I: Chemical Structure and Properties

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CHAPTER OVERVIEW

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1.1: From Democritus to the 19th Century- Historical Developments in Chemistry

Chemistry is the study of the material world. What are different materials made of? How is their composition and structure related to their properties? How does one material become transformed into another? These are the sorts of questions that have driven the development of chemistry.

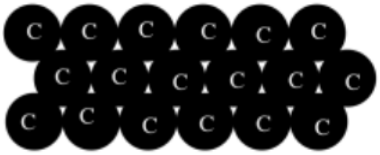
People have been using chemistry for a very long time. Medicines were obtained from plants in early societies all over the world. People made dyes for clothing and paints for houses. Metallurgy was practised in India and the Sahel, in Africa, before 1000 BC.

The Greek philosopher, Democritus, is often cited as the earliest person to formulate an idea of atoms, although similar ideas were recorded in India around the same time. Democritus thought that all things were made of atoms. Atoms were very small, he thought. They were also indivisible. Although you could cut a piece of wood in half, and cut each of those pieces in half, at some point you would reach the stage at which the wood could not be cut any longer, because you had a slice that was one atom thick.

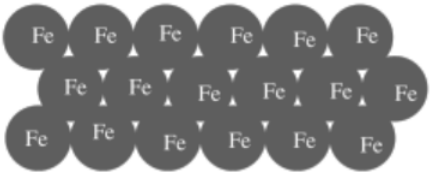
There were an infinite variety of atoms, Democritus thought, making up an infinite variety of materials in the world. The properties of those atoms were directly responsible for the properties of materials. Water was made of water atoms, and water atoms were slippery. Iron was made of iron atoms, and iron atoms were strong and hard.

nitrogen is made of nitrogen atoms

oxygen is made of oxygen atoms



carbon is made of carbon atoms



iron is made of iron atoms

We don't quite think of materials in the same way today, but we have retained some of the roots of these ideas. For example, we do know that matter is composed of atoms, and that there are different kinds of atoms that make different materials. However, we also know that those atoms can combine with each other in different ways to make lots of different materials.

All of the materials in the world around us are made from atoms.

A more practical aspect of chemistry has its roots in the Islamic Golden Age. Practitioners such as Jabir Ibn Hayyan developed laboratory apparatus and experimental methods to recrystallize and distill compounds from natural sources. Like Democritus, these early chemists wanted to know what the world is made of, but they were also trying to make improvements in practical applications such as tanning leather, making glass or rust-proofing iron.

? Exercise 1.1.1

Natural products are widely used in food, medicine and industrial applications. See if you can match the following natural products to their original, natural source.

i. vanillin a. coffee beans

ii. caffeine b. willow tree bark

iii. polyisoprene c. indigo plants

iv. aspirin d. yew tree needles

v. tannin e. vanilla beans

vi. the chemotherapy agent, paclitaxel f. rubber trees

vii. blue dye for jeans g. oak tree

The translation of Arabic texts into Latin helped spur the European Renaissance. Practical observations from the Islamic period, such as the fact that matter could be converted into different forms but did not disappear, gave rise to some of the most fundamental ideas of modern chemistry.

- Conservation of mass: matter can be converted from one form to another, but it does not disappear.

As is usually true in science, new developments in chemistry built on earlier work as well as the work of contemporary colleagues, continually improving our understanding of nature in small steps. In the 1600's, Robert Boyle adopted the Islamic emphasis on experimental work. Among his experiments, he was able to isolate the hydrogen gas formed by reacting metals with acids, as other scientists were doing at that time. In the 1700's, Joseph Priestley isolated several different "airs" or gases, including oxygen. Henry Cavendish showed that hydrogen combined with oxygen to form water. Antoine Lavoisier argued that oxygen and nitrogen, the other major component of air, are elements -- materials that cannot be made from any other kind of atom. In contrast, water was not an element, because it could be made by combining atoms of oxygen and hydrogen. The free exchange of ideas allowed people to rapidly advance our understanding of the material world.

Lavoisier, in particular, was important in bringing a number of important ideas together. He clearly stated that elements were the basic unit of matter, that could not be obtained from other materials. Compounds were made by combining different elements. His careful use of a balance to weigh reactants and products of an experiment clearly confirmed the idea of conservation of mass: the total mass of products after a reaction equals the total mass of reactants. These conclusions were more sophisticated versions of earlier ideas, and Lavoisier was able to present them in a way that eventually gained wide acceptance.

- A compound is a mixture of different elements bonded together.
- Conservation of mass, revised: the total mass of products after a reaction equals the total mass of reactants.

In the 1800's one of the principle proponents of the developing atomic theory was John Dalton. He advanced the idea that all atoms of a particular element are identical (as far as he could tell at that time). An element is a fundamental atomic building block from which other materials are made. Dalton performed analyses to try to deduce the atomic weights of different elements. Taking these ideas together, he showed that a particular compound always contained the same elements in the same ratio.

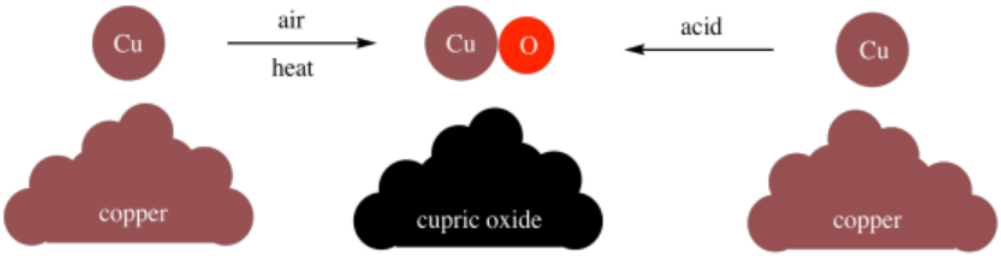
- An element is a fundamental atomic building block from which other materials are made.
- A compound is a mixture of different elements bonded together in a specific ratio.
- A compound may have a specific number of atoms of one type combined with a specific number of atoms of another type.
- Because all atoms have weight, we can also think of a compound as a specific weight of one kind of element combined with a specific weight of another element.

For example, water is a compound made from hydrogen and oxygen. It is crucial for life, of course. Water is about 1/9th hydrogen by weight; the other 8/9ths are oxygen. However, a different compound, hydrogen peroxide, is a rocket fuel. Hydrogen peroxide is only about 1/19th hydrogen by weight. Those specific ratios of hydrogen to oxygen are inherent qualities of each compound.

Left: a sailboat floating on water next to space-filling model of H_2O. Right: rocket taking off from a cloud of hydrogen peroxide next to space-filling model of H_2O_2.

Furthermore, Dalton found that he could make compounds through different methods. For example, he could make cupric oxide (CuO) by heating copper in air, or he could make it through various reactions involving copper and acids. It didn't matter how he

made the cupric oxide; the ratio of copper to oxygen was always the same in the product.



A pile of copper is transformed into cupric oxide via air and heat. A pile of copper is also transformed into cupric oxide via acid.

There is one other compound containing copper and oxygen in a different ratio; it is called cuprous oxide, and it has the formula Cu_2O. However, it is very different from cupric oxide. The most obvious difference is that cuprous oxide is red whereas cupric oxide is black. Once again, when elements are combined in different ratios, different materials are produced, and they have properties that differ from each other and from they elements of which they are comprised.

? Exercise 1.1.2

Ratios are commonly used in baking. Usually, ingredients must be combined in the correct proportions in order to make brownies or a cake.

Brownies: Cake:

1 cup sugar 1 cup sugar

2 eggs 2 eggs

1/2 cup butter 1/2 cup butter

1/2 teaspoon vanilla 1/2 teaspoon vanilla

1/2 cup flour 1-1/2 cup flour

1/3 cup cocoa 1/2 cup cocoa

1/4 teaspoon baking powder 1 teaspoon baking powder

1/4 teaspoon salt 1/4 teaspoon salt

1/4 teaspoon baking soda

1 c boiling water

a. Brownies and cake have a lot of ingredients in common. Looking at those ingredients that are found in both brownies and cake, do you see any difference in the proportions used? How do you think that affects the properties of the product?
b. The above cake recipe is just for one shallow cake pan. If you wanted a two-layer cake, what would you do with the recipe?
c. Suppose you are cleaning out your fridge and want to turn all of your eggs into brownies. If the above recipe makes sixteen 2" x 2" brownies, how many brownies could you make with a dozen eggs? How much flour would you need to accomplish your goal?

d. You want to make some brownies but you don't have any measuring cups or spoons. You notice that there is a really nice balance in the chem lab and you decide to measure your ingredients there (it's a terrible idea, by the way). You find a list of conversions, including the following:

1 cup flour = 125 g; 1 cup sugar = 200 g; 1 cup cocoa = 90 g.

How many grams of flour, sugar and cocoa would you need to use for a batch of brownies?

d. Why do you think a cup of flour does not weight the same as a cup of sugar or a cup of cocoa?

? Exercise 1.1.3

Mercury forms two different compounds with oxygen: mercuric oxide (HgO, which is red) and mercurous oxide (Hg_2O, which is black).

a. How many atoms of mercury combine with one atom of oxygen to form one unit of mercuric oxide, HgO?
b. How many atoms of mercury combine with one atom of oxygen to form one unit of mercurous oxide, Hg_2O?
c. Given the following approximate atomic weights, what is the total weight of one unit of mercuric oxide? 1 mercury atom (Hg): 200 amu; 1 oxygen atom (O) : 16 amu
d. What is the weight of one unit of mercurous oxide?

Answer a:

one atom of mercury with one atom of oxygen

Answer b:

two atoms of mercury with one atom of oxygen

Answer c:

200 amu (Hg) + 16 amu (O) = 216 amu (HgO)

Answer d:

2 x 200 amu (Hg) + 16 amu (O) = 416 amu (HgO)

? Exercise 1.1.4

It's pretty difficult to weigh an individual atom. Because we are working with ratios, we can always scale up and keep the ratio of atoms the same, and we will just make more of the compound we want. Instead of weighing things in atomic mass units, we usually weigh them in grams.

1 mercury atom (Hg): 200 amu; 1 mol mercury: 200 g

1 oxygen atom (O) : 16 amu; 1 mol oxygen (O): 16 g

1 hydrogen atom (H): 1 amu; 1 mol hydrogen (H): 1 g

200 amu of Hg plus 16 amu of O makes 216 amu of HgO, which is just on unit of HgO. An atom of mercury weighs 200 amu and an atom of oxygen weighs 16 amu, so one atom of mercury combined with one atom of oxygen weighs 216 amu.

A mole of mercury weighs 200 g. A mole of oxygen atoms weighs 16 g. A mole is just a scaled-up batch of atoms; it is just the atomic mass number of the atom, but weighed in grams instead of amu.

a. How much does a mole of HgO weigh?
b. How many grams of mercury would be needed in order to make one mole of Hg_2O?
c. How many grams of mercury would be needed to make 0.25 moles of HgO?
d. How many grams of oxygen would be needed to make 2.08 g Hg_2O?

Answer a:

200 g (Hg) + 16 g (O) = 216 g (HgO)

Answer b:

2 x 200 g (Hg) + 16 g (O) = 416 g (Hg_2O)

Answer c:

If one mole is 216 g of HgO, then 0.25 mole must be a quarter of that amount, or 54 g.

0.25 mol x 216 g/mol = 54 g

Alternatively written as

0.25 mol x 216 g mol^{-1} = 54 g

The amount of mercury is just a fraction of that: 200/216. So the answer is (200/216) x 54 g = 50 g.

Answer d:

What fraction of a mole is 2.08 g of Hg_2O, if one mole is 416 g?

2.08 g / 416 g mol^{-1} = 0.005 mol

Notice that when we divide *g* by *g* mol^{-1}, the grams cancel and the mol^{-1} becomes *mol*.

There is 1 mol of O in 1 mol of HgO, so 0.005 mol of O are needed for 0.005 mol HgO.

0.005 mol x 16 g mol^{-1} = 0.08 g O needed

? Exercise 1.1.5

Priestley isolated oxygen by heating up mercuric oxide. How much oxygen could be made by heating 1 g of HgO?

By the late 1800's, enough different elements had been isolated that people began to notice patterns in their properties. If you listed the elements out by weight, elements with similar properties seemed to occur at regular intervals throughout the list. A Russian chemistry teacher, Dmitri Mendeleev, came up with a convincing way to convey this "periodicity" in a table. This is the modern periodic table (an example is shown in figure 1.1.1).

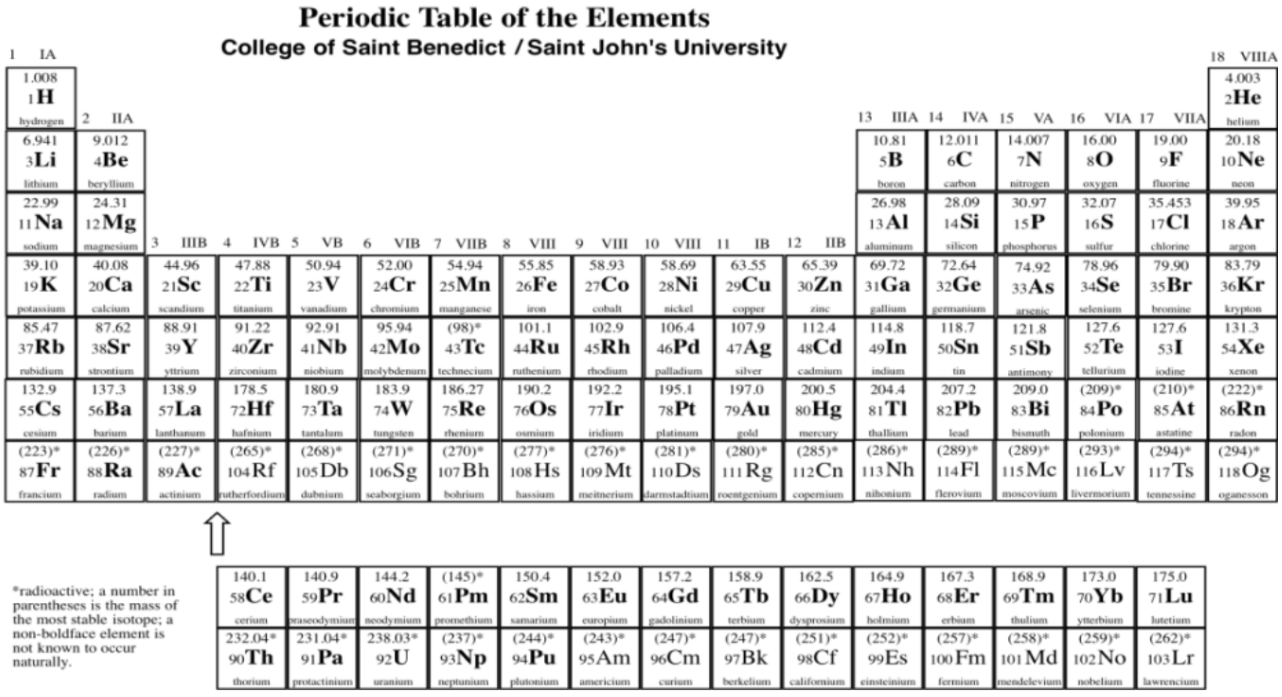
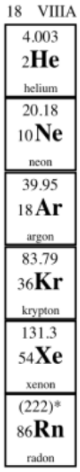


Figure 1.1.1: **The periodic table**

Download a copy of the periodic table.

The noble gases are an example of one of the groups in the periodic table. They have a number of properties in common. As the name suggests, all of the noble gases exist in the vapour phase at normal room temperature. They are all pretty unreactive; they do not undergo chemical changes very easily. In terms of structure, they each exist as individual atoms in nature. The rest of the elements in the periodic table don't really exist as individual atoms in nature. In one way or another, they cluster together with other atoms. They may bunch up with other atoms of the same kind, forming an element, or else form groups with atoms of different kinds, forming compounds. Noble gases rarely do either of those things.

Because of their similar qualities, Mendeleev put the noble gases together in one column in the periodic table. They are helium, neon, argon, krypton, xenon, and radon.



Exercise 1.1.6

a. Which of the following elements are in the same group as oxygen: silicon, sulfur, or neon?
b. Which of the following elements would have similar properties to carbon: silicon, nitrogen, sodium?
c. Which of the following elements would have similar properties to magnesium: calcium, lithium, potassium?
d. Which of the following elements would have similar properties to sodium: nitrogen, potassium, lithium?
e. Which of the following elements would have similar properties to nitrogen: oxygen, phosphorus,rubidium?
f. Which of the following elements are in the same group as fluorine: argon, iodine, or neon?
g. Which of the following elements are in the same group as gold: silver, copper, zinc?
h. Which of the following elements are in the same group as iron: ruthenium, copper, gold?

Answer a:

sulfur

Answer b:

silicon

Answer c:

calcium

Answer d:

potassium and lithium

Answer e:

phosphorous

Answer f:

iodine

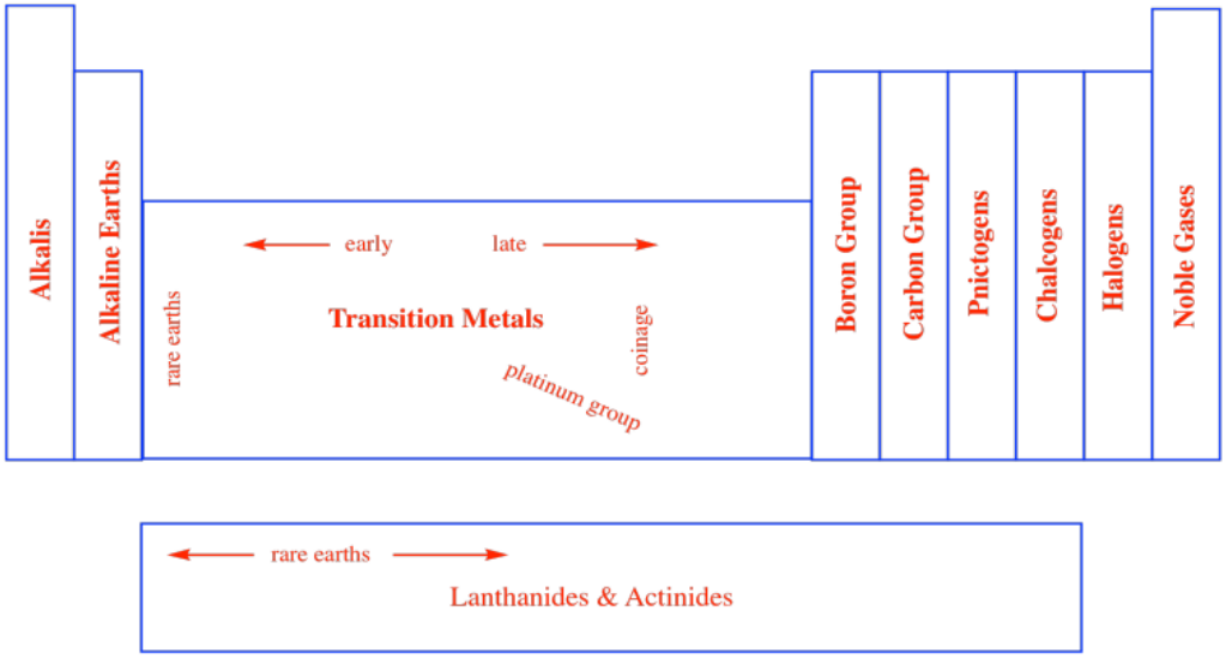
Answer g:

silver and copper

Answer h:

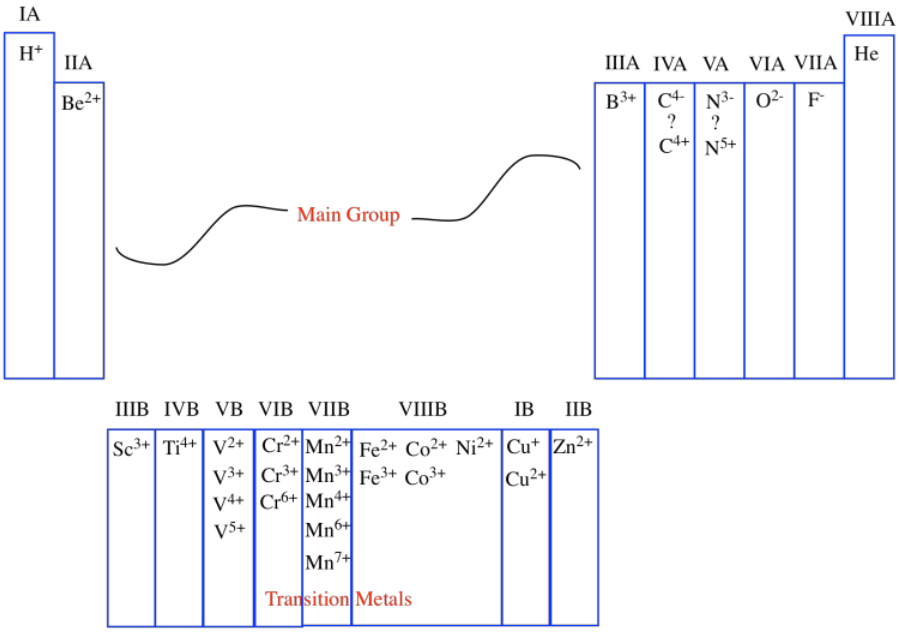
ruthenium

In a similar way, chemists began thinking about other columns in the periodic table as belonging in groups. Sometimes, these groups were given specific names, like the noble gases. There are the halogens, meaning "salt-makers", because they were often contained in salts. There are the chalcogens, "ore-makers", found in iron oxides such as haematite and taconite, for example. There are the pnictogens, "choke-makers", so called after the discovery that air is mostly composed of nitrogen, but nitrogen is not the part of air that we breathe. Other groups are simply referred to as the self-explanatory "carbon group" or "boron group" after the first element in the column.



Summary of the periodic table separated by groups. Labelled are the alkalis, alkaline earths, transition metals, boron group, carbon group, pnictogens, chalcogens, halogens, noble gases, and lanthanides and actinides.

Alternatively, the columns of the periodic table are often numbered. At one time, the columns were separated into different groups, with specific focus on two of them: the main group and the transition metals. The main group was Group A and the transition metals constituted Group B. Each successive column across these blocks of the periodic table was then numbered using Roman numerals.



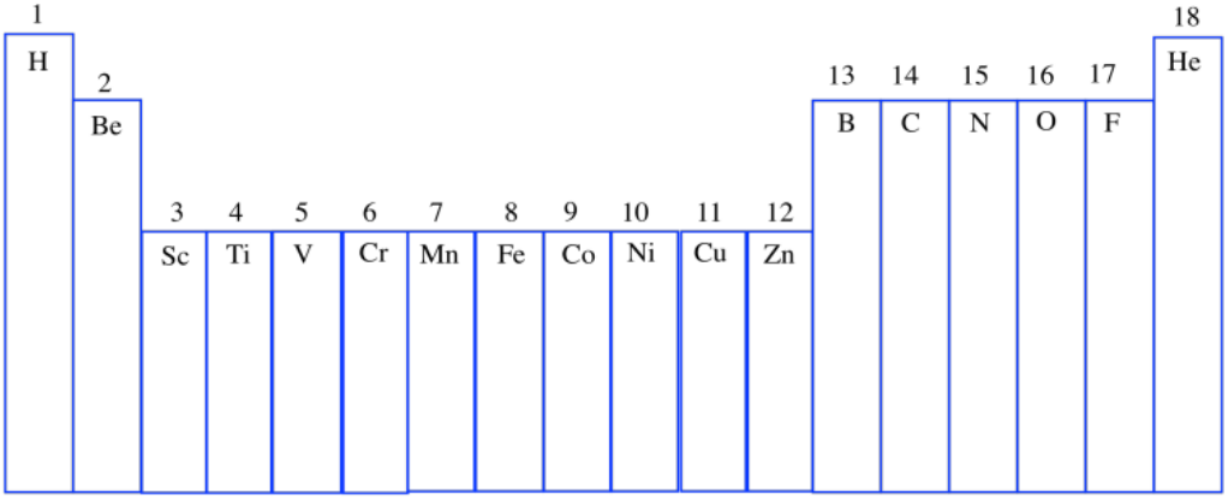
One of those periodic properties that is found in each column is the usual charge on an ion. Atoms sometimes capture extra electrons, which are negatively charged sub-atomic particles, becoming negatively charged overall. Other atoms sometimes lose their electrons, becoming positively charged as a result. To some extent, the column number corresponds to the charge on the common ions found in that column. For example, in the first column, the atoms are almost always found as ions with a +1 charge; in the second column, the atoms are almost always found as ions with a +2 charge, and so on.

That correlation breaks down after a while. Sometimes, as in the transition metals, the group number simply denotes the highest possible charge on an ion, although there may be many possible ions that are commonly observed. Eventually, as we move to the right, the correlation between group number and charge breaks down altogether. In the main group, the atoms farther to the right are not cations at all, but anions. Some, such as carbon and nitrogen, can be *formally* thought of as either anions or cations, depending on their environment.

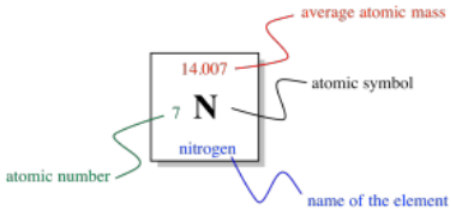
In a sense, although we like to be organized and number things from left to right, the periodic table is naturally organized from the edges inward. Atoms closest to the left edge build up positive charge according to how far away from the edge they are. Atoms closest to the right edge build up negative charge according to how far away from the edge they are. Atoms in the middle vary a lot more, though.

This edge-orientation is related to the stability of the noble gases and what are called "filled-shell configurations". We will get to those, and to the physical reasons for their stability, on a later page.

Now, eventually in science, someone always decides that there is a better way of doing things, and so if you have just purchased a brand-new periodic table to display on your bedroom wall, you might just see the Arabic numerals 1-18 across the top. This system is meant to be a simpler and cleaner way of doing things. (And once again, the Lanthanides and Actinides, those two lonely rows orphaned at the bottom of the periodic table, are more-or-less ignored. That's partly because, for reasons that are a little complicated at this point, they mostly behave as if they were part of Group 3.)



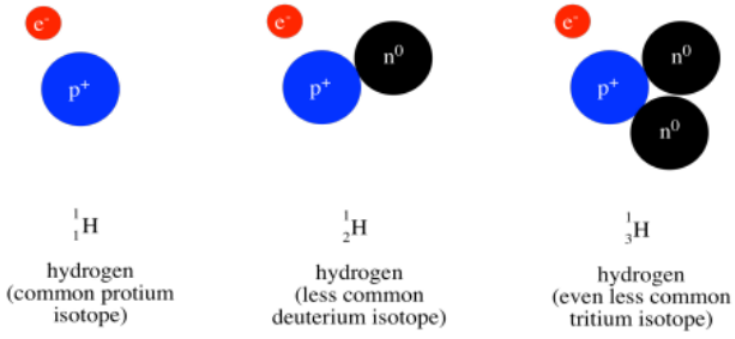
So, the columns in the periodic table are designed to show us which elements are related to each other. What else is shown in the table? If we look at just one square of the periodic table, we can see what it tells us about an individual element.



Breakdown of the square for nitrogen on the periodic table, highlighting the name, atomic number and symbol, and average atomic mass.

In the middle of the square, there is a Roman letter or a pair of Roman letters. The first letter is always a Roman capital. This one- or two-letter designation is the atomic symbol. It is usually the first couple of letters in the name of the atom, although the name isn't always in English. For example, the symbol for mercury is Hg, for hydrargyrum. That's the Latin name, meaning, roughly, "liquid silver".

Above the symbol, or sometimes above and to the left, is the atomic weight of the atom. The atomic mass is one of the properties of an element, but it turns out that a given element can have a range of atomic weights. Consequently, the average weight is shown in the periodic table. For example, the smallest atom, hydrogen, can have a weight of either 1, 2, or 3 atomic mass units (or amu). The average weight of a hydrogen atom is 1.008 amu. That fact tells us that most of the hydrogen atoms out there have a weight of 1 amu; relatively few of them have atomic weights of 2 amu or 3 amu.



Most of the mass of an atom comes from the nucleus of the atom, where relatively heavy particles, the protons and neutrons, are found. Hydrogen atoms always contain a proton, with a mass of 1 amu, but they can also contain varying numbers of neutrons, which also have a mass of 1 amu.

(Many scientists prefer the term "mass" when talking about atoms, reserving the term "weight" to describe how heavy something feels because of the pull of gravity. Here, we will use the term "force due to gravity" if we want to discuss the latter concept.)

The number to the lower left is called the atomic number. Notice that each element in the periodic table has a number assigned from 1 to 112. The elements are numbered in order from "smallest" to "largest", roughly speaking. Element 1, hydrogen, is the smallest, and element 112, copernium, is the largest (at least, that's as far as the teams of chemists and physicists who look for new elements have gotten so far). More correctly, the atomic number simply tells us the number of protons in the nucleus of an atom of a given element. Hydrogen always has one proton; copernium always has 112 of them.

Finally, the name of the element may or may not be written on the periodic table. The other three pieces of information are always there. Sometimes additional information is given, such as specific properties of the element.

? Exercise 1.1.7

Supply the following information about each element.

a. The atomic number of calcium.
b. The atomic symbol of sodium.
c. The atomic mass of oxygen.
d. The name of P.
e. The name of element 6.
f. The symbol of tin.
g. The atomic mass of sulfur.
h. The name of K.

Answer a:

20

Answer b:

Na

Answer c:

16.00

Answer d:

phosphorous

Answer e:

carbon

Answer f:

Sn

Answer g:

32.07

Answer h:

potassium

The periodic table as laid out by Mendeleev had predictive value. It presented the structure-property relationships of atoms. If you knew something about one element in the table, it would lead you to believe that other elements in the same column would have similar properties. Furthermore, there were gaps in the table where there ought to be an element, but none was known. It was predicted that these elements would eventually be discovered, and they were.

However, people were not satisfied with the idea of the atom as the basic building block of the universe. People wanted to know how atoms themselves were made. Ultimately, answering this question depended on the development of quantum mechanics. We will learn a little bit more about that view of the atom next.

Exercise 1.1.8

What is the approximate weight, to the nearest g, of a mol of each of the following elements?

a) neon, Ne, found in brightly-colored store signs

b) iron, Fe,used to make steel

c) copper, Cu, found in power lines

d) gold, Au, found in jewelery

e) silicon, Si, used in high-tech devices

Answer a:

Ne: 20 g/mol

Answer b:

Fe: 56 g/mol

Answer c:

Cu: 64 g/mol

Answer d:

Au: 197 g/mol

Answer e:

Si: 28 g/mol

Exercise 1.1.9

What is the weight, to the nearest gram, of a mol of each of the following compounds?

a) water, H_2O

b) baking soda, $NaHCO_3$

c) sand, which is mostly silica, SiO_2

d) table salt, NaCl

e) tantalum nitride, TaN, used in electronics

f) ammonia, NH_3, found in some cleaning solutions

g) sodium dihydrogen phosphate, NaH_2PO_4, used in toothpaste

h) acetic acid, CH_3CO_2H, which is dissolved in water to make vinegar.

Answer a:

H_2O: 18 g/mol (2 x H + 1 x O = 2 x 1 + 1 x 16 g/mol)

The molar weight of the atom was rounded to the nearest gram. In order to be very careful and avoid "error propagation", the more exact molar weight (to several decimal places) could be used and rounding could be performed *after* the calculation. In these cases, the result would be the same. The result could be different if very large numbers of atoms were found in the compound.

Answer b:

$NaHCO_3$: 84 g/mol (3 x O + 1 x Na + 1 x H + 1 x C = 3 x 16 + 1 x 23 + 1 x 1 + 1 x 12 g/mol)

Answer c:

SiO_2: 60 g/mol (1 x Si + 2 x O = 1 x 28 + 2 x 16 g/mol)

Answer d:

NaCl: 58 g/mol (1 x Na + 1 x Cl = 1 x 23 + 1 x 35 g/mol)

Answer e:

TaN: 195 g/mol (1 x Ta + 1 x N = 1 x 181 + 1 x 14 g/mol)

Answer f:

NH_3: 17 g/mol (1 x N + 3 x H = 1 x 14 + 3 x 1 g/mol)

Answer g:

NaH_2PO_4: 120 g/mol (1 x Na + 2 x H + 1 x P + 4 x O = 1 x 23 + 2 x 1 + 1 x 31 + 4 x 16 g/mol)

Answer h:

CH_3CO_2H: 60 g/mol (2 x C + 4 x H + 2 x O = 2 x 12 + 4 x 1 + 2 x 16 g/mol)

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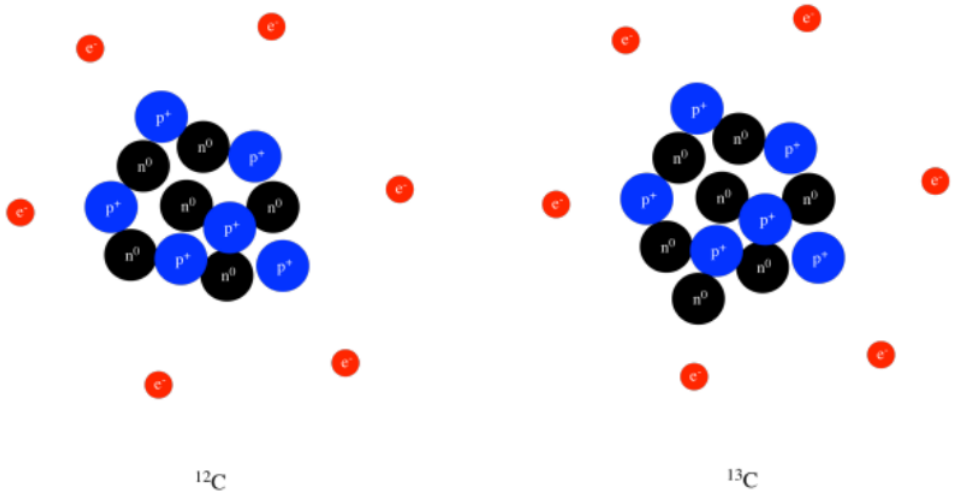
1.2: Old Quantum Mechanics- Basic Developments

Today, we know that atoms contain protons, neutrons and electrons. The protons have significant mass and a positive charge and are found in the nucleus of the atom. The neutrons have mass but no charge and are also found in the nucleus. The electrons have negative charge and very little mass and are found outside the atom's nucleus. The weight of an atom in atomic mass units is approximately the sum of its protons and neutrons, since the electrons don't have much mass.

For example, a typical carbon atom has six protons and six neutrons, and it has an atomic weight of 12 amu. A carbon also has six electrons, but they are so small that they don't contribute to carbon's weight.

- An element is defined by the number of protons in its nucleus.
- The number of protons in an atom is equal to the number of electrons, to balance the charge.

Some carbon atoms have an extra neutron or two, so carbon may have an atomic weight of 13 or even 14 amu. However, a carbon atom can't have an extra proton; an extra proton would make it a nitrogen atom. It is the six protons that make the atom behave like carbon. Many other elements may have slightly different atomic weights, depending on how many neutrons are found in the nucleus. Different atoms of the same element with different weights are called *isotopes*. For example, ^{12}C, ^{13}C and ^{14}C are all isotopes of carbon. They all have six protons, but different numbers of neutrons, as seen in a model of ^{12}C and ^{13}C, below.



- Neutrons are also in the nucleus.
- A neutron has a mass similar to a proton, but has no charge.
- Compared to protons and neutrons, the mass of an electron is very small.

? Exercise 1.2.1

An element's atomic number is just the number of protons in an atom of that element. Given the following atomic numbers and atomic weights, identify the number of protons, neutrons and electrons in an atom of the element.

a. oxygen: atomic number = 8, atomic weight = 16
b. phosphorus: atomic number = 15, atomic weight = 31
c. zinc: atomic number = 30, atomic weight = 65
d. gold: atomic number = 79, atomic weight = 197

Answer a:

O: 8 protons, 8 electrons, 8 neutrons

The atom is neutral overall, so the number of positively charged protons is equal to the number of negatively charged electrons. The atomic weight is provided almost entirely by the protons and neutrons, so the number of protons plus number of neutrons equals the atomic weight.

Answer b:

P: 15 protons, 15 electrons, 16 neutrons

Answer c:

Zn: 30 protons, 30 electrons, 35 neutrons

Answer d:

Au: 79 protons, 79 electrons, 118 neutrons

Exercise 1.2.2

If a proton's mass is 1.67 x 10^{-27} kg and the mass of an electron is 9.11 x 10^{-31} kg, how many times heavier is a proton than an electron?

Exercise 1.2.3

If carbon in nature is about 99% ^{12}C and 1% ^{13}C, then what is the average weight of a carbon atom?

Answer

Carbon: [(99 x 12 amu) + (1 x 13 amu)] / 100 = [1,188 + 13 amu] / 100 = 1,201 amu / 100 = 12.01 amu

Exercise 1.2.4

Note that ^{14}C is even rarer than ^{13}C, because ^{14}C is converted into ^{14}N via radioactive decay. In that event, a high-energy electron is emitted from the ^{14}C nucleus. Explain how that emission must convert the carbon into a nitrogen, and indicate how many protons and neutrons are found in the resulting nucleus.

Answer

The negatively charged electron's departure from the nucleus leaves behind a positive charge. A neutron is converted into a proton. The overall atomic weight remains the same, but the atom ends up with one more proton and one more electron. A ^{14}C is converted into a ^{14}N.

Exercise 1.2.5

Magnesium in nature is found in three major isotopes. It is nearly 79% ^{24}Mg, about 11% ^{25}Mg and 12% ^{26}Mg. What is the average weight of a magnesium atom?

Exercise 1.2.6

Chlorine in nature is found in two major isotopes: ^{35}Cl and ^{37}Cl. If the average atomic weight of chlorine is about 35.5, what percentage of each isotope is found in nature?

Answer

Suppose y is the decimal fraction of ^{35}Cl and z is the decimal fraction of ^{37}Cl.

35.5 amu = (y x 35 amu + z x 37 amu)/100 but y + z = 1

35.5 amu = (y x 35 amu + (1-y) x 37 amu)

35.5 amu = y x 35 amu - y x 37 amu + 37 amu

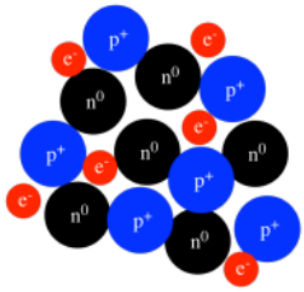
(37-35) x y amu = 37 amu - 35.5 amu

2 x y amu = 1.5 amu

y = 0.75 (75% ^{35}Cl)

z = 0.25 (25% ^{37}Cl)

A number of developments at the beginning of the twentieth century led to our current understanding of the structure of atoms and molecules a hundred years later. At that time, some people though protons, neutrons, and electrons were lumped together in the atom. This view of the atom was called the "pudding model" of the atom.



^{12}C

Ernest Rutherford first proposed that an atom contains a very small, positively charged nucleus surrounded by empty space. The electrons orbited far away from the nucleus.

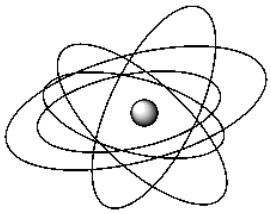


Figure 1.2.1: Rutherford's model of an atom: a nucleus with electrons far away, and lots of empty space.

Rutherford was explaining the result of an experiment in which alpha particles (positively charged helium ions) were fired at a gold foil. Most of these particles passed through the foil easily, suggesting there was a lot of empty space in the material. However, some of the particles bounced directly back, having collided with the small, highly charged nuclei. The positive alpha particles were powerfully repelled by the positive nuclei, because like charges repel each other. He didn't really know much about the location of the electrons, the negatively charged particles in the atom, but believed they orbited the nucleus like planets around the sun.

Why weren't the electrons found in the nucleus? If electrons are attracted to protons, it seems like that's where they should be. Niels Bohr suggested that electrons are found only in specific, allowed orbits at different distances from the nucleus.

That conceptual leap to specific, allowed orbits marks the introduction of quantum mechanics into the understanding of the atom. Quantum mechanics is based on the idea that on a very small scale, many properties only have specific values (like 1, 2, 3...) instead of any value at all (like all the possible fractions between these integers). In other words, in the world around us, we usually view things like walking up a ramp. We can heat a pot of water just a little bit warmer, and just a little bit warmer than that, and so on. On the atomic scale, however, the world is more like walking up a set of stairs. Maybe you could heat the water to 30 ^{o}C or 40 ^{o}C, but heating to 35 ^{o}C would be impossible, because heat only comes in 10 degree packages. That is, in fact, how the quantum world really works, but on the human scale, the steps involved are so tiny that we cannot notice them.

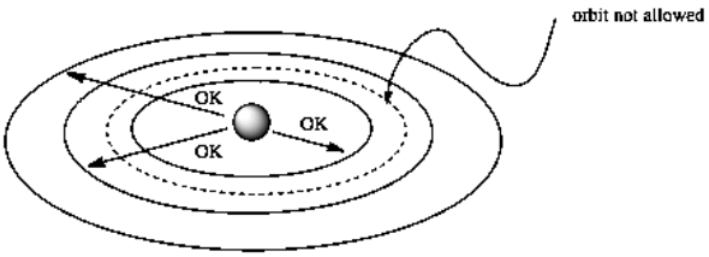
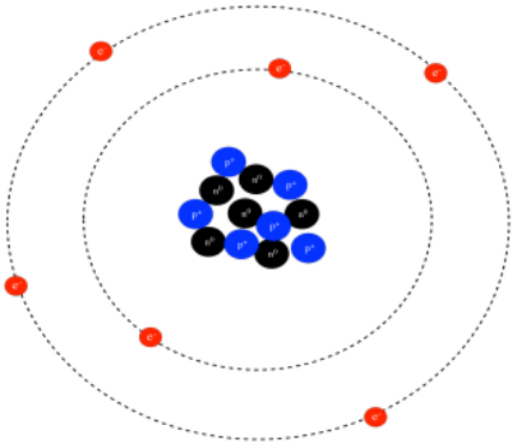


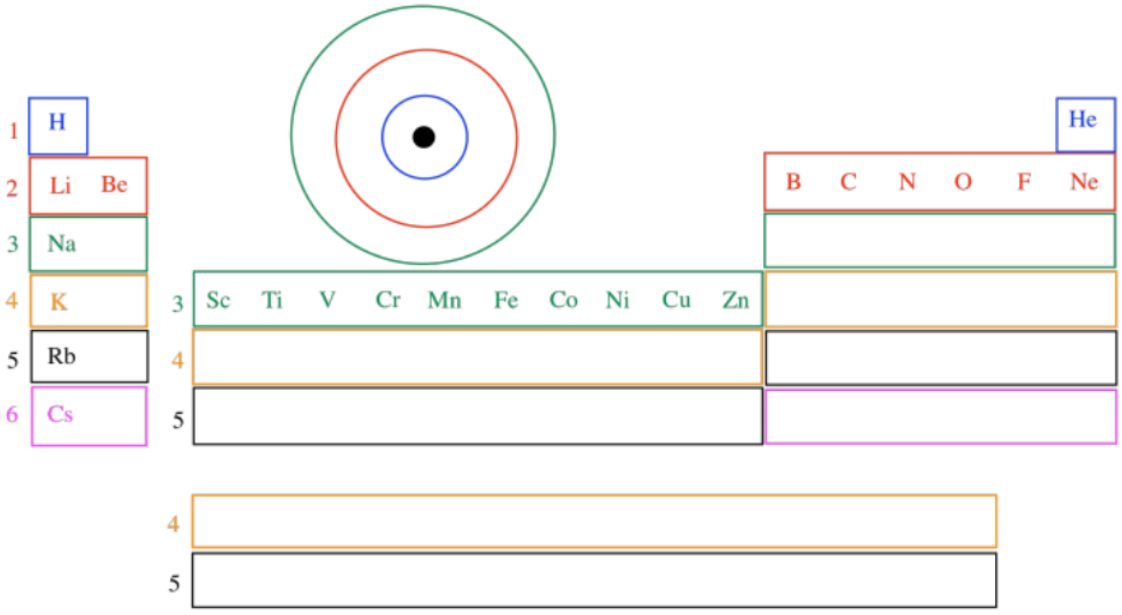
Figure 1.2.2: In the Bohr model of an atom, electrons could be found only at certain allowed distances from the nucleus. Diagram showing that orbits must be at specific distances from the nucleus, not in-between two orbits.

Bohr's model was also consistent with the earlier idea of the periodic table of the elements. The idea is that electrons are found in different "shells" that are each further and further from the nucleus. Each of those shells corresponds roughly to a different row in the periodic table. Hydrogen and helium have electrons only in the first shell, and we see those two elements in the first row of the periodic table. Carbon and oxygen's outermost electrons are found in the second shell, so they show up in the second row of the periodic table.



^{12}C

Each row in the periodic table corresponds to an outer layer of electrons that are found further from the nucleus than the outermost electrons in the row before it. We are going to see eventually that there is a further variation on this idea, but it is still pretty much the way we see the periodic table today. Hydrogen starts the first shell, lithium the second, sodium (the Latin, natrium) the third, potassium (Latin, kalium) the fourth, and so on.



The variation we are going to see involves that dip in the middle of the periodic table. Scandium through zinc have outer electrons that are only in the third shell, not the fourth. The third and the fourth shell overlap a little bit, so that some electrons actually start to go into the fourth shell (as in potassium and calcium), then finish filling the third shell across the transition metals. The reasons for that also have to do with quantum mechanics, but we will need to learn a little more about energy and waves before we see why.

Bohr showed that electrons might be found in specific orbits around the nucleus. He also showed that electrons in these different orbits have specific amounts of energy. By doing this mathematically, he was offering an explanation to an important problem. People knew that atoms can absorb energy (they can be heated in a flame, for example) and give the energy back again in the form

of light. Rather than give off light of all colors when excited, atoms only give off very specific colors. For example, heating lithium salts in a flame produces a red color, but heating sodium salts produces an orange color, whereas potassium salts produce a purple color, and so on.

These colors can be separated and studied using a prism. When people did that, they found that a given atom does not produce just one pure color of light, but several different ones. When separated by a prism, the light given off by an excited compound could be seen against a dark surface as several different, colored lines. These were called emission lines.

It had been known since the early 1800's that light had wave properties, and that light of different colors had different wavelengths. For example, red light consistes of electromagnetic waves, with a wavelength of about 700 nm, but blue light's wavelength is about 450 nm. That means a color can actually be measured numerically. Because of that fact, people can look for mathematical relationships between the emission lines observed for different atoms. Those mathematical relationships may reveal something about the atoms themselves.

Furthermore, it was known that different wavelengths of light corresponded to different amounts of energy. In one of the first developments in quantum mechanics, Max Planck in 1900 proposed that light travels in bundles called photons. Although they are particles, these photons do have wave properties. The amount of energy in a photon of light corresponds to its wavelength.

By proposing that electrons could be found only in specific orbits, specific distances away from the nucleus, Bohr was trying to explain observations from atomic spectroscopy reported by another scientist named Rydberg. Rydberg had found a mathematical relationship between the wavelengths of these emission lines. Bohr thought that, when energy was added, electrons could be excited from one energy level (or orbit) to a higher one. When the electron relaxed back to its original orbit, it gave off the energy it had gained in the form of light. The specific emission lines occur because electrons are found at very specific energy levels in an atom, so a drop from one level to another always produces the same amount of light energy. That specific amount of light energy has a specific color.

Figure 1.2.3: The correspondence between color, wavelength and energy.
Left: High energy blue light with short wavelength. Right: low energy red light with long wavelength.

Bohr then used the mathematical relationships describing electrostatic attraction and centripetal force to show that his model of the atom was consistent with Rydberg's relationship. In fact, he could use his model to predict the emission lines of an atom.

? Exercise 1.2.7

Bohr's explanation of atomic structure built on Rydberg's observation of a numerical series in spectral emission lines. Solving a series involves finding a pattern in numbers. Find the patterns among the following sequences of numbers, and predict the next number in the sequence.

a. 1, 2, 3, 4...
b. 2, 4, 6, 8...
c. 3, 5, 7, 9...
d. 1, 4, 9, 16...
e. 2, 4, 8, 16...
f. 1, 1/2, 1/4, 1/9...

Answer a:

1, 2, 3, 4, 5... a series of whole numbers, or n.

Answer b:

2, 4, 6, 8, 10... a series of even numbers, or 2n (because every even number is two times another number).

Answer c:

3, 5, 7, 9, 11... a series of odd numbers, or 2n + 1 (because every odd number is one more than some even number).

Answer d:

1, 4, 9, 16, 25... a series of squares, or n^2.

Answer e:

2, 4, 8, 16, 32... a series in which each numer is double the last number, or 2^n.

Answer f:

1, 1/2, 1/4, 1/9, 1/16... a series of reciprocals of squares, or $1/n^2$.

Exercise 1.2.8

Bohr's idea depended partly on the use of Coulomb's Law of electrostatic attraction. Coulomb's law is expressed mathematically as follows:

$$F = \frac{kq_1q_2}{r^2} \tag{1.2.1}$$

in which F is the attractive force between two charged particles, q_1 and q_2 are the charges on the two particles, r is the distance between the two particles and k is a constant. A large value of F means that the charges are strongly attracted to each other.

a. Suppose q_1 is the charge on the nucleus of an atom and q_2 is the charge on an electron. What happens to the force of attraction between an electron and the nucleus when the charge in the nucleus increases? Explain.
b. Suppose r is the distance from the electron to the nucleus. What happens to the force of attraction between an electron and nucleus when the electron gets further from the nucleus?
c. Using the ideas of Coulomb's law, compare the attraction of an electron to the nucleus in a helium atom versus a hydrogen atom.

Answer a:

When q increases, F increases. The increase is linear: if q_1 doubles, F doubles. As the charge in the nucleus gets larger, the force of attraction gets larger.

Answer b:

When r increases, F decreases. The decrease is nonlinear: if r doubles, F drops by a factor of four, rather than a factor of two. As the distance from the nucleus gets longer, the attraction to the nucleus drops sharply.

Answer c:

Hydrogen and helium are both in the first row of the periodic table. To a rough approximation, the distance between nucleus and electron is similar in these two atoms. However, helium has a charge of 2+ in its nucleas, compared to the 1+ charge in the nucleus of a hydrogen atom. As a result, the attraction of an electron on helium to the nucleus would be about twice as great as the attraction of an electron on hydrogen to its nucleus.

Helium's electrons are much more tightly held than hydrogen's.

The situation is really much more complicated than that. For example, if helium's electrons are more tightly attracted to the nucleus than hydrogen's, then helium's electrons ought to be pulled closer to the nucleus than hydrogen's. That means helium's electrons are held even more tightly than we at first thought.

Another complicating factor is that helium has two electrons, whereas hydrogen has only one. An electron may be attracted to the nucleus, but electrons repel each other. That second electron in helium should offset the extra attraction to helium's more positive nucleus. That means helium's electrons may be less tightly attracted than we originally thought.

However, the effect of the second electron is much smaller than it first appears. That's because the second electron could be anywhere around the helium atom. It has a 50% chance of being further away from the first electron than that positively charged nucleus. The farther it is away, the smaller its influence. Helium's electrons are definitely more strongly attracted to the nucleus than are hydrogen's, but it is difficult to say exactly how much more without the help of some more sophisticated tools.

? Exercise 1.2.9

Max Planck described the energy of a photon using the following relationship:

$$E = h\nu \backslash) or E = \frac{hc}{\lambda}$$

In which E = energy; ν =frequency; λ = wavelength; c = speed of light; h = Planck's constant

a. What happens to the energy of light as its wavelength gets longer?
b. What happens to the energy of light as its frequency gets higher?

Answer a:

As wavelength gets longer (value of λ increases), energy decreases.

Answer b:

As frequency gets higher (value of ν increases), energy increases.

Other people were familiar with these ideas and already knew about the relationship between light and energy. Bohr's model of the atoms put all of these ideas together to successfully explain a specific atomic property:

color = wavelength = energy of light = energy between electron levels.

In other words, an excited electron can drop back to its original orbit by giving off a photon with an energy exactly the same as the difference in energy between the two orbits ("excited state" and "ground state" orbits).

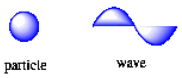


Figure 1.2.4: An electron can be thought of as both a particle and a wave.

However, Bohr did not explain why electrons would be found at specific energy levels in the first place. Louis de Broglie, a historian-turned-physicist, solved this problem with the idea of wave-particle duality. de Broglie put together the following ideas:

- All moving particles have wave properties.
- Electrons move around the nucleus and they have wavelengths.
- To maintain a complete standing wave along its orbit, an electron can only adopt orbits of specific circumferences. Otherwise, one end of the wave would not meet up with the other end, and it would interfere with itself.
- Orbits with specific circumferences have specific radii.
- Electrons are found at specific distances from the nucleus, but not at other distances.

One way to illustrate why an electron might have only certain allowed orbits is via the "particle in a box", a basic concept from quantum mechanics. If a particle has wave properties, then it has a wavelength. Its wavelength depends on certain conditions. By analogy, if you take a guitar string and attach it to the ends of a box, the string can only vibrate at certain frequencies. That's how guitarists can change the note played on a guitar string. By pressing one end of the string against a fret on the guitar neck, the length of the string is changed, and so is its allowed wavelength, so it makes a different sound.

The string can't move at the two points where it is held. That means the wave has to form in such a way that it returns to the same position at both ends. Because of that, certain wavelengths won't work, because the wave won't be able to return to that correct position at the far end.

Furthermore, the allowed wavelengths of a guitar string also depend on the thickness of the string. As a result, there are two conditions that control the tone that is played: which of the six guitar strings is plucked, and where the string is held against the frets.

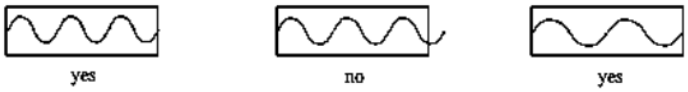


Figure 1.2.5: A particle in a box is allowed only certain wavelengths, based on the dimensions of the box.
Left: a wave in a box that does not extend outside the box, labelled "yes". Middle: a wave that extends outside the box, labelled "no". Right: a wave with a longer wavelength that does not extend outside the box, labelled "yes".

The same thing is true with very small particles that have wave properties. These particles can have only certain wavelengths that fit their surroundings. An electron has some property, analogous to the thickness of a guitar string, that limits its possible wavelengths. Given those limits, there are only certain orbits allowed the electron. If its orbit does not have the right circumference, the electron will not be able to form a complete wave along that orbit.

These ideas ushered in a revolution in science. Quantum mechanics is a very powerful tool. It can be used to accurately predict how molecules will behave. Unfortunately, the mathematics involved in quantum mechanics are one or two math courses beyond what most introductory chemistry students are familiar with. Even so, a qualitative feel for some of the consequences of quantum mechanics is important enough that we should explore it.

Exercise 1.2.10

Complete the table with the appropriate information.

Table for Exercise 1.2.10

Element Symbol	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Number of Electrons	Charge
H		1			1	
H		1			0	
H		1			2	
H		2			1	
H		3			1	
	4	9			2	+2
	6	12		6	6	
	12			13	12	0
	43			55	43	
	20	40				+2
Si	14	28				0
			19	28		+4
Fe			26	30	23	
	35			44		-1
K			22	17	21	
	15			15		0
	13	27				+3
S				16	16	0
Pd		106	46			+1
	24			28	21	

Element Symbol	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Number of Electrons	Charge
			50	68	50	
Hg	80			120	79	
	79			118	78	

Answer

Element Symbol	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Number of Electrons	Charge
H	1	1	1	0	1	0
H	1	1	1	0	0	+1
H	1	1	1	0	2	-1
H	1	2	1	1	1	0
H	1	3	1	2	1	0
Be	4	9	4	5	2	+2
C	6	12	6	6	6	0
Mg	12	25	12	13	12	0
Tc	43	98	43	55	43	0
Ca	20	40	20	20	18	+2
Si	14	28	14	14	14	0
K	19	47	19	28	15	+4
Fe	26	56	26	30	23	+3
Br	35	79	35	44	36	-1
Ti	22	39	22	17	21	+1
P	15	30	15	15	15	0
Al	13	27	13	14	10	+3
S	16	32	16	16	16	0
Pd	46	106	46	60	45	+1
Cr	24	52	24	28	21	+3
Sn	50	118	50	68	50	0
Hg	80	200	80	120	79	+1
Au	79	197	79	118	78	+1

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1.3: New Quantum Mechanics

Bohr's idea that electrons are found in different orbitals or energy levels was an important step in understanding the structure of an atom. Louis de Broglie's particle-wave relationship was also a crucial development.

Werner Heisenberg and Erwin Schrödinger were able to take these ideas and develop modern quantum mechanics. The main significance of quantum mechanics is the ability to very accurately predict physical properties using basic mathematical principles. Heisenberg and Schrödinger used different kinds of mathematics to explain atomic structure, but they ultimately reached similar results.

The key approach by Schrödinger was to recognize the factors influencing the energy of an electron in an atom. He saw that there would be contributions from Coulomb's law, because of attractive forces between the electron and the nucleus as well as repulsive factors between different electrons. In addition, Schrödinger recognized that there would be a kinetic energy component related to the wavelength of the electron. Schrödinger combined these factors into "the Schrödinger wave equation."

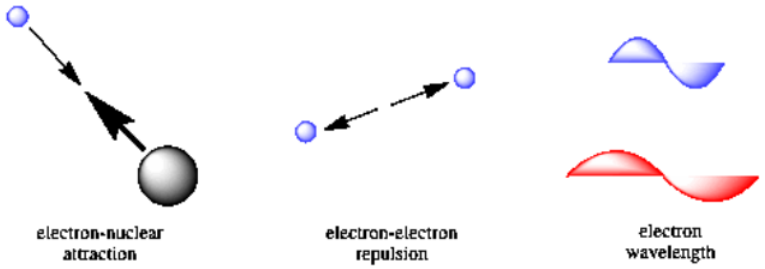

Figure 1.3.1: The factors Schrödinger accounted for in his wave equation. Each factor influences the energy of an electron. Left: electron-nuclear attraction. Middle: electron-electron repulsion. Right: two waveforms with different wavelengths.

Solving the wave equation is very useful. A solution to the equation, which is called a wave function, can indicate the energy of an electron in an atom. The solution can also be combined with other mathematical relations that will give specific predictions of different properties of atoms and molecules.

- The Schrödinger wave equation is an approach to describing an electron.
- The solution to the wave equation is called a wavefunction.

If you aren't familiar with how waves behave, you might start by looking here.

? Exercise 1.3.1

a. What happens to the energy of an electron as its wavelength gets shorter?
b. What happens to the energy of an electron as its wavelength gets longer?
c. If an electron is confined in a small space, what will happen to the electron's wavelength?
d. If an electron is allowed to expand into a large volume, what will happen to the electron's wavelength?

Answer a:

The energy of the electron gets higher.

Answer b:

The energy of the electron gets lower.

Answer c:

The wavelength gets shorter.

Answer d:

The wavelength gets longer.

Apart from showing us the energy of the electron, the wavefunction carries other information. One additional item is the idea of phase. This idea is illustrated with a sine wave (although a wavefunction of an electron is a more complex, three-dimensional wave).

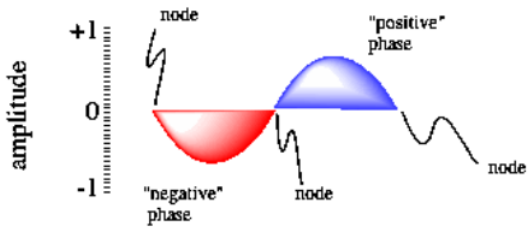

Figure 1.3.2: A sine wave, showing phase and nodal properties.

Diagram of a wave, showing amplitude on the y-axis. Nodes, negative phase, and positive phase are labelled.

One of the consequences of wave behavior is the presence of nodes along a wave. A node is a place where the wave changes phase; in a sine wave, the wave goes from a "trough" or valley or negative phase to a "peak" or hill or positive phase. A node is also place where the amplitude of the wave is zero. For an electron, the amplitude of the wave is *related to* the chance of an electron being found at that position (you'll see more about that below). We wouldn't find an electron at a node, but it could be in one of the other positions along the wave.

Other important consequences of wave properties in electrons include interference behavior. If two electrons are sent through parallel slits, a diffraction pattern results, like ripples from two different stones overlapping in a pond. That's because the waveforms of the two electrons interfere with each other. When the two waves overlap, they interact with each other in different ways, depending on whether they are in phase or out of phase.

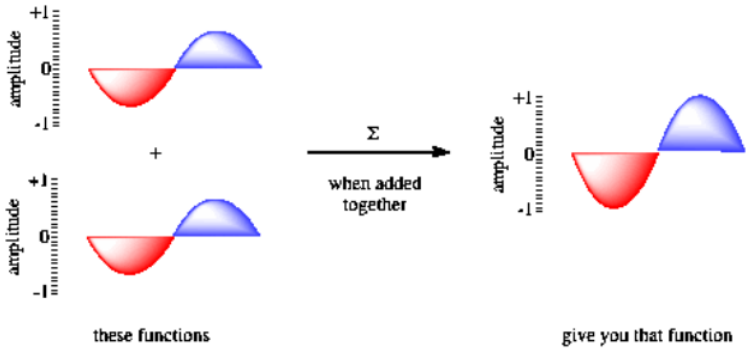

Figure 1.3.3: "Constructive interference" and wave addition. **The two waves are in phase with each other and give rise to a new, taller wave.**

If the waves are in phase with each other, constructive interference occurs, and a taller wave results. The peak of one wave adds onto the peak of another, and the trough of one wave falls into the trough of another. However, if the two waves are out of phase with each other, the peak of one falls into the trough of each other, and the wave disappears. That phenomenon is called destructive interference.

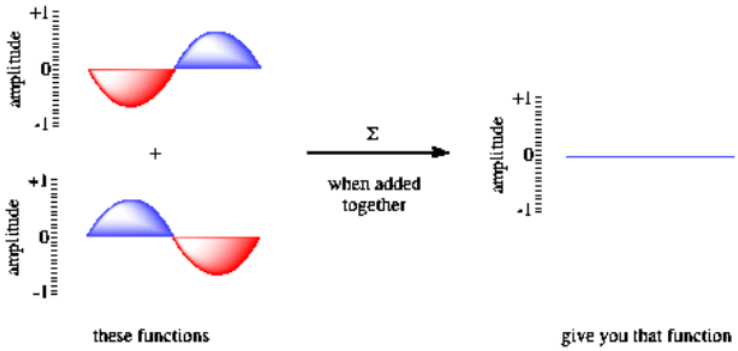

Figure 1.3.4: "Destructive interference" and wave addition. **The two waves are out of phase with each other and cancel each other out.**

One of the funny consequences of quantum mechanics is that you don't need two different electrons to cause an interference pattern. A single electron can be sent through a pair of parallel slits and result in an interference pattern. The electron passes through both slits at the same time. Sometimes an electron does not behave like a solid particle at all.

- Wave properties of electrons lead to interference patterns.

The wave properties of electrons also become important when considering bonding between atoms. As atoms are brought together to share electrons, constructuve and destructive interference between electrons leads to different consequences in different situations. We will look at these factors in a later chapter.

We mentioned that mathematical operations are sometimes performed on the wavefunction in order to predict other properties. For example, if you want to get an idea of where an electron is, you have to square the wavefunction. You take the wavefunction and multiply it by itself.

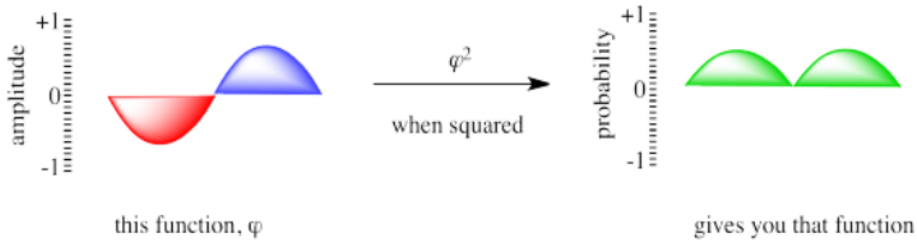

Figure 1.3.5: The chance of finding an electron at a particular position is predicted by the square of the wavefunction.
A wavefunction with one negative amplitude peak and one positive amplitude peak, when squared, gives two peaks with positive amplitude.

We lose some information when we perform math on the wavefunction. We no longer have "amplitude"; instead we have a probability. The curve we see is a statistical distribution that tells us where the electron is most likely to be found (the highest point on the curve) as well as many other places where the electron might also be found (the rest of the curve). We no longer have phase information, either; when the negative portion of the wave was multiplied by itself, it gave a positive number.

- The wavefunction can be used to narrow down the probable location of an electron.

? Exercise 1.3.2

What is the probability of finding an electron at a node?

Answer

The probability of finding an electron at a node is zero.

It is useful to keep the idea of particle-wave duality in mind, for a number of reasons. When we think of an electron as a particle, like a tennis ball, it is easy to expect that it will behave like a real tennis ball. After all, we know where the tennis ball is; you can see it, right there. But if an electron is a wave, like a wave on the ocean, it is not really restricted to one location. First of all, it's spread out (maybe over many miles, in the case of some waves). Secondly, it does not sit still long enough for you to decide it's exactly here or there. That's a little more like an electron. Also, if you had two holes in a wall, you could only throw a tennis ball through one hole at once. If a wave splashed against the wall, though, it could pass through both holes at once.

So, instead of thinking of an electron as a ball, maybe we should think about it as a cup of water. There's a stiff wind blowing, so there are waves on the surface of the water. Also, there's no gravity, so we can take the cup away and the water will hold together there, with its waves. Of course, the electron is no more liquid than it is a solid, but we often need familiar analogies to remind us of these different aspects of something we can't really see.

When Schrödinger worked out solutions for his equation, he found evidence of quantization again. Bohr had found that the distance between the electron and nucleus was quantized. However, Schrödinger found four different electronic properties that were quantized. One of these properties of an electron, called the principle quantum number, corresponds roughly to Bohr's quantized distance from the nucleus.

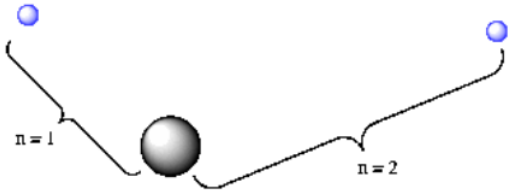

Figure 1.3.6: Schrödinger's math predicted that electrons should be found only at certain distances from the nucleus.

Two of the other properties have to do with the electron's direction from the nucleus. As it happens, a specific electron might be found in any direction from the nucleus. Alternatively, it might only be found in one direction or another.

Thinking in just two dimensions, suppose you have three tennis balls: a yellow one, a red one and a blue one. Imagine you are the nucleus of an atom and the tennis balls are electrons. In Bohr's model, the tennis balls might be found different distances away from you. Maybe one is five feet away, one is ten feet away, and one is twelve feet away. They cannot be found three feet away from you, or nine feet away or eleven feet away. They have to be found at those exact distances. However, they might be found in any direction: in front of you, behind you, to the left or right. They could all be lying in the same direction or all in different directions.

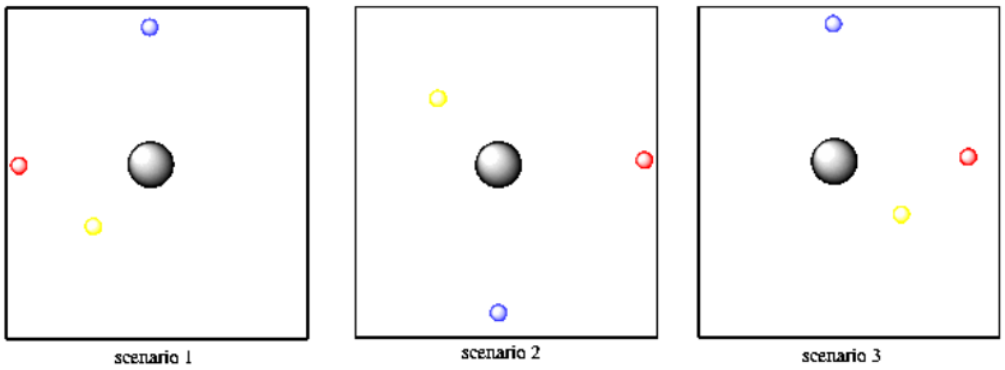

Figure 1.3.7: Schrödinger also found that particular electrons were restricted to lie in certain directions from the nucleus.

Three different scenarios showing an atome with three color-coded electrons. In all three scenarios, each electron is a different distance from the nucleus, but the value of the distances remain the same.

What Schrödinger's math seemed to be saying was that there was an additional restriction on where electrons could be found. In addition to a specific distance, the electron might be found only in certain directions from the nucleus. That direction relied on those other two quantized properties, called the magnetic and azimuthal quantum numbers. For one set of values, the electron could be found in any direction at all. For another set of values, though, the electron was restricted to lie along one particular axis.

- According to Schrödinger's solution, an electron in an atom is described by a group of "quantum numbers".
- The quantum numbers limit an electron to a general distance from the nucleus (like the shell in the Bohr model).
- Other quantum numbers limit the electron to certain regions of space around the atom.

In this model, maybe the yellow tennis ball has to be five feet way, but can be in any direction. But maybe the blue tennis ball has different quantum numbers. It is ten feet away and it can only be directly in front of you or directly behind you, but cannot be to your left or right. The red tennis ball, on the other hand, can only be found to your left or right, but never in front of you or behind you.

There is also a fourth quantum number, and it is called spin. Spin can't be described very well because it does not have an analogous big-world property such as distance or direction. However, it is an inherent property of an electron that can have either of two values. These values are sometimes called alpha and beta, or sometimes +1/2 and -1/2.

Despite the abstract nature of spin, it does have a real physical quality associated with it: if you place an electron in a magnetic field, it will interact differently with the magnetic field, depending on the value of its spin. Hence, spin is closely associated with magnetic properties of materials.

One of the basic rules of quantum mechanics is that no two electrons on the same atom can have the same two quantum numbers. You'll need some extra tennis balls to see how that works. Suppose you have two red balls, two yellow and two blue. The first yellow ball is found five feet away from you, in any direction. The second yellow tennis ball is also found five feet away from you

and in any direction. So far, the yellow tennis balls have the same properties, so they must have different spin. Of course, you can't tell that they have different spins unless you put them in a very strong magnetic field, but you know they are different because you have faith that Schrödinger did his math correctly.

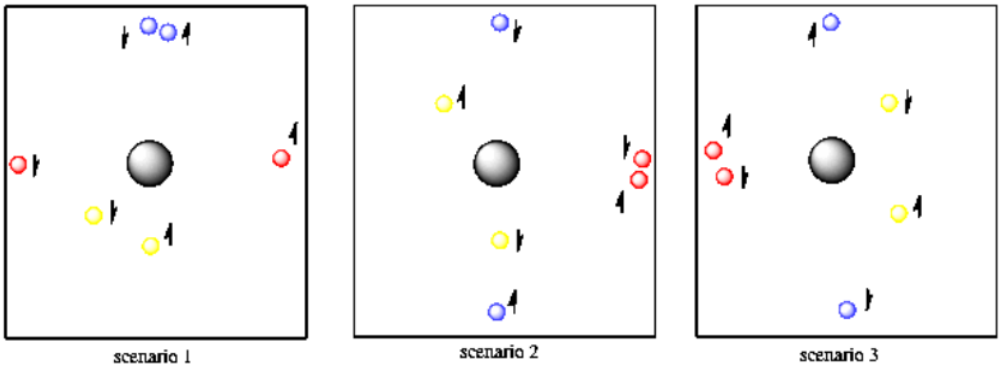

Figure 1.3.8: Spin (shown symbolically with an arrow) allows two different electrons to be the same distance from the nucleus and in the same direction, with the same energy

The two blue balls are ten feet away from you and they can only be found in front of you or behind you. It does not matter which. They could both be in front of you or both behind you or one in either direction. They also have two different spins.

Finally, the two red balls are also ten feet away from you, but they are found to your right or left (or both). They don't have to be a different distance away from you than the blue ones because they already have a different directional property, so we can repeat the distance property. The red balls also have two different spins, but you are having trouble telling which is which.

- Spin is another quantum mechanical property of electrons.
- Two electrons in the same atom with all other quantum numbers the same must have different spin.
- Spin has no real "big world" analogy. However, two electrons with different spin interact differently with a strong magnetic field.

One more thing. The quantum world is a little more subtle than that. The quantum world also involves concepts such as the uncertainty principle. The uncertainty principle says it is difficult to find an electron's exact location. Instead, we work with probability. Instead of being five feet away exactly, we only know that the yellow ball has a very good chance of being five feet away. There is a slight chance it is four and a half feet away, and a very small chance it is only four feet away.

Similarly, the red tennis ball may not be exactly in front of you, although it is probably no more than a few feet to the left or right. The blue tennis balls may also be a few feet off their axis someplace. We can't predict exactly where they will be.

? Exercise 1.3.3

Let's do an exercise in pointillism. You will need a pencil, a ruler, and pens of four different colors. Gel pens work better than ballpoint pens. In a pinch, you could use crayons, colored pencils or colored markers.

a. Draw a line in pencil 6 cm long. Mark the midpoint of the line.
b. Draw a second line 6 cm long and perpendicular to the first line, so that the midpoints of the two lines intersect. You should have a nice X or cross with arms 3 cm long.
c. Lightly draw in dashed lines, 10 cm long, halfway in between the prvious lines, so that the midpoints of all the lines intersect. You should have a new X or cross with arms 5 cm long, superimposed on the old cross but rotated by 45 degrees.
d. Choose one of the solid lines to work on. Place two marks along that line, 1 cm away from the midpoint in each direction. Using the first pen, start putting dots on the paper, centered on one of those 1 cm points. Keep adding dots as you move away from that 1 cm point in all directions, but there should be fewer and fewer dots as you go out. Expand your dots the same distance in all directions. Try not to cross the dashed lines, however. Aim for about a hundred dots (or 50 if you aren't very patient or if you are using a marker). You should end with a roughly circular mass of dots, centered 1 cm from the midpoint; the mass should get fainter along its edges and heavier and darker towards its center.
e. Now do the same thing, using the same pen, at the other 1 cm point along the same line.
f. Now do the same thing, with a second pen, 1 cm away from the midpoint in both directions along the second solid line.
g. Now do the same thing, with a third pen, 3 cm away from the midpoint in both directions along the first solid line.

h. Now do the same thing, with a fourth pen, 3 cm away from the midpoint in both directions along the second solid line. You should end up with four pairs of colored spots. Each spot should have higher value (heavier and darker) in the center and should fade to lower value away from its center.

Answer

Your drawing is beautiful. You should put it on your fridge, or else send it to your mother.

What you have produced is a simplified, two-dimensional electron probability map. Each color corresponds to a different "orbital", described by a set of principle, azimuthal and magnetic quantum numbers. Suppose your four colors describe the probability of finding a $2p_x$, a $2p_y$, a $3p_x$ and a $3p_y$ electron. With each dot, you sucessfully found the electron. The collection of dots tells you where a particular electron is most likely to be found; the highest value corresponds to the highest probability of locating an electron.

Compare and contrast your sets of dots with each other.

? Exercise 1.3.4

Construct another pointillist electron probability map, showing a two-dimensional slice through a 2s and 3s orbital in two different colors. Start with the same cross drawn in pencil, but this time when you put down dots with the first pen, centerd 1 cm from the midpoint of the cross, don't restrict them along one line. Let them be any direction from the midpoint. Use a hundred dots. Add a second set of dots with the second pen, centerd 3 cm from the midpoint of the cross, and in any direction from the midpoint. Compare and contrast the two sets of dots with each other, and with your previous map.

Why do electrons sort themselves out this way? One of the factors affecting electrons is electrostatic repulsion. They repel each other. To minimize that repulsion, the first pair of electrons might be a certain distance from the nucleus. A second pair may be a little farther away, so they're not too close to the first two. Once we reach a certain distance from the nucleus, electrons may be spread out enough that more than one pair could be found at that distance. Still, it is best to keep them a little farther away from each other. One pair may lie along one axis, and another pair may lie along a perpendicular axis. Of course, there is some repulsion between two electrons within the same pair, but the repulsion is actually decreased a little by having opposite spins (this is called spin pairing).

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1.4: Quantum Numbers

On the very, very small scale of the universe, things don't behave exactly as we are used to. Electrons are one example. They are not solid objects. They are waves. Or are they? On the nanoscale, things can be both particles and waves. An individual particle like an electron has mass, but it is spread out, not located in one position, and it has a wavelength.

The recognition of the wave properties of the electron provided a breakthrough in understanding its properties. Schrödinger's wave equation allowed scientists to make predictions about the electronic structure of atoms. Where are the electrons found? What is their energy?

The wavefunction is a mathematical expression that describes the electron. It can be plotted, like a graph, although it is a graph in three dimensions instead of two. The three-dimensional plot of the wavefunction is sometimes called an orbital. Often, chemists find it useful to look at pictures of orbitals in order to gain some sense of where electrons may be and how they may behave. Orbitals are something like the wave form of the electron.

In another sense, orbitals are related to probability maps -- the wavefunction squared reveals the probability of an electron being located at a particular position in space. It might be helpful to picture them that way. Suppose you could take a series of pictures of an electron and superimpose all of those pictures, like time-lapse photography. The result might look something like the drawing below, in which every dot represents where the electron showed up in one of our pictures. It's impossible to predict exactly where the electron would show up in the next picture, but it would be a pretty good guess that it would show up somewhere in the same rough circle as it did all of the other times.

1s

Of course, in three-dimensional space, we would be looking at a sphere instead of a circle. Maybe our picture is just a thin slice through the middle of that sphere. In the very center of the sphere, we would find the nucleus of the atom. So this electron is found within a certain distance of the nucleus, but it can be found in any direction. We call an electron that behaves this way an s electron.

The drawing above is labelled 1s, specifically. An atom can have many s electrons, but this is the one that is closest to the nucleus. It is the first s electron we would encounter if we started at the nucleus and moved outward through the atom.

Other electrons have different distributions about the atom. They are more likely to be located in different places. In solving the Schrödinger wave equation, it turns out that there are four variables that must be restricted to certain values if the equation is to have a sensible solution. The values of these variables determine where the electron is likely to be found around the atom, and roughly how much energy it will have.

The four quantum numbers are given the symbols *n*, *m*, *l*, and *s*. If you need to, you might remember that via the word aNiMaLS. Each quantum number tells you something different about the electron that it describes. The first one, *n*, tells you about distance. This number has to be an integer, so it could be 1, 2, 3, 4,... How far is the electron from the nucleus? If $n = 1$, the electron is as close to the nucleus as it could be; if $n = 4$, it is further away.

We sometimes think of *n* as describing the "shell" of the atom. Think of the old Bohr model of the atom, with electrons being found at different distances from the nucleus. It's like the atom is a set of Russian nested dolls, with one shell outside another. The first shell ($n = 1$) is close to the nucleus, the second ($n = 2$) is farther out, and so on.

The second number, *m*, tells you about spatial distribution, or shape. Maybe we know how close the electron is to the nucleus, but can it be found anywhere within a certain distance, or only in certain directions? This number has to be an integer, and it has to be less than *n*. If $n = 1$, $m = 0$. If m = 0, there is no "shape" preference, and the orbital is spherical. These numbers describe our 1s orbital, above.

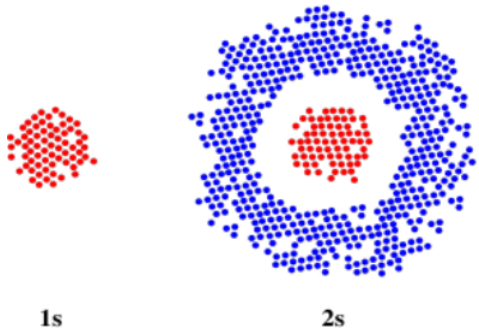
The third number, *l*, can be a positive or a negative integer. It can be anywhere from $+m$ to $-m$. If $n = 1$, and $m = 0$, then $l = 0$, too. The number *l* roughly correlates to orientation: in what direction is the orbital oriented? If there is only one possible value of *l*, then there must be only one possible orientation. That's true for something spherical; it does not matter which direction you look at it, because it will always look the same.

The final number is *s*. That's the spin quantum number and it can have only two values, regardless of the values of the other quantum numbers. It is either +1/2 or -1/2. Spin does not have a very tangible explanation in the macroscopic world, but if electrons have opposite spin values then they can occupy the same orbital. Thus, one pair of electrons can be described by each orbital.

Every electron in an atom must have a unique set of quantum number. If *n*, *m*, and *l* are the same for two electrons, then *s* must be different.

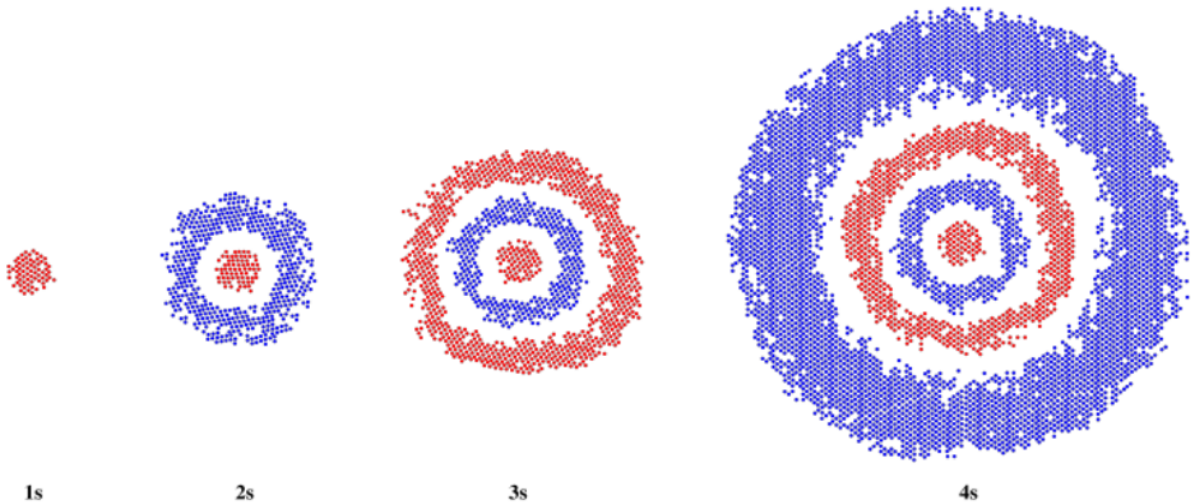
What happens when $n = 2$? In that case, the electron could be farther from the nucleus. The orbital will be bigger. In this case, *m* could either equal 0 again, or it could equal 1. If $m = 0$, like in the case of the 1s orbital, the orbital will be spherical. It will be a 2s orbital. Of course, $l = 0$, too, because *l* can only range from $+m$ to $-m$. This orbital will be spherical, too, because $m = 0$. It will look just like a 1s orbital, only bigger.

However, if we could look at a thin slice through the orbital, we would see a difference between a 1s and a 2s orbital. The 1s orbital is uniform throughout, but the 2s orbital has a phase change. Remember, it is a wave, and it has peaks and troughs. This is a three-dimensional, spherical wave, but it has a trough nested inside and the peak is on the outside (or vice versa).



Two clusters of electrons. Left: 1s: a single circle of electrons. Right: 2s: a circle of electrons surrounded by another circle.

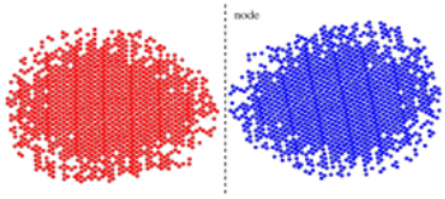
If we go further from the nucleus, we may encounter a 3s orbital and a 4s orbital. These, too, would look like bigger 1s orbitals from the outside. However, a thin slice through the middle would reveal the phase behavior of the orbotal, with peaks and troughs alternating from the center to the edge.



Electron depictions in levels 1s, 2s, 3s, and 4s. With each level, another concentric circle of electrons is added.

But let's step back for a moment. If n = 2, then m = 0 or 1, because m can be any integer less than n. We looked at the case in which m = 0; that's an s orbital. What if m = 1? The quantum number m describes the number of nodal planes that slice through the center of an orbital. If m = 1, we would take the regular s orbital and chop it through the middle (or loop a rope around the middle and tie

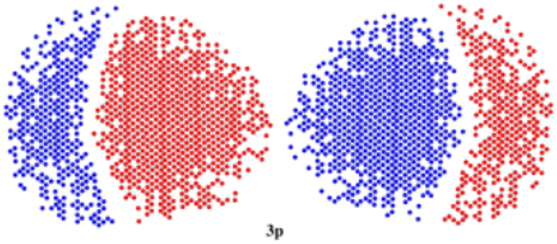
it tight) to get two different halves. These halves would be out of phase with each other. This type of orbital is called a p orbital. It has two lobes. On lobe is on one side of the nucleus and the other lobe is on the other side of the nucleus.



2p

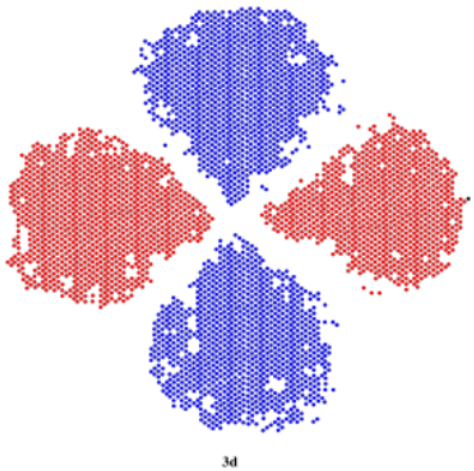
If m = 1, then l = 1, 0, or -1. That means this p orbital could be oriented in any of three directions. Since we are really talking about three different electrons, and they would repel each other, then they will get as far as possible from each other. The easiest way to do that, if you can imagine x, y, and z axes meeting at the nucleus, is to have one p orbital pointing along the x axis, one along the y axis, and one along the z axis. These three p orbitals are called $2p_x$, $2p_y$, and $2p_z$.

Just like with the s orbital, we could also have p orbitals farther from the nucleus. We can't have one closer to the nucleus; there isn't enough room closer in to the nucleus, and the quantum rules prevent a p orbital at energy level n = 1. A 3p orbital would look just like a 2p orbital, and could lie in three different directions. However, if we could take a thin slice through its middle and pull it out, we could see the same internal phase changes that we saw in the 2s, 3s, and 4s orbitals.



3p

So we can have one spherical s orbital at energy level 1, another spherical s orbital at energy level two, and three propellor-shaped or dumbell-shaped p orbitals at energy level 2. What about energy level 3? If n = 3, then m = 0, 1, or 2. That means there is a third shape possible at this level. To see the shape, we would take a p orbital and pinch it in half again, but in a direction perpendicular to the one we chose the first time. This would result in a cloverleaf shape. This is called a d orbital. There would be five different orientations of a d orbital, because l = 2, 1, 0, -1, or -2.

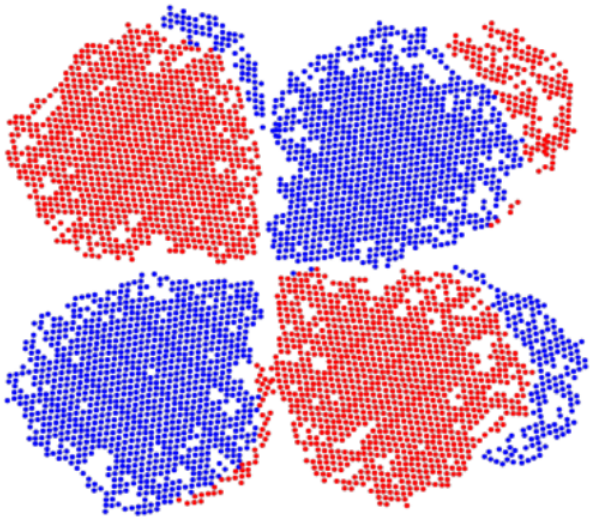


3d

The d orbitals can point their lobes between the axes: the d_{xy} has lobes in the xy plane but between the x and y axes; the d_{yz} is in the yz plane with lobes between the y and z axes; the d_{xz} is in the xz plane and its lobes point between the x and z axes. The two remaining d orbitals point along the axees. The $d_x2_{-y}2$ orbital points the lobes of its cloverleaf along the x and y axes. The d_z2

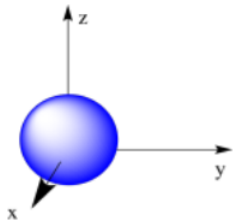
orbital is not a clover shape like the others; it looks like a p orbital emerging from a donut. The two lobes extend along the z axis, and the donut (usually called the toroid) sits in the xy plane.

We could go one step further, although you are not likely to encounter the next level (many students only need to work with s and p orbitals). If $n = 4$, we could have s, p, or d orbitals for the values of m that we have seen before, but if $m = 3$, then we will have to chop the d orbital shape into additional lobes again, producing a funky f orbital. There are actually several ways this happens, producing several different shapes; only one is illustrated below. An f orbital can have seven possible orientations.



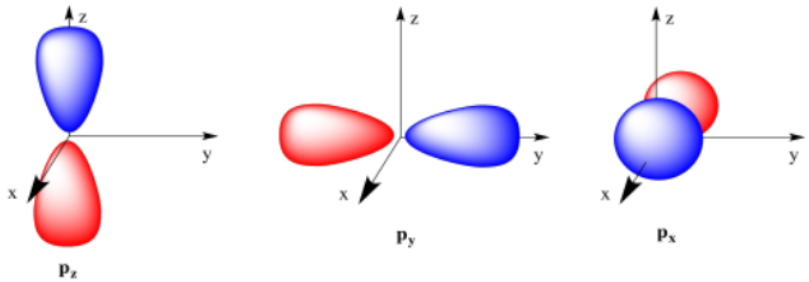
4f

More commonly, the overall shapes of these orbitals are depicted in "cartoon" form. For example, an s orbital is usually just shown as a ball or sphere.



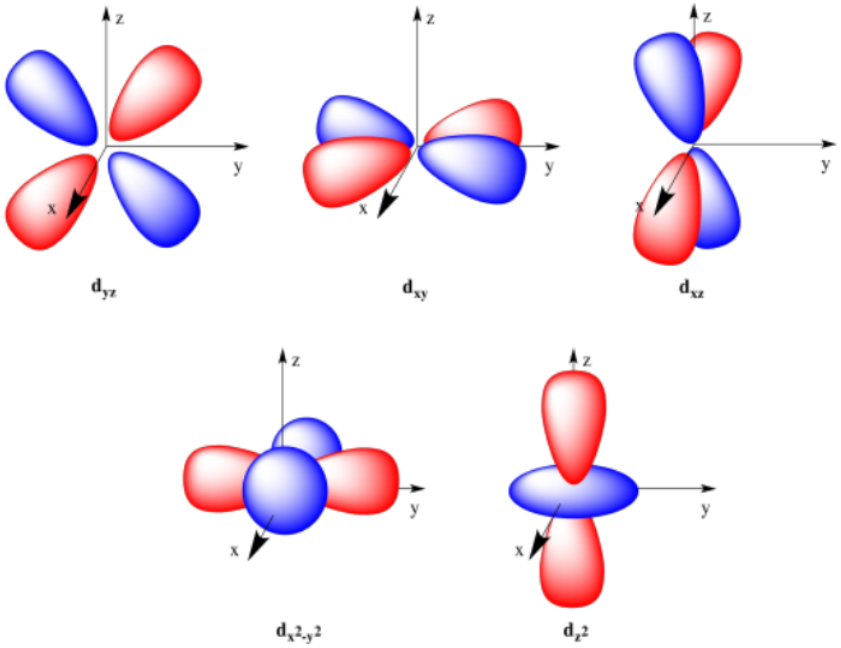
s

The three p orbitals are shown here. Each one is a dumbell shape pointing in a different direction along Cartesian coordinates (x, y, z).



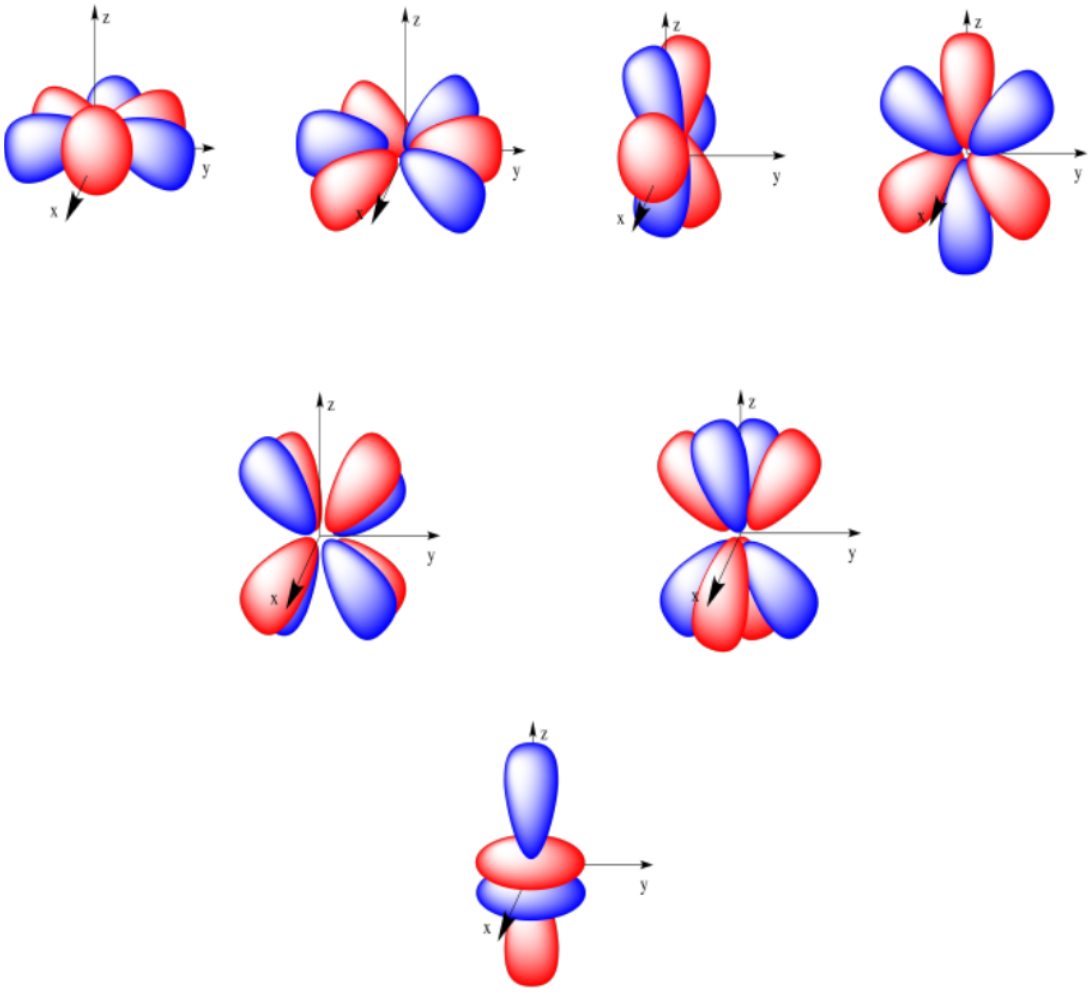
p_z p_y p_x

There are five d orbitals. Four of them are cloverleaf shapes, but the fifth contains a toroid (or donut shape).



Five d orbitals. d(yz), d(xy), d(xz), and d(x2-y2) are shaped as clover leaves. d(z2) has a donut shape.

The seven f orbitals are shown below. Four of them look like orange segments, lying on one plane. Two of them look like the cloverleaf d orbitals that have split into two layers. The last one is like the d_z2 orbital, only it has two toroids instead of one.



We can summarize quantum numbers in a couple of ways. Remember, quantum numbers are just variables in the Schrödinger wave equation that have to take certain values in order for the equation to have a sensible solution. These values are usually integers, and they depend on each other. There is something different about the quantum numbers that describe each electron in an atom; in part, that helps to keep the electrons away from each other.

- Quantum numbers are constrained to specific values.
- Each electron in an atom has a unique set of quantum numbers.

number	*n*	*m*	*l*	*s*
rules	integer	less than *n*	-*m* to +*m*	1/2 or -1/2

For example, the 1s electrons on a helium atom have to be different from each other somehow. They have the same values of *n*, *m*, and *l*, so s is different.

number	*n*	*m*	*l*	*s*
rules	integer	less than *n*	-*m* to +*m*	1/2 or -1/2
1st set (1s)	1	0	0	1/2
	1	0	0	-1/2

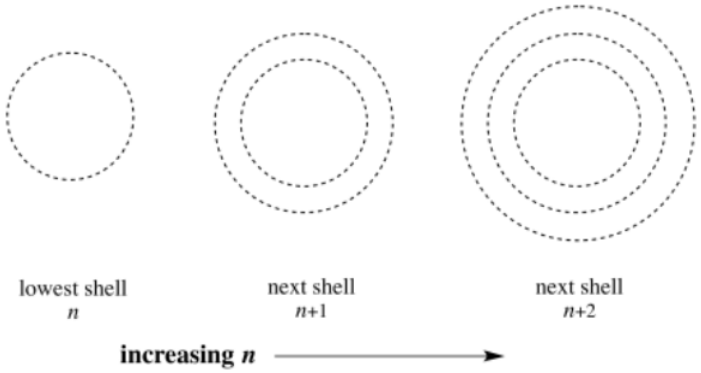
As we proceed to the second "shell" of electrons around the atom, m can vary, and so can l. That means we get different shapes and orientations of the allowed waves for the electron. We'll ignore s in the following table; in each case, there are two possibilities, *s* = 1/2 and *s* = -1/2; two electrons can be described by each orbital.

number	*n*	*m*	*l*	orbital description
rules	integer	less than *n*	-*m* to +*m*	
1st set (1s)	1	0	0	spherical
2nd set (2s)	2	0	0	spherical
3rd set (2p)	2	1	-1	dumbbell (orthogonal directions)
	2	1	0	
	2	1	-1	

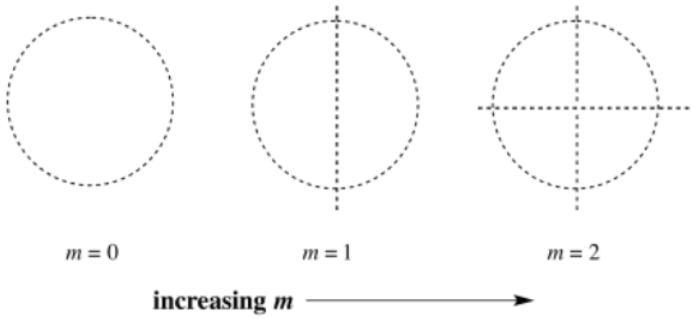
When we get to the 3rd shell, there are even more variations.

number	*n*	*m*	*l*	orbital description
rules	integer	less than *n*	-*m* to +*m*	
4th set (3s)	3	0	0	spherical
5th set (3p)	3	1	-1	dumbbell
	3	1	0	
	3	1	1	
6th set (3d)	3	2	-2	cloverleaf
	3	2	-1	
	3	2	0	
	3	2	1	
	3	2	2	

Overall, the quantum number *n* indicates the shell in which an electron is found. That is, it indicates distance from the nucleus.



In addition, *n* can also indicate the number of spherical nodes in an orbital. As we saw in the progression of s orbitals, each type of orbital (s, p, d, f) becomes "nested" when we move to higher levels; a 2s orbital is like a 1s orbital nested inside a bigger, spherical shell, with a spherical node in between the two parts. A 3s orbital contains one more spherical node (two total), and so on.



A set of three circles. m-values shown are 0, 1, and 2. As m increases by 1, a new dividing line cuts the circle in half.

Quantum number m indicates the shape of the orbital. Is the orbital divided into different lobes? Described in a different way, it indicates how many nodes or nodal planes there are between these lobes. An s orbital is completley shpherical, with no lobes. A p orbital has a nodal plane cutting it in half, forming two lobes. A d orbital has two nodal planes, usually resulting in four lobes, and so on.

If the orbital does have a non-spherical shape, *l* corresponds to different directions in which it can be oriented. Of course, *s* is the spin, and two electrons in the same orbital have to have opposite spins.

? Exercise 1.4.1

Provide labels (e.g. 1s, 3p, etc) for the following orbital descriptions.

a. a spherical orbital in the second shell of the atom.
b. a dumbbell-shaped orbital in the third shell of the atom.
c. a cloverleaf-shaped orbital in the third shell of the atom.
d. an orange-slice shaped orbital in the fifth shell of the atom.
e. an orbital that looks like one ball nested inside a second ball netsed inside a third ball

Answer a:

2s

Answer b:

3p

Answer c:

3d

Answer d:

5f

Answer e:

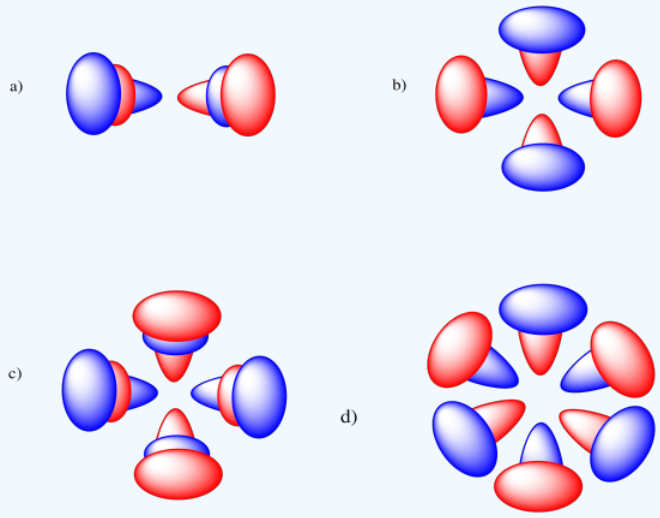
4s

Exercise 1.4.2

Draw cartoons of the following orbitals.

a. a 4p orbital.
b. a 4d orbital
c. a 5d orbital
d. a 6f orbital

Answer

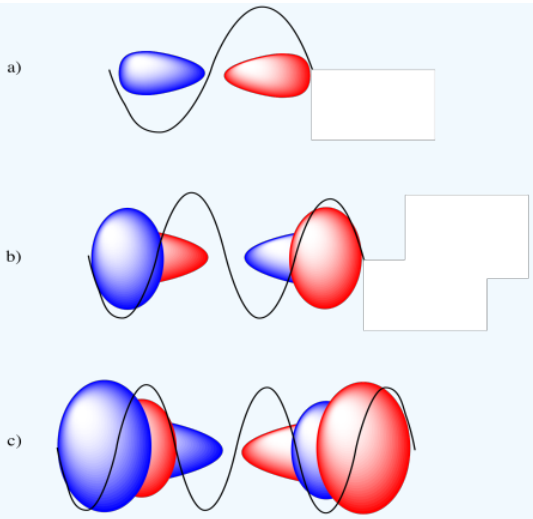


Exercise 1.4.3

As we go to higher shells in the atom, we start to see additional spherical nodes in the orbitals. Make a sketch of each orbital below, and superimpose a repeating sine wave over the drawing such that the nodes in the sine wave correspond to the nodes in the orbital.

a. a 2p orbital
b. a 3p orbital
c. a 4p orbital

Answer



From one end of the orbital to another, the 2p orbital covers a full sine wave, a 3p orbital covers two full sine waves, and a 4p orbital covers three full sine waves.

What happens to the number of sine wavelengths as we go from one shell to the next?

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1.5: The Aufbau Process

The quantum mechanical model lets us take an atom and make predictions about its properties. All we need to know is how many protons it has (and how many electrons, which is the same as the number of protons for a neutral atom). We can predict the properties of the atom based on our vague idea of where its electrons are and, more importantly, the energy of those electrons.

How electrons fill in their positions around an atom is called the *Aufbau Process* (German: "building-up" process). The Aufbau Process is all about keeping electrons at their lowest possible energy.

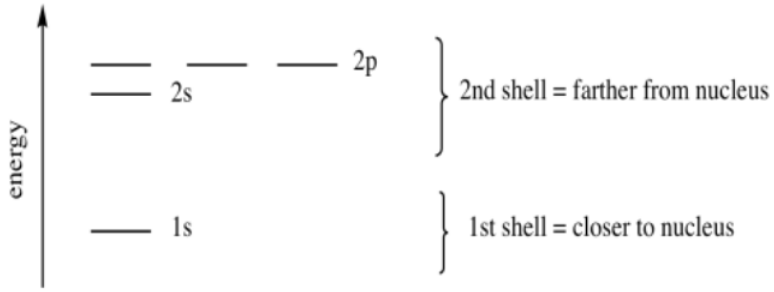
A corollary of Coulomb's law is that the energy of an electron is affected by attractive and repulsive forces. The closer an electron to the nucleus, the lower its energy. The closer an electron is to another electron, the higher its energy.

Of course, a basic principle of thermodynamics is that a system will proceed to the lowest energy possible. That means, if an atom has only one electron, the electron will have quantum numbers that place it at the lowest possible energy. It will be as close as possible to the positive nucleus.

If an atom has a second electron, it will also be as close as possible to the nucleus. It could have the same quantum numbers as the first electron, except for spin. There is a trade-off, of course, because those two electrons will be close enough to repel each other. However, if it is a choice between that and taking a position much farther from the nucleus, the second electron will go ahead and pair up. These two electrons are sometimes described as being "in the same orbital"; their first three quantum numbers are the same, so that are probably found somewhere in the same region of space. This first orbital, which has no directional restrictions, is called the 1s orbital.

Figure 1.5.1: The 1s orbital has no directional preference. It can be found in any direction from the nucleus.

There is only room for one orbital at this distance from the nucleus. A third electron has to occupy another orbital farther away, the 2s orbital. Again, this is a spherical orbital: the electron can be found in any direction. The 2 in 2s means the principle quantum number is two (corresponding to the second general energy level). The s is a code for other quantum numbers; it means the electron can be found in any direction, just like the 1s electrons.



A blank orbital diagram including 1s, 2s, and 2p. The second shell is higher in energy and farther from the nucleus.

The second energy level is large enough to accommodate additional orbitals, but they are a little farther from the nucleus. These are called the 2p orbitals. They are regions of space along the x, y and z axes. There are three orbitals of this type, and they are just called p_x, p_y and p_z to remind us that they are orthogonal to each other.

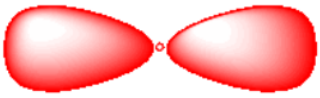


Figure 1.5.2: The $2p_x$ orbital has a directional preference. It can be found only along one axis.

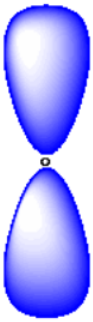
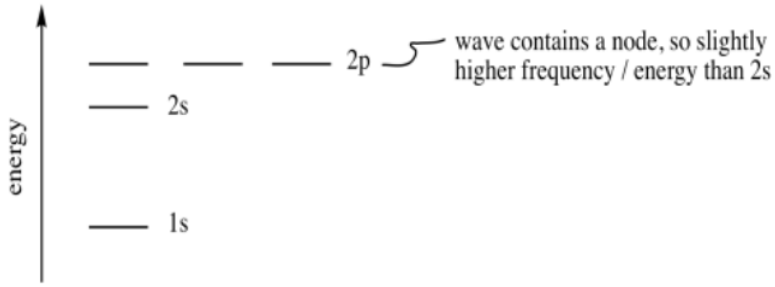


Figure 1.5.3: The $2p_y$ orbital has a directional preference. It can be found only along one axis.

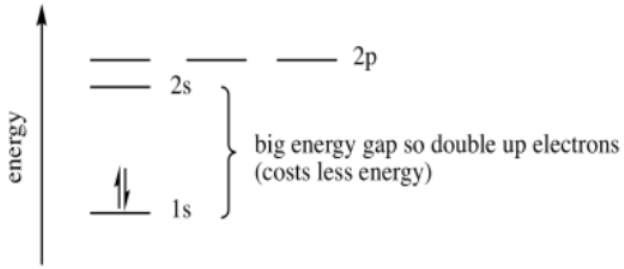
Expressed in a different way, an electron with principle quantum number 2 can have four different combinations of its other quantum numbers. These combinations are denoted 2s, $2p_x$, $2p_y$ and $2p_z$. The three 2p combinations are a little higher in energy than the 2s orbital.



An orbital diagram including 1s, 2s, and 2p. The 2p orbital contains a node, so it is slightly higher in frequency and energy than 2s.

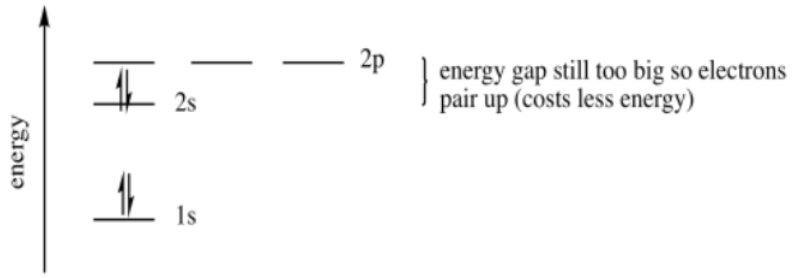
Why is the 2p level higher than the 2s level? That's related to the wave behavior we saw before. With a node in the middle, the 2p orbital behaves as a higher-frequency wave than the 2s orbital. A higher-frequency wave has higher energy. So, a p orbital, with one node, is always higher in energy than an s orbital, with no node.

Once again, we have several energy levels available for an electron, but they will surround the atom in a way that lowers energy. A second electron remains in the lower-energy 1s orbital.



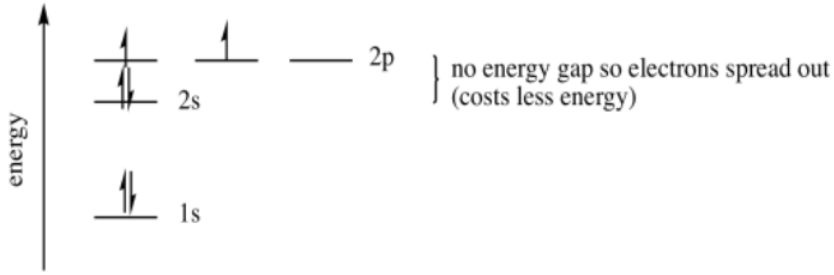
An orbital diagram including 1s, 2s, and 2p. 1s has two electrons in it. The other orbitals are blank.

A third electron will go into the 2s orbital. It's the lowest in energy. What about a fourth? Does it go into the 2s or a 2p? Once again the pairing energy is not quite as big as the energy jump up to the 2p orbital. The fourth electron pairs up in the 2s orbital.



Orbital diagram with 1s, 2s, and 2p. 1s and 2s have two electrons in them. The energy gap is still too big between 2s and 2p, so the electrons pair up in 2s.

A fifth electron goes into one of the 2p orbitals. It does not matter which one. We will say it is the p_x, arbitrarily. A sixth electron again could either pair up in the p_x, or it could go into the p_y. But the p_y level is really the same as the p_x, just in a different direction. The energy is the same. That means a sixth electron will go into the p_y rather than pair up in the p_x, where it would experience extra repulsion.



Orbital diagram with 1s, 2s, and 2p. 1s and 2s are both filled with two electrons. The 2p shell has two electrons total, with two orbitals having one each. The third orbital is empty.

Note that the p orbitals are often drawn a little differently. For example, p orbitals are usually drawn in a way that shows that they have phase. Either the two lobes are colored differently to show that they are out of phase with each other, or they are shown with one lobe shaded and the other left blank.

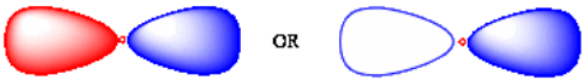


Figure 1.5.4: The $2p_x$ orbital shown with phase information.

A p orbital with both lobes out-of-phase. Left: the two lobes are colored red and blue. Right: one lobe is blank, the other is filled in with blue.

This pattern of "filling" electrons is generally followed for all of the elements. The tally of how many electrons are found in each orbital is called the electron configuration. For example, hydrogen has only one electron. Its ground state configuration (that means, assuming the electron hasn't been excited to another orbital via addition of energy) is $1s^1$.

On the other hand, an atom with six electrons, such as the element carbon, has the configuration $1s^2 2s^2 2p_x^1 2p_y^1$. There is one electron in each of two p orbitals in order to avoid repulsion, which would happen if they were in the same one.

? Exercise 1.5.1

Write electron configurations for the following elements.

a. oxygen, O
b. sulfur, S
c. silicon, Si
d. nitrogen, N
e. argon, Ar
f. neon, Ne

Answer a:

O: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

Answer b:

S: $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_x^2 3p_y^1 3p_z^1$

Answer c:

Si: $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_x^1 3p_y^1$

Answer d:

N: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

Answer e:

Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$

Answer f:

Ne: $1s^2 2s^2 2p^6$

Electron configuration and the periodic table

You may already know that electron configuration is the reason the periodic table works the way it does. Mendeleev and others noticed certain elements had very similar properties, and that's because they have very similar electron configurations. Lithium has configuration $1s^2 2s^1$ and its alkali sister, sodium, has configuration $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$. In both cases, the last electron added is an unpaired s electron. The last electron, or last few electrons, added to an atom generally play a strong role in how the atom behaves. This "frontier" electron is the one at the outer limits of the atom. If the atom is to interact with anything, the frontier electron will encounter the thing first. In contrast, the "core" electrons closer to the nucleus are more protected from the outside.

- The order of electrons in an atom, from lowest to highest energy, is:
  - 1s
  - 2s
  - 2p

There are some shortcuts we take with electron configurations. We tend to abbreviate "filled shells" (meaning all the possible orbitals with a given principle quantum number are filled with electrons) and filled "sub-shells" (like 2s or 2p). First of all, in the case of p orbitals, if all the p orbitals are filled, we might just write $2p^6$ instead of $2p_x^2 2p_y^2 2p_z^2$, because there is only one way all the orbitals could be filled. However, we wouldn't necessarily write $2p^2$ instead of $2p_x^1 2p_y^1$, because we may wish to make clear that the configuration does not involve two electrons in one p orbital at that point, as in $2p_x^2 2p_y^0$.

Also, we dispense with orbital labels entirely to ignore core electrons in a filled shell. For example, instead of writing $1s^2 2s^1$ for lithium, we can write [He]$2s^1$. Instead of writing $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$ for sodium, we write [Ne]$3s^1$. The [He] means all the electrons found in a helium atom, which is a noble gas. The [Ne] means all the electrons found in a neon atom. A noble gas is an unreactive element with a filled shell: helium, neon, argon, krypton, xenon or radon.

[He] = $1s^2$ so [He]$2s^1$ = $1s^2 2s^1$

[Ne] = $1s^2 2s^2 2p^6$ so [Ne]$3s^1$ = $1s^2 2s^2 2p^6 3s^1$

The electrons beyond the noble gas shell are called the valence electrons.

? Exercise 1.5.2

Write abbreviated electron configurations for the following elements.

a. chlorine, Cl
b. calcium, Ca
c. aluminum, Al
d. phosphorus, P

Answer a:

Cl: $[Ne]3s^2 3p_x^2 3p_y^2 3p_z^1$

Answer b:

Ca: $[Ar]4s^2$

Answer c:

Al: $[Ne]3s^2 3p_x^1$

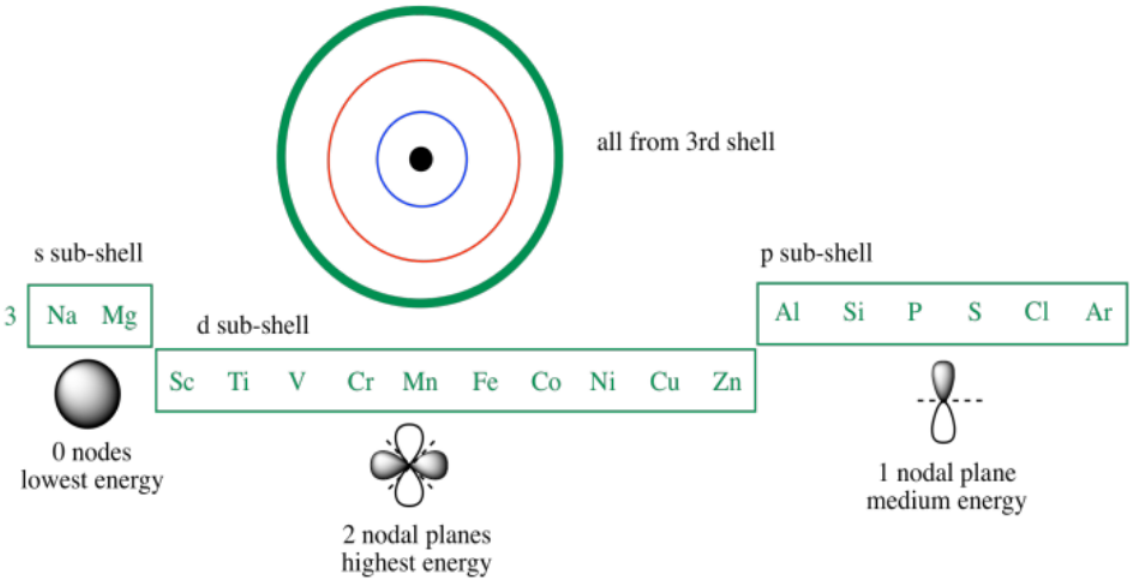
Answer d:

P: $[Ne]3s^2 3p_x^1 3p_y^1 3p_z^1$

Principle quantum number 3 actually allows a third set of orbitals. These are called the d orbitals. The d orbitals are a little like p orbitals, but they are two-dimensional rather than one-dimensional. A d electron, for example, might extend along the x axis *and* the y axis, but not in between the axes.

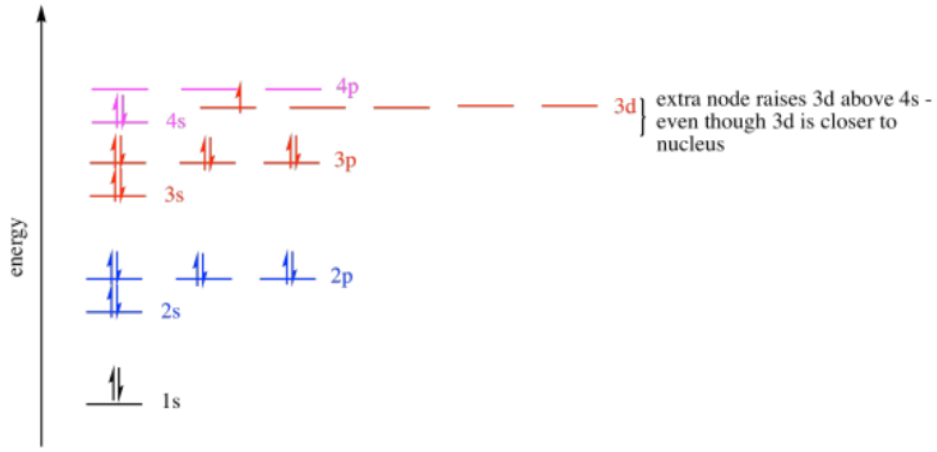
The d orbitals have five allowed orientations. They can be found along the x and y axes (called d_{xy}), along the x and y axes (called d_{xz}), or along the y and z axes (called d_{yz}). Alternatively, they might be found in between the axes instead, rotated 45 degrees away from one of the other d orbitals. One of these, called the $d_x2_{-y}2$ orbital, is found between the x and y axes. In the same way, you could imagine an orbital between the x and z and between the y and z axes, but that would make six different orientations. Quantum mechanical rules don't allow that. As a result, two of the possible combinations collapse into a mathematical sum, making just one orbital. We call this one the d_z2 orbital.

If we look at the third row in the periodic table, we see those three sub-shells (the s, then the p, then the d). Again, the 3s sub-shell fills first. With fewer nodes, this orbital is lower in energy than either the 3p or the 3d. The 3d orbital has more nodes than the 3p, so it is even higher in energy than the 3p. In fact, it is even a little higher in energy than the 4s orbital, the first sub-shell of the next shell.



A breakdown of the third shell. a and Mg have the s subshell, with zero nodes and the lowest energy. The p subshell, with elements Al through Ar, have one nodal plane and medium energy. The d subshell, with elements Sc through Zn, have two nodal planes and the highest energy.

So, the 3d orbitals are higher in energy than the 3p orbitals. The 3d level is very similar in energy to the 4s level. For that reason, calcium's last electrons go into a 4s orbital, not a 3d orbital. Calcium behaves much like magnesium as a result.



Orbital diagram from 1s to 4p. The extra node raises 3d above 4s, even though 3d is closer to the nucleus.

- The order of electrons in an atom, from lowest to highest energy, is:
  - 1s
  - 2s
  - 2p
  - 3s
  - 3p
  - 4s
  - 3d
  - 4p
- As a consequence, all of the alkali metals (Li, Na, K, Rb, Cs, Fr) have similar properties, because they have similar electron configurations [Noble]s^1
- All of the alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra) have similar properties, because they have similar electron configurations [Noble]s^2

? Exercise 1.5.3

Write abbreviated electron configurations for the following elements.

a. iron, Fe
b. nickel, Ni
c. mercury, Hg
d. lead, Pb
e. arsenic, As
f. titanium, Ti

Answer a:

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

Answer b:

nickel, Ni: [Ar]$4s^2 3d^8$

Answer c:

mercury, Hg: [Xe]$6s^2 4f^{14} 5d^{10}$

Answer d:

lead, Pb: [Xe]$6s^2 4f^{14} 5d^{10} 6p^2$

Answer e:

arsenic, As: [Ar]$4s^2 3d^{10} 4p^3$

Answer f:

titanium, Ti: $[Ar]4s^2 3d^2$

Complications in transition metals

Some subtle variations are encountered across the transition metals. Filling the d orbitals is not as straightforward as the s and p orbitals. For example, in the first row of the transition metals, all but two elements have configurations $[Ar]4s^2 3d^x$. However, chromium has configuration $[Ar]4s^1 3d^5$, and copper has configuration $[Ar]4s^1 3d^{10}$. Similarly, two elements in the third row of the transition metals do not have the configuration $[Xe]6s^2 5d^x$. Platinum has configuration $[Xe]6s^1 5d^9$, and gold has configuration $[Xe]6s^1 5d^{10}$. Things are even worse in the second row of transition metals, in which half of the elements do not follow the "correct" order of filling. Niobium is $[Kr]5s^1 4d^4$, molybdenum is $[Kr]5s^1 4d^5$, ruthenium is $[Kr]5s^1 4d^7$, silver is $[Kr]5s^1 4d^{10}$, and palladium does not have any s electrons at all in its outer shell: it is $[Kr]4d^{10}$.

Sc = $[Ar]4s^2 3d^1$ and Ti = $[Ar]4s^2 3d^2$ and V = $[Ar]4s^2 3d^3$ but Cr = $[Ar]4s^1 3d^5$

What's going on? The main reason things are complicated here is that the 4s and 3d levels are quite close to each other in energy (as are 5s and 4d, and 6s and 5d). As a result, slight changes are causing the electron configuration to vary from one element to the next. Pairing energy is certainly a culprit; that's the amount of energy it costs to put two electrons in the same orbital. If the electron configuration is $[Ar]4s^2 3d^x$, then two electrons are always being forced to occupy the same space, the 4s orbital. That costs energy, because electrons repel each other. Pairing energy changes from one element to another, but by the time we reach chromium, pairing energy is evidently high enough (or the difference in energy between the 4s and 3d levels is low enough) that the energy is lower if the electrons just spread themsleves out.

So, a balance has to be struck between pairing energy and orbital energy. Both are changing as we move from one element to the next. Sometimes the pairing energy of the s orbital is small compared to the energy jump to the d orbital, so two electrons go into an s orbital. Sometimes the pairing energy of the s orbital is large compared to the energy jump to the d orbital, so the electron goes in a d orbital. Of course, the pairing energy of the d orbitals also plays a role in some cases, and it also varies from one element to another.

Well, what are you supposed to do with that information? Usually, you are expected to know the most general rule (such as filling like $[Ar]4s^2 3d^x$). Twenty-one out of thirty transition metals have two s electrons and some number of d electrons. Sometimes, you are expected to know the most common exceptions; those are chromium and copper (there's a lot more chromium and copper in the world than there is niobium), and they are relatively easy to remember because one has a half-filled d shell and the other has a completely filled d shell.

- Most transition metals have two s electrons and some d electrons.
- Copper and chromium have only one s electron; the other one is "promoted" into a d orbital.
- You can keep track those two exceptions if you remember that copper has one electron in each d orbital and copper has an electron pair in each d orbital ("half-filled d" and "filled d" is a good rule to remember).

One more important thing to know is that these cases describe only the transition metals in their elemental state. They do not apply to compounds, in which the transition metal is found bound with atoms of different types to form salts or other materials. The atoms in a chunk of silver metal have the electronic configuration $[Kr]5s^1 4d^{10}$, but the atoms in a silver ion, which have one less electron, have configuration $[Kr]4d^{10}$. The missing electron is lost from the s orbital, not from the d. In general, compounds and ions of the transition metals do not have s electrons in the valence shells. For example, the atoms in pure molybdenum metal may have configuration $[Kr]5s^1 4d^5$, but the molybdenum atoms in compounds, if they still have all their electrons, have configuration $[Kr]4d^6$.

- Most often, transition metals in ions and compounds have only d electrons in their valence shell.

Why would compounds be different? The difference is easiest to see in the case of ions, in which the metal loses one or more electrons. Because it not longer has the same amount of electrons as protons, it becomes positively charged (it has more positive protons than it has negative electrons). The positive charge causes the electrons to become more attracted to the nucleus; that atom contracts or shrinks.

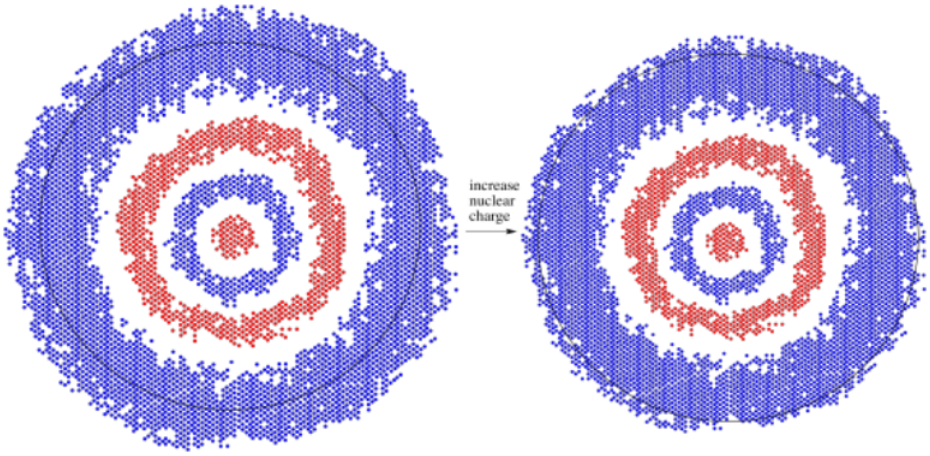


Figure 1.5.5: A 4s orbital responds to an increase in positive charge when an electron is lost to form a cation.
Two atoms, represented as four concentric circles. Increasing nuclear charge reduces the diameter of the atom.

Different orbitals may have different responses to this change in the metal atom. Because the d orbital is one level below the s orbital of similar energy (it is a 3d orbital, for example, compared to a 4s orbital), it is closer to the nucleus. It experiences that positive charge more strongly and contracts more than the s orbital. As a result, its energy is lowered even more than the s orbital's energy by this stronger electrostatic interaction with the nucleus.

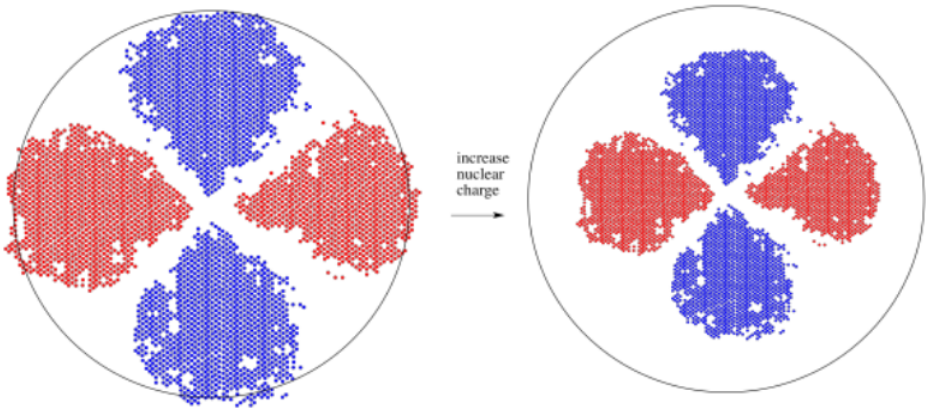
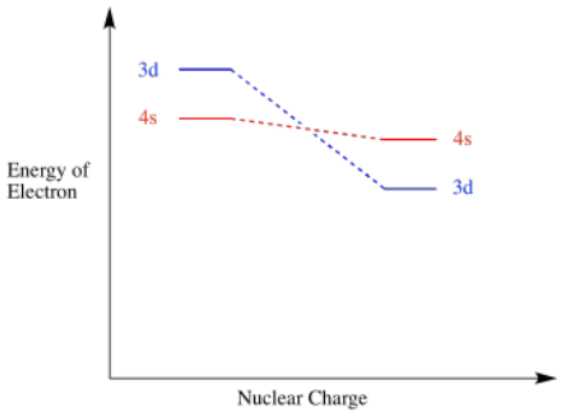


Figure 1.5.6: A 3d orbital responds to an increase in positive charge when an electron is lost to form a cation.

As a result of the charge when a transition metal atom becoms an ion, the 3d level falls below the 4s level. Remember, these two orbitals are very close in energy to begin with, so small changes can reverse their order. Similarly, the 3d level generally falls below the 4s level anytime a transition metal joins other atoms to become part of a compound.



A chart: nuclear charge vs. energy of electron. Initially, 3d is higher than 4s in energy. Both 3d and 4s orbitals decrease in energy as nuclear charge increases. However, 4s decreases slower than 3d.

The way the 3d electrons fall in energy with increasing charge is one of the factors making the electron configurations of transition metals complicated.

- In ions and compounds, the d orbital is lower in energy than the s orbital of the next level, not the other way around.

Exercise 1.5.4

Draw an orbital filling diagram (arrows and energy levels) for:

Reminder: The filling diagrams for transition metals and transition metal ions/complexes differ.

A. Ni

B. Co^{+2}

C. Fe^{+3}

D. Ti^{+4}

E. V

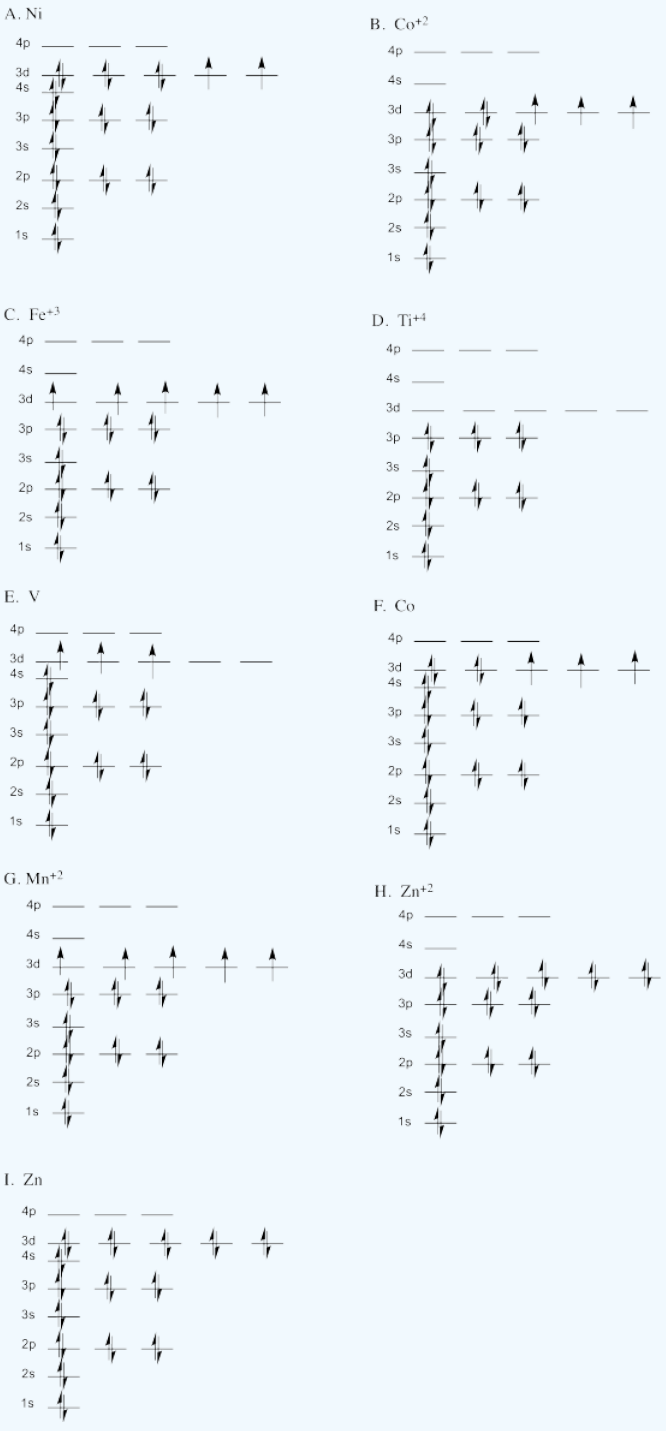
F. Co

G. Mn^{+2}

H. Zn^{+2}

I. Zn

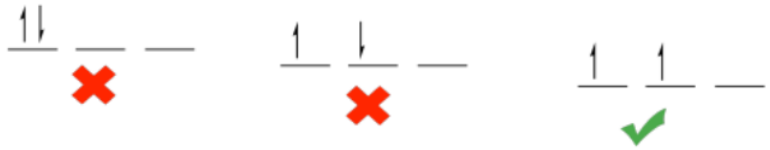
Answer



Finishing Touches

Earlier, we saw that electrons tend to go into unfilled orbitals before pairing up in the same one, provided other orbitals are available at the same energy level.

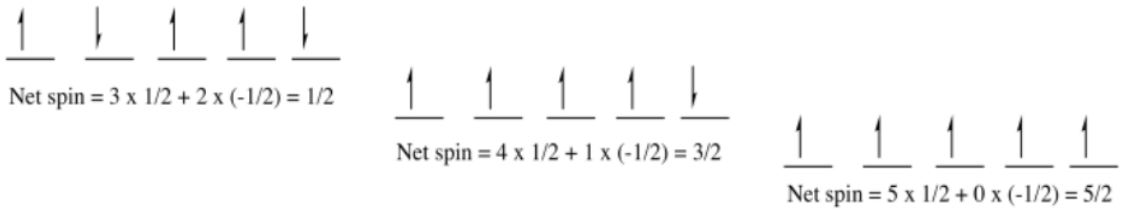
This idea is part of *Hund's rule*. Hund's rule says, in part, that if you have two electrons, and there are two orbitals available at the same energy level, then one electron will go into each orbital. It's partly about avoiding electron-electron repulsion that would occur if you put two electrons into the same orbital -- that is, into the exact same region of space.



Left: incorrect: two electrons in one orbital with two blank orbitals. Middle: incorrect: two electrons in two orbitals, but with opposite spins. Right: correct: two electrons in two orbitals, both with spin up.

It's partly something else though, and that is a quantum mechanical bias toward *high multiplicity*. Multiplicity refers to the number of *unpaired* electrons there are in an atom or molecule. By paired, we mean two electrons that have opposite spin. Remember, spin is a fundamental quantum mechanical property of an electron. It can only have two values, and the numerical values seem arbitrary but it's important to know that the two possible options are opposite numbers: they can be either +1/2 or -1/2. Unpaired electrons would be those that don't have a partner somewhere with an opposite spin value.

To illustrate that idea, consider the following drawing. It shows three different ways a set of five electrons might fill in a group of five orbital (maybe the 3d level; suppose these are the valence electrons on a vanadium atom). Often, electrons in orbital diagrams are indicated by arrows, with the direction of the arrow indicating the spin. An up arrow means spin = 1/2; a down arrow means spin = -1/2.



Three different shells with different net spins. All shells have one electron per orbital and a total of five orbitals. Left, highest: three up electrons and two down electrons give a net spin of 1/2. Middle: four up electrons and one down electron give a net spin of 3/2. Right, lowest: five up electrons gives a net spin of 5/2.

In two cases, some of the electrons are paired; they have a partner somewhere with opposite spin. The multiplicity is basically a tally of how many unpaired electrons are left over; you get the multiplicity by adding up the spin value of all the electrons. One case has all the electrons unpaired. All of the electrons have the same spin. Multiplicity is maximized in this case. *Hund's rule* says this case has the lowest energy.

What about if two electrons occupy the same orbital? We could still maximize multiplicity by keeping their spins "parallel"; that is, they could both have spin = 1/2 or both spin = -1/2. That does not happen, though. Remember the quantum rule that no two electrons on the same atom can be described by the same set of quantum numbers. In other words, each electron on the atom must have a unique identity. This rule has a name, too: the *Pauli exclusion principle*.

- Electrons always occupy the lowest energy orbital available.
- Multiplicity is maximised; electrons are given the same spins when possible.
- However, when they are found in the same orbital, two electrons must have opposite spin.

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1.6: The Periodic Table and Periodic Trends

The aufbau process is a set of rules that allows us to predict the electronic configuration of an atom if we know how many electrons there are in the atom. If the periodic table is used as a tool, this process is pretty easy.

For atoms found in the first two columns of the periodic table (figure 1.6.1), the configuration is a closed shell of core electrons, plus s electrons in a new shell. For example, potassium has a configuration [Ar]$4s^1$. These atoms are often called the alkali and alkaline earth elements. Alkali elements, from the first column, have a configuration ending in s^1; alkaline earth elements, from the second column, have configurations ending in s^2. Together, these elements are often called the s-block elements, because their valence electrons are s electrons. Remember, the valence electrons are the ones beyond the noble gas core. In the case of potassium, they are the ones beyond [Ar].

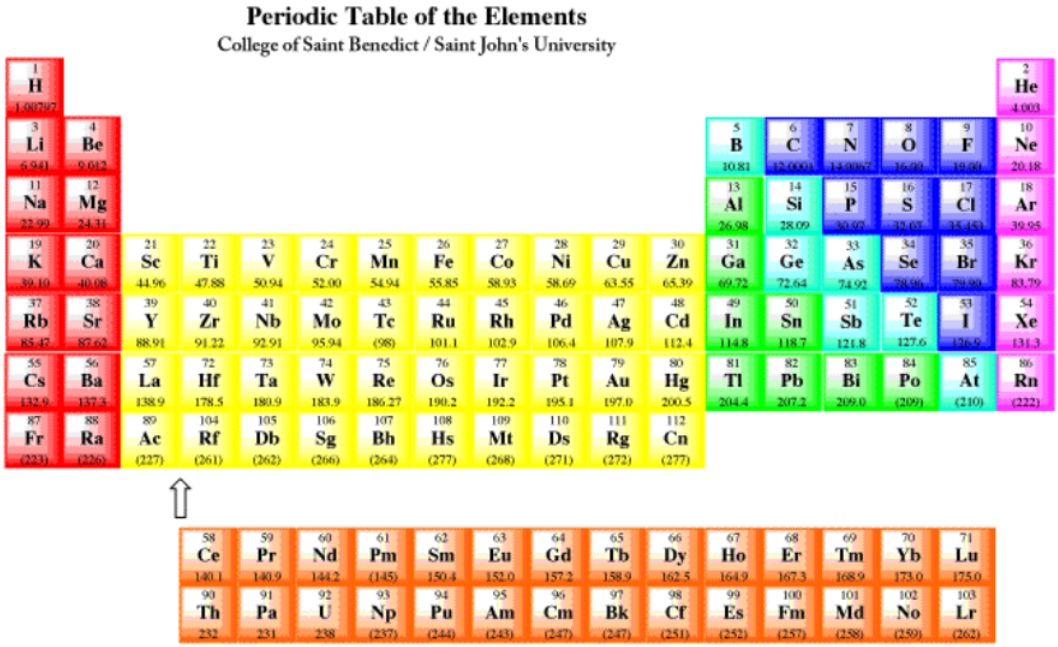


Figure 1.6.1: **The periodic table. Red elements are the alkali and alkaline earth metals (s-block). Yellow elements are the transition metals (d-block). Orange elements are the lanthanides and actinides (f-block). Green, blue and purple elements are the p-block; together with the s-block, they are called the main group elements. The main group is divided into metals (green), metalloids (teal), non-metals (blue) and noble or inert gases (purple).**

The first two and the last six columns of the periodic table are called the main group elements. Alternatively, they are sometimes called the s-block and p-block elements, respectively. For example, phosphorus has a configuration, [Ne]$4s^2 4p_x^1 p_y^1 p_z^1$, or simply [Ne]$4s^2 4p^3$.

The middle block of the periodic table consists of the transition metals or the d-block elements. For example, scandium has configuration [Ne]$4s^2 3d^1$.

The final two rows of the periodic table are the lanthanides and actinides. Collectively, they are called the f-block elements. Samarium, for example, is [Xe]$6s^2 4f^6$. These elements could really be inserted at the left-hand side of the d-block in the appropriate rows. Notice that lanthanum, element 57, is followed by hafnium, element 72, in the table. The element that really occurs next is element 58, cerium, and it is shown in the lanthanide row down below. The f-block elements are usually shown below in order to save space.

Really, the periodic table should look like this:

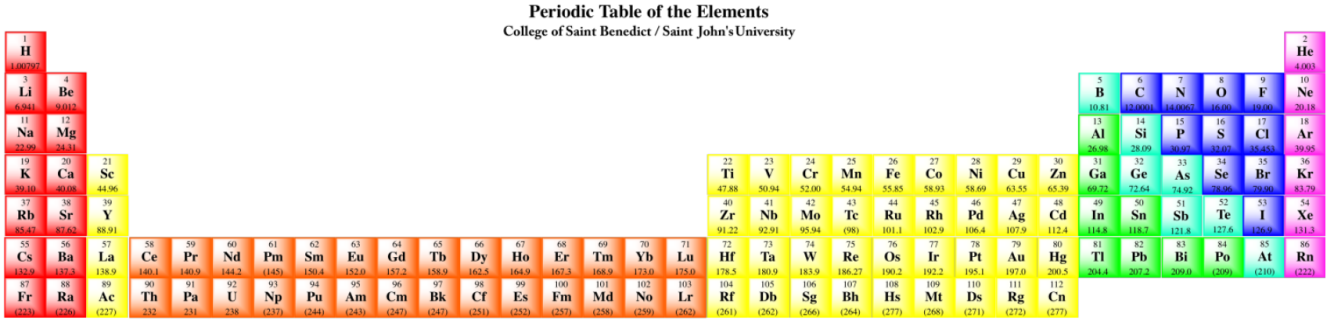


Figure 1.6.2: **The periodic table shown with the lanthanides in their proper places.**
The periodic table, with the lanthanide and actinide series between the alkali earth metals and the transition metals.

- The periodic table is divided into columns of atoms with similar electron configurations.
- Atoms with similar electron configurations have similar properties.

Chemical reactions depend on the movement of electrons. In a reaction, one atom may accept electrons from another atom. One atom may donate electrons to another atoms. The valence electrons are the outermost electrons in an atom; they are closest to the surface of an atom. That fact makes the valence electrons more likely to interact with other atoms. The valence are also the highest-energy electrons in an atom, and most likely to participate in a reaction.

For these reasons, atoms with similar electron configurations generally behave in similar ways. The repeating properties in each row of the periodic table, as observed by Mendeleev and others, reflect the repeating electron configurations in subsequent rows. The periodic table organizes atoms with similar configurations and properties together in columns.

? Exercise 1.6.1

For the following elements, suggest two other elements that would have similar properties.

a) zinc, Zn b) calcium, Ca c) oxygen, O d) chlorine, Cl e) chromium, Cr

Answer a:

Zn: Cd, Hg

Answer b:

Ca: Mg, Ba

Answer c:

O: S, Se

Answer d:

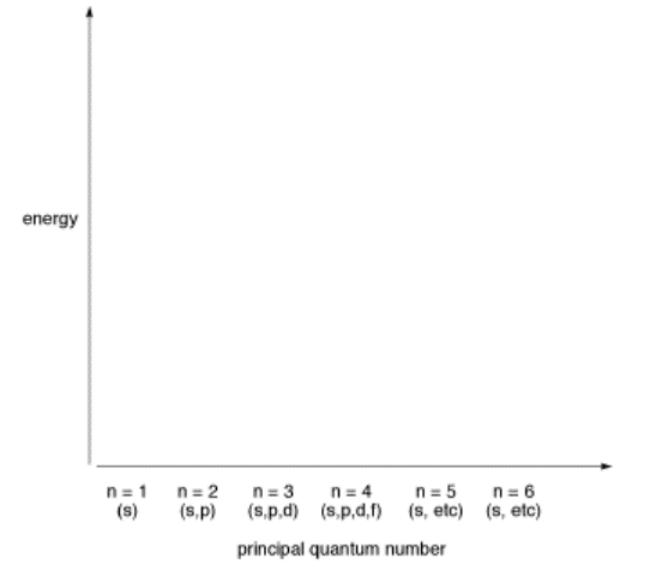
Cl: F, Br

Answer e:

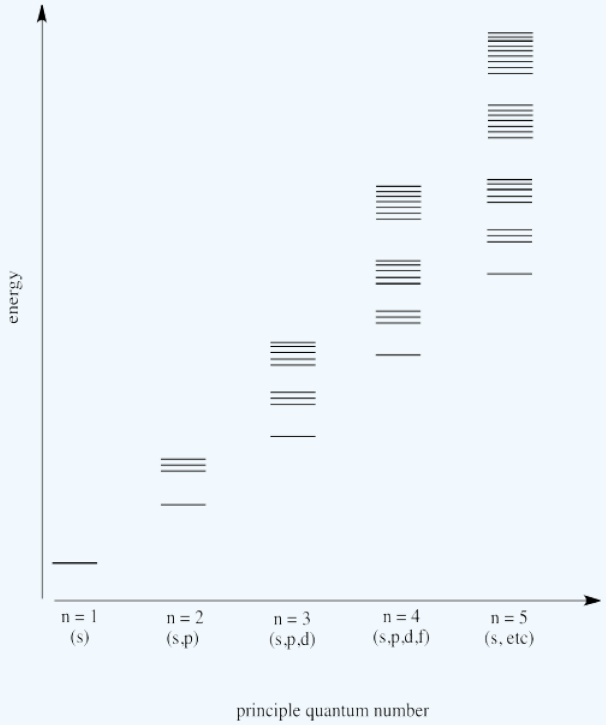
Cr: Mo, W

? Exercise 1.6.2

Make a diagram showing the energy levels of different orbitals, arranged by principal quantum number.



Answer



Answer

"Periodic trends" refer to the way in which physical properties of atoms change across the periodic table. One of the most commonly used periodic trends in chemistry is electronegativity. Electronegativity is closely connected to the basic idea of chemical reactions: the transfer of an electron from one neutral atom to another. It refers to how strongly an atom attracts electrons from other atoms.

- Electronegativity is a measure of an atom's ability to draw electrons towards itself, or the ability of the nucleus to hold electrons tightly.

There are many scales of electronegativity, based on different physical measurements. Usually, electronegativity is set to an approximately 4-point scale. Atoms with electronegativity of around 4 draw electrons very strongly toward themselves. Atoms with electronegativity of 1 (or lower) only weakly draw electrons toward themselves.

The following data use the Allen scale of electronegativity. The Allen scale uses spectroscopic measurements to estimate the energy of valence electrons in an atom. From these values, the relative attraction of the atom for its valence electrons is placed on a 4 point scale (approximately).

Table 1.6.1: **The Allen electronegativity values of the second-row elements.**

Element	Electronegativity (Allen scale)
Li	0.912
Be	1.576
B	2.051
C	2.544
N	3.066
O	3.61
F	4.193
Ne	4.789

Some electronegativity scales do not have values for the noble gases, because they are based on experimental measurements of compounds, and noble gases do not commonly form compounds with other elements. Instead, they exist as single atoms. The Allen scale just depends on the ability of an atom to interact with light, which is something even noble gases can do. As a result, noble gases are also given electronegativity values on this scale. However, on many scales, fluorine would be the most electronegative atom here. As a result, fluorine is usually thought of as the most electronegative element.

Often it is useful to plot data on a graph. That way, we can get a better look at the relationship. For example, a quick glance at Figure AT5.2. shows that there is a smooth increase in electronegativity as we move across a row in the periodic table.

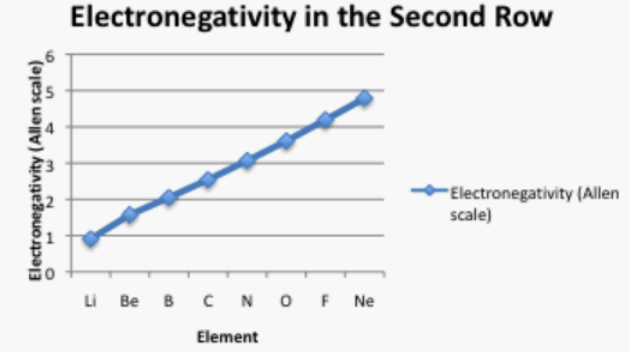


Figure 1.6.3: **A plot of electronegativity versus atomic number in the second row of the periodic table.**
A chart of elements in the second row vs. electronegativity. Electronegativity increases linearly as atomic number increases.

? Exercise 1.6.3

Take a look at the graph in figure 1.6.3. Can you explain why the electronegativity increases as atomic number increases?.

Answer

The atomic number is the number of protons in the nucleus. For two atoms in the same row of the periodic table, the outermost electrons are roughly the same distance away from the nucelus. The more positive protons there are in the nucleus, the more tighly held are the electrons.

? Exercise 1.6.4

Suppose you need an electron. You have a boron atom and an oxygen atom. You try to take an electron away from one. Use Figure 1.6.3. to predict which atom will give up the electron more easily.

Answer

Take it from the boron. The oxygen atom is holding its electrons much more tightly.

? Exercise 1.6.5

Suppose you have an electron. You are able to send it into a vessel that contains a carbon atom and a fluorine atom. Use Figure 1.6.3. to predict which atom is more likely to take the electron.

Answer

According to the drawing, the neon would take the electron, because of all the atoms depicted in the graph, neon attracts electrons most strongly. However, there is a complication. Although neon strongly attracts its own electrons, it can't accommodate an extra electron as easily as could fluorine, the next-best candidate. In "Lewis" terms, neon has a "full octet". In quantum terms, an additional electron would have a higher principle quantum number and be placed in the next "shell", farther from the nucleus. With spin-pairing, fluorine can accept another electron into its valence shell.

? Exercise 1.6.6

A covalent chemical bond is a pair of electrons shared between two atoms. Suppose you have a carbon-oxygen bond. Will the electrons be shared evenly between the two atoms, or will one atom pull the electrons more tightly towards itself? Use Figure 1.6.3. to make your prediction.

Answer

The oxygen would pull the electrons in the bond more tightly to itself.

What is happening as we move across a row in the periodic table? Why does electronegativity increase?

Keep in mind that the only difference from one element to the next is the number of protons in the nucleus. The number of protons is called the atomic number. If you know the number of protons you have, then you know what atoms you have. Electronegativity may have something to do with the number of protons in the nucleus. In fact, it should. The more protons there are in the nucleus, the more strongly electrons should be attracted to it. Each additional proton should add more electrostatic attraction for an electron. Fluorine, with nine protons, should attract electrons much more strongly than lithium, which has only three protons.

- Moving across a row of the periodic table, as protons are added to the nucleus, electrons are held more tightly.
- Electronegativity increases across a row in the periodic table.

It seems like that effect should be offset by the increasing number of electrons in the atom. Each time a proton is added, so is an electron. That electron should repel other electrons in the atom, cancelling out the effect of more protons in the nucleus.

However, the structure of the atom minimizes electron-electron repulsion a little bit. Remember that all the protons are in one place, the nucleus. All the electrons are a relatively great distance from the nucleus, in many different directions. Chances are, an additional electron is much farther away; it may be twice as far away as an additional proton in the nucleus. It may be all the way on the other side of the atom. Because electrons are spread out in the atom, and the distances between them is pretty large, the repulsive effect is a little smaller than the attractive effect of additional protons.

We can see that this trend is generally true across the periodic table, with a few exceptions here and there.

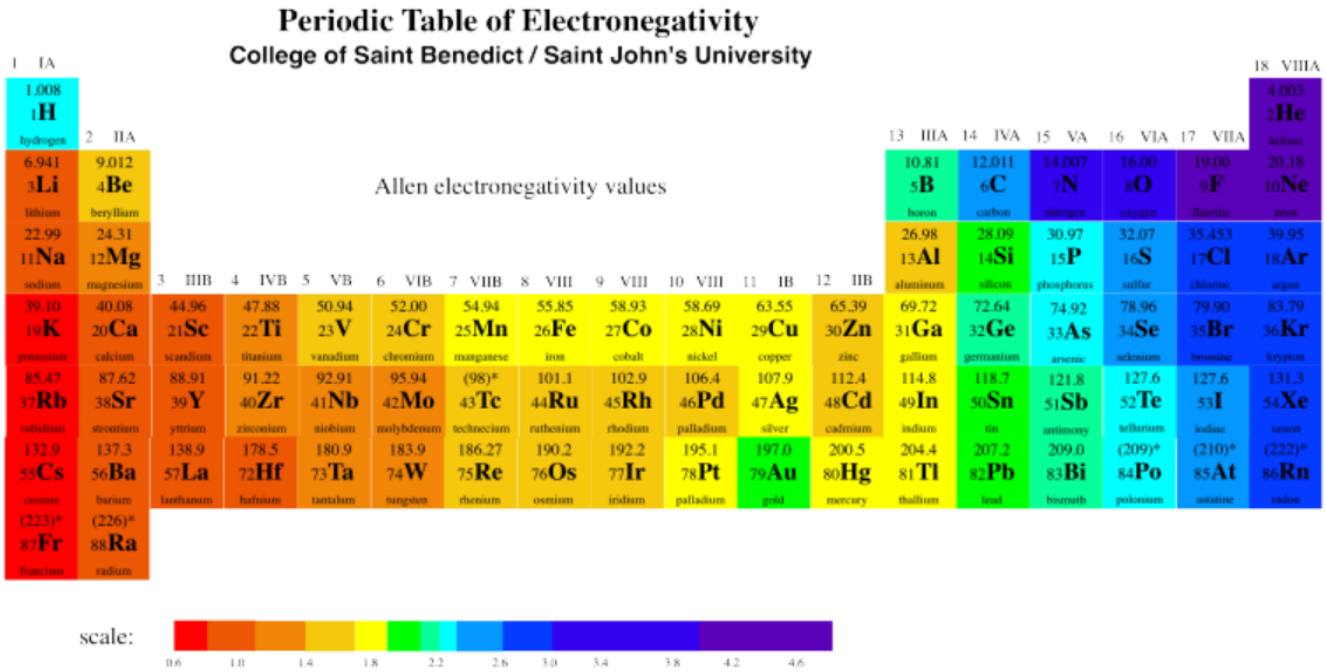


Figure 1.6.4: Electronegativity trends across the periodic table. Download a copy.

What happens as we move down a column in the periodic table? Table 1.6.2. shows the Allen electronegativities of the alkali metals. These elements are also called the Group 1 elements or the Group IA elements. The "Group 1" designation is used because they are the first column or group in the periodic table. The data are also presented in Figure 1.6.5.

***Table* 1.6.2*:* The Allen electronegativity values of the alkali elements.**

Element	Electronegativity (Allen scale)
H	2.3
Li	0.912
Na	0.869
K	0.734
Rb	0.706
Cs	0.659
Fr	0.67

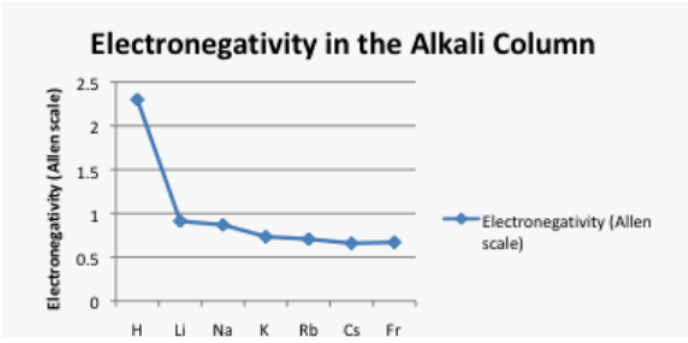


Figure 1.6.5: Plot of the Allen electronegativity values of the alkali elements.

Chart of electronegativity in the alkalie column. Hydrogen has the highest electronegativity, decreasing sharply at lithium. Electronegativity falls very slightly as period number increases.

There is a different trend here. In this case, lithium (atomic number 3) has more protons than hydrogen (atomic number 1). However, hydrogen is a lot more electronegative than lithium. Francium, with 87 protons in its nucleus, is the least electronegative alkali element.

? Exercise 1.6.7

Take a look at the graph in Figure 1.6.5. Can you explain why the electronegativity decreases as atomic number increases, going down this column?

Answer

Moving from one row to the next in the periodic table signifies that the outermost electron is in a shell farther from the nucleus. Those outermost electrons are less tightly held if they are farther from the nucleus.

? Exercise 1.6.8

An ionic chemical bond is a pair of ions attracted by their opposite charges. A cation is a positively charged ion; it may be an atom that has lost an electron. An anion is a negatively charged ion; it may be an atom that has gained an extra electron. Ions can form by moving an electron from one atom to another.

a. Suppose you have an ionic cesium-fluorine bond. Which ion is the cesium and which is the fluorine? Use Figure 1.6.3 and Figure 1.6.5. to make your prediction. Cesium is Cs.
b. Suppose you have an ionic sodium-oxygen bond. Which ion is the sodium and which is the oxygen? Use Figure 1.6.3 and Figure 1.6.5. to make your prediction. Sodium is Na (from the Latin, natrium).
c. Suppose you have an ionic potassium-hydrogen bond. Which ion is the potassium and which is the hydrogen? Use Figure 1.6.3 and Figure 1.6.5. to make your prediction. Potassium is K (from the Latin, kalium).

Answer a:

Cs^+ F-

Answer b:

Na^+ O^-

Answer c:

K^+ H^-

Periodic Trends and Atomic Radius

The biggest difference between two atoms in the same group (column) in the periodic table is the principal quantum number. Remember, that corresponds to the "valence shell". Think of electrons as forming layers around the nucleus. Electrons with principal quantum number one form a first layer. Those with principal quantum number 2 form a second layer, and so on. Each layer is further away from the nucleus. Remember, electrostatic attraction gets weaker as charges get further away from each other. As electrons get further from the nucleus, they are less tightly held.

- Moving down a column in the periodic table, valence electrons are held less tightly because they get further from the nucleus.
- Electronegativity decreases as we move down a column in the periodic table.

We can see this general size trend in the following periodic table. This table presents covalent radii, which are related to the sizes of the atoms (although not exactly the same; data on atomic radii are not available for all atoms, however).

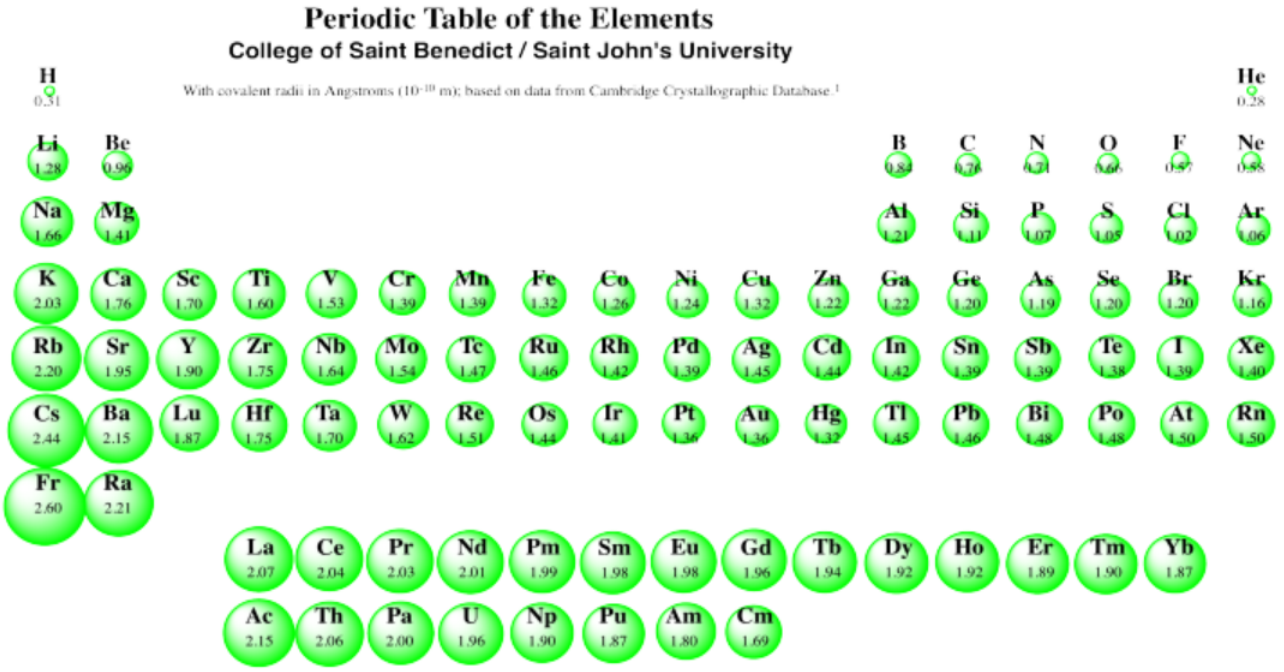


Figure 1.6.6: Covalent radii of the atoms. Download a copy here.

We can clearly see the expanding radii of atoms if we look at Group 1, the first column; these elements are called the alkali metals. Hydrogen, at the top, is very small. Lithium is much bigger. Sodium is much bigger than lithium, however, and potassium is much bigger than sodium. And so on: francium is bigger than cesium, which is bigger than rubidium, which is bigger than potassium.

Each time an electron is added to an orbital that is significantly farther from the nucleus, of course it is going to result in a bigger atom. Remember, the atom is mostly empty space, and its size is described by the outermost reaches of its electrons. So when we go to the next principal quantum number -- that is, to the next row in the periodic table, from the first row to the second row, for example -- the next electron is much further away from the nucleus. It has to be that way, because electrons repel each other. They can't all be equally close to the nucleus, because there would be too much repulsion. Instead, they form these layers, and when the first layer is so full that there would be too much repulsion if anothe relectron were added, we start the next layer.

Of course, the very first layer is very, very small. There just isn't that much room so close to the nucleus. For the first row, only two electrons are allowed. Then they have to start the next layer. For the second row, eight electrons are allowed; that's the origin of something called the "octet rule" (think "octopus") for common compounds, which you'll see later on. Eventually we get to eighteen electrons in a shell, then thirty two, as the shells get bigger and bigger like layers of an onion, or like nested Russian dolls.

There is another important trend if you look carefully. As you move from left to right across the periodic table, from one group to the next, the atoms get bigger. That does not make any sense, does it? If we are adding more electrons, why would the atom get smaller?

The key thing is, not only are we adding more electrons, but we are also adding more protons in the nucleus. The new electrons we are adding are all roughly equidistant from the nucleus; they are all equally close to the protons. So as the charge on the nucleus gets bigger, those electrons are all more strongly attracted to the center. The atom shrinks.

Eventually, we get to the point at which we couldn't possibly add more electrons; the radius has shrunk so much that repulsion would become too great if we added one more electron. Then we just start another row. Just before that point, however, we hit a sweet spot: the point at which the attraction between the nucleus and the outermost electrons is so strong, and the electrons are held so tightly, that the atom becomes very, very stable. This last column in the table contains the noble gases, which are particularly stable and unreactive.

Exercise 1.6.9

Why does electronegativity fall so sharply between hydrogen and lithium, and much more subtly between lithium and sodium?

Answer

The attraction for an electron falls off with $1/r^2$. As the value of r gets larger and larger, the quantity $1/r^2$ will begin to approach a limit (of zero). As a result, the difference between two successive values of $1/r^2$ in a series gets smaller and smaller.

Exercise 1.6.10

Which atom, in the following pairs, is more electronegative?

a. magnesium, Mg, or calcium, Ca
b. lead, Pb, or tin, Sn
c. silver, Ag, or antimony, Sb
d. gallium, Ga, or arsenic, As
e. tungsten, W, or copper, Cu
f. thallium, Tl, or sulfur, S

Answer a:

Mg > Ca

Answer b:

Sn > Pb

Answer c:

Sb > Ag

Answer d:

As > Ga

Answer e:

Cu > W

Answer f:

S > Tl

Exercise 1.6.11

Electron ionization is the energy that must be added in order to pull an electron away from an atom.

a. Why do you think energy has to be used to pull an electron away from an atom? What is holding the electron there?
b. Explain the general trend in ionization energies seen in the following table (a larger value means more energy must be added to remove a first electron from the atom).

Answer a:

The electron is held by its attraction to the nucleus.

Answer b:

As the number of protons in the nucleus increases, the electron becomes more tightly held, and harder to remove.

The relationship is similar to the one seen for electronegativity, and not coincidentally. Electronegativity can be calculated in a number of ways, but one of those ways uses the ionization energy as a factor.

Electronegativity is a calculated value, whereas ionization energy is an experimentally determined one. This difference brings up an important philosophical distinction. To a beginning student, an experimental value seems faulty, whereas a

calculated value sounds good. To an experienced chemist, an experimental value is verifiable; it is real. In contrast, a calculated value is enhanced in prestige only if it can be shown to agree with experiment.

Table 1.6.3 **The ionization energies of the second row elements.**

Element	Ionization Energy (eV)
Li	5.392
Be	9.322
B	8.298
C	11.26
N	14.534
O	13.618
F	17.422
Ne	21.564

? Exercise 1.6.12

Sometimes a plot of the data can be revealing. Ionization energies do not follow a smooth trend. Explain why it is a little easier to remove an electron from boron and oxygen than expected. (Electron configurations may be helpful here.)

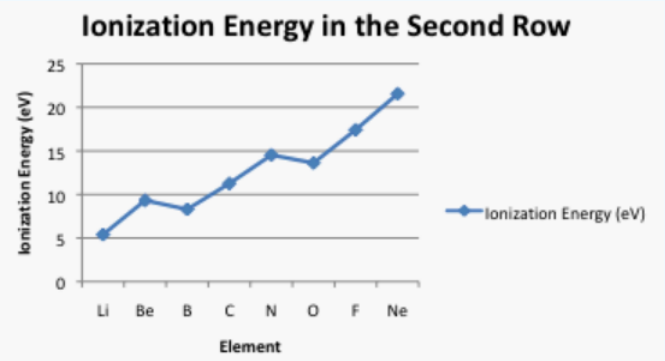


Figure 1.6.7: Plot of the ionization energies of the second row elements.AnswerIn order to escape the atom, an electron must gain energy. As shown in problem Exercise 1.6.2, the 2p energy level is higher than the 2s energy level. That means a 2p electron already has more energy than a 2s electron. The 2p electron will not need as much additional energy in order to escape from the atom. As a result, boron's ionization energy is a little lower than beryllium's.The additional protons in the nucleus of carbon and nitrogen more than make up for that effect.In the case of oxygen, the next electron is just added to a 2p level, but in this case it must be paired with another electron in the same region of space (in the same "orbital"). The repulsion between these electrons, or "pairing energy", slightly destabilizes the oxygen, so less energy will be needed to remove an electron.Once again, the continued addition of extra protons eventually compensates for this pairing effect.

? Exercise 1.6.13

Explain the trend in the following data on ionization energy.

Table 1.6.4: **The ionization energies of the alkali elements.**

Element	Ionization Energy (eV)
H	13.598
Li	5.392
Na	5.139
K	4.341
Rb	4.177
Cs	3.894

Answer

AnswerAs with electronegativity, ionization energy decreases as the distance to the nucleus increases because of the 1/r2 relationship in Coulomb's Law.

Exercise 1.6.14

Electron affinity is the energy released when a free electron is picked up by an atom.

a. Why would energy be released when a free electron is taken by an atom?
b. Explain the general trend in the following electron affinity data.

Element	Electron Affinity (kJ/mol)
H	-73.5
Li	-60.4
Na	-53.2
K	-48.9
Rb	-47.4
Cs	-46
Fr	-44.5

Answer a:

Answer b:

Table 1.6.5: The electron affinities of the alkali elements.Answer a:Energy is released because of the attraction of the free electron to a nucleus. The electron moves to lower energy as it becomes stabilized by its interaction with the nucleus.Answer b:The electron can get much closer to the hydrogen nucleus thanto the lithium nucleus, and so on. More energy will be released owing to the strong interaction between the electron and the hydrogen nucleus compared to the interaction between the electron and the lithium (or sodium or potassium...) nucleus.

Exercise 1.6.15

a. Explain a *general* trend in the following electron affinity data.
b. There are several exceptions to the general trend. Why do beryllium and neon have such low electron affinities (almost zero)?
c. Nitrogen also has an electron affinity that is close to zero. Why?

Element	Electron Affinity (kJ/mol)
Li	-60.4
Be	0
B	-27
C	-123.4
N	7
O	-142.5
F	-331.4
Ne	0

Answer a:

Answer b:

Answer c:

Answer a:The data zig-zags, but broadly speaking there is an increase in electron affinity as the number of protons in the nucleus increases.Answer b:Beryllium and neon have zero electron affinity because the next electron in each case would be added to a higher energy level. In the case of beryllium, the next electron would go into the 2p energy level. An electron added to neon would go into the 3s energy level.Answer c:Although the next electron added to nitrogen would be added to a 2p level, it would have to be paired in the same region of space as an electron that was already there. The pairing energy in this case must be enough to offset the attraction of the electron to the nucleus.

? Exercise 1.6.16

Usually, elements become bigger as we go down a column in the periodic table. However, in a phenomenon called "the lanthanide contraction", some elements are actually smaller than the ones in the row above them. Specifically, osmium, iridium, platinum, gold, and mercury are smaller than their relatives, ruthenium, rhodium, palladium, silver, and cadmium, respectively.

Use the periodic table in Figure 1.6.2. to offer a possible explanation for this phenomenon.

Answer

Perhaps the simplest explanation is this: The addition of 14 extra protons between lanthanum and hafnium, compared to between yttrium and zirconium, results in a considerable contraction of the atom. The electrons are pulled inward by the added positive charge in the nucleus. Thus, elements in the third row of the transition metal block are not as large as might otherwise be expected, and in some cases are even smaller than their precedent elements.

Note that this is not the only explanation. Relativistic effects are also believed to play a role in the behaviour of these massive elements. Einstein's theory of relativity states that objects get heavier the faster they move. The velocity of an electron can be shown to increase with the charge in the nucleus of the atom. Thus, atoms that have very high atomic numbers have very, very fast electrons, and consequently very heavy ones. These heavy electrons sink toward the heavy nucleus, and the atom shrinks further.

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1.7: Atoms- Solutions to Selected Problems

Exercise 1.1.3

a. one atom of mercury with one atom of oxygen.
b. two atoms of mercury with one atom of oxygen.
c. 200 amu (Hg) + 16 amu (O) = 216 amu (HgO)
d. 2 x 200 amu (Hg) + 16 amu (O) = 416 amu (HgO)

Exercise 1.1.4

a. 200 g (Hg) + 16 g (O) = 216 g (HgO)
b. 2 x 200 g (Hg) + 16 g (O) = 416 g (Hg_2O)
c. If one mole is 216 g of HgO, then 0.25 mole must be a quarter of that amount, or 54 g.

$$0.25mol \times 216 \frac{g}{mol} = 54g$$

Alternatively written as

$$0.25mol \times 216g\,mol^{-1} = 54g$$

The amount of mercury is just a fraction of that: 200/216. So the answer is $\frac{200}{216} \times 54g = 50g$.

d) What fraction of a mole is 2.08 g of Hg_2O, if one mole is 416 g?

$$\frac{2.08g}{416g\,mol^{-1}} = 0.005mol$$

Notice that when we divide *g* by *g mol*$^{-1}$, the grams cancel and the *mol*$^{-1}$ becomes *mol*.

There is 1 mol of O in 1 mol of HgO, so 0.005 mol of O are needed for 0.005 mol HgO.

$0.005mol \times 16g\,mol^{-1} = 0.08g$ O needed

Exercise 1.1.6

a) sulfur b) silicon c) calcium d) potassium and lithium

e) phosphorus f) iodine g) silver and copper h) ruthenium

Exercise 1.1.7

a) 20 b) Na c) 16.00 d) phosphorus

e) carbon f) Sn g) 32.07 h) potassium

Exercise 1.1.8

a) Ne: 20 g/mol b) Fe: 56 g/mol c) Cu: 64 g/mol d) Au: 197 g/mol e) Si: 28 g/mol

Exercise 1.1.9

a. H_2O: $18\frac{g}{mol}(2 \times H + 1 \times O = 2 \times 1 + 1 \times 16\frac{g}{mol})$
b. $NaHCO_3$: $84\frac{g}{mol}(3 \times O + 1 \times Na + 1 \times H + 1 \times C = 3 \times 16 + 1 \times 23 + 1 \times 1 + 1 \times 12\frac{g}{mol})$
c. SiO_2 : $60\frac{g}{mol}(1 \times Si + 2 \times O = 1 \times 28 + 2 \times 16\frac{g}{mol})$
d. NaCl : $58\frac{g}{mol}(1 \times Na + 1 \times Cl = 1 \times 23 + 1 \times 35\frac{g}{mol})$
e. TaN : $195\frac{g}{mol}(1 \times Ta + 1 \times N = 1 \times 181 + 1 \times 14\frac{g}{mol})$
f. NH_3 : $17\frac{g}{mol}(1 \times N + 3 \times H = 1 \times 14 + 3 \times 1\frac{g}{mol})$
g. NaH_2PO_4 : $120\frac{g}{mol}(1 \times Na + 2 \times H + 1 \times P = 4 \times O = 1 \times 23 + 2 \times 1 + 1 \times 31 + 4 \times 16\frac{g}{mol})$
h. CH_3CO_2H : $60\frac{g}{mol}(2 \times C + 4 \times H + 2 \times O = 2 \times 12 + 4 \times 1 + 2 \times 16\frac{g}{mol})$

Tthe molar weight of the atom was rounded to the nearest gram. In order to be very careful and avoid "error propagation", the more exact molar weight (to several decimal places) could be used and rounding could be performed *after* the calculation. In these cases, the result would be the same. The result could be different if very large numbers of atoms were found in the compound.

Exercise 1.2.1

a) O: 8 protons, 8 electrons, 8 neutrons

The atom is neutral overall, so the number of positively charged protons is equal to the number of negatively charged electrons. The atomic weight is provided almost entirely by the protons and neutrons, so the number of protons plus number of neutrons equals the atomic weight.

b) P: 15 protons, 15 electrons, 16 neutrons

c) Zn: 30 protons, 30 electrons, 35 neutrons

d) Au: 79 protons, 79 electrons, 118 neutrons

Exercise 1.2.3

Carbon: $\frac{(99\times12amu)+(1\times13amu)}{100} = \frac{1188+13amu}{100} = \frac{1201amu}{100} = 12.01amu$

Exercise 1.2.4

The negatively charged electron's departure from the nucleus leaves behind a positive charge. A neutron is converted into a proton. The overall atomic weight remains the same, but the atom ends up with one more proton and one more electron. A ^{14}C is converted into a ^{14}N.

Exercise 1.2.6

Suppose y is the decimal fraction of ^{35}Cl and z is the decimal fraction of ^{37}Cl.

$35.5amu = \frac{(y\times35amu+z\times37amu)}{100}$ but y + z = 1

$$35.5amu = (y\times35amu+(1-y)\times37amu)$$

$$35.5amu = y\times35amu - y\times37amu + 37amu$$

$$(37-35)\times yamu = 37amu - 35.5amu$$

$$2\times yamu = 1.5amu$$

$$y = 0.75(75\%^{35}Cl)$$

$$z = 0.25(25\%^{37}Cl$$

Exercise 1.2.7

a. 1, 2, 3, 4, 5... a series of whole numbers, or n.
b. 2, 4, 6, 8, 10... a series of even numbers, or 2n (because every even number is two times another number).
c. 3, 5, 7, 9, 11... a series of odd numbers, or 2n + 1 (because every odd number is one more than some even number).
d. 1, 4, 9, 16, 25... a series of squares, or n^2.
e. 2, 4, 8, 16, 32... a series in which each numer is double the last number, or 2^n.
f. 1, 1/2, 1/4, 1/9, 1/16... a series of reciprocals of squares, or $1/n^2$.

Exercise 1.2.8

a. When q increases, F increases. The increase is linear: if q_1 doubles, F doubles. As the charge in the nucleus gets larger, the force of attraction gets larger.
b. When r increases, F decreases. The decrease is nonlinear: if r doubles, F drops by a factor of four, rather than a factor of two. As the distance from the nucleus gets longer, the attraction to the nucleus drops sharply.
c. Hydrogen and helium are both in the first row of the periodic table. To a rough approximation, the distance between nucleus and electron is similar in these two atoms. However, helium has a charge of 2+ in its nucleas, compared to the 1+ charge in the

nucleus of a hydrogen atom. As a result, the attraction of an electron on helium to the nucleus would be about twice as great as the attraction of an electron on hydrogen to its nucleus.

Helium's electrons are much more tightly held than hydrogen's.

The situation is really much more complicated than that. For example, if helium's electrons are more tightly attracted to the nucleus than hydrogen's, then helium's electrons ought to be pulled closer to the nucleus than hydrogen's. That means helium's electrons are held even more tightly than we at first thought.

Another complicating factor is that helium has two electrons, whereas hydrogen has only one. An electron may be attracted to the nucleus, but electrons repel each other. That second electron in helium should offset the extra attraction to helium's more positive nucleus. That means helium's electrons may be less tightly attracted than we originally thought.

However, the effect of the second electron is much smaller than it first appears. That's because the second electron could be anywhere around the helium atom. It has a 50% chance of being further away from the first electron than that positively charged nucleus. The farther it is away, the smaller its influence. Helium's electrons are definitely more strongly attracted to the nucleus than are hydrogen's, but it is difficult to say exactly how much more without the help of some more sophisticated tools.

Exercise 1.2.9

a. As wavelength gets longer (value of λ increases), energy decreases.
b. As frequency gets higher (value of ν increases), energy increases.

Exercise 1.2.10

Periodic of Elements in a Table

Element Symbol	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Number of Electrons	Charge
H	1	1	1	0	1	0
H	1	1	1	0	0	+1
H	1	1	1	0	2	-1
H	1	2	1	1	1	0
H	1	3	1	2	1	0
Be	4	9	4	5	2	+2
C	6	12	6	6	6	0
Mg	12	25	12	13	12	0
Tc	43	98	43	55	43	0
Ca	20	40	20	20	18	+2
Si	14	28	14	14	14	0
K	19	47	19	28	15	+4
Fe	26	56	26	30	23	+3
Br	35	79	35	44	36	-1
Ti	22	39	22	17	21	+1
P	15	30	15	15	15	0
Al	13	27	13	14	10	+3
S	16	32	16	16	16	0
Pd	46	106	46	60	45	+1

Element Symbol	Atomic Number	Mass Number	Number of Protons	Number of Neutrons	Number of Electrons	Charge
Cr	24	52	24	28	21	+3
Sn	50	118	50	68	50	0
Hg	80	200	80	120	79	+1
Au	79	197	79	118	78	+1

Exercise 1.3.1

a. The energy of the electron gets higher.
b. The energy of the electron gets lower.
c. The wavelength gets shorter.
d. The wavelength gets longer.

Exercise 1.3.2

The probability of finding an electron at a node is zero.

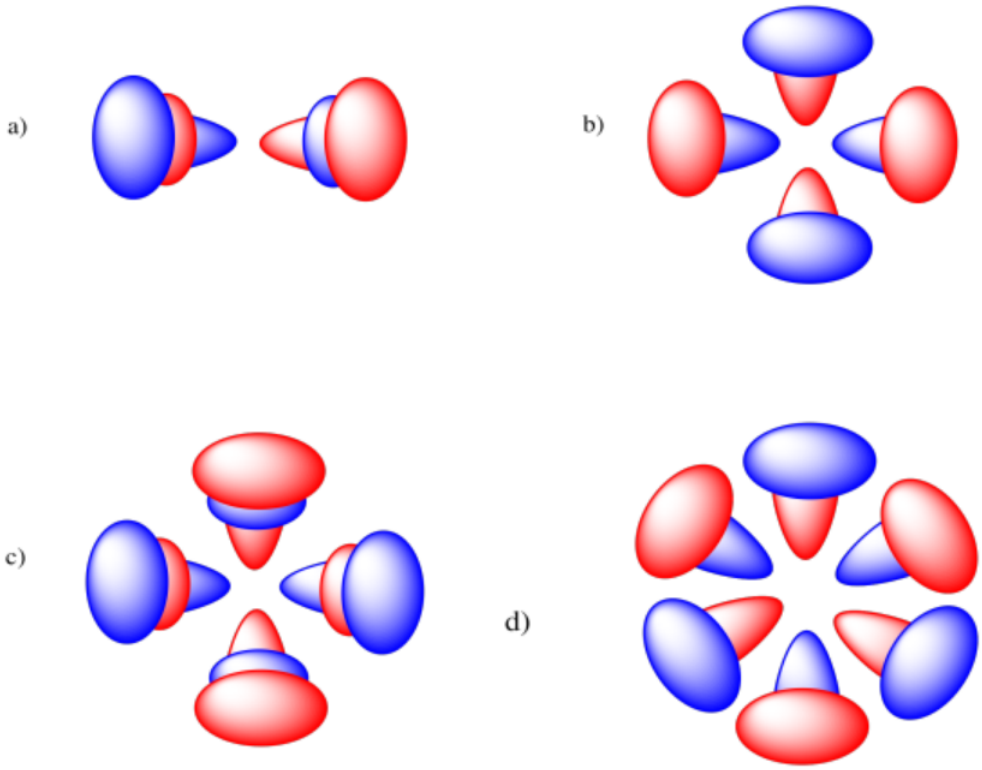
Exercise 1.3.3

Your drawing is beautiful. You should put it on your fridge, or else send it to your mother.

Exercise 1.4.1

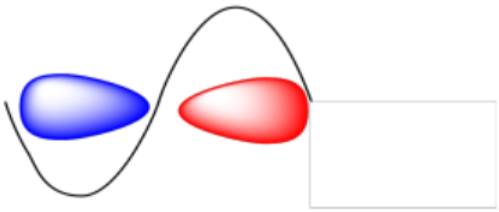
a) 2s b) 3p c) 3d e) 5f e) 4s

Exercise 1.4.2

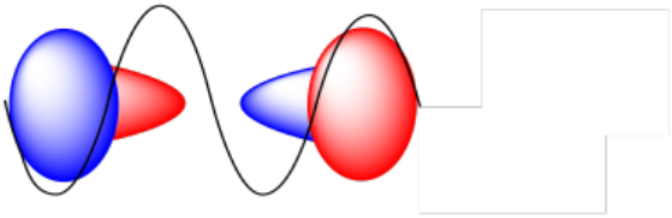


Exercise 1.4.3

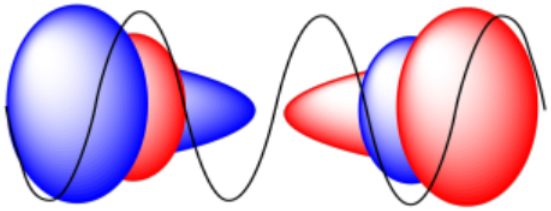
a)



b)



c)



From one end of the orbital to another, the 2p orbital covers a full sine wave, a 3p orbital covers two full sine waves, and a 4p orbital covers three full sine waves.

Exercise 1.5.1

a. O: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
b. S: $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_x^2 3p_y^1 3p_z^1$
c. Si: $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_x^1 3p_y^1$
d. N: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
e. Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$
f. Ne: $1s^2 2s^2 2p^6$

Exercise 1.5.2

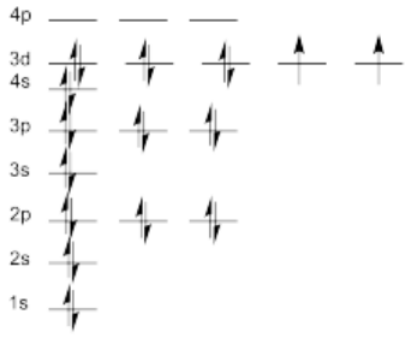
a. Cl: $[Ne]3s^2 3p_x^2 3p_y^2 3p_z^1$
b. Ca: $[Ar]4s^2$
c. Al: $[Ne]3s^2 3p_x^1$
d. P: $[Ne]3s^2 3p_x^1 3p_y^1 3p_z^1$

Exercise 1.5.3

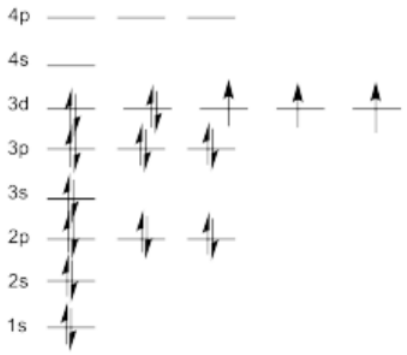
a. iron, Fe: $[Ar]4s^2 3d^6$
b. nickel, Ni: $[Ar]4s^2 3d^8$
c. mercury, Hg: $[Xe]6s^2 4f^{14} 5d^{10}$
d. lead, Pb: $[Xe]6s^2 4f^{14} 5d^{10} 6p^2$
e. arsenic, As: $[Ar]4s^2 3d^{10} 4p^3$
f. titanium, Ti: $[Ar]4s^2 3d^2$

Exercise 1.5.4

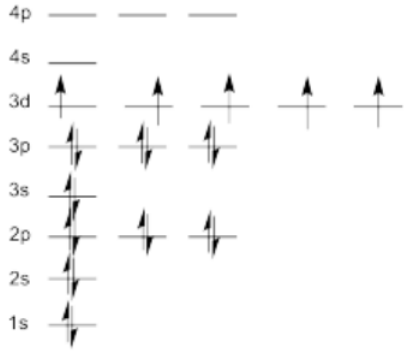
A. Ni



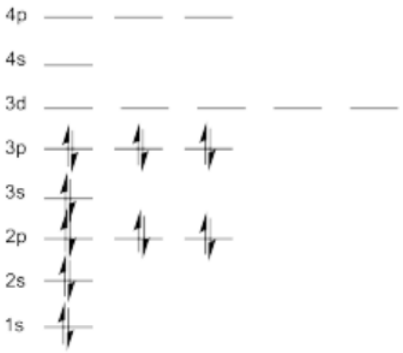
B. Co^{+2}



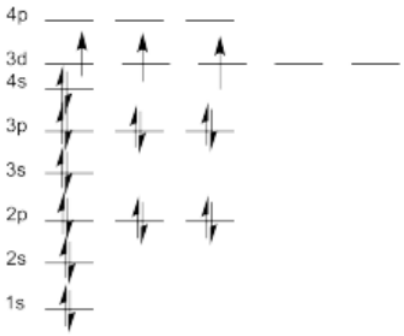
C. Fe^{+3}



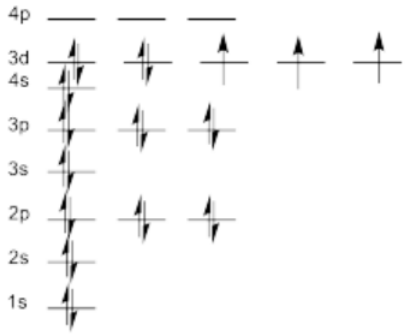
D. Ti^{+4}



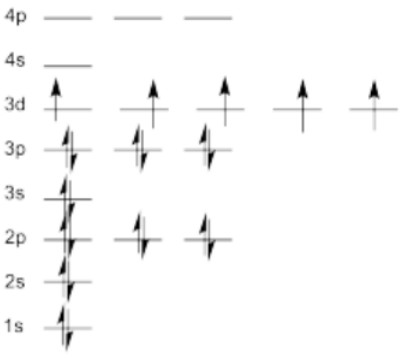
E. V



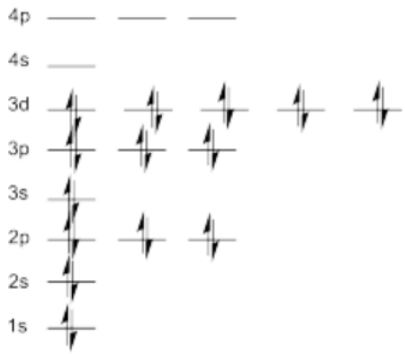
F. Co



G. Mn^{+2}



H. Zn^{+2}



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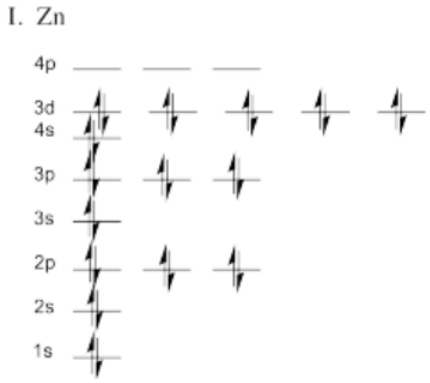
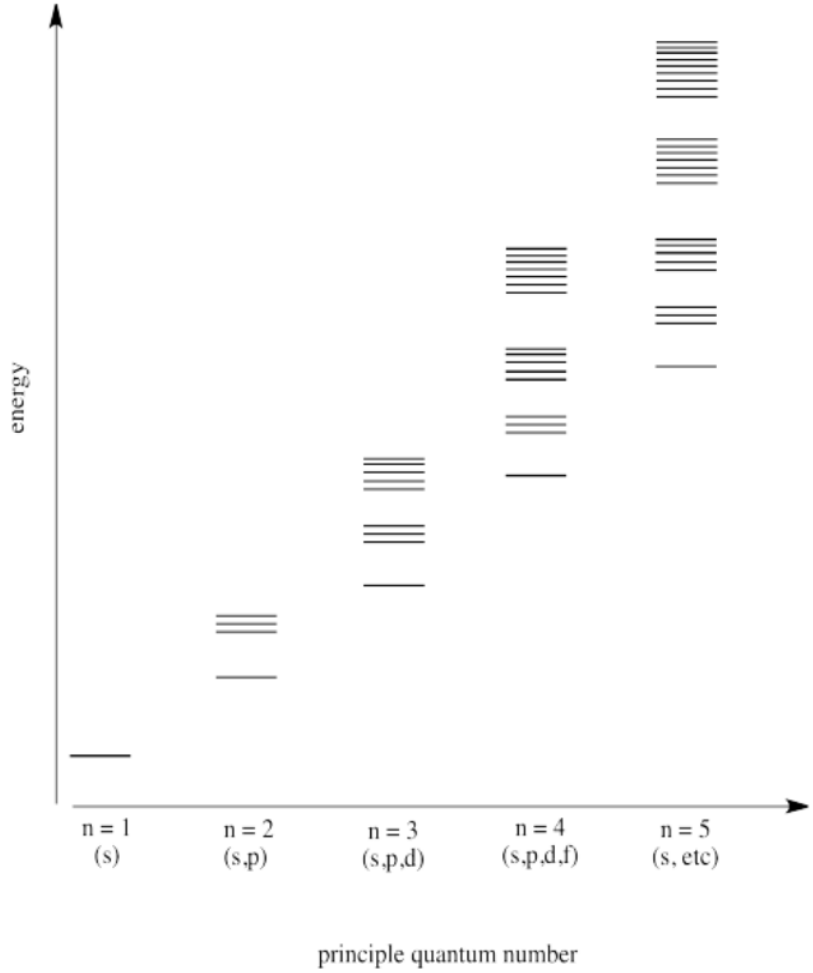


Exercise 1.6.1

a. Zn: Cd, Hg
b. Ca: Mg, Ba
c. O: S, Se
d. Cl: F, Br
e. Cr: Mo, W

Exercise 1.6.2



Exercise 1.6.3

The atomic number is the number of protons in the nucleus. For two atoms in the same row of the periodic table, the outermost electrons are roughly the same distance away from the nucelus. The more positive protons there are in the nucleus, the more tighly held are the electrons.

Exercise 1.6.4

Take it from the boron. The oxygen atom is holding its electrons much more tightly.

Exercise 1.6.5

According to the drawing, the neon would take the electron, because of all the atoms depicted in the graph, neon attracts electrons most strongly. However, there is a complication. Although neon strongly attracts its own electrons, it can't accommodate an extra electron as easily as could fluorine, the next-best candidate. In "Lewis" terms, neon has a "full octet". In quantum terms, an additional electron would have a higher principle quantum number and be placed in the next "shell", farther from the nucleus. With spin-pairing, fluorine can accept another electron into its valence shell.

Exercise 1.6.6

The oxygen would pull the electrons in the bond more tightly to itself.

Exercise 1.6.7

Moving from one row to the next in the periodic table signifies that the outermost electron is in a shell farther from the nucleus. Those outermost electrons are less tightly held if they are farther from the nucleus.

Exercise 1.6.8

a. Cs^+ F-
b. Na^+ O^-
c. K^+ H^-

Exercise 1.6.9

The attraction for an electron falls off with $1/r^2$. As the value of r gets larger and larger, the quantity $1/r^2$ will begin to approach a limit (of zero). As a result, the difference between two successive values of $1/r^2$ in a series gets smaller and smaller.

Exercise 1.6.10

a. Mg > Ca
b. Sn > Pb
c. Sb > Ag
d. As > Ga
e. Cu > W
f. S > Tl

Exercise 1.6.11

a. The electron is held by its attraction to the nucleus.
b. As the number of protons in the nucleus increases, the electron becomes more tightly held, and harder to remove.

The relationship is similar to the one seen for electronegativity, and not coincidentally. Electronegativity can be calculated in a number of ways, but one of those ways uses the ionization energy as a factor.

Electronegativity is a calculated value, whereas ionization energy is an experimentally determined one. This difference brings up an important philosophical distinction. To a beginning student, an experimental value seems faulty, whereas a calculated value sounds good. To an experienced chemist, an experimental value is verifiable; it is real. In contrast, a calculated value is enhanced in prestige only if it can be shown to agree with experiment.

Exercise 1.6.12

In order to escape the atom, an electron must gain energy. As shown in problem AT5.2., the 2p energy level is higher than the 2s energy level. That means a 2p electron already has more energy than a 2s electron. The 2p electron will not need as much additional energy in order to escape from the atom. As a result, boron's ionization energy is a little lower than beryllium's.

The additional protons in the nucleus of carbon and nitrogen more than make up for that effect.

In the case of oxygen, the next electron is just added to a 2p level, but in this case it must be paired with another electron in the same region of space (in the same "orbital"). The repulsion between these electrons, or "pairing energy", slightly destabilizes the oxygen, so less energy will be needed to remove an electron.

Once again, the continued addition of extra protons eventually compensates for this pairing effect.

Exercise 1.6.13

As with electronegativity, ionization energy decreases as the distance to the nucleus increases because of the $1/r^2$ relationship in Coulomb's Law.

Exercise 1.6.14

a. Energy is released because of the attraction of the free electron to a nucleus. The electron moves to lower energy as it becomes stabilized by its interaction with the nucleus.
b. The electron can get much closer to the hydrogen nucleus thanto the lithium nucleus, and so on. More energy will be released owing to the strong interaction between the electron and the hydrogen nucleus compared to the interaction between the electron and the lithium (or sodium or potassium...) nucleus.

Exercise 1.6.15

a. The data zig-zags, but broadly speaking there is an increase in electron affinity as the number of protons in the nucleus increases.
b. Beryllium and neon have zero electron affinity because the next electron in each case would be added to a higher energy level. In the case of beryllium, the next electron would go into the 2p energy level. An electron added to neon would go into the 3s energy level.
c. Although the next electron added to nitrogen would be added to a 2p level, it would have to be paired in the same region of space as an electron that was already there. The pairing energy in this case must be enough to offset the attraction of the electron to the nucleus.

Exercise 1.6.16

Perhaps the simplest explanation is this: The addition of 14 extra protons between lanthanum and hafnium, compared to between yttrium and zirconium, results in a considerable contraction of the atom. The electrons are pulled inward by the added positive charge in the nucleus. Thus, elements in the third row of the transition metal block are not as large as might otherwise be expected, and in some cases are even smaller than their precedent elements.

Note that this is not the only explanation. Relativistic effects are also believed to play a role in the behavior of these massive elements. Einstein's theory of relativity states that objects get heavier the faster they move. The velocity of an electron can be shown to increase with the charge in the nucleus of the atom. Thus, atoms that have very high atomic numbers have very, very fast electrons, and consequently very heavy ones. These heavy electrons sink toward the heavy nucleus, and the atom shrinks further.

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CHAPTER OVERVIEW

2: Metals

2.1: Introduction to Metals
2.2: A Layer of Metal Atoms
2.3: Building Metal Atoms in Three Dimensions
2.4: Application Problems with Metals
2.5: Metals- Solutions to Selected Problems

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2.1: Introduction to Metals

Most of the elements found on earth are metals. A look at the periodic table shows that these elements occupy the entire left-hand stretch of the table, from the main group, through the transition metals, lanthanides, actinides, alkali and alkaline earth elements.

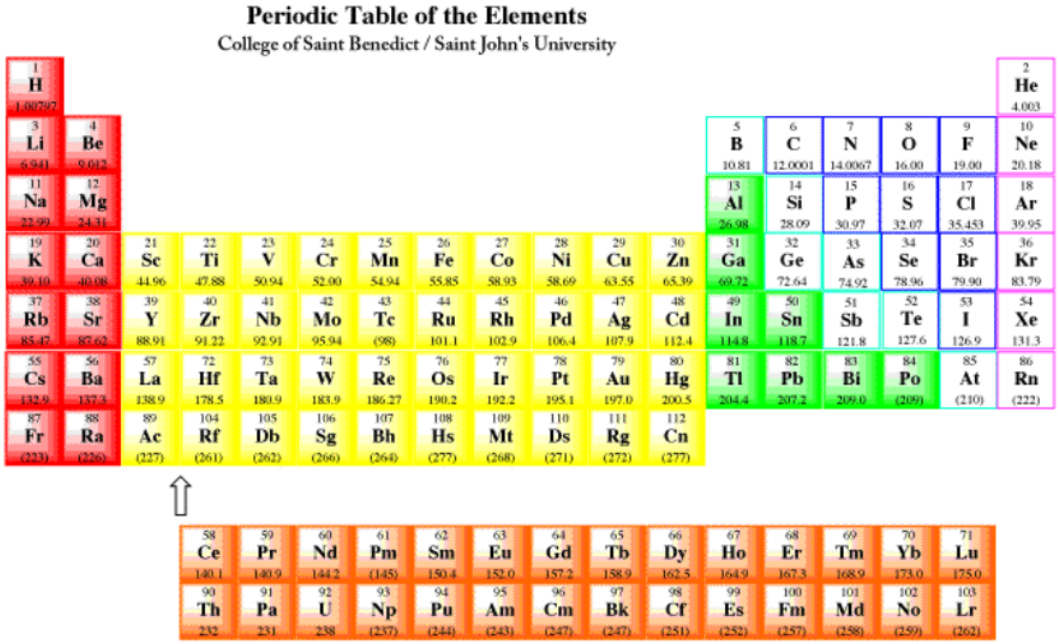

Figure 2.1.1: **The periodic table, showing metals in full color and non-metals in white boxes.**

One element included here, hydrogen, is rarely classified as a metal. On earth, hydrogen is a gas, and it is usually classified as a non-metal, like oxygen and nitrogen. However, at very low temperatures and very high pressures, hydrogen is a solid, and under the right conditions it is expected to behave more like a metal. It is thought that gas giants, such as Jupiter and Saturn in our solar system, may have metallic hydrogen cores.

Metallic elements are not generally found as single atoms. Instead, the atoms in an element such as iron cluster together to make a larger structure. The materials formed in this way have some similar properties. Metals are shiny. Metals are malleable; they can be bent and formed into different shapes (at least when heated). Metals are good conductors of electricity.

- In metals, large groups of atoms cluster together.
- Metal atoms form large, extended arrays, with the atoms repeating in specific patterns throughout the solid.

The properties of metals are really important. The fact that metals are malleable allows them to be formed into sheets that can be used to make cars, airplanes, railway lines, cargo containers and ships, as well as more delicate items such as jewelry and surgical tools. A related property, ductility, allows metals to be stretched into long, thin wires. Together with the conductivity of metals, this property allows transmission lines to carry electricity from generating stations to people like you. Sometimes, the source of electricity is hundreds of miles away; electricity used to power a laptop in New York may come from places like La Grande Baleine or James Bay, in northwestern Quebec.

Some of these properties can be understood by thinking about the structure of metallic elements. A great deal of our structural understanding of metals and other materials comes from x-ray diffraction studies. A very focused beam of x-rays can be sent into a material, where they will bounce off the atoms and scatter in different directions. The outcome sounds chaotic, but if the solid is highly organized, the x-rays behave in very predictable ways. The result is an x-ray diffraction pattern. A diffraction pattern is a little like the pattern of ripples on a pond when a stone is thrown into calm water. The pattern can be studied and decoded mathematically to find the locations of the atoms within the material.

- X-ray diffraction can reveal the atomic-level structures of highly ordered materials such as metals.

What does x-ray diffraction tell us? Evidently, a chunk of metal is not just a mass of atoms stuck together randomly. Instead, the atoms arrange themselves in neat layers in very specific ways. These layers of atoms sit on top of each other to form a three-dimensional solid.

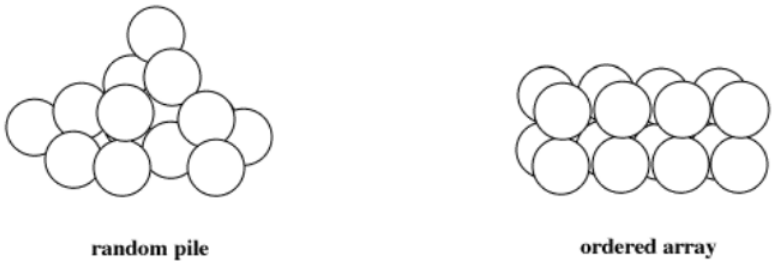

Figure 2.1.2: **A pile of atoms versus an ordered array of atoms.** Left: a cartoon of a pile of atoms. Right: a cartoon of a square rectangle of atoms arranged in an orderly array.

One of the properties that results from this organized arrangement of atoms is the malleability of metals. If you take a nice, soft metal such as copper, after annealing it in a fire or oven, it can be bent and shaped easily. With copper, this can be done even after the metal has cooled to room temperature. When you bend the copper, you are actually causing layers of atoms to slide over each other, until you stop bending and they come to rest in a new location.

Figure 2.1.3: **A force (bold arrow) pushes a layer of atoms past another layer of atoms, making a new shape.**

If you have ever done this, you'll know that the more you work with the copper, the harder it is to bend. That's because while you are sliding layers of atoms back and forth, occasionally an atom (or an entire row of atoms) slips out of place. It is no longer part of a smooth layer, and so other atoms can't slide past it as easily. This situation is called a defect. Once there are enough defects in the metal, it is impossible to bend the material anymore.

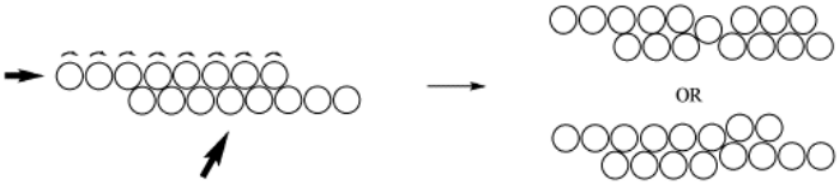

Figure 2.1.4: **A defect can be caused by forces pushing atoms out of alignment. This displaced atom or layer in an ordered array of atoms lowers the malleability of the metal.** Left: two rows of atoms out of alignment. A force acts on the lower row. Right: atoms shifted out of alignment.

- Metal atoms are found in organized layers.
- Because these layers can roll over each other, metals can be worked into different shapes.

? Exercise 2.1.1

An alloy is a mixture of two metals. Steel is an alloy of iron with any of a number of other elements, such as chromium or vanadium. Alloys are often harder than metals composed of a pure element. Show how alloying introduces a defect into the metal, and how that makes the metal stronger.

Answer

The second metal atom is a different size than the principle metal atom. It will not quite fit into the array of atoms. Consequently, the atoms will not be able to slide past each other as easily.

What is it that holds these metal atoms together? To answer that question, it's important to realize where metallic materials are found in the periodic table. The bottom left part of the periodic table is where the least electronegative elements are found. In fact, all of these elements lose electrons easily, and they are frequently found as cations in naturally-occurring compounds. For example, hematite is a common iron ore, containing iron cations (Fe^{3+}) and oxygen anions (O^{2-}). The formula of this compound is Fe_2O_3, meaning there is always a ratio of three oxygen anions for every two iron cations in hematite.

Exercise 2.1.2

Show how the ratio of elements in hematite leads to a charge-balanced (overall neutral) compound.

Answer

2 Fe: (3^+) x 2 = (6^+)

3 O: (2^-) x 3 = (6^-)

Fe_2O_3: neutral

Many of the atoms in a metallic material are present as cations. But where did their lost electrons go? Well, those electrons are still in the material, moving between the iron atoms and cations. In a piece of iron, the attraction between the iron cations and the freely moving electrons helps hold the metal together. This way of thinking about metals is sometimes called the "electron sea" model of bonding.

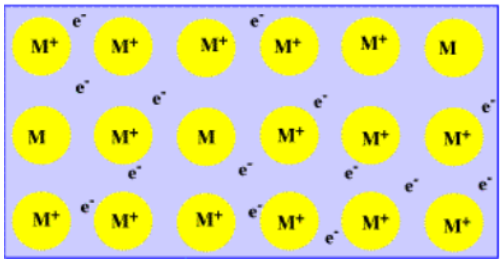

Figure 2.1.5: **Metal cations in an electron sea.**

- Bonding in metals is often described through the "electron sea model".
- Metal ions are surrounded by delocalized electrons.
- Delocalized electrons are not restricted to one atom or another; they are distributed across several atoms in the solid.

Why do metals conduct electricity? Electricity is the movement of electrons through a material. But the conduction of current through a metal probably takes place through a series of events. If an electron is introduced at one end of the material, it will probably be attracted by a metal cation. It may even be captured by that metal. Sometimes, we describe this electron as moving into a "hole"; a hole, in conductivity terms, is just a positive charge that captures an electron. But remember that metals are still pretty electropositive (the opposite of electronegative), and that metal atom is likely to lose another electron. This may not be the same electron as the one you put in; it is probably another one. That electron may in turn be captured by another hole on another metal. That metal may lose another electron, and so on. Electrons will hop and skip from one metal to another throughout the material. An electric current results because these hopping electrons in the metal move away from the electrons that are being supplied at one end. They move towards the other end, instead.

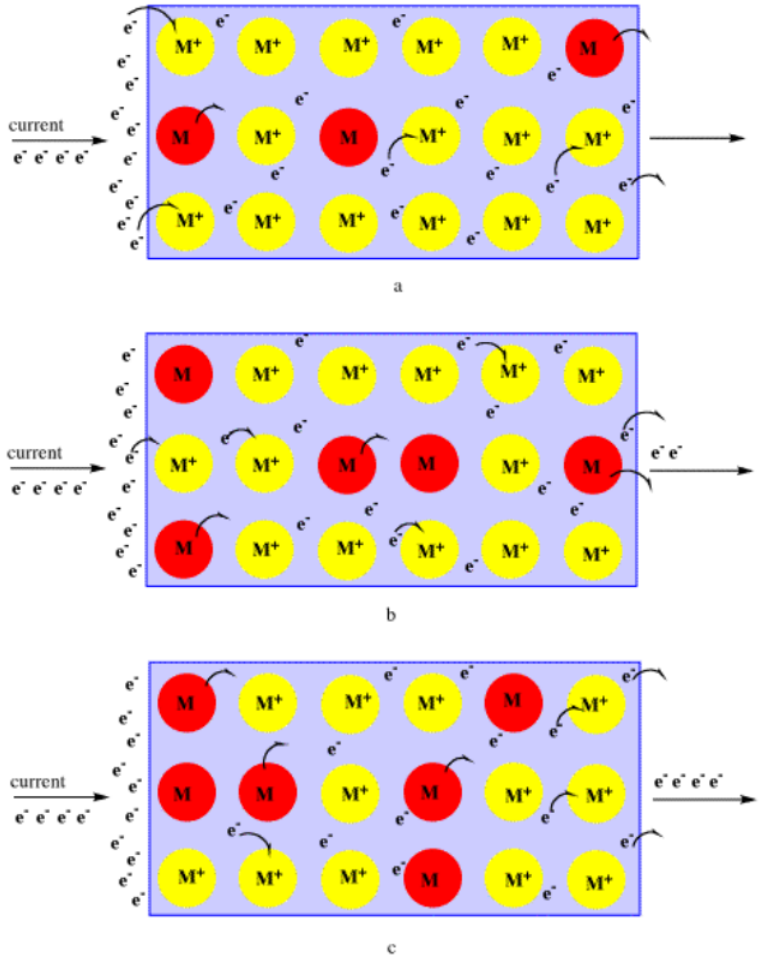

Figure 2.1.6: **Electrical conductance in a metal.** Diagram showing how, when a current of electrons is added, the electrons move from metal cation to metal cation, attracted by the positive charges.

The shininess of metals is also attributed to the electron-sea aspect of metallic bonding. Collisions between incoming photons and the "free" electrons at the surface of a metal cause the photons to bounce off the surface. The reddish color of copper results from a limit on the wavelengths of visible light that bounce off the metal.

- The electron sea model is used to explain several unique properties of metals.

So far, we have looked at the electron sea model purely in terms of electrostatics: the negatively charged electron is attracted to the positively charged nucleus. However, we already saw in the discussion of quantum mechanics in the atom that kinetic energy and the wavelength of the electron is also an important factor in chemistry.

Figure 2.1.7: Symbolic drawing of the longest possible wavelength of an electron that is confined to one atom (left) compared to an electron that is delocalized over a group of atoms (right). Left: Diagram of a wave shortened to fit over one atom. Right: Row of five atoms, showing one wave with a much longer wavelength than at left.

? Exercise 2.1.3

Suppose the following boxes are half-filled with water. Show the longest wavelength possible in each of the boxes.

Answer

The longer the box, the longer the possible wavelength.

In the electron sea model of metallic bonding, the electrons can be delocalized. They are no longer confined to a single atom, but can be spread out over multiple atoms. As a result, the wavelength of the electron increases. Because wavelength is inversely proportional to energy, as an electron's wavelength increases, its energy goes down. As a result, spreading electrons out over a group of metals results in a decrease in energy because of the wave properties of electrons.

- Delocalization is an important concept in chemistry.
- Delocalization is related to the "particle-in-a-box" concept: the longer the container, the longer the possible wavelength.
- By spreading out over a larger group of atoms, an electron can adopt a longer wavelength.
- An electron with a longer wavelength has a lower energy.

Some of the properties of metals can be understood, given a basic outline of the structure of a metal. We are going to look in more detail at exactly how metal atoms arrange themselves into solids, before we look at some of the ways metals form compounds with other elements.

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2.2: A Layer of Metal Atoms

Metals are composed of atoms in ordered layers. These atoms form a three-dimensional, crystalline structure. That means that the individual units within the solid -- the atoms, in this case -- are organized in a regularly repeating pattern, like the stars on the American flag.

Three-dimensional things can be difficult to think about. It's much easier to start in two dimensions. On this page, we're going to look at a couple of ways that metal atoms could arrange themselves in a single layer. We'll build up from there later on. In the meantime, we'll try to develop familiarity with a number of terms that are used to describe crystalline structures.

Simple Squares

We live in a Cartesian society. Our houses and buildings are mostly square, our rooms are square, our streets are straight and meet at right angles, unless we live in a meandering place on the water, like Boston or Venice. It's probably easiest to imagine layers of atoms that form nice squares.

Suppose a group of atoms forms a nice, straight line. Another group forms a second line, and each atom in the second line sits directly behind an atom in the first line. A third row forms in the same way. The resulting layer has neat rows and columns of atoms. The pattern of atoms regularly repeats as you look from right to left, and as you look from front to back.

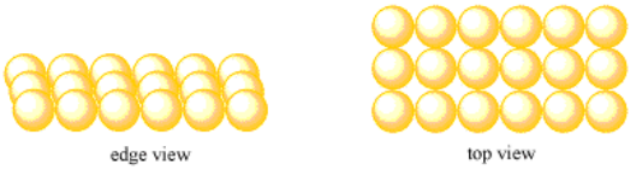


Figure 2.2.1: **A simple square layer of atoms.**

We will call this type of layer a simple square layer.

- In a square layer, atoms are arranged in rows and columns.

Hexagonal Layers

Some metals atoms may be arranged in simple square layers. Others adopt a slightly different arrangement.

Start with the same, neat line of atoms in the first row. This time, when the second row of atoms forms, we won't put them directly behind the atoms in the first row. We'll put them just in between the atoms in front. Each atom in the second row sits behind two atoms in the first row, as if it were peeking between them, like kids in a kindergarten class photo (before they all squirm around).

The third row will also be slightly offset from the row in front of it. If you look carefully, you can see that puts each of the third row atoms directly behind an atom in the first row, but an extra row farther away. The fourth row will be slightly offset from the third, and so on.

Figure 2.2.2: **A hexagonal layer of atoms.**

We still have a crystalline structure. There is a regularly repeating pattern as we look from left to right. There is also a repeating pattern as we move from front to back, but now that pattern repeats every other row, instead of every row.

This type of layer is called a hexagonal layer. Sometimes, it is called a close-packed layer.

- In a hexagonal layer, the rows are offset from each other by half an atom.
- Each atom in a hexagonal layer is surrounded by six other atoms.

Exercise 2.2.1

a. Look at the simple square layer. Can you find repeating patterns in other directions (rather than left-right or front-back)? If so, in what direction?
b. Look at the hexagonal layer. Can you find repeating patterns in other directions (rather than left-right or front-back)? If so, in what direction?

Answer a:

The pattern also repeats diagonally.

Answer b:

The pattern also repeats diagonally.

Exercise 2.2.2

We usually think of atoms as little spheres, or circles if we are working in just two dimensions. How might other shapes form an organized layer? Draw an organized layer for each of the following shapes, using about a dozen units in each case.

a. squares.
b. triangles (equilateral: all sides the same length).
c. hexagons.
d. pentagons.

In each case, is there only one way to pack the shapes in a regular way? Can you find repeating patterns in the layer? If so, in what direction?

Are there any shapes that seemed more difficult to arrange in a repeating layer?

Answer

The squares can form a number of regularly repeating patterns. The rows can exactly repeat (an aaa pattern), or they can be shifted slightly, so that every other row exactly repeats the first row (an ababab pattern). They could even be shifted so that every third row is an exact repeat of the first (abcabcabc).

The pentagons do not form a repeating layer in two dimensions.

Holes

Unlike some other geometric shapes, circles do not pack together with no space in between them. The spaces in between atoms within a layer are called holes. Note that the use of the word "holes" here has nothing to do with holes in conductivity-speak. On this page, holes are just spaces between atoms. In conductivity, holes are places where there is positive charge that could capture an electron.

Sometimes, the spaces between the atoms are described in other ways, such as "interstitial sites".

Later on, these interstitial sites or holes will be important in building compounds from mixtures of elements. You will see that the empty spaces in an array of atoms leave room for a second kind of atom to pack into the same structure.

Exercise 2.2.3

Holes generally have particular shapes. The shapes vary, depending on how the atoms are arranged. For example, how would you describe the shape of the holes in the following layers:

a. simple square packing.
b. hexagonal or close packing.

Answer a:

In the simple square packing, the holes are roughly diamond shaped.

Answer b:

In the hexagonal pattern, the holes are roughly triangular.

You can come up with an answer by looking at a drawing, or you can try packing a layer of dimes or pennies or quarters (as long as they are all the same) and look at the spaces between them

Unit Cells

The simplest repeating unit in a pattern is sometimes called the unit cell. In a layer, the unit cell can be traced again and again over the layer, so that every part of the layer is accounted for (but depending where you start tracing, you might run out of room at the edges).

Figure 2.2.3: **A simple row of atoms. The unit cell is a repeating unit along the row.**
Left: a single unit cell comprised of two halves of two neighboring atoms. Right: several unit cells lined up, showing that unit cells repeat.

Because each layer is composed of individual atoms, we might call a single atom the unit cell. However, we also use the unit cell to illustrate the spatial relationship between the atoms in the layer. For that reason, we often shift the unit cell to show multiple atoms.

For example, in a row of atoms, a unit cell might be a square. The ends of the square would cut through two neighbouring atoms. The unit cell contains two half-atoms, for a total of one atom. The square could be repeated in a straight line to reproduce the row of atoms.

- The unit cell is the smallest repeating unit in the structure.
- The unit cell shows the pattern that is found in the structure.

In a layer of atoms, the unit cell might once again be thought of as a single atom. However, we can more clearly show the relationships between these atoms by choosing a slightly different cell. The unit cell in a simple square layer is just a square that contains the corners of four neighbouring atoms. The unit cell in a hexagonal layer is a rhombus that contains the corners of four neighbouring atoms.

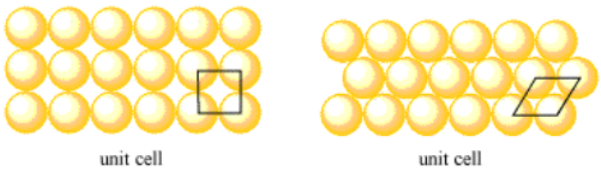


Figure 2.2.4: **The unit cell in a simple square layer (left) and in a hexagonal layer (right).**
Left: a square unit cell in a square array of atoms. Right: a hexagonal array of atoms, showing different angular shape of the unit cell.

? Exercise 2.2.4

In the following cases, show that the given unit cells repeat throughout the structure.

a. simple square layer: a square unit cell
b. hexagonal layer: a rhombic unit cell

Note: in the hexagonal layer, you can find an additional way to do this if you *rotate* copies of the unit cell to get unit cells facing in three different directions.

? Exercise 2.2.5

In the following cases, show what fractions of atoms are found in the unit cell. Add the fractions to find the combined total of atoms in the unit cell.

a. simple square layer: a square unit cell
b. hexagonal layer: a rhombic unit cell

Packing Efficiency

Packing efficiency is one of the questions people wonder about in crystal structures. It deals with how tightly the atoms are packed together in a structure. Often, the more tightly packed the structure, the better (but it does not always happen that way).

Figure 2.2.5: **Packing efficiency refers to how tightly atoms are packed together.**

Why might tighter packing of metal atoms be favored? It has to do with the fact that the metal atoms are interacting with each other. The closer they are together, the more strongly they can interact.

There are a couple of ways we can think about that interaction. In the simplest idea of the electron-sea model, metal atoms have become metal cations, and are surrounded by electrons. The closer the metal atoms can get to the electrons, the more strongly they will interact. In general, we think of the metal atoms as sharing their electrons; the closer the metal atoms are to each other, the more efficiently the electrons can be shared.

Let's just work with that idea of electrostatic attraction. Imagine a group of atoms in a simple square layer. All of the atoms are touching their neighbors on either side. Let's think about the distance between a nucleus and an individual electron in the electron sea. We know that the nucleus is in the center of the atom. We don't know exactly where a free electron is, but let's assume it is in the center of the nearest hole. Remember, the closer the electron is to the nucleus, the lower the energy.

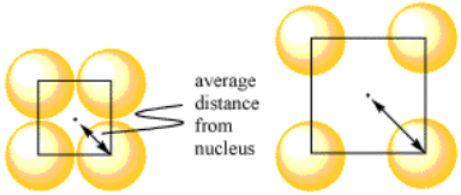


Figure 2.2.6: **Packing efficiency has an influence on the strength of interactions between metal nuclei and the electrons in the "electron sea".**

For comparison, maybe there is another set of atoms, also in a simple square layer. Suppose they are well-separated from each other; maybe they are far enough apart that you could fit an extra atom between each pair if you wanted to. If the free electron is in the same place -- the middle of the nearest hole -- you can see that it is much farther from the nucleus in this case. The force of attraction is much lower in this case, and the overall energy is not as low.

- Most metals pack very efficiently together to form a solid.
- Efficient packing leads to stronger bonding interactions.

That first case, with atoms packed more tightly together, may be preferable, because of the stronger interaction between the metal nucleus and the free electron. For reasons like this, understanding the packing efficiency in a crystal can be very important.

Exercise 2.2.6

Go to your piggy bank and break out a bunch of pennies, nickels, quarters or dimes. You will need at least four of each, but nine of them is a good number. Pack one type of coin into the following layers:

a. simple square
b. hexagonal or close packed

Answer a:

Using quarters, the distance is about 5 mm.

Answer b:

Using quarters, the distance is about 2.5 mm.

A free electron would be closer to the atoms in a hexagonal close packed layer. There would be stronger electron-ion attraction in that case.

In each case, measure the distance from the edge of one coin to the center of the hole.

In which case is the free electron closer to the atom? Does the packing system (the type of layer) have an effect on how tightly bonded that atoms are?

Exercise 2.2.7

Go to your piggy bank and break out a bunch of quarters AND a bunch of dimes. You will need at least four of each, but nine of them is a good number. Pack each type of coin into the following layers:

a. simple square
b. hexagonal or close packed

Answer a:

Using dimes, the distance is about 3.5 mm.

Answer b:

Using dimes, the distance is about 1.5 mm.

A free electron would be closer to the atoms if the atoms were smaller. There would be stronger electron-ion attraction in that case.

In each case, measure the distance from the edge of one coin to the center of the hole.

In which case is the free electron closer to the atom? Does the size of the atom have an effect on how tightly bonded that atoms are?

Exercise 2.2.8

When a metal melts, the atoms go from a tightly-bound, regular array of atoms to a loosely-bound set of mobile atoms.

Compare the melting points of the following metals, given in degrees Celsius.

potassium: 64 cesium: 29 lithium 181 sodium: 98 francium: 27

a. Can you determine any trends among these values?
b. Can you provide a physical explanation for your observation? (You may have found a trend, but can you explain it?)

Answer a:

melting points (and force of attraction between atoms): Fr < Cs < K < Na < Li

Answer b:

This trend mirrors the sizes of the atoms. Lithium is the smallest and francium the largest. The electron / ion attraction is greatest in Li and weakest in Fr.

Exercise 2.2.9

Packing efficiency is often determined more rigorously in terms of the percentage of a unit cell that is actually occupied by atoms. What is the total area of a unit cell in the following layers?

a. simple square layer.
b. hexagonal layer.

Answer a:

The total area of this square is

$$Area = w^2$$

in which w = width of the unit cell. The width of the unit cell is

$$w = 2r$$

in which r = radius of titanium atom.

$$Area = 4r^2 = 4(2.00 \times 10^{-10} m)^2 = 4(4.00 \times 10^{-20} m^2) = 1.60 \times 10^{-19} m^2$$

Answer b:

The total area of this rhombus is

$$Area = s^2 sin\theta$$

in which s = one side of unit cell and θ = an angle of the unit cell (either 60° or 120°). But

$$s = 2r$$

in which r = radius of titanium atom.

$$Area = (2 \times 2.00 \times 10^{-10} m)^2 sin(60) = 1.60 \times 10^{-19} (0.87) m^2 = 1.39 \times 10^{-19} m^2$$

You can assume the atoms are titanium. Titanium has an atomic radius of 2.00 Angstroms (or 2.00 x 10^{-10} m).

Exercise 2.2.10

How many titanium atoms are there in a unit cell in the following layers?

a. simple square layer.
b. hexagonal layer.

Answer a:

$$4 \times \frac{1}{4} = 1\ atom$$

Answer b:

$$2 \times \frac{1}{6} + 2 \times \frac{1}{3} = \frac{2}{6} + \frac{4}{6} = 1\ atom$$

You may need to add up fractions of titanium atoms to arrive at the answer. The answer may or may not be a whole number.

Exercise 2.2.11

What is the area occupied by a titanium atom?

(If you think the question is ambiguous, assume we're concerned about the area of a cross-section of the atom at its widest part. It is a spherical atom, but we are dealing with its projection in two dimensions, i.e. its shadow when the sun is directly overhead.)

Answer

The cross-sectional (two dimensional) area of a titanium atom is the area of a circle

$$Area = \pi r^2$$

$$Area = 3.1415 \times (2.00 \times 10^{-10} m)^2 = 3.1415 \times 4.00 \times 10^{-20} m^2 = 1.257 \times 10^{-19} m^2 = 1.26 \times 10^{-19} m^2$$

Exercise 2.2.12

In the following cases, what percentage of the unit cell is filled with titanium atoms?

a. simple square layer.
b. hexagonal layer.

Answer a:

$$Efficiency = \frac{occupied}{total} \times 100\% = \frac{1.26 \times 10^{-19} m^2}{1.39 \times 10^{-19} m^2} \times 100\% = 91\%$$

Answer b:

$$Efficiency = \frac{occupied}{total} \times 100\% = \frac{1.26 \times 10^{-19} m^2}{1.39 \times 10^{-19} m^2} \times 100\% = 91\%$$

> *A greater percentage of space is occupied in hexagonal close packing.*

The percentage of unit cell that is occupied by atoms is called "the packing efficiency".

Coordination Number

There are a number of terms used in describing the relationships between atoms and the atoms to which they are directly bonded. For example, we use the term "coordination number" to describe the number of other atoms that a specific atom is touching in a regular layer.

Exercise 2.2.13

What is the coordination number of an atom in

a. simple square layer
b. hexagonal layer

Answer a:

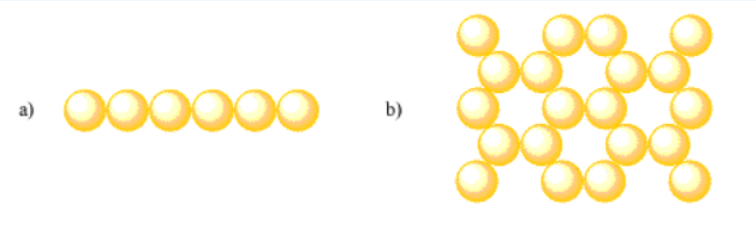
coordination number = 4

Answer b:

coordination number = 6

Exercise 2.2.14

What is the coordination number of an atom in the following layers:



Answer a:

Answer b:

Answer a:Assuming the pattern extends linearly, coordination number = 2. Otherwise, coordination number = 2 for interior atoms and coordination number = 1 for terminal atoms.Answer b:Assuming the pattern extends in two dimensions, coordination number = 3. Otherwise, coordination number = 3 for interior atoms, coordination number = 2 for side edge atoms and coordination number = 1 for corner atoms.Images for Exercise 2.2.14 a and b. a is a single row of six atoms. b is a hexagonal arrangement of atoms; each hexagon has an empty center and is composed of six atoms.

Coordination Geometry

Take a look at all of the atoms surrounding one specific atom in a layer. If you were to draw a line from the center of one of these atoms to the next, and go all the way around until you got back to the beginning, you would get a specific shape. That shape is described as the coordination geometry of the central atom. It's closely related to the coordination number. In two dimensions, two atoms with the same coordination number always have the same coordination geometry. Occasionally in three dimensions, two atoms with the same coordination number can have different coordination geometries; the atoms that they are touching may be arranged in slightly different ways.

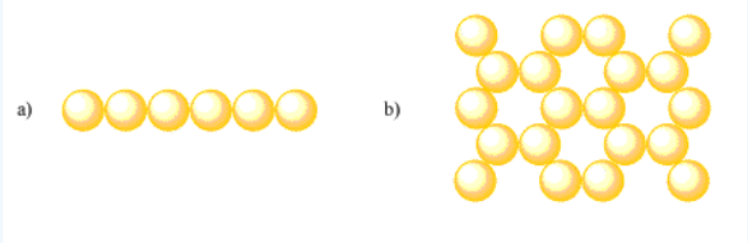
Exercise 2.2.15

What is the coordination geometry of an atom in

a. simple square layer
b. hexagonal layer

Exercise 2.2.16

What is the coordination geometry of an atom in the following layers:



Images for Exercise 2.2.16 a and b. a is a single row of six atoms. b is a hexagonal arrangement of atoms; each hexagon has an empty center and is composed of six atoms.

Lattice

Sometimes, the arrangement of atoms in a crystal is referred to as "an array" or "a lattice". At this point, an array or lattice is just the two-dimensional network of atoms in a layer. Later, we will see three-dimensional arrays of atoms. Metallic solids are usually three-dimensional, not two-dimensional. However, as we start to build up to a third dimension, you will see that most of the ideas on this page have analogies in 3D.

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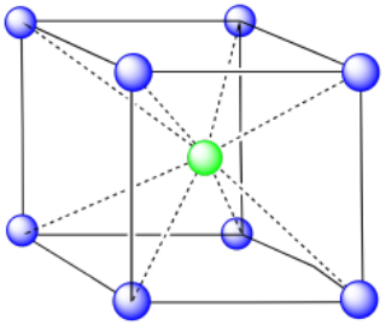
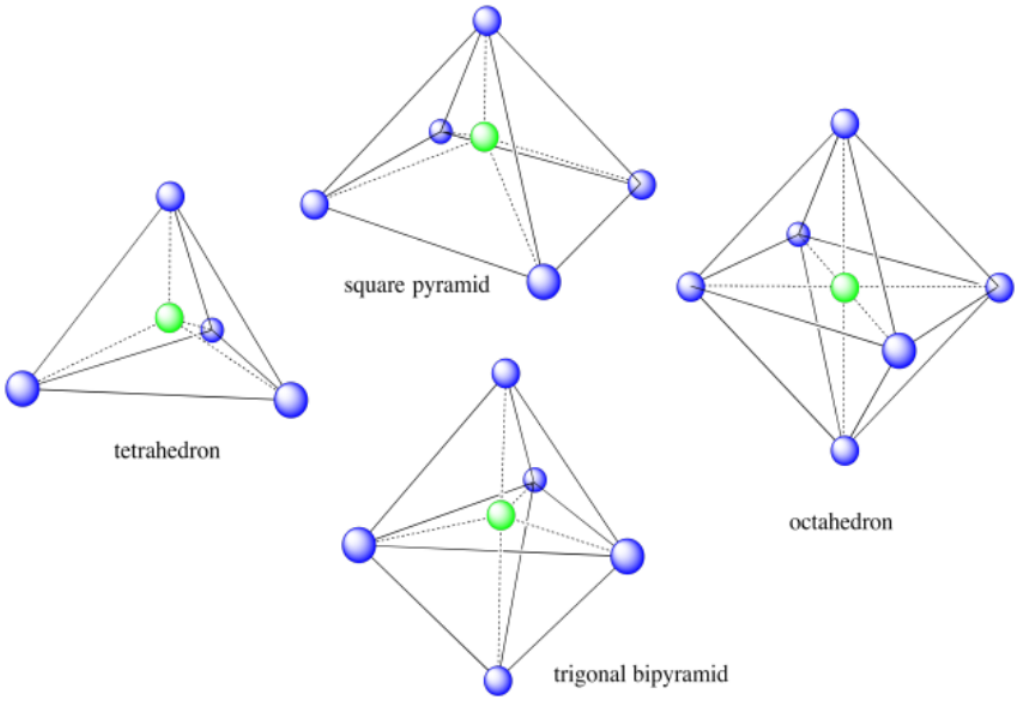
2.3: Building Metal Atoms in Three Dimensions

What sort of structures compose the world around us? What sort of shapes do we see in the building blocks of the material world? The ancient Greeks placed special significance on certain perfect shapes, or Platonic solids. These shapes were considered to be perfect because they were so regular, with equally sized sides arranged at identical angles to each other, so that the solid would look the same when viewed from different angles. For example, a cube has four square sides, all connected at right angles to each other. These Platonic solids were sometimes associated with the classic elements as perceived at the time: earth, air, fire and water.



As it happens, the Greeks were not that far from the truth. Certain solids do appear frequently in the structures of nature, including the classic Platonic solids. These shapes just happen to describe the natural way that a group of atoms might arrange themselves when they come together to build a larger structure. Very often, we find an atom at the center of a Platonic solid, with other atoms arranged around it to form the corners of the solid.

In addition to the cube shown above, the tetrahedron and octahedron are extremely common Platonic solids found in natural structures. A couple of non-Platonic solids that we sometimes see are the square pyramid (think of the ones in Egypt) and the trigonal bipyramid; however, we won't encounter those in nature for a few more chapters.



Models of a tetrahedron, square pyramid, octahedron, and trigonal bipyramid, showing spheres at the vertices and the centers of each shape.

? Exercise 2.3.1

For each of the following solids, identify the number of (i) corners and (ii) faces.

a) cube b) tetrahedron c) square pyramid d) trigonal bipyramid e) octahedron

Answer a:

(i) 8

(ii) 6

Answer b:

(i) 4

(ii) 4

Answer c:

(i) 5

(ii) 5

Answer d:

(i) 5

(ii) 6

Answer e:

(i) 6

(ii) 8

We will see cubic, octahedral and tetrahedral shapes cropping up as we look at the structures of extended solids such as metals and salts. In the solid state, metals are very neat, orderly structures. Metal atoms form a three-dimensional, crystalline structure. We will start thinking about those structures by seeing how they can be built up from simpler, two-dimensional layers.

Building up from Squares: Simple Cubic Packing

Take a simple square layer of atoms. Suppose another layer forms on top of that one, with atoms arranged in the same way as the first layer. Each atom in the second layer sits directly on top of an atom in the first layer.

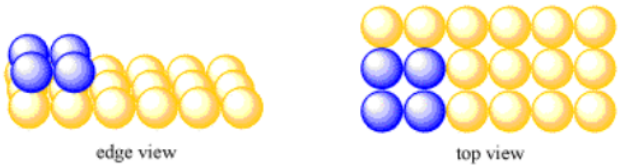


Figure 2.3.1: **Adding a second layer of atoms to a simple square layer.**
An edge and top view of a single rectangular layer of yellow atoms with a small square of blue atoms on top, overlaid directly on top of the bottom atoms.

This is a very neat, ordered, simple structure. All of the atoms are lined up in straight rows, aisles and columns. The structure looks exactly the same if viewed along the x-axis, along the y-axis, or along the z-axis.

The simplest repeating unit in three dimensions is usually thought of as a box or cube with atoms at each of its eight corners. Alternatively, we might think of the repeating unit as a cube with one atom in its center. However, it's useful to see the relationships between multiple atoms in the unit cell. For that reason, we usually picture the unit cell as the cube with an atom at each corner. Because each of those corners is shared between several unit cells, it is better to think of each unit cell as only owning a fraction of each corner atom.

- A simple cubic unit cell is based on a square layer.
- Squares of atoms are repeated in the x, y and z directions.

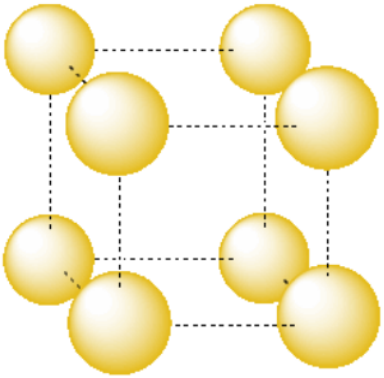


Figure 2.3.2: **A simple cubic unit cell. The atoms are separated so that you can see their relationship more clearly.**

In the following sections, unit cells will be shown with atoms separated even further from each other because the relationships between the atoms are even more complex. In the case of a simple cubic packing system, the unit cell would be shown as follows:

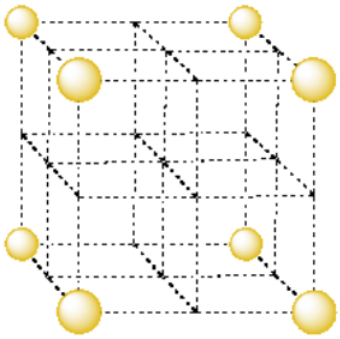


Figure 2.3.3: **A simple cubic unit cell. The atoms are separated so that you can see their relationship more clearly.**
A set of eight unit cells arranged in a cube: four on top and four on bottom. Eight atoms at the vertices are shown.

? Exercise 2.3.2

Take a look at the simple cubic unit cell.

a. What fraction of an atom is found in each corner of the simple cubic unit cell?
b. How many corners are there in the cube?
c. What is the total number of atoms in the simple cubic unit cell?

Answer a:

1/8 atom at each corner

Answer b:

8 corners in a cube

Answer c:

$8 \times \frac{1}{8} = 1$ atom per simple cube

Building up from Squares: Body-Centered Cubic Packing

That isn't the only way a three-dimensional solid could be built up from a simple square layer. Remember from the discussion of layers that atoms can sit a little more tightly together by staggering, so that one atom does not sit directly behind another. Instead, an atom in the second row sits behind a pair of atoms in the first row, and right in between them as viewed from the front. This sort of staggering happens easily in three dimensions, too.

In fact, if you take four oranges and make a square with them, and then decide to place a fifth orange on top of that layer, where is the obvious place to put this last orange? You would put it right in the middle of the first four, perched in the little valley on top of

them.

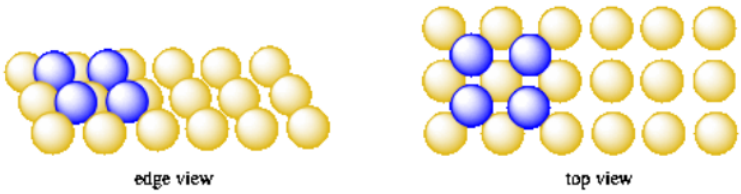


Figure 2.3.4: **Another cubic unit cell. The atoms are arranged based on a simple square layer.**
Edge and top view of a single layer of yellow atoms with four blue atoms on top. The four blue atoms are arranged in a square and rest in the corner spaces between the yellow atoms.

If you have a whole produce box full of oranges, you can make a bigger first layer of oranges, and start placing additional oranges in all of the little square valleys between the oranges of the first layer. Soon you will find that you have built a second, simple square layer. It is just like the first layer, but offset by half a unit cell to the side and half a unit cell to the back.

You can keep adding more layers until you run out of oranges or the whole thing falls down and rolls away. If you do so, you might notice that all the oranges in the third layer sit directly above the oranges in the first layer, and all the oranges in the fourth layer sit directly above the ones in the second layer. That's because each new layer is offset by half a unit cell, so every two layers, that shift adds up to one unit cell, and the oranges line up again. This pattern is sometimes described as an ABABAB pattern; that means the odd layers line up exactly with each other, and the even layers line up exactly with each other.

- Body-centered cubic packing allows the second layer of atoms to get a little closer to the atoms in the first layer.

The unit cell in this system, like the simple cubic system, is a cube with an eighth of an atom (or orange) at each corner. However, the corner atoms are not found in adjacent layers, but in alternating layers (such as the first and the third). An atom from the middle layer is also included in the cell; the entire atom is right in the center of the unit cell. This packing system is called body-centered cubic.

- The unit cell of a body-centered cubic system is a lot like the simple cubic unit cell.
- The body-centered cubic unit cell has an extra atom in its center.

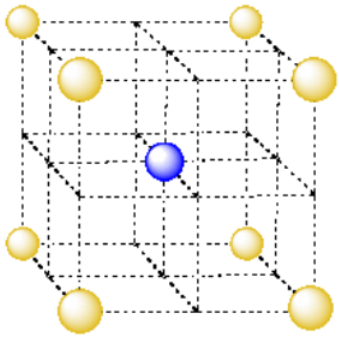


Figure 2.3.5: **A body-centered cubic unit cell.**

One important note: in a body-centered cubic system (and the other systems to follow), the atoms in the first layer are not quite touching each other. By backing off slightly from each other within a layer, there are closer interactions from one layer to another. The extra room allowed by spreading an individual layer out a little bit allows subsequent layers of atoms to nestle more deeply in those valleys. Stronger bonding interactions result from those close connections between layers.

By the way, you would have a hard time building up a simple cubic structure with oranges, unless you glued them together or used slightly flattened oranges, like clementines. There is more structural support in the body-centered cubic structure, because the oranges resting in valleys are distributing their weight to and getting support from four oranges beneath them, not just one.

? Exercise 2.3.3

Take a look at the body-centered cubic unit cell.

a. What fraction of an atom is found in each corner of the body-centered cubic unit cell?

b. How many corners are there in the cube?
c. Are there atoms anywhere else in the cube?
d. What is the total number of atoms in the body-centered cubic unit cell?

Answer a:

1/8 atom at each corner

Answer b:

8 corners in a cube

Answer c:

1 atom in middle of cube

Answer d:

$1 + 8 \times \frac{1}{8} = 2$ atoms per body-centered cube

Building up from Hexagonal Layers: Hexagonal Close Packing

Some metal atoms form hexagonal layers. Instead of being in close contact with four neighbouring atoms in a layer, an atom in a hexagonal layer is in close contact with six neighbouring atoms.

Do you still have your oranges? Suppose you start with a hexagonal layer of them. When another layer of oranges is added on top of a hexagonal layer, the new oranges don't sit right on top of the ones in the first layer. Instead, they sit in the little valleys between the oranges of the first layer. This is a little like the second layer of body-centered cubic packing. The difference is, in body centered cubic packing, all of the valleys between the oranges of the first layer are occupied by oranges from the second layer. In hexagonal packing, each orange in the first layer has six small valleys around it. You can't easily fit six oranges into all of those valleys at the same time; there isn't enough room. Instead, only *every other* valley is occupied by an orange, forming the second layer.

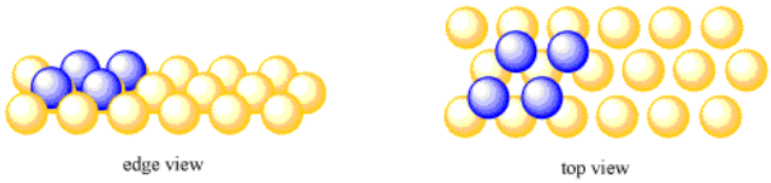


Figure 2.3.6: **Adding a second layer of atoms to a hexagonal layer.**
Edge and top view of a hexagonal layer of yellow atoms. Four blue atoms rest in the gaps between the yellow atoms.

In the drawing, you might notice that the atoms in one layer are separated slightly from each other. That's also to the second layer of atoms to fit more deeply into the valleys between the atoms in the first layer. Some close interaction between the atoms within a layer is given up in order to get better interactions between the atoms in different layers. It's a trade-off that leads to slightly stronger interactions overall.

Again, just like the systems based on simple squares, the second layer that forms looks a lot like the first. It is another hexagonal layer. It is shifted away from the first layer by half an atom to the side, and half an atom to the front or back.

- Hexagonal layers are not usually stacked with atoms directly on top of each other.
- Hexagonal layers get a little closer to each other by shifting so that atoms above can sit in valleys below.
- There isn't room for every valley to be occupied by an atom. Every other valley is left open.

Once we begin to add a third layer, we have a choice. Just like with the second layer, we can't add a new orange into every valley. We will have to add them into every other valley. We can either add them directly over the oranges in the first layer, or directly over the valleys that were left empty when we filled in the second layer.

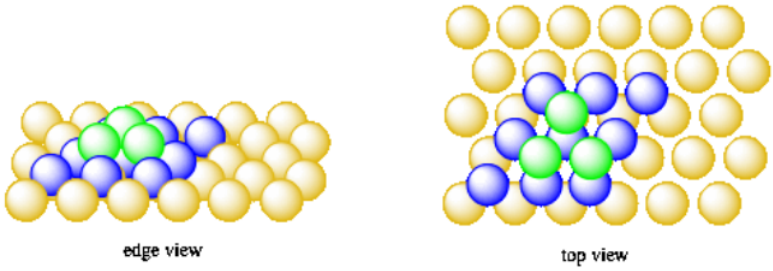


Figure 2.3.7: **Adding the third layer of atoms (green). There are two different ways to add this layer.**

Edge and top view of several layers of atoms. The bottom layer of yellow atoms is arranged hexagonally. The second layer of nine blue atoms rests in the spaces between the yellow atoms. The top layer of three green atoms rests in the spaces between the blue atoms.

Let's put them directly over the oranges in the first layer. When we add the oranges for the fourth layer, we'll put them directly over the ones in the second layer. This system of packing is called hexagonal close-packing.

- In hexagonal close packing, the third layer of atoms is directly above the first layer.
- This system is a little like body-cenetered cubic, but with a hexagonal base instead of a square one.

Before we consider the unit cell in this system (which is a little more complicated than in the cubic packing systems), let's take a look at these layers of atoms, with a little bit greater separation.

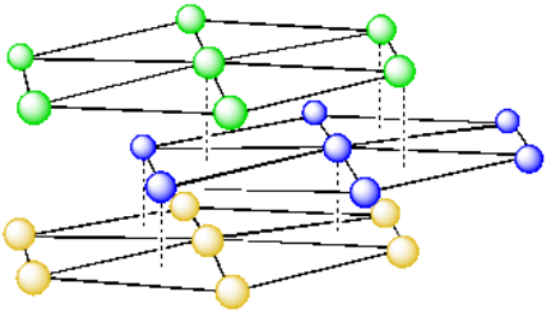


Figure 2.3.8: **Three hexagonal layers of atoms. The atoms in the top layer lie directly above the atoms in the bottom layer.**

Three layers of seven atoms. Each layer is colored green, blue, and yellow, from top to bottom. The atoms are arranged hexagonally at the vertices and center of the hexagon. The atoms of each layer are positioned so that an atom is at the farthest distance of the layer below it.

Because the atoms in the top layer are directly over the atoms in the bottoms layer, we can think of these two layers as being identical. We can show that by drawing them in the same color.

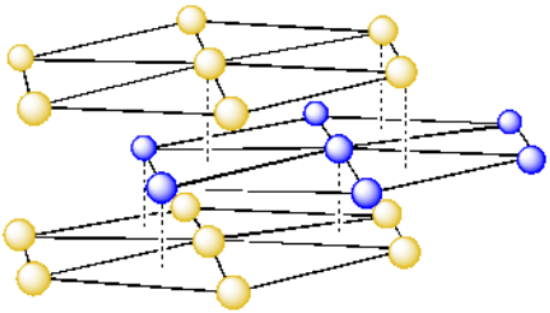


Figure 2.3.9: **Another view of three hexagonal layers of atoms.**

Three layers of seven atoms. The top and bottom layers are colored yellow, and the middle layer is blue. The atoms are arranged hexagonally at the vertices and center of the hexagon. The atoms of each layer are positioned so that an atom is at the farthest distance of the layer below it.

In a hexagonal single layer, the unit cell was a rhombus. We could use that to build the unit cell for a hexagonal close packed system. We would just add walls into the cell to build the simplest repeating unit.

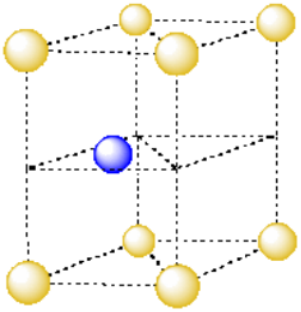


Figure 2.3.10: **The unit cell for a hexagonal close-packed system.**

A unit cell composed of two cubes with four atoms at the vertices. In the cube's interior, one atom is in the center of a triangle made by the diagonal cut through one square face.

Exercise 2.3.4

The pattern of layers in the simple cubic packing system was AAAAAA; each layer was placed so that each atom was directly above an atom in the layer below it. The pattern of layers in the body centered cubic arrangement was ABABAB; each atom in a layer was directly above one that was two layers down. Which pattern fits hexagonal close packing?

Answer

Hexagonal close packed pattern is ABAB.

Exercise 2.3.5

Take a look at the hexagonal close-packed unit cell.

a. What fraction of an atom is found in each corner of the hexagonal close-packed cubic unit cell?
b. Adding up all those fractions, how many corner atoms are within the cell?
c. Are there atoms anywhere else in the cell?
d. What is the total number of atoms in the hexagonal close-packed unit cell?

Answer a:

At both the top and bottom layer, two atoms are 1/3 within the cell and two atoms are 1/6 within the cell.

Answer b:

That makes $2 \times (2 \times \frac{1}{3} + 2 \times \frac{1}{6}) = \frac{4}{3} + \frac{4}{6} = \frac{4}{3} + \frac{2}{3} = 1$ atom total in corners

Answer c:

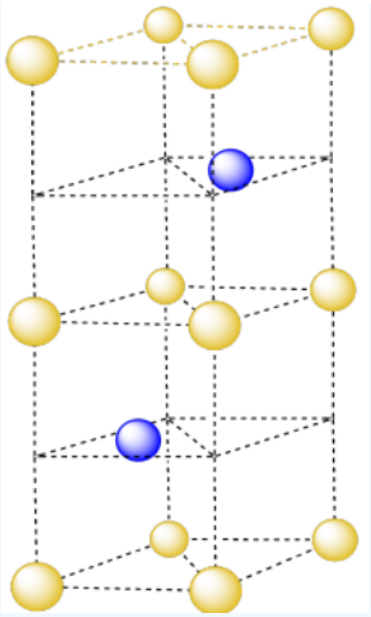
1 atom inside the cell.

Answer d:

2 atoms total.

Exercise 2.3.6

In the following variation on hexagonal close packing, the two unit cells appear to be slightly different.



Two hexagonal unit cells stacked on top of each other. The central atoms in the unit cells are on opposite sides.

a. What is the relationship between the two unit cells in the above structure?
b. How would you describe the relationships between the layers in the above structure (i.e. ABCABC etc)?

Answer

The pattern in this variation is ABACA.

Building up from Hexagonal Layers: Cubic Close Packing (or Face-Centered Cubic Packing)

Start with the same hexagonal layer of oranges. Once again, when another layer is added on top of that hexagonal layer, the new oranges don't sit right on top of the ones in the first layer. Instead, they sit in the little valleys between the oranges of the first layer. Remember, in hexagonal packing, each orange in the first layer has six small valleys around it. You can't easily fit six oranges into all of those valleys at the same time; there isn't enough room. Instead, only every other valley is occupied by an orange, forming the second layer.

Again, just like in the other systems, the second layer looks a lot like the first. It is another hexagonal layer. It is shifted away from the first layer.

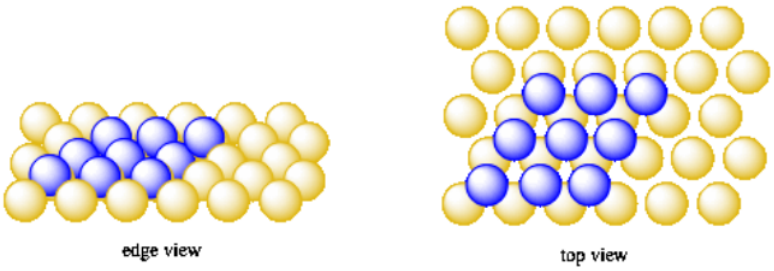


Figure 2.3.11: **Adding a second layer, just like before.**

Edge and top view of a hexagonal layer of yellow atoms. Four blue atoms rest in the gaps between the yellow atoms.

Once we begin to add a third layer, we have a choice. Just like with the second layer, we can't add a new orange into every valley. We will have to add them into every other valley. We can either add them directly over the oranges in the first layer, or directly over the valleys that were left empty when we filled in the second layer.

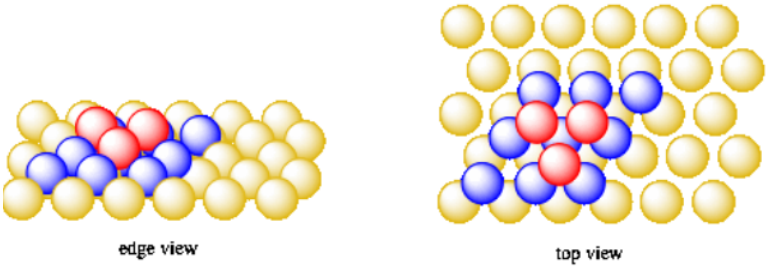


Figure 2.3.12: **Adding a third layer. This time, the atoms in the third layer are not directly above the atoms in the first layer.**
Edge and top view of several layers of atoms. The bottom layer of yellow atoms is arranged hexagonally. The second layer of nine blue atoms rests in the spaces between the yellow atoms. The top layer of three red atoms rests in the spaces between the blue atoms.

This time, let's put them directly over the holes in the first layer that were not filled before. When we add the oranges for the fourth layer, we'll put them directly over the oranges in the first layer. The oranges in the fifth layer will sit above the ones in the second layer, and the ones in the sixth layer will sit over those in the third layer.

- In cubic close-packing, the layers are actually hexagonal (also called "close-packed").
- In the third layer, the atoms do not lie directly above atoms in the first layer.
- Instead, the atoms in the third layer sit above the empty valleys from the first layer.

This system of packing is called cubic close-packing or face centered cubic packing.

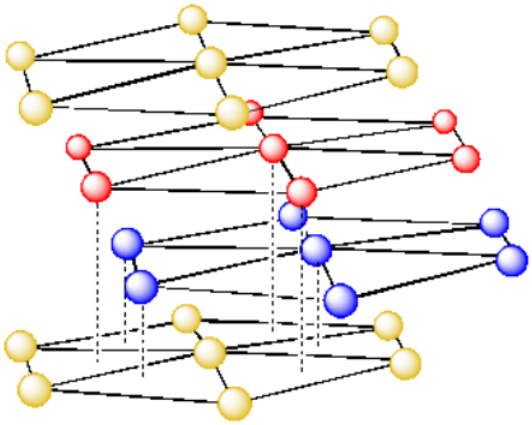


Figure 2.3.13: **Adding a third layer. This time, the atoms in the third layer are not directly above the atoms in the first layer.**
Four hexagonal layers of atoms, colored yellow, red, blue, and yellow from bottom to top. The top and bottom layers of yellow atoms are directly above each other.

? Exercise 2.3.7

The pattern of layers in the simple cubic packing system was AAAAAA. The pattern of layers in the body centered cubic arrangement was ABABAB. How would you describe the pattern in cubic close-packing?

Answer

ABCABC.

? Exercise 2.3.8

The unit cell in the hexagonal close-packed system was based on a unit cell from a single layer. Propose a similar unit cell for a cubic close-packed system.

a. What two-dimensional unit cell forms the base of this three-dimensional unit cell?
b. How many layers does the cubic close-packed unit cell cut through?
c. Draw the cubic close-packed unit cell.

Answer a:

The rhombus-shaped hexagonal unit cell.

Answer b:

4 layers.

Hey, wait a minute. Why do they call it cubic packing if the unit cell is based on a rhombus instead of a square? Maybe there is another way of looking at this structure. Maybe there is an alternative unit cell.

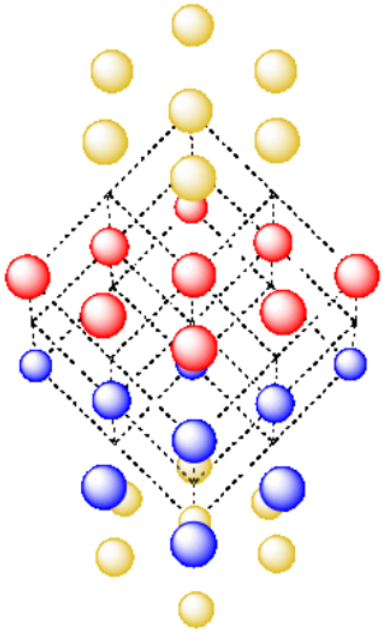


Figure 2.3.13: **Another look at cubic close-packing. This time, we will look for a cubic unit cell.**

Top view of four hexagonal layers of atoms, colored yellow, red, blue, and yellow from top to bottom. None of the layers directly match up with each other.

There is a cubic unit cell, but it is harder to see. The cube is tipped on one of its corners. We will strip away some of the extra atoms in the hexagonal layers so we can get a better look.

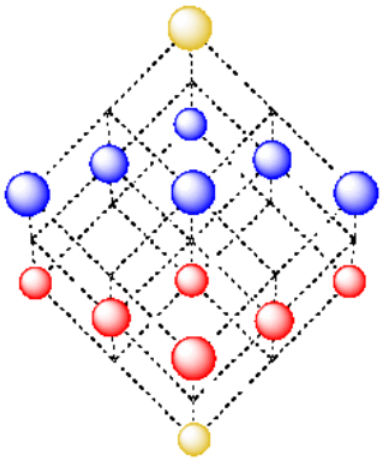


Figure 2.3.14: **Another look at cubic close-packing.**

Top view of hexagonal unit packing. Three layers of atoms, colored blue, red, and yellow from top to bottom, are shown.

There is an atom in the lowest layer that forms one corner of the cube. The opposite corner of the cube is an atom in the fourth layer. That atoms sits directly above the one in the first layer, the bottom corner of the cube. In between, three faces of the cube are tilted downwards. There is an atom in the middle of each of these faces; together with atoms at the three corners in between them,

these form a second layer in the structure. There are also three faces tilted upwards. There is an atom in the center of each of these faces; together with atoms at the three corners in between them, these form a third layer in the structure.

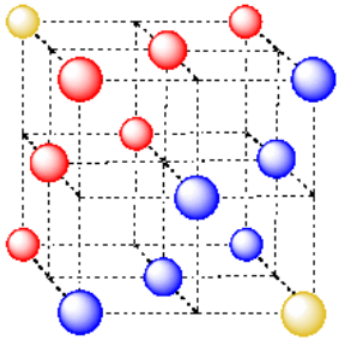


Figure 2.3.15: **A final look at cubic close-packing.**

Note that this cube has an atom in the center of each face; hence the name, face-centered cubic.

- A cubic close-packed takes the name "cubic" from the presence of a cubic unit cell.
- This cubic unit cell is oriented diagonally to the close-packed layers.
- This cubic unit cell has an atom in the ceneter of each face; it is also called "face-centered cubic".

? Exercise 2.3.9

Take a look at your new cubic close-packed unit cell.

a. What fraction of an atom is found in each corner of the cubic close-packed cubic unit cell?
b. How many corners are there in the cell?
c. Are there atoms anywhere else in the cell?
d. What is the total number of atoms in the cubic close-packed unit cell?

Answer a:

1/8 atom at each corner

Answer b:

8 corners in a cube

Answer c:

1/2 atom on each face of cube

Answer d:

$6 \times \frac{1}{2} + 8 \times 18 = 4$ atoms per face-centered cube

The type of packing adopted by a metal actually has some influence on the physical properties of the metal. For example, the metals that are closely associated with metal-working during antiquity, such as lead, gold, silver, and copper, generally adopt cubic close-packed structures. These metals have high values of "physical ductility" -- an index of how easily they can be stretched into wire. Titanium, cobalt, and zinc are hexagonal close-packed and have moderate values of physical ductility. Metals that adopt body-centered cubic packing, such as iron, tungsten, and chromium, usually have lower physical ductility.

This trend isn't a strict rule; some body-centered metals are more ductile than some cubic close-packed metals. Nevertheless, metal packing seems to be one factor in how easily metals can be stretched, bent, and worked. The reason it plays a role is because of the presence of "slip planes" in metal structure. Remember the idea that rows of metal atoms can slide across each other? It turns out that cubic close-packed metals form rows in lots of different directions, so their atoms can slip past each other pretty easily. In contrast, that central atom in a body-centered cubic cell acts like a speed bump for the layer of atoms above and below it, slowing down their movement.

Exercise 2.3.10

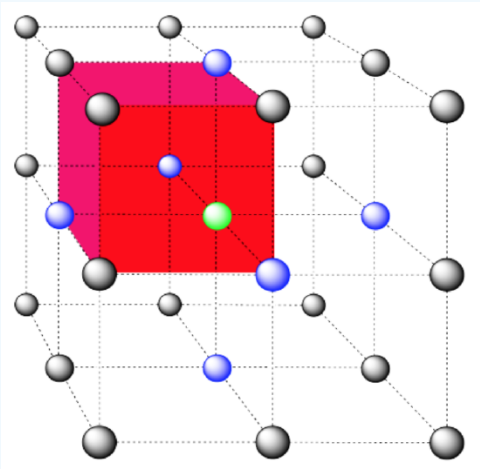
We saw previously that the number of near neighbors of a metal atom is called the coordination number. What is the coordination number in each of the following cases?

a. an atom at the corner of a simple cubic cell. Remember, it is surrounded by other unit cells, too.
b. an atom in the center of a body-centered cubic cell.
c. an atom in the corner of a body-centered cubic cell.
d. an atom in the corner of a face-centered cubic cell.
e. an atom on the face of a face-centered cubic cell.

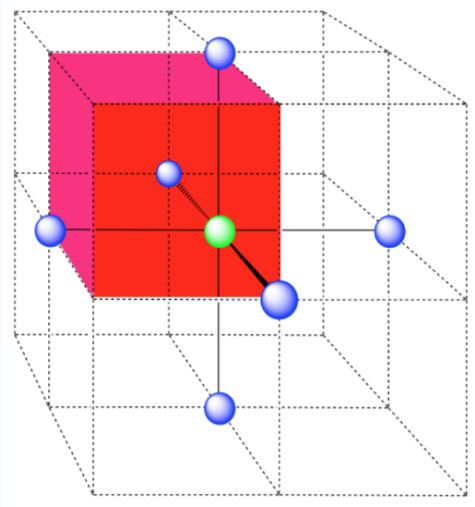
Answer a:

coordination number = 6 (3 within the cube, along the three adjacent edges, plus three on adjacent cubes).

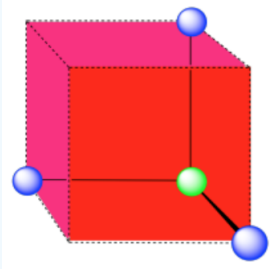
In the picture, consider the green atom coordinated by its nearest neighbors, the blue atoms. One unit cell is highlighted in red.



Here is the coordination environment without the surrounding atoms.

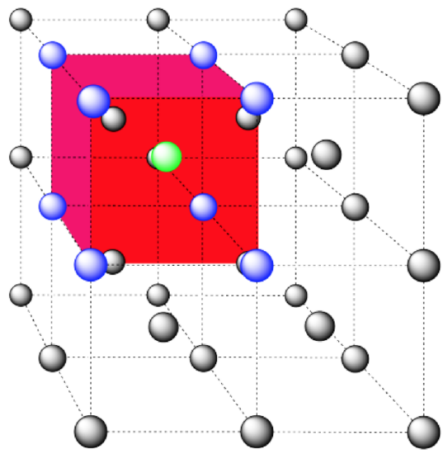


A single unit cell is shown for comparison. The three other nearest atoms are in cells below, behind and to the right of the one shown.

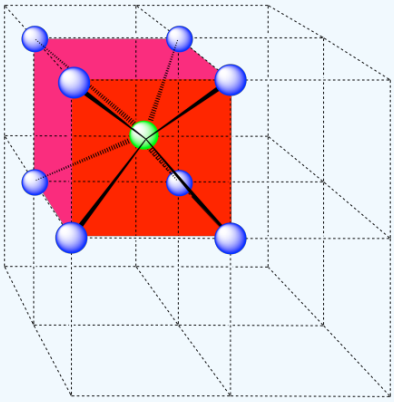


Answer b:

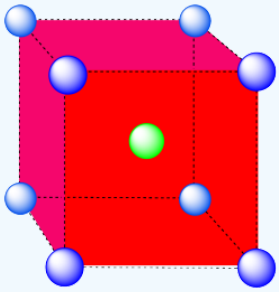
coordination number = 8 (corners of the cube).



Here is the coordination environment without the surrounding atoms.

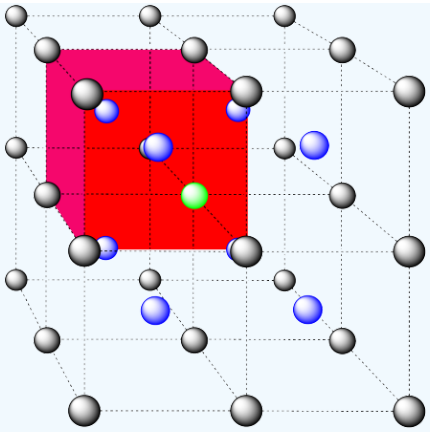


A single unit cell is shown below for simplicity. All of the coordinated atoms are found within the cell.

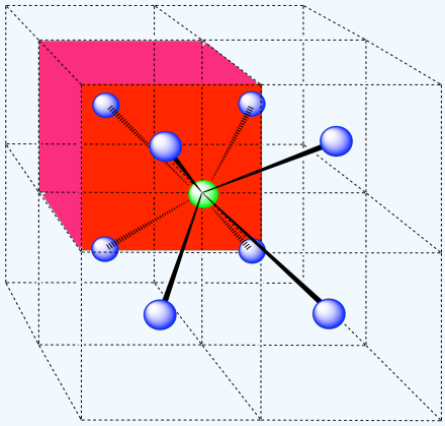


Answer c:

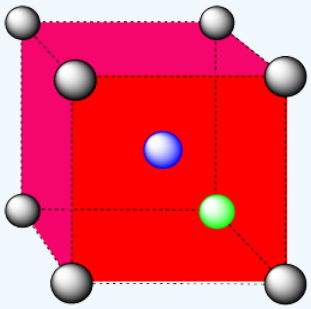
The closest atoms are in the centers of the adjacent cells; the other corners are further away; coordination number = 8.



Here is the coordination environment without the surrounding atoms.

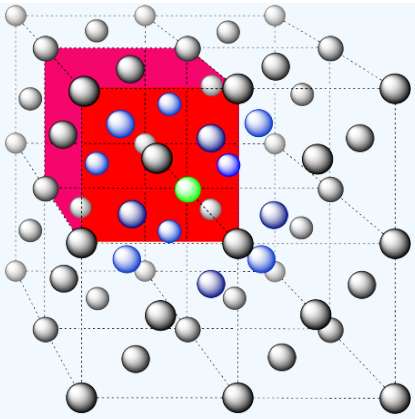


A single unit cell is shown below, for simplicity. Because the atom is in a corner, there are eight other cells arranged around this one: one on the right, two behind, and then four more below.

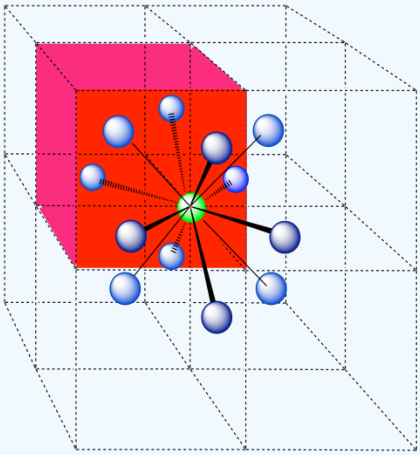


Answer d:

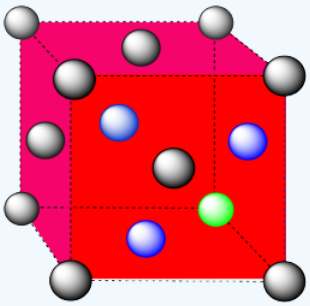
The closest atoms are on the faces adjacent to the corner position; these faces are found along three planes, with four faces surrounding the corner on each plane; coordination umber = 12.



Here is the coordination environment, without the atoms that are further from the green one.

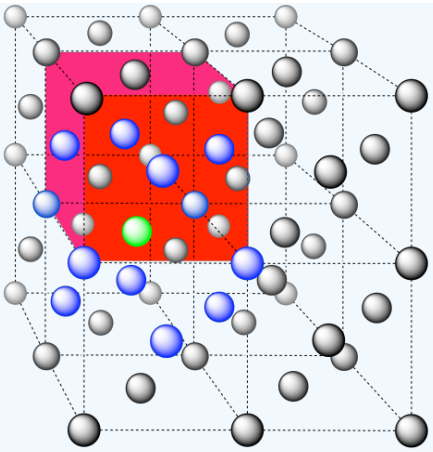


A single unit cell is shown below. Because the atom is in a corner, there are seven other cells arranged around this one: one on the right, two behind, and then four more below.

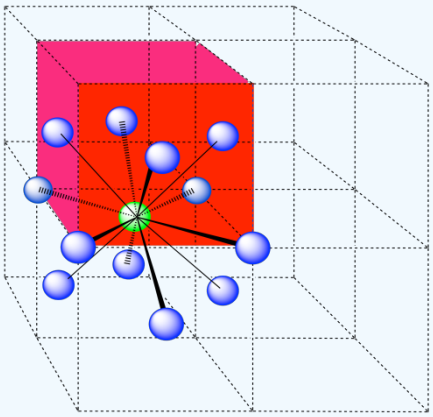


Answer e:

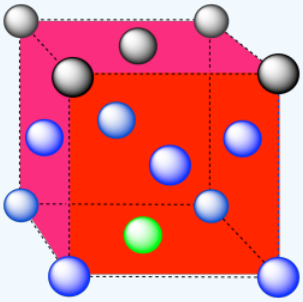
The closest atoms are at the corners around the face (4), as well as the atoms in the middle of each adjacent face (8); coordination number = 12.



Here is the coordination environment without the other atoms.



A single unit cell is shown below. There is another cell directly below it.



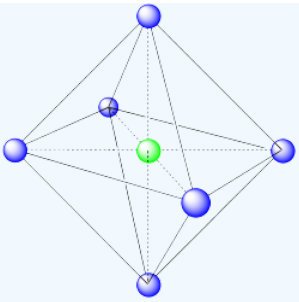
? Exercise 2.3.11

Coordination geometry is related to the coordination number. What is the coordination geometry in each of the following cases?

a. an atom at the corner of a simple cubic cell. Remember, it is surrounded by other unit cells, too.
b. an atom in the center of a body-centered cubic cell.
c. an atom in the corner of a body-centered cubic cell.

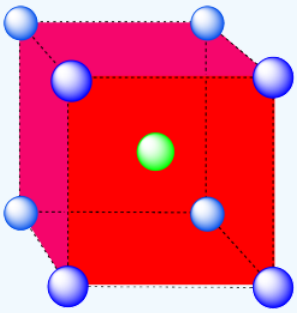
Answer a:

Octahedral. An octahedron has six vertices and eight faces.



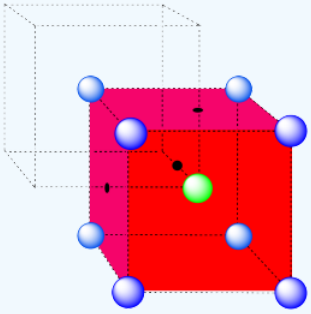
Answer b:

Cubic. A cube has eight vertices and six faces.



Answer c:

This is also a cube, translated from the last one (i.e. the cube is just shifted to a different position in the lattice).



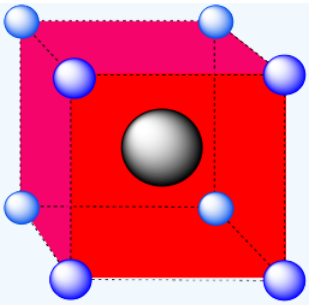
Exercise 2.3.12

We learned earlier about the holes or interstitial spaces between atoms in a layer. There are also holes between atoms in a three dimensional structure. For example, how would you describe the shape of the holes in the following cases:

a. the hole in the middle of a simple cubic cell.
b. a hole between the central atom and the face of a body-centered cubic cell.
c. the hole right in the middle of the face of a body-centered cubic cell.
d. the hole between the atoms forming a valley in one hexagonal layer and the atom sitting in the valley.
e. the hole between the atoms forming an empty valley in one hexagonal layer and the atoms in the layer above.

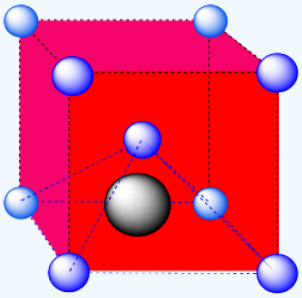
Answer a:

A cubic hole.



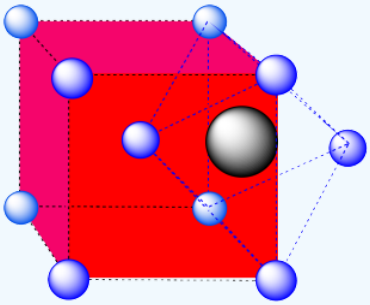
Answer b:

A square pyramidal hole. The atom in the hole is above a square of atoms, with an additional atom right above it.



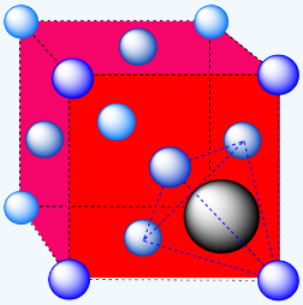
Answer c:

An octahedral hole. The atom occupying the hole has been pushed all the way to the face of the cube. It is right in the middle of a square of atoms. One of the vertices is in the center of the next cube.



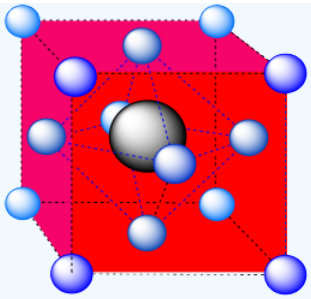
Answer d:

A tetrahedral hole. Note that the layers in the cubic closest-packed system run diagonally through the cubic unit cell. The atom in the hole sits above a trio of atoms on three adjacent faces, and is topped by the atom in the corner of the cube. Because a tetrahedron is so symmetric, the arrangement can be described in a number of other ways, choosing any three surrounding atoms as the base and the fourth atom as the cap of the tetrahedron.



Answer e:

An octahedron. Again, the hexagonal layers run diagonally through the unit cell.



Exercise 2.3.13

Packing efficiency is often determined in terms of the percentage of the volume of a unit cell that is actually occupied by atoms.

In the following cases, calculate the volume of the entire unit cell.

a. a simple cubic unit cell.
b. a body-centered cubic unit cell.
c. a face-centered cubic unit cell.
d. a hexagonal close-packed unit cell (remember, this cell is a rhombic prism, not a cube).

You can assume the atoms in the cell are titanium. Titanium has an atomic radius of 2.00 Angstroms (or 2.00 x 10^{-10} m).

Exercise 2.3.14

How many atoms are there in a unit cell in the following layers?

a. a simple cubic unit cell.
b. a body-centered cubic unit cell.
c. a face-centered cubic unit cell.
d. a hexagonal close-packed unit cell (remember, this cell is a rhombic prism, not a cube).

You may need to add up fractions of titanium atoms to arrive at the answer. The answer may or may not be a whole number.

Exercise 2.3.15

What is the volume occupied by a titanium atom?

Exercise 2.3.16

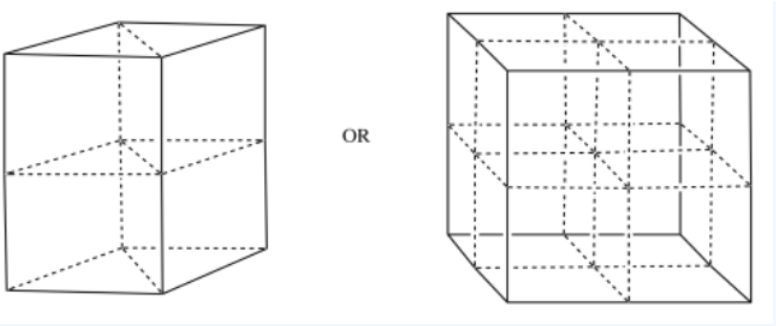
In the following cases, what percentage of the unit cell would be filled with titanium atoms?

a. a simple cubic unit cell.
b. a body-centered cubic unit cell.
c. a face-centered cubic unit cell.
d. a hexagonal close-packed unit cell.

The percentage of unit cell that is occupied by atoms is called "the packing efficiency".

Exercise 2.3.17

Use the appropriate template to draw one unit cell for each of the following metals.

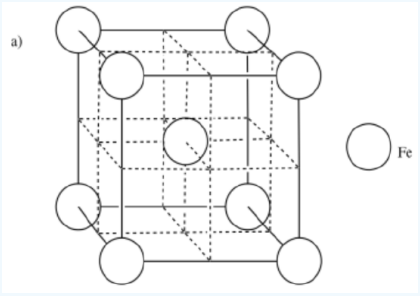


Left: rectangular prism composed of two cubes with diagonals drawn in. Right: cube divided into eight smaller cubes. The word "OR" is between the two diagrams.

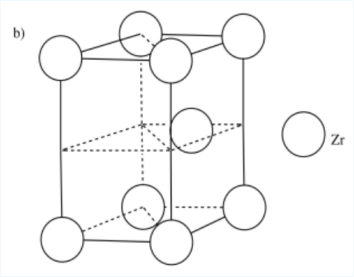
a) iron, Fe, is BCC b) zirconium, Zr, is HCP c) copper, Cu, is FCC

d) manganese, Mn, is BCC e) platinum, Pt, is CCP f) osmium, Os, is HCP

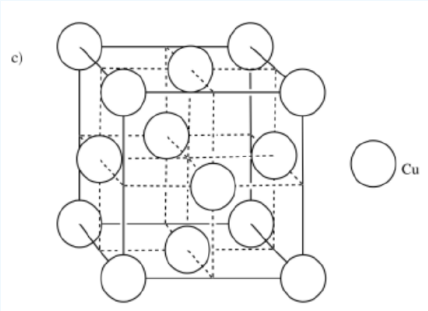
Answer a:



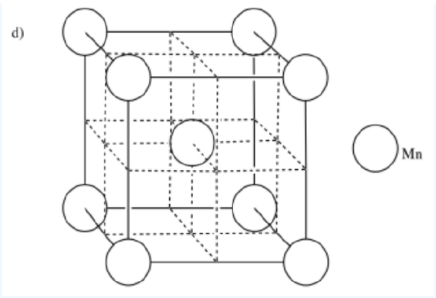
Answer b:



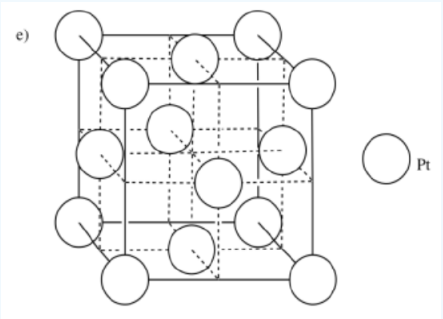
Answer c:



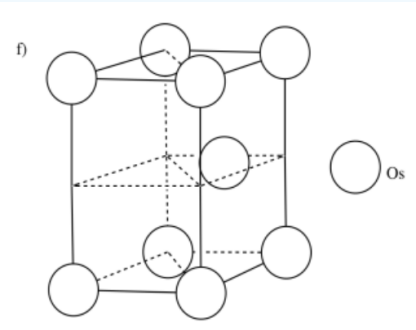
Answer d:



Answer e:



Answer f:



Want to see some additional information? Try these other sites that provide three-dimensional pictures of how atoms pack together.

Kings College Crystal Packing Lab

Naval Research Lab site

Bodner site at Purdue

Solid State site at Liverpool

Davidson College Crystals

Visualization of solid state structures: unit cells, etc.

Oxford University Solid Structures

Visualization of solid state structures: unit cells, etc.

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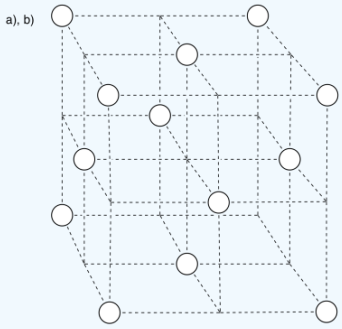
2.4: Application Problems with Metals

Exercise 2.4.1

Maraging steel is an alloy, Fe_3Ni, that forms a face-centered cubic unit cell. It is used for high-strength applications such as in the forging of fencing swords (epées).

a. Draw a cube.
b. Add circles to denote atoms in a face-centered cubic array.
c. Calculate the number of atoms in the unit cell (always show work).
d. Shade in selected atoms in the unit cell to give a 3:1 ratio of iron:nickel in the unit cell.
e. Add a legend with shaded and non-shaded circles so that it is clear which circle represents which atom.
f. Face centered cubic can also be thought of as forming hexagonal layers. The layers alternate to give which pattern? ABABAB or ABCABCABC
g. In the cubic diagram you made, put a letter beside each atom to indicate which of those layers (A or B or C) it is found in.
h. Why does the addition of nickel to the steel make the material more difficult to bend or break?

Answer a), b

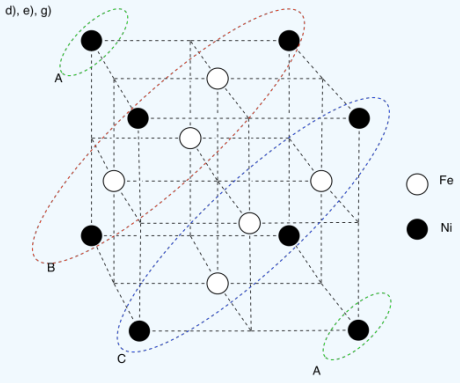


Answer c

There are eight atoms in the corner; each is shared by eight neighbouring cubes. There are six atoms on the faces; each is shared by two neighbouring cubes.

atoms = $8(\frac{1}{8})+6(\frac{1}{2})=1+3=4$ atoms

Answer d), e), g



Answer h

Nickel is a little smaller than iron. A row of atoms rolling along in the layer above would fall into the "pothole" caused by the smaller nickel atom and get stuck.

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2.5: Metals- Solutions to Selected Problems

Exercise 2.1.1

The second metal atom is a different size than the principle metal atom. It will not quite fit into the array of atoms. Consequently, the atoms will not be able to slide past each other as easily.

Exercise 2.1.2

$$2Fe:\ (3^+) \times 2 = (6^+)$$

$$3O:\ (2^-) \times 3 = (6^-)$$

Fe_2O_3: neutral

Exercise 2.1.3

The longer the box, the longer the possible wavelength.

Exercise 2.2.1

The pattern also repeats diagonally.

Exercise 2.2.2

The squares can form a number of regularly repeating patterns. The rows can exactly repeat (an aaa pattern), or they can be shifted slightly, so that every other row exactly repeats the first row (an ababab pattern). They could even be shifted so that every third row is an exact repeat of the first (abcabcabc).

The pentagons do not form a repeating layer in two dimensions.

Exercise 2.2.3

In the simple square packing, the holes are roughly diamond shaped.

In the hexagonal pattern, the holes are roughly triangular.

Exercise 2.2.6

a. Using quarters, the distance is about 5 mm.
b. Using quarters, the distance is about 2.5 mm.

A free electron would be closer to the atoms in a hexagonal close packed layer. There would be stronger electron-ion attraction in that case.

Exercise 2.2.7

a. Using dimes, the distance is about 3.5 mm.
b. Using dimes, the distance is about 1.5 mm.

A free electron would be closer to the atoms if the atoms were smaller. There would be stronger electron-ion attraction in that case.

Exercise 2.2.8

a. melting points (and force of attraction between atoms): Fr < Cs < K < Na < Li
b. This trend mirrors the sizes of the atoms. Lithium is the smallest and francium the largest. The electron / ion attraction is greatest in Li and weakest in Fr.

Exercise 2.2.9

a) The total area of this square is

$$Area = w^2$$

in which w = width of the unit cell. The width of the unit cell is

$$w = 2r$$

in which r = radius of titanium atom.

$$Area\ = 4r^2 = 4(2.00 \times 10^{-10} m)^2 = 4(4.00 \times 10^{-20} m^2) = 1.60 \times 10^{-19} m^2$$

b) The total area of this rhombus is

$$Area\ = s^2 sin\theta$$

in which s = one side of unit cell and θ = an angle of the unit cell (either 60° or 120°). But

$$s = 2r$$

in which r = radius of titanium atom.

$$Area\ = (2 \times 2.00 \times 10^{-10} m)^2\ sin(60) = 1.60 \times 10^{-19}\ (0.87) m^2 = 1.39 \times 10^{-19} m^2$$

Exercise 2.2.10

a. $4 \times \frac{1}{4} = 1\ atom$
b. $2 \times \frac{1}{6} + 2 \times \frac{1}{3} = \frac{2}{6} + \frac{4}{6} = 1\ atom$

Exercise 2.2.11

The cross-sectional (two dimensional) area of a titanium atom is the area of a circle

$$Area\ = \pi r^2$$

$$Area\ = 3.1415 \times (2.00 \times 10^{-10} m)^2 = 3.1415 \times 4.00 \times 10^{-20} m^2 = 1.257 \times 10^{-19} m^2 = 1.26 \times 10^{-19} m^2$$

Exercise 2.2.12

a. $Efficiency\ = \frac{occupied}{total} \times 100\% = (\frac{1.26 \times 10^{-19} m^2}{1.60 \times 10^{-19} m^2}) \times 100\% = 79\%$
b. $Efficiency\ = (\frac{occupied}{total}) \times 100\% = (\frac{1.26 \times 10^{-19} m^2}{1.39 \times 10^{-19} m^2}) \times 100\% = 91\%$

A greater percentage of space is occupied in hexagonal close packing.

Exercise 2.2.13

a. coordination number = 4
b. coordination number = 6

Exercise 2.2.14

a. Assuming the pattern extends linearly, coordination number = 2. Otherwise, coordination number = 2 for interior atoms and coordination number = 1 for terminal atoms.
b. Assuming the pattern extends in two dimensions, coordination number = 3. Otherwise, coordination number = 3 for interior atoms, coordination number = 2 for side edge atoms and coordination number = 1 for corner atoms.

Exercise 2.3.0

a. (i) 8; (ii) 6
b. (i) 4; (ii) 4
c. (i) 5; (ii) 5
d. (i) 5; (ii) 6
e. (i) 6; (ii) 8

Exercise 2.3.1

a. 1/8 atom at each corner
b. 8 corners in a cube
c. $8 \times \frac{1}{8} = 1$ atom per simple cube

Exercise 2.3.2

a. 1/8 atom at each corner
b. 8 corners in a cube
c. 1 atom in middle of cube
d. \(1 + 8 \times \frac{1}{81 + 8 x 1/8 = 2 atoms per body-centered cube

Exercise 2.3.3

Hexagonal close packed pattern is ABAB.

Exercise 2.3.4

a. At both the top and bottom layer, two atoms are 1/3 within the cell and two atoms are 1/6 within the cell.
b. That makes $2 \times (2 \times \frac{1}{3} + 2 \times \frac{1}{6}) = \frac{4}{3} + \frac{4}{6} = \frac{4}{3} + \frac{2}{3} = 1$ atom total in corners
c. 1 atom inside the cell.
d. 2 atoms total.

Exercise 2.3.5

The pattern in this variation is ABACA.

Exercise 2.3.6

ABCABC.

Exercise 2.3.7

a. The rhombus-shaped hexagonal unit cell.
b. 4 layers.

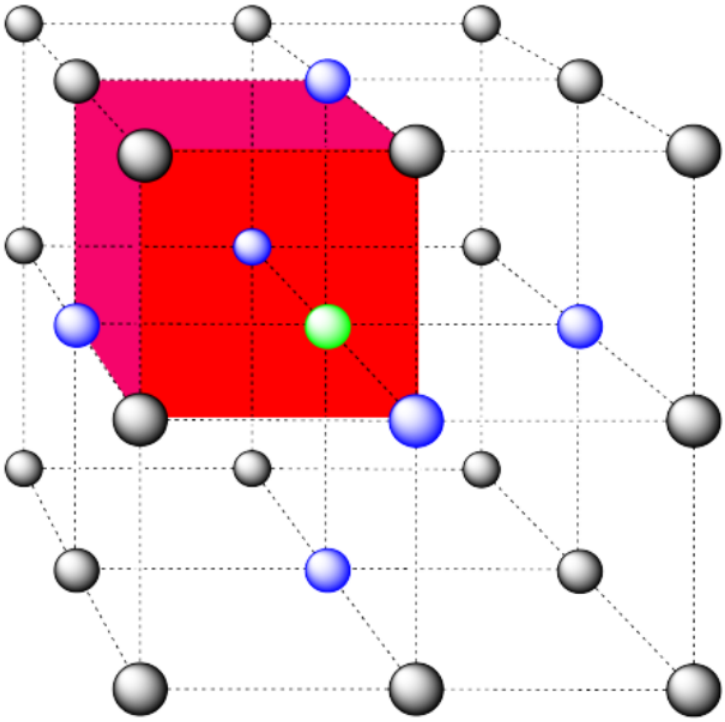
Exercise 2.3.8

a. 1/8 atom at each corner
b. 8 corners in a cube
c. 1/2 atom on each face of cube
d. $6 \times \frac{1}{2} + 8 \times \frac{1}{8} = 4$ atoms per face-centered cube

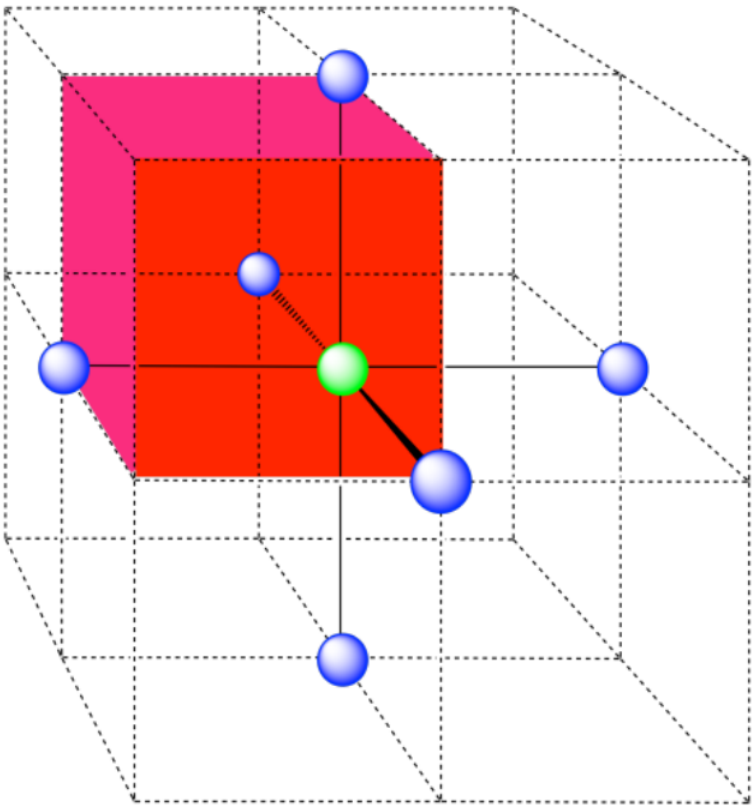
Exercise 2.3.9

a) coordination number = 6 (3 within the cube, along the three adjacent edges, plus three on adjacent cubes).

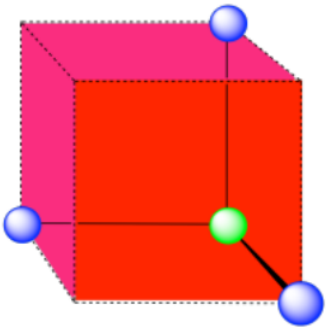
In the picture, consider the green atom coordinated by its nearest neighbors, the blue atoms. One unit cell is highlighted in red.



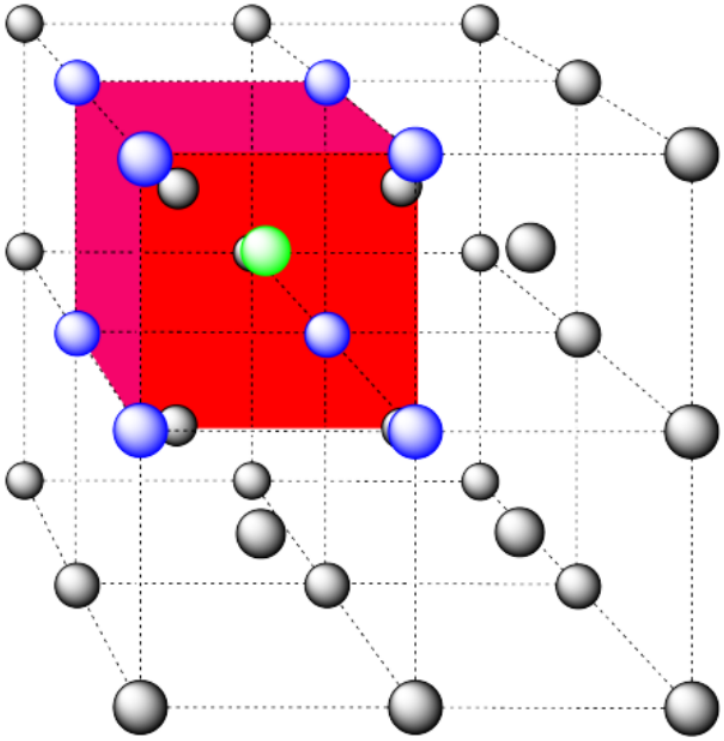
Here is the coordination environment without the surrounding atoms.



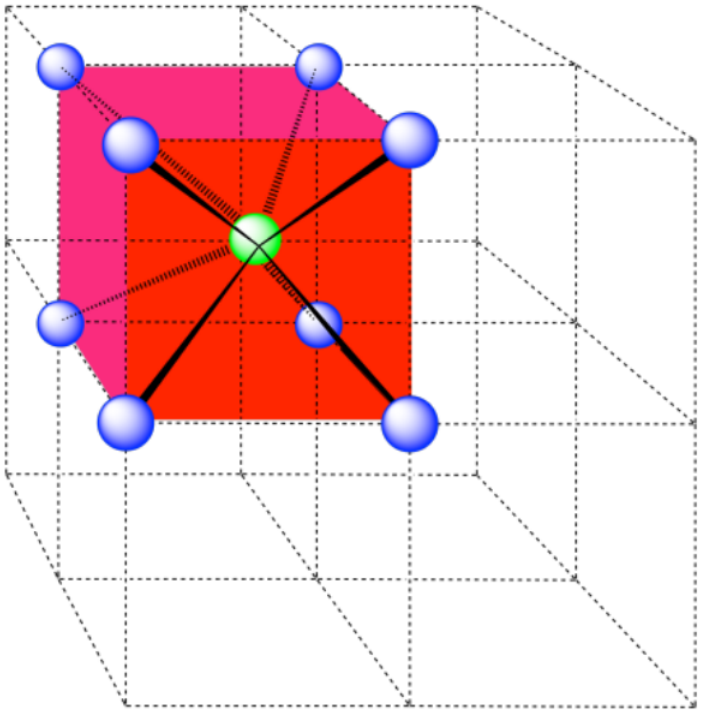
A single unit cell is shown for comparison. The three other nearest atoms are in cells below, behind and to the right of the one shown.



b) coordination number = 8 (corners of the cube).

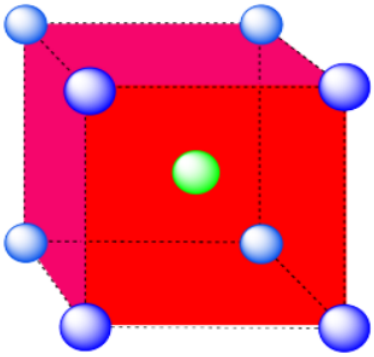


Here is the coordination environment without the surrounding atoms.

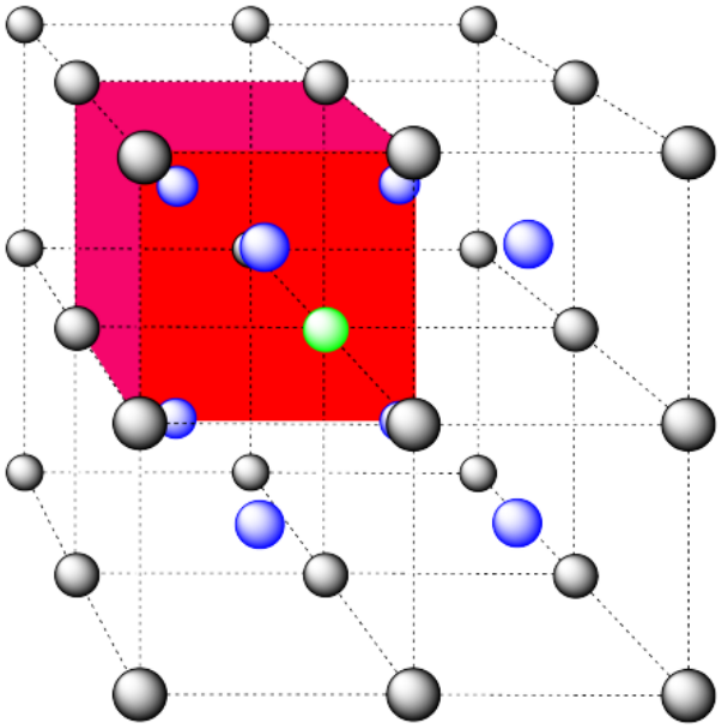


Answer to Exercise 2.3.9b. One unit cell is highlighted in red. Extraneous atoms outside of the highlighted unit cell are removed.

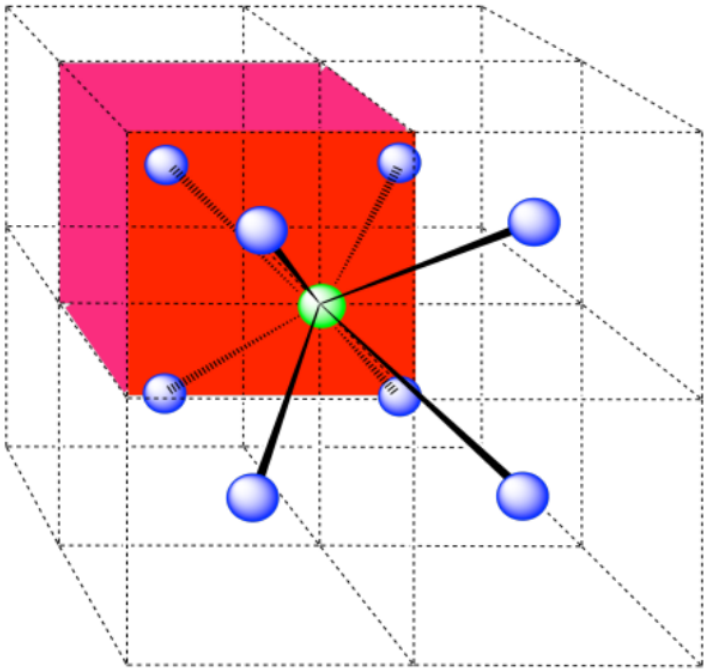
A single unit cell is shown below for simplicity. All of the coordinated atoms are found within the cell.



c) the closest atoms are in the centers of the adjacent cells; the other corners are further away; coordination number = 8.

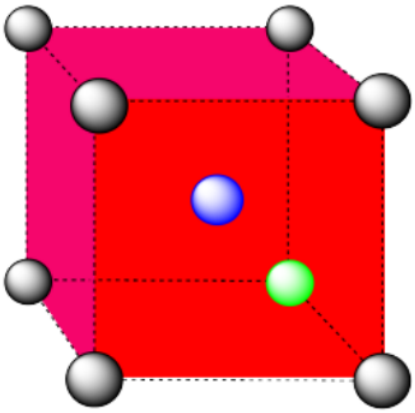


Here is the coordination environment without the surrounding atoms.

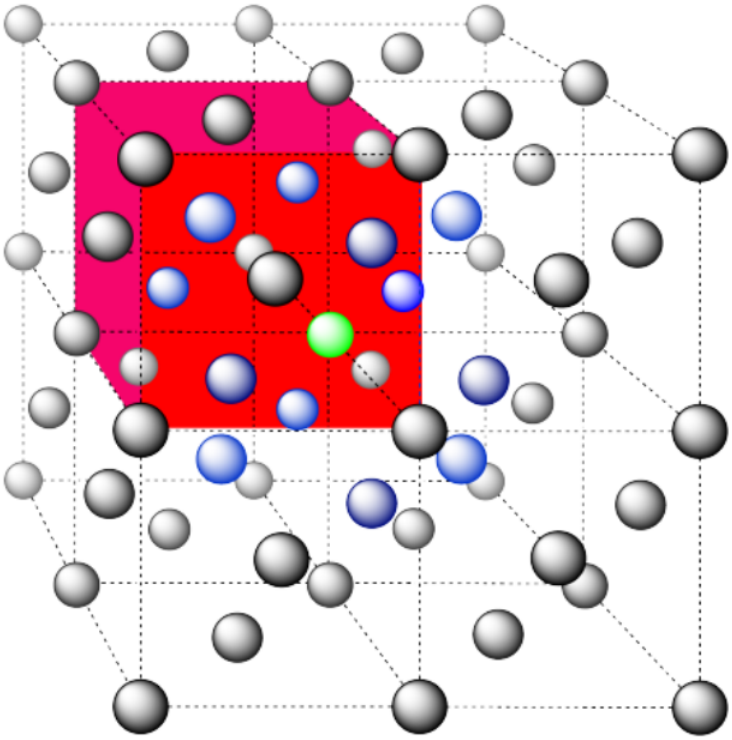


Answer to Exercise 2.3.9c. One unit cell is highlighted in red. Extraneous atoms outside of the unit cell are removed. Projection lines are added to emphasize the location of the atoms in 3D space.

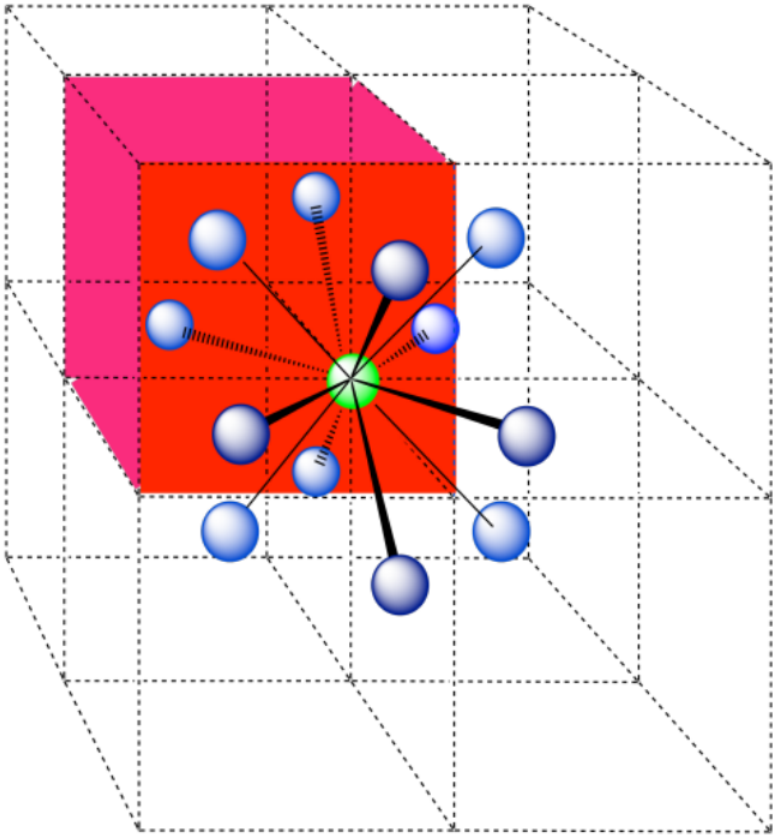
A single unit cell is shown below, for simplicity. Because the atom is in a corner, there are eight other cells arranged around this one: one on the right, two behind, and then four more below.



d) The closest atoms are on the faces adjacent to the corner position; these faces are found along three planes, with four faces surrounding the corner on each plane; coordination number = 12.

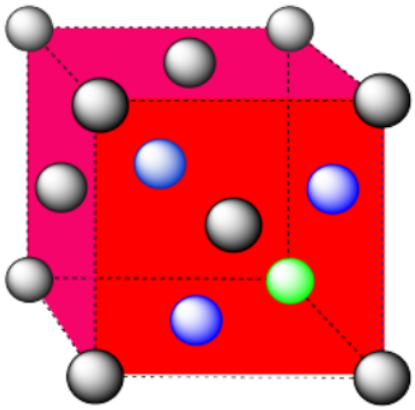


Here is the coordination environment, without the atoms that are further from the green one.

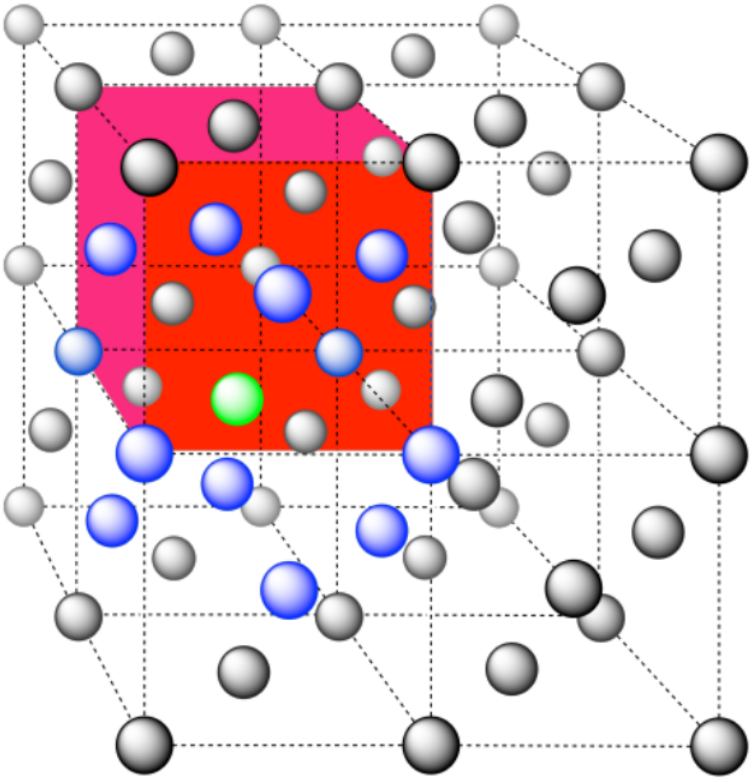


Answer to Exercise 2.3.9d. One unit cell is highlighted in red. Extraneous atoms outside of the unit cell are removed. Projection lines are added to emphasize the location of the atoms in 3D space.

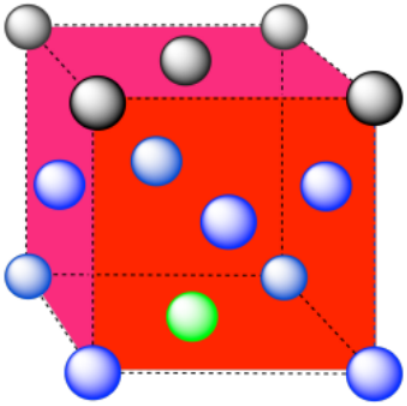
A single unit cell is shown below. Because the atom is in a corner, there are seven other cells arranged around this one: one on the right, two behind, and then four more below.



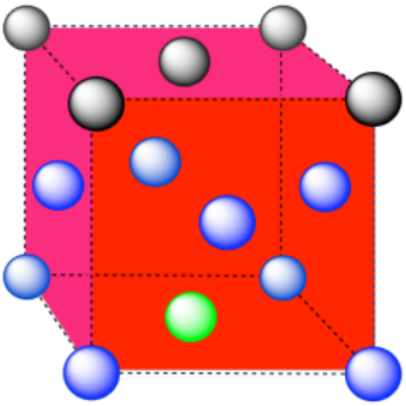
e) The closest atoms are at the corners around the face (4), as well as the atoms in the middle of each adjacent face (8); coordination number = 12.



Here is the coordination environment without the other atoms.

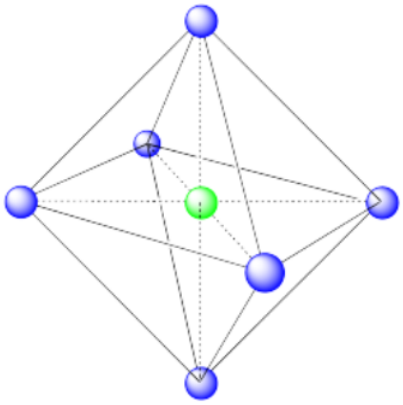


A single unit cell is shown below. There is another cell directly below it.

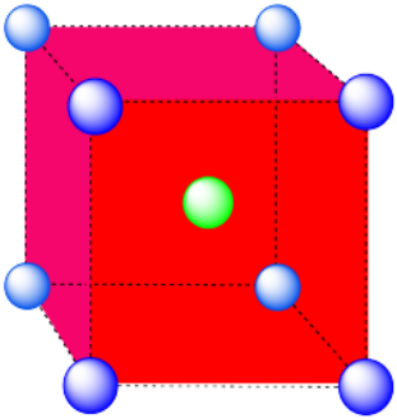


Exercise 2.3.10

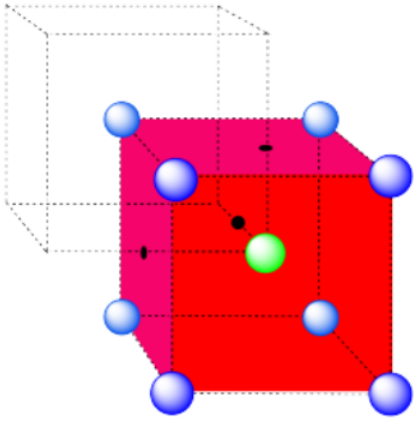
a) Octahedral. An octahedron has six vertices and eight faces.



b) Cubic. A cube has eight vertices and six faces.

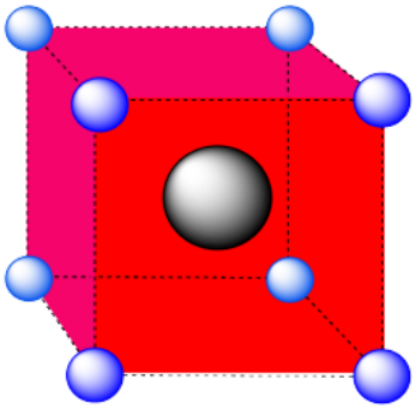


c) This is also a cube, translated from the last one (i.e. the cube is just shifted to a different position in the lattice).



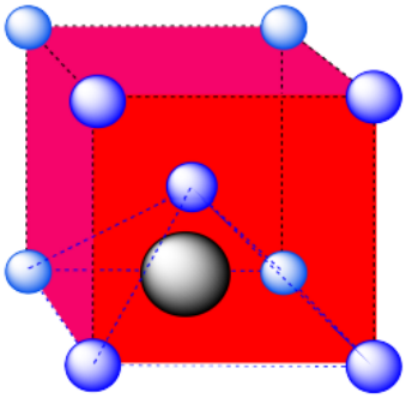
Exercise 2.3.11

a) A cubic hole.

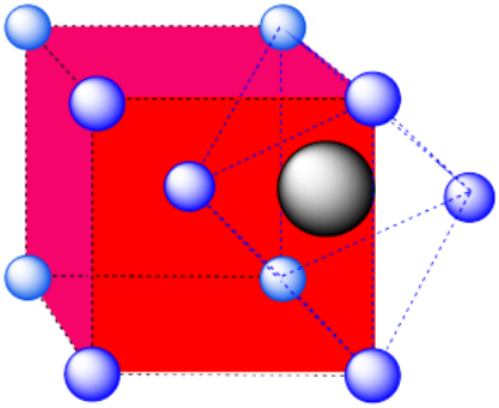


Answer to Exercise 2.3.11a. A red square unit cell with coordination number of 8. A large hole is in the center.

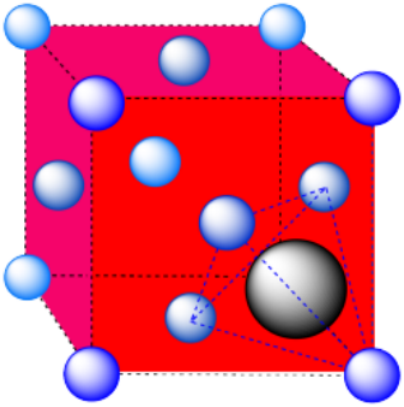
b) A square pyramidal hole. The atom in the hole is above a square of atoms, with an additional atom right above it.



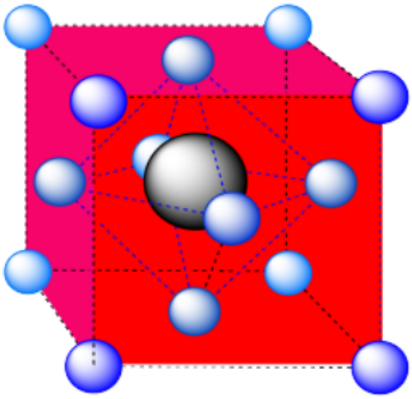
c) An octahedral hole. The atom occupying the hole has been pushed all the way to the face of the cube. It is right in the middle of a square of atoms. One of the vertices is in the center of the next cube.



d) A tetrahedral hole. Note that the layers in the cubic closest-packed system run diagonally through the cubic unit cell. The atom in the hole sits above a trio of atoms on three adjacent faces, and is topped by the atom in the corner of the cube. Because a tetrahedron is so symmetric, the arrangement can be described in a number of other ways, choosing any three surrounding atoms as the base and the fourth atom as the cap of the tetrahedron.

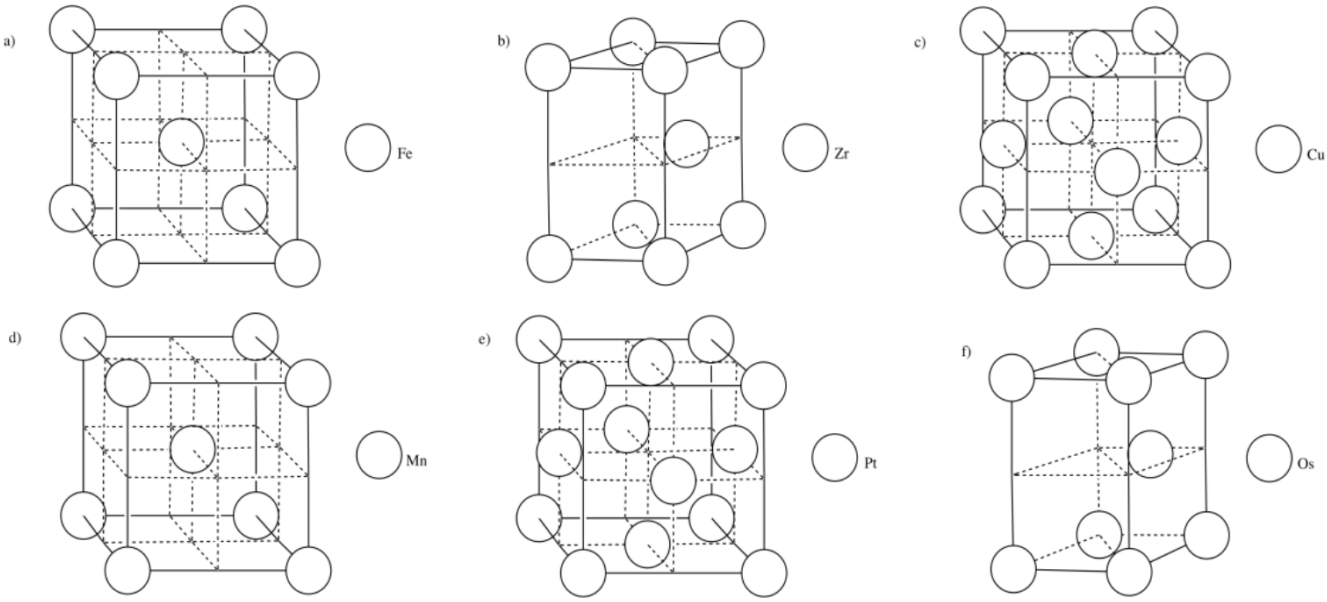


e) An octahedron. Again, the hexagonal layers run diagonally through the unit cell.

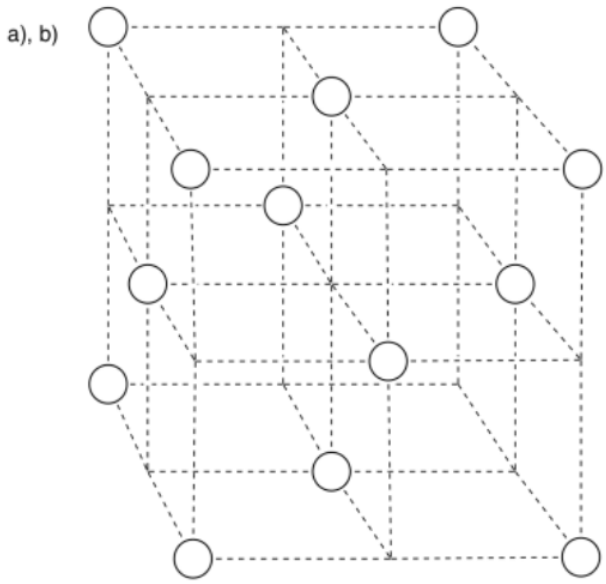


Answer to 2.3.11e. An octahedral figure with a hole in the center is positioned at the heart of a red cube with a coordination number of 8.

Exercise 2.3.16

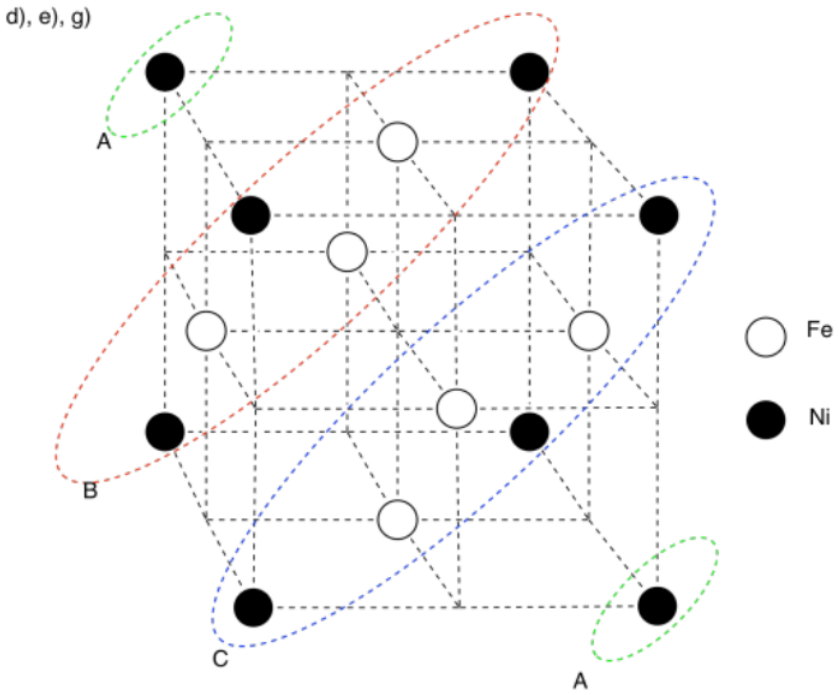


Exercise 2.4.1



c) There are eight atoms in the corner; each is shared by eight neighbouring cubes. There are six atoms on the faces; each is shared by two neighbouring cubes.

$$\#\ atoms = 8(\frac{1}{8}) + 6(\frac{1}{2}) = 1 + 3 = 4\ atoms$$



h) Nickel is a little smaller than iron. A row of atoms rolling along in the layer above would fall into the "pothole" caused by the smaller nickel atom and get stuck.

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CHAPTER OVERVIEW

3: Ionic Compounds

3.1: Ionic Atoms
3.2: Counterions
3.3: Physical Properties
3.4: Solubility
3.5: Structures of Ionic Solids
3.6: Application Problems
3.7: Naming Ionic Compounds
3.8: Ionic Compounds- Solutions for Selected Problems

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3.1: Ionic Atoms

Periodic trends tell us that some atoms gain electrons easily to obtain a stable configuration; these atoms have a high electron affinity. These atoms are principally found in nature as anions (ANN-eye-ons). Anions are atoms that have gained extra electrons, and have overall negative charge. Examples include the halogens, such as chlorine and bromine.

- Atoms in the upper right section of the periodic table can easily form anions.

One of the most commonly-used periodic properties is electronegativity. A look at the periodic table shows the high electronegativity of atoms in the upper right part of the table. The relatively high positive charge in the nuclei of these atoms makes their attraction for electrons very strong.

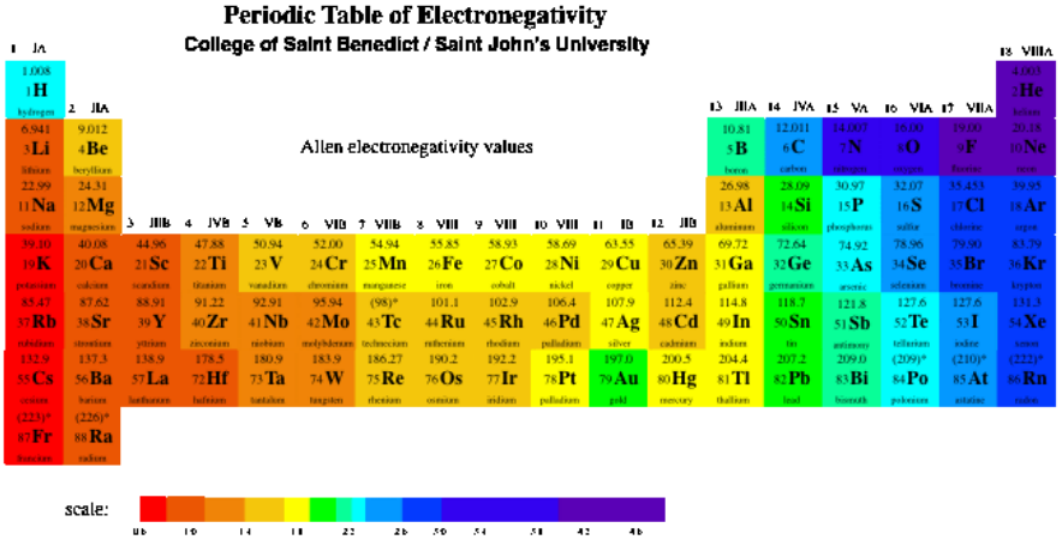

Figure 3.1.1: Electronegativity in the periodic table.

Another thing to remember is that atoms towards the right hand side of the periodic table are likely to gain enough electrons to attain the same electron configuration as a noble gas.

The noble gases are exceptional in the periodic table because they do not easily undergo reactions with other elements. In a chemical reaction, electrons are somehow redistributed between atoms. The noble gases have particularly stable electron configurations, however, and do not gain or lose electrons easily. This is true even though they have high electronegativities; in the case of noble gases, high electronegativity might be thought of as a measure of the stability of the electrons in these elements. However, they have a "closed shell" configuration, meaning that any additional electrons would have to go into a much higher energy level in the next "shell". Other atoms can gain a similarly stable electron configuration by gaining or losing electrons. For example, if oxygen gains two electrons, it attains the same electron configuration as neon. Oxygen is frequently found as an O^{2-} anion in many compounds.

Periodic trends also tell us that some atoms lose electrons easily to obtain a stable configuration; these atoms have a low ionization potential. These atoms are principally found in nature as cations (CAT-eye-ons). Cations are atoms that have lost electrons, so that they have an overall positive charge. Examples include the alkalis, such as sodium and potassium.

- Atoms in the vast expanses to the lower left part of the periodic table easily become cations.

Just as some elements attain a noble gas configuration by gaining some extra electrons, other elements can more easily gain that configuration by losing some electrons. For a sodium atom, it is simply closer to get to the same configuration as neon than it is to get to the same configuration as argon. Sodium is frequently found as Na^{+} in many compounds.

In general, atoms that have an overall charge are called ions (EYE-ons). In an ion, the number of protons in the nucleus is not exactly balanced by the number of electrons, so there is either an overall positive or an overall negative charge on the atom.

What happens to these atoms as they gain or lose an electron? Of course, having an overall charge on an atom introduces an additional electrostatic problem. Two atoms might not repel each other, but two cations would. In the electron sea model of metals, metal cations exist in a block of metal. Those like charges should push the metal cations away from each other, but most metals

don't spontaneously fly apart into tiny particles. The cations are partly held together by the presence of delocalized electrons in the block of metal. The attraction of the delocalized electrons for the metal cations offsets any repulsion between the metal cations.

For that reason, we will see that cations are generally found in the presence of anions, and vice versa, so that repulsive forces between like-ions are balanced by attractive forces with oppositely-charged ions.

? Exercise 3.1.1

Given the following pairs of atoms, which one is most likely to give up an electron?

a. tantalum or vanadium
b. mercury or zinc
c. silicon or sulfur
d. tungsten or copper

Answer a:

Ta (tantalum) is lower in the periodic table than V (vanadium)

Answer b:

Hg (mercury) is lower in the periodic table than Zn (zinc)

Answer c:

Si (silicon) is to the left in the periodic table compared to S (sulfur)

Answer d:

W (tungsten) is to the left and lower in the periodic table compared to Cu (copper)

? Exercise 3.1.2

Provide the electron configuration for the following atoms or ions (without using the nobel gas abbreviation for the outermost shell). If the atom or ion has the same electron configuration as a noble gas, state which noble gas it resembles.

a. oxygen, O
b. oxide, O^{2-}
c. calcium, Ca
d. calcium ion, Ca^{2+}
e. aluminum, Al
f. aluminum ion, Al^{3+}
g. nitrogen, N
h. nitride, N^{3-}
i. chlorine, Cl
j. chloride, Cl^{-}

Answer a:

$[He]2s^2 2p_x^2 2p_y^1 2p_z^1$

Answer b:

$[He]2s^2 2p_x^2 2p_y^2 2p_z^2$

Answer c:

$[Ar]4s^2$

Answer d:

[Ar]

Answer e:

$[Ne]3s^2 2p_x^1$

Answer f:

[Ne]

Answer g:

$[He]2s^2 2p_x^1 2p_y^1 2p_z^1$

Answer h:

$[He]2s^2 2p_x^2 2p_y^2 2p_z^2$

Answer i:

$[Ne]2s^2 2p_x^2 2p_y^2 2p_z^1$

Answer j:

$[Ne]2s^2 2p_x^2 2p_y^2 2p_z^2$

Notice the change in the name of chloride: frequently, when an element becomes an anion, the end of its name changes to "ide". A chlorine atom that has an extra electron is called a chloride ion. An oxygen atom with two extra electrons (to get to the same electron configuration as neon) is called oxide. A nitrogen atom with three extra electrons (to get to the same electron configuration as neon) is called nitride.

There are other changes that occur when an atom is ionized (when an atom loses or gains an electron, becoming an ion). Cations tend to be relatively small. The higher than normal ratio of positive to negative charge causes the remaining electrons to contract towards the nucleus.

- A cation is always smaller than a neutral atom of the same element.

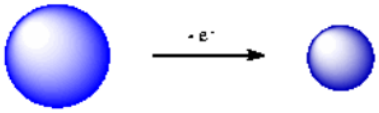

Figure 3.1.2: A cation is smaller than the atom from which it was formed.
Diagram of an atom losing an electron. After the electron is lost, the atom becomes smaller in diameter.

For similar reasons, anions tend to be relatively large. The low ratio of positive to negative charge causes the remaining electrons to repel each other more and expand away from the nucleus.

- An anion is always much larger than a neutral atom of the same element.

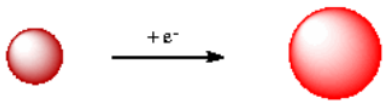

Figure 3.1.3: An anion is larger than the atom from which it was formed.

As a result, many of the elements in the periodic table are very different in size depending on whether they form cations or anions.

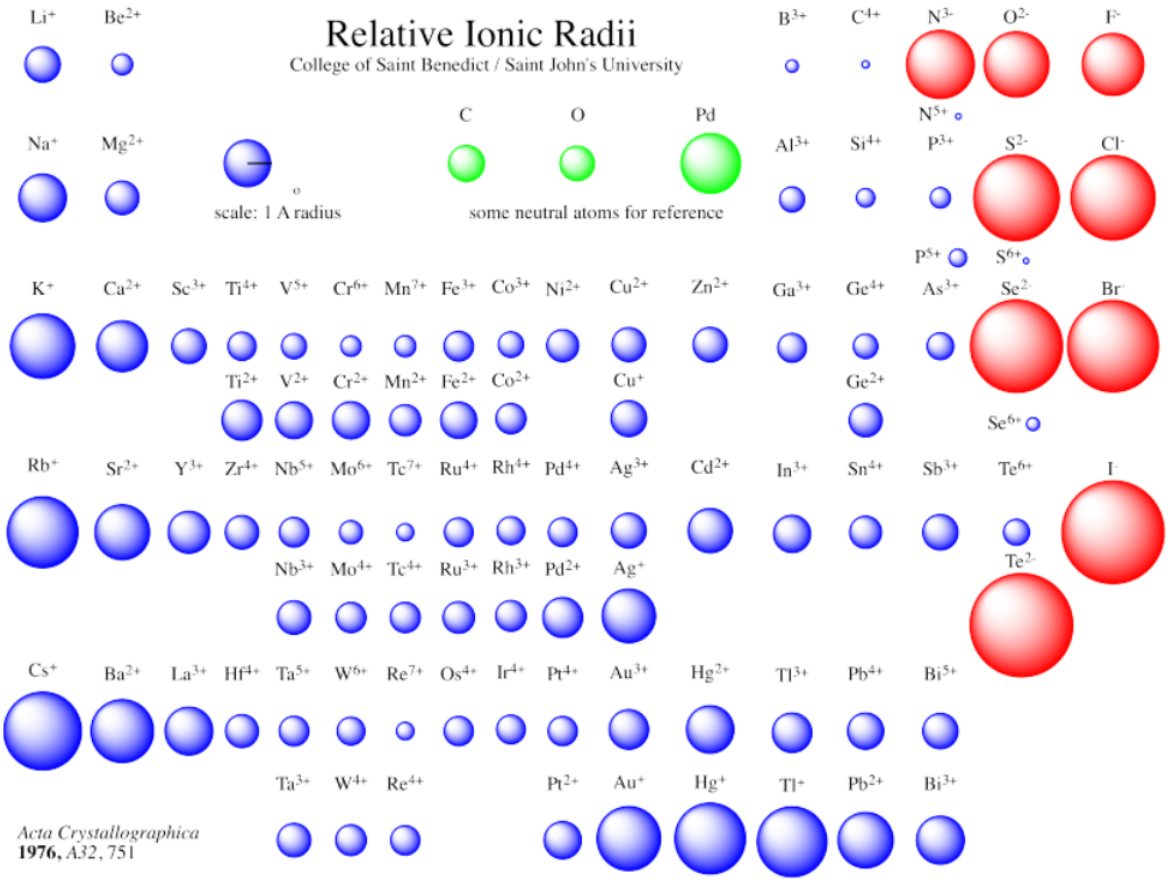

Figure 3.1.4: Periodic table showing relative sizes of common ions. Cations are in blue; anions are in red. In many cases, if multiple "oxidation states" or charges are possible, two examples are shown.

In describing the size of an atom or ion, typically the radius is reported rather than the diameter. Note that different units are sometimes used to report the measured sizes of atoms or ions. The most common unit is an Angstrom, Å. An Angstrom is 10^{-10} m; it is based on the metric system although it is not, strictly speaking, a metric unit. Alternatively, sometimes atomic and ionic radii are reported in nanometers, nm (10^{-9} m) or picometers, pm (10^{-12} m). The reason for the prevalence of the Angstrom is that this unit is about the size of an atom; most atoms have radii between 0.75 and 2 Å. An atom with a 1.0 Å radius has a radius of 100 pm, or 0.10 nm.

? Exercise 3.1.3

Given the following atomic radii, select the correct radius for the given ion.

a. Li : 0.134 nm. Li^+ : 0.076 or 0.176 nm?
b. O : 0.073 nm. O^{2-} : 0.040 or 0.140 nm?
c. Cs : 0.235 nm. Cs^+ : 0.167 or 0.267 nm?
d. H : 0.037 nm. H^- : 0.024 or 0.144 nm?

Answer a:

0.076 nm; smaller

Answer b:

0.140 nm; larger

Answer c:

0.167 nm; smaller

Answer d:

0.144; larger

Exercise 3.1.4

Given the following ionic radii, select the correct radius for the given atom.

a. Pb^{2+} : 0.119 nm. Pb : 0.054 or 0.154 nm?
b. F^{-} : 0.133 nm. F : 0.071 or 0.171 nm?
c. Pd^{2+} : 0.086 nm. Pd : 0.057 or 0.128 nm?
d. I^{-} : 0.220 nm. I : 0.133 or 0.235 nm?

Answer a:

0.154; larger

Answer b:

0.071; smaller

Answer c:

0.128; larger

Answer d:

0.133; smaller

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3.2: Counterions

Compounds are mixtures of elements bonded together to make one material. Compounds can contain two or more elements. Those elements have to be found in a specific ratio. Two materials that contain the same two elements bonded together, but in different ratios, are two different compounds. Two materials that contain two different pairs of elements bonded together, but in the same ratio, would still be different compounds.

In nature, elements are found bound up in compounds more often than not. One common way for elements to be bound together is to form a salt. Salts are found very frequently in the earth's crust. A salt contains both anions and cations. Cations are not generally found alone. Anions are not generally found alone. They need counterions to balance out their charges.

Imagine two atoms get together to form a salt. A sodium atom comes together with a fluorine atom. The sodium atom lets one of its electrons go, and the fluorine atoms snatches it up. Now there is a sodium cation and a fluoride anion. The two ions are held together by the attractive forces between their opposite charges. They have formed a salt.

- Anions and cations are always found together.
- The charges on the cations must balance the charges on the anions.

For example, sodium chloride is a very common ionic compound. It is the main component of table salt, used in cooking. Sodium chloride contains sodium ions, each with a +1 charge, and chloride ions, each with a -1 charge. Overall, the compound has no charge, because the positive sodiums balance out the charge on the negative chlorides, and vice versa.

$$\mathrm{Na^+ + Cl^- = NaCl\ (no\ overall\ charge)} \tag{3.2.1}$$

In a similar way, other ionic compounds form so that there is no overall charge on the compound. Magnesium oxide forms in a ratio so that the positive charges on the magnesium balance the negative charges on the oxygen.

$$\mathrm{Mg^{2+} + O^{2-} = MgO\ (no\ overall\ charge)} \tag{3.2.2}$$

However, sodium oxide would need to form in a different ratio in order to keep the positive and negative charges balanced. Instead of forming in a one-to-one ratio, there would need to be double the number of sodium ions as oxygen ions in order to have the charges cancel each other exactly.

$$\mathrm{2\,Na^+ + O^{2-} = Na_2O\ (no\ overall\ charge)} \tag{3.2.3}$$

The two positive charges on the two sodium cations balance out the two negative charges on the oxide anion.

? Exercise 3.2.1

What would be the ratio of elements if each of the following ions formed a salt with chloride ions, Cl^-?

a) K^+ b) Fe^{3+} c) Mo^{6+} d) Zr^{4+}

Answer a:

1:1 K:Cl or KCl

Answer b:

1:3 Fe:Cl or $FeCl_3$

Answer c:

1:6 Mo:Cl or $MoCl_6$

Answer d:

1:4 Zr:Cl or $ZrCl_4$

? Exercise 3.2.2

What would be the ratio of elements if each of the following ions formed a salt with oxide ions, O^{2-}?

a) Li^+ b) Fe^{3+} c) Cr^{6+} d) Ti^{4+}

Answer a:

Li:O 2:1 or Li_2O

Answer b:

Fe:O 2:3 or Fe_2O_3

Answer c:

Cr:O 1:3 or CrO_3

Answer d:

Ti:O 1:2 or TiO_2

Exercise 3.2.3

What would be the ratio of elements if each of the following ions formed a salt with nitride ions, N^{3-}?

a) Li^+ b) Ta^{3+} c) W^{6+} d) Co^{2+}

Answer a:

Li:N 3:1 or Li_3N

Answer b:

Ta:N 1:1 or TaN

Answer c:

W:N 1:2 or WN_2

Answer d:

Co:N 3:2 or Co_3N_2

Exercise 3.2.4

Some compounds are more complicated. In the following polyoxoanions, the metal and oxide charges do not quite cancel. Given the charge on the metal, and assuming oxide has a 2- charge, what would be the overall charge on the polyoxoanion? Suggest the right ratio of counterion(s) that could balance the charge in each case (e.g. 3 Li^+ ions, etc).

a) WO_4^{n-} (W^{6+}) b) $V_4O_{12}^{n-}$ (V^{5+}) c) $Mo_4O_{14}^{n-}$ (Mo^{6+}) d) $Cr(OH)_6Mo_6O_{18}^{n-}$ (OH^-, Cr^{4+}, Mo^{6+})

Answer a:

Li_4WO_4 because tungstate anion would be 4-

Answer b:

$Li_4V_4O_{12}$ because the tetravanadate ion would be 4-

Answer c:

$Li_2Mo_4O_{14}$ because the tetramolybdate ion would be 2-

Answer d:

$Li_2Cr(OH)_6Mo_6O_{18}$ because the complex polyoxoanion would be 2-

Ionic compounds have no overall charge. Instead, they consist of anions and cations found together to balance charge. The number of positive charges in an ionic compound equal the number of negative charges. Overall, the charge is balanced out.

Why does the charge need to be balanced out? Imagine a bottle of sodium cations. There are a few problems with the cations in that bottle. First of all, the cations will all repel each other. You'd better stand back when you take the lid off. The repulsion between the sodium atoms will make them erupt out of the bottle like a volcano.

By the way, what happened to all of the electrons when somebody made that bottle of sodium ions? Did they also make a jar of electrons with the leftovers? Did the two bottles sit on their shelves in a factory in Milwaukee until someone in Cleveland ordered a bottle of sodium ions and somebody in Tampa ordered a bottle of electrons?

The problem with that story lies in Coulomb's law, the mathematical relationship that talks about the force of attraction between two charges. A transformation of Coulomb's law deals with the energy needed to separate opposite charges. It would take a lot of energy to separate a whole bottle of electrons from a whole bottle of sodium cations, and even more energy to send one bottle to Cleveland and another to Tampa. You would need a power station to generate a bazillion gigawatts of energy to get the job done.

On the other hand, people really can generate cations or anions in instruments such as mass spectrometers. They can even keep those ions for a while in "ion traps". They would only do this with extremely small numbers of ions, though (nowhere near a visible amount), and it does take a generous amount of power. Once they switch the mass spectrometer off, the ions won't stick around for long.

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3.3: Physical Properties

The strong electrostatic forces of attraction of a cation for its surrounding anions, and the strong electrostatic forces of attraction of an anion for its surrounding cations, keep the compound together.

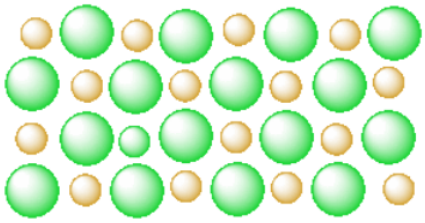


Figure 3.3.1: A salt in the solid state. The ions are tightly packed together in an ordered arrangement.

Most of the time, we think of ionic compounds as solids. In the solid state, the ions are very close together. The forces of attraction between cations and anions are very high. In the liquid (melted) state, the ions would move around independently, and would be able to move a little farther apart from each other. In order to accomplish this independent movement, a great deal of energy would have to be supplied to get over the strong forces of attraction in the solid state. It takes a lot of heat to supply enough energy to convert them into liquid.

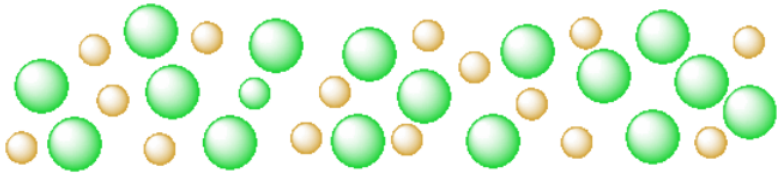


Figure 3.3.2: A salt in the liquid (melted)state. The ions are still close together but more mobile and less ordered.

An ionic compound of two types of atoms. There is still some order to their arrangement, where the larger green atoms are preferentially surrounded by smaller yellow atoms, but the order is not rigid.

- Ionic compounds often have high melting points.

In the gas phase, ions would be very far from each other and would move very freely. They would no longer attract each other very strongly because of the distances between ions. In order to convert an ionic compound into vapour, an enormous amount of energy would have to be supplied to overcome the attractions in the solid or liquid phase. Often, so much energy is supplied that they undergo decomposition into different compounds rather than boiling.

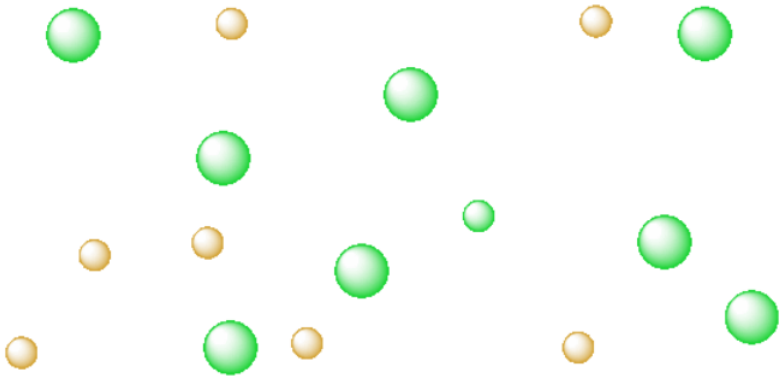


Figure 3.3.3: A salt in the vapor state. The ions are far apart and randomly arranged.

- Ionic compounds have extremely high boiling points.

The changes of state in ionic compounds are governed by simple electrostatic forces between the ions. These electrostatic forces are governed by Coulomb's Law, in which the force of attraction depends on the amount of charge and the distance between the ions. That means that there are sometimes predictable variations in the properties of ionic compounds.

For example, among the potassium halides, the melting point is lowest for the iodide (681 ^{o}C) and highest for the fluoride (858 ^{o}C). The reason for that comes from the distance dependence in Coulomb's law.

Iodide is a bigger ion than bromide, chloride or fluoride. That means the distance between atoms is greater in potassium iodide than in potassium fluoride. In other words, the average distance between the positive potassium nucleus and the negative electrons surrounding the anion is greater for iodide than for chloride or fluoride. Note that this average distance really amounts to the distance between the two nuclei.

The greater the distance between ions, the lower the forces of attraction. The ions in potassium iodide can move around more easily than the ions in potassium fluoride. Potassium iodide has a lower melting point than potassium fluoride.

- Compounds containing smaller ions often have higher melting points than similar compounds that contain larger ions.

? Exercise 3.3.1

Select the compound that would have the lowest melting point in each of the following pairs.

a) KCl or LiCl b) NaF or NaBr c) CaO or BeO d) LiF or KBr

Answer a:

KCl would have the lowest melting point. It would be easier to melt than LiCl because the smaller Li^+ ion would more strongly attract the counterion, owing to the smaller distance separating the opposite charges.

Answer b:

NaBr would have a lower melting point than NaF.

Answer c:

CaO would have a lower melting point than BeO.

Answer d:

KBr would have a lower melting point than LiF.

There is another factor, too: the force of attraction between ions also depends on the magnitude of the charges involved. The greater the size of the charge on an ion, the greater the force of attraction for its counterion.

For example, calcium fluoride, CaF_2, has a lower melting point (1418 ^oC) than calcium oxide, CaO (2572 ^oC).

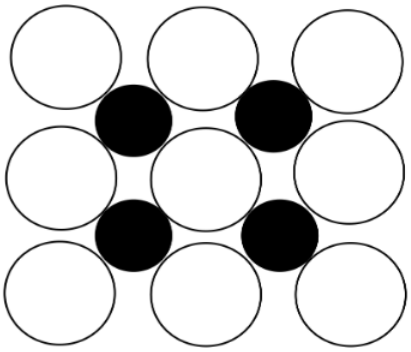
This difference is probably not due to differences in the distance between the charges. Fluoride and oxide are almost the same size, and if anything fluoride is a little smaller. Based on interionic distance alone, fluoride could have a slightly higher melting point than calcium oxide.

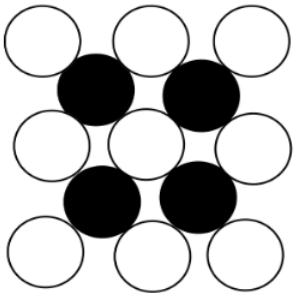
However, each fluoride has a 1- charge, but the oxide has a 2- charge. As a result of this greater charge, the force of attraction between an oxide and a calcium ion is stronger than the force of attraction between a fluoride and a calcium ion. It is more difficult to get the calcium and oxide ions to move away from each other, and the melting point is higher than for calcium fluoride.

- Compounds containing more highly charged ions often have higher melting points than similar compounds that contain lower charged ions.

? Exercise 3.3.2

Select which of the following compounds would have the lowest melting point. Assume that the cations and the anions in each structure are all +1 or -1, respectively.

a. 

b. 

Answer

AnswerThe answer is (a). The sum of the cation and anion radius is longer; therefore the distance betwwen the two is longer, so the force of attraction will be weaker.Exercise 3.3.2a and 3.3.2b. a is composed of nine large white atoms in a square with four small black atoms in the corners. b is composed of nine smaller white atoms in a square with the same four black atoms in their corners.

? Exercise 3.3.3

Select the compound that would have the highest melting point in each of the following pairs.

a) KCl or $CaCl_2$

b) NaF or Na_2O

c) CaO or NaF

Answer a:

$CaCl_2$

Answer b:

Na_2O

Answer c:

CaO

? Exercise 3.3.4

The melting point of NaCl is 801°C. Estimate (guess!) the melting point of the following compounds. (More important than the actual number you come up with is whether it is larger or smaller than the melting point of NaCl and by a lot or a little.)

a) KCl

b) NaF

c) Na_2O

d) MgS

Answer a:

A little lower since K^+ is a little larger than Na^+ (actual= 770°C)

Answer b:

A little higher since F^- is a little smaller than Cl^- (actual =930°C)

Answer c:

A lot higher since the anion charge is 2x higher (actual =1275°C (sublimes but doesn't melt))

Answer d:

A whole lot higher since cation and anion charge are 2x higher (actual = 2000+ °C (decomposes above this temp))

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3.4: Solubility

One of the other general properties of ionic compounds is that they often have some solubility in water. The oceans, of course, are saltwater. In a mixture, two or more materials are mixed together but they remain essentially separate, like sand and water. You can still easily tell the difference between the sand and the water, because even if you shake them up they will separate again on their own.

In a mixture, two or more materials are mixed together but they remain essentially separate, like sand and water. You can still easily tell the difference between the sand and the water, because even if you shake them up they will separate again on their own.

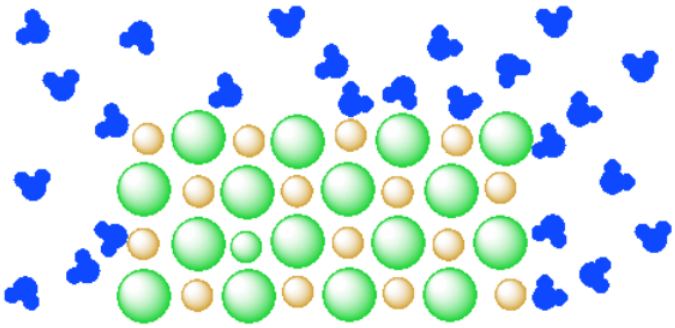

Figure 3.4.1: A mixture of an insoluble salt (orange and green ions) and water (blue molecules). The two components remain separate from each other.

Diagram of water molecules adhering to atoms in an ionic solids. The H atoms of water are attracted to the green atoms of the solid, while the oxygen atoms are attached to the yellow atoms in the solid.

In a suspension, one or more materials is mixed into a liquid, and the mixture becomes somewhat homogeneous. Instead of having easily identifiable layers, the liquid looks the same throughout. However, suspensions are generally cloudy liquids. Milk is a suspension. It contains water, fats and proteins. They may settle out into separate layers eventually, but it takes time.

In a solution, one or more materials is mixed into a liquid, and the mixture becomes a completely homogeneous liquid. Solutions are transparent, not cloudy. They may be colored or colorless, but you can always see through them. Saltwater is a solution.

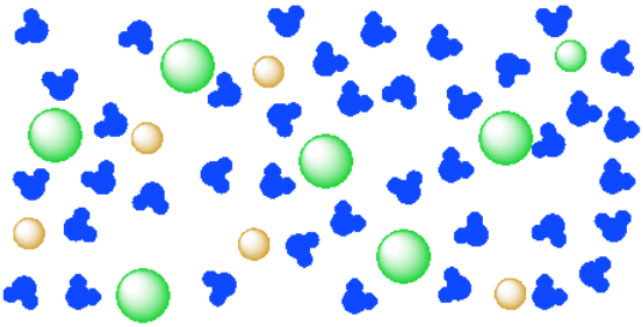

Figure 3.4.2: A solution of a salt (orange and green ions) in water (blue molecules). The ions of the salt are completely distributed throughout the water.

You can't see chunks of salt in the solution because the salt particles are too small for you to see. The salt is separated into individual ions, surrounded by water molecules.

Of course, if you put some salt in water, it might not dissolve right away. You might have to stir it for a while.

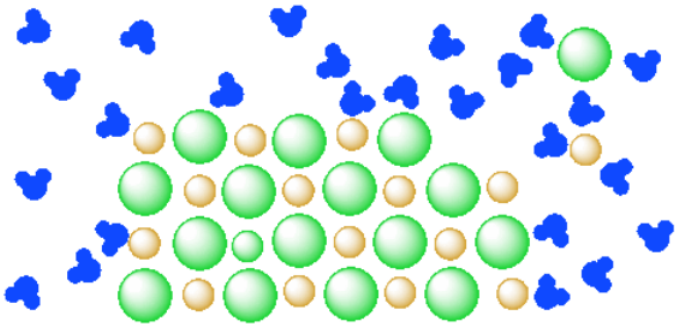

Figure 3.4.3: A mixture of a salt (orange and green ions) and water (blue molecules). The salt is beginning to dissolve in the water.

Eventually more of the salt would dissolve in the water.

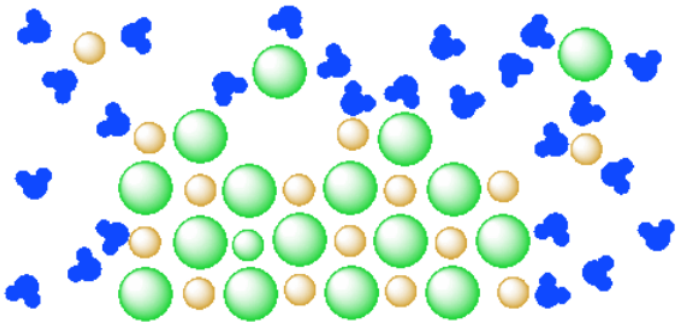

Figure 3.4.4: A mixture of a salt (orange and green ions) and water (blue molecules). The salt continues to dissolve in the water.

An ionic compound being dissolved in water. Several ions are starting to dissociate from the solid, carried away by water molecules.

However, at some point, the system might come to "equilibrium": the water has dissolved all of the salt that it can, so the rest of the salt stays solid. This equilibrium may be "dynamic": different ions may become dissolved in the water or may be deposited from solution into the solid state. However, the overall ratio of dissolved ions to water stays the same.

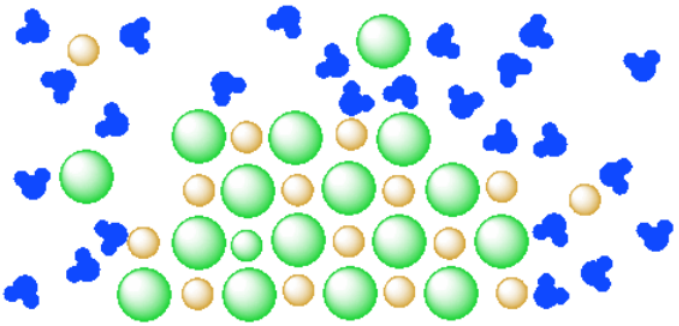

Figure 3.4.5: A mixture of a salt (orange and green ions) and water (blue molecules). The salt is partly dissolved in the water but has reached equilibrium.

An ionic compound being dissolved in water. Several ions are starting to dissociate from the solid, carried away by water molecules.

? Exercise 3.4.1

Let's take a look at the idea that a given amount of water is only able to dissolve a specific amount of salt.

a. In the diagram above, how many water molecules are there?
b. How many units of salt (an anion and a cation) are dissolved?
c. If there were only a dozen water molecules present, how many units of salt would dissolve?
d. If a hundred water molecules were present, how many units of salt would dissolve?

Answer a:

25 waters.

Answer b:

2 units (2 anions and 2 cations).

Answer c:

Half the water might only dissolve half the salt: 1 unit.

Answer d:

Four times the water may dissolve four times the salt: 4 units.

Why do salts dissolve in water? Water is a molecular compound; the atoms are directly attached to each other, rather than being ions that are attracted to each other. Because of electronegativity differences, the oxygen in water has a partial negative charge and the hydrogens have partial positive charges. Ionic compounds can dissolve in polar liquids like water because the ions are attracted to either the positive or negative part of the molecule.

Note that there is a sort of tug-of-war involved when things dissolve in water. The water is pulling individual ions away from the solid. The solid is pulling individual ions back out of the water. There exists an equilibrium at some point, based on how strongly the water attracts the ions, versus how strong the ionic solid attracts the ions.

You might expect to be able to predict vaying degrees of solubility in water for different ionic compounds. You would just use the principles of Coulomb's law that we used in melting points. The smaller the ions, the closer together they would be, and the harder it would be for the water molecules to pull the ions away from each other.

? Exercise 3.4.2

Predict which of the following pairs should be more soluble in water, based on what you know about Coulombic attraction between ions.

a. LiF or NaF
b. NaK or KF
c. BeO or LiF

Answer a:

LiF should be more soluble.

Answer b:

KF should be more soluble (but keep reading).

Answer c:

LiF should be more soluble.

? Exercise 3.4.3

Although lithium fluoride and magnesium oxide contain cations and anions of roughly the same size, lithium fluoride is much more soluble in water (2.7 g/L) than magnesium oxide (0.087 g/L) at room temperature. Propose a reason why.

Answer

The MgO contain more highly charged ions (Mg^{2+} and O^{2-}) than LiF (Li^{+} and F^{-}) and so it is more difficult to separate the ions from their solid state.

However, the trends we saw in melting points in ionic compounds become more complicated when it comes to solubility. The water solubility of alkali chlorides does not follow a simple trend (Table 3.4.1).

Table 3.4.1 Water solubility among alkali chlorides.

Table 3.4.1 Water solubility among alkali chlorides.

Compound	Water Solubility in g/100 mL at 20°C
LiCl	83
NaCl	359
KCl	344

Lithium chloride is certainly the least water-soluble of the three compounds. That makes sense, since the lithium ions are small and the attraction for the chloride would be stronger over that shorter distance. However, we would expect potassium chloride to be the most soluble by far, and it is hardly different from sodium chloride.

? Exercise 3.4.4

Propose an explanation for why the water solubility of the alkali chlorides does not simply increase as the cation gets larger.

Answer

The ions interact with the water via electrostatic interactions, too. The same distance factor that allows small ions to attract each other more strongly also allows small ions to interact more strongly with the water.

If we change the halides, we see similar trends.

Table 3.4.2 Water solubility among lithium halides.

Table 3.4.2 Water solubility among lithium halides.

Compound	Water Solubility in g/100 mL at 20°C
LiCl	83
LiBr	166
LiI	150

Once again, it isn't surprising that the lithium chloride is the least soluble, but the most soluble seems to be the lithium bromide, not the lithium iodide.

This sort of behavior, in which we start to see a trend but it then reverses, often means there is more than one factor at work. In this case, there are a couple of other factors, some of which are more complicated. One of them simply involves the fact that there are two interactions going on here. We are not just overcoming the attraction of the ionic solid for individual ions, like when something melted. In this case, there is also the attraction of the water for the ion to think about. That attraction should also be governed by Coulomb's Law. At some stage, there must be a tipping point, when the factors that increase attraction between the ions also increase the attraction between the ion and the water. One or the other of these factors may become the dominant player under different circumstances.

- Several interactions are involved in dissolution.
- Cation - anion attraction is just one of these interactions.
- Cation - water and anion - water interactions are important, too.
- Water - water interactions also play a role.

Remember that an additional factor that influences lattice energy is the amount of charge. If we look at solubility of some alkaline earth chlorides and compare them to alkali halides, we can see the difference charge makes. Alkali metals are in the first column of the periodic table and their ions have a +1 charge. Alkaline earth metals are in the second column of the periodic table and their ions have a +2 charge.

Table 3.4.3 Water solubility among alkali and alkaline earth chlorides.

Table 3.4.3 Water solubility among alkali and alkaline earth chlorides.

Compound	Water Solubility in g/100 mL at 20ºC
LiCl	83
$BeCl_2$	15
$MgCl_2$	54

We expect the higher charges in beryllium and magnesium chloride to result in higher lattice energies. If the ions in beryllium chloride become harder to separate, then it will be more difficult to dissolve this compound in water. Instead, the ions will remain tightly stuck together.

? Exercise 3.4.5

Let's review some basic points about ionic solids.

a. Define lattice energy.
b. What two properties affect the lattice energy of an ionic compound?
c. Does a stronger or weaker lattice energy result in a stronger ionic bond?
d. How will a strong lattice energy affect melting and boiling points of a crystal lattice?
e. How will a strong lattice energy affect solubility of a crystal lattice?

Answer a:

The lattice energy of an ionic solid is a measure of the strength of bonds in that ionic compound.

Answer b:

Charge of ion (directly related to lattice energy); Radius of each ion (inversely related to lattice energy)

Answer c:

Stronger lattice energy results in a stronger bond. The stronger the bond, the more energy required to separate ions.

Answer d:

Stronger lattice energy results higher mp or bp.

Answer e:

Stronger lattice energy results in less soluble crystal lattice.

? Exercise 3.4.6

In each pair, determine which compound will have a higher lattice energy.

a. NaCl or NaBr
b. KF or CaF2
c. MgO or Na2O
d. KF or CsCl
e. RbBr or CaCl2

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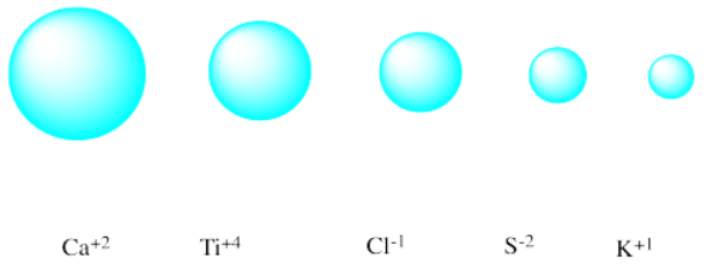
3.5: Structures of Ionic Solids

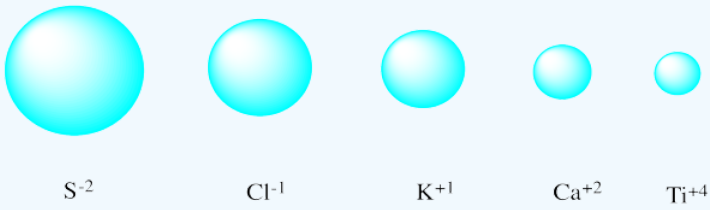
The structure of ionic solids is determined by how the cations and anions can pack together. Generally, one of the ions adopts a standard packing structure, like the metal atoms in a metallic solid. The counterions then fit into the holes or interstitial spaces among these ions. It is pretty common for the anions to form a close-packed structure, and for cations to find room in the resulting holes, but sometimes it is the other way around.

Exercise 3.5.1

Match each isoelectronic ion with the correct picture of its radius.



Answer



AnswerDiagrams of five atoms, ordered left to right from largest to smallest atomic radii. Answer choices, from left to right: Ca2+, Ti4+, Cl1-, S2-, K1+.

Exercise 3.5.2

Why might anions more commonly pack into a close-packed structure, rather than the cations?

Answer

Generally, but not always, anions are bigger than cations, so cations can pack efficiently into the holes between the anions.

The holes between the atoms have particular coordination numbers and geometries. There are many possible holes of different shapes where a counterion can find room. However, some of these geometries are very common.

For example, in the center of a simple cube, there is room for an additional atom. This atom is described as sitting in a cubic hole.

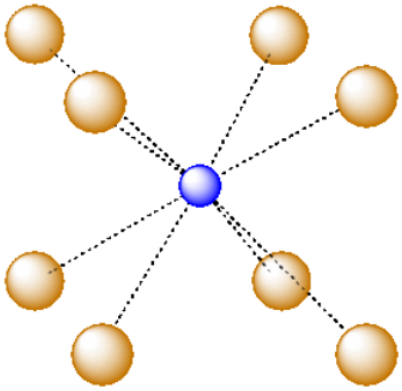


Figure 3.5.1: An ion in a cubic hole.

The above drawing emphasizes the relationship between the central atom and the atoms that form the corners of the cube. The central atom is in a cubic coordination geometry. Alternatively, we could describe the coordination number of the central atom. Instead of describing the shape formed by the surrounding atoms, we simply count the number of near neighbors. In this case, the coordination number of the central atom is 8. We can think of the central atom as sharing ionic bonding with its eight near neighbors.

An atom in a cubic hole might be viewed more easily if we draw lines between the various atoms at the corners of the cube, however. In that way,we can see more clearly the cubic shape of the cage in which the central atom is sitting.

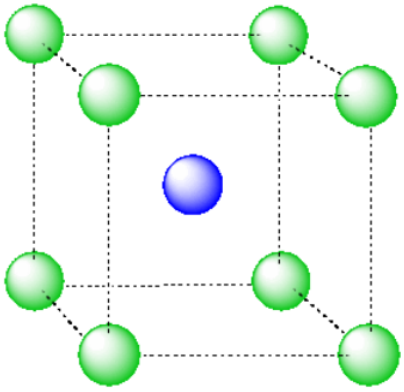


Figure 3.5.2: An alternative view of an ion in a cubic hole.

Another common interstitial space in ionic solids is an octahedral hole. An octahedral hole forms in between two close-packed layers. Because the atoms in the layers are packed more tightly than in a simple cube, this octahedral hole is generally a little smaller than a cubic hole.

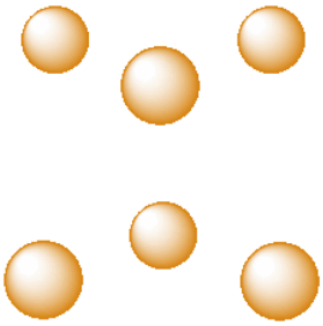


Figure 3.5.3: An octahedral hole.

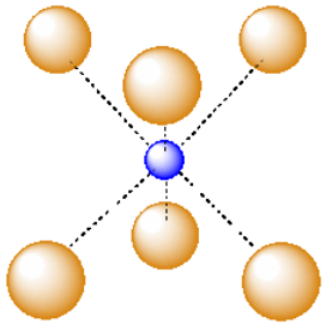


Figure 3.5.4: An atom in an octahedral hole.

Six orange atoms arranged at the vertices of an octahedron. At the center of the octahedron is a single blue atom.

A third, common type of interstitial space is a tetrahedral hole. Tetrahedral holes, like octahedral holes, are found between two close-packed layers.

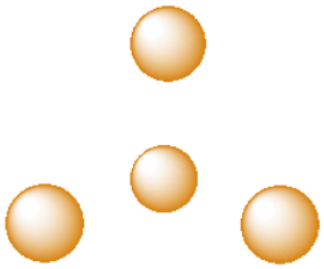


Figure 3.5.5: A tetrahedral hole.

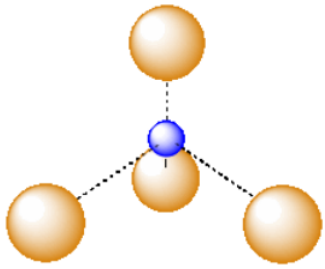


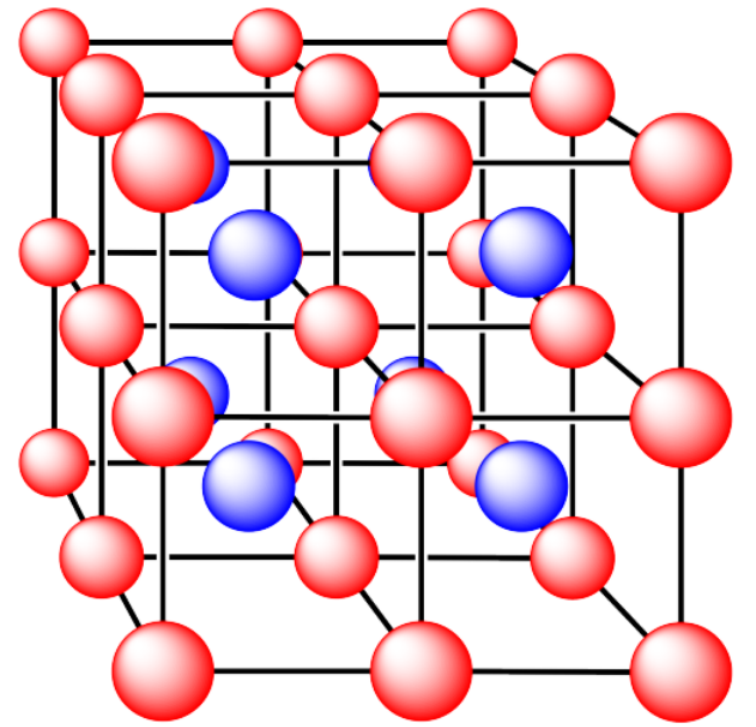
Figure 3.5.6: An atom in a tetrahedral hole.

? Exercise 3.5.3

In the following structures, the anions are represented in red and the cations are represented in blue. For each structure,

a. identify the type of unit cell that is visible
b. identify the type of hole occupied by the counter ion
c. identify the fraction of those holes that are occupied
d. identify the number of anions and cations in the unit cell
e. state the empirical formula (the lowest possible ratio of atoms in the material)

i. The ions are formed from cesium and chlorine



Answer i. a):

Answer i. b):

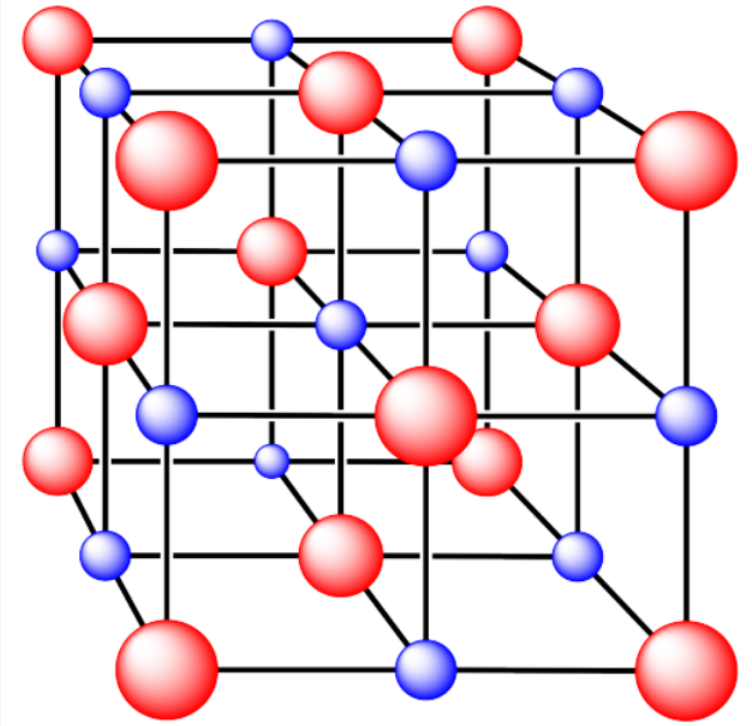
Answer i. c):

Answer i. d):

Answer i. e):

Answer i. a):simple cubicAnswer i. b):cubic holeAnswer i. c):coordination number = 8Answer i. d):all occupiedAnswer i. e):8 x 1/8 Cl and 1 Cs (or vice versa, depending on how you define a unit cell)An ionic compound composed of eight cubes. Red atoms are at the vertices of each cube, and several blue atoms are at the core of each cube.

ii. The ions are formed from sodium and chlorine.



Answer ii. a):

Answer ii. b):

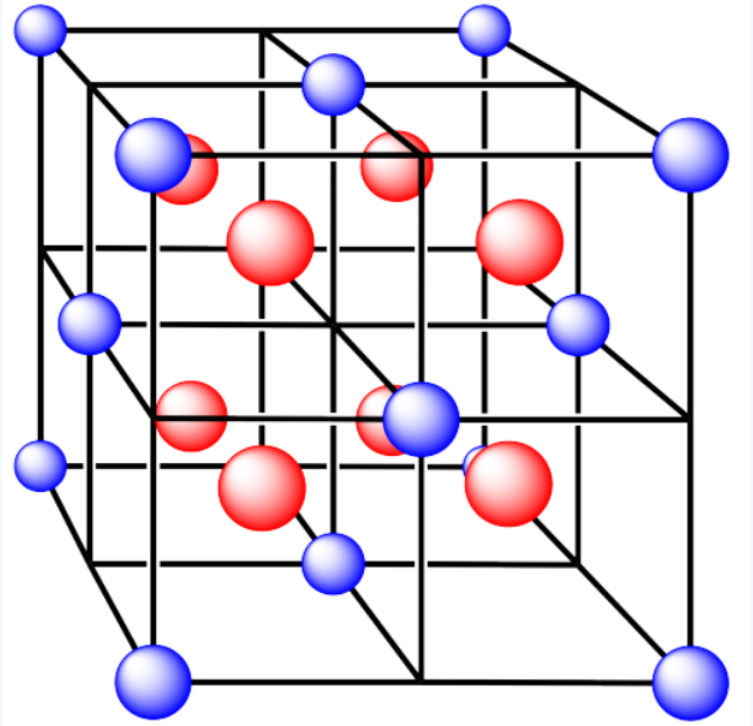
Answer ii. c):

Answer ii. d):

Answer ii. e):

Answer ii. a):face centered cubicAnswer ii. b):octahedral holeAnswer ii. c):coordination number = 6Answer ii. d):all occupiedAnswer ii. e):6 x 1/2 plus 8 x 1/8 = 4 Cl and 1 plus 12 x 1/4 = 4 Na (or vice versa, depending on how you define a unit cell)An ionic compound composed of eight cubes. Half of the vertices have red atoms, and the other vertices have blue atoms.

iii. The cations are formed from calcium and the anions are formed from fluorine.



Answer iii. a):

Answer iii. b):

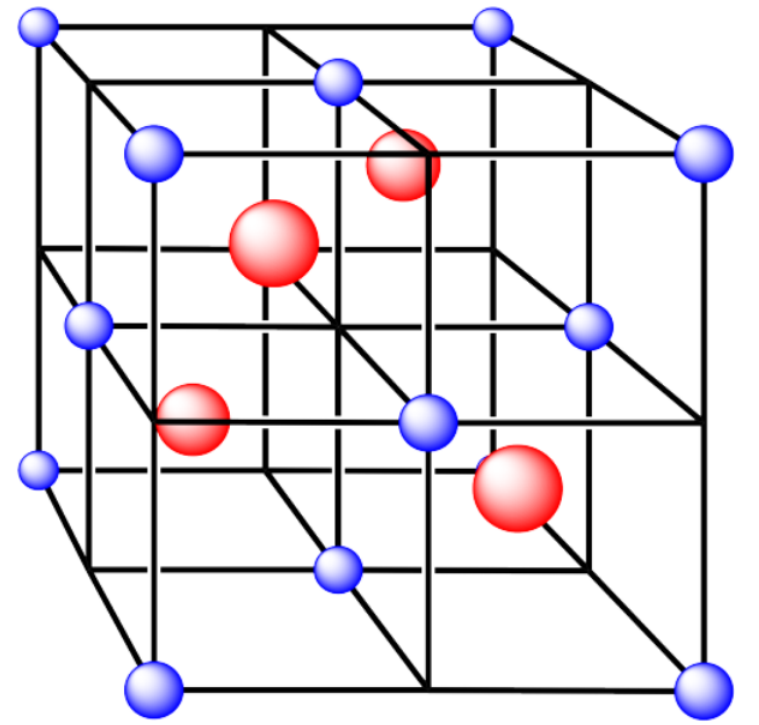
Answer iii. c):

Answer iii. d):

Answer iii. e):

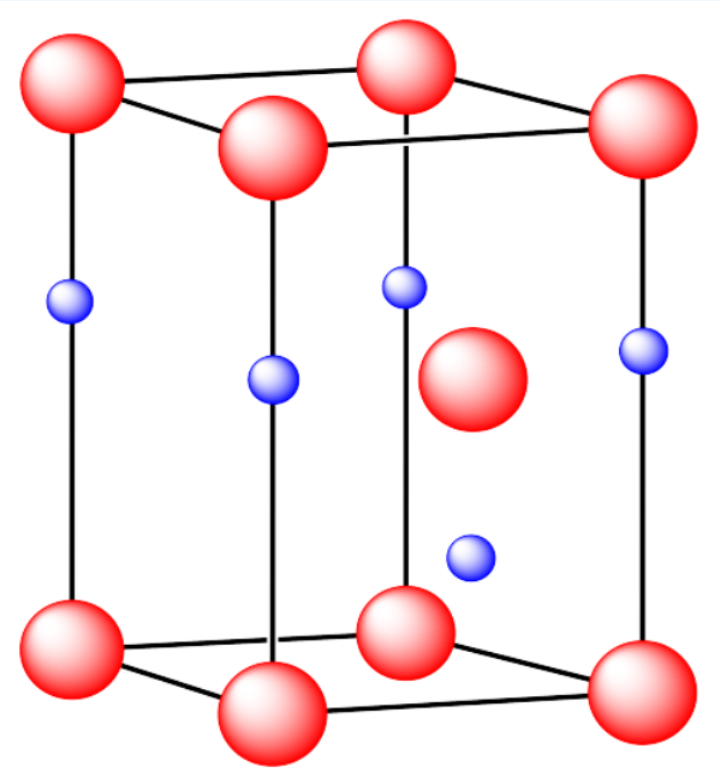
Answer iii. a):face centered cubicAnswer iii. b):tetrahedral holeAnswer iii. c):coordination number = 4Answer iii. d):all occupiedAnswer iii. e):6 x 1/2 plus 8 x 1/8 = 4 Ca and 8 FAn ionic solid composed of eight cubes. Blue atoms are at every other vertex. Red atoms are at the center of each cube.

iv. The cations are formed from zinc and the anions are formed from sulfur.



An ionic compound composed of eight cubes. Every other tex has a blue atom. Four of the eight cubes have red atoms at their centers, arranged opposite to each other.

v. The cations are formed from zinc and the anions are formed from sulfur.



One single rectangular prism. Eight red atoms are at its vertices. Four blue atoms are along the midway point of each vertical edge. One red atom is on the front face of the prism. One blue atom is towards the bottom right of the prism.

Additional Information on solid structures:

Liverpool Solid State

Visualization of solid state structures: unit cells, etc.

Davidson College Crystals

Visualization of solid state structures: unit cells, etc.

Oxford University Solid Structures

Visualization of solid state structures: unit cells, etc.

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3.6: Application Problems

Exercise 3.6.1

Gallium arsenide is used in the electronics industry as a semiconductor. You can start by thinking of gallium arsenide as arsenide ions forming a face-centered cubic unit cell.

a) Draw that face-centered cubic unit cell.

b) Place the gallium ions in half of the tetrahedral holes.

c) Shade one kind of atom in and add a legend to your diagram.

d) Calculate the total number of arsenic atoms in the unit cell.

e) Calculate the total number of gallium atoms in the unit cell.

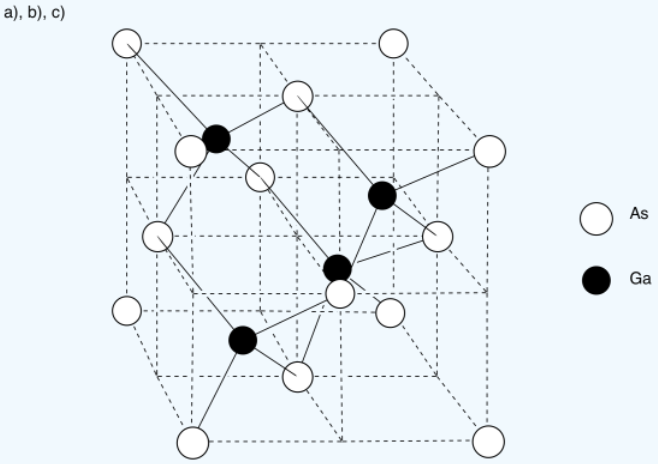
f) What is the formula of gallium arsenide, based on that ratio?

g) What would be the charge on each ion, based on its location in the periodic table?

h) The melting point of gallium arsenide would be (higher / lower) than CsI.

i) In reality, both ions have much less charge than expected. Why isn't gallium arsenide fully ionic?

Answer a), b), c



Answer d

There are eight arsenic atoms in the corner; each is shared by eight neighbouring cubes. There are six atoms on the faces; each is shared by two neighbouring cubes.

atoms = $8(\frac{1}{8})+6(\frac{1}{2})=1+3=4$ arsenic atoms

Answer e

Each gallium atom is entirely within the cell. There are 4 gallium atoms.

Answer f

The formula is just the ratio of each atom in the material. Since the 4:4 ratio is the same thing as a 1:1 ratio, the formula is just GaAs.

Answer g

Arsenic is to the right of gallium in the periodic table, so arsenic must be more electronegative; it must be the anion, and gallium the cation.

Arsenic is three atoms from the right edge of the periodic table; as an ion, a 3- charge makes sense. To balance the charge, gallium must have a 3+ charge.

Answer h

Cesium is larger than gallium, and iodine is larger than arsenic, so in terms of internuclear distance, there would be less attraction between the cesium and iodide ions than between the (closer) gallium and arsenide ions. Also, if the charge on gallium and arsenide are 3+ and 3-, respectively, and the charges on cesium and iodide are only 1+ and 1-, respectively, then there should be much greater attraction between the gallium and arsenide ions.

The melting point of gallium arsenide (mp = 1,238 ^{o}C) should be higher than that of cesium iodide (mp = 632 ^{o}C).

Answer i

The atoms are so close together in the periodic table that it isn't likely that arsenic should completely steal three electrons away from gallium; the difference in electronegativity isn't great enough.

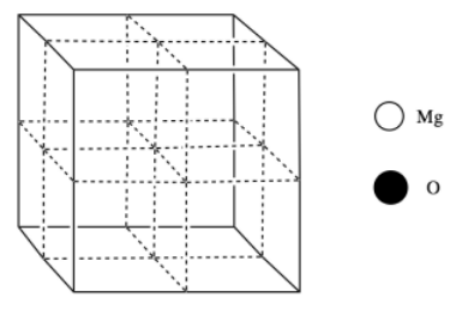
? Exercise 3.6.2

Electronic devices rely on an interface between copper, a conductor of electricity, and silicon, a semiconductor. However, copper atoms tend to diffuse through silicon, disrupting its semiconductor properties. A barrier layer is therefore used in between, usually magnesium oxide or titanium nitride. Let's take a look at the structure of these materials.

a. Based on its position in the periodic table, what is the charge on oxide ion in magnesium oxide?
b. Based on its position in the periodic table, what is the charge on magnesium ion in magnesium oxide?
c. Therefore, to balance charge, what is the formula of magnesium oxide?

Magnesium oxide has a rock salt structure. Oxide ions form a face-centered cubic cell, and magnesium ions occupy the octahedral holes.

d) Add the atoms to the figure according to the legend.



e) Calculate how many atoms of each kind there are in the cell.

f) What is the electronic configuration of a Mg atom (you can use noble gas abbreviation)?

g) What is the electronic configuration of a Mg ion in magnesium oxide?

h) Which is bigger: magnesium, or magnesium ion? Why?

i) What is the electronic configuration of an oxide ion in magnesium oxide?

j) Which is bigger: oxide ion, or magnesium ion? Why?

Alternatively, sometimes titanium nitride (TiN) is used as the barrier layer instead of magnesium oxide.

k) Based on its position in the periodic table, what is the charge on nitride ion in titanium nitride?

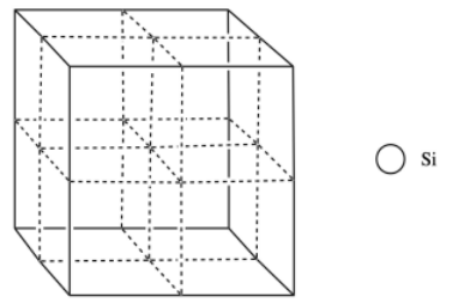
l) Therefore, what is the charge on titanium in titanium nitride?

Titanium nitride, like magnesum oxide, adopts a rock salt structure. It has a melting point that is a little higher than that of magnesium oxide (2 930 ^{o}C vs. 2 852 ^{o}C).

m) Explain, in terms of lattice energy, why the melting point of titanium nitride is a little higher than the melting point of magnesium oxide.

In the structure of silicon, imagine a face-centered cubic cell, but with extra silicon atoms that occupy half of the tetrahedral holes.

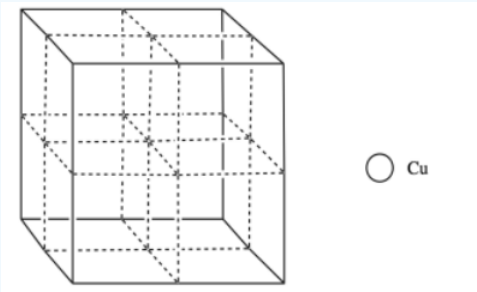
n) Add the atoms to the figure to show the structure of silicon.



o) What is the coordination number of a silicon in a tetrahedral hole?

Copper usually forms a face-centered cubic cell. However, researchers found that body-centered cubic copper can be formed during laser ablation at room temperature (Wu, F; Narayan, *J. Cryst. Growth. Des.* **2013**, *13*, 5018-5024.). When grown on a magnesium oxide surface, this body centered copper forms a more durable layer than the normal FCC form.

p) Add the atoms to the figure to form body-centered cubic copper.



q) What is the electronic configuration of copper (you can use noble gas configuration)?

r) Explain why copper is a good conductor of electricity. Add a picture to support your explanation.

s) Why isn't silicon as good a conductor of electricity as copper?

Answer a

O^{2-}

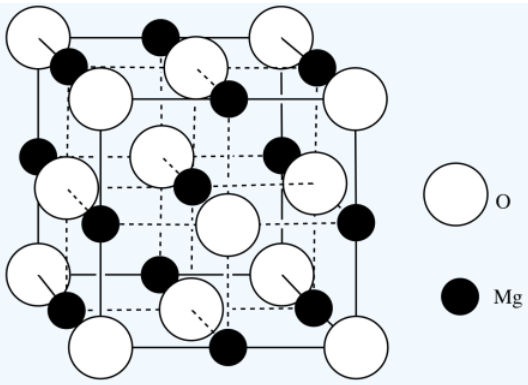
Answer b

Mg^{2+}

Answer c

MgO

Answer d



Answer d to Exercise 3.6.2s. An ionic material composed of eight cubes. Atoms of Mg and O are placed alternately at each vertex.

Answer e

O: 8(1/8) corners + 6(1/2) faces = 4 atoms; Mg: 12(1/4) edges + 1 center = 4 atoms; MgO

Answer f

$[Ne]3s^2$

Answer g

[Ne] or $[He]2s^22p^6$

Answer h

magnesium; the positive charge on the ion causes the remaining electrons to contract

Answer i

[Ne] or $[He]2s^22p^6$

Answer j

oxide; they have the same electron configuration, but magnesium has more protons in its nucleus to attract the electrons.

Answer k

N^{3-}

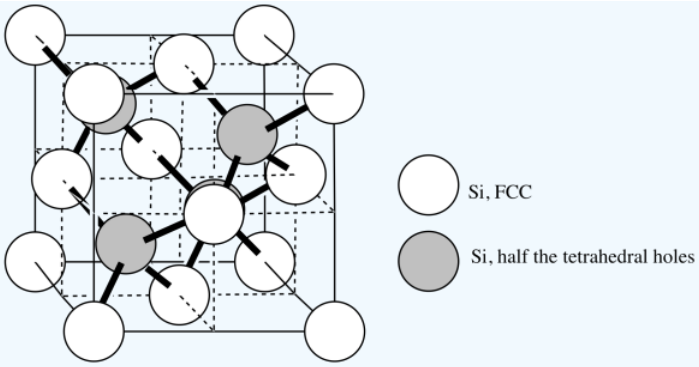
Answer l

Ti^{3+}

Answer m

The higher charge on the ions in TiN would lead to a higher force of attraction between the ions, and thus a higher lattice energy would be required to remove ions from the lattice. That attraction thus lowers the mobility of the ions, so the compound does not melt as easily. However, the fact that both Ti3+ and N3- are slightly larger than Mg2+ and O2- helps explain why the melting points are not extremely different; Coulomb's Law says that the increased attraction of the higher charges should be partly offset by the greater size of the ions.

Answer n

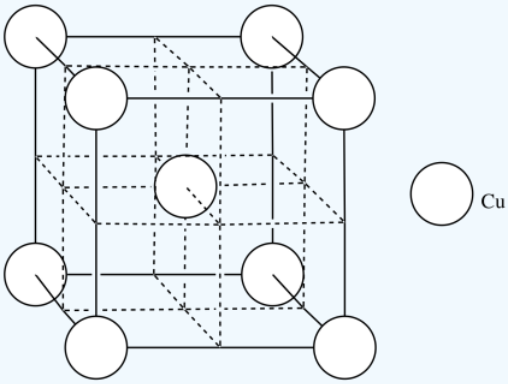


Answer n to Exercise 3.6.2s. Two types of silicon atoms are shown: the white atoms are face-centered cubic, labeled FCC, and the shaded atoms are centered in half the tetrahedral holes.

Answer o

CN = 4

Answer p



Answer q

$[Ar]4s^{1}3d^{10}$ (remember, this is one of those cases in which the 3d level is slightly below the 4s level)

Answer r

Copper's low electronegativity allows it to form an electron sea model of metallic bonding. Copper ions are surrounded by the loosely-held electrons that are allowed to flow through the material.

Answer s

Silicon is too electronegative to form an electron sea structure like a metal.

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3.7: Naming Ionic Compounds

Sometimes, it is useful to be able to recognize the name of a compound and know how to translate it into the structure. You might need to go the other direction, too; if you see a formula -- the ratio of atoms in a compound -- you may want to be able to name the compound.

Take a common ionic compound such as table salt or rock salt, which has the formula NaCl. To name this compound systematically, we just name the two ions of which it is composed: sodium and chlorine. We leave the name of the cation exactly as it is in the periodic table, but we change the ending of the anion's name to *-ide*. We name the cation first and the anion second.

- Name the cation first and the anion second.
- Change the ending of the anion to *-ide*.

In this case, sodium is the cation and chlorine is the anion, so the name for NaCl is sodium chloride.\

How did we know which one was the cation and which was the anion? For one thing, when we write the formula of a simple ionic compound, we usually writethe elements in the same order: cation before anion. If you didn't know that, or if for some reason the formula did not appear in that order, you should still be able to work it out based on the layout of the periodic table. The key is usually found in the elements that form the first two columns of the periodic table. These are the alkali and alkaline earth metals. They are very commonly found in ionic compounds, and they are reliably found as cations in those compounds.

The alkali metals are always found as 1+ or monovalent cations, such as Na^+, K^+, or Li^+. The reason, of course, is that these metals all have one electron in a shell that has been newly started; that shell is far from the nucleus, so the electron is ot held very tightly and it is lost pretty easily.

A similar thing is true for the alkaline earth metals such as magnesium or calcium. These metals have two electrons in the outermost shell, and there still are not enough protons in that distant nucleus to hold those electrons tightly. As a result, both of these electrons are easily lost, and so magnesium is most often found as Mg^{2+} and calcium is usually found as Ca^{2+}.

Once you have identified the cation, you can quickly decide that the other atom in the formula must be the anion.

? Exercise 3.7.1

Provide formulae for the following names.

a) lithium fluoride b) sodium iodide c) potassium bromide d) magnesium chloride

e) calcium oxide f) beryllium sulfide g) sodium oxide h) lithium nitride

Answer a:

LiF

Answer b:

NaI

Answer c:

KBr

Answer d:

$MgCl_2$

Answer e:

CaO

Answer f:

BeS

Answer g:

Na_2O

Answer h:

Li_3N

A similar line of reasoning works with atoms on the other side of the periodic table. Halogens, such as fluorine and chlorine, are frequently found as halide ions, such as fluoride, F-, and chloride, Cl-. However, the halogens and other elements toward the right hand side of the periodic table display a little more versatility that the alkali and alkaline earth metals. Consequently, if you spot chlorine or oxygen in a structure, you can't always be sure it is acting as a simple anion.

For example, there are host of compounds that are "polyatomic ions", clusters of atoms bound tightly together that have an overall charge. Many of these ions contain oxygen. Although oxygen does exist as a simple oxide anion, O^{2-}, that isn't the case in these examples. Because the oxoanions are very common, they have their own names. That lets us distinguish chloride, Cl^-, and oxide, O^{2-}, from chlorate, ClO_3^-. Some of the most common oxoanions are found in the table below.

Most Common Oxoanions

series	**lowest # oxygens**			**highest # oxygens**
chlorine	hypochlorite, ClO^-	chlorite, ClO_2^-	chlorate, ClO_3^-	perchlorate, ClO_4^-
sulfur		sulfite, SO_3^{2-}	sulfate, SO_4^{2-}	persulfate, SO_5^{2-}
phosphorus	hypophosphite, $H_2PO_2^-$	phosphite, HPO_3^{2-}	phosphate, PO_4^{3-}	
nitrogen		nitrite, NO_2^-	nitrate, NO_3^-	

All of these anions have oxygen atoms bound to a central atom of another kind. For example, in chlorate, four oxygen atoms are attached to a central chlorine atom. (The only exception, and it probably isn't important at this point, is persulfate; it has four oxygen atoms attached to a central sulfur atom, and the fifth oxygen hangs from one of the other oxygen atoms.) The names of each of these ions seem a little random until you consider them together. Then, it becomes clear that the names offer clues to the structure. The ending *-ate* always means more oxygens than *-ite*, although neither one corresponds to a specific number of oxygen atoms. The prefix *per-* always means an extra oxygen (beyond what we see in the *-ate* ion), whereas the prefix *hypo-* means even fewer oxygens than in the *-ite* ion.

However, none of those names would signal to us that hydrogen atoms are also attached to the central atom, in addition to the oxygens, but that's what we have in phosphite and hypophosphite.

In addition to these examples, there are a few carbon-based oxoanions that are pretty common: carbonate (CO_3^{2-}), formate (HCO_2^-) and acetate ($CH_3CO_2^-$). Like some of the phosphorus examples, the last two are rather complicated, with hydrogens attached to the central carbons as well as the oxygens seen in all the other cases.

There are also a few polyatomic cations, but they aren't as common as these anions. The most prevalent one in ammonium, NH_4^+.

? Exercise 3.7.2

Provide formulae for the following names.

a) sodium nitrate b) potassium perchlorate c) lithium sulfate

d) ammonium phosphate e) magnesium carbonate f) calcium hypochlorite

g) sodium acetate h) beryllium chlorate

Answer a:

$NaNO_3$

Answer b:

$KClO_4$

Answer c:

Li_2SO_4

Answer d:

$(NH_4)_3PO_4$

Answer e:

$MgCO_3$

Answer f:

$Ca(OCl)_2$

Answer g:

NaO_2CCH_3

Answer h:

$Be(ClO_3)_2$

Towards the middle of the periodic table, it becomes a lot harder to predict the charges on cations. It's not like in those first few columns, where if something is from the first column, its charge is 1+, and if it is from the second column, its charge is 2+. What if a metal comes from the seventh column in the periodic table? Is it guaranteed to be a 7+ cation? Not exactly, because that is an awful lot of electrons to lose. In the middle portion of the periodic table, the transition metals, charges can vary from one case to another, and the same metal could be found with different charges in different compounds. One of the familiar examples if iron, which can most commonly be found as a ferric ion, Fe^{3+}, or as a ferrous ion, Fe^{2+} (although other charges are also possible).

To help sort that problem, the charge on these cations is often given in the name. For example, we might refer to iron (III) chloride, $FeCl_3$, vs. iron (II) chloride, $FeCl_2$ (in addition to the common names ferric chloride and ferrous chloride, respectively). The Roman numeral tells you about the positive charge on the cation.

Arabic numeral to Roman numeral Conversion Table

Arabic numeral	Roman numeral
1	I
2	II
3	III
4	IV
5	V
6	VI
7	VII
8	VIII

? Exercise 3.7.3

Provide formulae for the following names.

a) tantalum (V) chloride b) chromium (III) fluoride c) lead (II) bromide

d) mercury (II) chloride e) tungsten (VI) oxide f) molybdenum (IV) sulfide

Answer a:

$TaCl_5$

Answer b:

CrF_3

Answer c:

$PbBr_2$

Answer d:

$HgCl_2$

Answer e:

WO_3

Answer f:

MoS_2

Exercise 3.7.4

Provide names for the following formulae.

a) LiCl b) Na_2S c) LiO_2CCH_3 d) $Mg(NO_2)_2$ e) $Na_2(SO_3)_2$

f) $PbSO_4$ g) OsO_4 h) $Pb(NO_3)_4$

Answer a:

lithium chloride

Answer b:

sodium sulfide

Answer c:

lithium acetate

Answer d:

magnesium nitrite

Answer e:

sodium sulfite

Answer f:

lead (II) sulfate

Answer g:

osmium (VIII) oxide

Answer h:

lead (IV) nitrate

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3.8: Ionic Compounds- Solutions for Selected Problems

Exercise 3.1.1

a. Ta (tantalum) is lower in the periodic table than V (vanadium)
b. Hg (mercury) is lower in the periodic table than Zn (zinc)
c. Si (silicon) is to the left in the periodic table compared to S (sulfur)
d. W (tungsten) is to the left and lower in the periodic table compared to Cu (copper)

Exercise 3.1.2

a. $[He]2s^2 2p_x^2 2p_y^1 2p_z^1$
b. $[He]2s^2 2p_x^2 2p_y^2 2p_z^2$
c. $[Ar]4s^2$
d. [Ar]
e. $[Ne]3s^2 2p_x^1$
f. [Ne]
g. $[He]2s^2 2p_x^1 2p_y^1 2p_z^1$
h. $[He]2s^2 2p_x^2 2p_y^2 2p_z^2$
i) $[Ne]2s^2 2p_x^2 2p_y^2 2p_z^1$
j) $[Ne]2s^2 2p_x^2 2p_y^2 2p_z^2$

Exercise 3.1.3

a. 0.076 nm; smaller
b. 0.140 nm; larger
c. 0.167 nm; smaller
d. 0.144; larger

Exercise 3.1.4

a. 0.154; larger
b. 0.071; smaller
c. 0.128; larger
d. 0.133; smaller

Exercise 3.2.1

a. 1:1 K:Cl or KCl
b. 1:3 Fe:Cl or $FeCl_3$
c. 1:6 Mo:Cl or $MoCl_6$
d. 1:4 Zr:Cl or $ZrCl_4$

Exercise 3.2.2

a. Li:O 2:1 or Li_2O
b. Fe:O 2:3 or Fe_2O_3
c. Cr:O 1:3 or CrO_3
d. Ti:O 1:2 or TiO_2

Exercise 3.2.3

a. Li:N 3:1 or Li_3N
b. Ta:N 1:1 or TaN
c. W:N 1:2 or WN_2
d. Co:N 3:2 or Co_3N_2

Exercise 3.2.4

a. Li_4WO_4 because tungstate anion would be 4-
b. $Li_4V_4O_{12}$ because the tetravanadate ion would be 4-
c. $Li_2Mo_4O_{14}$ because the tetramolybdate ion would be 2-
d. $Li_2Cr(OH)_6Mo_6O_{18}$ because the complex polyoxoanion would be 2-

Exercise 3.3.1

a. KCl would have the lowest melting point. It would be easier to melt than LiCl because the smaller Li^+ ion would more strongly attract the counterion, owing to the smaller distance separating the opposite charges.
b. NaBr would have a lower melting point than NaF.
c. CaO would have a lower melting point than BeO.
d. KBr would have a lower melting point than LiF.

Exercise 3.3.2

The answer is (a). The sum of the cation and anion radius is longer; therefore the distance betwwen the two is longer, so the force of attraction will be weaker.

Exercise 3.3.3

a. $CaCl_2$
b. Na_2O
c. CaO

Exercise 3.3.4

a. A little lower since K^+ is a little larger than Na^+ (actual= 770°C)
b. A little higher since F^- is a little smaller than Cl^-. (actual =930°C)
c. A lot higher since the anion charge is 2x higher. (actual =1275°C (sublimes but doesn't melt))
d. A whole lot higher since cation and anion charge are 2x higher. (actual = 2000+ °C (decomposes above this temp))

Exercise 3.4.1

a. 25 waters.
b. 2 units (2 anions and 2 cations).
c. Half the water might only dissolve half the salt: 1 unit.
d. Four times the water may dissolve four times the salt: 4 units.

Exercise 3.4.2

a. LiFshould be more soluble.
b. KF should be more soluble (but keep reading).
c. LiF should be more soluble.

Exercise 3.4.3

The MgO contain more highly charged ions (Mg^{2+} and O^{2-}) than LiF (Li^+ and F^-) and so it is more difficult to separate the ions from their solid state.

Exercise 3.4.4

The ions interact with the water via electrostatic interactions, too. The same distance factor that allows small ions to attract each other more strongly also allows small ions to interact more strongly with the water.

Exercise 3.4.5

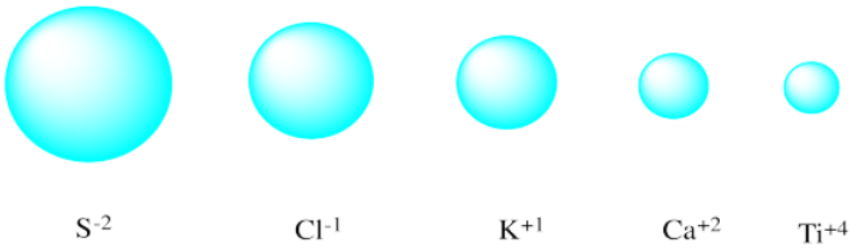
a. The lattice energy of an ionic solid is a measure of the strength of bonds in that ionic compound.
b. Charge of ion (directly related to lattice energy); Radius of each ion (inversely related to lattice energy)
c. Stronger lattice energy results in a stronger bond. The stronger the bond, the more energy required to separate ions.
d. Stronger lattice energy results higher mp or bp.

e. Stronger lattice energy results in less soluble crystal lattice.

Exercise 3.4.6

a. NaCl NaBr
b. KF CaF2
c. MgO Na2O
d. KF CsCl
e. RbBr CaCl2

Exercise 3.5.1



Answer to Exercise 3.5.1. From left to right, largest to smallest atoms, are sulfur with -2 charge, chlorine with -1 charge, potassium with +1 charge, calcium with +2 charge, and titanium with +4 charge.

Exercise 3.5.2

Generally, but not always, anions are bigger than cations, so cations can pack efficiently into the holes between the anions.

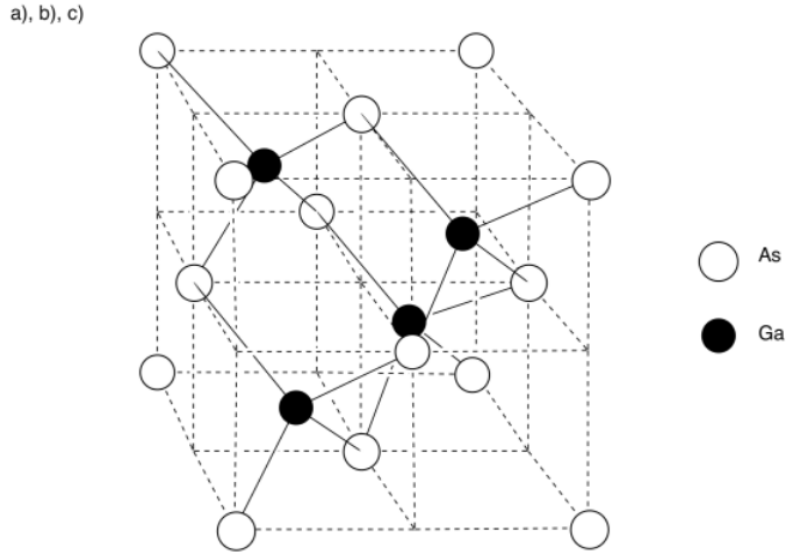
Exercise 3.5.3

i. a) simple cubic; b) cubic hole; c) coordination number = 8; d) all occupied; e) 8 x 1/8 Cl and 1 Cs (or vice versa, depending on how you define a unit cell); f) CsCl

ii. a) face centered cubic; b) octahedral hole; c) coordination number = 6; d) all occupied; e) 6 x 1/2 plus 8 x 1/8 = 4 Cl and 1 plus 12 x 1/4 = 4 Na (or vice versa, depending on how you define a unit cell); f) NaCl

iii. a) face centered cubic; b) tetrahedral hole; c) coordination number = 4; d) all occupied; e) 6 x 1/2 plus 8 x 1/8 = 4 Ca and 8 F ; f) CaF_2

Exercise 3.6.1



d) There are eight arsenic atoms in the corner; each is shared by eight neighbouring cubes. There are six atoms on the faces; each is shared by two neighbouring cubes.

$\#\ atoms = 8(\frac{1}{8}) + 6(\frac{1}{2}) = 1 + 3 = 4$ arsenic atoms

e) Each gallium atom is entirely within the cell. There are 4 gallium atoms.

f) The formula is just the ratio of each atom in the material. Since the 4:4 ratio is the same thing as a 1:1 ratio, the formula is just GaAs.

g) Arsenic is to the right of gallium in the periodic table, so arsenic must be more electronegative; it must be the anion, and gallium the cation.

Arsenic is three atoms from the right edge of the periodic table; as an ion, a 3- charge makes sense. To balance the charge, gallium must have a 3+ charge.

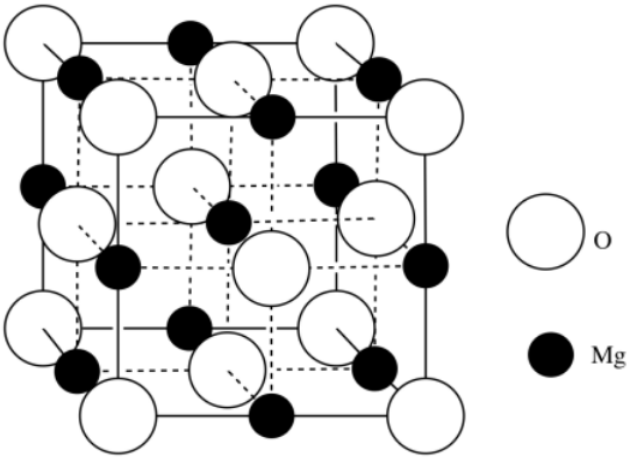
h) Cesium is larger than gallium, and iodine is larger than arsenic, so in terms of internuclear distance, there would be less attraction between the cesium and iodide ions than between the (closer) gallium and arsenide ions. Also, if the charge on gallium and arsenide are 3+ and 3-, respectively, and the charges on cesium and iodide are only 1+ and 1-, respectively, then there should be much greater attraction between the gallium and arsenide ions.

The melting point of gallium arsenide (mp = 1,238 ^{o}C) should be higher than that of cesium iodide (mp = 632 ^{o}C).

i) The atoms are so close together in the periodic table that it isn't likely that arsenic should completely steal three electrons away from gallium; the difference in electronegativity isn't great enough.

Exercise 3.6.2

a) O^{2-} b) Mg^{2+} c) MgO



e) O: 8(1/8) corners + 6(1/2) faces = 4 atoms; Mg: 12(1/4) edges + 1 center = 4 atoms; MgO

f) [Ne]$3s^2$ g) [Ne] or [He]$2s^2 2p^6$

h) magnesium; the positive charge on the ion causes the remaining electrons to contract

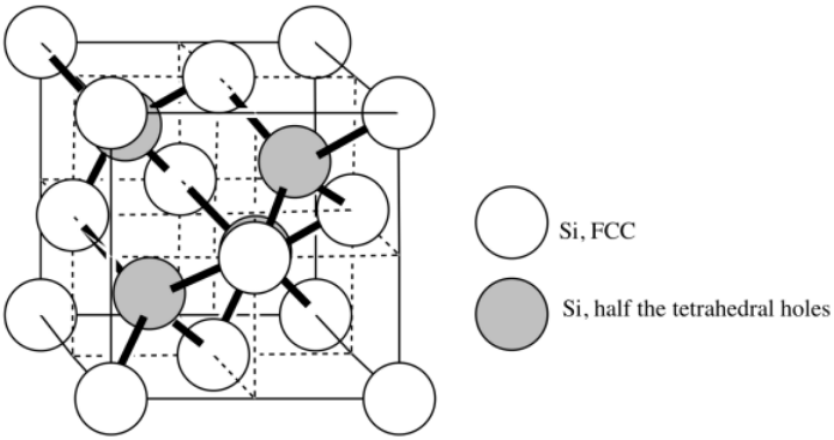
i) [Ne] or [He]$2s^2 2p^6$

j) oxide; they have the same electron configuration, but magnesium has more protons in its nucleus to attract the electrons.

k) N^{3-} l) Ti^{3+}

m) The higher charge on the ions in TiN would lead to a higher force of attraction between the ions, and thus a higher lattice energy would be required to remove ions from the lattice. That attraction thus lowers the mobility of the ions, so the compound does not melt as easily. However, the fact that both Ti3+ and N3- are slightly larger than Mg2+ and O2- helps explain why the melting points are not extremely different; Coulomb's Law says that the increased attraction of the higher charges should be partly offset by the greater size of the ions.

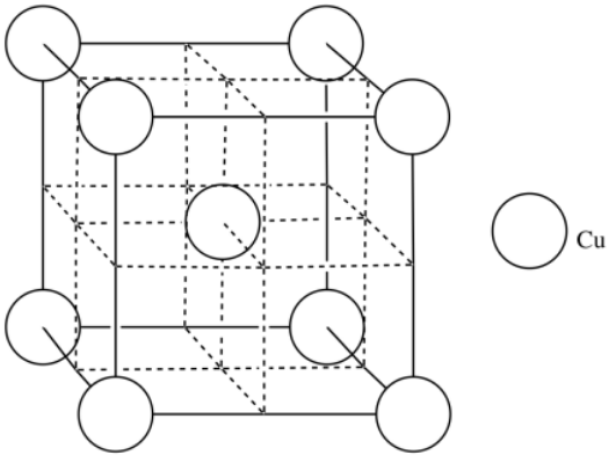
n)



Answer to Exercise 3.6.2n. An ionic solid composed of silicon in two arrangements: in the face-centered cubic position, and in the tetrahedral holes.

o) CN = 4

p)



q) [Ar]$4s^1 3d^{10}$ (remember, this is one of those cases in which the 3d level is slightly below the 4s level)

r) Copper's low electronegativity allows it to form an electron sea model of metallic bonding. Copper ions are surrounded by the loosely-held electrons that are allowed to flow through the material.

s) Silicon is too electronegative to form an electron sea structure like a metal.

Exercise 3.7.1

a) LiF b) NaI c) KBr d) $MgCl_2$ e) CaO f) BeS g) Na_2O Li_3N

Exercise 3.7.2

a) $NaNO_3$ b) $KClO_4$ c) Li_2SO_4 d) $(NH_4)_3PO_4$ e) $MgCO_3$ f) $Ca(OCl)_2$ g) NaO_2CCH_3 h) $Be(ClO_3)_2$

Exercise 3.7.3

a) $TaCl_5$ b) CrF_3 c) $PbBr_2$ d) $HgCl_2$ e) WO_3 f) MoS_2

Exercise 3.7.4

a) lithium chloride b) sodium sulfide c) lithium acetate d) magnesium nitrite e) sodium sulfite

f) lead (II) sulfate g) osmium (VIII) oxide h) lead (IV) nitrate

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CHAPTER OVERVIEW

4: Introduction to Molecules

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4.1: Why do Molecules Matter?

Molecules aren't everything

To get a good idea of what a molecule is, let's first look at what a molecule isn't.

Not all things are composed of molecules. Many common rocks and minerals are composed mostly of silica. Silica is a non-molecular network solid with the approximate formula SiO2. Its structure keeps going on in all directions. The chunk of silica shown below shows just 14 silicon atoms, but a real chunk of silica could contain 14 thousand or 14 million silicon atoms, or just about any other number.

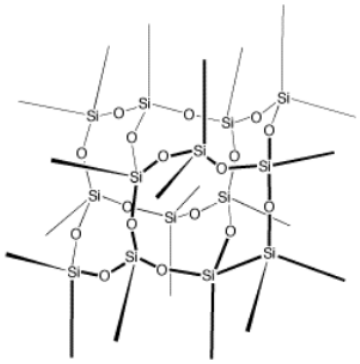


Figure 4.1.1: A representative chunk of a non-molecular solid.

Diagram of a solid composed of silicon and oxygen. The bonds are different lengths and angles, unlike a lattice structure.

In contrast, a molecule is made from a particular number of atoms, and so it has a particular size. The atoms in silica are not collected into discrete units of a particular size; instead, they can be arranged in very large arrays of different sizes. A unit of silica could contain a million silicon atoms or a billion of them.

Molecules contain a specific combination of atoms in a specific ratio. That isn't exactly true in silica. There really are about twice as many oxygen atoms as silicon in silica and the atoms are arranged in a particular way, but the Si:O ratio can vary slightly, and there are also small amounts of hydrogen (but so small an amount that we ignore it in the formula).

Copper metal is also a non-molecular solid, with legions of copper atoms bonded together to form one united mass. The copper atoms are arranged in a particular way, and the metal has a very specific formula (Cu), but like silica, a unit of copper could contain a million copper atoms or a billion of them.

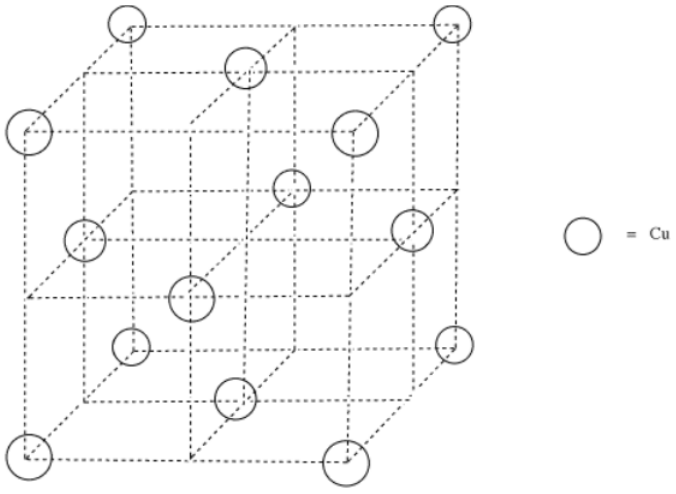


Figure 4.1.2: A representative chunk (or unit cell) of a metal.

Rocks and metals are non-living, inorganic materials. We are often interested in with chemicals used by biological systems. Those compounds are overwhelmingly molecular.

- not all compounds are molecules

- some compounds form larger structures that don't have a well-defined size, although they may have a specific ratio of atoms
- metals form large structures that do not come in regular chunks

Origins and scope of inorganic and organic chemistry

Sometimes you will hear the terms "organic chemistry" and "inorganic chemistry", as in "I've got an inorganic chem lab today" or "I just did really well on my o-chem test". Sometimes high school or first year chemistry is called "inorganic", but that isn't really a good description. What do these terms really mean?

The realization during the European Renaissance that there is an entire chemistry unique to living things gave rise to the study of organic chemistry. Researchers working in medical schools labored to discover the active principles that could be found in herbal remedies and spices, which at that time formed an important part of the treatment of disease. The chemistry of the biological world seemed completely separate from that of the mineral world, and consequently organic chemistry developed as a separate discipline from inorganic chemistry.

- organic chemistry is based on the chemistry of organisms
- the chemistry of organisms overwhelmingly involves carbon compounds
- more generally, organic chemistry is the chemistry of carbon compounds
- inorganic chemistry is the chemistry of the rest of the periodic table

Organic compounds are based on only a few elements from the upper part of the periodic table. The principle component of organic molecules is carbon. Carbon atoms are able to bond with each other to form bigger and bigger structures.

In addition, organic compounds frequently contain hydrogen, oxygen and nitrogen; phosphorus and sulfur are occasionally seen as well. With just these atoms, the major classes of structural biomolecules can be made (lipids, proteins and nucleic acids). Most small, biologically relevant molecules contain only this small group of atoms, including hormones, neurotransmitters and compounds involved in chemical ecology.

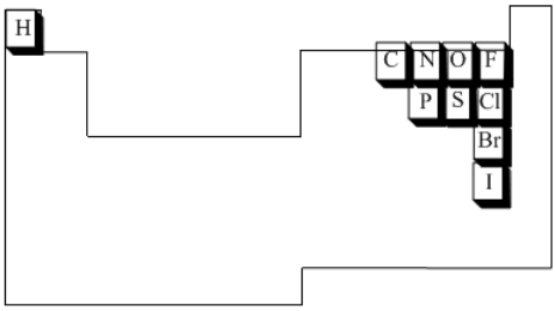


Figure 4.1.3: The "organic" part of the periodic table.
Abbreviated periodic table, with only hydrogen, carbon, nitrogen, fluorine, phosphorus, sulfur, chlorine, bromine, and iodine.

Some marine organisms produce halogenated compounds containing bromine, chlorine or iodine. These compounds don't perform an obvious function in these organisms. Many halogenated organic compounds are toxic, and so it is possible that marine organisms use these compounds as a self-defense measure; chemical warfare is not unheard of in nature.

In addition, halogenated compounds are sometimes useful in carrying out organic reactions in the laboratory or in industry.

Occasionally other elements play extremely important roles in biological molecules; for example, vitamin B12 contains a cobalt atom bonded to a carbon, and plays an important role as a regulatory agent. However, by and large, organic and biological compounds contain very few elements: C, H, O, N, occasionally S and P, and sometimes halogens.

Applications of organic chemistry are wide-ranging. An obvious practical area is the pharmaceutical industry, because small organic molecules are frequently biologically active. However, one of the earliest industrial applications of organic chemistry was the dyestuff and paint industry, because many pigments can be made from organic compounds. It has been argued that the development of this industry in Germany in the 1800's was closely connected to the rise of that country as a major industrial power. Today, Germany is still an important center for research and development in chemistry. One of the biggest applications is polymer chemistry, which involves very large molecules or "macromolecules" that are useful as plastics and other materials. Most organic polymers are derived from petroleum, but a growing fraction of them come from agricultural materials such as corn and soybeans.

- pharmaceuticals are an important application of organic chemistry

- pigments, paints and dyes are historically very important in organic chemistry
- one of the biggest applications of organic chemistry is polymer chemistry

Inorganic chemistry is just the rest of chemistry. It is the part that is not principally based on carbon. It turns out that there is a lot of important inorganic chemistry in biology, as well. Frequently, metal ions play crucial roles in There are important applications of inorganic chemistry, too. Many important materials are inorganic, such as ceramics and solid-state materials used as conductors and semiconductors. Many industrial catalytic processes, such as refining petroleum or making detergent, require catalysis by transition metals. Metals themselves are important in society, and often inorganic chemistry is required to extract metals out of natural ores.

- materials science offers important applications of inorganic chemistry
- catalysis offers important applications of inorganic chemistry
- mining and metallurgy often depends on inorganic chemistry

In Living Systems, the Focus is Often on Molecules

Biological structures like DNA, proteins and cells all depend on molecules. A strand of DNA is a very long molecule, and so is a protein. Cells are complicated, organized structures built up from huge numbers of smaller molecules.

There are lots of important small molecules in biology, too. Neurotransmitters like epinephrine are pretty simple molecules, but without them our nervous system couldn't work. Oxygen, containing just two oxygen atoms, is a very simple molecule, and it is certainly essential to living things.

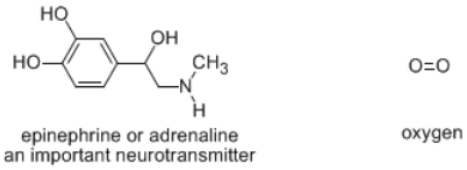


Figure 4.1.4: Two examples of molecules.
Left: structural formula of epinephrine, also known as adrenaline. Right: structural formula of oxygen, a diatomic molecule.

Molecules aren't only found in biology. Sulfur is a molecule that is found naturally in the earth. It contains a group of sulfur atoms connected in a ring, like a daisy chain. Carbon nanotubes and fullerenes are carbon-containing molecules that can be found in meteorites as well as some kinds of steel.

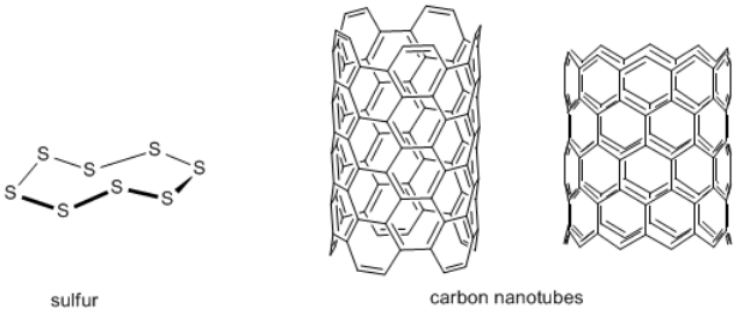


Figure 4.1.5: Some non-biological molecules.
Left: eight atoms of sulfur in a ring. Right: carbon nanotubes, composed of hexagons in a hollow cylinder.

In general, this is a course about structural chemistry. Chemistry is specifically the study of matter and energy: the stuff from which the universe is made. Because many of the readers of this text will be biology majors and pre-medical students, we will be especially careful to pay attention to the stuff living things are made of. Organic chemistry is the study of organic matter, meaning the stuff from which living things are made. Many of the examples in these pages on molecules and their properties are related somehow to living things.

In a molecule, a specific combination of atoms is arranged in a specific way. The atoms are all held in place by bonds that connect them to other atoms. The atoms in a specific compound are always found in the same places from one molecule to the next. This information has been shown using x-ray crystallography and tunneling electron microscopy, two methods that can give us pretty good pictures of where the individual atoms can be found within a compound or an element. This unique arrangement gives the molecule unique physical and biological properties.

While there are a number of ways in which eight carbons, two oxygens, four nitrogens and ten hydrogens can combine to form molecules with the formula C8H10N4O2, one unique arrangement of these atoms forms the structure of caffeine, with the accompanying stimulant effect on your nervous system.

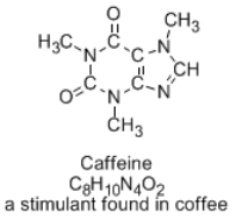


Figure 4.1.6: Caffeine, a molecule with special significance at the college level

You wouldn't want to ingest just any molecule that happened to have the same formula as caffeine. Other combinations of atoms in the ratio C8H10N4O2 could be ineffective at best or poisonous at worst. The structures may be connected using a different order of atoms; sometimes, we say they have a different connectivity. These other structures are described as "isomers" of caffeine.

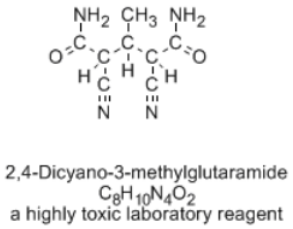


Figure 4.1.7: This molecule is not caffeine; it is an isomer of caffeine.

- Compounds that have the same formulae but different connectivities are called isomers.

These atoms remain bonded together in the same way throughout the lifetime of the molecule, regardless of whether the molecule is frozen in the solid phase, has melted into the liquid phase, or floats through the air in the gas phase.

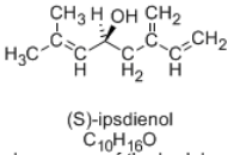


Figure 4.1.8: This molecule can float through the air from one beetle to another, but all the atoms stay connected together.

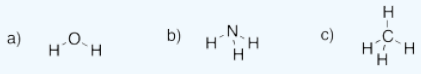
When a female bark beetle produces and secretes a sex pheromone in order to attract a mate, the pheromone can be carried on currents of air to male bark beetles, whose antennae can intercept individual pheromone molecules, completely intact, still in the same form as when they were secreted by the female, no matter how far away she is. The male recognizes the structure of the molecule; it can clearly tell if it has just intercepted the proper pheromone or some subtle imposter that also happens to have the formula $C_{10}H_{16}O$.

? Exercise 4.1.1

Draw the following molecules. In each case, the hydrogens are all bonded to the non-hydrogen atom.

a) water, H_2O b) ammonia, NH_3 c) methane, CH_4

Answer

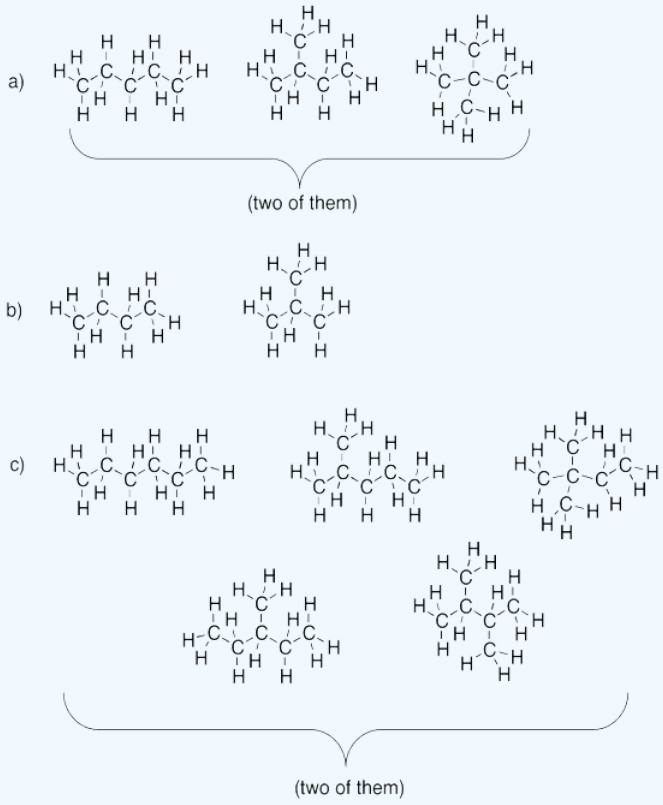


Exercise 4.1.2

Draw three isomers for each the following formulae. Assume each carbon can make 4 bonds and each hydrogen can make only one bond.

a) C_5H_{12} b) C_4H_{10} c) C_6H_{14}

Answer



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4.2: Lewis Structures

In order to think about some of the compounds that can be made with this small collection of elements, we will need a way to visualize on paper how these atoms are connected with one another.

At one time, people thought of the atoms in these compounds as charged spheres (such as oxygen anions, O^{2-}, or carbon cations, C^{4+}) that were simply pulled together by their opposing charges, like piles of sticky jellybeans. However, there are some limitations to this way of looking at compounds. We know that in most organic compounds, it is common to find two carbon atoms connected together, which is not likely to happen if all carbons are found as charged cations; in that case, they would simply repel each other.

In the early twentieth century, G.N. Lewis used some simple observations about the periodic table to propose an alternate model of how atoms can be bonded together. This model still influences the way we think about molecules today.

First of all, Lewis noted that if you count up the number of electrons in all the atoms in almost any known molecular compound, such as water (H_2O), ammonia (NH_3) or carbon dioxide (CO_2), you get an even number (10, 10 and 22, respectively, in these examples).

Number of electrons...

	O	H	H	Total
H_2O	8	1	1	10

	N	H	H	H	Total
NH_3	7	1	1	1	10

	C	O	O	Total
CO_2	6	8	8	22

Figure 4.2.1: A tally of numbers of electrons in some small molecules.

From this observation he eventually proposed the notion that electrons are more stable if found in pairs. Two atoms with odd numbers of electrons may therefore gain stability if they come together to form an even number overall.

- molecules usually contain even numbers of total electrons

For example, hydrogen, with 1 electron, plus fluorine, with 9 electrons, come together to form hydrogen fluoride, with 10 electrons. The new pair of electrons that forms from the unpaired electron in fluorine and the single electron in hydrogen, Lewis thought, is the bond that holds the two atoms together.

Figure 4.2.2: A tally of numbers of electrons in a small molecule, hydrogen fluoride, showing the electrons as dots.

The synthesis reaction of a hydrogen atom and a fluorine atom. One electron from hydrogen and nine from fluorine, both odd numbers, give hydrogen fluoride, a compound with an even number of ten electrons.

To simplify electron counting, one need only consider the valence electrons when thinking about bonding; one could ignore the core electrons, which are simply groups of electrons that already number the same as a noble gas. Thus, we consider fluorine's seven valence electrons instead of all nine; we consider nitrogen's five valence electrons and not all seven.

	Number of electrons...				or	Number of *valence* electrons....			
	O	H	H	Total		O	H	H	Total
H_2O	8	1	1	10		6	1	1	8
	N	H	H	H	Total	N	H	H	H	Total
NH_3	7	1	1	1	10	5	1	1	1	8
	C	O	O	Total		C	O	O	Total
CO_2	6	8	8	22		4	6	6	16
	H	F	Total			H	F	Total	
HF	1	9	10			1	7	8	

Figure 4.2.3: A tally of numbers of *valence* electrons in some small molecules.

Rows, from top to bottom: water, ammonia, carbon dixodie, and hydrogen fluoride. Left column: total number of electrons. Right column: number of valence electrons.

- valence electrons are the electrons in an outer shell of an atom
- counting only valence electrons simplifies electron counting

Lewis made a couple of additions to this idea based on the layout of the periodic table. People were aware of the remarkable stability of the noble gases, and so it seemed that there was something particularly stable about the number of electrons found in these elements. These are even numbers, of course: 2 for helium, 10 for neon, 18 for argon, 36 for krypton and so on. In terms of valence electrons, neon has 8, argon has 8, krypton has 18 and so on. Lewis suggested that any atom could become more stable if it could share enough electrons from its neighbors to obtain the same electron count as a noble gas.

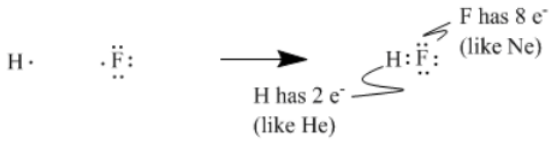

Figure 4.2.4: A tally of numbers of *valence* electrons in hydrogen fluoride.

Formation of full electrons shells in the synthesis of hydrogen fluoride. Hydrogen has two electrons, like helium, and fluorine has eight electrons, like neon.

- when an atom is found in a molecule, it usually has the same number of valence electrons as the noble gas in the same row
- this electron count includes unshared electrons as well as shared electrons
- for electron-counting, shared pairs are counted for both atoms that share the electrons

The fact that organic and biological chemistry, which constitutes a majority of familiar molecules, takes place mostly in the second row of the periodic table allows us to think of the Lewis model as "the octet rule", from the Latin word for eight: second-row elements form bonds so that they can have eight valence shell electrons, like neon.

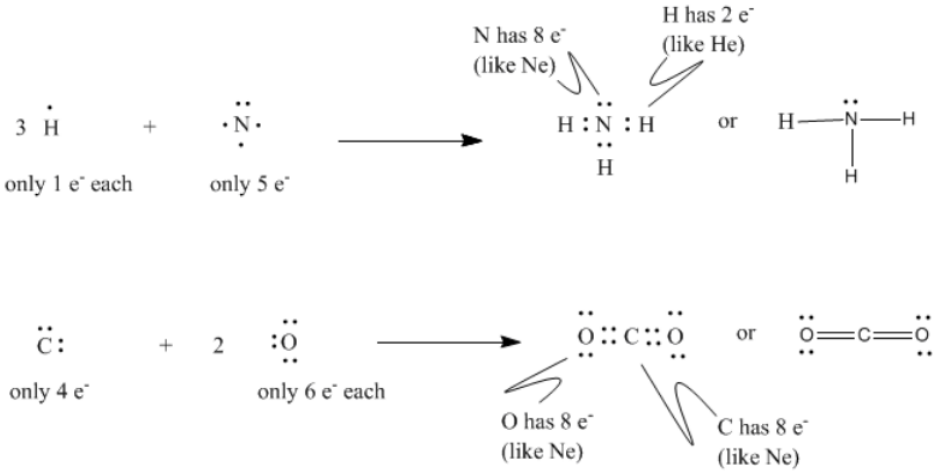

Figure 4.2.5: A tally of numbers of electrons in some small molecules, using Lewis structures.
Top: synthesis of ammonia from three moles of hydrogen and one mole of nitrogen. Nitrogen, in ammonia, has one lone pair and a complete electron shell. Bottom: synthesis of carbon dioxide from carbon and two moles of oxygen. Both oxygens have two lone pairs and two bonds to carbon.

- most common biological or organic molecules are made from atoms in the second row of the periodic table
- it is common to see atoms with 8 electrons, like neon, in many molecules
- the Lewis "octet" rule says atoms frequently have 8 valence electrons in molecules
- atoms in other rows sometimes have larger numbers of electrons

Lewis structures are drawings that we use to show how the electrons in a molecule are arranged in a stable way. They let us verify that each atom in the molecule has an octet.

Note that a pair of electrons that forms a bond is usually written as a line instead of a pair of dots. This modification of a Lewis structure is sometimes called a Kekule structure. For the most part, Kekule structures will be used in these pages.

? Exercise 4.2.1

Try drawing Kekule structures for the following diatomic molecules:

a) Cl_2 b) H_2 c) HCl d) F_2

Answer

What happens if a compound is actually an ion? A positive or negative charge tells you something about the structure. If there is a negative charge there must be an extra electron in the structure, so that the proton : electron ratio is no longer balanced. If the charge is two minus, there must be two extra electrons. For the same reason, a positive charge means an electron is missing from the structure.

- a negative charge means extra electron(s)
- a positive charge means missing electron(s)

? Exercise 4.2.2

Try drawing Kekule structures for the following ions:

a) HO^- b) $MgCl^+$ c) HS^- d) OCl^-

Answer

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4.3: Lewis Structures and Multiple Bonding

The Basics

Let's go over some of the main things you need to consider if you want to draw Lewis structures. Lewis structures will be the principal way you communicate ideas about molecules in this course, so it is best to get some practice with them as soon as possible.

Here's what you need to do:

a. count up the valence electrons in the atoms that will be bonded together.
b. place the atoms beside each other on paper.
c. arrange the given electrons around the atoms so that each atom has an octet.
d. these electrons can be shared between the atoms (these are called bonding pairs) or held by one atom or the other (these are called nonbonding pairs or "lone pairs")

Occasionally, you will need to share more than one pair of electrons between two atoms so that all atoms can obtain an octet. That's what happens in the structure of carbon monoxide, CO.

Figure 4.3.1: Carbon monoxide: both atoms have octets.

Carbon has 4 valence electrons and oxygen has 6, for a total of 10 electrons. That's 5 pairs. If carbon and oxygen share a pair of electrons, there will be four pairs left. You could put three pairs on the oxygen and one pair on the carbon. The oxygen has four pairs, including the lone pair and the shared pairs. Carbon only has two pairs. That isn't an octet, and if possible the molecule will avoid that situation.

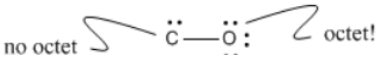


Figure 4.3.2: Carbon monoxide: not all the atoms have octets.

A carbon and oxygen atom with a single bond. Carbon has one lone pair while oxygen has three. Carbon does not have an octet, while oxygen does.

There could be one bond, and two lone pairs on each atom. That isn't much better. Now neither atom has an octet.

Figure 4.3.3: Carbon monoxide: neither atoms have octets.

Figure 4.3.4: Carbon monoxide: neither atoms have octets.

That means we can only have three bonds between the carbon and oxygen -- a total of six electrons. The other four electrons could become lone pairs -- one on carbon and one on oxygen. Now both atoms have an octet.

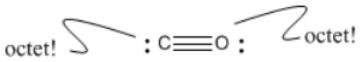


Figure 4.3.5: Carbon monoxide: both atoms have octets.

A carbon and oxygen atom with three bonds. Both have a single lone pair of electrons and a complete octet.

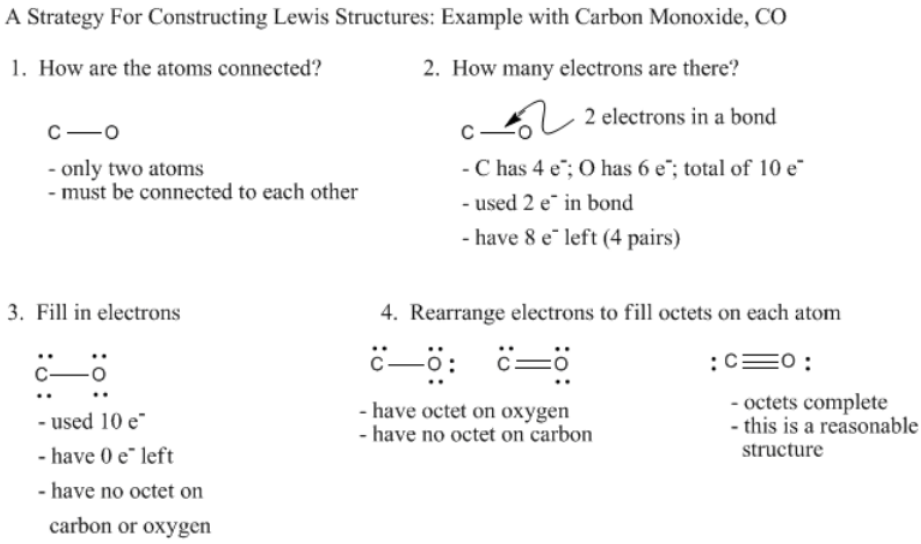


Figure 4.3.6: A *beginning* set of instructions for completing a Lewis structure.

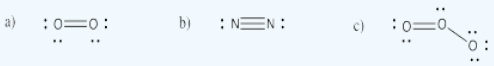
Steps for constructing lewis structures. Step one: connect the atoms together. Step two: calculate how many valence electrons are present. Step 3: fill in electrons. Step 4: rearrange electrons to fill octets on each atom.

? Exercise 4.3.1

Try drawing Lewis structures for the following molecules:

a) O_2 b) N_2 c) O_3

Answer



Consequences of multiple bonding: bond distances

Are there really three bonds between the carbon and oxygen in carbon monoxide? How could we tell?

Multiple bonds have important consequences. A bond is a pair of electrons shared by two atoms. Since both atoms need the pair of electrons to complete an octet, the atoms must stay close to the electron pair and close to each other in order to be stable. Hence, a bond is also an attractive force between atoms. That idea means additional bonds between two atoms leads to additional attraction between the atoms. Two atoms with multiple bonds should be more tightly bound to each other than two atoms with fewer bonds.

- a double bond between two atoms is shorter than a single bond between the same two atoms
- a triple bond between two atoms is shorter than a double bond between the same two atoms
- a quadruple bond between two atoms is shorter than a triple bond between the same two atoms

Experimental data suggests that this is true. Microwave spectroscopy is a technique that can be used to measure bond distances (the distance from one atom to the next) in molecules in the gas phase. The data on carbon monoxide indicates that the C-O distance is about 1.13 A (1 A = 10^{-10} m). In carbon dioxide, CO_2, the distance is 1.16 A. The shorter distance in carbon monoxide suggests the carbon and oxygen are held a little more tightly together than they are in carbon dioxide, in which the Lewis structure shows only a double bond.

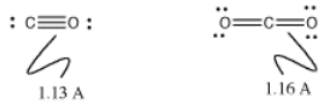


Figure 4.3.7: A comparison of experimentally determined bond distances.

Comparison of bond length between carbon monoxide (1.13 Ångstroms) and carbon dioxide (1.16 Ångstroms).

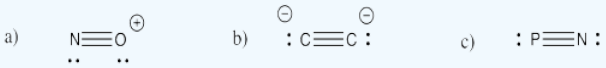
The additional bond between a pair of atoms is often called a pi bond (pronounce "pie" bond). The first bond between a pair of atoms is sometimes called a sigma bond. Carbon monoxide has one sigma bond and two pi bonds.

Exercise 4.3.2

Draw structures for the following molecules and ions.

a) NO^+ b) C_2^{2-} c) PN

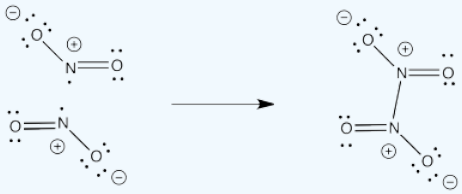
Answer



Exercise 4.3.3

NO_2 is a brown gas (connectevity O-N-O) that comes from car exhausts. It is partly responsible for smog in large cities. NO_2 dimerizes at low temperature to form N_2O_4, a colorless gas. Dimerization refers to two molecules coming together to form one, bigger structure. Show why this phenomenon happens with NO_2, with the help of structures.

Answer



Exercise 4.3.4

Do you expect the NO_2^- anion to dimerize? Explain.

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4.4: Lewis Structures and Polyatomic Molecules

Connectivity

Thinking about how atoms and electrons are arranged in a molecule gets harder when there are more than two atoms. Often you need to decide how the atoms are arranged before writing the Lewis structure.

Let's draw the structure for carbonic acid, H_2CO_3. First we need to know which atoms are connected together. That will tell us which atoms are sharing electrons.

We could put one atom in the middle of the structure and arrange all the others around it. That may work sometimes, but often it gives the central atom too many bonds. A second-row atom can't have more than eight electrons in its valence shell. As a result, a carbon can't have more than four bonds, because there is no room for more electrons.

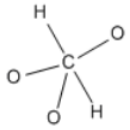


Figure 4.4.1: A carbon atom with a problem: too many valence electrons.

We could try to attach all the atoms in a string. Long strings of atoms like this are not very common. There may be several reasons why this sort of arrangement isn't very stable. First, when we consider formal charge a little later, you will see that placing all the atoms in a row may cause unnecessary charge separation. Second, some atoms such as oxygen are not very stable when bonded to other atoms of the same kind. Repulsion between lone pairs may contribute to this instability. Because carbon often has no lone pairs, it is an exception and it can bond to itself.

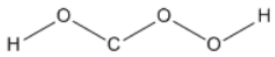


Figure 4.4.2: A long string of atoms may still have problems when you start adding in the rest of the electrons.
A proposed structure for carbonic acid: a line of atoms in the order hydrogen-oxygen-carbon-oxygen-oxygen-hydrogen.

Note that when we try to arrange the atoms in either way, we would probably avoid putting a hydrogen in the middle. That's because hydrogen's octet is just two electrons, so it can usually only make one bond. Knowing the number of bonds that other atoms usually form can also be helpful.

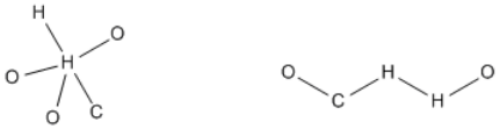


Figure 4.4.3: Hydrogen atoms with problems: usually, atoms with lower numbers of valence electrons must be nearer the edge of the molecule.
Two structures for carbonic acid. Left; hydrogen at center, with five bonds to the other atoms. Right: two hydrogens in the interior positions of a chain of atoms.

Valence

Valence is the number of bonds an element usually forms - for example, the valence of carbon is four, nitrogen is three, oxygen is two, fluorine and hydrogen are one. Valence usually corresponds to the number of electrons needed to form an octet. However, there are exceptions: boron would need 5 electrons to form an octet, but since it only has three electrons to share, it can only form three covalent bonds.

Table 4.4.1 Typical valences (number of bonds formed) for several second-row atoms.

Table 4.4.1 Typical valences (number of bonds formed) for several second-row atoms.

atom	B	C	N	O	F
valence	3	4	3	2	1

Keeping valence in mind can help Lewis structures go more easily. In the case of carbonic acid, carbon might go in the middle, since it must form the most bonds to obtain an octet. Also, having two of the oxygens connected to hydrogens as well as to carbon helps them to attain their normal valence as well.

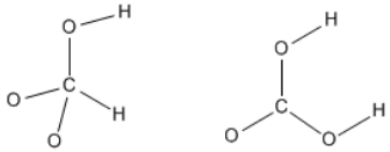


Figure 4.4.4: Knowledge of valence suggests the structure on the right is more likely.

Once the connectivity has been filled in, we have a skeletal structure of the compound. Now we just need to fill in the extra electrons. Six from each oxygen is 18; four from carbon makes 22; one from each hydrogen makes 24 total electrons.

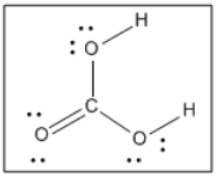


Figure 4.4.5: Adding in the remaining 14 electrons leads to this structure.

The correct structure for carbonic acid. The central carbon has two bonds to an oxygen, and single bonds to two groups consisting of an oxygen and a hydrogen.

Coming up with a Lewis structure requires a number of steps, but it usually follows a familiar pattern.

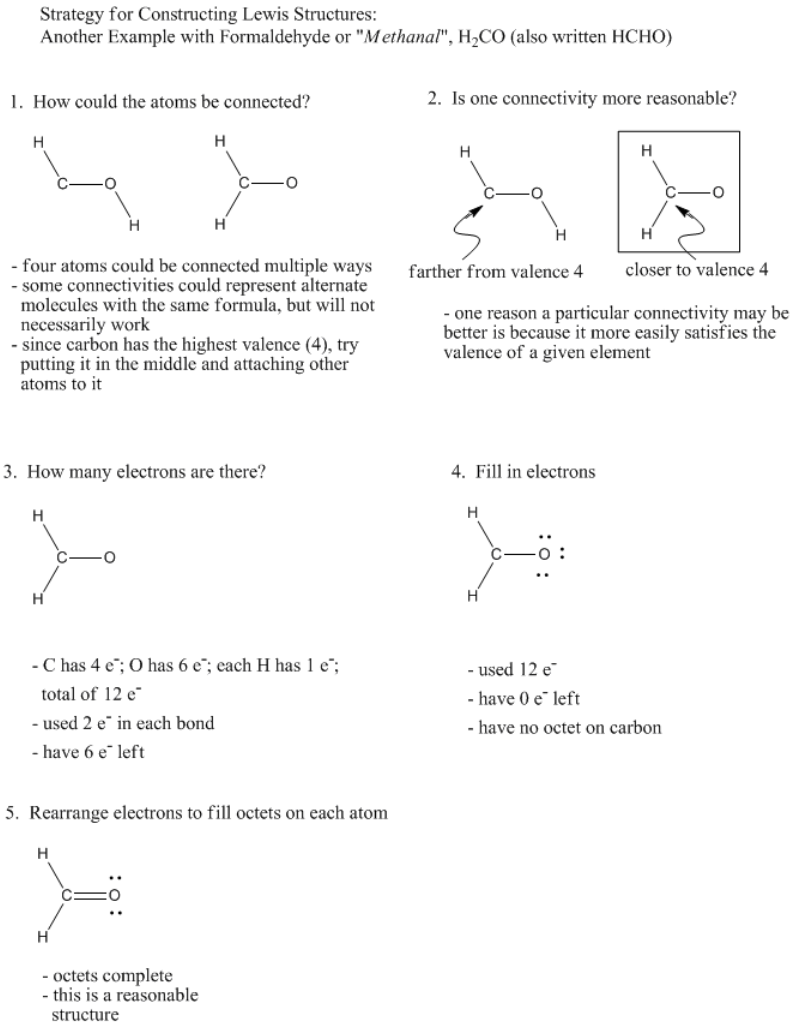


Figure 4.4.6: A set of instructions for constructing a Lewis structure.

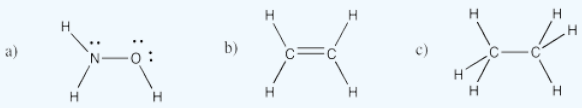
Steps for constructing lewis structures with formaldehyde as an example. Step 1: Connect the atoms. Since carbon has the highest valence of four, try putting it in the middle and attaching other atoms to it. Step 2: Is one connectivity more reasonable? One particular connectivity may be better because it more easily satisfies the valence of a given element. Step 3: Count how many electrons are used and how many are left over. Step 4: Fill in remaining electrons. Step 5: Rearrange electrons to fill octets on each atom.

Exercise 4.4.1

Use the idea of valence to construct Lewis structures of the following compounds:

a) hydroxylamine, H_3NO b) ethene, C_2H_4 c) ethane, C_2H_6

Answer



Exercise 4.4.2

Elements in the third row of the periodic table often behave similarly to elements in the second row. Use the idea of valence to construct Lewis structures of the following compounds:

a) PH_3 b) CS_2 c) SiH_4 d) PCl_3

Answer

Sometimes there will be more than one "correct" way to draw a Lewis structure for a given set of atoms. As an example, there are two different structures in nature with the formula C_2H_6O. These compounds, methyl ether and ethanol, are called *isomers*, meaning they are formed from the same (*iso*) things (*mer*).

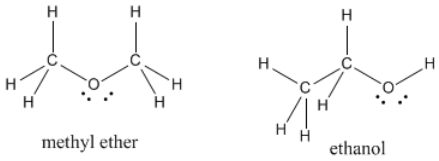


Figure 4.4.1:

To help distinguish between isomers, formulae are sometimes written with structural abbreviations. Instead of writing C_2H_6O for both these compounds, we would write CH_3OCH_3 for methyl ether, suggesting the first carbon is connected to three hydrogens and an oxygen, the oxygen is connected to the second carbon, and the second carbon is connected to another three hydrogens.

In a similar way, ethanol would be abbreviated as CH_3CH_2OH.

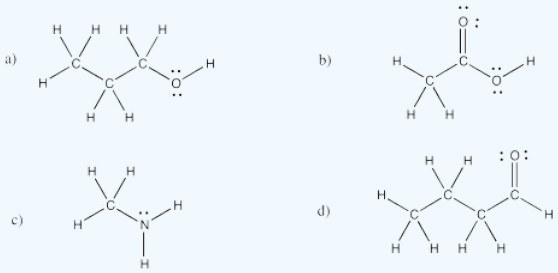
Exercise 4.4.3

Draw Lewis or Kekule structures for the following compounds:

a) propanol, $CH_3CH_2CH_2OH$ b) acetic acid (or ethanoic acid), CH_3CO_2H

c) methylamine, CH_3NH_2 d) butanal, $CH_3CH_2CH_2CHO$

Answer

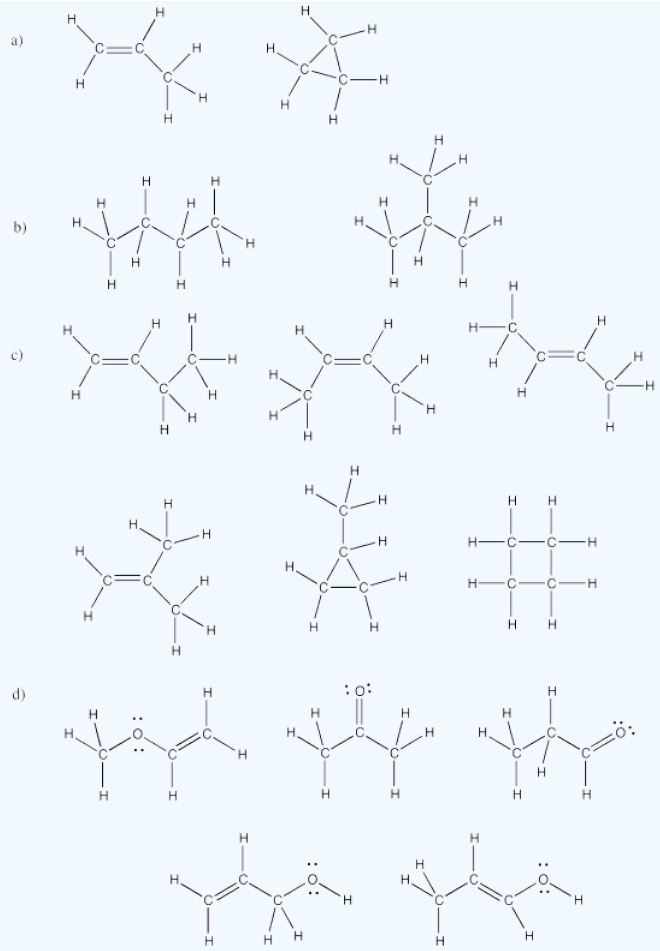


Exercise 4.4.4

Draw at least two isomers for each of the following formulae:

a) C_3H_6 b) C_4H_{10} c) C_4H_8 d) C_3H_6O

Answer



Sometimes, the decision about connectivity involves additional factors, other than valence. Here is a more detailed set of instructions:

Steps for Guessing Connectivity

IF the connectivity is not provided and you need to draw a Lewis Structure,

A. The first atom listed in the formula is often in the middle of the structure.

B. Most simple structures, especially for inorganic species, have an atom in the middle with several atoms connected to and branching out from this central one (as opposed to a linear chain of atoms). Thus, choose the middle atom to be

1. The atom in the lowest row of the periodic table (most likely to be able to use d orbitals to form more than 2 bonds as needed for "branching" structures)

2. The atom more in the center of the periodic table (group 4, then 3 or 5, etc) -has highest valence (valence=number of bonds formed)

3. The least EN atom is often in the middle.

C. Many simple structures are symmetric. This is not a law of nature but a simple observation!

X-M-X often favored over X-X-M

D. Oxyacids often have H's on O's; for example, $HClO_4$ has the connectivity H-O-ClO_3. The chlorine is attached to four different oxygen atoms, but one oxygen atom is also attached to a hydrogen.

E. Avoid three and four membered rings--they are not common, especially among inorganic species.

F. Avoid bonds between electronegative atoms (F-F, O-O, O-F, etc) . Such bonds are weak and tend to make molecules unstable, if not non-existent. Obviously the situation cannot be avoided in molecules like O_2, OF_2, F_2, etc.

Exercise 4.4.5

Provide structures for the following compounds. Remember to think about common valences.

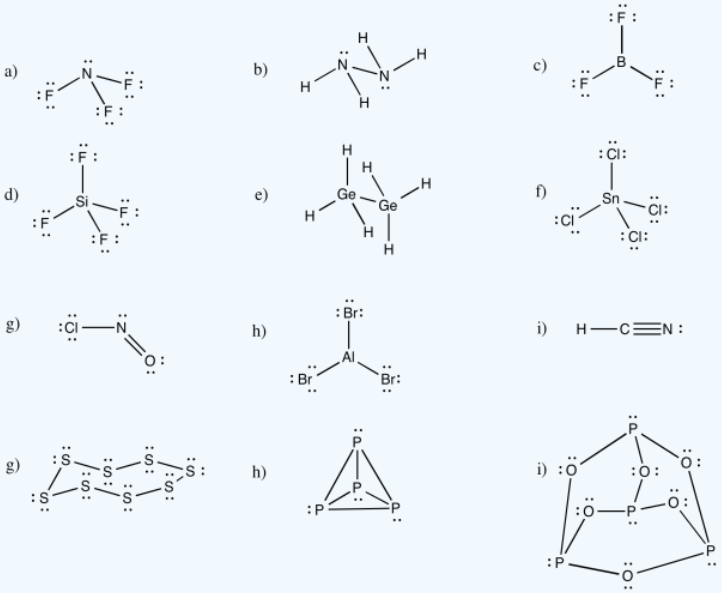
a) NF_3 b) N_2H_4 c) BF_3

d) SiF_4 e) Ge_2H_6 f) $SnCl_4$

g) ClNO h) $AlBr_3$ i) HCN

j) S_8 k) P_4 l) P_4O_6

Answer



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4.5: Lewis and Formal Charge

Looking at the structure of a molecule can help us to understand or to predict the behavior of that compound. One of the tools that we will eventually use to understand reactivity is formal charge. That is because reactivity has to do with the reorganization of electrons between atoms. New chemical bonds are formed by sharing electrons. Old chemical bonds are broken when one atom takes the bonding electrons away from another atom.

- chemical reactions occur via attraction and donation of electrons

Formal charge can help us to understand the behavior of carbon monoxide, CO. When exposed to transition metal cations such as the iron in hemoglobin (Fe2+), the carbon is attracted to and binds to the metal. In the case of hemoglobin, because the carbon monoxide binds very strongly to the iron, the CO blocks the position where oxygen would normally be bound and carbon monoxide poisoning results.

- formal charge can help us predict how a molecule behaves
- atoms with positive formal charges often attract electrons
- atoms with negative formal charges often donate electrons

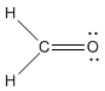
Why does the molecule behave in this way? There are actually a number of reasons. However, the fact that the carbon is attracted to a metal cation begs the question: Is the carbon an anion? Yes, in a sense. In a Lewis structure of the compound, the carbon has a formal negative charge. You will see why below.

Formal charges are an important book-keeping device that we use in Lewis structures. They tell us if one atom is donating extra electrons to another to give it an octet. If an atom needs to donate more electrons than normal in order for everyone to get an octet, it will have a positive formal charge. If an atom donates fewer electrons than normal and everyone still has an octet, it must be getting extra electrons from somewhere else. It will have a negative formal charge.

- formal charge is often present if the atom does not have its usual number of bonds
- valence rules can act as flags to alert you that formal charges are present

To help us think about formal charges, let's look at a few small molecules that all contain carbon-oxygen multiple bonds but that are slightly different from each other. Formaldehyde (CH_2O) is a chemical that is used to preserve tissues; you may be familiar with its odour from anatomy lab. Carbon monoxide results from burning fossil fuels; it is also an important industrial chemical used in manufacturing detergents. Carbonate is an anion that is found in many forms. Calcium carbonate is found in limestone and chalk, for instance.

Look at the structure of formaldehyde. Oxygen has a normal valence of two, and it has two bonds in formaldehyde, so there is no formal charge on the oxygen. Carbon has a normal valence of four, and it has four bonds here. There is no formal charge on carbon. There are no formal charges on the hydrogens either.



Carbon monoxide has a structure that is very similar to formaldehyde. It does not have any hydrogens, though. With ten electrons total, the only way to get an octet on both atoms is to make three bonds between carbon and oxygen.

Oxygen has normal valence two, but here it is making three bonds. It is sharing an extra pair of its electrons with carbon to make that third bond. If it is sharing a pair of electrons, we can think of it keeping one for itself and giving the other to carbon. Since it gives one of its electrons to carbon, it has formal charge +1.

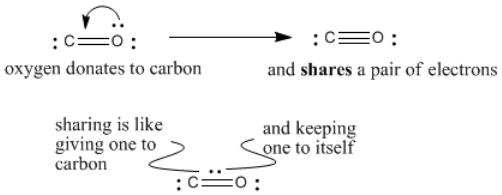


Diagram of how each bond in carbon monoxide is like oxygen keeping one electron of a lone pair and donating one electron to carbon.

Carbon has normal valence four, but here it is only making three bonds, even though it has an octet. How did it get an octet with only three bonds? It got an extra electron from somewhere (the oxygen). It has formal charge -1.

Structural formula of carbon monoxide with three bonds and one lone pair on both carbon and oxygen. Carbon has a negative formal charge and oxygen has a positive formal charge.

Notice that overall the carbon monoxide molecule is neutral. Oxygen has a plus charge and carbon has a minus charge. These charges cancel to give an overall neutral molecule.

What we are really doing when we assign formal charge is comparing how many electrons the atom brought with it from the periodic table to how many it has now. If the atom brought four electrons of its own and it is now sharing eight, things are even. It brought four to share and got four from its neighbors in an even trade. If it only brought three of its own and is now sharing eight, it got more electrons than it gave, and it will have a negative charge.

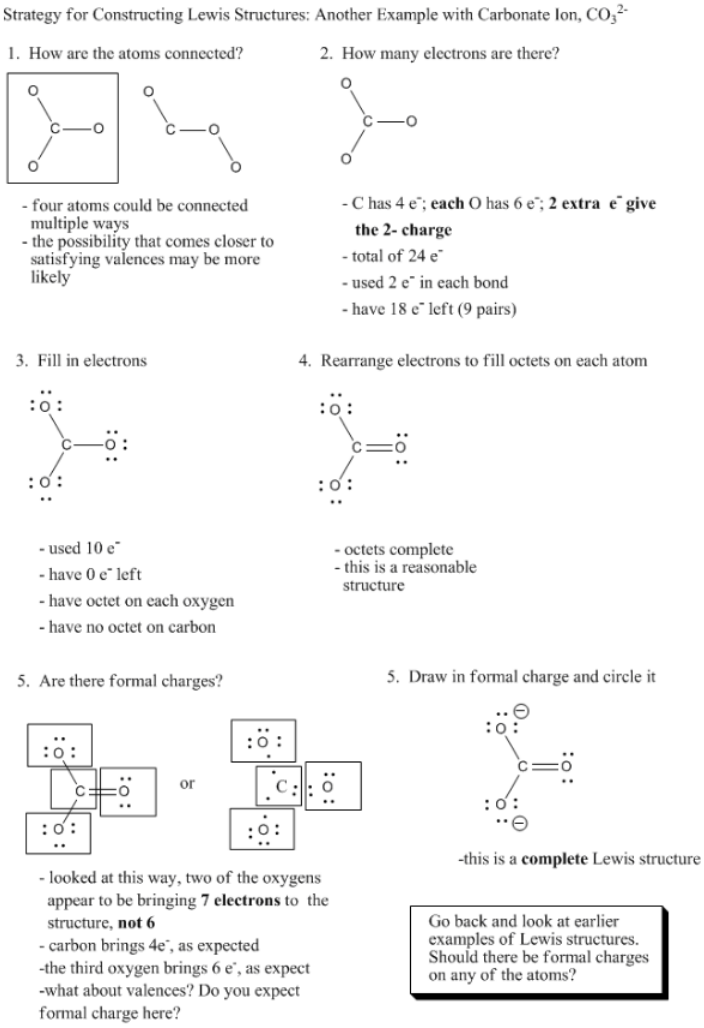
To determine formal charge:

- check the number of electrons on the atom in the periodic table
- check the number of electrons entirely owned by the atom in the molecule; *this is different than looking for an octet*
- "entirely owned" electrons include any electrons in lone pairs, since they belong completely to one atom
- "entirely owned" electrons also include half of the electrons in the bonds to the atom, since it is sharing each of those pairs with other atoms.

Compare the number of entirely owned valence electrons in the periodic table to those entirely owned by the atom in the molecule.

- if the number of entirely owned electrons on the atom in the molecule is higher than in the periodic table, the atom has a negative charge
- if the number of entirely owned electrons on the atom in the molecule is lower than in the periodic table, the atom has a positive charge
- the formal charge is additive: if the atom has two extra electrons in the molecule, it has a two minus charge. If it is two short, it has a two plus charge.

Remember, electron counting to determine an octet counts all of the bonding and nonbonding electrons equally. It is done simply to determine whether the atom has a noble gas configuration right now. Electron counting to determine formal charge is done to keep track of who has given electrons to whom when making the molecule. If, in getting to an octet, atoms have received more electrons than they have given, their electron/proton ratio has changed, and they become charged.



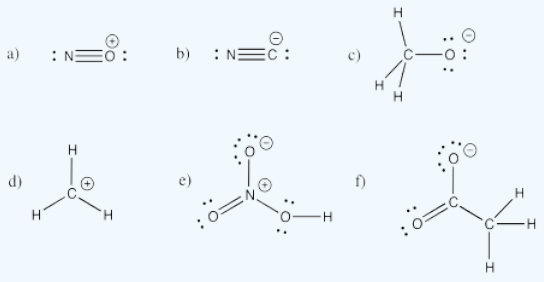
Instructions for drawing Lewis structures, with carbonate ion as an example. Step 1: Connect the atoms together. The arrangement with carbon at the center comes closest to satisfying valences. Step 2: Count up the total electrons. In carbonate, there are twenty-four total electrons, with six used in the initial connections. Step 3: Fill in electrons. No electrons remain after adding lone pairs. Step 4: Rearrange electrons to fill octets, giving carbon one double bond to an oxygen. Step 5: Calculate formal charges and draw them in.

? Exercise 4.5.1

Draw Lewis or Kekule structures for the following molecules, remembering to include formal charges, if any (and notice that some of these molecules are ions):

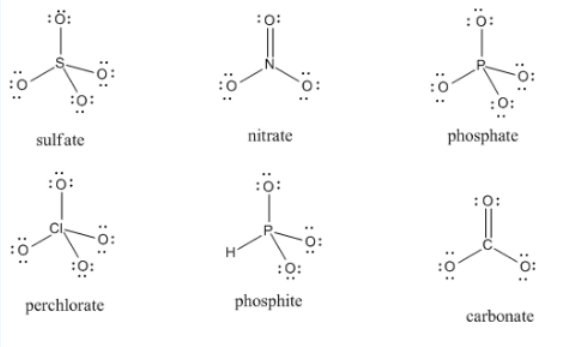
a) NO^+ b) CN^- c) CH_3O^- d) CH_3^+ e) HNO_3 f) $CH_3CO_2^-$

Answer



Exercise 4.5.2

Given the structures below, assign any missing formal charges.



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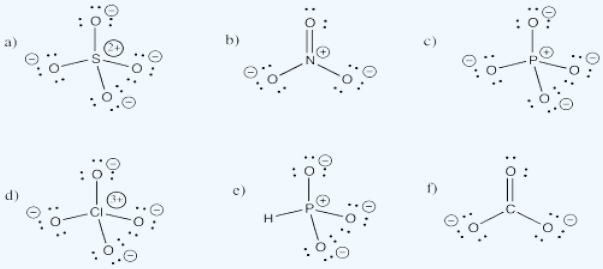
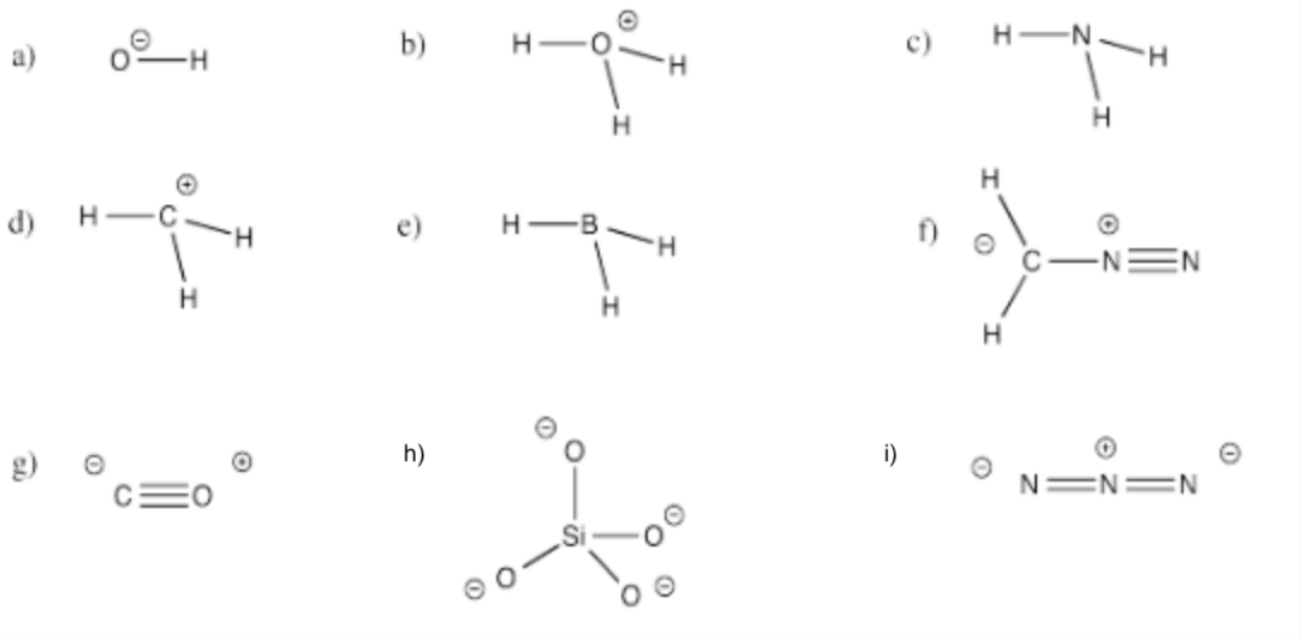


AnswerExercise 4.5.2. From left to right, top to bottom: structural formulas for sulfate, nitrate, phosphate, perchlorate, phosphite, and carbonate.

Exercise 4.5.3

Given the structures below, draw in the missing electrons, if any.



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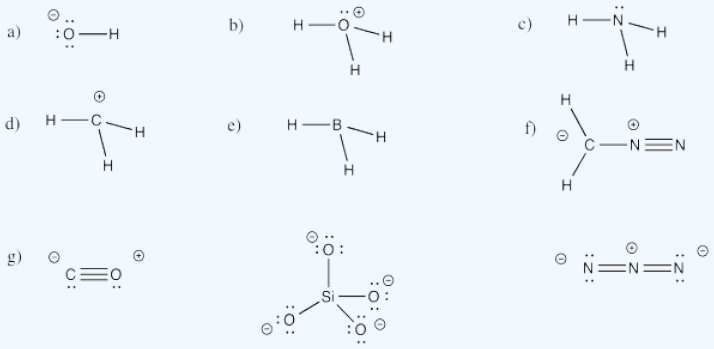

Answer

Exercise 4.5.4

Label all atoms in the following compounds with the correct non-zero formal charge.

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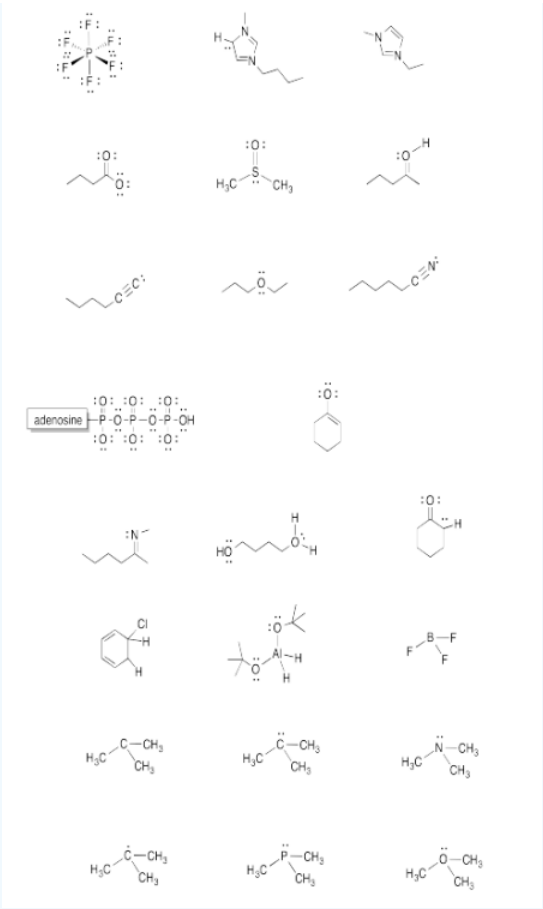

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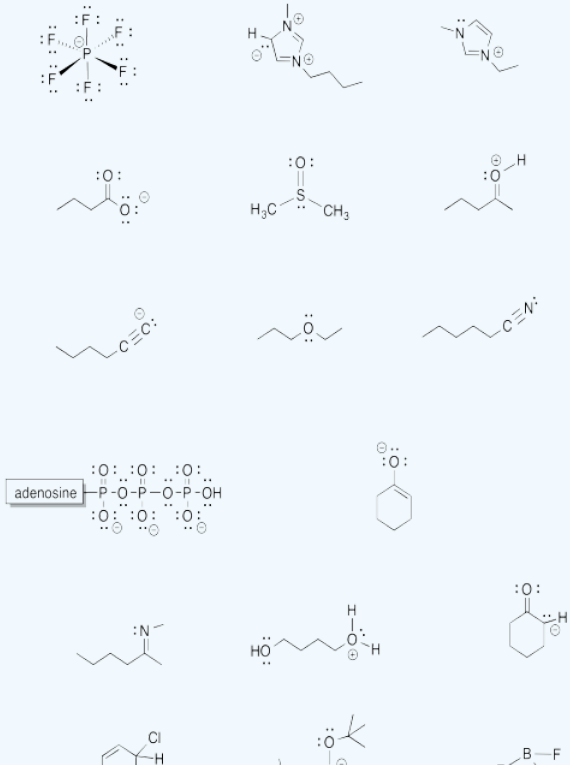

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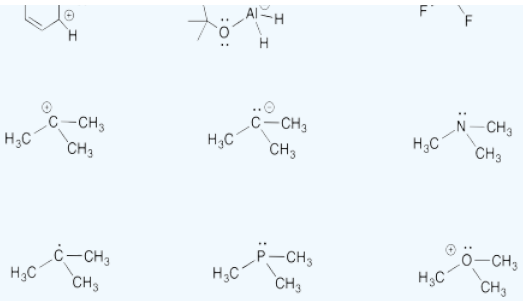

Answer

Exercise 4.5.5

Provide structures for the following oxoanions (anions with oxygens attached to another atom) of chlorine:

a) hypochlorite, ClO^- b) chlorite, ClO_2^- c) chlorate, ClO_3^- d) perchlorate, ClO_4

Exercise 4.5.6

Provide structures for the following oxoanions of sulfur:

a) sulfite, SO_3^{2-} b) sulfate, SO_4^{2-} c) thiosulfate, $S_2O_3^{2-}$

d) disulfate, $S_2O_7^{2-}$ e) persulfate or peroxomonosulfate, SO_5^{2-}

Exercise 4.5.7

Provide structures for the following oxoanions of phosphorus:

a) phosphate, PO_4^{3-} b) phosphite, HPO_3^{2-} c) hypophosphite, $H_2PO_2^-$

Note that hydrogen atoms in some phosphorus oxoanions are attached to the phosphorus atom.

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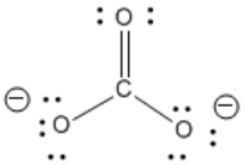
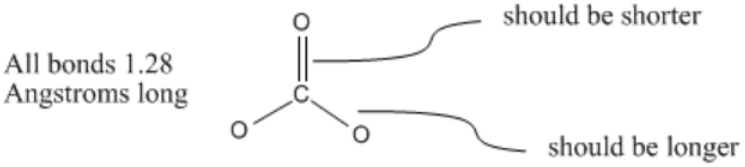
4.6: The Need for Resonance Structures

The carbonate anion shown below has one double bond and two single bonds. Normally, the number of bonds between two atoms in the Lewis structure can tell you how closely the two atoms are held. That means there is one C-O bond in the molecule that is shorter than the other two.



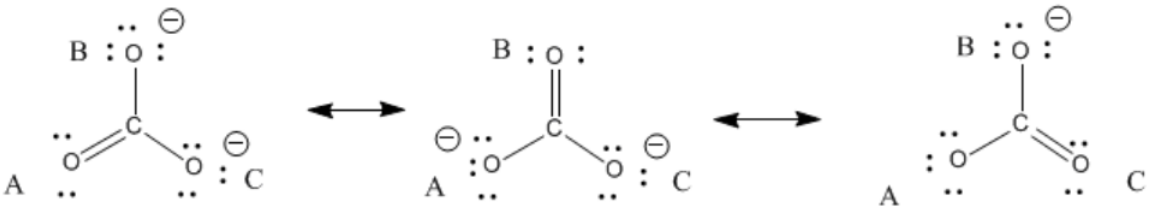
However, carbonate ion is an exception to the rule. In fact, carbonate ion is a symmetric, trigonal planar molecule. All three carbon-oxygen bond distances are about 1.28 Angstroms long.



A diagram of carbonate anion, showing that all bonds are 1.28 Ångstroms long when the double bond should be shorter than the single bonds.

You cannot draw a Lewis structure that would suggest all three bonds are the same length. Instead, you can use resonance structures to understand this fact. Resonance structures are just alternate Lewis structures that take into account different possible arrangements of lone pairs and multiple bonds for a given skeletal structure. In carbonate, there are three ways to arrange these extra electrons.

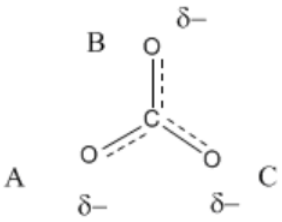
If you label the oxygen atoms A, B and C, as shown below, then A has a double bond in 1/3 of the structures you could draw, but it would have a single bond in the other 2/3 of the ways in which you could draw the structure. The same is true for the atoms B and C.



Resonance of electrons across atoms in the carbonate anion, placing the double bond in a new position across three different structures.

In fact, carbonate really has about 1-1/3 bonds between each carbon and oxygen. Furthermore, there is not a full negative charge on any of the oxygens but about two-thirds of a negative charge on each of the three oxygens.

Occasionally we might draw a structure that shows partial bonds between atoms as dashed lines to suggest, in this case, 1-1/3 bonds instead of either one bond or two. We might also write $\delta-$ ("delta minus") to denote a partial negative charge.



The limitation of this type of drawing is that it fails to show us exactly how many electrons we are dealing with. Later in the course, it will be very important to keep track of all the electrons in molecules as they undergo chemical reactions. Consequently, we almost always draw out different possible Lewis structures and keep in mind that the structure is something like a combination of all of them.

When we have structures that differ only in the way their electrons are arranged, but have exactly the same connectivity between the atoms, we refer to the set of structures as *resonance structures*. The double ended arrows between the resonance structures is the symbol we use to say that we have two or more different ways of drawing the same structure, and that we need to take all of the structures into account to understand how the molecule really behaves.

There is a subtlety here. The compound is not one structure or the other, and it is not an equilibrium where the structure changes back and forth rapidly. It is a superposition, in which a single molecule can behave like all three structures at the same time.

? Exercise 4.6.1

Draw sets of resonance structures for the following compounds.

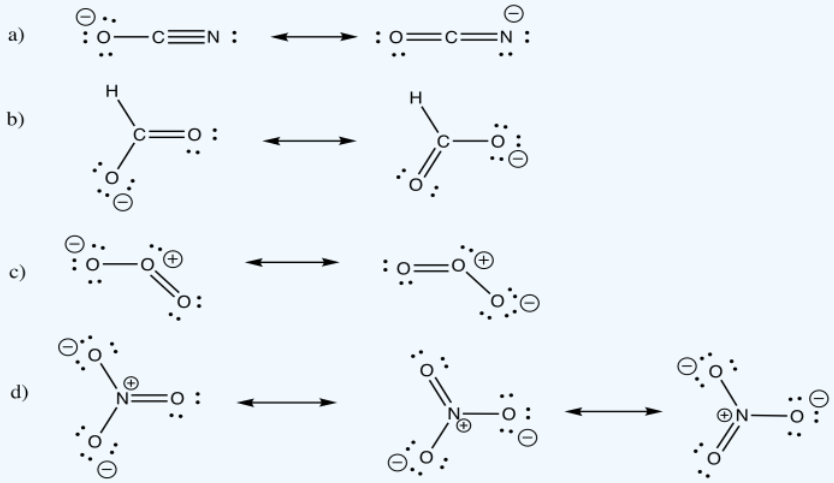
a) cyanate ion, NCO^- (a linear structure) e) azide ion, NNN^-

b) formate ion, HCO_2^- f) diazomethane, CH_2NN

c) ozone, O_3 (a bent or "boomerang" structure) g) enolate ion, CH_2CHO^-

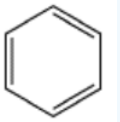
d) nitrate ion, NO_3^-

Answer



? Exercise 4.6.2

All of the bonds in benzene (below) are the same bond distance (1.39 A). Show why this is true.



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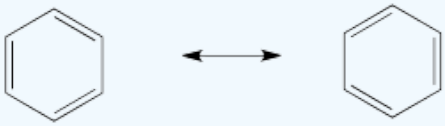
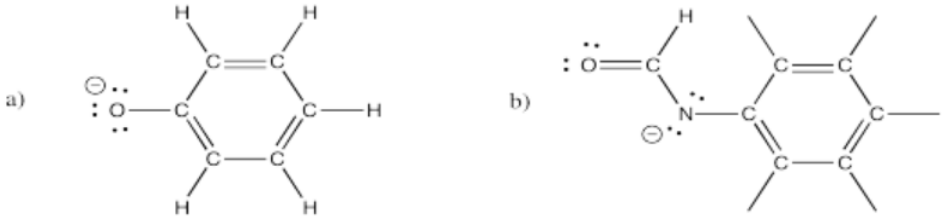


Answer

Exercise 4.6.3

There are several resonance structures for each of the following ions. Show at least three for each.



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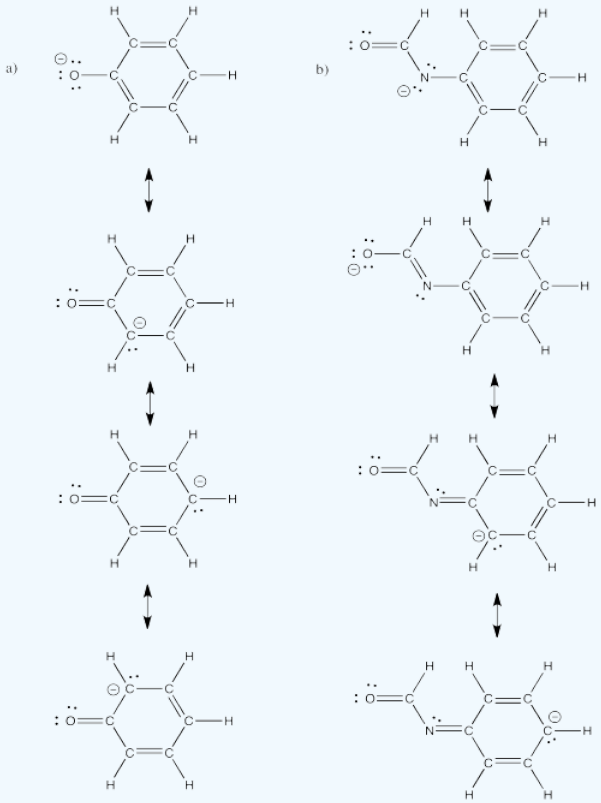
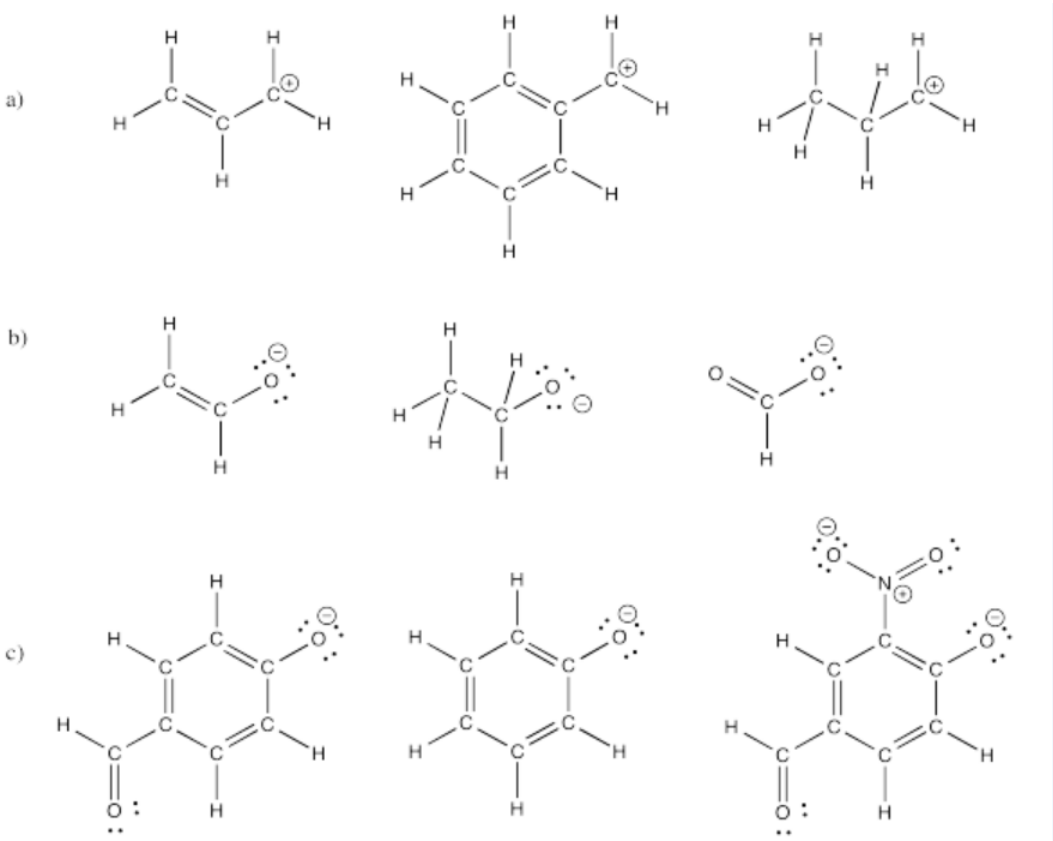


Answer

Exercise 4.6.4

Problem IM6.4.

Ions can be greatly stabilized by delocalization. That is, if a charge can be spread out over several atoms by resonance, the charge is more stable. Use this idea to predict the relative stabilities of the following ions (rank them from most stable to least stable).



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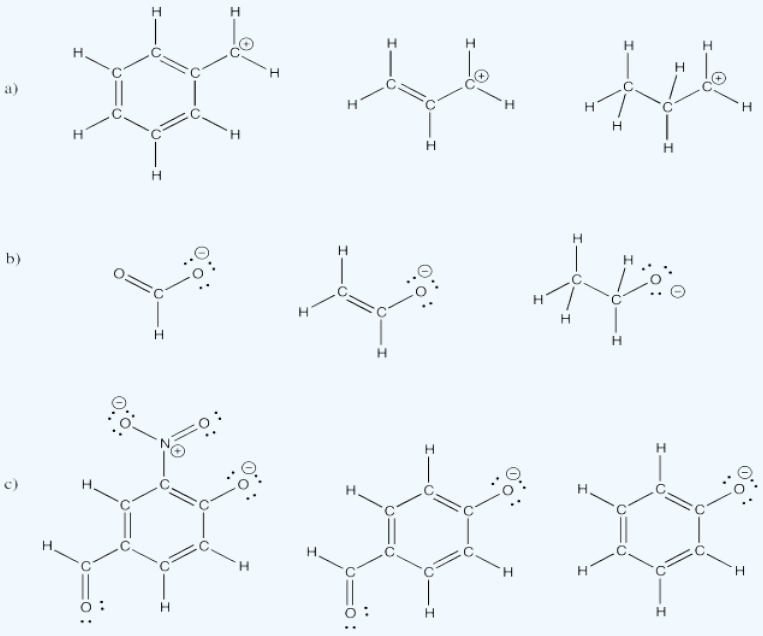

Answer

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Exercise 4.6.5

Draw resonance structures for the following molecules.

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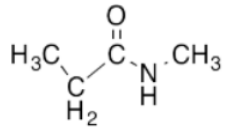
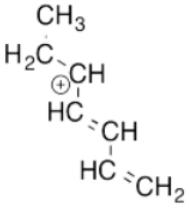
A.



B.



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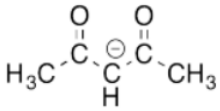

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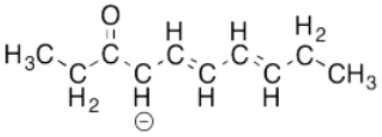
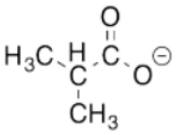
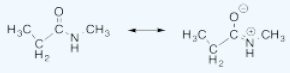


E.

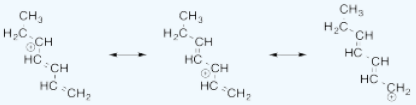


Answer

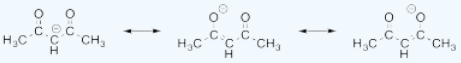
A.



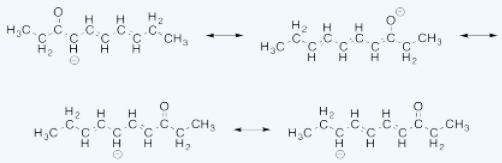
B.



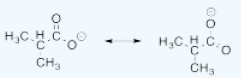
C.



D.



E.



Answer

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4.7: Which Bonds are Ionic and Which are Covalent?

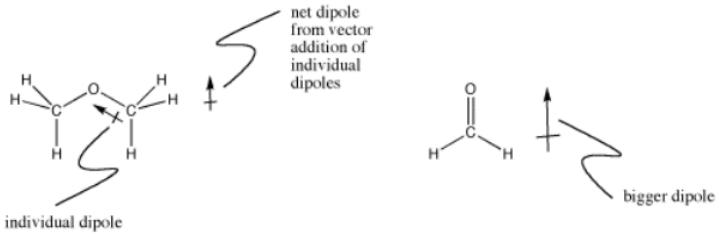
Cells contain lots of water. One of the roles of the water is to dissolve different materials. For example, there are many different ionic compounds (salts) in cells. Ions are used to maintain cell potentials and are important in cell signaling and muscle contraction.

How can you tell if a compound is ionic or covalent?

There is not a simple answer to this question. Many bonds are somewhere in between. In a polar covalent bond, a pair of electrons is shared between two atoms in order to fulfill their octets, but the electrons lie closer to one end of the bond than the other. There is more negative charge toward one end of the bond, and that leaves more positive charge at the other end.

Looking at the electronegativity values of different atoms helps us to decide how evenly a pair of electrons in a bond is shared. Electronegativity increases toward the upper right hand corner of the periodic table because of a combination of nuclear charge and shielding factors. Atoms in the upper right hand corner of the periodic table have a greater pull on their shared bonding electrons, while those in the lower left hand corner have a weaker attraction for the electrons in covalent bonds.

In a carbon-oxygen bond, more electrons would be attracted to the oxygen because it is to the right of carbon in its row in the periodic table. Compounds like , dimethyl ether, CH_3OCH_3, are a little bit polar. Formaldehyde, CH_2O, is even more polar. Electrons in pi bonds are held more loosely than electrons in sigma bonds, for reasons involving quantum mechanics. That allows the oxygen to pull the electrons toward it more easily in a multiple bond than in a sigma bond.

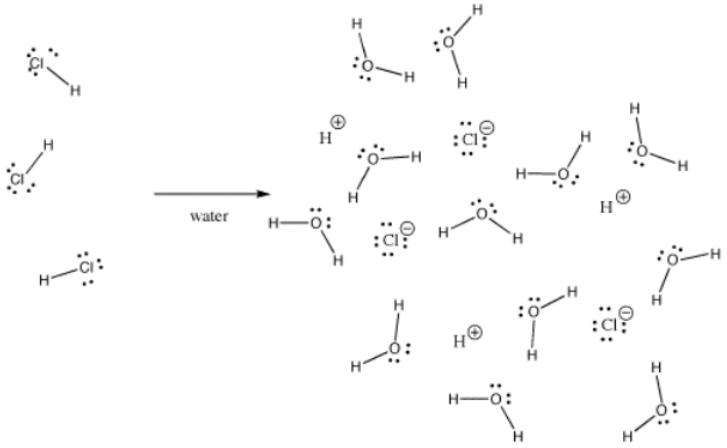


Left: net dipole and individual dipole in dimethyl ether. Right: net dipole of formaldehyde, larger in size than that of dimethyl ether.

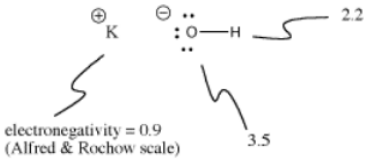
Not all polarities are easy to determine by glancing at the periodic table. The direction of the dipole in a boron-hydrogen bond would be difficult to predict without looking up the electronegativity values, since boron is further to the right but hydrogen is higher up. As it turns out, the hydrogen is slightly negative.

A bond is ionic if the electronegativity difference between the atoms is great enough that one atom could pull an electron completely away from the other one. That situation is common in compounds that combine elements from the left-hand edge of the periodic table (sodium, potassium, calcium, etc.) with elements in the extreme upper right hand corner of the periodic table (most commonly oxygen, fluorine, chlorine). Sodium chloride is an ionic compound.

Many bonds can be covalent in one situation and ionic in another. For instance, hydrogen chloride, HCl, is a gas in which the hydrogen and chlorine are covalently bound, but if HCl is bubbled into water, it ionizes completely to give the H+ and Cl- of a hydrochloric acid solution. Even in gaseous HCl, the charge is not distributed evenly. The chlorine is partially negative and the hydrogen is partially positive.



Potassium hydroxide, KOH, contains one bond that is covalent (O-H) and one that is ionic (K-O). Hydrogen is tricky because it is at the top of the periodic table as well as the left side. It is just electropositive enough to form ionic bonds in some cases. It is just electronegative enough to form covalent bonds in other cases.



Ions of potassium hydroxide. Potassium has electronegativity of 0.9; oxygen has electronegativity of 3.5; hydrogen has electronegativity of 2.2.

In KOH, the K-O bond is ionic because the difference in electronegativity between potassium and oxygen is large. The difference in electronegativity between oxygen and hydrogen is not small. An O-H bond can sometimes ionize, but not in all cases.

Sometimes ionization depends on what else is going on within a molecule. Because the K-O bond in potassium hydroxide is ionic, the O-H bond is not very likely to ionize. There is already a negative charge on oxygen. Charge separation costs energy, so it is more difficult to put a second negative charge on the oxygen by ionizing the O-H bond as well. Frequently first ionizations in molecules are much easier than second ionizations.

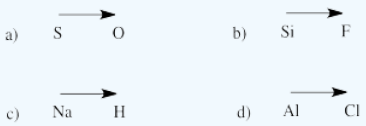
Exercise 4.7.1

Predict the direction of polarity in a bond between the atoms in the following pairs:

a) sulfur-oxygen b) silicon-fluorine

c) hydrogen-sodium d) chlorine-aluminum

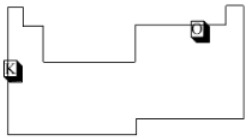
Answer



Because it is so common that an element from the extreme left hand of the periodic table is present as a cation, and that elements on the extreme right carry negative charge, we can often assume that a compound containing an example of each will have at least one ionic bond.

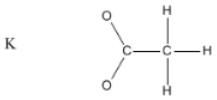
Strategy for Constructing Lewis Structures: Another Example with Potassium Acetate, CH_3CO_2K

1. Is this an ionic compound?



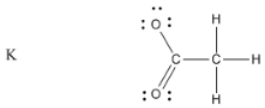
-potassium is from the far left edge of the periodic table
-oxygen is from the top right corner
-together in one compound, these two elements may form an ionic bond

2. What is the comnnectivity?



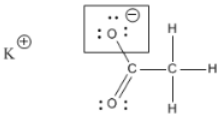
-treat potassium as a separate cation.
- the abbreviated formula suggests one carbon has 3 H connected while the other has 2O

3. Fill in electrons



- K has no e⁻ left (gave away to become cation)
- each C: 4 e⁻; each O: 6e⁻; each H:1 e⁻; negative charge: 1 e⁻; total 24 e⁻
- used 12 e⁻ in bonds
- have 12 e⁻ left (6 pairs)
- sharing one pair allows all atoms to have octet

5. Are there formal charges?

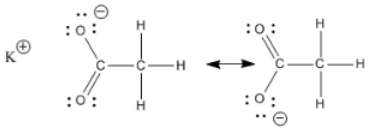


- K has one e⁻ in the periodic table but none here; it has a plus charge
- one O has 6 e⁻ in the periodic table but appears to be bringing 7 e⁻ here

or

- one of the oxygens has an octet, but one bond less than its valence
- it has one electron to itself that it normally shares
- it has a negative charge

5. Are there other important resonance structures?



-there is probably not one short C=O double bond and one long C-O single bond
-it is somewhere in between

Exercise 4.7.2

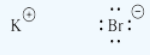
Draw structures of the following compounds. Each one contains at least one anion and cation.

a) KBr b) LiOH c) KNO_3 d) $MgSO_4$ e) Na_3PO_4 f) Na_2SO_3

g) $LiClO_4$ h) $NaClO_3$ i) KNO_2 j) $Ca(ClO_2)_2$ k) Ca_2SiO_4 l) Na_3PO_3

m) NaOCl n) Mg_2SnO_4

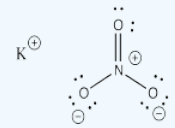
Answer

a) 

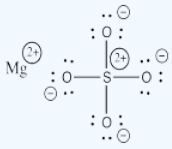
potassium bromide

b)

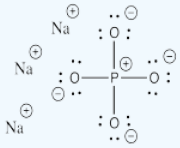
lithium hydroxide

c) 

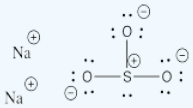
potassium nitrate

d) 

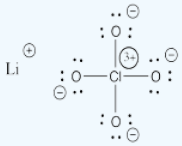
magnesium sulfate

e) 

sodium phosphate

f) 

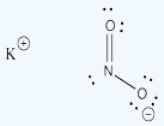
sodium sulfite

g) 

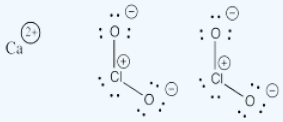
lithium perchlorate

h)

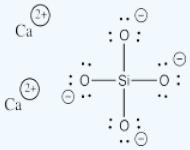
sodium chlorate

i) 

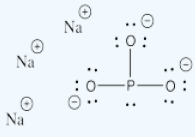
potassium nitrite

j) 

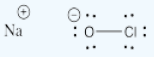
sodium chlorite

k) 

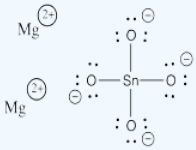
calcium orthosilicate

l) 

sodium phosphite

m) 

sodium hypochlorite

n) 

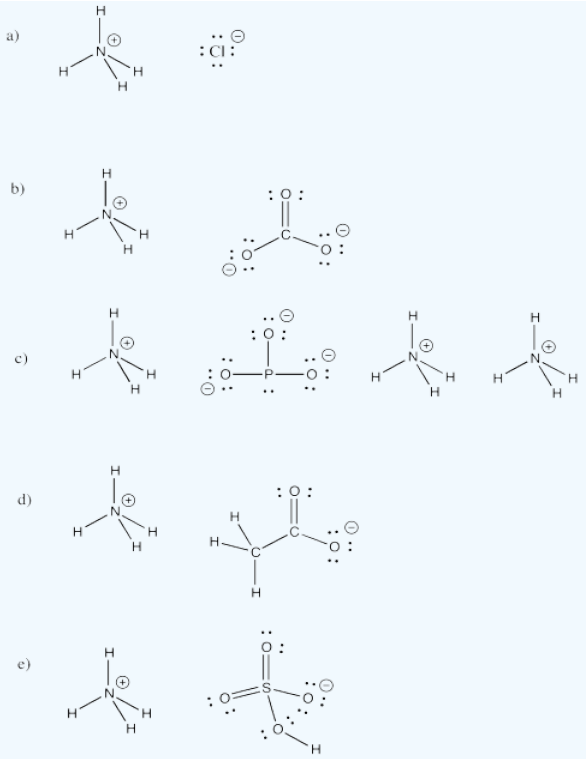
calcium orthosilicate

? Exercise 4.7.3

Ammonium ion, NH_4^+, is a common molecular ion. Draw structures for the following compounds that include this ion.

a) NH_4Cl b) $(NH_4)_2CO_3$ c) $(NH_4)_3PO_3$ d) $NH_4CH_3CO_2$ e) NH_4HSO_4

Answer



Exercise 4.7.4

Many anions have names that tell you something about their structure.

Table with Anions names

prefix- or -suffix	common meaning	example name	example formula
-ide	atom is present as anion	chloride	Cl^-
-ate	atom is present as an oxyanion; usually a common form	chlorate	ClO_3^-
-ite	atom is present as an oxyanion, but with fewer oxygens (or lower "oxidation state") than another common form	chlorite	ClO_2^-
per-	atom is present as an oxyanion, but with even more oxygens than the "-ate" form	perchlorate	ClO_4^-
hypo-	atom is present as an oxyanion, but with even fewer oxygens than the "-ite" form	hypochlorite	ClO^-

Using the table as a guide, propose names for the following anions:

a) Br^- b) O^{2-} c) F^- d) CO_3^{2-} (common oxyanion) e) NO_3^- (common oxyanion) f) NO_2^-

g) S^{2-} h) SO_4^{2-} (common oxanin) i) SO_3^{2-} j) SO_5^{2-} k) C^{4-} l) N^{3-} m) As^{3-}

n) PO_4^{3-} (common oxyanion) o) PO_3^{3-} p) I^- q) IO_3^- (common oxyanion) r) IO_4^-

Answer a

bromide

Answer b

oxide

Answer c

fluoride

Answer d

carbonate

Answer e

nitrate

Answer f

nitrite

Answer g

sulfide

Answer h

sulfate

Answer i

sulfite

Answer j

persulfate

Answer k

carbide

Answer l

nitride

Answer m

arsenide

Answer n

phosphate

Answer o

phosphite

Answer p

iodide

Answer q

iodate

Answer r

periodate

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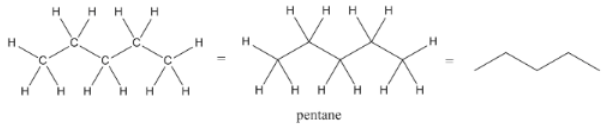
4.8: Line Drawings

Line drawings

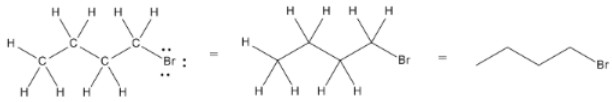
Lewis structures can tell us a lot about how atoms come together to make molecules. They can also be cumbersome, especially if we are dealing with very large molecules. Drawing a line instead of a pair of dots for bonding pairs of electrons makes it easier to draw structures. There are other abbreviations that are helpful in some situations.

Because organic chemistry is based on the compounds of carbon, we would have to draw the letter C over and over again unless we had a shortcut. In line structures, we drop the label "C" for the carbon atoms. Anytime there is a joint between two bonds (drawn as a vertex in a zig-zag line), the atom attached to that bond is assumed to be a carbon unless written otherwise.



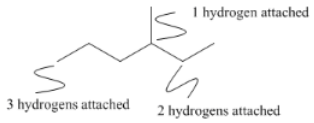
pentane

The atom at the end of a zig-zag line would also be a carbon, unless it is explicitly written as another atom.



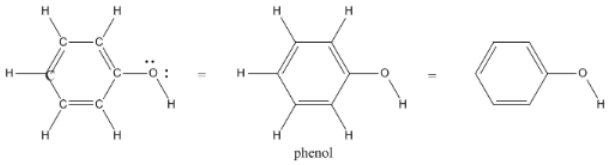
1-bromobutane

Taken even further, we will omit the hydrogens from our structures, since the compounds of carbon almost always contain hydrogen as well. Since we know carbon has a valence of four, we always know how many hydrogen atoms are attached to each carbon in order to reach that valence. A carbon with two bonds drawn in must have two hydrogens on it. A carbon with only one bond drawn to it must have three hydrogens.



Breakdown of a skeletal structure. Three hydrogens are attached to a terminal carbon. Two hydrogens are attached to a carbon surrounded by two other carbons. One hydrogen is attached to a carbon with bonds to three other carbons.

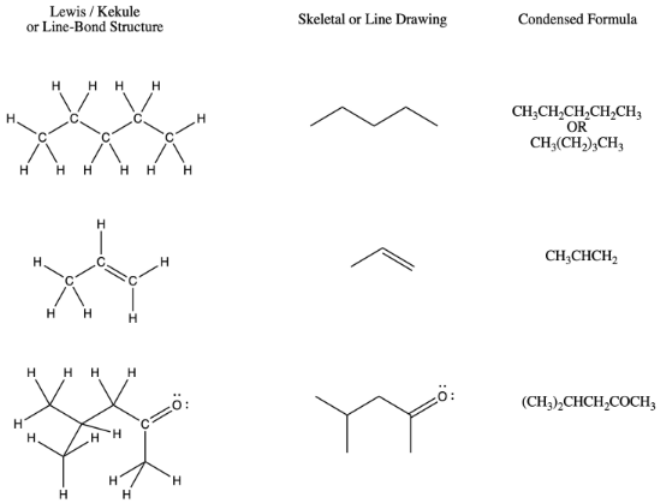
Note that the hydrogens are not normally omitted if they are attached to heteroatoms (atoms other than carbon, such as oxygen or nitrogen).



phenol

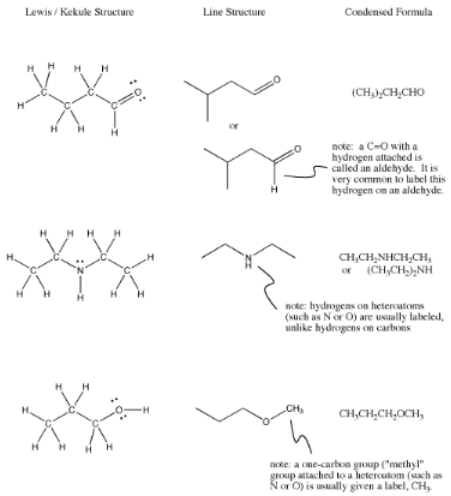
You will also note that lone pairs are frequently left out when we use line structures, so you will have to add them back in to think about Lewis structures. Adding the lone pairs back to the heteroatoms in line structures is a good habit to get into, because later in the course we will be very concerned with keeping track of where all the electrons are.

Below is a summary, showing the relationship between Lewis/Kekule structures, line structures and condensed formulae for a few different compounds.



Lewis structures, skeletal structures, and condensed formulas for pentane, propene, and 4-methyl-2-pentanone.

Remember, in phenol, the hydrogen attached to oxygen was labeled in the line structure. Sometimes there are exceptions in line structures, in which atoms that you might not think about labeling usually do get labels. The most common exceptions are shown below.



Lewis structures, line structures, and condensed formulas of 3-methylbutanal, diethyl amine, and 1-methoxypropane.

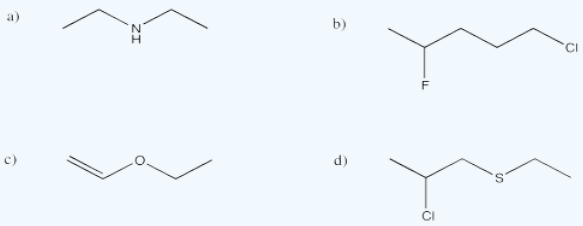
? Exercise 4.8.1

Translate the following condensed formulae into line drawings.

a) $CH_3CH_2NHCH_2CH_3$ b) $CH_3CHFCH_2CH_2CH_2Cl$

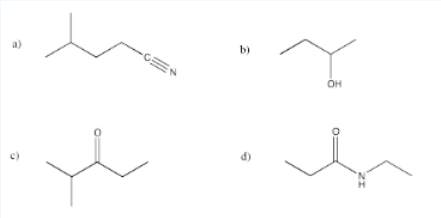
c) $CH_2CHOCH_2CH_3$ d) $CH_3CHClCH_2SCH_2CH_3$

Answer



Exercise 4.8.2

Translate the following structures into condensed formula.



Answer a

Answer b

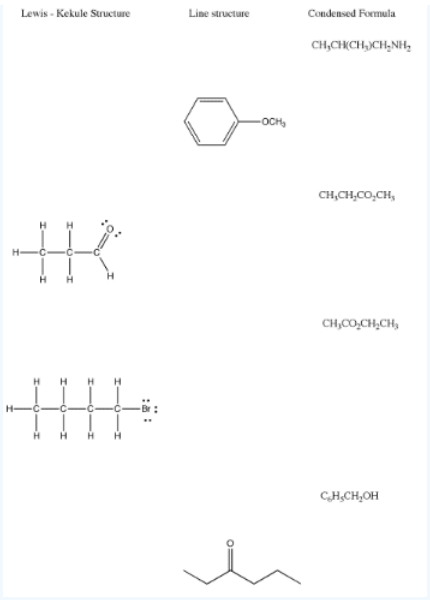
Answer c

Answer d

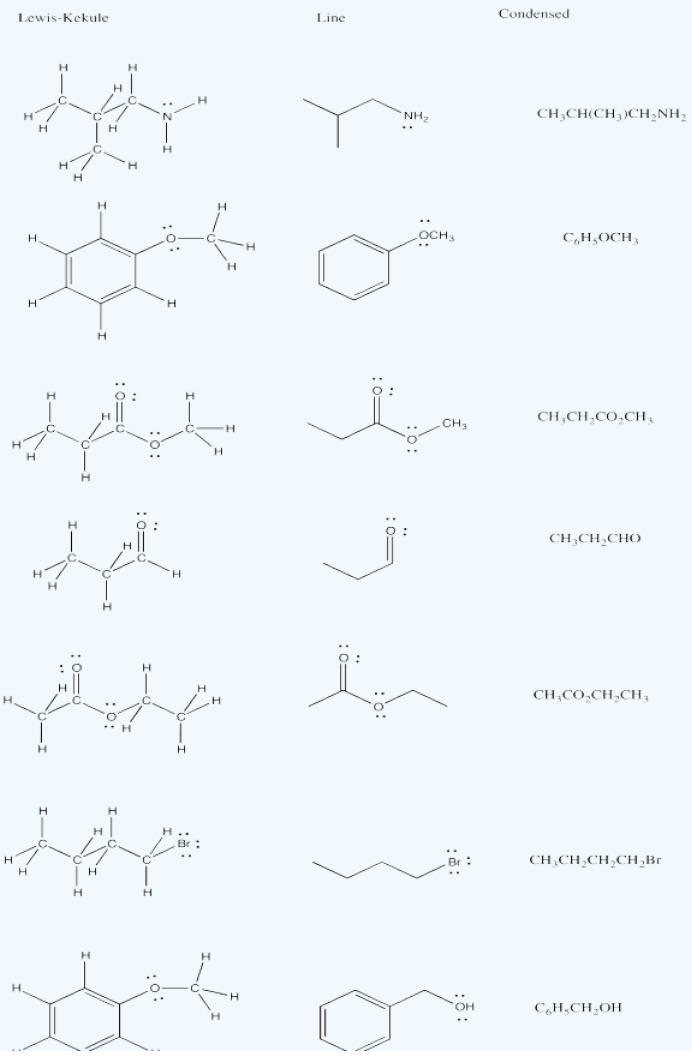
Answer a(CH3)2CHCH2CH2CNAnswer bCH3CH2CH(OH)CH3Answer c(CH3)2CHCOCH2CH3Answer dCH3CH2CONHCH2CH3

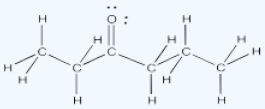
Exercise 4.8.3

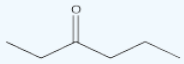
Try filling in the missing line drawing, Lewis / Kekule structures or condensed formulae in each line of the table below.


Lewis - Kekule Structure
Line structure
Condensed Formula
CH3CH(CH3)CH2NH2
OCH3
CH3CH2CO2CH3
CH3CO2CH2CH3
Br
C6H5CH2OH
O

Answer


Lewis-Kekule
Line
Condensed
CH3CH(CH3)CH2NH2
C6H5OCH3
CH3CH2CO2CH3
CH3CH2CHO
CH3CO2CH2CH3
CH3CH2CH2CH2Br
C6H5CH2OH





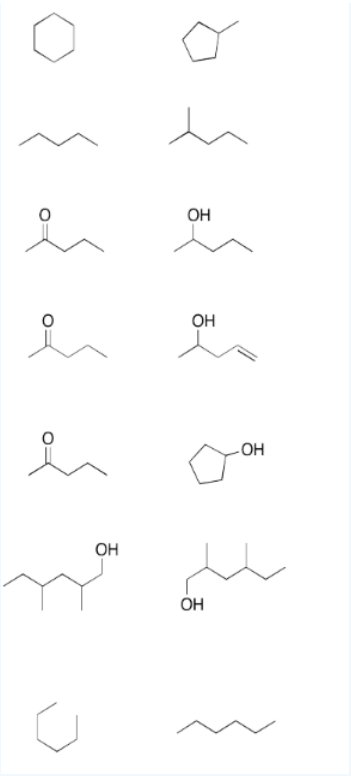
$CH_3CH_2COCH_2CH_2CH_3$

Answer

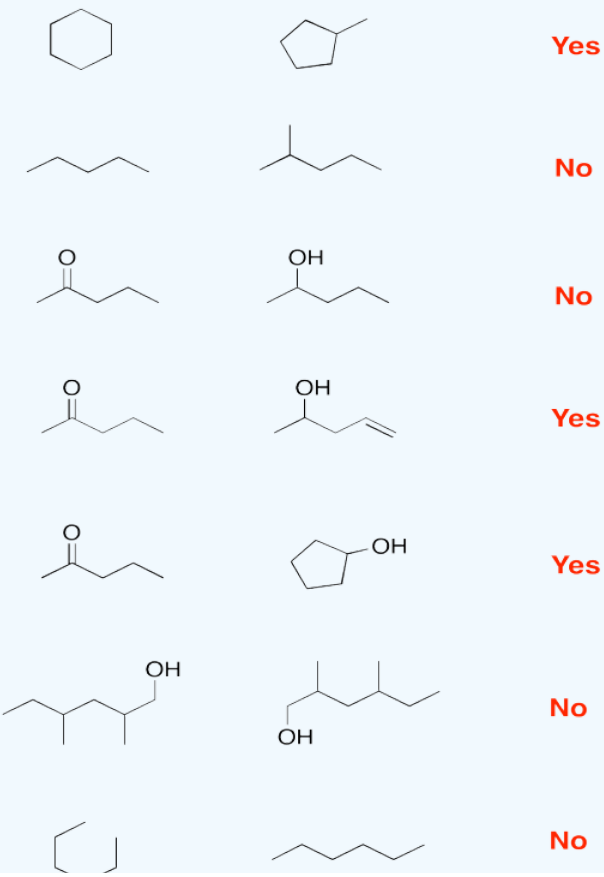
Exercise 4.8.4

Look at the following pairs of compounds. Are the compounds constitutional isomers? (Hint: You may need to add in all hydrogens)

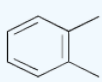
https://chem.libretexts.org/@go/page/191162

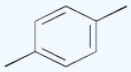


Answer

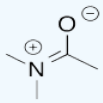


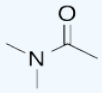
https://chem.libretexts.org/@go/page/191162





Yes





No

Answer

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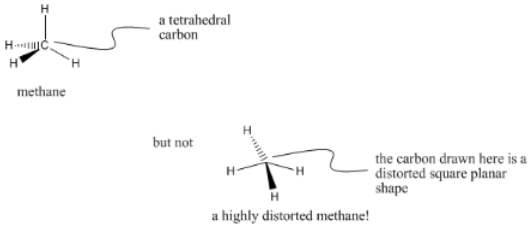
4.9: Three Dimensional Drawings

Our purpose in this chapter is to be able to represent the structure of a molecule. When we draw the Lewis structure for methane, it is only a 2-dimensional representation, but really the compound has a three-dimensional shape. The central carbon in methane is tetrahedral, with the four hydrogens at the alternate corners of a cube.

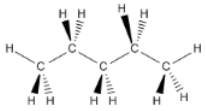
We can draw a tetrahedron by making a vertex between two lines, then attaching a wedged line and a hatched line to the outside of the corner. The black, wedged line is read as "this atom is towards us". The hatched line is read as "this atom is farther away from us". Although the drawing is flat, the hatched and wedged lines is a shorthand notation for 3-dimensionality.



Representing the three-dimensional shape of a molecule can be done on paper, but only if we are very careful about drawing conventions such as wedge-dash drawings.

Carbons that have bonds to four *different* neighbors are always tetrahedral. The neighbors arranged around a tetrahedral carbon are around 109° apart. Sometimes, for reasons we won't go into here, tetrahedral carbons are called sp3 carbons.

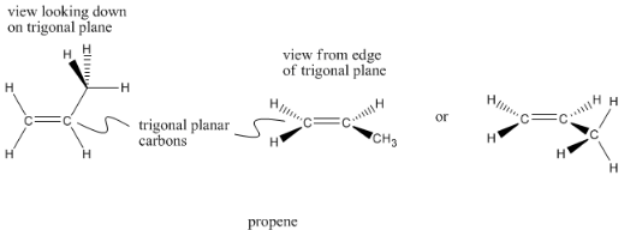
Pentane is a compound that contains four tetrahedral carbons in a row. Each tetrahedral carbon could be shown with wedge - dash projections.



It is also very common to use computer drawing programs to show the shapes of molecules. You can view the three-dimensional structure of pentane in many different ways. Three of the most common ways are shown here. Ball & Stick is an easy way to see where all the atoms are and how they are connected. Wireframe allows you to see connections without having your view obscured by atoms. Space-filling models are meant to most closely show you the shape of the molecule, although the atoms involved get obscured in this view.

Go to **Animation IM9.1.** A three-dimensional model of pentane.

Carbons double bonded to one neighbor, and consequently bonded to three different neighbors overall, are trigonal planar. The neighbors are all in the same plane and are about 120° apart. Trigonal planar carbons are sometimes described as sp2 carbons.

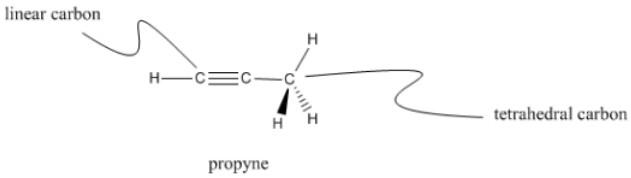


Propene has two trigonal planar carbons as well as one tetrahedral carbon. Notice that a trigonal planar carbon is flat if viewed from one direction, but not if viewed from the other. Sometimes you will see trigonal carbons drawn differently, if the drawer wants you to look at the molecule from one direction or the other.

See if you can find both kinds of carbon on the model below.

Go to **Animation IM9.2.** A three-dimensional model of propene.

Carbons that have only two different neighbors are linear; each neighbor is 180° apart from the other. Linear carbons are sometimes called sp carbons.



Kekule structure of propyne, showing linear arrangement of triple bond and tetrahedral arrangement of hydrogens around the terminal, single-bonded carbon.

Propyne has two linear carbons as well as one tetrahedral carbon. See if you can find both kinds of carbon on the model below.

Go to **Animation IM9.3.** A three-dimensional model of propyne.

Saying a carbon is sp or sp2 is only giving the shape of one atom within a molecule. The molecule itself may have a particular shape which is determined by the geometries of it constituent atoms, but which can't be described simply in words as "tetrahedral" or "linear".

Pentane is roughly a zig-zag shape. In a space-filling model, it resembles a fat caterpillar inching along. Propene is almost boomerang-shaped. Propyne is shaped like a dart; it has a pointed end and a feathered end.

Other molecules have more complicated shapes. The shape of ginkgolide B (a natural product isolated from the medicinally interesting *ginkgo biloba* tree) is hard to describe. However, it is clear that individual carbons in ginkgolide B are mostly tetrahedral, with just a couple of trigonal planar ones.

Go to **Animation IM9.4.** A three-dimensional model of ginkgolide B.

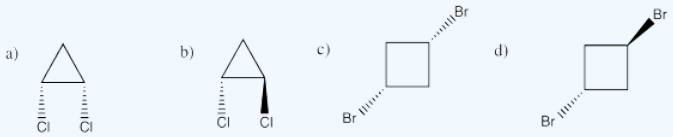
Understanding the overall shape of a molecule is particularly important in various aspects of biochemistry. For example, the effect of any drug in the body is strongly influenced by the shape of the drug and how that shape can interact with specific receptors.

? Exercise 4.9.1

Cis and trans cyclic isomers have two substituents attached to a ring. The cis isomer has both substituents on the same face of the ring. The trans isomer has substituents on opposite faces of the ring. Use wedge-dash projections to draw the shapes of the following molecules:

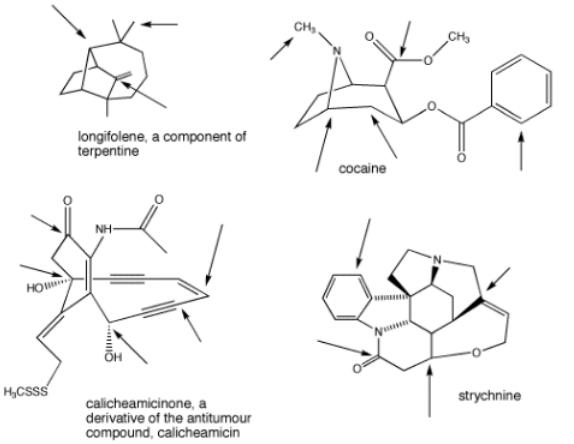
a. *cis*-1,2-dichlorocyclopropane, $C_3H_4Cl_2$ (the numbers mean there is a chlorine on the first carbon and a chlorin on the second carbon)
b. *trans*-1,2-dichlorocyclopropane, $C_3H_4Cl_2$ c) *cis*-1,3-dibromocyclobutane, $C_4H_6Br_2$ d) *trans*-1,3-dibromocyclobutane, $C_4H_6Br_2$
c. *cis*-1,3-dibromocyclobutane, $C_4H_6Br_2$
d. *trans*-1,3-dibromocyclobutane, $C_4H_6Br_2$

Answer

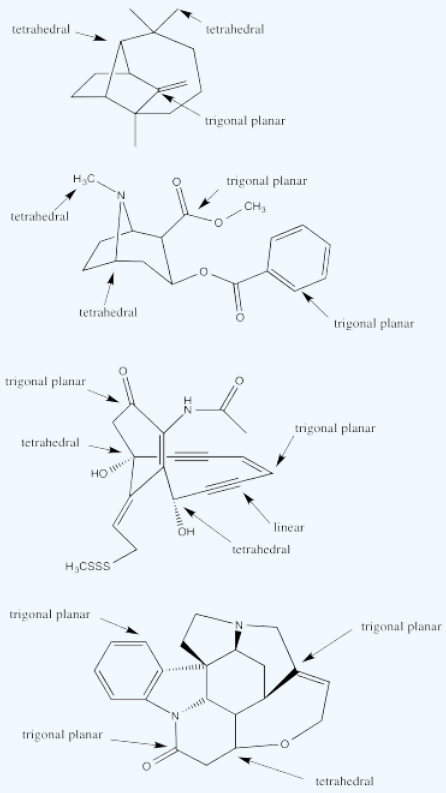


? Exercise 4.9.2

Identify the geometry at the indicated carbons in the following molecules:



Answer



AnswerExercise 4.9.2, showing structural formulas for longifolene, cocaine, calicheamicinone, and strychnine.

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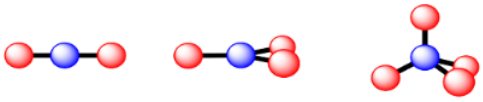
4.10: Other Geometries

Previously, we looked at a few common geometries of carbon atoms in molecules. Carbon most often has four neighbouring atoms in the molecule, and in that case it is tetrahedral. However, sometimes there are only two or three neighbouring atoms, and so linear or trigonal planar geometries are also pretty common.

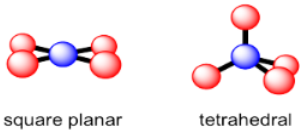


These geometries are found throughout the periodic table for atoms that have 2, 3 or 4 neighbouring atoms within a molecule. However, there are also some other molecular geometries that are pretty common.

Earlier, we looked at the environments of atoms or ions within solid structures and considered the "coordination number" of the atom or ion. Remember, the coordination number is just the number of atoms in close contact with a central atom. We can think about the geometry around a particular atom in a molecule the same way.

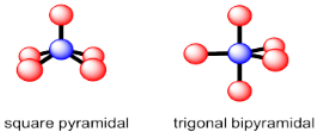
Coordination number 4

There are actually two different geometric options that occur with some regularity for coordination number 4. Tetrahedral geometry, which we have seen, maximizes the distances between neighbors. That could be advantageous because it minimizes crowding. In fact, tetrahedral geometry is the most common geometry for tjis coordination number. However, a second geometry is available for a limited number of compounds. In square planar geometry, all four neighbors are found in the same plane and are roughly 90 degrees apart from each other. This geometry is most often observed for certain compounds of palladium and platinum as well as a few other transition metals.



Coordination number 5

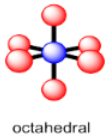
In the case of five neighboring atoms, there are two geometries that are roughly equally prevalent. In a trigonal bipyramidal structure, the central atom is surrounded by three neighbors that form a trigonal plane around it. The last two neighbors are above and below this plane. These two neighbors are roughly colinear with the central atom. The trigonal planar positions referred to as "equatorial"; the other two positions are called "axial".



The other common five coordinate geometry is square pyramidal. In this case, the central atom sits above a base of four neighbors; those four positions form a square plane together. A fifth atom occupies the space above the central atom.

Coordination number 6

Almost all examples of atoms with coordination number six can be described as having an octahedral geometry. Four of the neighbors form a square plane around the central atom, with one atom above this plane and one below it. As with the trigonal bipyramid, these positions can be described as equatorial and axial, respectively.

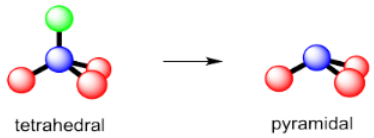


Electronic vs. molecular geometry

There is a striking difference between geometries around transition metals, in the middle of the periodic table, compared to main group p-block elements, in the right hand part of the periodic table. The geometry around a transition metal is simply based on the number of atoms bonded to it. Each surrounding atom takes up some space and so a geometry is adopted to give those atoms roughly equal space around the central atom.

In the p-block, things are generally quite different. It's not just the neighbouring atoms that take up space; the valence electrons on the central atom also have to be accommodated. Thus, in ammonia, NH_3, we need to consider not just the three hydrogen atoms that are bonded to the nitrogen, but nitrogen's own lone pair as well, in order to determine the geometry. That's four objects to fit around the nitrogen atom. The normal geometry for four things is tetrahedral. Thus, ammonia takes on a tetrahedral shape. It isn't trigonal planar.

That's sometimes called the overall *electronic* geometry. It is the geometry of everything, including lone pair electrons. To see the relationship between the *atoms* -- the nitrogen and its three nieghbouring hydrogens -- just ignore the electron pair for a minute. The nitrogen sits above a trigonal base of three hydrogen atoms. The *molecular geometry* -- that shape formed by the nitrogen and the three hydrogens -- is pyramidal.



Comparison of tetrahedral and pyramidal arrangements, showing the removal of one group of electron density to form the pyramidal shape.

This phenomenon, in which the geometric relationship between atoms is influenced by where the electrons are on a central atom, is pretty common around chalcogens and pnictogens -- that is, oxygen and the other atoms in its column of the periodic table, as well as nitrogen and the other atoms in its group. In those cases, lone pairs appear to force the surrounding atoms a little closer to each other.

? Exercise 4.10.1

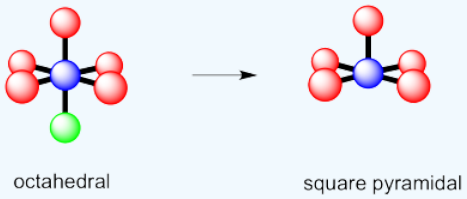
Suppose a compound had a central atom surrounded by six groups, including bonds to other atoms as well as its own lone pairs.

a. What is its overall "electronic" geometry?
b. What would be its molecular geometry if it had one lone pair?
c. What would be its molecular geometry if it had two lone pairs?

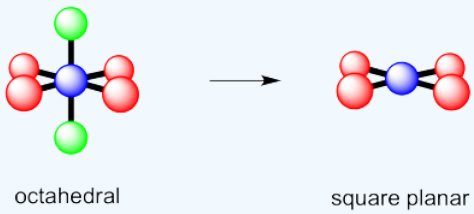
Answer a

octahedral

Answer b



Answer c



Exercise 4.10.2

Suppose a compound had a central atom surrounded by five groups, including bonds to other atoms as well as its own lone pairs.

a. What is its overall "electronic" geometry?
b. What would be its molecular geometry if it had one lone pair?
c. What would be its molecular geometry if it had two lone pairs?

Answer a

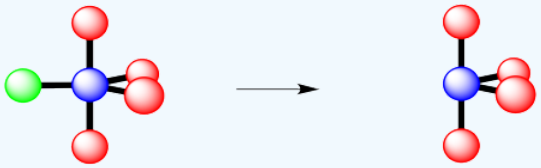
trigonal bipyramidal

Answer b

This time there could be two different answers.

If the lone pair occupies one of the axial positions, it would be pretty close to three other atoms.

If the lone pair occupies one of the equatorial positions, it would be pretty close to only two other atoms. The other equatorial atoms are pretty far away.

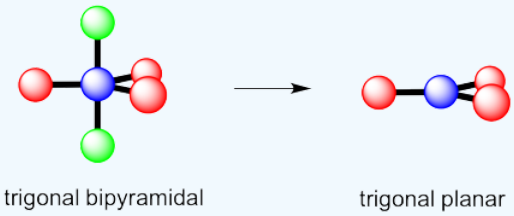


Exercise 4.10.2, answer to b, showing removal of the side group of electron density to form a different arrangement than in the above.

The rule is that the lone pair goes in the less crowded position, so this molecule would be see-saw shaped.

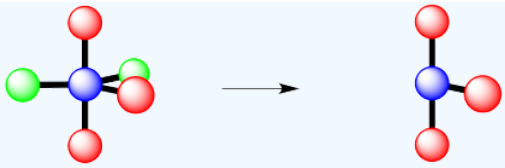
Answer c

Again, there are two possible geometries. One of them would be trigonal planar, a pretty common geometry.



Exercise 4.10.2, answer to c, showing the removal of the two vertical groups to form another arrangement.

However, that places the lone pairs in the more crowded positions. Instead, the molecule is going to be tee shaped.



Exercise 4.10.2, answer to c, showing the removal of the two horizontal groups to form a different arrangement than the one above.

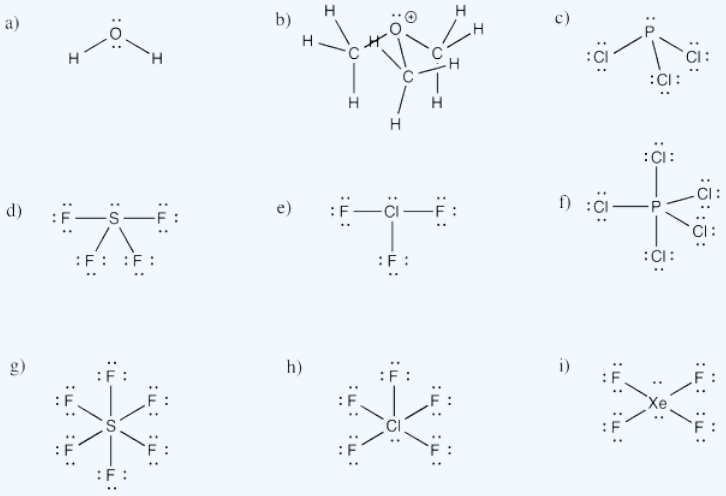
Exercise 4.10.3

Draw structures for the following compounds.

a) H_2O b) $(CH_3)_3O^+$ c) PCl_3 d) SF_4 e) ClF_3 f) PCl_5

g) SF_6 h) ClF_5 i) XeF_4

Answer



Exercise 4.10.4

What is the molecular geometry of each of the compounds in problem Exercise 4.10.3?

Answer a

bent

Answer b

pyramidal at O, although tetrahedral at C

Answer c

pyramidal

Answer d

see-saw

Answer e

tee

Answer f

trigonal bipyramidal

Answer g

octahedral

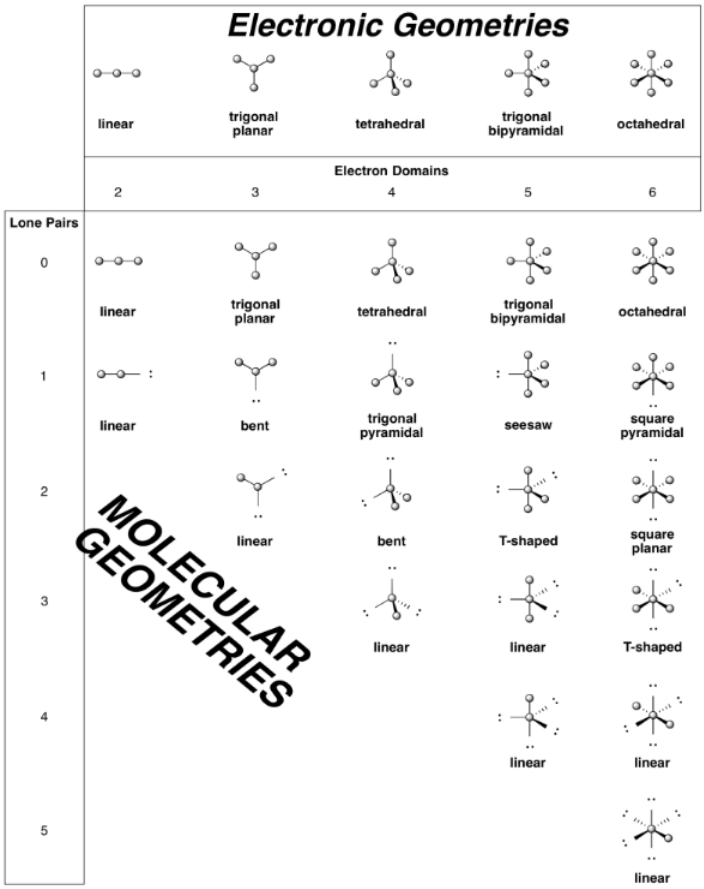
Answer h

square pyramidal

Answer i

square planar

Some common geometries are summarized in the table below.



In cases where the molecular geometry is different from the electronic geometry, we sometimes need to make choices about which position a lone pair is more likely to occupy. The general rule is that lone pairs occupy the less crowded site. It is as if the lone pair takes up more space than a bond to an atom. That might seem surprising, because it leaves the atoms in the molecule crowded together. Although these cases are not very common, they are observed in a number of compounds from the p-block. Some examples are summarized in the table below.

Example	Electron Domains	Electronic Geometry	Molecular Geometry
	5	trigonal bipyramidal	see-saw
	5	trigonal bipyramidal	T-shaped

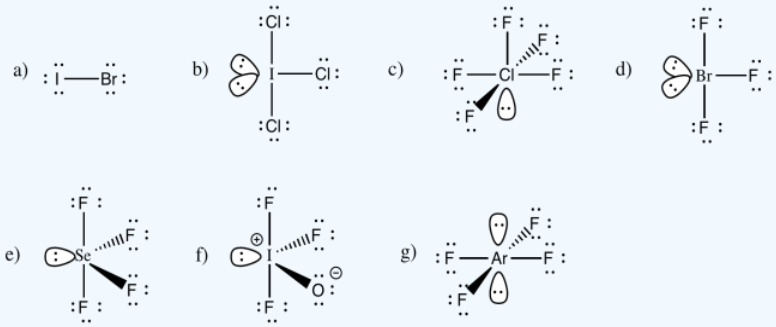
Table. Column headings, left to right: example, electron domains, electronic geometry, molecular geometry. First row, left to right: Lewis structure of sulfur tetrafluoride with lone pair, 5 electron domains, trigonal bipyramidal electronic geometry, see-saw molecular geometry. Bottom row, left to right: chlorine trifluoride with two lone pairs, five electron domains, trigonal bipyramidal electronic geometry, and T-shaped molecular geometry.

Exercise 4.10.5

Draw structures for the following compounds.

a) IBr b) ICl_3 c) ClF_5 d) BrF_3 e) SeF_4 f) IOF_3 g) ArF_4

Answer



(probably; it hasn't been made before)

Answers to Exercise 4.10.5, a through g. Below g is the note "(probably; it hasn't been made before)".

Exercise 4.10.6

Occasionally, atoms can have an even higher number of bonds than we have seen so far. Predict a reasonable geometry for iodine heptafluoride, IF_7.

Answer

You may be able to imagine some other possibilites for this number of neighbors, but IF_7 adopts a pentagonal bipyramid shape.

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4.11: Controversial Lewis Structures

There is sometimes controversy in science. Argument can be an important part of how we arrive at a better understanding of things. In the context of molecules and structures, there have been long-running controversies about how to draw certain phosphorus and sulfur compounds. A look at that controversy can tell us some things about how different chemists think about bonding.

The controversy concerns how to draw, and think about, the bonding in a number of "high-valent" sulfur and phosphorus compounds, in which the sulfur or phosphorus atom is bonded to more than the usual number of neighbors.

Sulfate ion, SO_4^{2-}, is an example of a high-valent sulfur compound. Sulfur, like oxygen, frequently forms two bonds. In sulfate, the sulfur is attached to four different atoms.

We could draw that structure in two ways. A structure that obeys the octet rule would have a single bond to each oxygen. That would satisfy the octet of sulfur. In order to fill in the right number of electrons for this group of atoms, each oxygen will have a negative formal charge. Sulfur will have a charge of plus two.

A different way to draw the structure would include double bonds between sulfur and two of the oxygen atoms. That structure would have less charge separation than the other structure. However, the sulfur would have twelve electrons in its valence shell, not eight. It would exceed its octet.

Can an atom have more than eight electrons in its valence shell? Lots of them can, if they are further down the periodic table. Whether sulfur and phosphorus can is much less clear. Frequently, the fact that these are 3rd row atoms is considered significant. After all, the d electrons begin in the third row. Perhaps sulfur and phosphorus can accommodate extra electrons because they have d orbitals. The d orbitals don't have any electrons in them, yet, so maybe they can accept some from other aroms via bonds.

Many theoretical chemists (including experts in sulfur and phosphorus chemistry) are convinced that this scenario just isn't possible. The d level in these atoms is just too high in energy. Other atoms can't possibly donate electrons to sulfur and phosphorus in this way.

And yet, many chemists (including experts in sulfur and phosphorus chemistry) still draw sulfate with double bonds. Why would they make such a mistake in the face of reason?

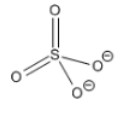
Partly, it has to do with experimental evidence. Remember, "experimental" sounds wishy-washy and tentative to non-scientists, but to a chemist the term really means "reality-based". One of the reasons people draw double bonds in many sulfur and phosphorus compounds is that the bonds simply behave like double bonds. That is, they are stronger and shorter than single bonds. We might not think about those bonds in exactly the way we think about double bonds in other situations, but the experimental evidence says that there is some additional attraction between the sulfur and oxygen atoms in these cases.

There is additional evidence that sulfur and phosphorus can "exceed the octet" or form "Lewis-disobedient" structures. Compounds like phosphorus pentafluoride (PF_5) clearly require more than four bonds to sulfur. Without five bonds, we would need to draw one of the fluorides as an anion. It's certainly possible that this could be the true structure, but there is evidence from X-ray crystallography that all of the fluorines are attached to phosphorus in PF_5, as well as in the related PF_6^- anion (hexafluorophosphate, a very common molecular ion in X-ray crystallographic studies).

So, sulfur and phosphorus really can form additional bonds. The only true controversy about the octet rule in sulfur and phosphorus chemistry is a little too subtle to explore very deeply at this point: it's whether sulfur can form a *double bond* in these cases. The issue has to do with ideas from molecular orbital theory, which is a later chapter, and how well d orbitals can form "pi bonds" with the p orbital on oxygen.

? Exercise 4.11.1

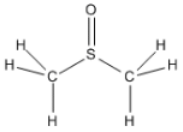
Fill in any missing lone pairs on the following structures.



sulfate

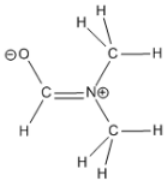
hexafluorophosphate

tetrafluoroborate

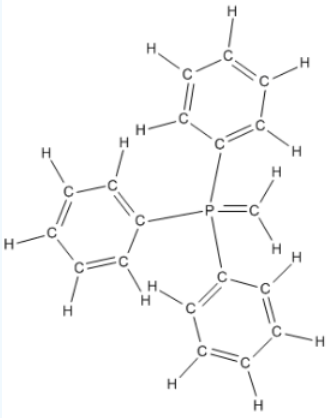


dimethylsulfoxide (DMSO)

antimony pentafluoride

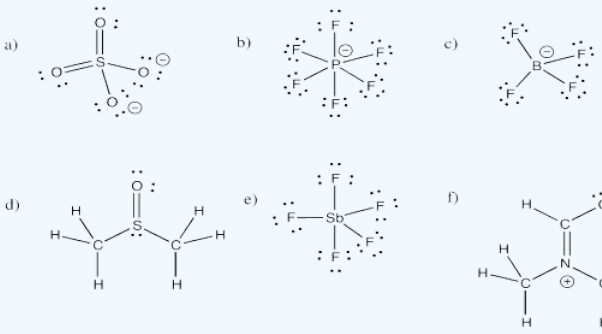


dimethylformamide (DMF)



triphenylphosphonium methylidene

Answer

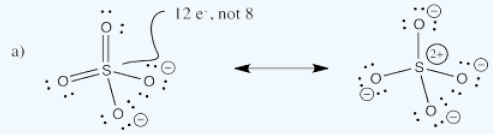


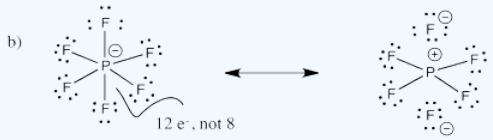
Answer

Exercise 4.11.2

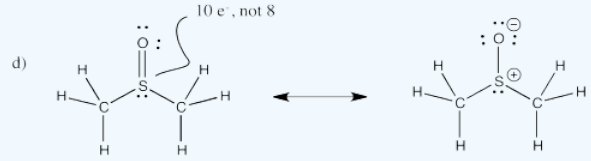
Indicate whether each of the structures in Exercise 4.11.1 (IM11.1) obeys the octet rule. If not, provide a resonance structure that obeys the octet rule.

Answer





c) obedient



f) obedient

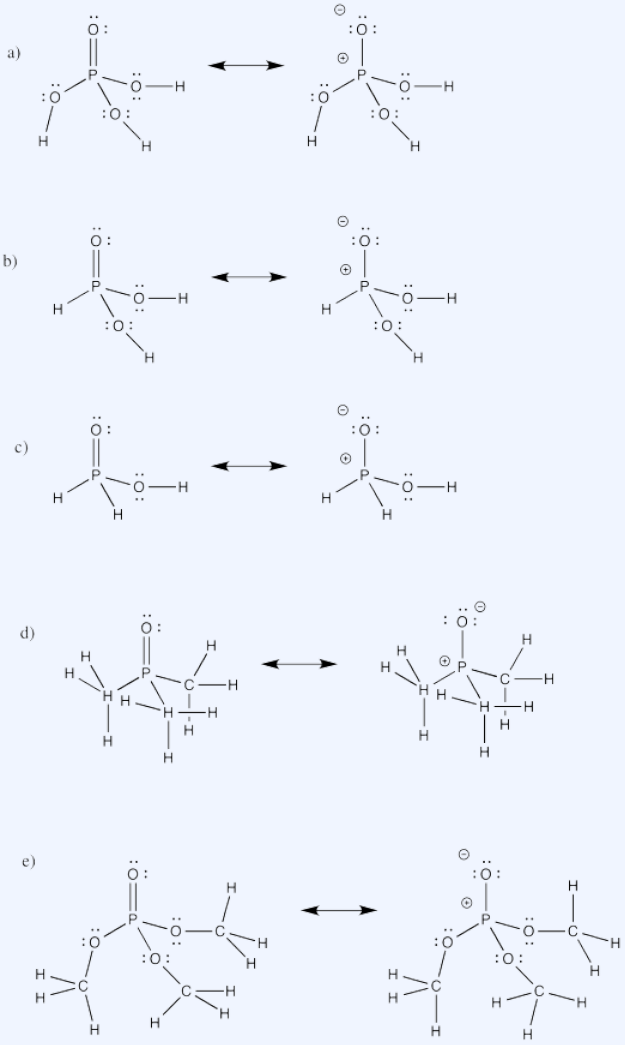
Exercise 4.11.3

Many oxyphosphorus compounds are commonly drawn in a way that is inconsistent with the octet rule. Draw two structures for each of the following compounds: one that obeys the octet rule but has higher charge separation, and one that has lower charge separation but exceeds the octet on phosphorus. (Note: in a few of the compounds, hydrogen is attached to phosphorus, as suggested in the condensed formula.)

a) H_3PO_4 or $PO(OH)_3$ b) H_3PO_3 or $HPO(OH)_2$ c) H_3PO_2 or $H_2PO(OH)$

d) $(CH_3)_3PO$ e) $(CH_3O)PO$

Answer



Exercise 4.11.4

Draw two structures for each of the following compounds: one that obeys the octet rule but has higher charge separation, and one that has lower charge separation but exceeds the octet on chlorine.

a) hypochlorite, ClO^- b) chlorite, ClO_2^- c) chlorate, ClO_3^- d) perchlorate, ClO_4^-

Exercise 4.11.5

Draw two structures for each of the following compounds: one that obeys the octet rule but has higher charge separation, and one that has lower charge separation but exceeds the octet on sulfur.

a) sulfite, SO_3^{2-} b) sulfate, SO_4^{2-} c) thiosulfate, $S_2O_3^{2-}$

d) disulfate, $S_2O_7^{2-}$ e) persulfate or peroxomonosulfate, SO_5^{2-}

Exercise 4.11.6

Global warming is a controversial topic in society but there is not a great deal of controversy about it in the scientific community. A summary of evidence can be found at the National Oceanic and Atmospheric Administration's website.

Explain some of the evidence that global warming is occurring and is linked to human activity. Why do you think there is little debate about these ideas among scientists, but lots of debate in the US public as a whole?

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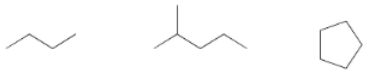
4.12: Organic Functional Groups

Organic compounds are very common in chemistry and biology. Some familiarity with some common types of compounds based on carbon and a few other elements will help you to understand organic chemistry and related fields.

The most common structural piece in organic chemistry is the carbon-carbon bond. Most organic compounds are filled with carbon-carbon bonds. Very often, a network of carbon atoms are single-bonded to each other, and to hydrogen atoms, to build up a complicated structure.

Other pieces, called functional groups, are attached to this framework. Functional groups are specific collections of atoms bonded together in a certain way. These collections of atoms are seen over and over in organic chemistry, and so they are given specific names. This appendix is meant to help you learn to recognize these functional groups. It will also help you learn how to talk about them.

Before looking at functional groups, let's look at simpler compounds that have no functional groups. Alkanes are compounds that contain only carbon and hydrogen, and that contain no double or triple bonds.



? Exercise 4.12.1

Translate the above structures into Lewis - Kekule structures.

Specific alkanes are given names that say something about their structures. Their names end in "ane"; that means they contain only single bonds, not double or triple bonds. A compound that contains no double or triple bonds is sometimes called "saturated". They are sometimes called "paraffinic" hydrocarbons, which means the same thing as saturated hydrocarbons.

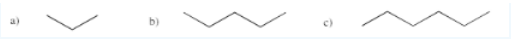
The name also contains a part that tells how many carbons are found connected in the chain. These prefixes are used throughout organic chemistry to name other kinds of compounds, so you need to memorize them.

Prefix and the number of Carbons they have

prefix	# carbons
meth	1
eth	2
prop	3
but	4
pent	5
hex	6
hept	7
oct	8
non	9
dec	10

? Exercise 4.12.2

Provide names for the following alkanes.



Answer a

Answer b

Answer c

Answer apropaneAnswer bpentaneAnswer chexane

The chain of carbons in an alkane is called an alkyl chain. Sometimes there are smaller alkyl chains attached to the main chain of an alkane. The same prefixes can be used to tell how many carbons are in these smaller branches.

Numbers are used to count how far along the chain these branches occur. You need to start on the end of the chain and count the carbons until you get to the place where the branch occurs. If there are two different possible chains, choose the longest chain as the base name. If there are two different directions possible, start at the one that gives the lowest numbers for the branches.

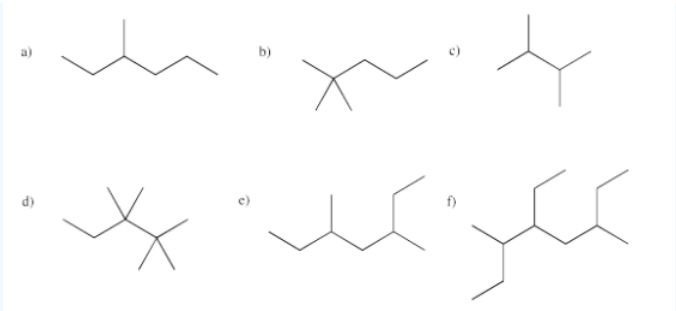
If there are two different branches of the same size on a chain, you need to say so. A different prefix is used to say how many of the same piece are present.

Prefix and the number groups they have

prefix	# of groups
di	2
tri	3
tetra	4
penta	5

? Exercise 4.12.3

Provide names for the following branched alkanes.



Answer a

Answer b

Answer c

Answer d

Answer e

Answer f

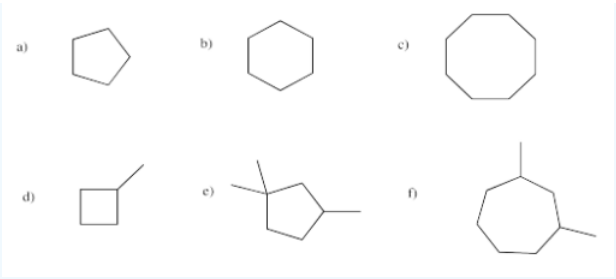
Answer a3-methylhexaneAnswer b2,2-dimethylpentaneAnswer c2,3-dimethylbutaneAnswer d2,2,3,3-tetramethylpentaneAnswer e3,5-dimethylheptaneAnswer f4-ethyl-3,6-dimethyloctane

"Aliphatic hydrocarbons" specifically refers to branched chains of saturated hydrocarbons. "Alicyclic hydrocarbons" are very similar but they contain rings of carbons. If a chain of carbons wraps around to form a ring, the prefix "cyclo" is used.

All these elements will be used in naming other compounds as well.

? Exercise 4.12.4

Provide names for the following cyclic alkanes.



Answer a

Answer b

Answer c

Answer d

Answer e

Answer f

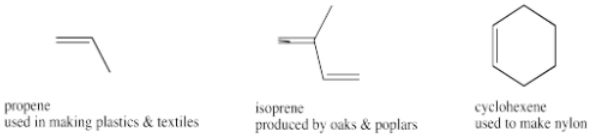
Answer acyclopentaneAnswer bcyclohexaneAnswer ccyclooctaneAnswer dmethylcyclobutaneAnswer e1,1,3-trimethylcyclopentaneAnswer f1,3-dimethylcycloheptane

Homoatomic functional groups

Any feature other than an alkyl chain is called a "functional group". A functional group is also just a place where reactions take place.

Homoatomic functional groups contain only carbon and hydrogen. They differ from alkyl groups only in having multiple C-C bonding.

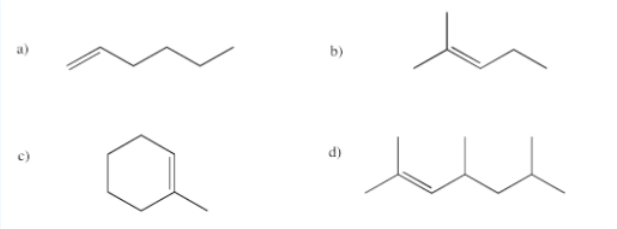
The C=C functional group is called an alkene. Simple compounds that contain C=C double bonds are also called alkenes. The term "olefin" also means alkene, and "unsaturated" or "olefinic" hydrocarbons contain double bonds.



In naming alkenes, the suffix "ene" is used instead of "ane". The base name of the alkene describes the length of the chain containing the double bond. A number says how far the double bond is from the nearest end of the chain.

? Exercise 4.12.5

Provide names for the following alkenes.



Answer a

Answer b

Answer c

Answer d

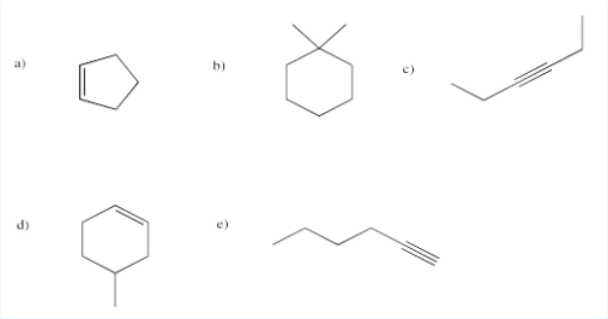
Answer a1-hexeneAnswer b2-methyl-2-penteneAnswer c1-methylcyclohexeneAnswer d2,4,6-trimethyl-2-heptene

The C-C triple bond is called an alkyne. "Acetylenic" hydrocarbons or alkynes are compounds that contain C-C triple bonds. These compounds are also examples of "unsaturated hydrocarbons".

acetylene or ethyne

? Exercise 4.12.6

Provide names for the following hydrocarbons.



Answer a

Answer b

Answer c

Answer d

Answer e

Answer acyclopenteneAnswer b1,1-dimethylcyclohexaneAnswer c3-hexyneAnswer d4-methylcyclohexeneAnswer e1-hexyne

? Exercise 4.12.7

Describe the geometries of the following carbons:

a) any carbon in pentane b) the second carbon in 2-butene c) the first carbon in 1-hexyne

Answer a

tetrahedral

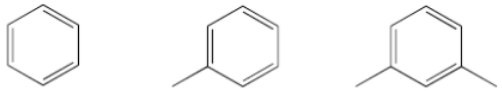
Answer b

trigonal planar

Answer c

linear

Aromatic compounds appear to contain C-C double bonds but they are very different from alkenes. The most common aromatic is benzene. Because benzene is a very common structural piece, you should be familiar with some of the language associated with it.



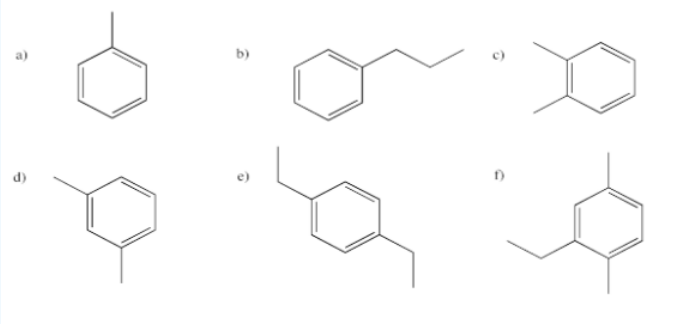
Benzene rings with two groups attached are common enough that different terms are used to describe their isomers. The terms *ortho-*, *meta-* and *para-* are used only to describe the relationship between two groups around benzene, and not any other compounds. These terms are sometimes abbreviated to *o-*, *m-* or *p-*. Alternatively, two groups attached to a benzene can simply be

numbered in order to make it clear where they are. If more than two groups are attached, numbering is used; terms such as "ortho" no longer apply.

Note that a benzene group is sometimes called a phenyl group. It is not called a benzyl group, nor a benzoyl group. Those two groups both contain a phenyl ring but they are not exactly the same.

? Exercise 4.12.8

Provide names for the following aromatics.



Answer a

Answer b

Answer c

Answer d

Answer e

Answer f

Answer amethylbenzeneAnswer bpropylbenzeneAnswer c1,2-dimethylbenzene or o-dimethylbenzene (also o-xylene)Answer d1,3-dimethylbenzene or m-dimethylbenzene (also m-xylene)Answer e1,4-diethylbenzene or p-diethylbenzeneAnswer f2-ethyl-1,4-dimethylbenzene

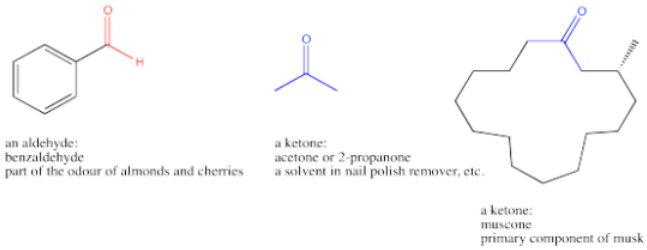
Heteroatomic Functional Groups: Carbonyls

Heteroatomic functional groups contain atoms other than carbon and hydrogen.

Probably the most important set of heteroatomic functional groups is the set that contains carbon-oxygen double bonds. The C=O group is called a carbonyl (carbon-EEL). Carbonyl compounds all contain the carbonyl group.

There are two subsets of carbonyl compounds: regular carbonyls and heteroatom-substituted carbonyls. In regular carbonyls, the carbon in the C=O group is attached only to carbon or hydrogen. It is not attached to additional heteroatoms such as nitrogen or oxygens.

There are two kinds of regular carbonyls. In ketones, the carbonyl carbon is attached only to other carbons. In aldehydes, the carbonyl carbon is attached to a hydrogen atom as well as a carbon.



an aldehyde:
benzaldehyde
part of the odour of almonds and cherries

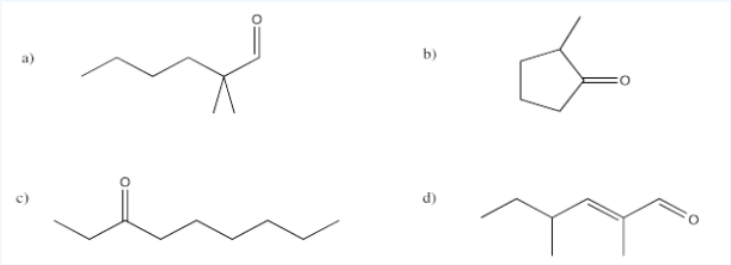
a ketone:
acetone or 2-propanone
a solvent in nail polish remover, etc.

a ketone:
muscone
primary component of musk

Aldehydes and ketones have specific naming conventions. The suffix for the name of an aldehyde is "-al"; whereas the suffix for the name of a ketone is "-one". In the case of a ketone, the location of the carbonyl along the chain can be described with a number. Otherwise, the names of aldehydes and ketones follow the rules we have seen for other organic compounds.

? Exercise 4.12.9

Provide names for the following compounds.



Answer a

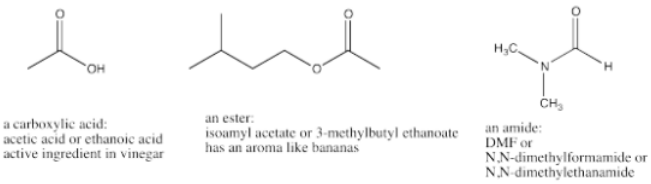
Answer b

Answer c

Answer d

Answer a2,2-dimethylhexanalAnswer b2-methylcyclopentanoneAnswer c3-nonanoneAnswer d2,4-dimethyl-2-hexenal

Heteroatom-substituted carbonyls all have a heteroatom attached to the carbonyl carbon. A heteroatom is an atom other than hydrogen or carbon, such as nitrogen, oxygen or chlorine. Heteroatom-substituted carbonyls are often called "carboxylic acid derivatives" or sometimes "carboxyloids".



a carboxylic acid:
acetic acid or ethanoic acid
active ingredient in vinegar

an ester:
isoamyl acetate or 3-methylbutyl ethanoate
has an aroma like bananas

an amide:
DMF or
N,N-dimethylformamide or
N,N-dimethylethanamide

In carboxylic acids, the carbonyl carbon is attached to an OH group. The OH group is often called a hydroxyl group. Fatty acids and amino acids are examples of biological compounds that contain carboxylic acids.

Two biologically important carboxyloids are amides and esters

In esters, the carbonyl carbon is attached to an oxygen, like in a carboxylic acid. However, the oxygen is not attached to a hydrogen. The oxygen is attached to a carbon. The properties of esters differ enough from carboxylic acids that they are given a different name. Glycerides are biological compounds that contain ester groups. Glycerides are found in fats.

In amides, the carbonyl carbon is attached to a nitrogen. Unlike esters and carboxylic acids, it does not matter whether the nitrogen is attached to a hydrogen or to another carbon. The presence of a hydrogen on the nitrogen changes the properties of the amide less dramatically than in esters and carboxylic acids.

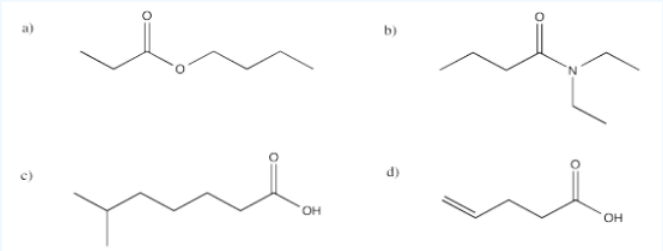
Because the amide does change subtly if there is a hydrogen attached to the nitrogen, there is a way to describe the presence ar absence of hydrogens. An amide with two hydrogens on the nitrogen is called a primary amide. The nitrogen is connected to only one (Latin for first: primus) carbon: the carbonyl carbon.

An amide with two carbons connected to the nitrogen is called a secondary amide (Latin for second: secondus). An amide with three carbons connected to the nitrogen is called a tertiary amide (Latin for third: tertius).

Naming simple examples of these compounds, as before, involves a change in the suffix of the name. The suffix for a carboxylic acid is "-oic acid". Esters really have a two-part name. The first part describes the group attached to the enchained oxygen atom of the ester, with the suffix "-yl". The second part describes the portion that contains the carbonyl, with the suffix "-oate". For an amide, the suffix is "amide". However, other groups attached to the nitrogen are usually prefixed with "*N*-"; this is a little like numbering the position of a group in previous examples, but this time it underscores that the group is attached to a nitrogen.

? Exercise 4.12.10

Provide names for the following carboxyloids.



Answer a

Answer b

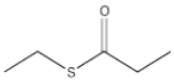
Answer c

Answer d

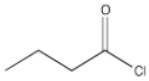
Answer abutyl propanoateAnswer bN,N-diethylbutanamideAnswer c6-methylheptanoic acidAnswer d4-pentenoic acid

A third biologically important carboxylic acid derivative contains a sulfur attached to the carbonyl carbon. Usually the sulfur is attached to another carbon as well. Because sulfur is in the same group in the periodic table as oxygen, this functional group is similar to an ester. It is called a thioester. It is much less common than amides and esters. A biological example of a thioester is acetyl conezyme A, which plays an important role in many biological reactions. In fact, the thioester plays the key role in the reactions of acetyl coenzyme A.

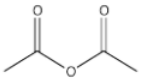
Naming thioesters is just like naming other esters, except that the prefix "thio-" is inserted into the second part of the name.



a thioester:
ethyl thiopropanoate



an acid chloride:
butanoyl chloride



an acid anhydride:
acetic anhysride or
ethanoic anhydride

Two other important carboxylic acid derivatives are not normally seen in biology. They are important because they are used synthetically or industrially to make the other carboxylic acid derivatives.

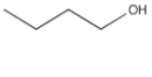
Acid anhydrides are prepared by heating carboxylic acids at high temperatures until water is lost. Acid anhydrides contain two carbonyl units, connected by an oxygen. Usually those two units are the same as each other. The name for an anhydride indicates the number of carbons in just one of those pieces (since the other one is the same) with the suffix "-oic (space) anhydride".

Acid chlorides have a chlorine atom attached to the carbonyl carbon. The name for an acid chloride contains the suffix "-oyl (space) chloride". Other acid halides (such as acid fluorides) are known, but they are less common than acid chlorides.

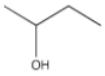
Simple Heteroatomic Functional Groups (No Carbonyls)

There are several heteroatomic functional groups that do not contain carbonyls.

Alcohols contain an OH or hydroxyl group, but the hydroxyl is not attached to a carbonyl.



a "primary" alcohol:
butanol or *n*-butanol



a "secondary" alcohol:
2-butanol or *sec*-butanol

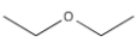
a "tertiary" alcohol:
2-methyl-2-propanol or *tert*-butanol

Sometimes alcohols are classed into sub-groups, as "primary", "secondary" or "tertiary". Those words just describe the carbon attached to the OH group. How many carbons are attached, in turn, to that carbon? Are there two, three, or just one? Those classifications have some influence on how reactive the alcohol will be under different conditions.

The suffix in the name of an alcohol is "ol". It does not matter whether the alcohol is described as a primary, secondary or tertiary one They are still named according to the same rule.

Phenols are alcohols in which the hydroxyl group is directly attached to a phenyl group, or benzene ring. Their behavior is different enough from other alcohols that they are sometimes thought of as a separate group. For one thing, they are somewhat acidic. Coming into contact with phenols, whether they are found in pine resin or, in a much more extreme case, poison ivy, can cause severe itching in the skin. Regular alcohols are much less likely to cause that reaction.

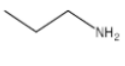
Ethers are kind of like alcohols in that they contain oxygen atoms. Ethers contain a C-O-C group, but neither carbon is part of a carbonyl. Generally, to name an ether, we list the two parts attached to the oxygen atom, and follow those two names with "ether".



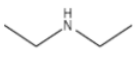
an ether: diethyl ether

Amines contain nitrogen atoms connected to three different atoms, but not connected to a carbonyl. If the nitrogen is attached only to one carbon, the functional group is a primary amine. If it is attached to two carbons, it is a secondary amine. If it is attached to three carbons, it is a tertiary amine. This classification system is a little bit different from the one used with alcohols, in that it refers to the number of things attached to the nitrogen itself. In oxygen compounds, the number of things attached to the oxygen determined whether we called it an alcohol or an ether.

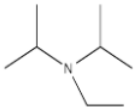
Naming amines is a little like naming ethers. We list the groups attached to the nitrogen, followed by "amine". Usually these groups are listed in alphabetical order. Sometimes, as with amides, the idea that a group is attached to the nitrogen is usually reinforced with the prefix "*N*-".



a "primary" amine:
propylamine

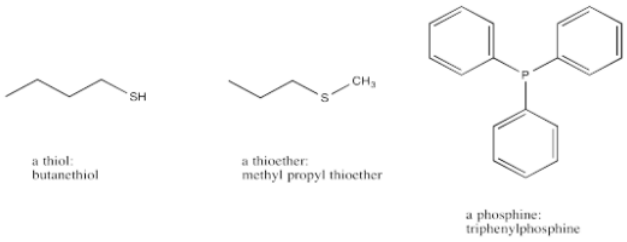


a "secondary" amine:
diethylamine



a "tertiary" amine:
N,*N*-diisopropylethylamine or
ethyldiisopropylamine

Thiols and thioethers are the sulfur analogues of alcohols and ethers. Phosphines are the phosphorus analogues of amines. None of these groups are as common as alcohols, ethers and amines. The sulfur-containing compounds are named in a similar way to their oxygen analogues, but with the suffix "-thioether" or "-thiol" used instead of "-ether" or "-ol". Similarly, phosphines have the suffix "-phosphine" instead of "-amine".

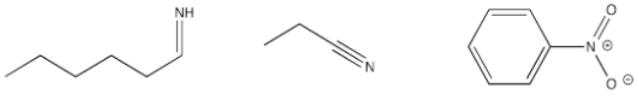


a thiol: butanethiol | a thioether: methyl propyl thioether | a phosphine: triphenylphosphine

Alkyl halides, or haloalkanes, are compounds that contain a halogen that is not attached to a carbonyl. These compounds are not common biologically, but they are important industrially. Usually halogens are treated like alkyl groups in terms of naming compounds that contain them. A halogen is described as a prefix ending in "-o", rather than the prefix ending in "-yl" that is used with alkyl groups. For example, an alkyl bromide is named as a bromoalkane, such as bromoethane or bromohexane.

bromobenzene | 1-iodopropane or propyl iodide | 2-chloropropane or isopropyl chloride | benzyl fluoride

There are a few other functional groups that contain multiple bonds to nitrogen. An imine is the nitrogen analogue of an aldehyde. An imine contains a carbon-nitrogen double bond. The carbon almost always has a hydrogen attached as well. The word "imine" is just appended to the name of the related aldehyde to describe a specific imine.



an imine: hexanal imine | a nitrile: propanenitrile | a nitro compound: nitrobenzene

A nitrile contains a carbon-nitrogen triple bond. The suffix for a nitrile is just "-nitrile".

A nitro group contains the NO_2 unit. "Nitro-" is usually added as a prefix to signal the presence of this group in a compound.

The fun group and their suffixes

fun group	suffix
none	ane
alkene	ene
alkyne	yne
ketone	one
aldehyde	al
carboxylic acid	oic acid
ester	-yl ...-oate
amide	amide
thioester	

Exercise 4.12.11

Provide names for each of the following compounds.

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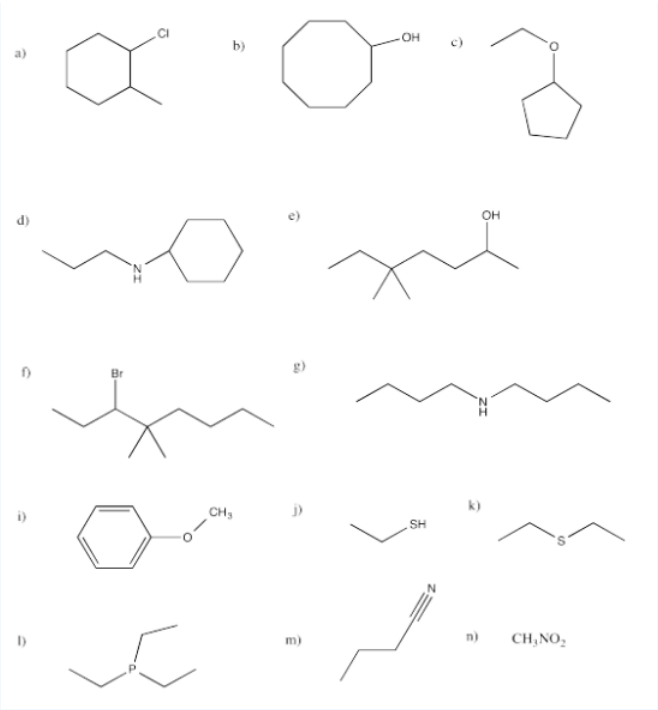


Answer a

Answer b

Answer c

Answer d

Answer e

Answer f

Answer g

Answer i

Answer j

Answer k

Answer l

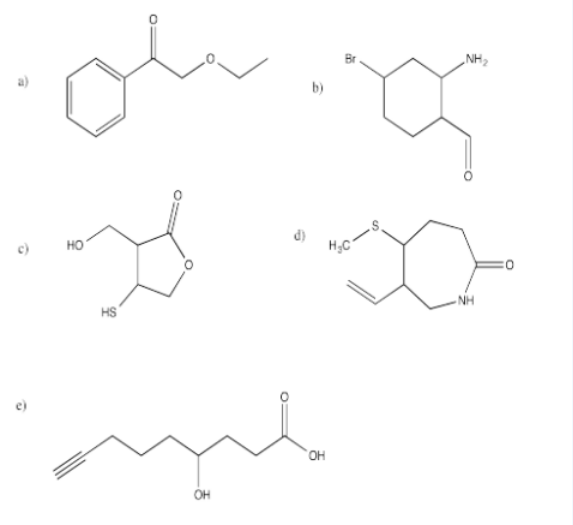
Answer m

Answer n

Answer a1-chloro-2-methylcyclohexaneAnswer bcyclooctanolAnswer cethyl cyclopentyl etherAnswer dN-propylcyclohexylamineAnswer e5,5-dimethylhelpan-2-olAnswer f3-bromo-4,4-dimethyloctaneAnswer gdibutylamineAnswer imethyl phenyl ether (or anisole)Answer jethane thiolAnswer kdiethyl thioetherAnswer ltriethylphosphineAnswer mbutanenitrileAnswer nnitromethaneNote that sometimes a number is located directly in front of the suffix for the group to which it refers.

? Exercise 4.12.12

Each of the following compounds contains three functional groups. Identify them.



Answer a

Answer b

Answer c

Answer d

Answer e

Answer abenzene (or aromatic), ketone, and etherAnswer bbromide, amine, and aldehydeAnswer calcohol, thiol, and esterAnswer dthioester, amide, and alkeneAnswer ealkyne, alcohol, and carboxylic acid

Exercise 4.12.13

Identify the circled functional groups.

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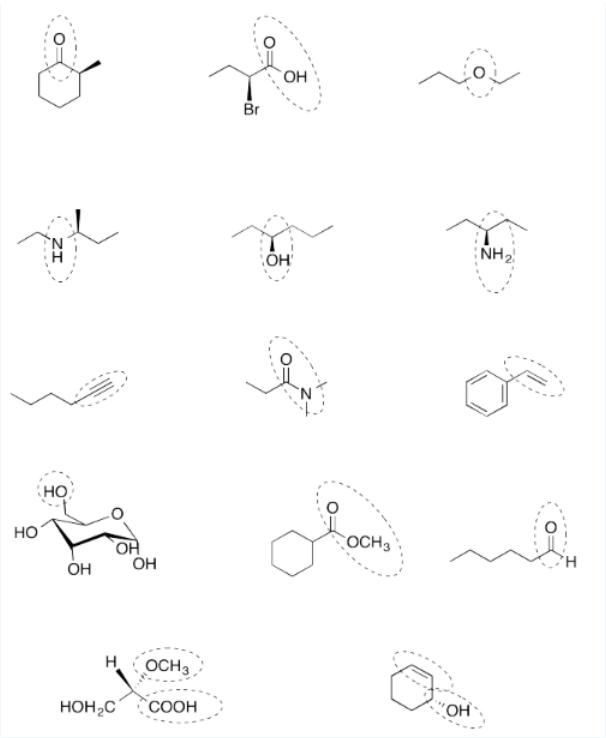

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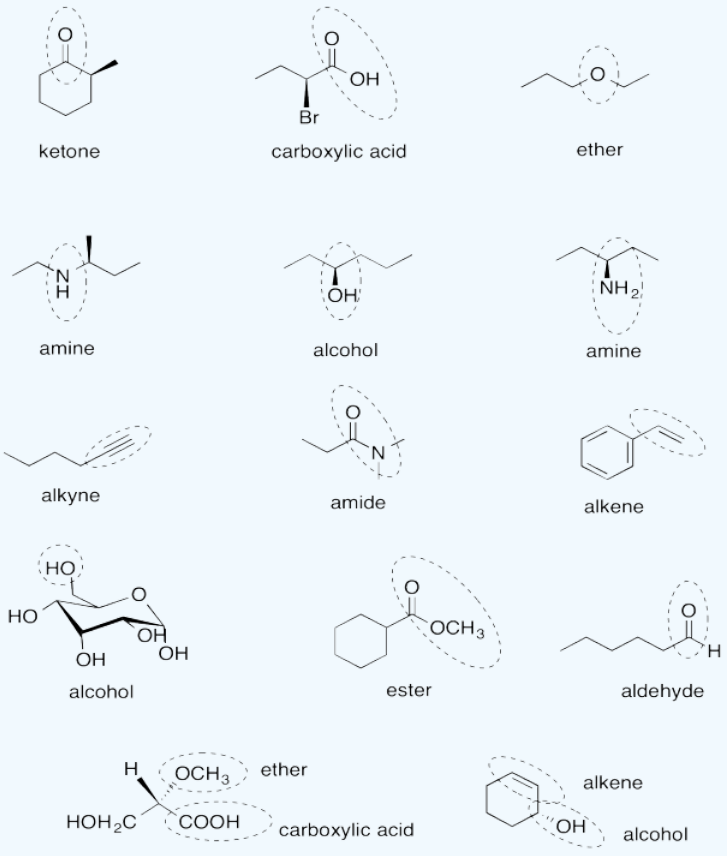

Answer

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Exercise 4.12.14

Identify the circled functional groups (more advanced level).

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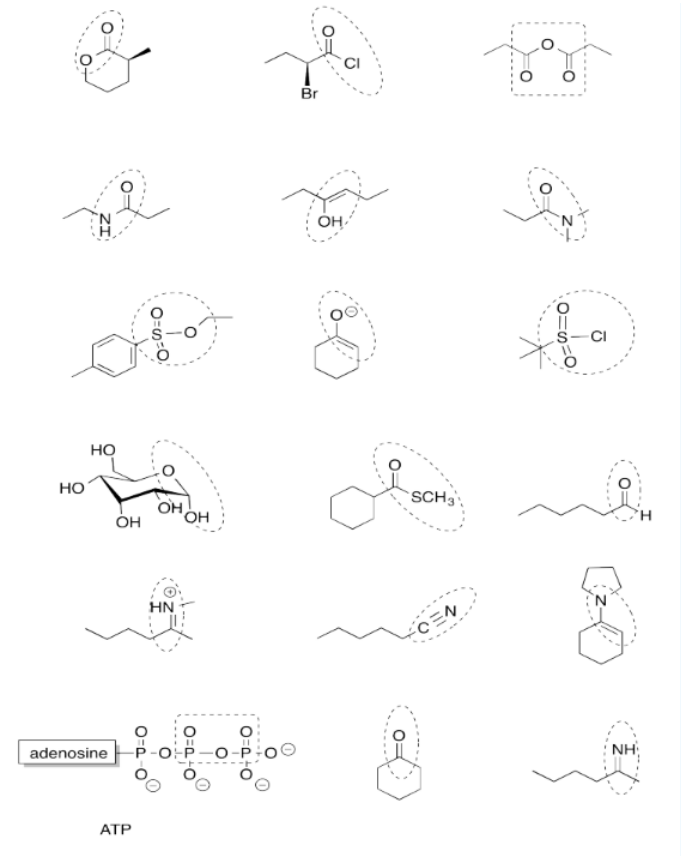

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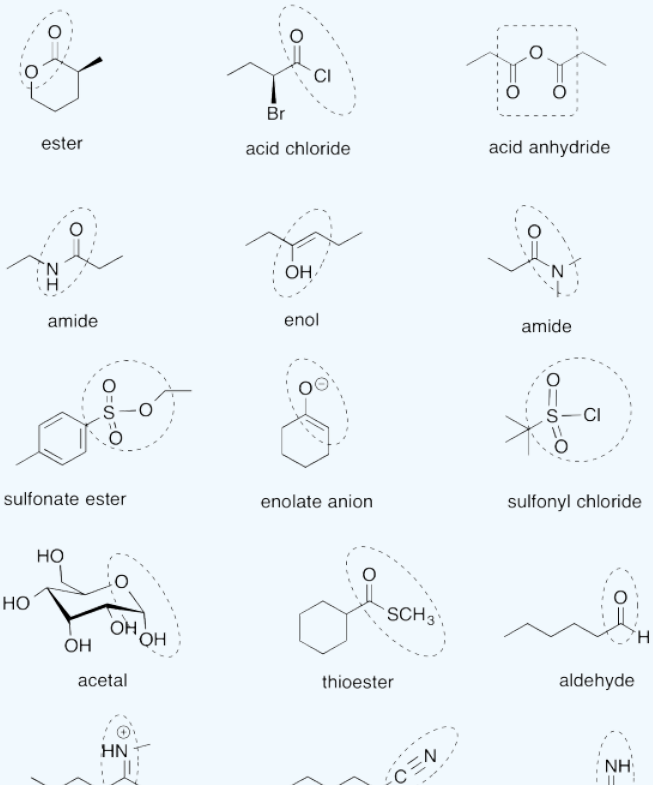

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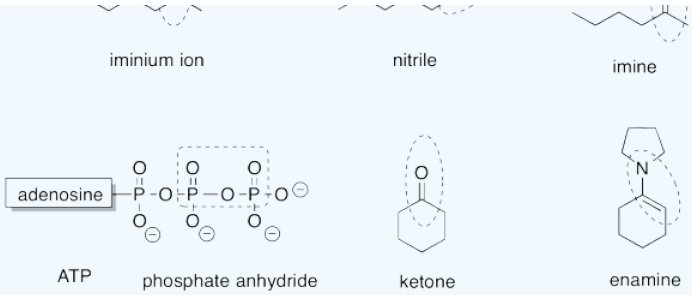

Answer

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4.13: Common Biomolecules

We have seen a number of common "functional groups" from organic chemistry. Functional groups are just collections of atoms that we frequently see, so that it becomes useful to recognize them. Organic compounds, by definition, are carbon-based compounds, usually derived from living things. However, there are a few specific classes of organic molecules that are so common in biology that they are termed "biomolecules". We are going to take a look at them here.

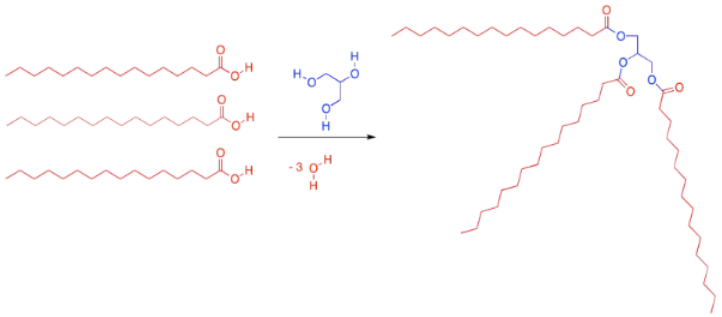
One common group of biomolecules is called "lipids". Lipids can really have lots of different structures. However, the most common type of lipid is an ester. An ester contains an O-C=O unit. Sometimes that group is termed an "ester linkage". We can think of that link as being formed when a carboxylic acid comes together with an alcohol. The carboxylic acid is shown below, in red; the alcohol is in blue.

This carboxylic acid is a particular kind called a fatty acid. It has a long carbon chain. When the alcohol oxygen connects to the carbonyl carbon in the fatty acid, the fatty acid loses its OH group. The alcohol also loses the hydrogen, or proton, from its OH group. That combination of things lost, H + OH, adds up to a water molecule. So every time a fatty acid combines with a alcohol molecule to form an ester linkage, a water molecule is made.

That formation of a water molecule gave rise to an old name for this reaction and others like it. It was called a condensation reaction. That term, "condensation", referred to the water or moisture that was formed during the reaction, like the condensation on the bathroom mirror when you take a shower.

In reality, exactly how these two molecules come together to form one molecule is slightly more complicated than what we are seeing here. At this point, however, this is all you need to know.

The most common kind of lipid in biology is a specific kind of ester called a "glyceride". A glyceride forms between a fatty acid and a glycerol unit. The glycerol unit, in blue, has three hydroxy groups (the OH part). These hydroxy groups are each capable of attaching to the carbonyl carbon in a fatty acid.

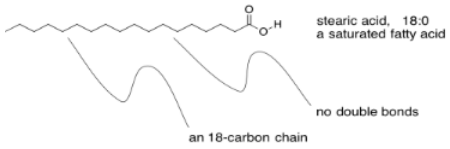


Three moles of n-hexdecanoic acid combine with 1 mole of glycerol to form a fatty acid through dehydration.

When the glycerol oxygen connects to the carbonyl carbon in the fatty acid, the fatty acid loses its OH group, and a proton is lost from the glycerol. So every time a fatty acid combines with a glycerol molecule, a water molecule is made, in addition to the lipid. That's three molecules of water lost, in total, from the original glycerol and fatty acids.

Ester linkages are important partly because they are reversible. Fatty acids can be conveniently stored as glycerides by attaching them to glycerol with ester linkages. However, ester linkages can break open again if water is added. The triglycerides can go back to being glycerol and fatty acids again. Those fatty acids can be used as fuel for the cells. The formation and breaking of ester linkages allows for these processes to be controlled, depending on whether energy is needed right now or should be stored for later.

Incidentally, there are a variety of fatty acids that can form triglycerieds, leading to a diversity of lipids with slightly different properties. There are fatty acids containing carbon chains of various lengths. There are fatty acids with one, two, or three C=C double bonds somewhere in their chains, and others without any. The ones that don't have any double bonds are called saturated fatty acids. Saturated fats are sometimes described by a shorthand notation that tells how long the chain is, followed by a colon, followed by a zero, indicating there are no C=C double bonds.



Unsaturated fats are sometimes described using a similar shorthand notation, but with a number after the colon indicating how many double bonds are present. That's followed by the symbol Δ, the Greek letter delta, with a supercsript number that tells how far the double bond is from the end of the chain.

Bond-line structure of oleic acid. The double bond of the eighteen-carbon chain begins at the ninth carbon.

Sometimes you will hear about omega-3 or omega-6 fatty acids, or some other variation. That's the Greek letter, ω, which is the last letter in the Greek alphabet. It stands for the last carbon in the chain, and the number after it tells you how far the double bond is from the end of the chain.

? Exercise 4.13.1

Draw the triglycerides that would result in each of the following cases.

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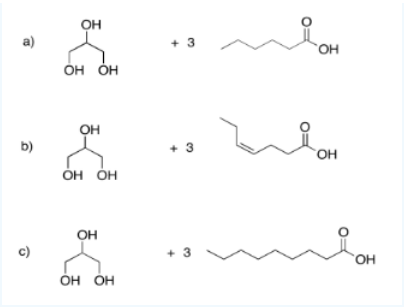

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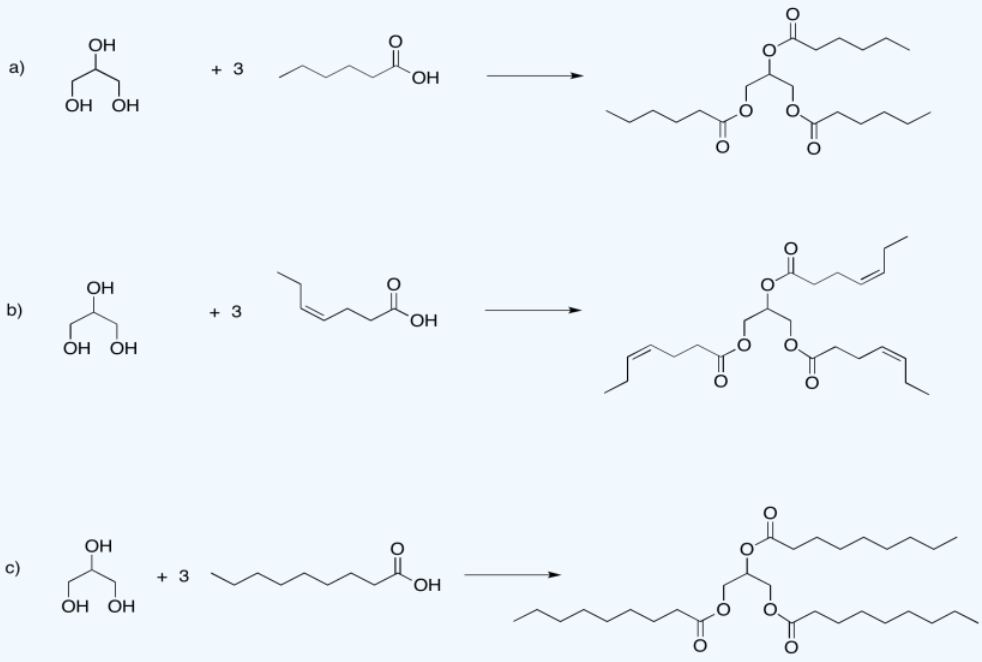
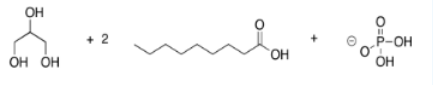


Answer

Exercise 4.13.2

Phospholipids are important in the formation of cell membranes. In a phospholipid, a phosphate replaces one of the alcohols that would otherwise make a triglyceride. Draw the pjospholipid that would result in the following case.



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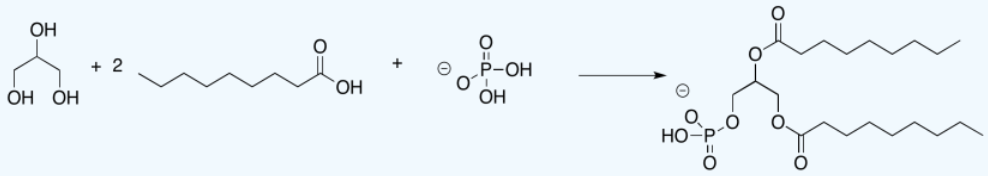


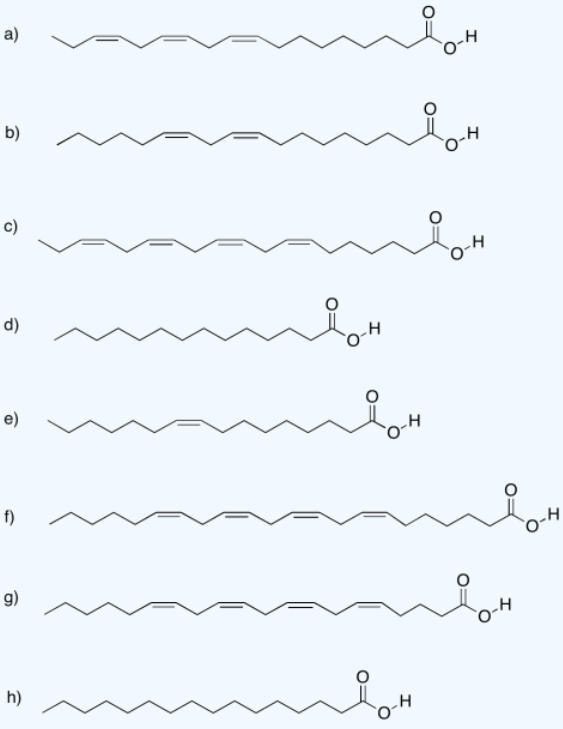
AnswerExercise 4.13.2. Chemical equation: glycerol plus two moles of nonanoic acid plus dihydrogen phosphite.

Exercise 4.13.3

Draw the following fatty acids, based on the notation given.

a. linolenic acid, 18:3 $\Delta^{3,6,9}$
b. linoleic acid, 18:2 $\Delta^{6,9}$
c. stearidonic acid, 18:4 $\Delta^{3,6,9,12}$
d. myristic acid, 14:0
e. palmitoleic acid, 16:1 Δ^{7}
f. adrenic acid, 22:4 $\Delta^{6,9,12,15}$
g. arachidonic acid, 20:4 $\Delta^{6,9,12,15}$
h. palmitic acid, 16:0

Answer



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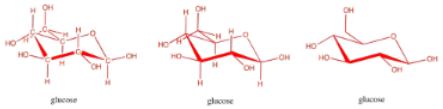
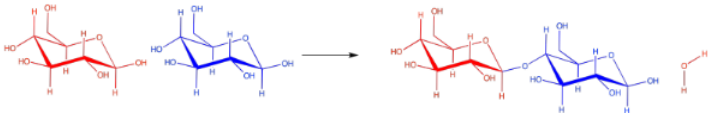
Carbohydrates are an even more crucial form of fuel storage for the cells. Carbohydrates are carbon-based molecules containing lots of OH groups. Glucose is an example. The drawings below are just a reminder that we usually work with skeletal line structures, like the one on the right, rather than the structures with atom labels, like the one on the left, because things get cluttered pretty quickly in the more explicit drawings. However, if you need to re-draw things with atoms to keep track of where everything is, don't be afraid to do that.



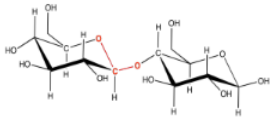
D-glucose depicted in chair conformation. Leftmost structure: all atoms are labelled, including carbons. Middle structure: carbons are unlabelled. Right structure: carbons and hydrogens bonded to carbons are unlabelled. Only oxygen atoms and hydroxy groups are labelled.

Carbohydrates, like fatty acids, are stored in a form in which they are linked together. When needed, they can be unlinked and the individual units, such as glucose, can be sent into energy-generating reactions.

Carbohydrates (or sugars) are connected by "ether linkages". An ether is just a C-O-C unit. In forming an ether linkage, two carbohydrates could come together, attaching one oxygen on one carbohydrate to a carbon on the next, and releasing a water molecule. It's another condensation reaction, like the ester-forming one. This time, a two-carbohydrate pair is formed, called a "disaccharide". The individual carbohydrates are called "monosaccharide"s.



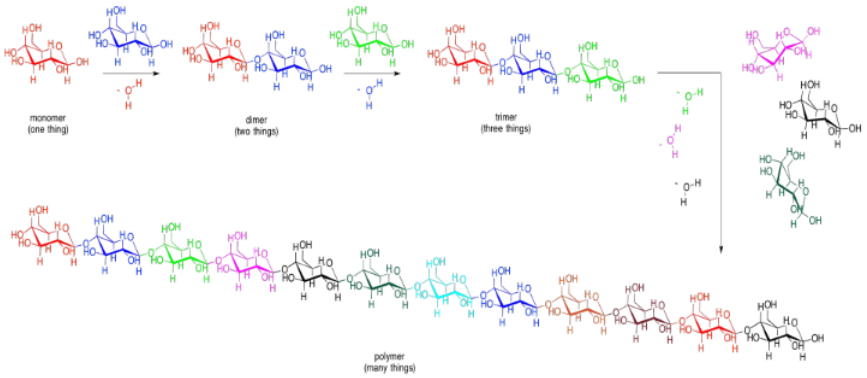
There are lots of carbons that the oxygen atom on a neighbouring carbohydrate might attach to, but the same one is always used. It's the carbon that already has two oxygens attached to it. The carbon in the right-hand corner of the red glucose molecules is an example. As a result, the particular kind of ether linkage between carbohydrates always looks more like C-O-C-O-C. You can see that pattern if you start from the left-hand corner of the blue glucose in the disaccharide, and move leftward across the gap onto the red glucose.



Two glucose molecules with a glycosidic linkage between them. The acetal carbon and the two oxygens it is bonded to are highlighted in red.

This sort of double-ether linkage is called a "glycoside linkage" in biochemistry. Don't get it confused with the triglyceride made from a fatty acid plus glycerol. In organic chemistry, this C-O-C-O-C unit is called an "acetal".

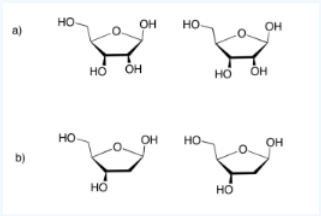
These bonds can be used to connect lots of carbohydrates together. Two monosaccharides can be linked to make a disaccharide. A third one would make a trisaccharide. Lots of them connected in a chain would be called a polysaccharide. Other small molecules can be connected in chains, too, although not always by glycoside or acetal linkages. When many small molecules have been connected into one big molecule, we call that molecule a "polymer". That word just means it is made of many things, all put together. A polysaccharide such as cellulose (below) is an example of a biological polymer.



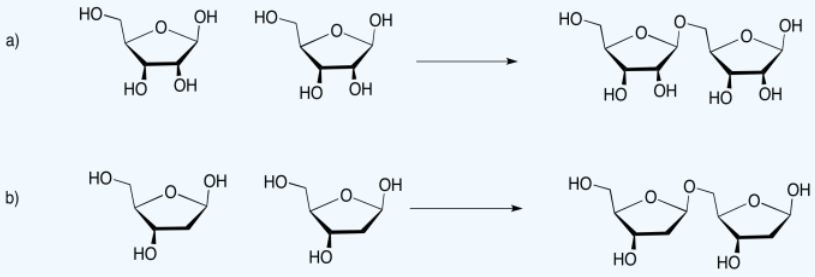
Schematic showing multiple monomers of carbohydrate being linked together via dehydration. A monomer is one unit. A dimer is two units. A trimer is three units. A polymer is many units.

Exercise 4.13.4

Draw the disaccharides that would result in each of the following cases. Make sure to use the acetal (glycoside) carbon on one molecule; you can link to the primary alcohol (the -CH_2-OH group) on the other.



Answer



Answer

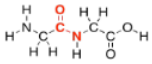
Amino acids are a third general class of biological molecules. Amino acids are important because they are collected together into polymers called proteins. Proteins function like machines; they carry out most of the tasks needed to keep an organism alive.

Amino acids get their name from the fact that they contain two different organic functional groups: an amine (NH_2) and a carboxylic acid (CO_2H). In order to make proteins, the amine nitrogen on one amino acid connects to the carbonyl carbon (on the C=O group) of the next. Once again, an OH is lost from one molecule and a proton from the other, to make water.

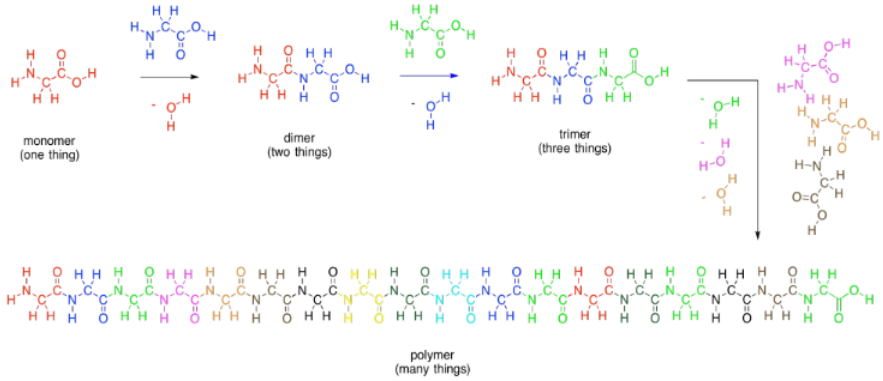
Chemical formula. Two amino acids combine via dehydration to form a peptide bond and dipeptide as well as water as a byproduct.

As in lipids, exactly how these two molecules eventually come together is slightly more complicated than that, but this picture is good enough for now. Two amino acids (two monomers) connect together to make one bigger molecule (a dimer) and a water molecule. That dimer is often called a "dipeptide". The bond that has formed between the nitrogen and the carbonyl is called an

"amide" bond in organic chemistry, becasue the funtional group formed is called an amide. In biochemistry, this bond is often called a "peptide linkage". It's what holds the two pieces together in a dipeptide.



As with carbohydrates, amino acids can be linked into long chains. They can make polymers. A polymer of amino acids is called a polypeptide. A protein is just an extremely large polypeptide, in which hundreds of amino acids are connected together in a long chain.



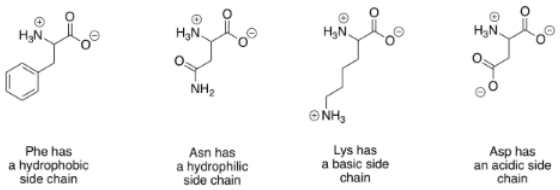
Progression of polypeptide chain length as amino acids are added. A monomer is one unit. A dimer is two units. A trimer is three units. A polymer is many units.

Lipids and carbohydrates are used for storage, among other things, and so it is useful to be able to undo ester linkages and acetal linkages, to get individual fatty acids and carbohydrates again when we need to consume energy. If we get desperate, we could also break down our proteins and polypeptides and get energy from them, but we don't usually use polypeptides for energy storage, because they have so many more valuable roles to play.

In fact, peptide bonds are a little stronger and harder to break than either ester linkages or acetal (glycosidic) linkages. That's because of a resonance contributor to the structure. Notice that oxygen is more electronegative than nitrogen. That oxygen is able to pull the lone pair on the nearby nitrogen closer, forming an N=C π bond that makes the amide stronger and more stable. We still have special enzymes that can break down proteins in our food, but it's not easy.

Two forms of the peptide bond, highlighted in red, in a dipeptide. Left: neutral form with carbon double-bonded to the oxygen and a lone pair on nitrogen. Right: the carbon is double-bonded to nitrogen and single-bonded to oxygen. Oxygen has a negative charge and three lone pairs. Nitrogen has no lone pairs and a positive charge.

There are a huge variety of proteins that can result from linking amino acids together in this way. That diversity largely results from the fact that lots of different compounds have the same basic amino acid structure, but with modified groups called "side chains". A few examples are shown below.



Skeletal structures of four amino acids. Left: Phenylalanine, with hydrophobic benzylic side chain. Middle left: Asparagine, with hydrophilic amide side chain. Middle right: Lysine, with basic amine side chain. Right: Aspartate, with acidic carboxylic acid side chain.

There are actually twenty common amino acids in biology. To help organize these compounds, people normally use four different categories that correspond to the properties of the side chains. Two groups of amino acids commonly have charged side chains under biological pH conditions. Acidic side chains give up a proton easily (H^+) and become negatively charged as a result; there

are two of these, aspartate and glutamate. (Aspartate is just the word for the negatively charged form of aspartic acid; that name is often used because it is shorter than "aspartic acid".) Basic side chains pick up protons easily and are positively charged as a consequence. There are three of them, although only two are usually protonated at neutral pH; the other becomes protonated under slightly more acidic conditions (lower pH).

The polar (or "hydrophilic") amino acids are those that would interact easily with polar water molecules in the cell. You can usually spot them by the presence of strong dipoles in the side chains. Strong dipoles are charge separations between two different atoms that have very different electronegativity values. For example, C-O and O-H bonds are polar. In contrast, the non-polar (or "hydrophobic") amino acids have side chains that lack strong dipoles. For example, C-C and C-H bonds are not very polar, because the electronegativity differences between the atoms are small.

Here are all of the common amino acids, arranged according to category, as they would appear when linked in a peptide chain.

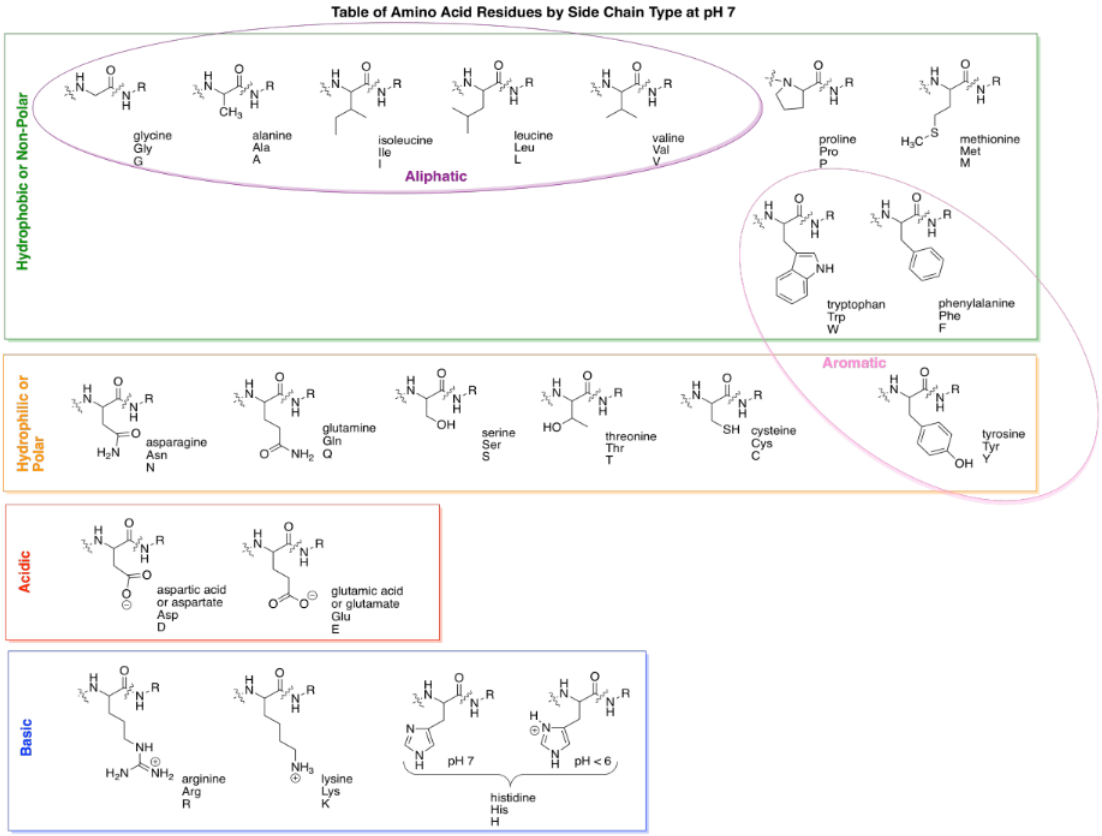


Table of amino acid residues by side chain type at pH 7. Amino acids are grouped into four categories: hydrophobic or nonpolar, hydrophilic, acidic, and basic.

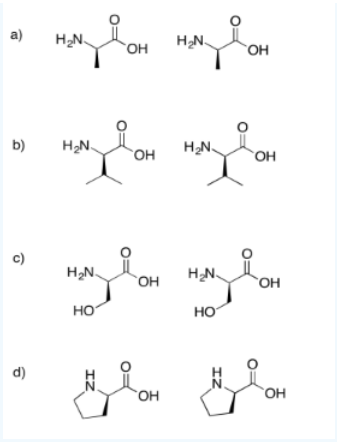
A couple of the amino acid side chains are sort of on the edge in terms of polarity, and some textbooks will place them in a different category. For example, tyrosine has an O-H bond and so is capable of hydrogen bonding with water. That makes it pretty hydrophilic. However, the majority of the side chain contains non-polar C-C and C-H bonds, so sometimes you will see it grouped with hydrophobic side chains.

One more pair of sub-groups you will sometimes see are the aromatic and aliphatic amino acids. Aliphatic ones contain carbon chains, but not other functional groups, whereas aromatics contain "aromatic rings" such as benzene. Aromatics are usually six-membered rings with double bonds alternating all the way around. They are flat groups that can stack on top of each other and sometimes that property can be important.

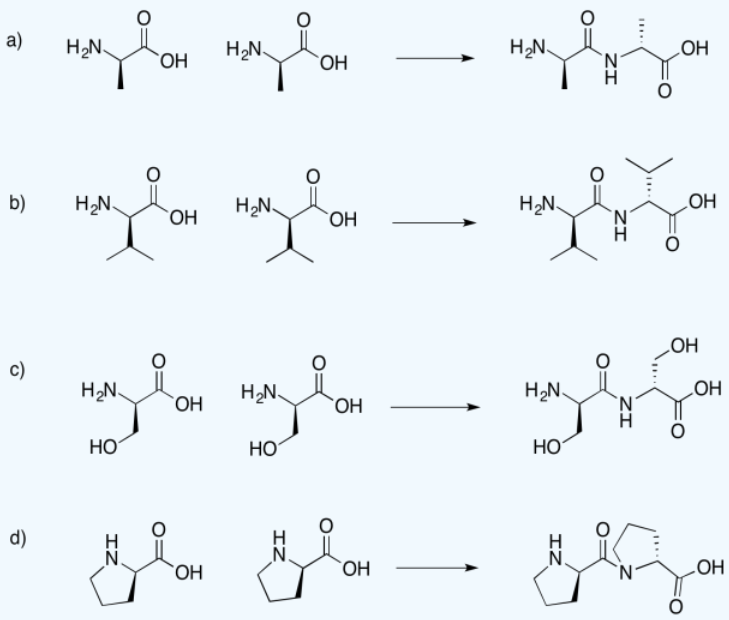
? Exercise 4.13.5

Draw the dipeptides that would result in each of the following cases.

If you don't know what the wedged and dashed lines in the drawing mean, don't worry about it. They just represent different orientations in space. You will learn about these representations in a later topic called "stereochemistry".



Answer



Answer

Exercise 4.13.6

Draw the possible dipeptides that would result in each of the following cases.

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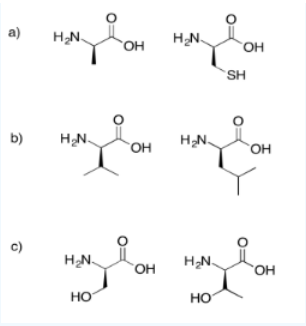
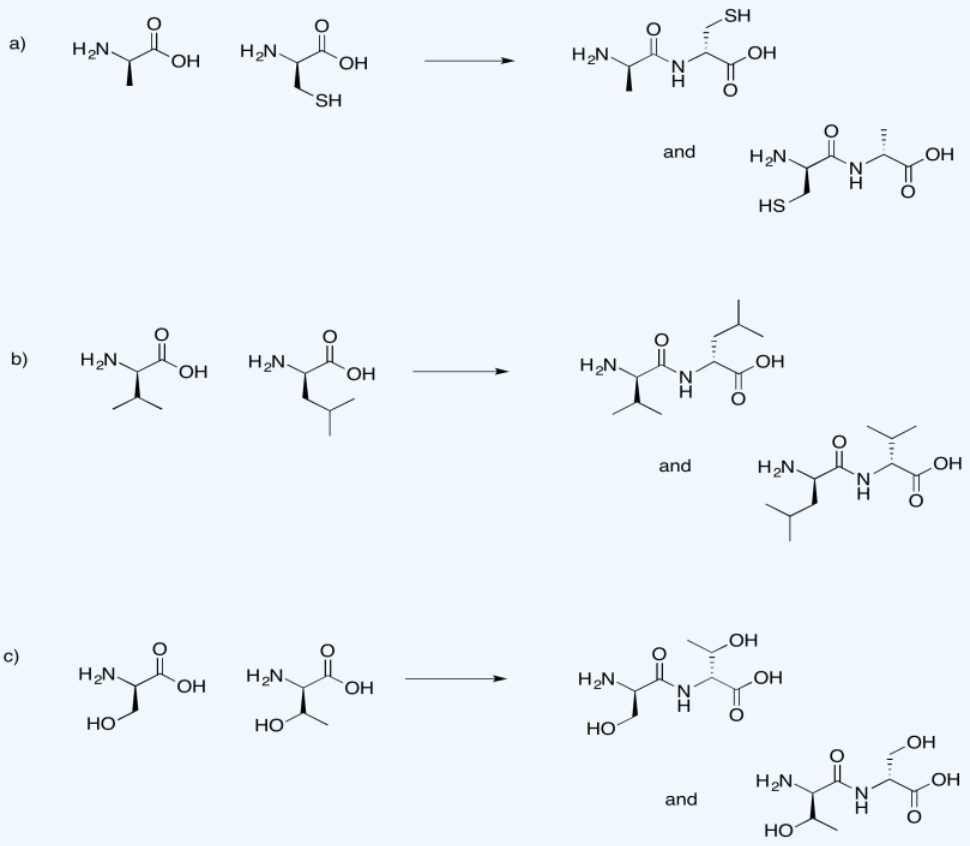


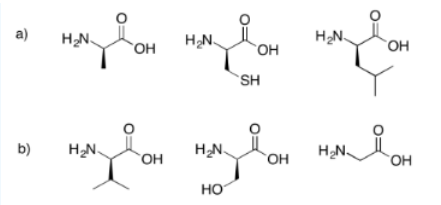
Answer



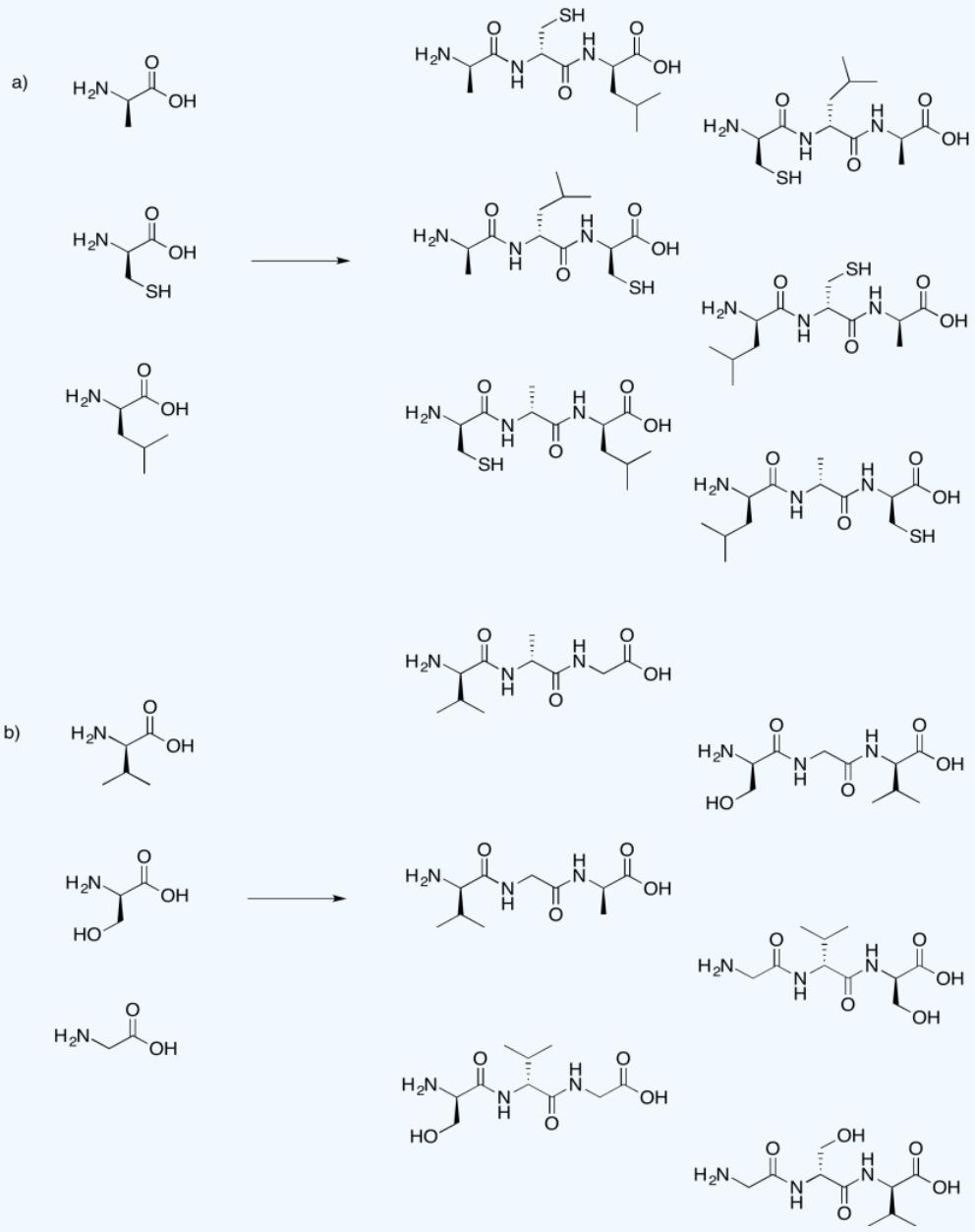
Answer

Exercise 4.13.7

Draw the possible tripeptides that would result in each of the following cases.



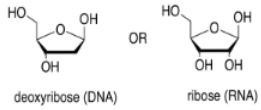
Answer



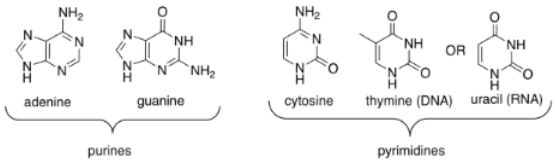
Answer

Possibly the most well-known biomolecules are the nucleic acids, DNA and RNA. These compounds are examples of co-polymers. Like complex carbohydrates, they are composed of individual molecules that have become covalently bonded to each other to form polymer chains. However, DNA and RNA always contain three different types of monomer: bases, sugars, and phosphates.

The sugar is the part that gives rise to the D in DNA or the R in RNA. Ribose, found in RNA, is a five-membered ring with oxygens on each carbon, mostly as OH groups. Deoxyribose, found in DNA, is almost identical, but is missing one OH group.



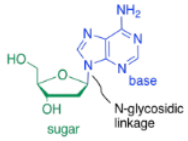
One of four different bases can attached to this sugar in DNA, and one of four different bases can be attached to this sugar in RNA. Three of those bases can be found in either molecule: adenine, cytosine, and guanine. The fourth is unique to either DNA (thymine) or RNA (uracil).



Bond-line structures of the nitrogenous bases. From left to right: adenine, guanine, cytosine, thymine (DNA), and uracil (RNA). A bracket groups adenine and guanine as the purines. A bracket groups cytosine, thymine, and uracil as pyrimidines.

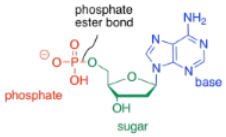
These five bases (so called because, like the basic amino acid side chains, they can pick up protons) fall into two categories. Pyrimidines (peer-IM-id-eens) each contain a six membered ring. Purines (PURE-eens) contain both a six-membered and a five-membered ring. These categories are important because of "base-pairing"; that's when a strand of DNA can bind to a complementary strand via hydrogen bonding between a base on one strand and another base on another. In base-pairing, a purine always binds to a pyrimidine partner: guanine to cytosine, and adenine to thymine (in DNA) or uracil (in RNA).

The bases are covalently bonded to sugars at the glycoside position - that same place sugars link to each other in carbohydrates. The new bond is called a N-glycoside bond. The new compound is called a nucleoside.



A diagram of an N-glycosidic linkage. The sugar is highlighted in green. The base is highlighted in blue.

The third type of molecule that comes together to form the nucleic acid co-polymer is a phosphate. It becomes covalently bonded to the primary alcohol group at the other end of the ring from the base. The bond between the phosphate and the sugar is called a phosphate ester bond. The new compound is called a nucleotide.



A diagram of a sugar-phosphate backbone with a nitrogenous base. The phosphate group is highlighted in red and attached with an ester bond to the sugar. The sugar is highlighted in green. The base is highlighted in blue.

To form a co-polymer, another phosphate ester bond forms with the sugar of another nucleotide. The phosphate between the two sugars is sometimes called a phosphodiester linkage, meaning that the phosphate is forming two esters at once to bridge the two sugars.

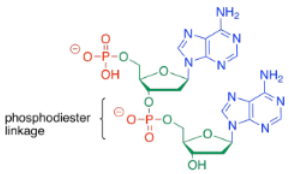
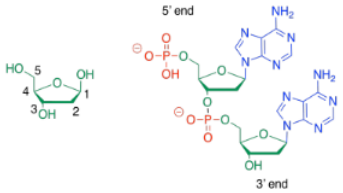


Diagram of a phosphodiester linkage between two nitrogeneous bases. The phosphate groups are highlighted in red. The sugar backbones are highlighted in green. The bases are highlighted in blue.

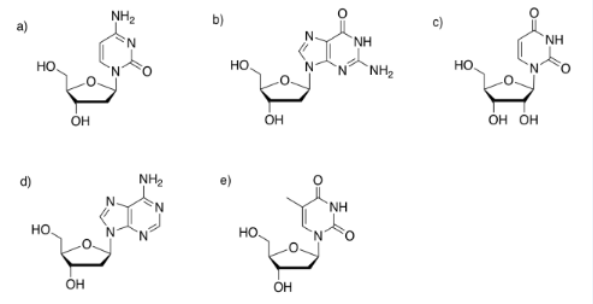
Sometimes, people will refer to the 3'-end or the 5'-end of a nucleic acid strand. Those numbers refer to a system of numbering the carbons in the sugars. If you are talking about the end of the DNA chain that is closest to carbon number 3 of the nearest sugar, you are talking about the 3' end.



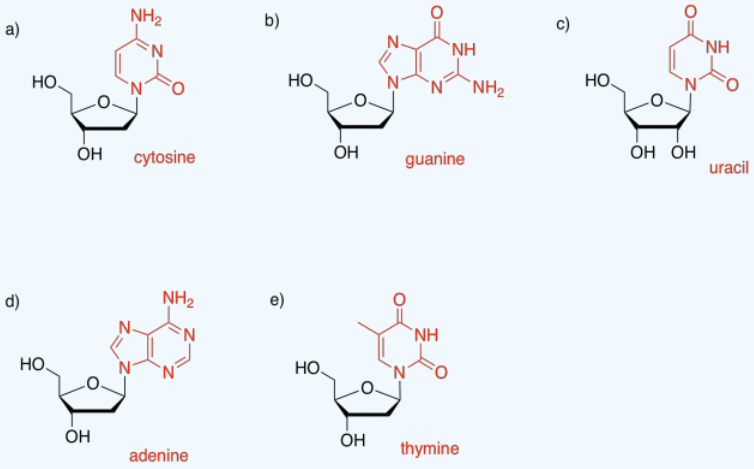
Left: deoxyribose with the carbons numbered. The deoxygenated carbon is labelled C2. Right: two deoxyriboses linked together. The hydroxy end on the 3' carbon of the bottom deoxyribose is labelled "3' end". The phosphate of the top deoxyribose is labelled "5' end".

Exercise 4.13.8

Identify the base in each of the following nucleosides.



Answer



Answer

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4.14: Drawings for Large Biological Compounds

Line structures will be the most common type of structural drawing you see in these pages. You will also see some others used for specific purposes, and those representations are explained here.

Sometimes even drawing a line structure is too much. Proteins often contain thousands of atoms. Presenting all that information about bonding could make the drawing hard to read, especially in a three-dimensional shape.

A picture of a molecule can be presented in several ways. A ball-and-stick model gives a pretty good idea of where all of the atoms are, and how they are connected. The balls represent the atoms and the sticks represent the bonds. An example of a ball-and-stick picture of a protein, bovine low molecular weight protein tyrosyl phosphate, binding to inorganic phosphate, is shown below.

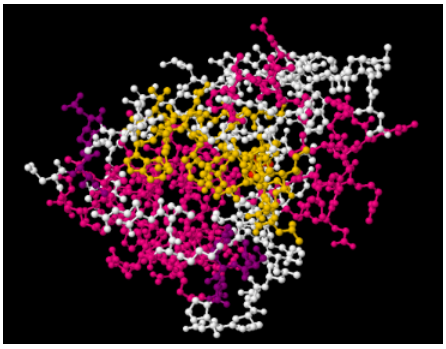

Figure 4.14.1: A ball-and-stick drawing of a protein, bovine low molecular weight protein tyrosyl phosphatase, binding to inorganic phosphate.

Go to **Animation IM14.1.** A three-dimensional model of bovine low molecular weight protein tyrosyl phosphatase, binding to inorganic phosphate.

There are a couple of problems with viewing a protein this way, though. The first problem is that we usually don't know where the hydrogen atoms are, so they are missing from the ball-and-stick structure. Why is that?

It's because protein structure is usually determined experimentally using X-ray crystallography. That means someone has gone to the trouble of isolating a pure sample of protein from an organism. They dissolved the protein very carefully, then coaxed the protein to form crystals. There are different ways to do that, but usually it involves cooling the solution, so that the solvent no longer has enough energy to keep all of the molecules dissolved, or else evaporating a little of the solvent, so that there is no longer enough solvent to keep everything dissolved. This process might take weeks. At that point, they could carefully lift a single crystal out of the solution and mount in on an X-ray diffractometer. When X-rays shine through the crystal, they essentially bounce off the atoms and scatter in different directions. By measuring where the X-rays land, and using some computer software that exploits those imaginary numbers that you learned about in high school but didn't think were useful for anything, the researcher can determine the location of every atom in the molecule (if they get lucky). Hydrogen atoms are just too small to locate with any certainty, however.

- X-ray diffractometry can reveal the location of every atom in a molecule, other than hydrogen.
- X-ray diffractometry requires that the compound is crystalline.

The other problem is that a ball-and-stick model of a protein contains an awful lot of atoms. The structure gets pretty complicated. The example here is a pretty small protein; its molecular weight is only about 35,000 D (D stands for Daltons; a Dalton is just another term for atomic mass unit or amu, but it is used more commonly in biochemistry and macromolecular chemistry). In larger proteins, its difficult to make sense of the pile of atoms we see in a ball-and-stick structure.

Similarly, we could view the protein in a space-filling model. The space-filling model probably gives a better picture of what the molecule would look like in terms of how much room it would take up, or what its overall shape would be. The advantage of this view is that it allows a biochemist to see how other molecules might interact with the protein.

For example, maybe a protein acts as an enzyme; it catalyses reactions that are essential for our survival. Bovine low molecular weight protein tyrosyl phosphatase is an example. It's bovine, which means it is found in cows. It's a phosphatase, which means it removes phosphate groups from other proteins. That is an important regulatory event in biochemistry. Adding a phosphate group or taking a phosphate group off another molecule, including another protein, often acts as an "on/off" switch, so that an organism can control when certain reactions take place. This is a tyrosyl phosphatase, so it specifically removes phosphate that has been added to

a tyrosine residue in the substrate protein. By looking at the space-filling model, a biochemist may be able to see where the tyrosine from the substrate can fit into the bovine low molecular weight tyrosyl phosphatase, so that the enzyme can do its job and chop off the phosphate.

The trouble is, most proteins look pretty much like blobs to the untrained eye. To make things a little easier, there are shortcuts that biochemists use when visualising proteins.

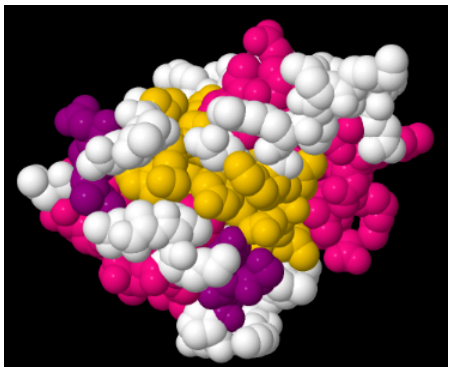

Figure 4.14.2: A space-filling drawing of bovine low molecular weight protein tyrosyl phosphatase with bound inorganic phosphate.

One abbreviation used in biochemistry is sometimes called a wireframe structure. In a wireframe structure, none of the atoms are labeled and all of the hydrogens are omitted. That means it is difficult to tell a carbon from a nitrogen. However, biological macromolecules like DNA and proteins are made of a few simple building blocks. A very experienced reader would remember the structures of these building blocks. She would be able to tell what atoms go in which place based on the shapes of the building blocks.

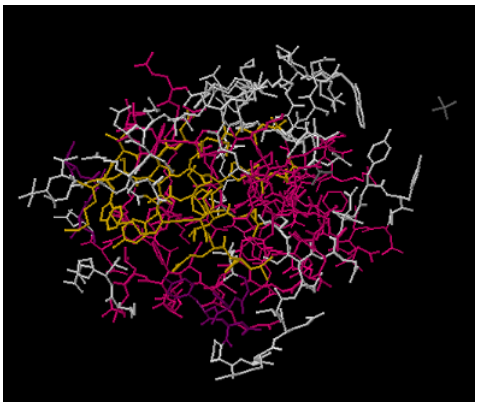

Figure 4.14.3: A wireframe drawing of bovine low molecular weight protein tyrosyl phosphatase with bound inorganic phosphate.

That's still a pretty complicated picture. There are other views that are simplified further.

A protein is made of amino acids strung together in a chain. The chain does not hang out in a long, straight line. It folds up into a coil, and the shape of that coil influences its biological activity. Sometimes a biochemist may be interested in how the chain of amino acids coils up. A backbone structure only shows the atoms that are connected directly in a row from one end of the chain to the next. Any atoms that hang out along the sides of the chain are left off.

Figure 4.14.4: A backbone drawing of bovine low molecular weight protein tyrosyl phosphatase with bound inorganic phosphate.

Those parts that were left off are pretty important in terms of the function of the protein. They are the parts that make alanine different from lysine, for example. However, if you are trying to see some basic shapes in the protein, they just end up getting in the way in the picture.

The order in which a chain of amino acids is connected together is called the primary structure of a protein. For example, the amino acids glycine, alanine, tyrosone and arginine could be connected in the order gly-ala-tyr-arg, or ala-gly-arg-tyr, or tyr-gly-ala-arg, and so on. These compounds are isomers of each other. Knowing which isomer we have tells us something about the protein.

The way that chain arranges itself is called the secondary structure. Very often, proteins coil up into spirals or helices. This helical structure is similar to that of DNA. Another possible secondary structure is a beta-sheet, which is sort of wavy, a bit like a sheet of corrugated steel. These secondary structures are held in place by hydrogen bonds between different amino acids. (You can see the structure-property relationship chapter to review hydrogen bonding).

In the backbone drawing of bovine low molecular weight tyrosyl phosphatase, you can see where parts of the backbone are coiled up into alpha-helices. These parts are coded in pink in the picture. You can also see some sections that form pleated beta-sheets. Those are the yellow, zig-zag sections next to each other.

Usually, the entire protein does not adopt the same secondary structure. There may be a section that coils into a helix and another section that forms a beta-sheet. The helical domain and the beta-sheet domain then arrange themselves and pack together somehow. The arrangement of domains in the protein is called tertiary structure.

Figure 4.14.5: A cartoon drawing of bovine low molecular weight protein tyrosyl phosphatase with bound inorganic phosphate.
A cartoon of a protein, showing alpha helices and beta sheets. Different sections of the protein are color coded.

Seeing the tertiary structure in a protein can be difficult even with a backbone structure. Instead, ribbon drawings or cartoon structures are used to convey how beta-sheets and helices are arranged in a protein.

Sometimes a protein is made of more than one chain of amino acids. The arrangement of different coils of amino acids all stuck together is called quaternary structure. Bovine low molecular weight tyrosyl phosphatase is a monomeric structure; it is just made of one protein chain, so we don't see a quaternary structure in this case.

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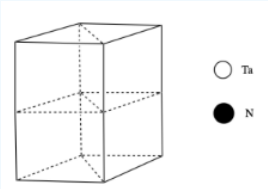
4.15: Application Problems

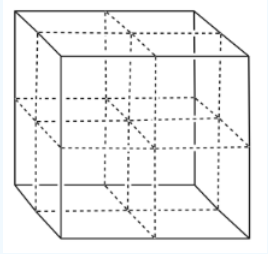
Exercise 4.15.1

Tantalum nitride (TaN) is a very hard material used in automobile transmissions and other high-performance applications.

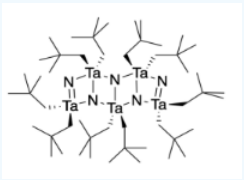
a. Given its position in the periodic table, what is the charge on nitride ion?
b. Therefore, what is the charge on tantalum in tantalum nitride?
c. Tantalum nitride most commonly adopts a hexagonal structure. The drawing below shows one unit cell. Place a tantalum atom in each corner of the unit cell.



d. Tantalum nitride is a layered structure. The nitrides lie in the same planes as the tantalum atoms. Within each layer, there is one nitrogen in between each pair of tantalum atoms. Add the nitrogens to each layer.
e. How many tantalums are in a unit cell? Show how you know.
f. How many nitrides are in a unit cell? Show how you know.
g. The resulting formula doesn't match our expectations. Add atoms to the middle layer to balance things out.
h. What is the coordination geometry of the atoms in the middle layer? Heating tantalum metal under dinitrogen or ammonia leads to formation of hexagonal tantalum nitride. What if other methods could lead to other structures of the same compound? These new structures could also have useful properties.
i. Tantalum nitride also forms a rare cubic phase. In this phase, assume the nitrides form a face-centered cubic array, with tantalum in the octahedral holes. Fill in the atoms.



Wolczanski (Cornell University) reported the synthesis of a molecular tantalum nitride compound (adapted with permission from Banaszak Holl, M. M.; Wolczanski, P. T.; Van Duyne, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 7989-7994; Copyright 1994 American Chemical Society).



j) There are two different molecular geometries at tantalum. Add two labels pointing to two tantalum atoms (example on right) describing their different geometries.

k) There are two different molecular geometries at nitrogen. Add two labels pointing to two nitrogen atoms (example on right) describing their different geometries.

l) There are two different tantalum-nitrogen bonds in this compound. Identify which bond length corresponds to which tantalum nitrogen bond(s) by adding two more labels to the drawing.

TaN = 194 nm and TaN = 212 nm

Heating this compound to 800 °C results in formation of the less common cubic form of tantalum nitride.

m) Propose a reason why this compound leads to formation of cubic tantalum nitride instead of hexagonal.

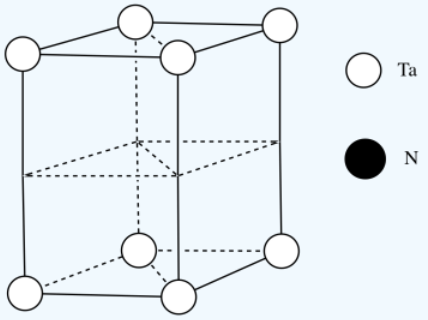
Answer a

N^{3-} would get to a noble gas configuration.

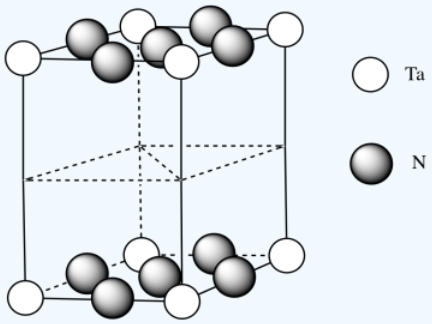
Answer b

Ta^{3+} would balance the charge in TaN.

Answer c



Answer d



Answer e

#Ta = (\frac{1}{6})(\frac{1}{2})(4)\) for the acute corners and (1/3)(1/2)(4) for the obtuse corners

$$= \frac{4}{12} + \frac{4}{6}$$

$$= \frac{4}{12} + \frac{8}{12}$$

= 1 (note that it's the same outcome as the corners of a cube)

Answer f

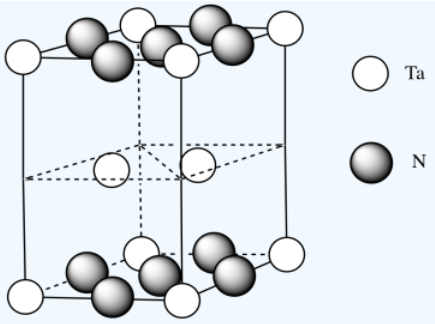
$\# = \frac{1}{4}(8)$ for the edges and $frac12(2)$for the faces

$$= 2 + 1$$

$$= 3$$

Answer g

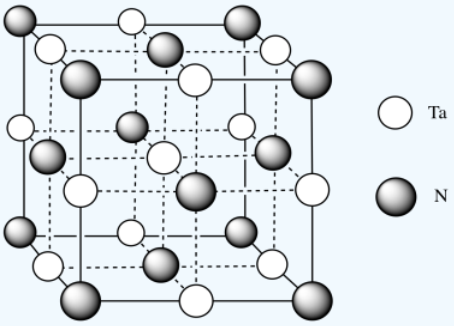
Need 2 more Ta.



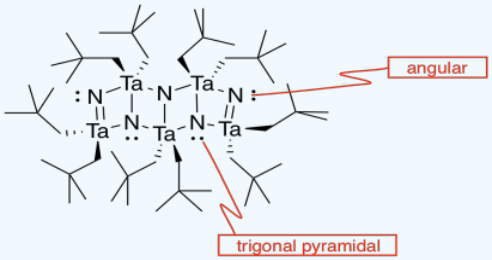
Answer h

Each tantalum has three nitrogens above and three below it. It's almost octahedral, but the top layer of nitrogens is lined up above the bottom layer rather than being twisted 120 degrees to form an octahedron. The geometry is a trigonal prism.

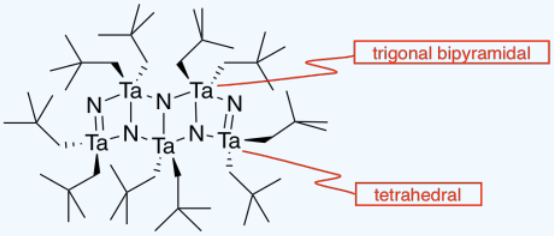
Answer i



Answer j

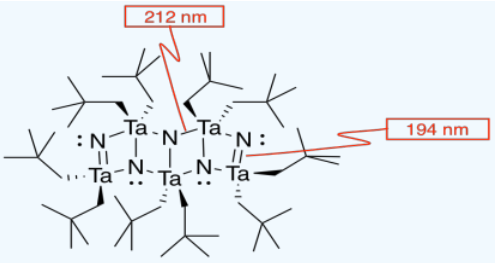


Answer k



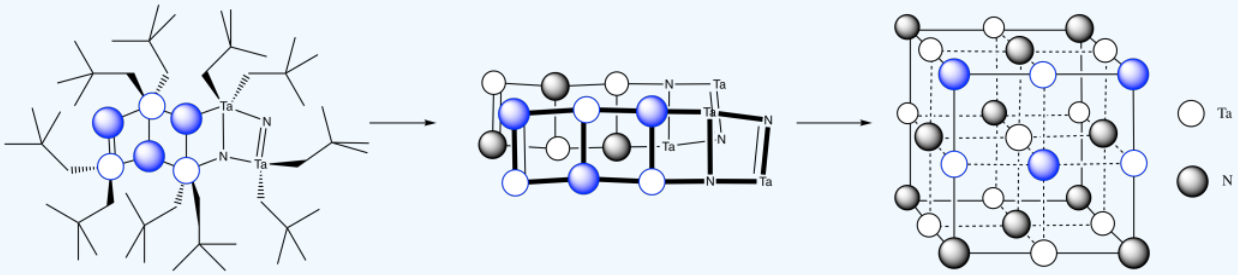
Answer l

The double bonds hold the atoms more closely together than the single bonds.



Answer m

You can imagine the molecules stacking together to make a cubic array of TaN.



Answer to Exercise 4.15.1m, with three steps showing formation of the tantalum nitride cubic cell from the lattice structure diagram.

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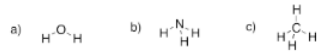
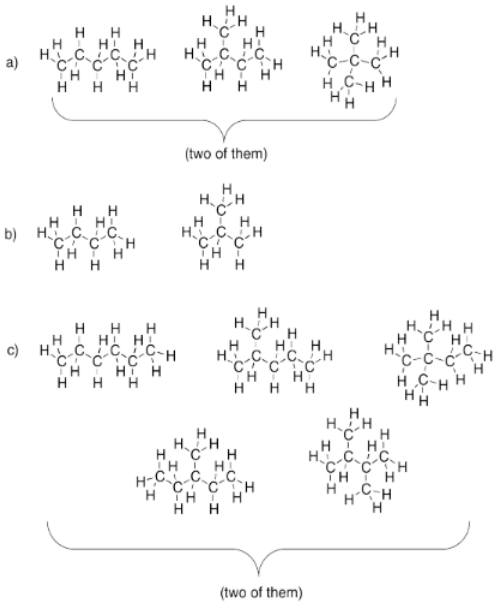
4.16: Solutions to Selected Problems

Exercise 4.1.1:



Exercise 4.1.2



Answers to Exercise 4.1.2, a through c. Underneath answers a and c are brackets surrounding the answers, labelled "(two of them)".

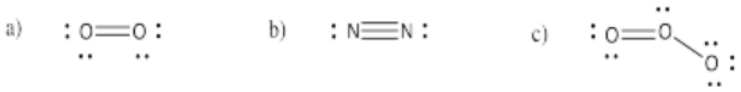
Exercise 4.2.1:

Answers to Exercise 4.2.1, a through d. In order: chlorine gas, hydrogen gas, hydrochloric acid, and fluorine gas.

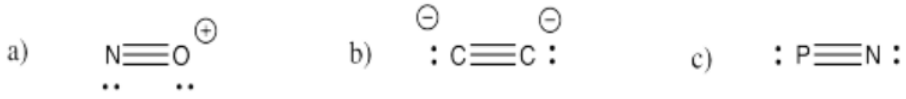
Exercise 4.2.2

Answers to Exercise 4.2.2, a through d. In order: hydroxide, magnesium chloride, thiol, and hypochlorite.

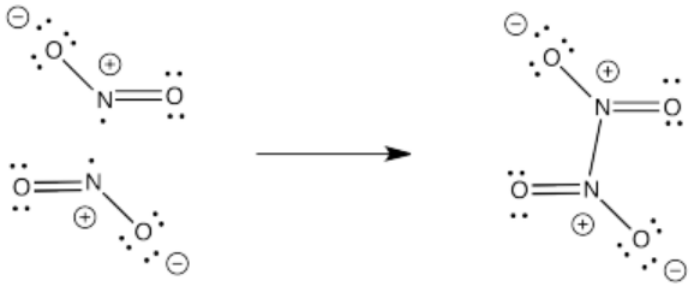
Exercise 4.3.1



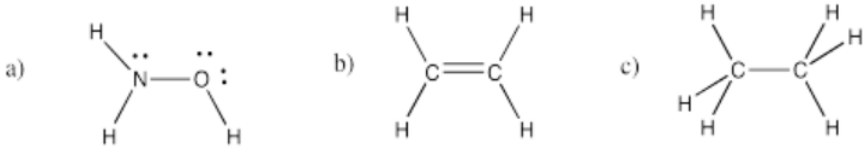
Exercise 4.3.2:



Exercise 4.3.3:



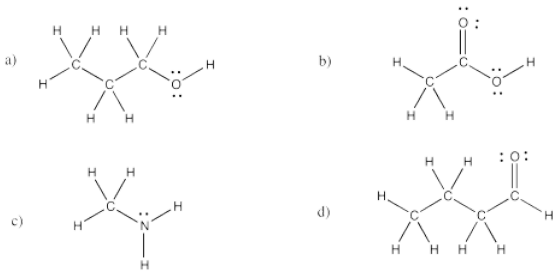
Exercise 4.4.1:

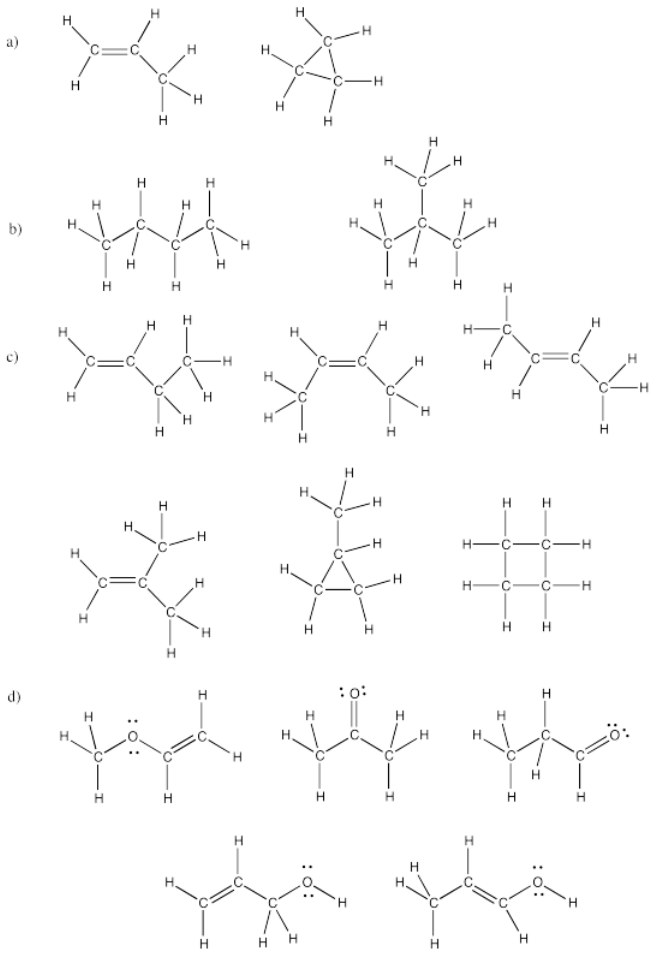


Exercise 4.4.2:

Answers to Exercise 4.4.2, a through d. In order: PH3, carbon disulfide, SiH4, and phosphorus trichloride.

Exercise 4.4.3:





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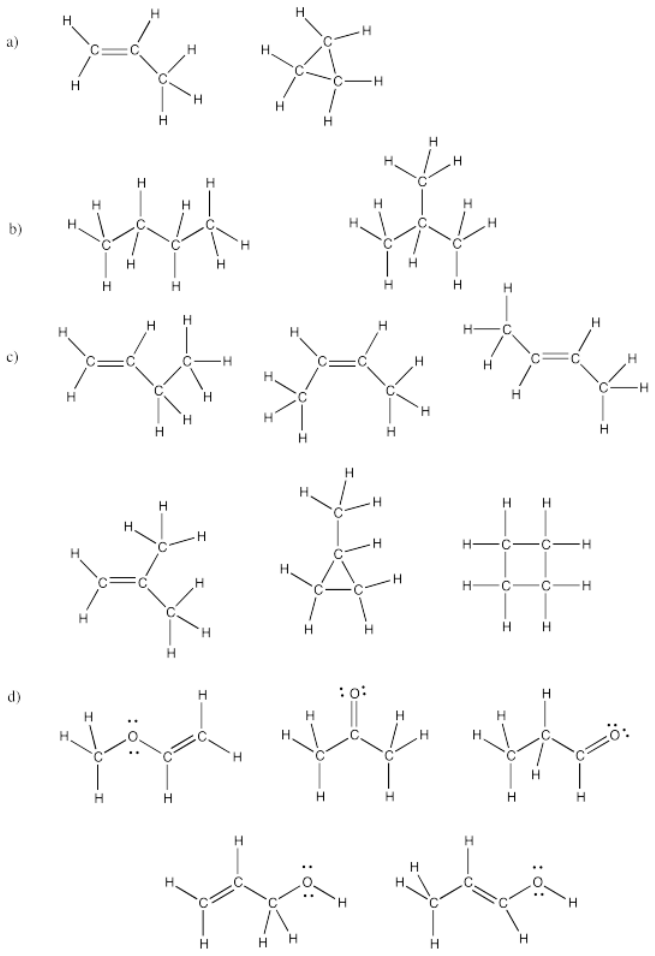
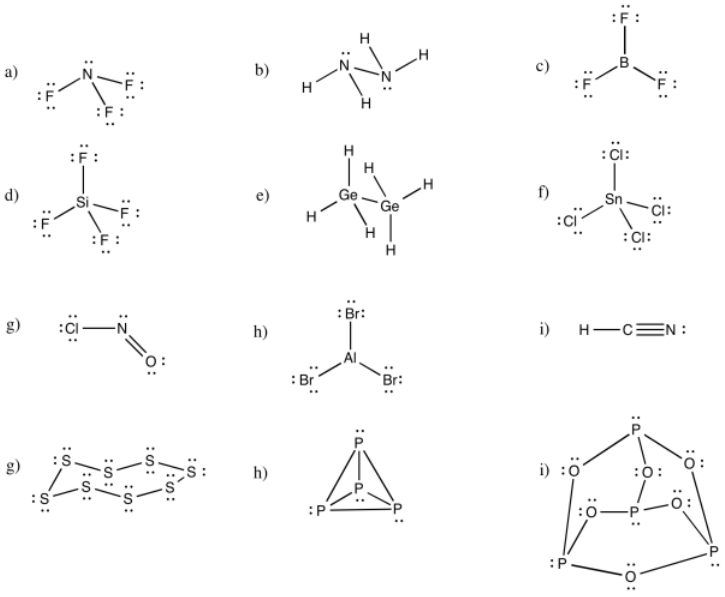


Exercise 4.4.5



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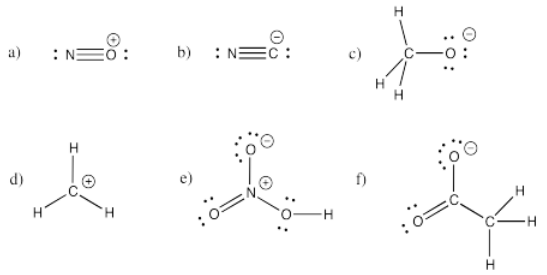
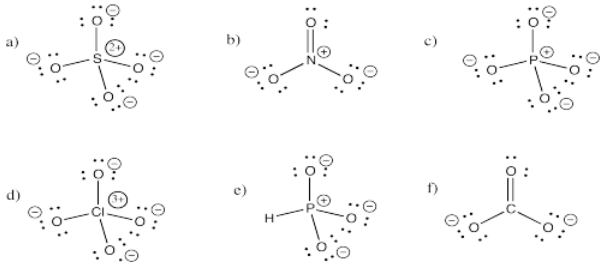
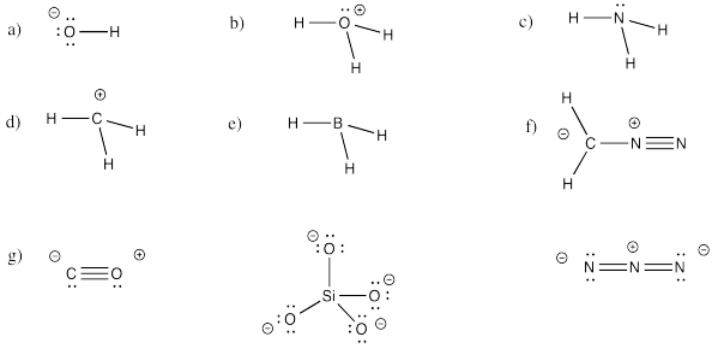


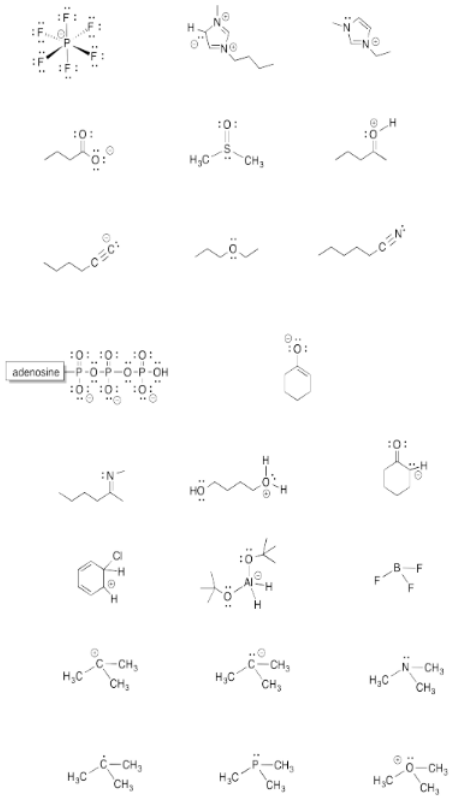
Exercise 4.5.2:



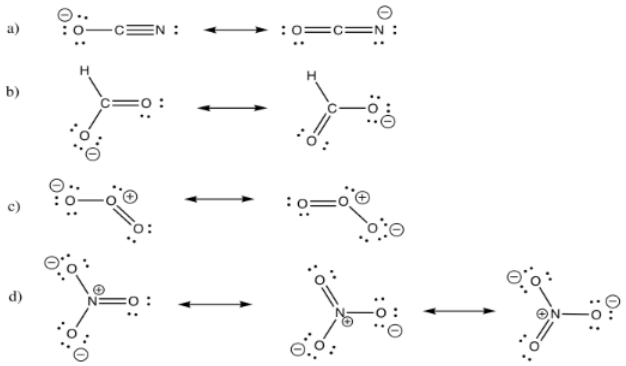
Exercise 4.5.3:



Exercise 4.5.4:



Exercise 4.6.1:



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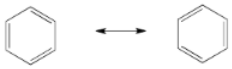
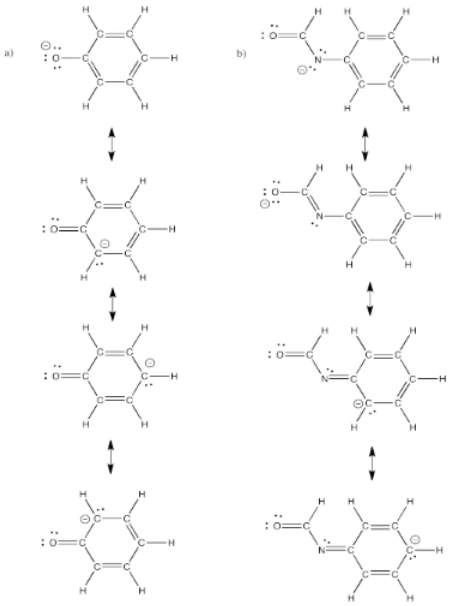


Exercise 4.6.3:



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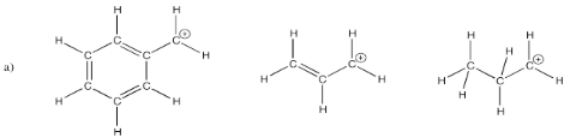

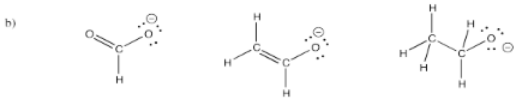

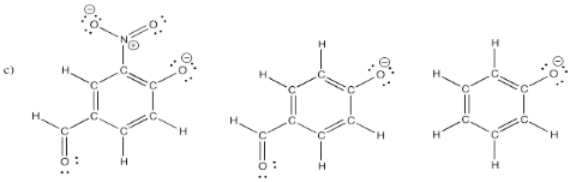

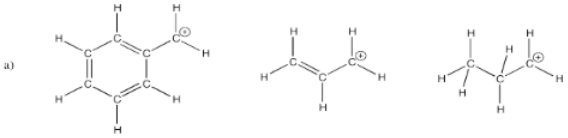

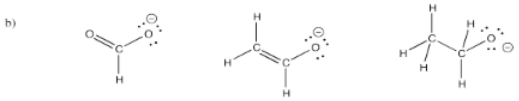

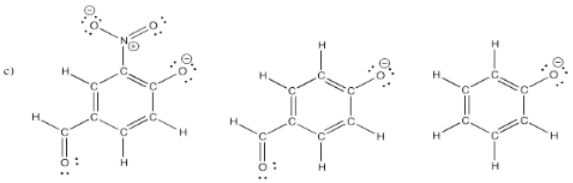

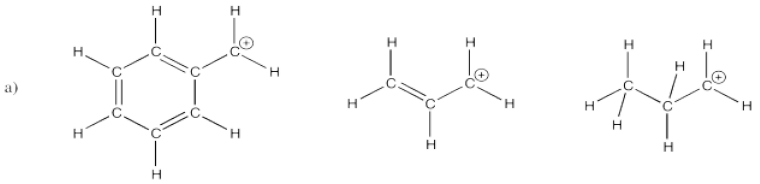

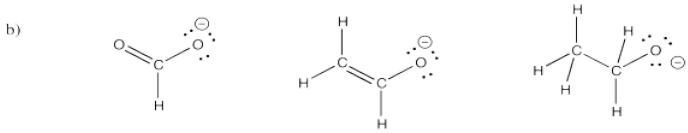

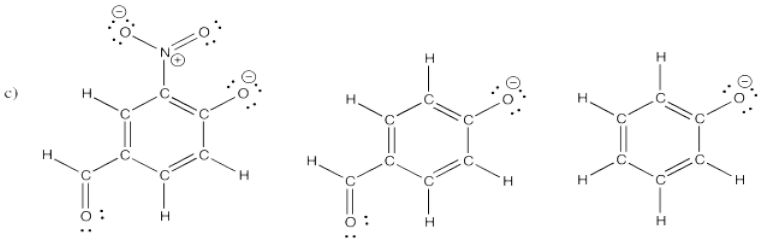

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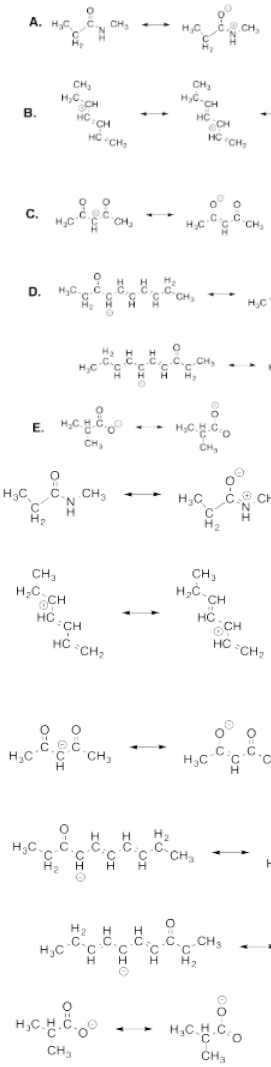
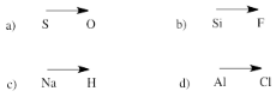


Exercise 4.7.1:



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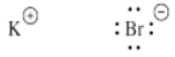
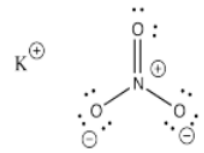
a) 

potassium bromide

b)

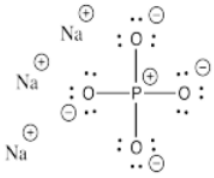
lithium hydroxide

c) 

potassium nitrate

d)

magnesium sulfate

e) 

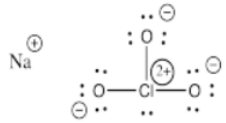
sodium phosphate

f)

sodium sulfite

g)

lithium perchlorate

h) 

sodium chlorate

a)

potassium bromide

b)

lithium hydroxide

c)

potassium nitrate

d)

magnesium sulfate

e)

sodium phosphate

f)

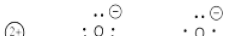
sodium sulfite

g)

lithium perchlorate

h)

sodium chlorate



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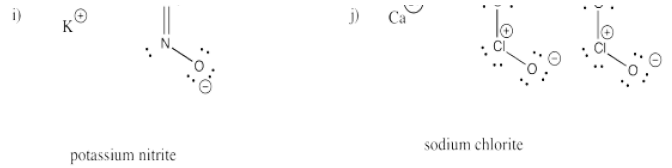
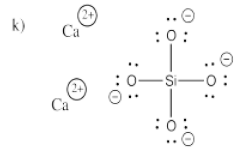
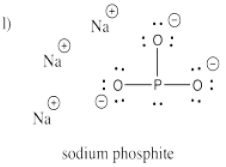


potassium nitrite

sodium chlorite

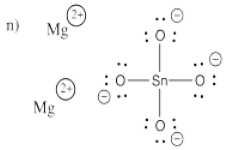


calcium orthosilicate



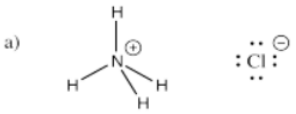
sodium phosphite

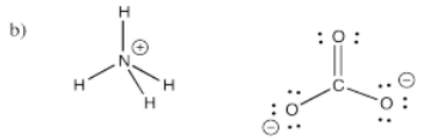
sodium hypochlorite

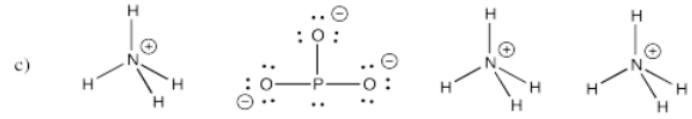


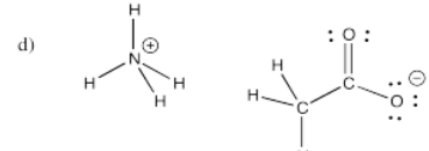
calcium orthosilicate

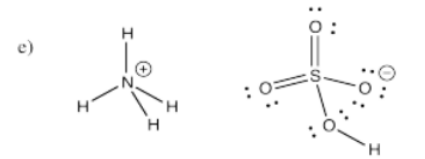
Exercise 4.7.3:











Exercise 4.7.4:

a) bromide b) oxide c) fluoride d) carbonate e) nitrate f) nitrite

g) sulfide h) sulfate i) sulfite j) persulfate k) carbide l) nitride m) arsenide

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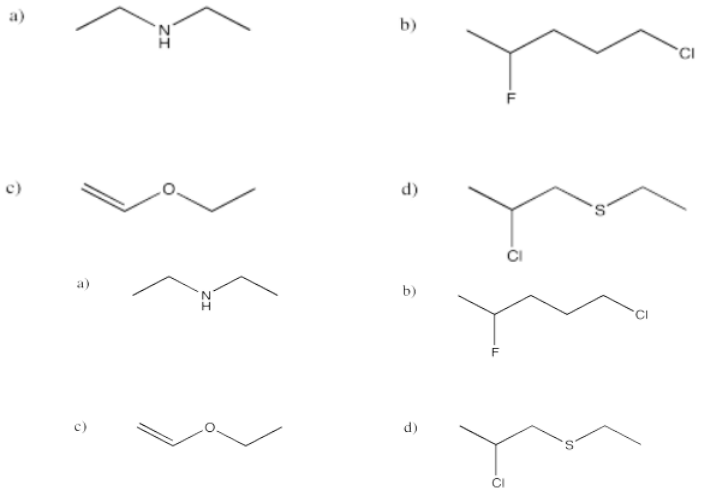
n) phosphate o) phosphite p) iodide q) iodate r) periodate

Exercise 4.8.1:

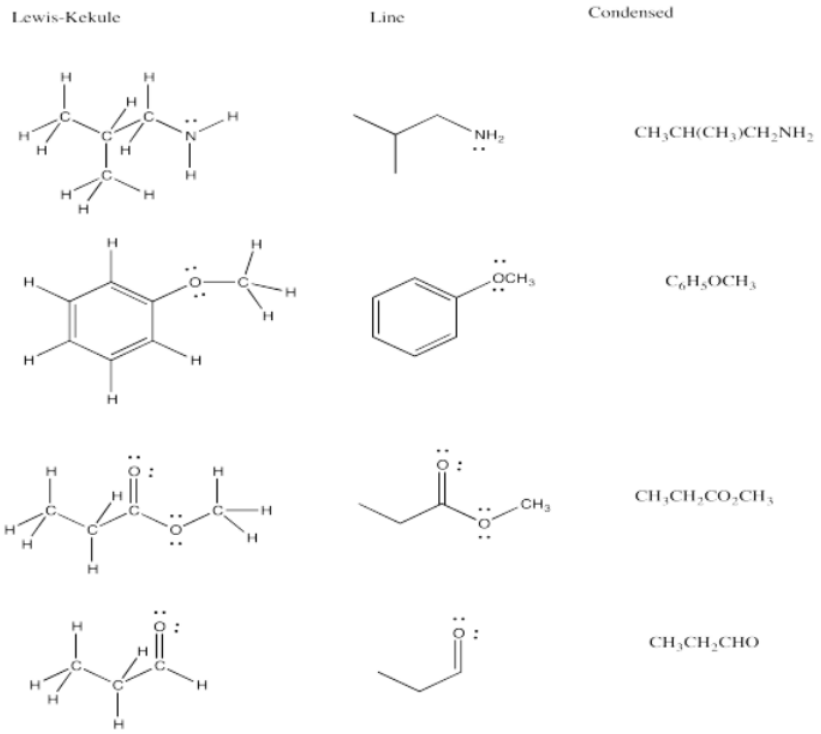


Exercise 4.8.2:

a) $(CH_3)_2CHCH_2CH_2CN$ b) $CH_3CH_2CH(OH)CH_3$

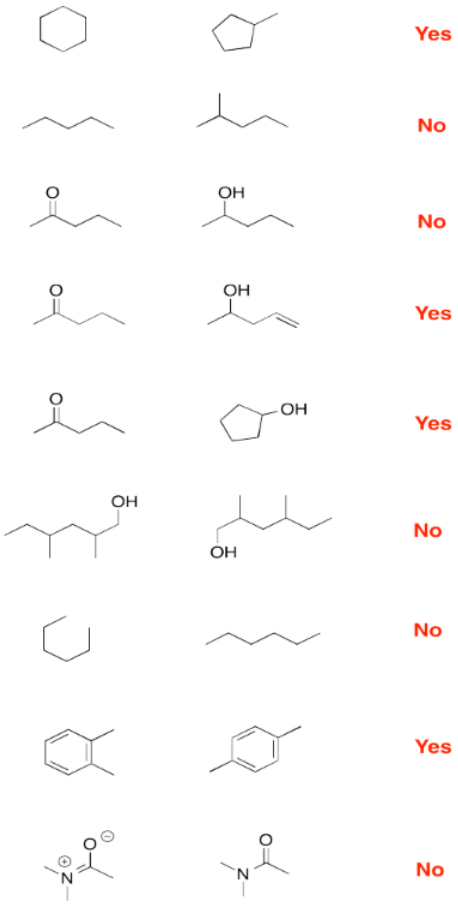
c) $(CH_3)_2CHCOCH_2CH_3$ d) $CH_3CH_2CONHCH_2CH_3$

Exercise 4.8.3:

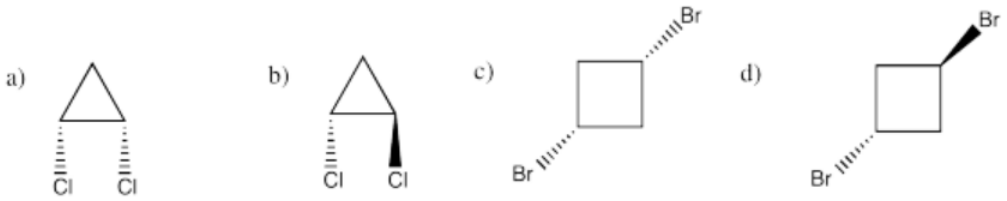


Answers to Exercise 4.8.3, with Lewis-Kekule structures, bond-line structures, and condensed formulae.

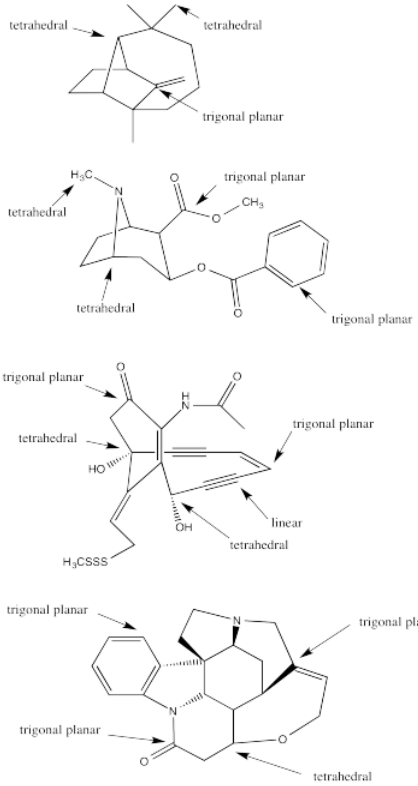
Exercise 4.8.4:



Exercise 4.9.1:



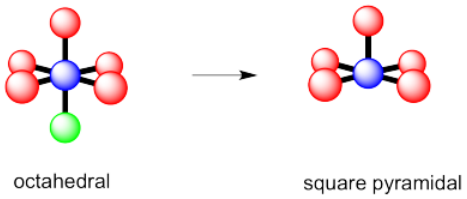
Exercise 4.9.2:



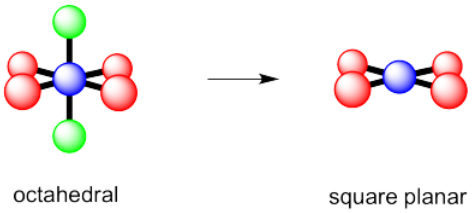
Exercise 4.10.1:

a) octahedral.

b)



c)



Exercise 4.10.2:

a. trigonal bipyramidal

b. This time there could be two different answers.

If the lone pair occupies one of the axial positions, it would be pretty close to three other atoms.

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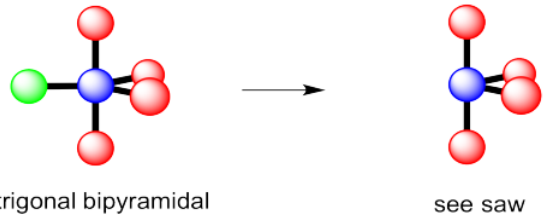
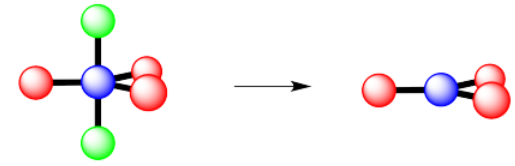
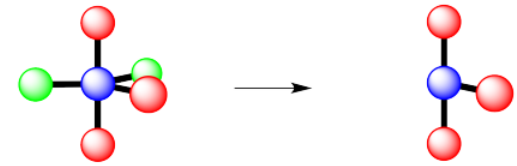
If the lone pairs occupies one of the equatorial positions, it would be pretty close to only two other atoms. The other equatorial atoms are pretty far away.



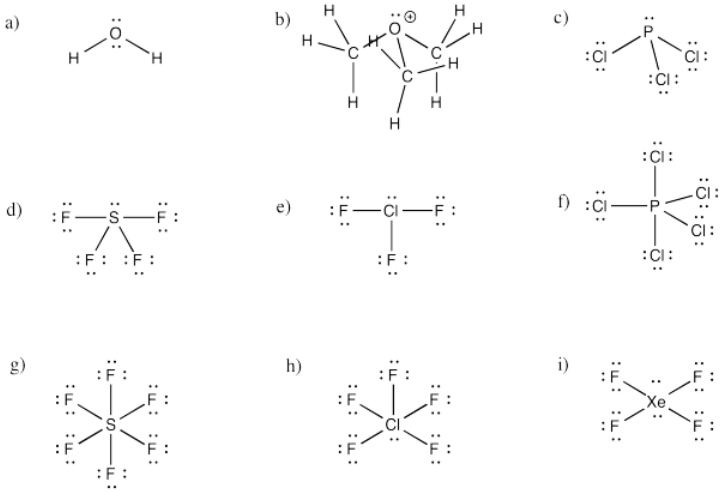
The rule is that the lone pair goes in the less crowded position, so this molecule would be see-saw shaped.

c) Again, there are two possible geometries. One of them would be trigonal planar, a pretty common geometry.





Exercise 4.10.3:



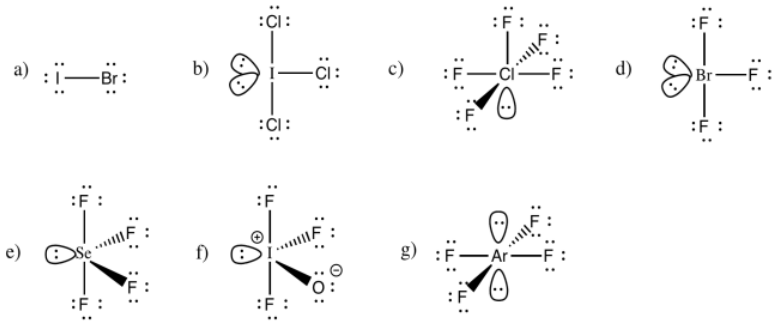
Exercise 4.10.4

a) bent b) pyramidal at O, although tetrahedral at C c) pyramidal

d) see-saw e) tee f) trigonal bipyramidal

g) octahedral h) square pyramidal i) square planar

Exercise 4.10.5:

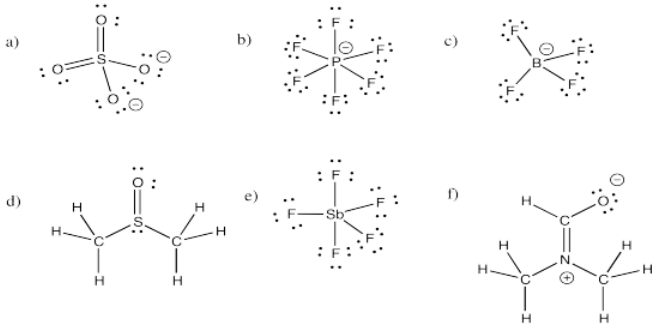


(probably; it hasn't been made before)

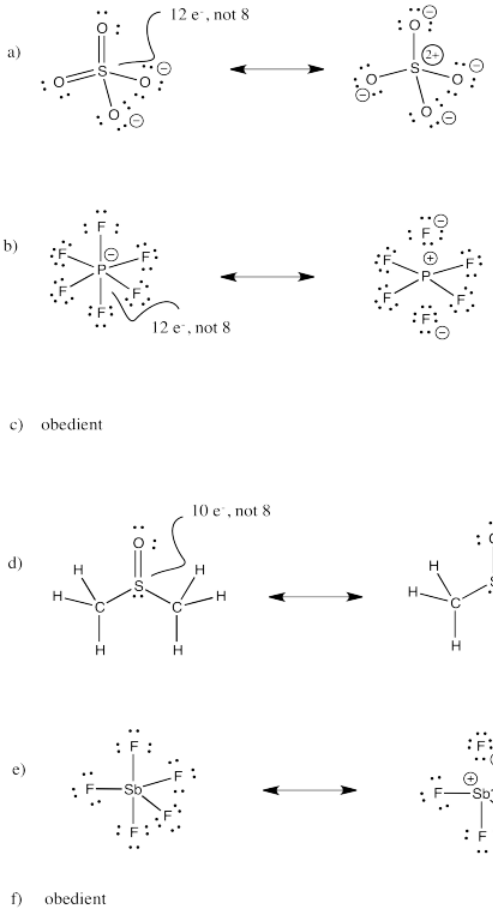
Exercise 4.10.6:

You may be able to imagine some other possibilites for this number of neighbors, but IF_7 adopts a pentagonal bipyramid shape.

Exercise 4.11.1:



Exercise 4.11.2:



Answers to Exercise 4.11.2, a through f, showing several Lewis structures with bonds being removed or the label "obedient".

Exercise 4.11.3:

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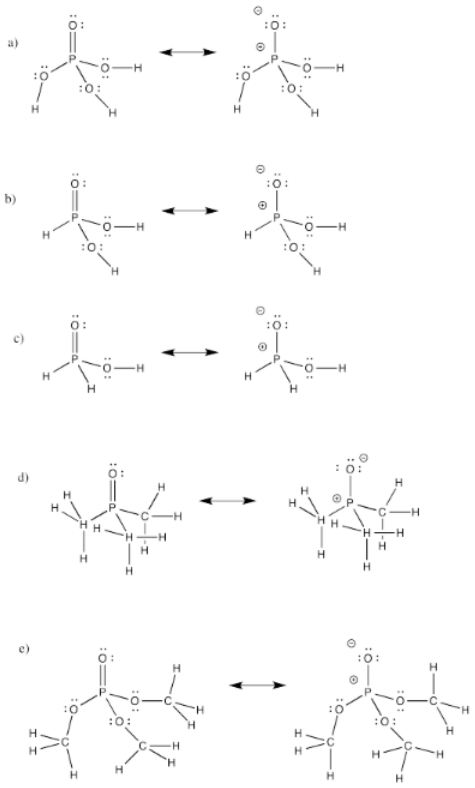


Exercise 4.12.2:

a) propane b) pentane c) hexane

Exercise 4.12.3:

a) 3-methylhexane b) 2,2-dimethylpentane c) 2,3-dimethylbutane

d) 2,2,3,3-tetramethylpentane e) 3,5-dimethylheptane f) 4-ethyl-3,6-dimethyloctane

Exercise 4.12.4

a) cyclopentane b) cyclohexane c) cyclooctane

d) methylcyclobutane e) 1,1,3-trimethylcyclopentane f) 1,3-dimethylcycloheptane

Exercise 4.12.5:

a) 1-hexene b) 2-methyl-2-pentene c) 1-methylcyclohexene d) 2,4,6-trimethyl-2-heptene

Exercise 4.12.6:

a) cyclopentene b) 1,1-dimethylcyclohexane c) 3-hexyne

d) 4-methylcyclohexene e) 1-hexyne

Exercise 4.12.7:

a) tetrahedral b) trigonal planar c) linear

Exercise 4.12.8:

a) methylbenzene b) propylbenzene c) 1,2-dimethylbenzene or *o*-dimethylbenzene (also *o*-xylene)

d) 1,3-dimethylbenzene or *m*-dimethylbenzene (also *m*-xylene) e) 1,4-diethylbenzene or *p*-diethylbenzene

f) 2-ethyl-1,4-dimethylbenzene

Exercise 4.12.9:

a) 2,2-dimethylhexanal b) 2-methylcyclopentanone

c) 3-nonanone d) 2,4-dimethyl-2-hexenal

Exercise 4.12.10:

a) butyl propanoate b) *N*,*N*-diethylbutanamide

c) 6-methylheptanoic acid d) 4-pentenoic acid

Exercise 4.12.11:

a) 1-chloro-2-methylcyclohexane b) cyclooctanol c) ethyl cyclopentyl ether

d) *N*-propylcyclohexylamine e), 5,5-dimethylheptan-2-ol f) 3-bromo-4,4-dimethyloctane

g) dibutylamine i) methyl phenyl ether (or anisole) j) ethane thiol k) diethyl thioether

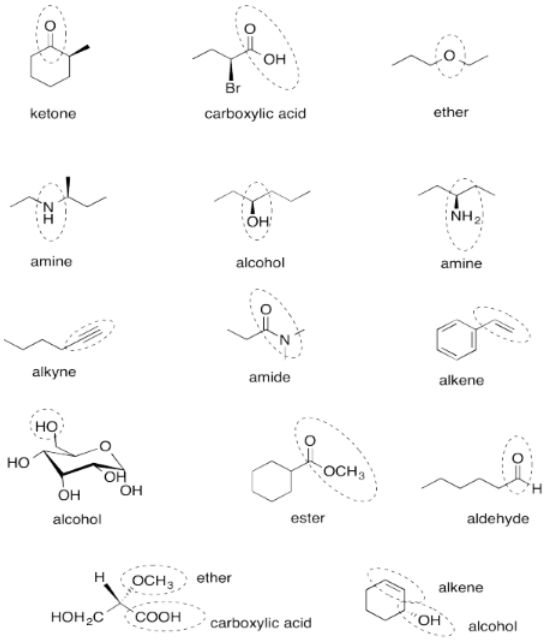
l) triethylphosphine m) butanenitrile n) nitromethane

Note that sometimes a number is located directly in front of the suffix for the group to which it refers.

Exercise 4.12.12

a. benzene (or aromatic), ketone and ether
b. bromide, amine and aldehyde
c. alcohol, thiol and ester
d. thioether, amide and alkene
e. alkyne, alcohol and carboxylic acid

Exercise 4.12.13



Exercise 4.12.14

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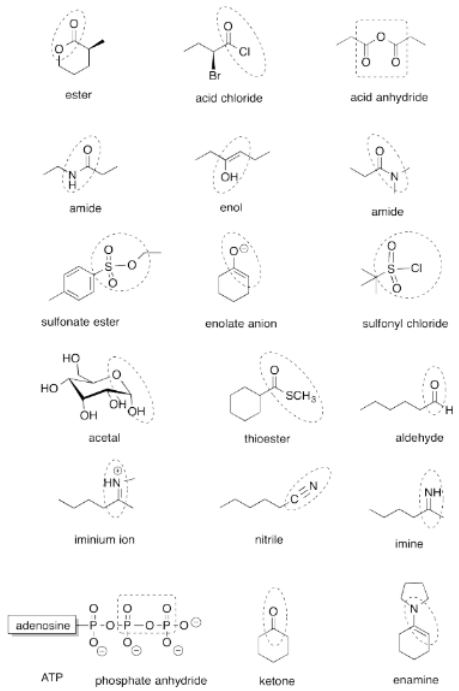
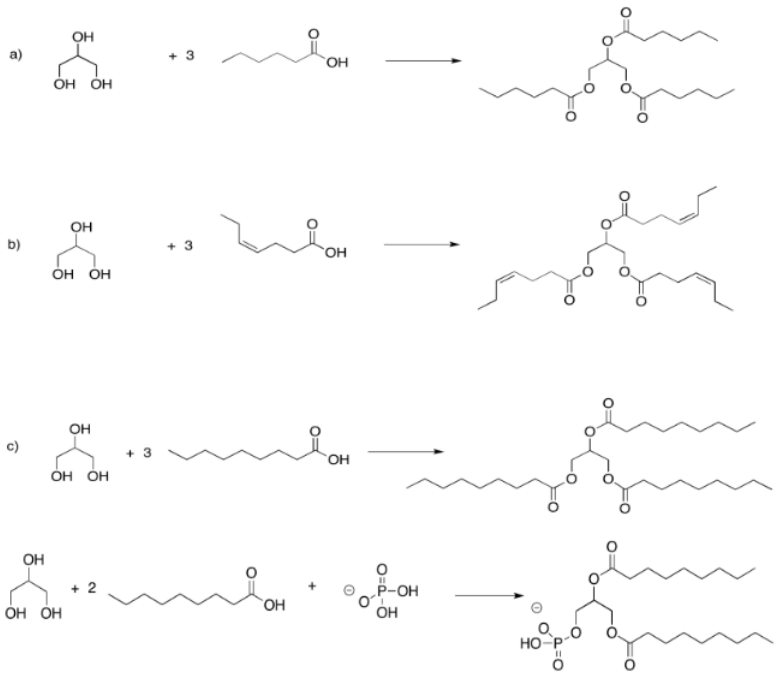


Exercise 4.13.1:



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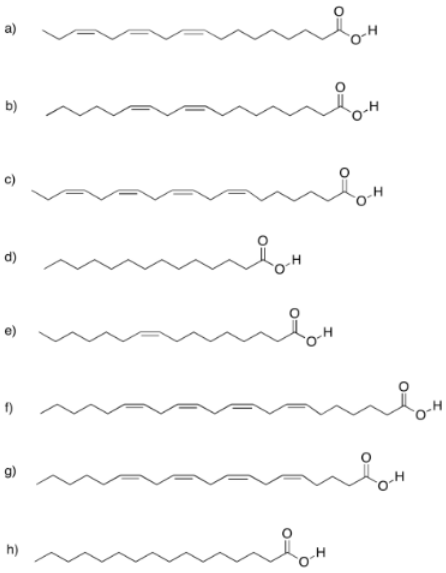
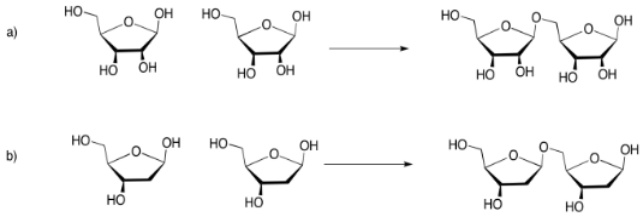


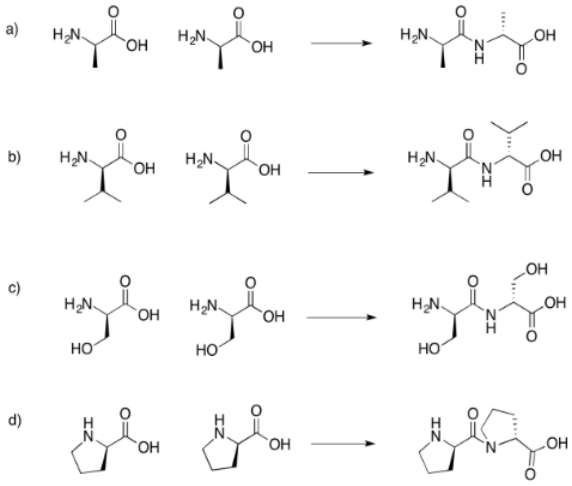
Exercise 4.13.4:



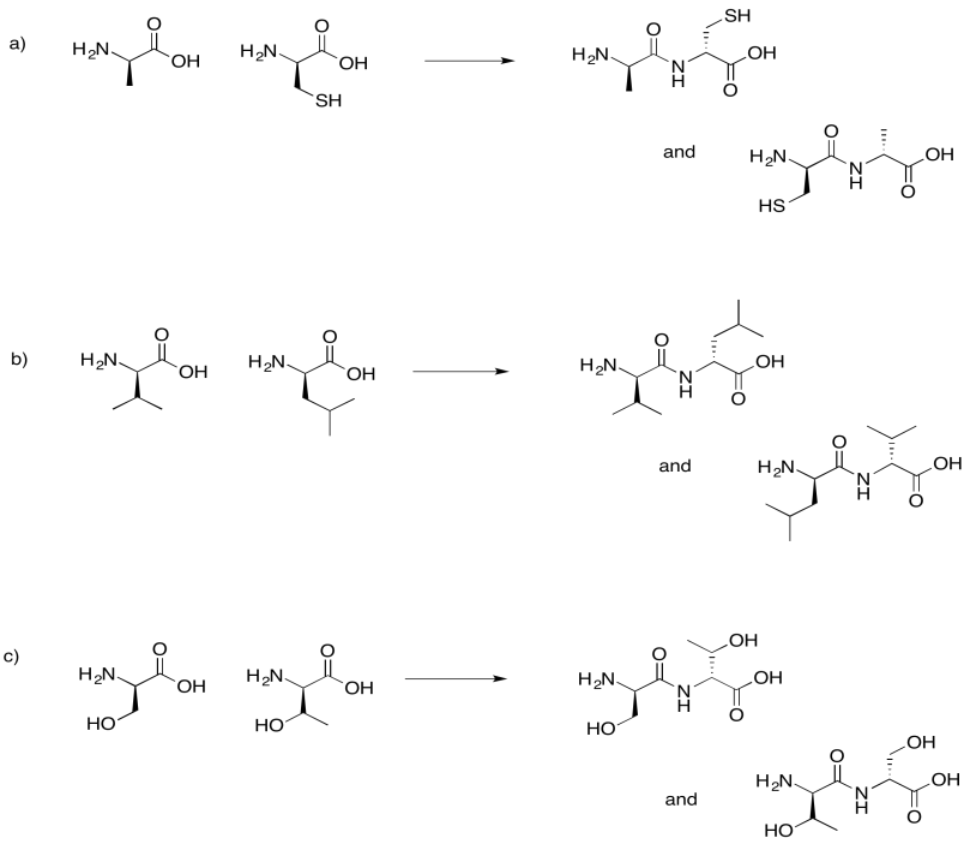
Answers to Exercise 4.13.4, a and b, showing formation of glycosidic linkages between ribose and deoxyribose, respectively.

Exercise 4.13.5:

If you don't know what the wedged and dashed lines in the drawing mean, don't worry about it. They just represent different orientations in space. You will learn about these representations in a later topic called "stereochemistry".



Exercise 4.13.6:



Answers to Exercise 4.13.6, a through c, showing different orientations of dipeptides formed from two amino acids.

Exercise 4.13.7:

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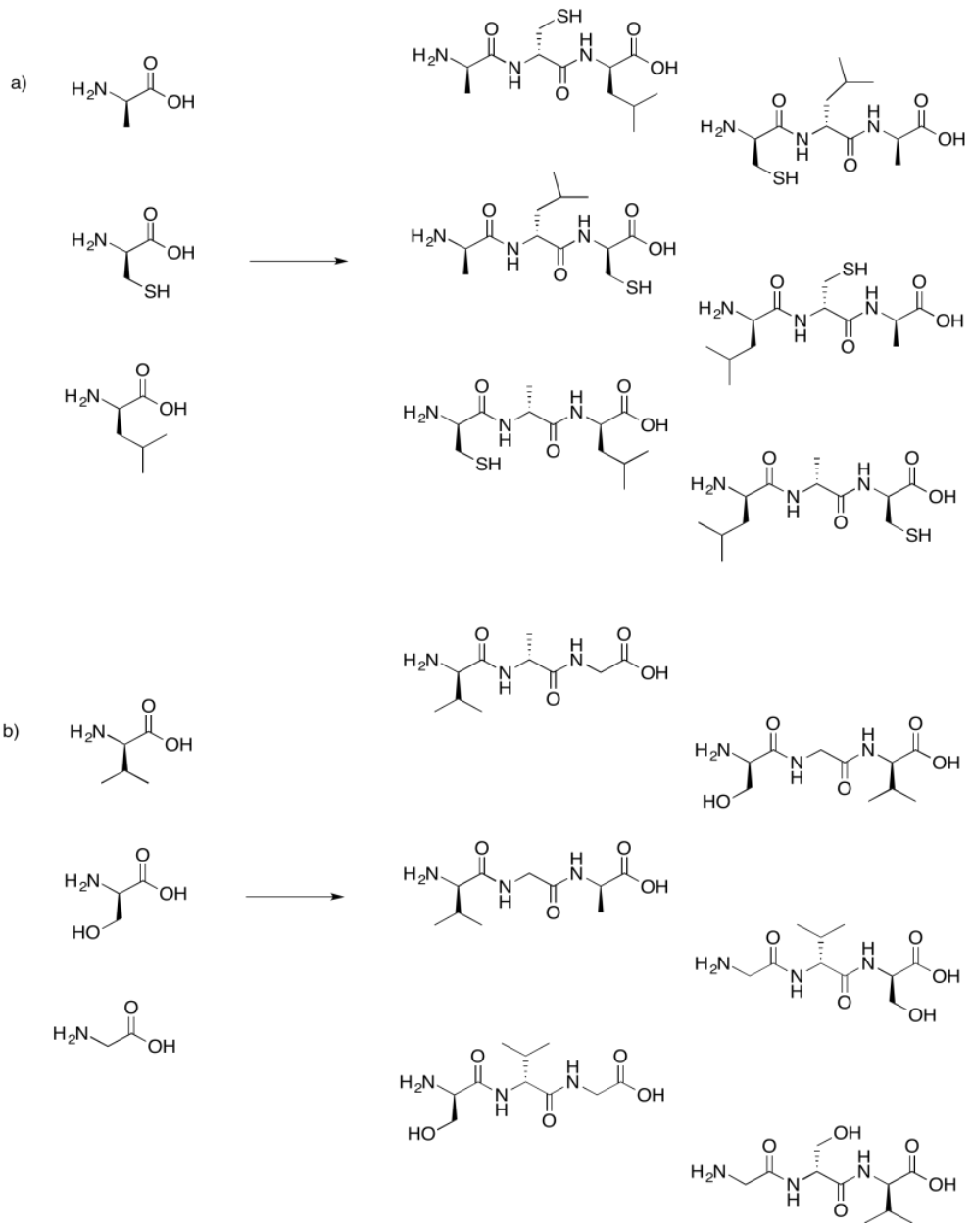
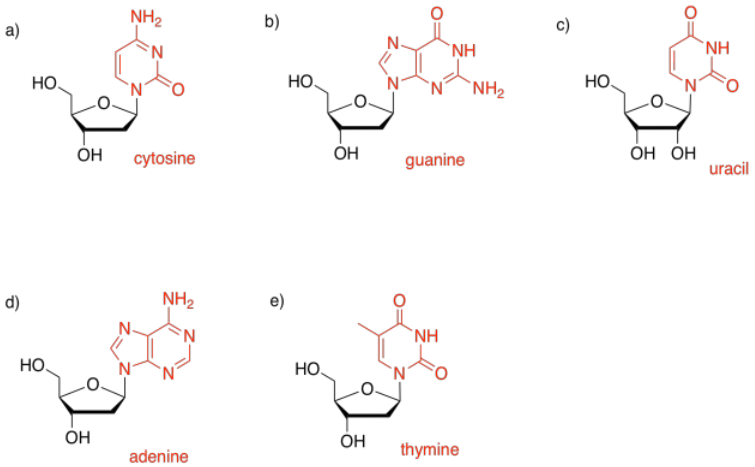


Exercise 4.13.8:



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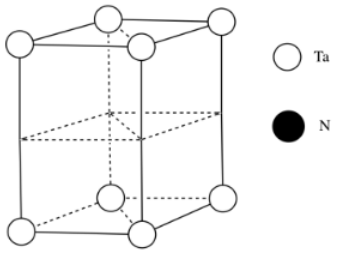
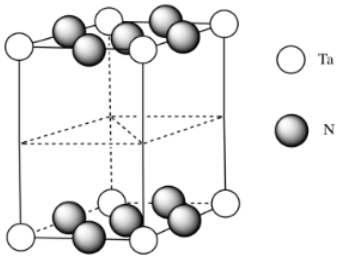
Exercise 4.15.1:

a. N^{3-} would get to a noble gas configuration.
b. Ta^{3+} would balance the charge in TaN.

c)



d)



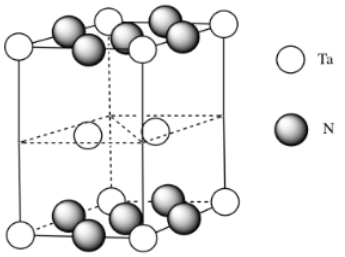
Answer to Exercise 4.15.1d, with unit cell filled in with tantalum and nitrogen on the top and bottom layers only.

e) $\#Ta = (\frac{1}{6})(\frac{1}{2})(4)$ for the acute corners and $(\frac{1}{3})(\frac{1}{2})(4)$ for the obtuse corners = $\frac{4}{12} + \frac{4}{6} = \frac{4}{12} + \frac{8}{12} = 1$

(note that it's the same outcome as the corners of a cube)

f) $\#N = \backslash(\frac{1}{4})(8)$ for the edges and $(\frac{1}{2})(2)$ for the faces = $2 + 1 = 3$

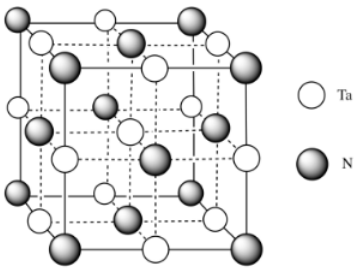
g) Need 2 more Ta.



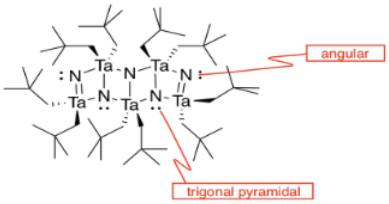
Answer to Exercise 4.15.1d, with unit cell filled in with tantalum and nitrogen. There are two atoms of tantalum in layer two.

h) Each tantalum has three nitrogens above and three below it. It's almost octahedral, but the top layer of nitrogens is lined up above the bottom layer rather than being twisted 120 degrees to form an octahedron. The geometry is a trigonal prism.

i)

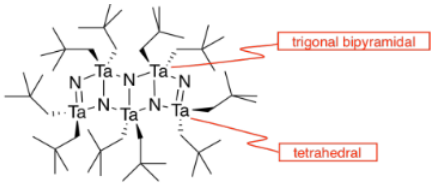


j)



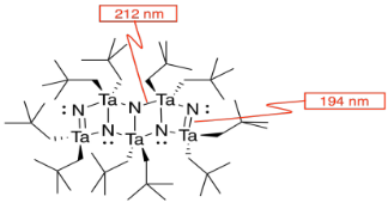
Structure of tantalum-nitrogen lattice, with geometries about different nitrogen atoms labelled as trigonal pyramidal and angular.

k)



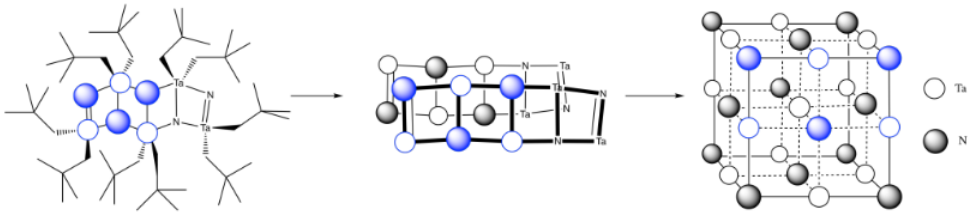
Answer to Exercise 4.15.1k. Structure of tantalum-nitrogen lattice, with geometries about different nitrogen atoms labelled as trigonal pyramidal and angular. The lone pairs are removed.

l) The double bonds hold the atoms more closely together than the single bonds.



Answer to Exercise 4.15.1k. Structure of tantalum-nitrogen lattice, with the single tantalum-nitrogen bonds labelled as 212 nanometers and the double bonds labelled as 194 nanometers.

m) You can imagine the molecules stacking together to make a cubic array of TaN.



Answer to Exercise 4.13.1m, showing how the structure of the tantalum-nitrogen solid can be modelled in different forms.

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CHAPTER OVERVIEW

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5.1: Introduction

One of the most important properties of molecules in the biological world is three-dimensional shape. Organisms interact with molecules based to a large extent on molecular shape. Many compounds fit together with cell-based receptors (which are themselves molecules of very particular shapes). When this happens, a biological response results: a signal to the brain, the onset of cell division, or other possibilities.

Because shape can influence how two molecules fit together, it can affect physical properties as well as biological ones. For example, if a compound is made of molecules that cannot fit together easily, London dispersion interactions are limited, and so the compound is less likely to be a solid.

Stereochemistry refers to the three-dimensional arrangement of atoms. When two compounds contain the same atoms that are connected in the same order, but have different intrinsic shapes, they are steroisomers.

In biology, stereoisomers result from chiral centers. Because biological molecules are comprised largely of carbon, and because carbon usually adopts a tetrahedral shape, there are often two different ways for four groups to be arranged around a carbon atom.

Sterochemistry are not just found in biology, however. Certain minerals contain right- or left-handed helices, and chiral molecules have been observed by astronomers. It is even possible that some of the chiral molecules found in early biology were influenced by templates from meteorites or other astronomical debris.

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5.2: Stereoisomers

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called stereoisomers.

- There may be more than one way to arrange the same groups around the same atom with the same geometry.
- This phenomenon is called stereochemistry.

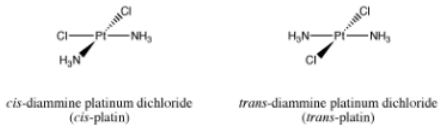


Figure 5.2.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases.

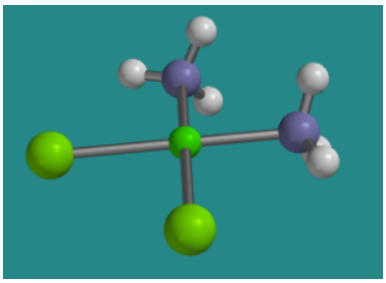


Figure 5.2.2: Ball-and-stick model of *cis*-platin. This compound is square planar at platinum. It is flat when viewed from the edge, and square when viewed from the face.

Go to **Animation SC2.1.** A three-dimensional model of *cis*-platin.

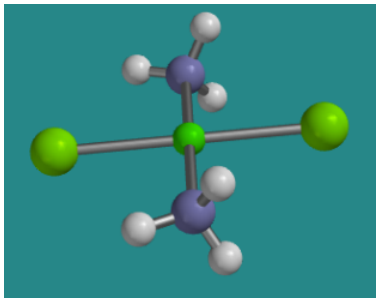


Figure 5.2.3: Ball-and-stick model of*trans*-platin. All the pieces are connected in the same way as in cis-platin, and the molecule is still square planar, but there is a different 3-dimensional arrangement.

Ball-and-stick model of a molecule, showing similar square planar geometry about the central atom as in Figure 5.2.2.

Go to **Animation SC2.2.** A three-dimensional model of *trans*-platin.

For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two ammines beside each other is called cis-platin.
- These two ligands are 90 degrees fom each other.
- The one with the ammines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but *trans*-platin forms pale yellow crystals and is more soluble than *cis*-platin in water.

- *Cis* and *trans* isomers have different physical properties.

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

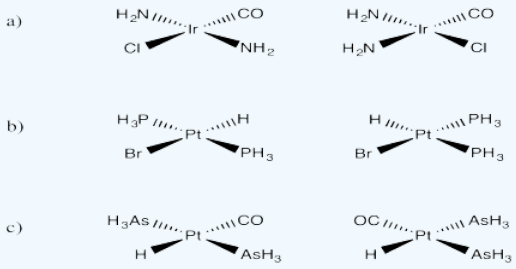
- *Cis* and *trans* isomers have different biological properties.

Exercise 5.2.1

Draw the cis and trans isomers of the following compounds:

a) $(NH_3)_2IrCl(CO)$ b) $(H_3P)_2PtHBr$ c) $(AsH_3)_2PtH(CO)$

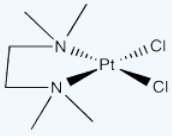
Answer



Exercise 5.2.2

Only one isomer of $(tmeda)PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

Answer



Needs to *cis*. The tmeda group is not long enough to reach the *trans* position

Still pictures of models obtained using Spartan 14 from Wavefunction, Inc., Irvine, California.

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5.3: Stereochemistry - Extra Problems

Optical rotation

Exercise 5.3.1

The (+) enantiomer of compound A has an optical rotation of 125°. If a pure sample of compound A has an optical rotation of 100°, what is the composition of the sample?

Answer

Pure = 125°

Optical purity = $\frac{100}{125} = 0.80$

$$\%Major = 80 + \frac{20}{2} = 90\%$$

$$\%Minor = 100 - 90 = 10$$

Exercise 5.3.2

The (+) enantiomer of compound B has an optical rotation of 100°. If a pure sample of compound B has an optical rotation of 95°, what is the composition of the sample?

Answer

Pure = 100°

Optical purity = $\frac{95}{100} = 0.95$

$$\%Major = 95 + \frac{5}{2} = 97.5\%$$

$$\%Minor = 100 - 97.5 = 2.5\%$$

Exercise 5.3.3

The (+) enantiomer of compound C has an optical rotation of 18°. If a pure sample of C contains 30% of the (+) enantiomer and 60% of the (-) enantiomer, what is the optical rotation value?

Answer

Pure = 18°

$$\%Major = 60\%$$

$$\%Minor = 40\%$$

Optical purity = $\frac{X}{18} = 20\%$

Solve for X:

$$X = 3.6^o$$

Exercise 5.3.4

The (+) enantiomer of compound D has an optical rotation of 25°. If a pure sample of D contains 80% of the (+) enantiomer and 20% of the (-) enantiomer, what is the optical rotation value?

Answer

Pure = 25°

$$\%Major = 80\%$$

$$\%Minor = 20\%$$

Optical purity $= \frac{X}{25} = 80 - 20 = 60\%$

Solve for X:

$$X = 15^o$$

The polarimetry experiment

Exercise 5.3.5

A pure sample of the naturally-occurring, chiral compound A (0.050 g) is dissolved in water (2.0 mL) and the solution is placed in a 0.5 dm cell. Three polarimetry readings are recorded with the sample: 0.625°, 0.706°, 0.682°. What is [a]?

Answer

$$[a] = \frac{observed\ rotation}{(l)(c)}$$

$$c = \frac{0.050g}{2.0mL} = 0.025\frac{g}{mL}$$

Average observed rotation $= \frac{0.625+0.706+0.682}{3} = 0.671^o$

$$[a] = \frac{0.671^o}{(0.025\frac{g}{mL})(0.5dm)} = 53.68^o$$

Exercise 5.3.6

A pure sample of the chiral compound B (0.540 g) is dissolved in ether (2.0 mL) and the solution is placed in a 1.0 dm cell. Three polarimetry readings are recorded with the sample: 1.225°, 1.106°, 1.182°. What is [a]?

Answer

$$[a] = \frac{observed\ rotation}{(l)(c)}$$

$$c = \frac{0.540g}{2.0mL} = 0.27\frac{g}{mL}$$

Average observed rotation $= \frac{1.225+1.106+1.182}{3} = 1.171^o$

$$[a] = \frac{1.171^o}{(0.27\frac{g}{mL})(1.0dm)} = 4.34^o$$

Exercise 5.3.7

A pure sample of the (+) enantiomer of compound C shows [a] = 42°. What would be the observed a if a solution of the sample was made by dissolving 0.250 g in 2.0 mL of acetontirile and was then placed in a 0.5 dm cell?

Answer

$$[a] = \frac{observed\ rotation}{(l)(c)}$$

$$c = \frac{0.250g}{2.0mL} = 0.125\frac{g}{mL}$$

$$42^o = \frac{observed\ rotation}{(0.125\frac{g}{mL})(0.5dm)}$$

observed rotation = 2.625°

Exercise 5.3.8

A student has prepared compound D in lab. She is sure the compound contains no impurities; a number of physical analyses have confirmed the structure and purity of the compound. A sample of compound D (0.10 g) is dissolved in methanol (2.0 mL) and the solution is placed in a 1.0 dm cell. Three polarimetry readings are recorded with the sample: 0.995°, 0.904°, 0.936°.

a. What is [a]?
b. The optical rotation of D has previously been reported as 25°. What is the optical purity of this sample?
c. What is the enantiomeric excess of this sample?
d. What is the composition of this sample?
e. Why did the previous analyses show that there was only one compound present?

Answer a

$$[a] = \frac{observed\ rotation}{(l)(c)}$$

$$c = \frac{0.10g}{2.0mL} = 0.05\frac{g}{mL}$$

Average observed rotation = $frac0.995 + 0.904 + 0.9363 = 0.945^o$

$$[a] = \frac{0.945^o}{(0.05\frac{g}{mL})(1.0dm)} = 18.9^o$$

Answer b

% optical purity = $\frac{(100)(18.9)}{25} = 75.6\%$

Answer c

enantiomeric excess = 75.6%

Answer d

$$\frac{100 - 75.6}{2} = 12.2\%$$

12.2% one enantiomer

87.8% other enantiomer

Answer e

Enantiomers differ in how they interact with plane polarized light, but not in other physical analyses.

Exercise 5.3.9

Suppose a student prepared a sample of a compound with known [a] = 40. The student did not realize that her sample contained 10% (by mass) of a non-chiral impurity. After correcting for c and l, what did she measure for [a]?

Answer

$$[a] = \frac{observed\ rotation}{(l)(c)}$$

$$40^o = \frac{observed\ rotation}{(l)(c)}$$

$$40^o = \frac{observed\ rotation}{(l)(1.1c)}$$

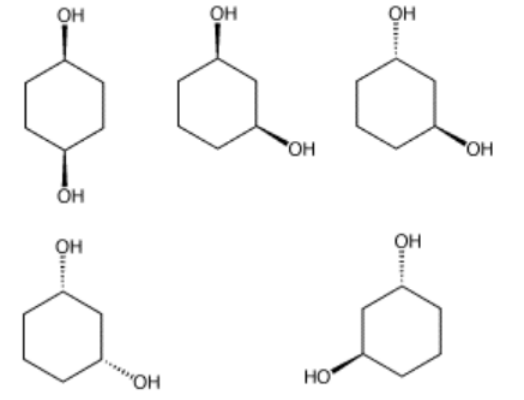
Observed rotation = 44^o

diastereomers and physical properties

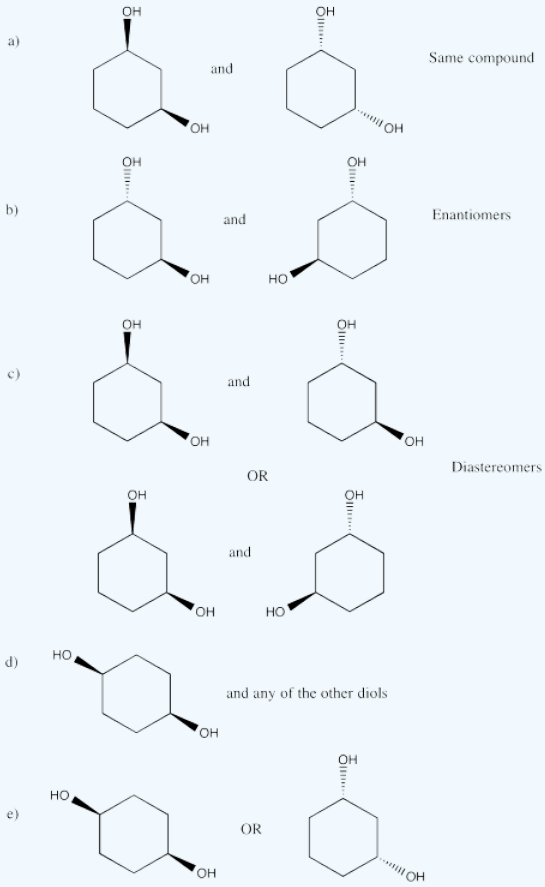
Exercise 5.3.10

From the following group of molecules, select:

a. a pair that are the same compound.
b. a pair that would have the same physical properties but opposite optical activities.
c. a pair that have different physical properties but the same connectivity.
d. a pair that have different connectivity.
e. a compound that contains chiral centers but has no optical activity.



Answer

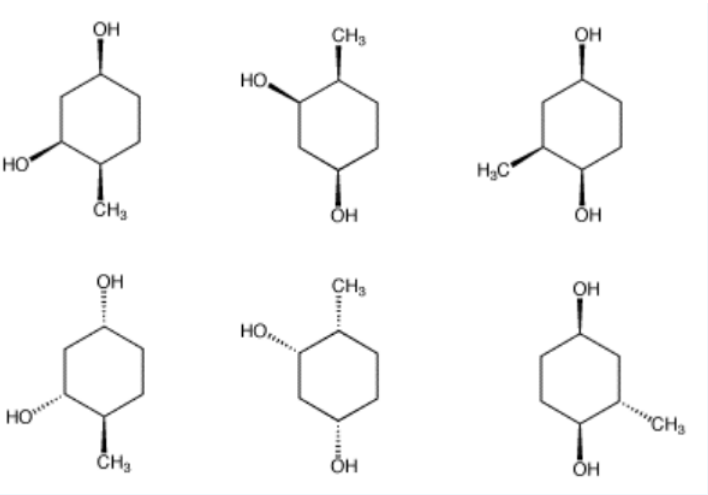


Answer

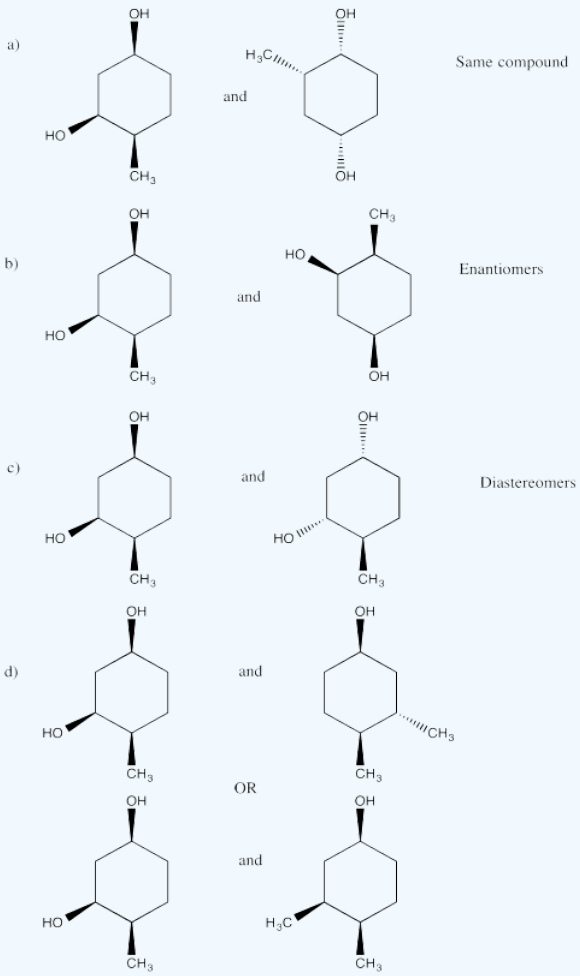
Exercise 5.3.11

From the following group of molecules, select:

a. a pair that are the same compound.
b. a pair that would have the same physical properties but opposite optical activities.
c. a pair that have different physical properties but the same connectivity.
d. a pair that have different connectivity.



Answer

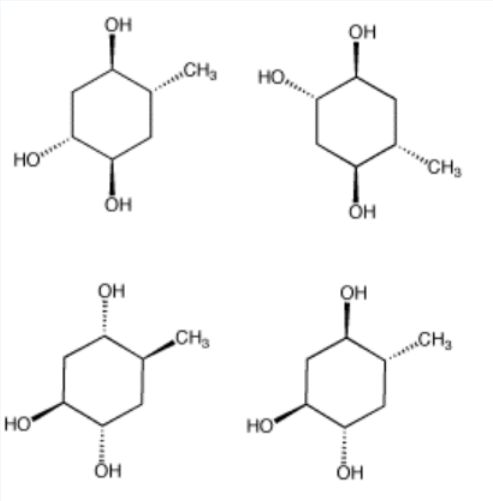


Answer

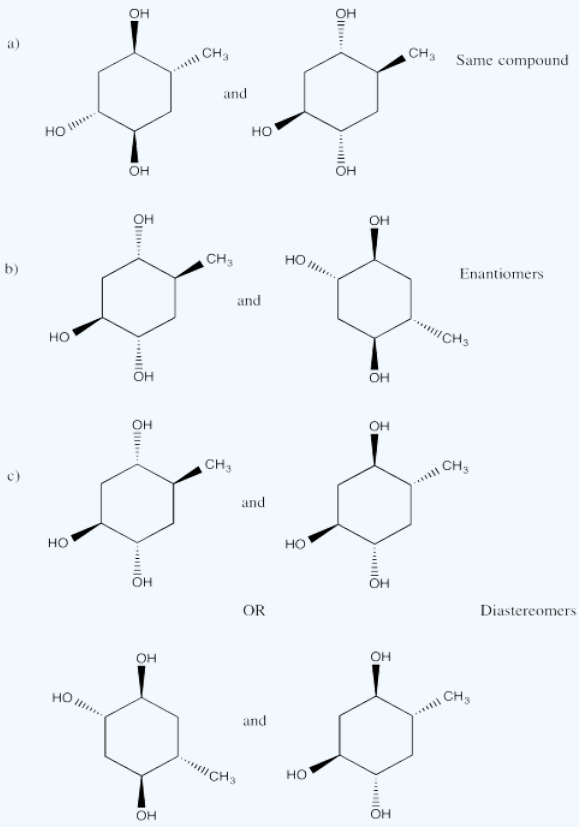
Exercise 5.3.12

From the following group of molecules, select:

a. a pair that are the same compound.
b. a pair that would have the same physical properties but opposite optical activities.
c. a pair that have different physical properties but the same connectivity.



Answer



Answer

Answers to Exercise 5.3.11, a through c. a is labelled "same compound". b is labelled "enantiomers". c is labelled "diastereomers".

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5.4: Enantiomers

An atom with four groups attached to it can also adopt a tetrahedral geometry. This geometry often occurs when the central atom is a little smaller. A tetrahedral geometry allows neighbouring groups to get a little farther from each other. The following model of methane shows a pretty simple example. The grey ball is a carbon atom and the four white balls are hydrogen atoms.

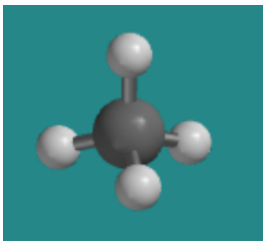


Figure 5.4.1: A ball-and-stick model of a simple tetrahedral compound: methane, CH_4.

Go to **Animation SC3.1.** A three-dimensional model of methane, CH_4.

Unlike square planar compounds, simple tetrahedral compounds do not have the same kind of *cis*- and *trans*- isomers. That is, two groups can't be placed on a tetrahedron so that they are opposite each other or beside each other. The relationship between any two groups on a tetrahedron is the same as the relationship between any other two groups on a tetrahedron.

Dichlorodimethylsilane is a compound that can be used to make silicone polymers. Like platin, it has two each of two groups attached to the central atom. However, the central tom is tetrahedral. There is only one way to arrange these four groups.

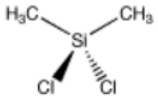


Figure 5.4.2: A ball-and-stick model of dichlorodimethylsilane.

Go to **Animation SC3.1.** A three-dimensional model of dichlorodimethylsilane.

However, if four different groups are attached to a tetrahedral atom, the four groups can be arranged in two possible ways. The two compounds that result are mirror images of each other. These two isomers are called enantiomers.

For example, suppose that tetrahedral silicon atom had four different groups attached to it: a hydrogen atom, a chlorine atom, a methyl group (that's a carbon with three hydrogens), and a hydroxy group (that's an oxygen with one hydrogen). There would be two slightly different ways to organize those four groups in space. In the picture below, hydrogen is white, chlorine is green, and oxygen is red, whereas silicon and carbon are both grey.

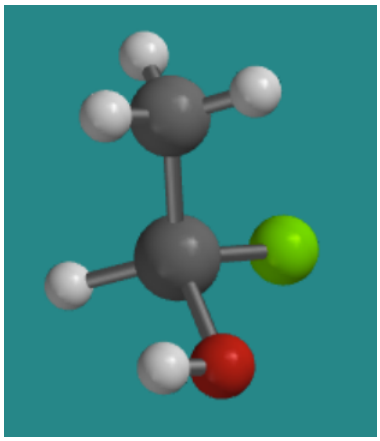


Figure 5.4.3: A ball-and-stick model of *R*-chlorohydroxymethylsilane, one of two stereoisomers.

Ball-and-stick molecule of a carbon with a methyl group, a hydrogen, a chlorine atom, and a silane group. The silane group points towards the camera.

Go to **Animation SC3.2.** A three-dimensional model of *R*-chlorohydroxymethylsilane.

Exercise 5.4.1

Turn the model so that the hydrogen attached to the silicon is hidden behind the molecule. In what direction would you travel if you traced from the chlorine to the oxygen to the carbon: clockwise or counter-clockwise?

Answer

Clockwise

This next picture shows a very similar molecule. The same groups are attached to the central silicon atom, but the are arranged in a slightly different way.

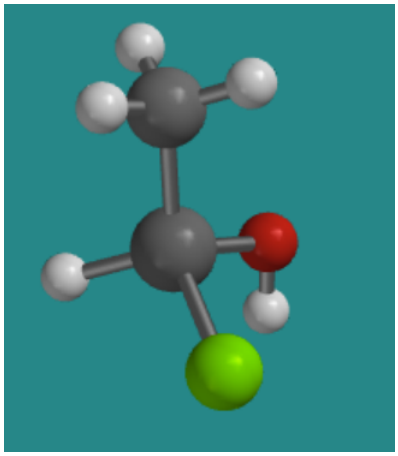


Figure 5.4.4: A ball-and-stick model of *S*-chlorohydroxymethylsilane, one of two stereoisomers.

Ball-and-stick molecule of a carbon with a methyl group, a hydrogen, a chlorine atom, and a silane group. The silane group points away from the camera to the right and the chlorine points towards the camera.

Go to **Animation SC3.3.** A three-dimensional model of *S*-chlorohydroxymethylsilane.

Exercise 5.4.2

Turn the model so that the hydrogen attached to the silicon is hidden behind the molecule. In what direction would you travel if you traced from the chlorine to the oxygen to the carbon: clockwise or counter-clockwise?

Answer

Counter-clockwise

Full disclosure: the molecule we are looking at isn't really a stable compound that you could pour out of a bottle from the chemistry stockroom. That's because one molecule would react with another one just like it, and then another one, and so on to form a long chain called a silicone polymer. That's the kind of material found in things like silly putty and silicone caulking.

Exercise 5.4.3

Let's try working without the three-dimensional model. The following ball-and-stick picture shows a silicon attached to a bromine (red), a chlorine (green), a fluorine (yellow) and a hydrogen. If you were looking at the molecule with the hydrogen hiddent behind it, in what direction would you travel if you traced from the bromine to the chlorine to the fluorine: clockwise or counter-clockwise?

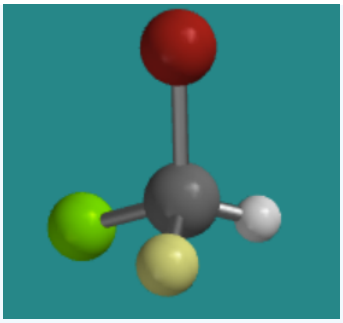


Figure 5.4.5:AnswerCounter-clockwiseBall-and-stick model of an sp3 atom with four different groups attached to it. Bromine is on top, chlorine is to the back left, hydrogen is to the back right, and fluorine points towards the camera.

Exercise 5.4.4

If you were looking at the molecule with the hydrogen hidden behind it, in what direction would you travel if you traced from the bromine to the chlorine to the fluorine: clockwise or counter-clockwise?

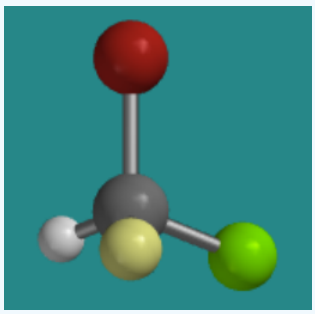


Figure 5.4.6:AnswerClockwiseBall-and-stick model of an sp3 atom with four different groups attached to it. Bromine is on top. Chlorine is to the back right. Hydrogen is to the back left. Fluorine points towards the camera.

There don't have to be four different atoms attached to the central atom to get two stereoisomers. There just have to be four different groups. Even if all four atoms attached to the central one are the same, if they have different things attached to them, then two three-dimensional arrangements are possible. The following compounds illustrate a more subtle example like that. This compound, by the way, is stable and can be isolated and stored; it's a real compound.

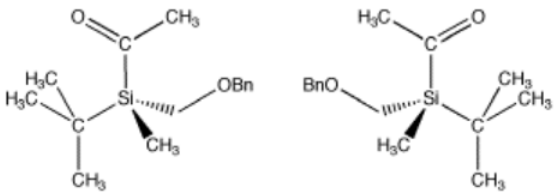


Figure 5.4.7: A pair of enantiomers. The (-) enantiomer is on the left and the (+) enantiomer is on the right. Note that the tetrahedral silicon atom has four different groups attached.

Two enantiomers of a molecule with silicon at center, with four different groups attached. The molecules are positioned so that their mirror image likeness is obvious.

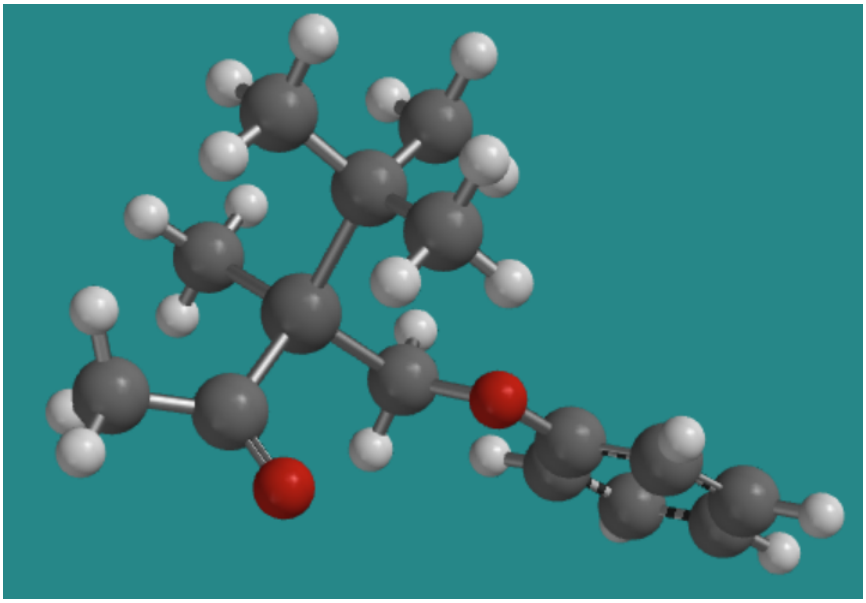


Figure 5.4.8: Another view of the (-) enantiomer; it's in a different orientation from the wedge/dash structure above.

Go to **Animation SC2.1.** A three-dimensional model of the (-) enantiomer

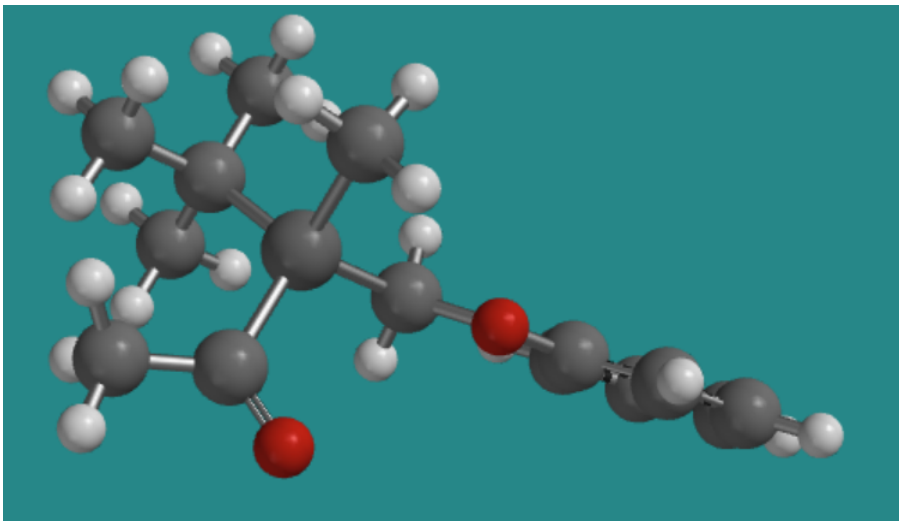


Figure 5.4.9: Another view of the (+) enantiomer; it's in a different orientation from the wedge/dash structure above.
Ball-and-stick model of the + enantiomer in Figure 5.4.7, top view, showing reversed (mirrored) positions of two groups.

Go to **Animation SC2.1.** A three-dimensional model of the (+) enantiomer.

- Enantiomers are pairs of compounds with exactly the same connectivity but opposite three-dimensional shapes.
- Enantiomers are not the same as each other; one enantiomer cannot be superimposed on the other.
- Enantiomers are mirror images of each other.

Two compounds with the exact same connectivity, that are mirror images of each other but that are not identical to each other are called enantiomers. The more common definition of an enantiomer is that it is not superimposable on its mirror image. It can be distinguished easily from its mirror image, just as a right hand can easily be identified and distinguished from a left hand.

- Compounds that occur in these pairs are called "chiral".
- "Chiral" comes from the Greek word for "hand".

It can be shown using group theory, the mathematics of symmetry, that an enantiomer may also be defined as a molecule that does not contain a mirror plane, meaning it cannot be divided into two identical and opposite halves.

- Enantiomers contain no mirror planes.
- Enantiomers do not contain two equal and opposite halves.

Unlike cis- and trans-isomers, two enantiomers have the same physical properties. they have the same melting point, the same solubility, and so on. Two compounds that are almost identical, but mirror images of each other, have exactly the same kinds of intermolecular attraction, so it may not be a surprise that their physical properties are identical.

- Enantiomers are another example of a type of stereoisomers.
- Two enantiomers have identical physical properties, except for optical rotation.

Optical rotation involves the interaction of plane-polarized light with a material. If a material is not symmetric, the light that passes through it will be rotated. That means if the waves making up the light are oscillating in one direction as they enter the material, they will have tilted slightly to oscillate in another direction when they emerge from the material. We will look at this phenomenon later.

- Two enantiomers have an equal but opposite rotational effect on plane-polarized light.
- (+) enantiomers rotate light in a clockwise direction.
- (-) enantiomers rotate light in a counterclockwise direction.

For example, in the chiral silicon compound shown above, the (+) enantiomer rotates plane-polarized light in a clockwise direction. It has a "standard optical rotation" of [a] = +12 (+/-2)^{o}. The (-) enantiomer rotates plane-polarized light in a counterclockwise direction. It has a "standard optical rotation" of [a] = -9.9 (+/-2)^{o}.

Exercise 5.4.5

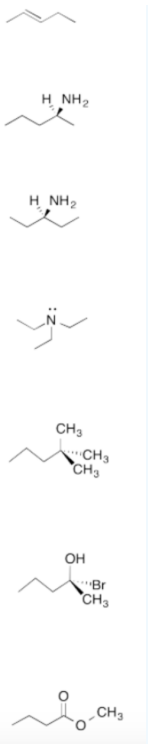
A certain compound exists in two forms; enantiomer A and enantiomer B. Enantiomer A has a molecular weight of 126 g/mol, a density of 0.995 g/mL, an optical rotation of [a] = 26^{o}, a melting point of 65 ^{o}C, a boiling point of 225 ^{o}C, and an odour of citrus fruit. What can you say about the corresponding properties of enantiomer B?

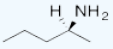
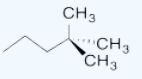
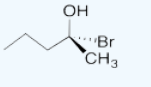
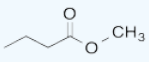
Answer

Enantiomer B has a molecular weight of 126 g/mol, a density of 0.995 g/mL, an optical rotation of [a] = -26^{o}, a melting point of 65^{o}C and a boiling point of 225^{o}C.

Exercise 5.4.6

Are these molecules chiral?
Draw the mirror image of each compound and determine if it is superimposable.



Mirror Image	Superimposable	Chiral?
	Yes	No
	No	Yes
	Yes	No
	Yes	No
	Yes	No
	No	Yes
	Yes	No

Seven different molecules. From top to bottom: 2-pentene, pentan-2-amine, pentan-3-amine, pentane, 2-bromo-2-pentanol, methyl butanoate.Figure 5.4.10:Answer

Answers to Exercise 5.4.6, with mirror images, yes/no statements for superimposability, and yes/no statements for chirality.

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Exercise 5.4.7

Find a mirror plane of symmetry in the following molecules. Some may have no mirror planes and thus are chiral. (Some may have several mirror planes, but it is only necessary to find one in order to determine that the molecule is not chiral.) Hint—there are low barriers to rotation about most single bonds. If any conformer can be drawn in which a molecule has a mirror plane, the molecule will not be chiral.

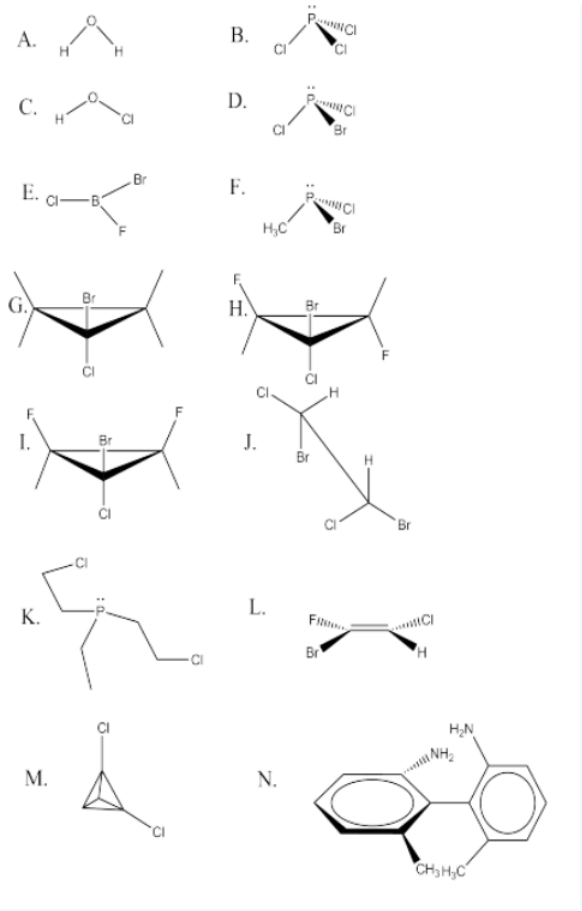

Figure 5.4.11:Answer A.The plane of the page is a mirror plane. There is also one perpendicular to the page that reflects one H into the other.Answer B.The plane of the page contains one P-Cl bond and bisects the other Cl's.Answer C.The plane of the page is a mirror plane.Answer D.Mirror plane contains P-Br bond and bisects the Cl's.Answer E.There is no lone pair on the B. Therefore all atoms lie in a mirror plane.Answer F.No mirror planes--the molecule is therefore chiral.Answer G.There is a plane perpendicular to the page that contains the Br and Cl and bisects the cyclopropane ring.Answer H.No mirror planes--the molecule is therefore chiral.Answer I.There is a plane perpendicular to the page that contains the Br and Cl and bisects the cyclopropane ring.Answer J.The C-C bond can be rotated by 60 degrees so that there is a plane perpendicular to the C-C bond axis.Answer K.The C-C bond in one of the chlorine-containing arms can be rotated so that there is a mirror plane that goes through the ethyl group (with no Cl's) and the P, and one chlorine containing arm is the reflection of the other.Answer L.Since a double bond is planar, there is a mirror plane that contains all six atoms.Answer M.There is a mirror plane that contains two C's and bisects the two Cls.Answer N.No mirror planes--the molecule is therefore chiral. The rings are not in the same plane due to the CH3 and NH2 groups, which bump into each other. They also prevent rotation around the C-C bond between the rings.

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Exercise 5.4.8

Select the picture that illustrates a mirror plane of symmetry in the following compound.

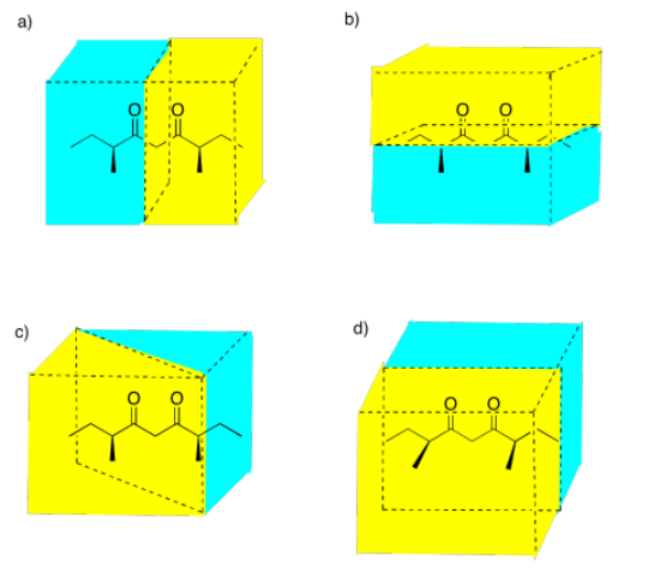

Figure 5.4.12:AnswerPicture (a)Possible answers to Exercise 5.4.8, showing different mirror planes between a molecule of (3S,7S)-3,7-dimethylnonane-4,6-dione

Exercise 5.4.9

Select the picture that illustrates a mirror plane of symmetry in the following compound.

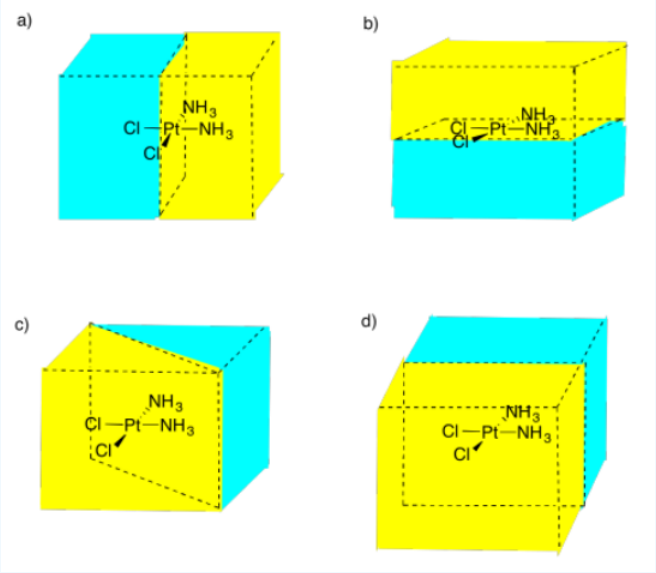

Figure 5.4.13:AnswerPicture (b)Possible answers to Exercise 5.4.9, showing different mirror planes between a molecule of platinum with two chlorine atoms and two ammonia groups.

Exercise 5.4.10

Select the picture that illustrates a mirror plane of symmetry in the following compound.

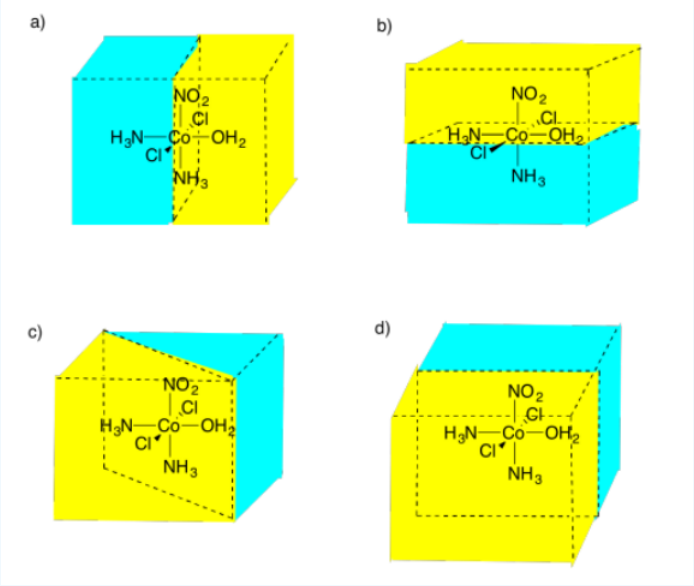

Figure 5.4.14:AnswerPicture (d)Possible answers to Exercise 5.4.10, showing different mirror planes between a molecule of cobalt with two chlorine atoms, two ammonia groups, a nitrate group, and an OH2 group attached.

Exercise 5.4.11

Select the picture that illustrates a mirror plane of symmetry in the following compound.

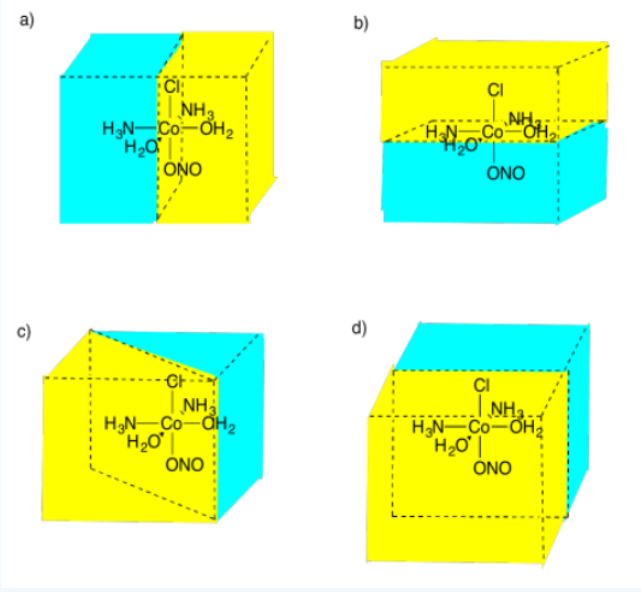

Figure 5.4.15:AnswerPicture (c)Possible answers to Exercise 5.4.11, showing different mirror planes between a molecule of cobalt with a nitrate group, two water groups, two ammonia groups, and a chlorine atom.

Still pictures of models obtained using Spartan 14 from Wavefunction, Inc., Irvine, California.

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5.5: Simple Organic Enantiomers- R and S configurations

Stereochemistry is most important to us because of the role it plays in biology. Biological compounds usually belong to a class of compounds called organic compounds, originally meaning compounds that come from organisms. More generally, organic compounds contain carbon. because carbon is usually a tetrahedral atom, there is great potential for enantiomers in organic compounds, including biological ones.

The compound shown below contains a carbon connected to a hydrogen, a bromine, a chlorine and a fluorine. A tetrahedral atom connected to four different things is called a chiral center; it is a place where two different arrangements are possible.

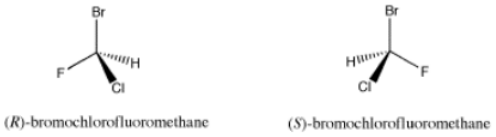


Figure 5.5.1: A pair of simple organic enantiomers.

This is not likely to be a naturally-occurring compound, although some marine organisms do make organic compounds containing bromine and chlorine. However, compounds similar to this one are sometimes used as general anaesthetics for surgical purposes. It is used as an example here because the chiral center is easy to see.

- A chiral center is a tetrahedral atom connected to four different groups.
- R and S configurations refer to the three-dimensional relationship of these groups around the chiral center.
- Assignment of R and S configuration follows a well-defined set of arbitrary rules. Anyone can follow these rules and arrive at the same configuration for the same structure.
- About half of S enantiomers rotate light in the (+) direction and about half rotate light in the (-) direction. R and S configurations do not correlate directly with optical rotation values; these are two ***unrelated*** systems for describing enantiomers.

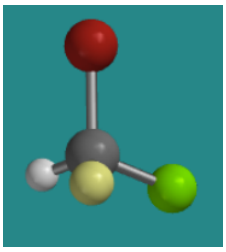


Figure 5.5.2: Ball-and-stick model of (*R*)-bromochlorofluoromethane.

Ball-and-stick model of bromochlorofluoromethane. Bromine is on top of the central carbon, fluorine points towards the camera, hydrogen is to the back left, chlorine is to the back right.

Go to **Animation SC4.1.** A three-dimensional model of (*R*)-bromochlorofluoromethane.

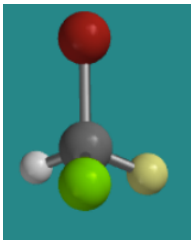


Figure 5.5.3: Ball-and-stick model of (*S*)-bromochlorofluoromethane.

Ball-and-stick model of bromochlorofluoromethane. Bromine is on top of the central carbon, chlorine points towards the camera, hydrogen is to the back left, fluorine is to the back right.

Go to **Animation SC4.2.** A three-dimensional model of (*S*)-bromochlorofluoromethane.

Rules for assigning *R* & *S* configuration:

- Find the chiral center(s).
- Compare the four atoms attached to the chiral center. What are their atomic numbers from highest to lowest?

- The highest atomic number has first priority; the second highest has second priority and so on.
- Turn the molecule so that the group with the lowest priority is away from you.
- Look at the three other groups. If they proceed in a clockwise direction from highest to second to third highest priority; the chiral center has the *R* configuration.
- If they proceed in a counterclockwise direction from highest to second to third highest priority; the chiral center has the *S* configuration.

Note

If two atoms connected to the chiral center have the same atomic number, you have to use a tie-breaker to decide which one gets higher priority. The tie-breaking rules are described on the next page; basically, you look at the next atoms attached to the ones that are the same.

Exercise 5.5.1

Explain the reasons for the assignment of configurations R and S in the models above. Assume red is bromine, bright green is chlorine and pale green is fluorine.

Answer

Priority of groups:

1 Br (red)

2 Cl (bright green)

3 F (pale green)

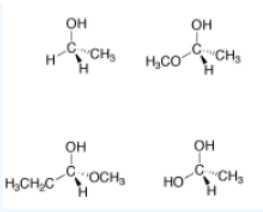
4 H (white)

In the molecule in Figure 5.5.2 (SC4.2), with the low-priority hydrogen pointed away, bromine is at the top, chlorine is clockwise from the bromine, and fluorine is clockwise from the chlorine. It therefore has an assigned configuration of *R*.

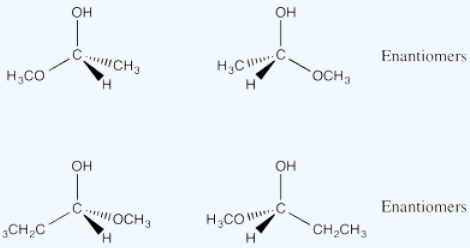
In the molecule in Figure 5.5.3 (SC4.3), with the low-priority hydrogen pointed away, bromine is at the top, chlorine is counterclockwise from the bromine, and fluorine is counterclockwise from the chlorine. Thus, it has an assigned configuration of *S*.

Exercise 5.5.2

Which of the following compounds have enantiomers? If they exist, draw them.



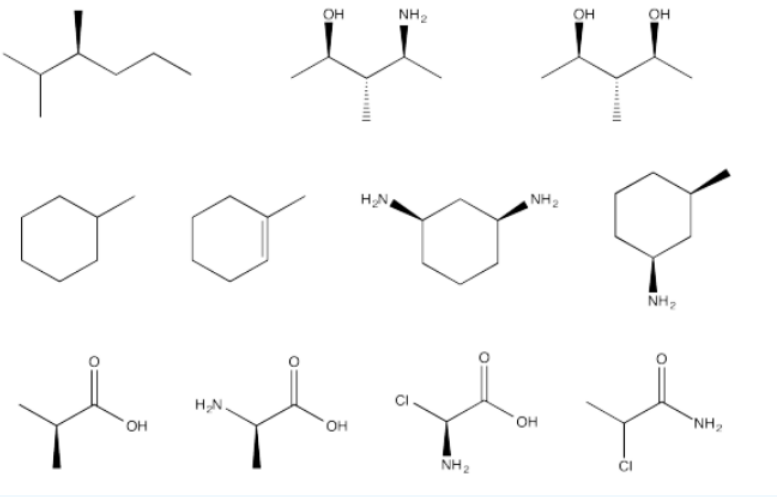
Answer



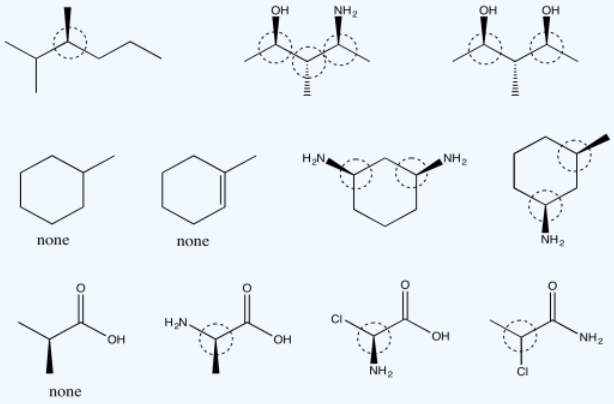
AnswerExercise 5.5.2, showing four different molecules with stereochemistry. Clockwise from top left: ethanol, 1-methoxy-1-ethanol, 1-ethoxy-1-propanol, 1,1-ethanediol.

Exercise 5.5.3

Circle the stereocenters in the following compounds.



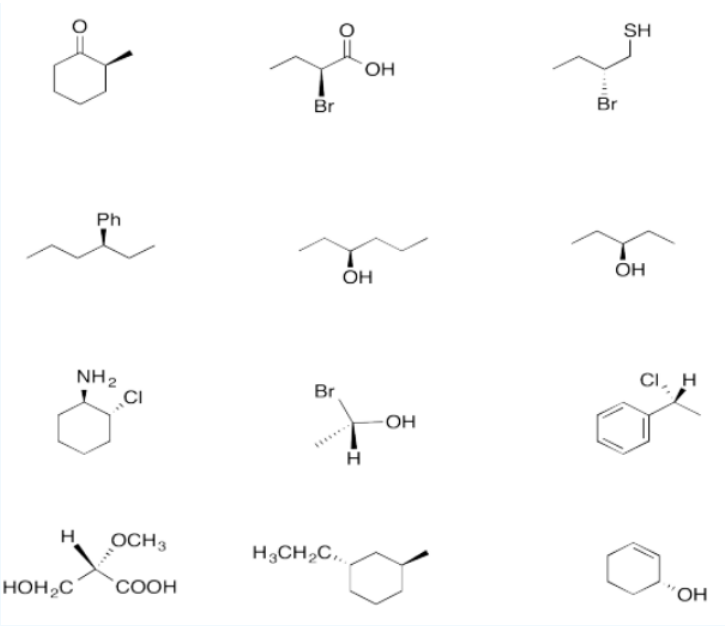
Answer



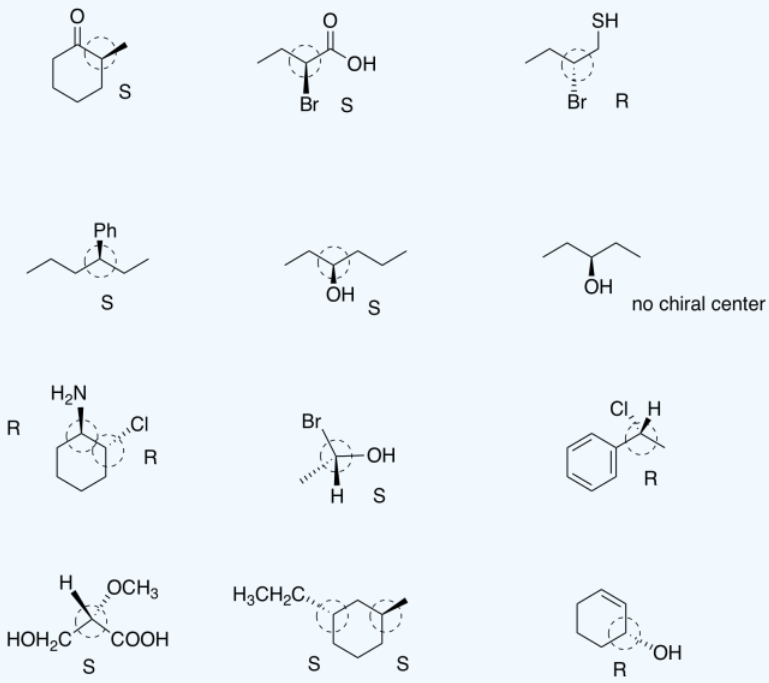
Answer

Exercise 5.5.4

Assign configuration of the stereocenters (*R* or *S*) in the following compounds.



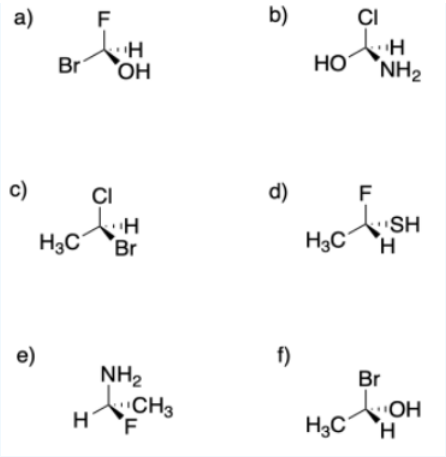
Answer



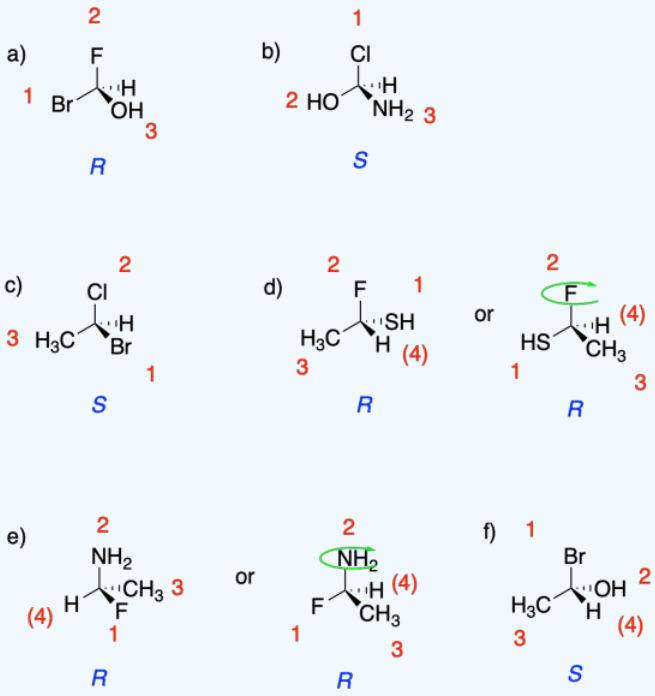
Answer

Exercise 5.5.5

Assign configurations (R or S) to the chiral centers in these molecules.



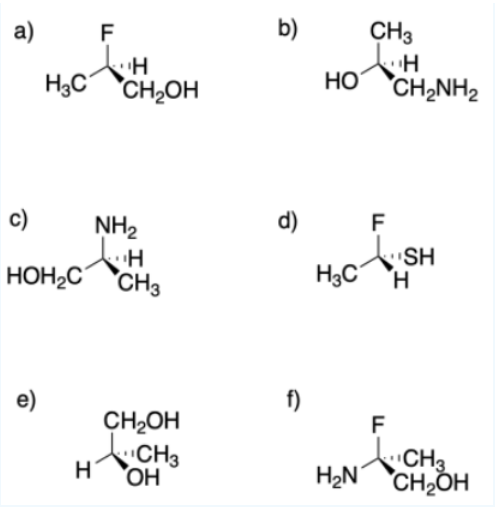
Answer



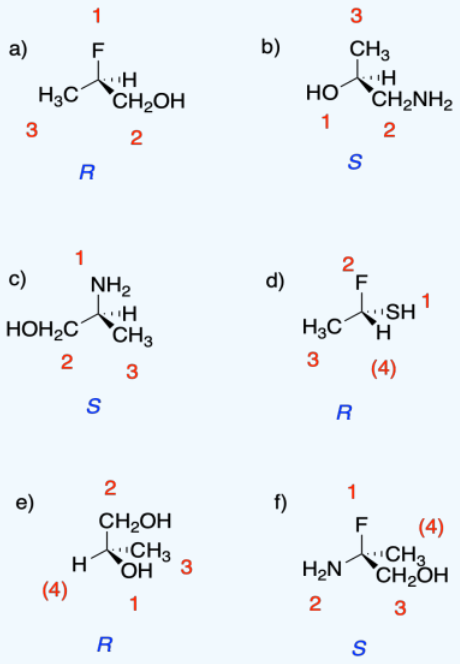
Answer

Exercise 5.5.6

Assign configurations (R or S) to the chiral centers in these molecules.



Answer



Answer

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5.6: Biological Small Molecules

There are a number of important biomolecules that could occur as enantiomers, including amino acids and sugars. In most cases, only one enantiomer occurs (although some fungi, for example, are able to produce mirror-image forms of these compounds). We will look later at some of these biomolecules, but first we will look at a compound that occurs naturally in both enantiomeric forms.

Carvone is a secondary metabolite. That means it is a naturally-occurring compound that is not directly connected to the very basic functions of a cell, such as self-replication or the production of energy. The role of secondary metabolites in nature is often difficult to determine. However, these compounds often play roles in self-defense, acting as deterrents against competitor species in a sort of small-scale chemical warfare scenario. They are also frequently used in communications; this role has been studied most extensively among insects, which use lots of compounds to send information to each other.

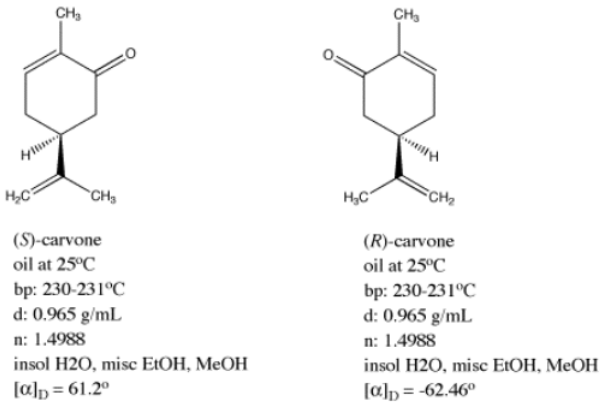


Figure 5.6.1: The two naturally-occurring enantiomers of carvone.

Comparison of R- and S-carvone. Left: S-carvone [a]D is 61.2 degrees. Right: R-carvone [a]D is -62.46 degrees. Both molecules are oil at 25C, have a boiling point at 230-231C, have density of 0.965g/mL, n of 1.4988, are insoluble in water, and miscible in ethanol and methanol.

Carvone is produced in two enantiomeric forms. One of these forms, called (-)-carvone, is found in mint leaves, and it is a principal contributor to the distinctive odor of mint. The other form, (+)-carvone, is found in caraway seeds. This form has a very different smell, and is typically used to flavour rye bread and other Eastern European foods. The structural connectivity in these two compounds appears to be identical, but they aren't the same in three dimensions, as you will find if you build models of them. Instead, (+)- and (-)-carvone are mirror images of each other, like a right hand and a left hand.

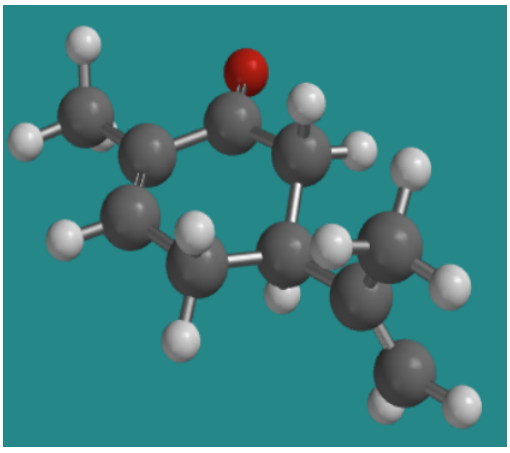


Figure 5.6.2: Ball-and-stick model of (*R*)-carvone.

Go to **Animation SC5.1.** A three-dimensional model of (*R*)-carvone.

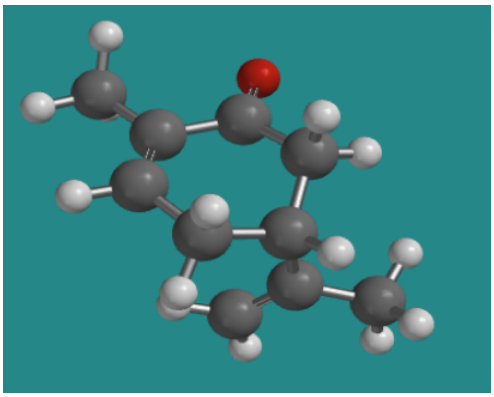


Figure 5.6.3: Ball-and-stick model of (*S*)-carvone.

Go to **Animation SC5.2.** A three-dimensional model of (*S*)-carvone.

Note that (+)-carvone is the same thing as (S)-carvone. The (+) designation is based on its positive optical rotation value, which is experimentally measured. The (S) designation is determined by the Cahn-Ingold-Prelog rules for designating stereochemistry, which deal with looking at the groups attached to a chiral center and assigning priority based on atomic number. However, carvone's chiral center actually has three carbons attached to it; they all have the same atomic number. We need a new rule to break the tie.

- If two substituent groups have the same atomic number, go one bond further to the next atom.
- If there is a difference among the second tier of atoms, stop.
- The group in which you have encountered a higher atomic number gets the highest priority.
- If there is not a clear difference, proceed one additional bond to the next set of atoms, and so on, until you find a difference.

In carvone, this decision tree works as follows:

- .The chiral center is connected to a H, a C, a C and a C.
- The H is lowest priority.
- One C eventually leads to a C=O. However, at the second bond from the chiral center, this C is connected to a C and two H's.
- A second C is also part of the six-membered ring, but the C=O is farther away in this direction. At the second bond from the chiral center, this C is connected to a C and two H's, just like the first one.
- The third C is part of a little three-carbon group attached to the six-membered ring. At the second bond from the chiral center, it is connected to only one H and has two bonds to another C (this is counted as two bonds to C and one to H).
- Those first two carbon groups are identical so far.
- However, the third group is different; it has an extra bond to C, whereas the others have an extra bond to H. C has a higher atomic number than H, so this group has higher priority.
- The second-highest priority is the branch that reaches the oxygen at the third bond from the chiral center.

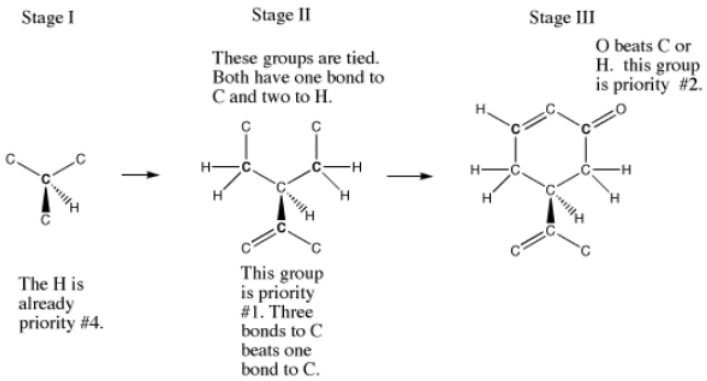


Figure 5.6.4: Comparing atoms step-by-step to assign configuration.

Stages 1, 2, and 3 of assigning priority to different parts of carvone at a chiral center. Stage 1: H is already priority #4, with three bonds to carbon left. Stage 2: two groups are tied, with one bond to carbon and two to H each. The carbon with a double bond to another carbon and a single bond to another carbon is priority #1, since it has three bonds to carbon. Stage 3: The carbon with a ketone group is priority #2, since O beats C or H.

How different, exactly, are these two compounds, (+)- and (-)-carvone? Are they completely different isomers, with different physical properties? In most ways, the answer is no. These two compounds have the same appearance (colorless oil), the same boiling point (230 ° C), the same refractive index (1.499) and specific gravity (0.965). However, they have optical rotations that are almost exactly opposite values.

- Two enantiomers have the same physical properties.
- Enantiomers have opposite optical rotations.

Clearly they have different biological properties; since they have slightly different odors, they must fit into slightly different nasal receptors, signaling to the brain whether the person next to you is chewing a stick of gum or a piece of rye bread. This different shape complimentarity is not surprising, just as it isn't surprising that a left hand only fits into a left handed baseball glove and not into a right handed one.

There are other reasons that we might concern ourselves with an understanding of enantiomers, apart from dietary and olfactory preferences. Perhaps the most dramatic example of the importance of enantiomers can be found in the case of thalidomide. Thalidomide was a drug commonly prescribed during the 1950's and 1960's in order to alleviate nausea and other symptoms of morning sickness. In fact, only one enantiomer of thalidomide had any therapeutic effect in this regard. The other enantiomer, apart from being therapeutically useless in this application, was subsequently found to be a teratogen, meaning it produces pronounced birth defects. This was obviously not a good thing to prescribe to pregnant women. Workers in the pharmaceutical industry are now much more aware of these kinds of consequences, although of course not all problems with drugs go undetected even through the extensive clinical trials required in the United States. Since the era of thalidomide, however, a tremendous amount of research in the field of synthetic organic chemistry has been devoted to methods of producing only one enantiomer of a useful compound and not the other. This effort probably represents the single biggest aim of synthetic organic chemistry through the last quarter century.

- Enantiomers may have very different biological properties.
- Obtaining enantiomerically pure compounds is very important in medicine and the pharmaceutical industry.

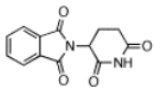


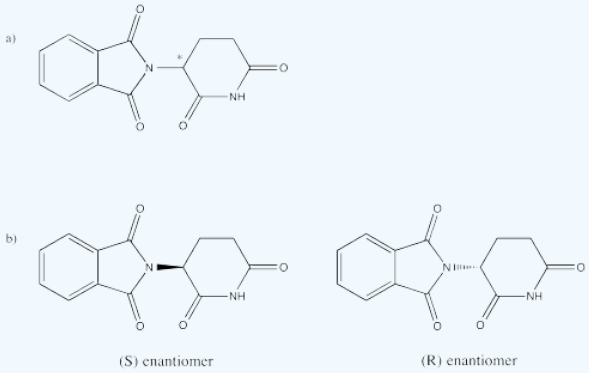
Figure 5.6.5: Thalidomide.

Exercise 5.6.1

a) Draw thalidomide and identify the chiral center with an asterisk.

b) Draw the two possible enantiomeric forms of thalidomide.

Answer



Exercise 5.6.2

Draw the two enantiomeric forms of 2-butanol, $CH_3CH(OH)CH_2CH_3$. Label their configurations.

Answer

Exercise 5.6.3

Sometimes, compounds have many chiral centers in them. For the following compounds, identify four chiral centers in each, mark them with asterisks, and identify each center as R or S configuration.

The following is the structure of dysinosin A, a potent thrombin inhibitor that consequently prevents blood clotting.

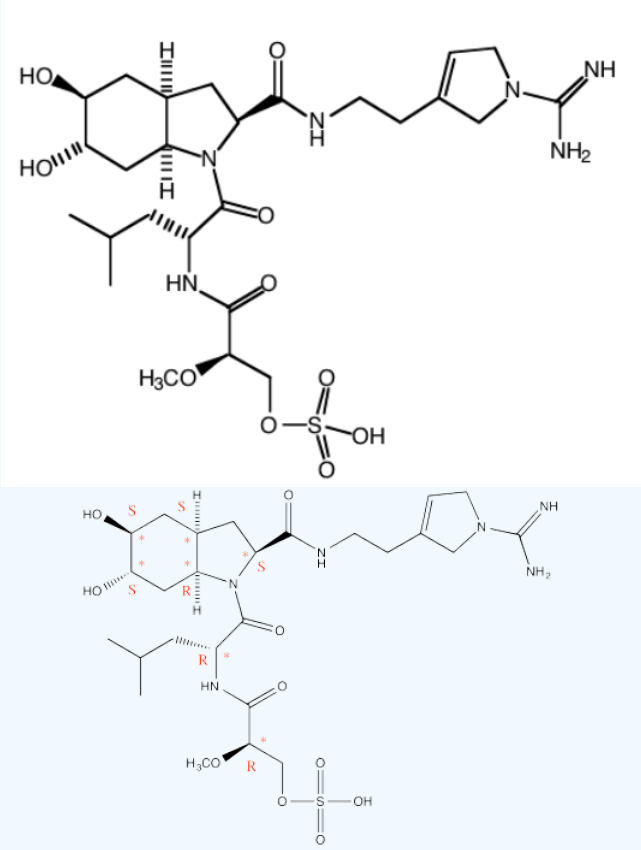


Figure 5.6.6 Answer

Ginkgolide B (below) is a secondary metabolite of the ginkgo tree, extracts of which are used in Chinese medicine.

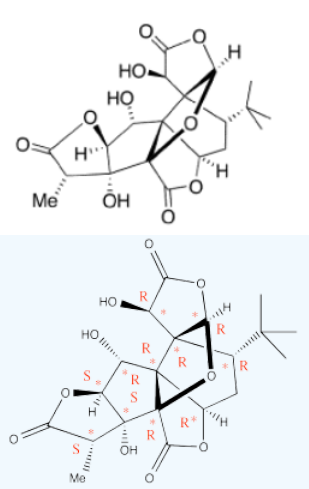


Figure 5.6.7:Answer

Sanglifehrin A, shown below, is produced by a bacteria that may be found in the soil of coffee plantations in Malawi. It is also a promising candidate for the treatment of organ transplant patients owing to its potent immuno-suppressant activity.

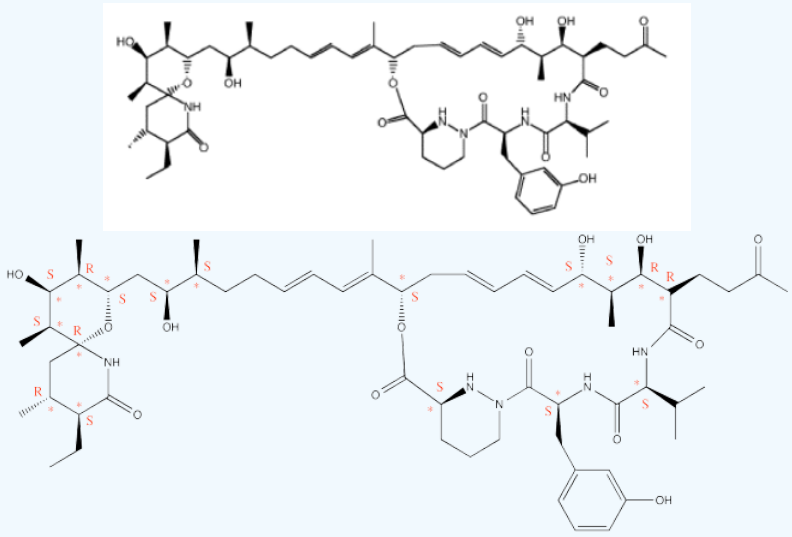


Figure 5.6.8:Answer

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5.7: Optical Rotation

- An equal mixture of two enantiomers is called a racemic mixture or racemate.
- If two enantiomers rotate plane-polarized light in opposite directions, a racemate will not rotate light at all. The effects of the two enantiomers will cancel out.

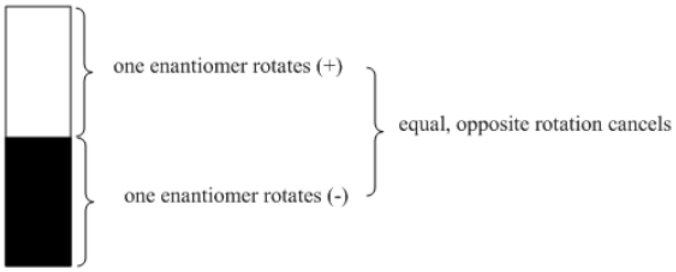


Figure 5.7.1: Optical rotation canceled out in a racemic mixture.

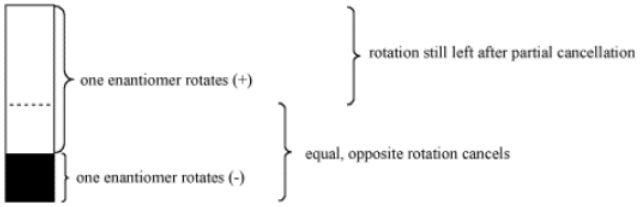


Figure 5.7.2: Optical rotation only partially canceled in a non-racemic mixture of enantiomers

e "optical purity" is a comparison of the optical rotation of a pure sample of unknown stereochemistry versus the optical rotation of a sample of pure enantiomer. It is expressed as a percentage. If the sample only rotates plane-polarized light half as much as expected, the optical purity is 50%.

Optical purity also corresponds to "enantiomeric excess". If the unknown sample rotates light 50% as much as a sample of pure enantiomer, it must contain 50% enantiomeric excess; the other 50% is a racemic mixture. In other words, if the sample is 75% of one enantiomer and 25% of the other, 50% of the mixture will simply cancel out in terms of optical activity. The remaining 50% will still exert optical activity, but only half as much as if the sample were 100% of that enantiomer.

These relationships could be expressed in formulae:

$$\text{Optical purity (op)} = \frac{\text{(optical rotation of pure compound)}}{\text{(optical rotation of pure enantiomer)}} \times 100\%$$

Enantiomeric excess (ee) = optical purity (that is, these numbers are always the same, although they represent different things)

$$\%\text{major enantiomer} = \text{enantiomeric excess} + \frac{100 - \text{enantiomeric excess}}{2} = 50 + \frac{\text{enantiomeric excess}}{2}$$

$$\%\text{minor enantiomer} = 100 - \%\text{ major enantiomer}$$

Exercise 5.7.1

The (+) enantiomer of compound A has an optical rotation of 75°. If a sample containing only compound A has an optical rotation of 50°, what is the composition of the sample?

Answer

A pure sample of A would have $[\alpha] = 75^o$

Optical purity or enatiomeric excess $= \frac{50}{75} = 66\%$

% major enantiomer $= 66 + \frac{34}{2} = 83\%$

% minor enantiomer $= 100 - 83 = 17\%$

Exercise 5.7.2

The (+) enantiomer of compound B has an optical rotation of 50º. If a sample containing only B contains 10% of the (+) enantiomer and 90% of the (-) enantiomer, what is the optical rotation value?

Answer

$$\%major = 90\%$$

$$\%minor = 10\%$$

Optical purity or enantiomeric excess $= \frac{X}{-50} = 90 - 10 - 80\%$

Solve for X.

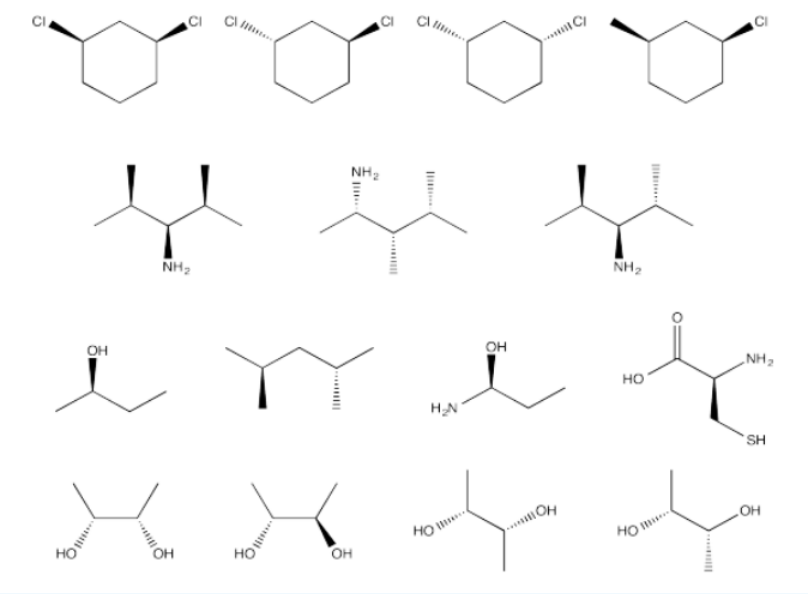
$$X = -40^{\circ}$$

Exercise 5.7.3

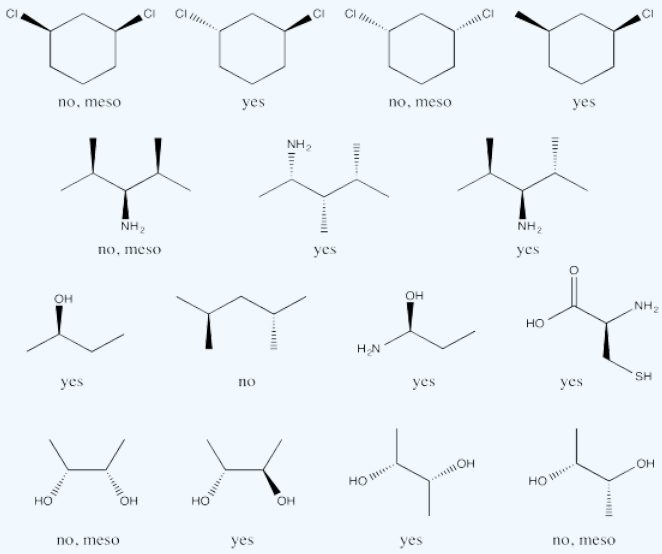
The (-) enantiomer of compound C has an optical rotation of -60. A sample of compound C is shown by chiral gas chromatography to contain only (-) C and no (+) C, but NMR analysis suggests the sample is about 50% ethyl acetate by weight. Predict the measured optical rotation of a 1 g/mL solution in dichloromethane, measured in a 1 dm cell.

Exercise 5.7.4

Which of the following compounds are optically active?



Answer



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5.8: The Polarimetry Experiment

In measuring optical rotation, plane-polarized light travels down a long tube containing the sample. If it is a liquid, the sample may be placed in the tube as a pure liquid (it is sometimes called a neat sample). Usually, the sample is dissolved in a solvent and the resulting solution is placed in the tube.

There are important factors affecting the outcome of the experiment.

- Optical rotation depends on the number of molecules encountered by the light during the experiment.
- Two factors can be controlled in the experiment and must be accounted for when comparing an experimental result to a reported value.

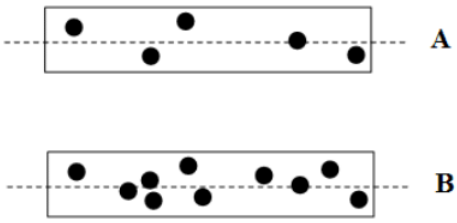

Figure 5.8.1: The effect of concentration on optical rotation.

- The more concentrated the sample (the more molecules per unit volume), the more molecules will be encountered.
- Concentrated solutions and neat samples will have higher optical rotations than dilute solutions.
- The value of the optical rotation must be corrected for concentration.

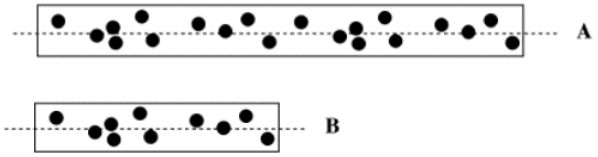

Figure 5.8.2: The effect of path length on optical rotation.

- The longer the path of light through a solution of molecules, the more molecules will be encountered by the light, and the greater the optical rotation.
- The value of the optical rotation must be corrected for the length of the cell used to hold the sample.

In summary:

$$[\alpha] = \frac{\alpha}{c \times l}$$

- a is the measured optical rotation.
- c is the sample concentration in grams per deciliter (1 dL = 10 mL).
- That is, c = m / V (m = mass in g, V = volume in dL).
- l is the cell length in decimeters (1 dm = 10 cm = 100 mm)
- The square brackets mean the optical rotation has been corrected for these variables.

Exercise 5.8.1

A pure sample of the naturally-occurring, chiral compound A (0.250 g) is dissolved in acetone (2.0 mL) and the solution is placed in a 0.5 dm cell. Three polarimetry readings are recorded with the sample: 0.775°, 0.806°, 0.682°.

a) What is [a]?

b) What would be the [a] value of the opposite enantiomer?

Answer a:

$$[a] = \frac{a}{(c)(l)}$$

$$c = (\frac{0.250g}{2mL})(\frac{10mL}{1dL}) = 1.25\frac{g}{dL}$$

$$a = \frac{0.775^o + 0.806^o + 0.682^o}{3} = 0.754^o$$

$$[a] = \frac{a}{(c)(l)} = \frac{0.754^o}{(1.25\frac{g}{dL})(0.5dm)} = +1.21^o$$

Answer b:

-1.21°

Exercise 5.8.2

A pure sample of the (+) enantiomer of compound B shows [a] = 32°. What would be the observed a if a solution of the sample was made by dissolving 0.150 g in 1.0 mL of dichloromethane and was then placed in a 0.5 dm cell?

Answer

$$[a] = \frac{a}{(c)(l)}$$

$$[a] = 32^o$$

$$c = (\frac{0.150g}{1mL})(\frac{10mL}{1dL}) = 1.5\frac{g}{dL}$$

$$[a] = \frac{a}{(c)(l)} = 32^o = \frac{a}{(1.5\frac{g}{dL})(0.5dm}$$

Solve for a.

$$a = +24^o$$

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5.9: Carbohydrates and Diastereomers

So far, we have mostly been looking at compounds that contain one chiral center -- that is, one tetrahedral carbon atom with four different groups attached to it. Could there be more than one chiral center? Of course. For example, if carbohydrates have an OH group on every carbon in a chain, we might get a number of chiral centers in one molecule. Thinking in Fischer projections, that means each of the OH groups on the chiral centers could be drawn either on the right or on the left.

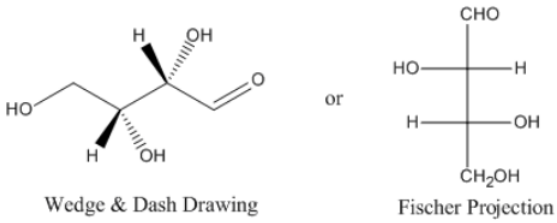
Of course, two compounds with multiple chiral centers could still be enantiomers. Maybe we have two carbohydrates, one with all of the OH groups on the right in the Fischer projection, the other with all of them on the left. Those two compounds would still be the exact opposite of each other. They would still be enantiomers.

Suppose instead that only some of the chiral centers were opposite, and others were the same. The compounds would no longer be exact mirror images of each other. The mirror would be flawed. These isomers would be called diastereomers.

We know that enantiomers have the same physical properties. Diastereomers do not. For example, they have different melting points, because the two isomers cannot pack together in exactly the same way, and the intermolecular attractions are different in each case.

- Diastereomers only occur in compounds containing more than one chiral center.
- In a pair of diastereomers, some of the chiral centers are the same in the two molecules, but others are different.
- Diastereomers are stereoisomers that are not mirror images of each other.

Threose is an example of a biological molecule (a carbohydrate) that contains two chiral centers.



D-threose

Figure 5.9.1: Pictures of D-threose.

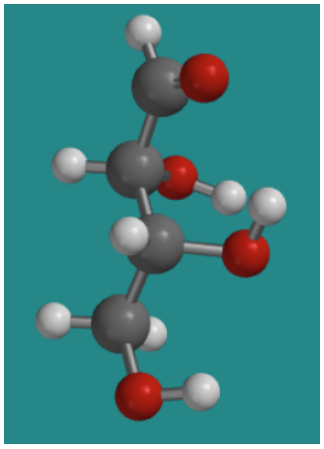


Figure 5.9.2: A ball-and-stick model of D-threose.

Fischer projections are sometimes used in showing carbohydrates and other chain compounds with many chiral centers. Fischer projections are Picasso-esque drawings in which the point of view alternates from one carbon to the next. The chiral centers are easy to compare in Fischer projections because you simply have to decide whether groups are on the same side or opposite sides of the vertical line.

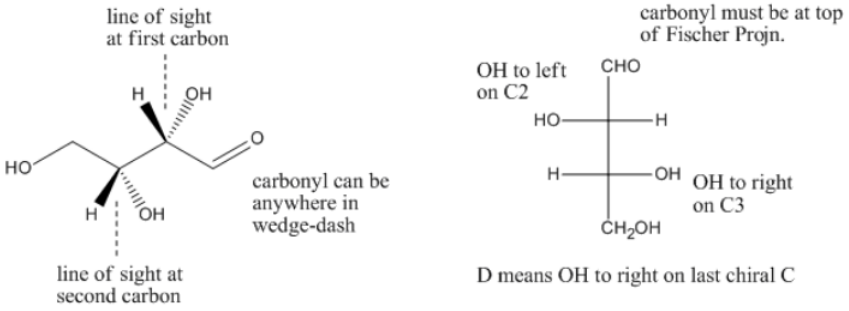


Figure 5.9.3: A little more insight into D-threose.

D-threose is chiral and it does have an enantiomer. Its enantiomer is called L-threose. L-threose has exactly the same physical properties as D-threose, except for one. A solution of D-threose rotates a beam of plane-polarized light to the right, whereas a solution of L-threose rotates the plane to the left.

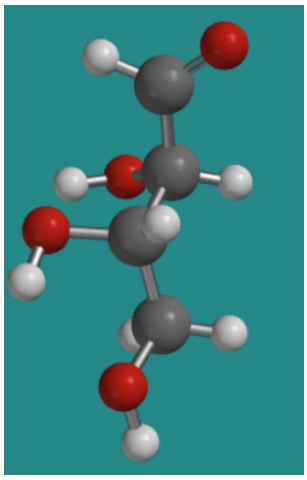


Figure 5.9.4: A ball-and-stick model of L-threose.

However, D-threose also has other stereoisomers that are NOT its mirror image. These isomers are called diastereomers. These compounds have different physical properties from threose, so they have a completely different common name. That's because common names for compounds were often coined before anyone knew about the structure of the compound.

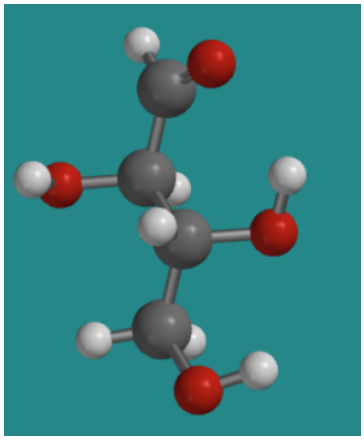


Figure 5.9.5: A ball-and-stick model of D-erythrose.

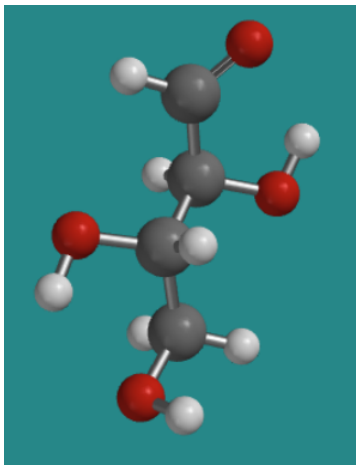


Figure 5.9.6: A ball-and-stick model of L-erythrose.

The relationships between D-threose and its stereoisomers can be seen in wedge-dash projections. The family of aldobutanoses -- that is, four-carbon dugars containing an aldehyde group -- is presented together below.

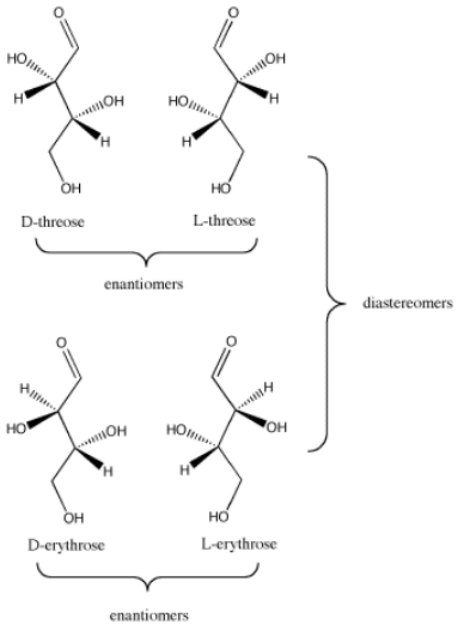


Figure 5.9.7: The relationship between D-threose and its enantiomer, L-threose; also, the relationship between D-threose and its two diastereomers, D- and L-erythrose.

Alternatively, these relationships can be viewed in Fischer projections.

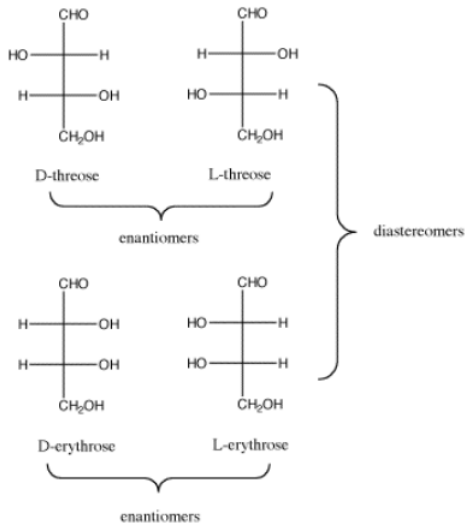


Figure 5.9.8: The relationship between D-threose and its enantiomer, L-threose; also, the relationship between D-threose and its two diastereomers, D- and L-erythrose.

Alternatively, these relationships can be viewed in Fischer projections.

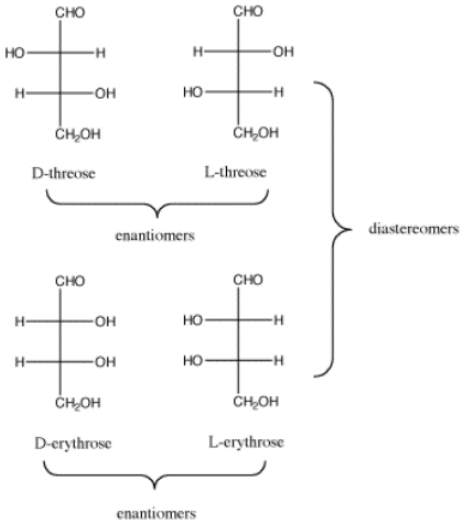


Figure 5.9.9: The relationship between D-threose and its enantiomer, L-threose; also, the relationship between D-threose and its two diastereomers, D- and L-erythrose. Once more with Fischer.

- In a pair of diastereomers, some chiral centers are the same and some are opposite. The molecule is neither identical to nor the mirror image of its diastereomer.
- D-threose is the enantiomer of L-threose. The two are non-identical, but they are mirror images of each other.

It may help to look at three-dimensional models of these sugars.

Go to **Animation SC9.1.** A three-dimensional model of D-threose.

Go to **Animation SC9.2.** A three-dimensional model of L-threosee.

Go to **Animation SC9.3.** A three-dimensional model of D-erythrose.

Go to **Animation SC9.4.** A three-dimensional model of L-erythrose.

Exercise 5.9.1

Take a look at the three-dimensional model of D-threose using the stick model.

a. If you turn it so that the carbonyl is at the top and the OH and H of the first chiral carbon are coming towards you, is the first OH on the right or on the left?

b. If you turn it so that the carbonyl is at the top and the OH and H of the second chiral carbon are coming towards you, is the first OH on the right or on the left?

Answer a:

left

Answer b:

right

Exercise 5.9.2

Take a look at the three-dimensional model of L-threose using the stick model.

a. If you turn it so that the carbonyl is at the top and the OH and H of the first chiral carbon are coming towards you, is the first OH on the right or on the left?
b. If you turn it so that the carbonyl is at the top and the OH and H of the second chiral carbon are coming towards you, is the first OH on the right or on the left?

Answer a:

right

Answer b:

left

Exercise 5.9.3

Take a look at the three-dimensional model of D-erythrose using the stick model.

a. If you turn it so that the carbonyl is at the top and the OH and H of the first chiral carbon are coming towards you, is the first OH on the right or on the left?
b. If you turn it so that the carbonyl is at the top and the OH and H of the second chiral carbon are coming towards you, is the first OH on the right or on the left?

Answer a:

right

Answer b:

right

Exercise 5.9.4

Take a look at the three-dimensional model of L-erythrose using the stick model.

a. If you turn it so that the carbonyl is at the top and the OH and H of the first chiral carbon are coming towards you, is the first OH on the right or on the left?
b. If you turn it so that the carbonyl is at the top and the OH and H of the second chiral carbon are coming towards you, is the first OH on the right or on the left?

Answer a:

left

Answer b:

left

- When there is one chiral center present, two stereoisomers result.

- When there are two chiral centers present, four stereoisomers result.
- For each additional chiral center, the number of stereoisomers doubles.

Carbohydrates can be classified according to their stereochemistry, forming a sort of carbohydrate family tree. They are considered to originate from the simplest carbohydrate, glyceraldehyde. Addition of a new carbon to the C=O unit of glyceraldehyde produces two possible isomers, because a new steresocenter is formed. From there, additional carbohydrates can be built up, one carbon at a time. In the carbohydrate family tree, glyceraldehyde is great-grandmother.

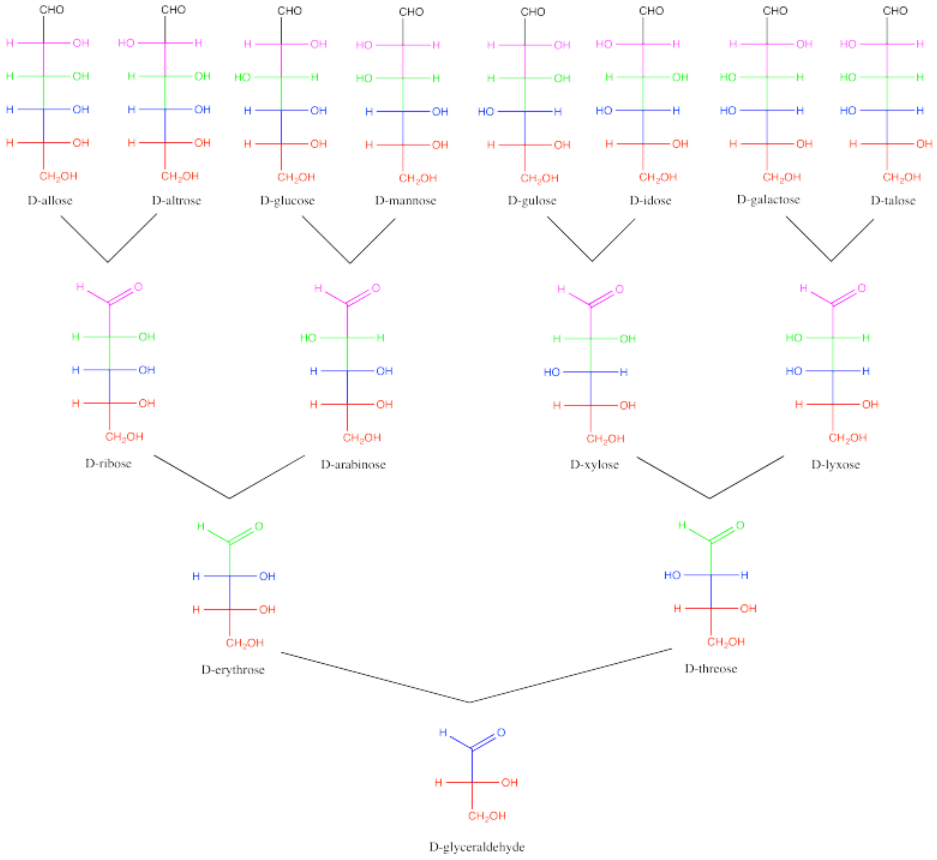


Figure 5.9.10: Relationships among a family of D-carbohydrates.

Exercise 5.9.5

What are the absolute configurations of the two chiral centers in D-threose? (You will need to number the carbons on which the chiral centers are found. For example, if an *S* center is found on the second carbon along the chain and an *R* center is found on the fourth carbon along the chain, the configuration is *2S,4R*. Note that you should number the chain from the highest-priority end, which has a carbon with the most bonds to oxygen.)

Answer

D-threose

2*S*, 3*R*

Exercise 5.9.6

What are the absolute configurations in L-threose? What do you notice about the relationship between the configurations in D- and L- threose?

Answer

L-threose

2*R*, 3*S*

D- and L-threose are enantiomers of one another

Exercise 5.9.7

What are the absolute configurations in L-erythrose? What do you notice about the relationships between the configurations in L-erythrose and L- threose?

Answer

L-erythrose

2*S*, 3*S*

L-erythrose and L-threose are diastereomers of one another.

Exercise 5.9.8

Suppose a compound contained three chiral centers.

a. How many possible stereoisomers would there be?
b. How many different pairs of enantiomers would there be?
c. Suppose you selected a pair of diastereomers from this group. How many possible pairs could you choose from?

Answer a:

$(2)^3$ = 8 possible stereoisomers

RRR; SSS; RRS; SSR; RSS; SRR; SRS; RSR

Answer b:

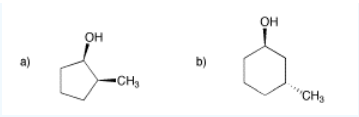
4 pairs

Answer c:

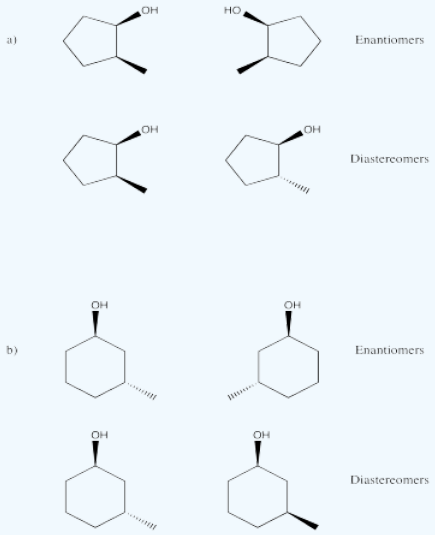
12 different possible pairs of diastereomers

Exercise 5.9.9

Draw one enantiomer and one diastereomer for each of the following compounds.



Answer



Exercise 5.9.10

Draw one enantiomer and one diastereomer for each of the following compounds.

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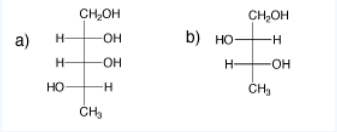
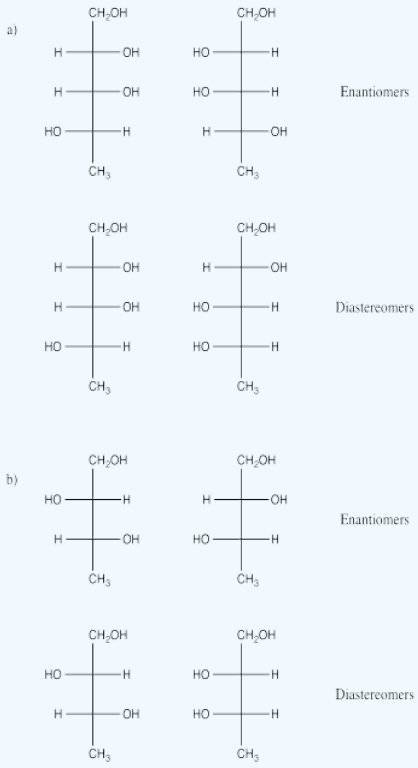


Answer



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5.10: Diastereomers and Physical Properties

- In a pair of diastereomers, some chiral centers are the same and some are opposite. The molecule is neither identical to nor the mirror image of its diastereomer.

Threitol is a metabolite closely related to carbohydrates. D-threitol is the enantiomer of L-threitol. The two are non-identical, but they are mirror images of each other. Both compounds can be crystallized, forming needle-like crystals. Both have melting points of 88-89ºC. D-threose has an optical rotation $[a]_D$= - 4.0 (c, 7 in H_2O, but L-threose has an optical rotation $[a]_D$= + 4.6 (c, 6 in H_2O). You might notice that these two numbers are not exactly opposites, but if you have ever tried measuring an optical rotation yourself, you know that this is pretty good.

- Enantiomers have identical physical properties, except that the optical rotation is opposite.

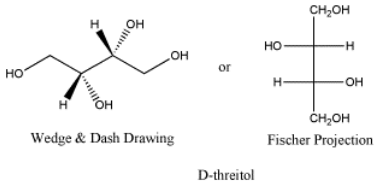


Figure 5.10.1: D-threitol, a reduced form of threose.

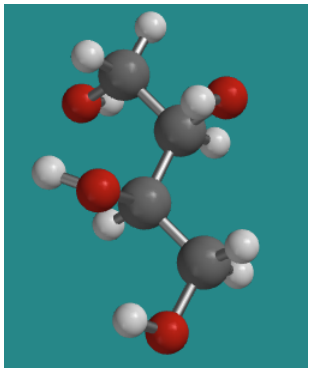


Figure 5.10.2: A ball-and-stick model of D-threitol.

Here is the other anantiomer. Once again, the Fischer projection makes it really easy to see the difference, but navigating back and forth between Fischer and wedge-dash can be tricky. The ball-and-stick model is rotated a little compared to the model of D-threose; see if can confirm that this is really the enantiomer.

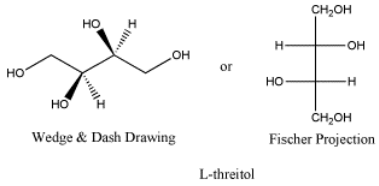


Figure 5.10.3: . L-threitol, the enantiomer of D-threitol

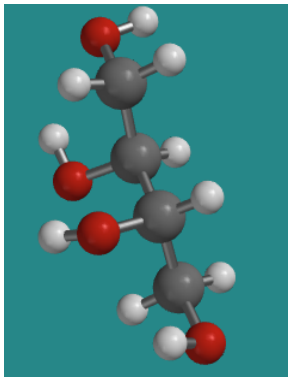


Figure 5.10.4: A ball-and-stick model of L-threitol.

Go to **Animation SC10.2.** A three-dimensional model of L-threitol.

Erythritol: a meso compound

Erythritol is a diastereomer to both L-threose and D-threose. It has one identical chiral center and one opposite one. Erythritol is a solid with a melting point of 121ºC and no optical rotation. Erythritol has properties that are different from threitol.

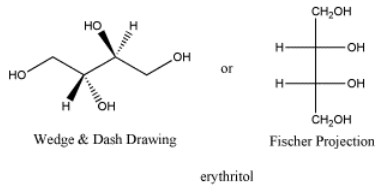


Figure 5.10.5: Erythritol, the diastereomer of threitol.

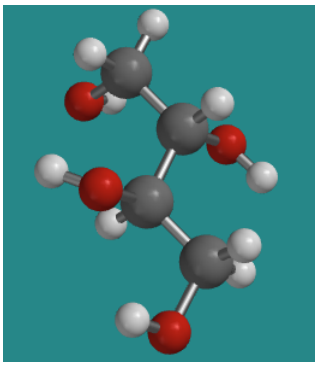


Figure 5.10.6: A ball-and-stick model of D-threitol.

Go to **Animation SC10.3.** A three-dimensional model of erythritol.

- Diastereomers have different physical properties.
- They do not have the same overall shape.
- They fit together in different ways, and experience different intermolecular attractions.

The fact that erythritol contains chiral centers but has no optical rotation is unusual. Erythritol is chiral but not optically active. It is a special case called a meso compound.

- A meso compound contains two identical, opposite chiral centers.
- Rotation of plane-polarized light is canceled between these two centers, just like in a racemic mixture.
- Meso compounds are not optically active and do not have enantiomers, because the mirror image of a meso compound is itself.

It may be easier to see the mirror symmetry within erythritol if it is in a less-stable conformation. In the following model, the carbon backbone is held in a curled-up, eclipsed conformation rather than the usual zig-zag, staggered conformer. You might notice in the animation that this is really what we are looking at in a Fischer projection: the backbone is always curling away from us, with attached groups projecting towards us on either side. Here, the top half of the molecule is just a reflection of the bottom half.

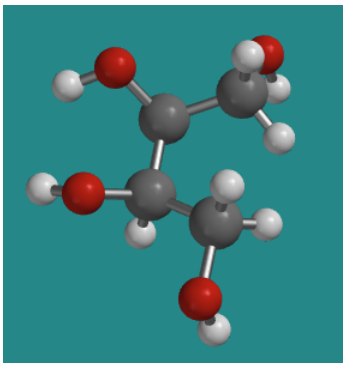


Figure 5.10.7: A ball-and-stick model of erythritol in an eclipsed conformation.

Go to **Animation SC10.4.** Another three-dimensional model of erythritol.

Exercise 5.10.1

What are the absolute configurations of each chiral carbon in:

a. D-threitol?
b. L-threitol?
c. erythritol?

Answer a:

D-threitol → 2R, 3S

Answer b:

L- threitol → 2S, 3S

Answer c:

erythritol → 2S, 3R or 2R, 3S (a meso compound)

Exercise 5.10.2

In problem 5.10.1, you should have numbered the carbons corresponding to each chiral center when you were denoting the absolute configuration. How did you know which end of the chain to start counting from?

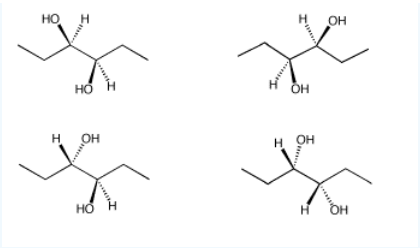
Answer

It does not matter which end you start counting from on these compounds since they are constituted the same.

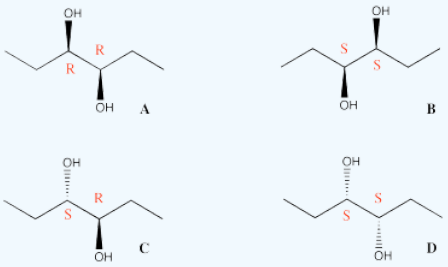
Exercise 5.10.3

From the following group of molecules, select:

a. a pair that are the same compound.
b. a pair that would have the same physical properties but opposite optical activities.
c. a pair that have different physical properties.
d. a compound that contains chiral centers but has no optical activity.



Answer



a) **B** and **D**

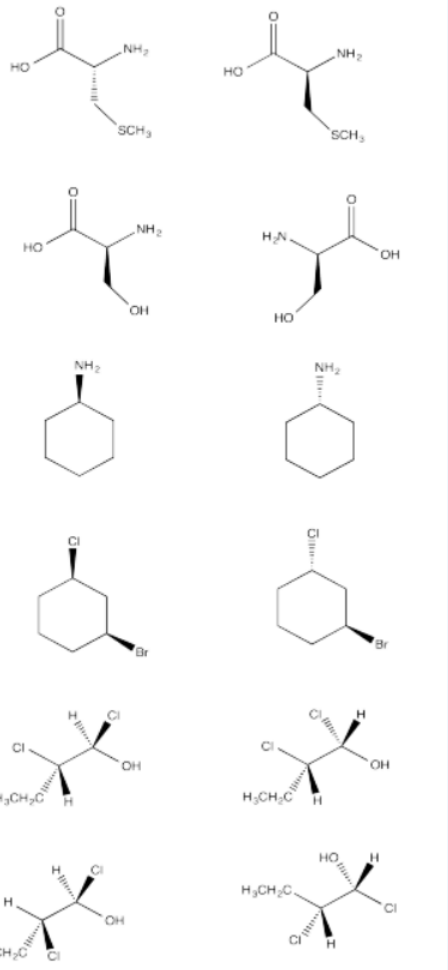
b) **A** and **D** or **A** and **B**

c) **A** and **C** or **B** and **C** or **D** and **C**

d) **C**

Exercise 5.10.4

What is the isomeric relationship between the following pairs of molecules (diastereomers, enantiomers, constitutional isomers, identical)?



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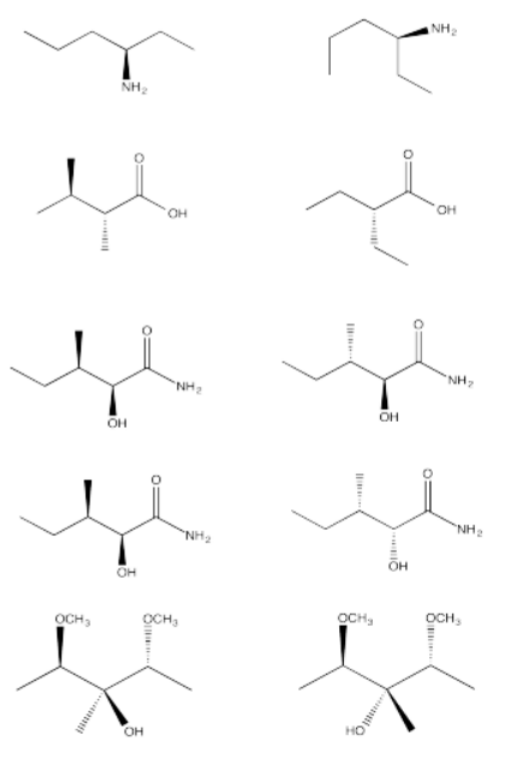
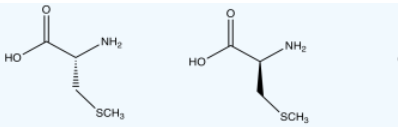
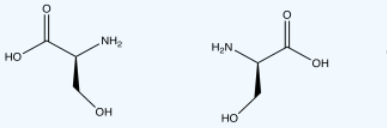
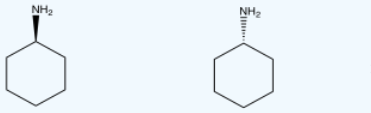


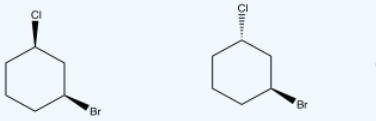
Answer

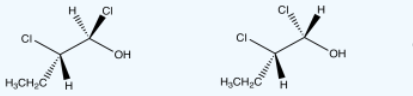
https://chem.libretexts.org/@go/page/191218

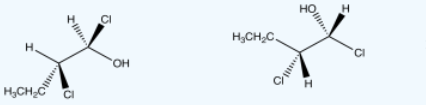

enantiomers


enantiomers


identical

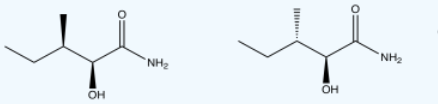

diastereomers

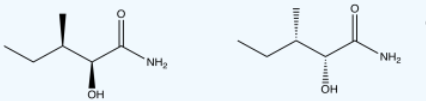

diastereomers


identical

enantiomers

constitutional isomers


diastereomers


enantiomers

identical

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5.11: Carbohydrates in Cyclic Form

Carbohydrates are complicated molecules. In solution, they slowly change into different isomers. In water, most carbohydrates can change from one form to another quickly; they are described as being in equilibrium with different structures. That means they can change back and forth.

The most prevalent form for most carbohydrates is a ring. One of the oxygens farther along the chain can reach around and bond to the carbon in the C=O at the head of the chain. When that happens, there are two possible orientations of the oxygen at the head of the chain. The two stereoisomers that result are diastereomers. Some of the chiral centers are the same, but one is different.

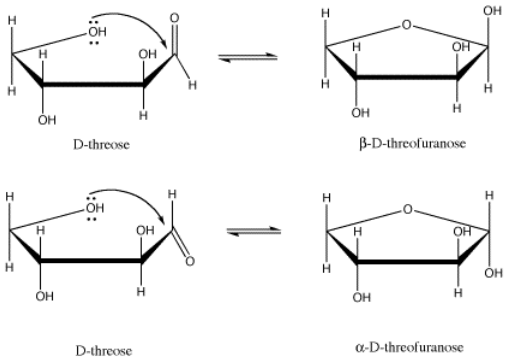


Figure 5.11.1: D-threose and its two possible five-membered-ring forms.

For example, D-threose can form two different five-membered rings (that is, rings made from a circle of five atoms). In carbohydrates, a five-membered ring with an oxygen in it is called a furanose (another common form, a six-membered ring, is called a pyranose). There are two diastereomers formed. they are sometimes called anomers. That means they differ in 3D space at the anomeric center; the anomeric center is the C=O carbon to which an oxygen binds to form the ring.

These drawings, by the way, are called Haworth projections. They are commonly used in biochemistry to depict the cyclic forms of sugars. They seem to suggest a funny see-saw shape for the carbon atoms, but the idea here is not to convey the shape of the molecule perfectly. Just like in Fischer projections, the main concern is to quickly convey stereochemical relationships. In a Haworth projection, you can easily see whether two groups are *cis* to each other or *trans* to each other.

Note that a Haworth projection of an odd-numbered ring is always drawn with the ring oxygen in the back. We are looking at the ring from the edge and slightly above, so the "back" is the upper edge of the polygon. It's just like if you were looking at a swimming pool, and the far corner of the pool appeared in your field of vision above the near corner. For an even-numbered ring, the same idea applies, but the ring oxygen is always drawn on the top edge and to the right.

If you want to get an idea of the true shape of the molecule, you can see it in the ball-and-stick models below. **[NOT AVAILABLE]**

Go to **Animation SC11.1.** A three-dimensional model of β-D-threofuranose.

Go to **Animation SC11.2.** Another three-dimensional model of α-D-threofuranose.

- Carbohydrates are normally found in their cyclic forms, not their chain forms.
- For every ring a carbohydrate can form, there are always two diastereomeric forms called anomers.

The two terms, α and β, that described the two different stereoisomers of the cyclic form of threose refer to the position of the OH group on the newly formed chiral center (the old C=O was trigonal planar, not tetrahedral, so it was not chiral). The terms are defined by looking at the Haworth projection of the molecule. If the new OH is in the upper position, it is termed β (think butterfly); it is is in the lower position, it is termed α (think ant).

Carbohydrates do not always make five-membered rings. Sometimes they make six-membered rings instead. A five-membered ring with an oxygen in it is called a furanose. A six-membered ring with an oxygen in it is called a pyranose. Ribose is a five-carbon sugar that could make either a five-membered or a six-membered ring, although we usually see it in its five-membered ring.

The presence of different diastereomers that can change back and forth complicates things. If you wanted to measure the optical activity of a sugar, you would probably open a bottle of the solid carbohydrate, dissolve some up in water and put the sample in a

polarimeter. However, the optical rotation would change over time as the pure solid slowly turned into other isomers. This process is called mutarotation (which means changing optical rotation). For this reason, the time at which a measurement was performed is often reported with optical rotation values of carbohydrates. For example, the optical rotation value for D-threose may be listed as $[\alpha]_D$ -12.3 (20 min, c = 4, water).

Carbohydrates are important partly because they are structural units in biology. Carbohydrates are incorporated into DNA and RNA as well as important enzymatic cofactors such as ATP, NADH and Acetyl Coenzyme A. Very frequently, the unique pieces attached to the carbohydrates to make these different molecules are attached via the anomeric carbon.

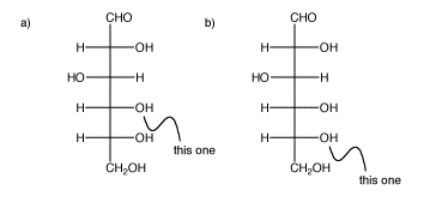
- Specific OH groups on carbohydrates are frequently substituted with other groups to make more complex molecules.

One more piece of terminology may be useful to review here. There are terms used in ring structures to describe whether two groups are attached to the same face or on opposite faces. For example, in β-D-threofuranose, the second hydroxy group is *cis* to the one on the anomeric center, but in α-D-threofuranose, the second hydroxy group is *trans* to the one on the anomeric center.

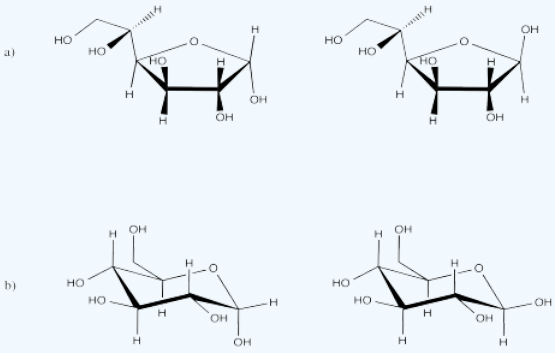
- Two groups on the same face of a ring are described as being *cis* to each other.
- Two groups on the opposite faces of a ring are described as being *trans* to each other.
- The terms *cis* and *trans* can be applied to any rings, not just carbohydrates.

Exercise 5.11.1

In the following carbohydrate, glucose, show the cyclic structures that would form if the indicated oxygen bonded to the carbonyl carbon (the C=O in the CHO group at the top). You should move a proton from one oxygen to another so that all the atoms have the usual number of bonds.

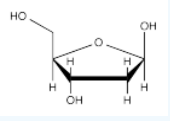


Answer



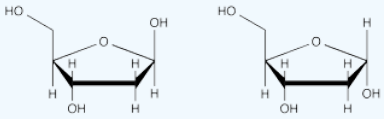
Exercise 5.11.2

β-deoxyribofuranose (below) is a building block of DNA.



a. What is the relationship between the two hydroxy (OH) groups that are directly attached to the 5-membered ring?
b. In the other possible 5-membered ring form of deoxyribose, what is the relationship between the two hydroxy (OH) groups that are directly attached to the 5-membered ring?

Answer



β-deoxyribofuranose α-deoxyribofuranose

a) Trans

b) Cis

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5.12: Biological Building Blocks- Amino Acids

One of the most important classes of biological chiral compounds is the family of amino acids. Amino acids are building blocks that are used to make peptides and proteins. Peptides can be used as hormones, carrying messages throughout the body. Proteins can be used as factories to carry out transformations, such as the formation of a neurotransmitter or the degradation of a toxin. The structure of peptides and proteins depend on the structures of the amino acids that make them. In turn, these shapes determine into what receptors peptide-based hormones can fit, and also what substrates protein-based enzymes can accept.

- Almost all of the naturally-occurring amino acids are chiral. In general, these compounds all have the same L-configuration.
- The peptides and proteins made from amino acids are therefore chiral as well.
- Chirality plays an important role in recognizing substrates and producing other chiral products.

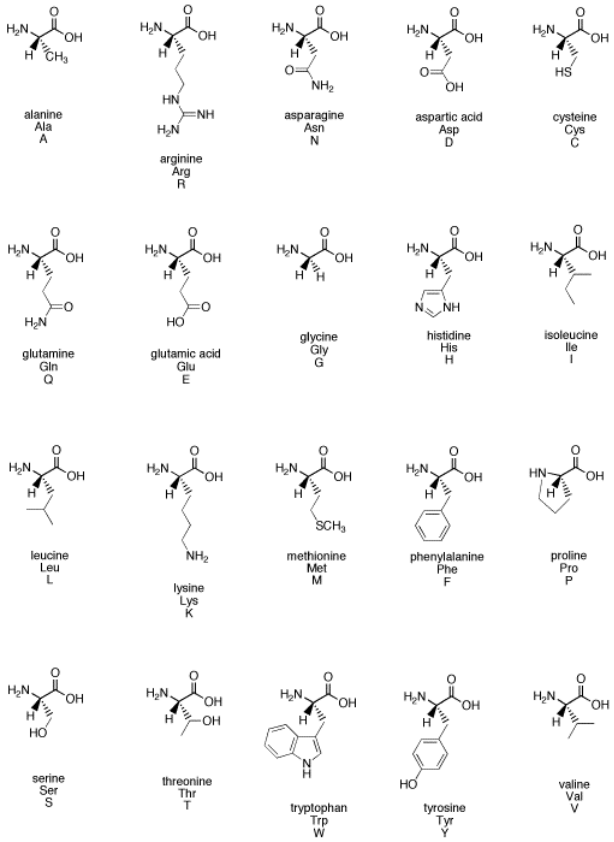


Figure 5.12.1: The common biological amino acids.

Go to **Animation SC12.1.** A three-dimensional model of L-leucine.

A few bacteria and fungi are capable of making the opposite enantiomer of the normal amino acids. In those compounds, the amino group and the hydrogen on the chiral carbon have switched positions.

Go to **Animation SC12.1.** A three-dimensional model of D-alanine.

Amino acids get their name from two "functional groups" or groups of atoms common to all these compounds. One of these groups is a carboxylic acid, the (C=O)OH on each amino acid. Later, we will look at how carboxylic acids can donate protons. The other common group is an amine, the NH_2 group connected to a tetrahedral carbon in most of these compounds. Later, we will see how amines can accept protons. In general, amines are bases.

Exercise 5.12.1

One of the amino acids is not chiral. Which one?

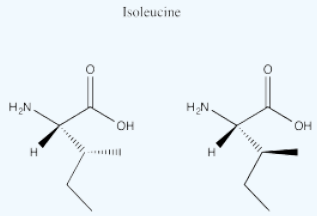
Answer

Glycine

Exercise 5.12.2

One of the amino acids has an enantiomer and also has diastereomers. Which one? Draw both diastereomers.

Answer



Exercise 5.12.3

One of the amino acids does not have an NH_2 group. Which one?

Answer

Proline

Exercise 5.12.4

Which of the amino acids contain more than one carboxylic acid?

Answer

Glutamic acid and aspartic acid

Exercise 5.12.5

Which of the amino acids contains more than one amine?

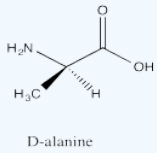
Answer

Arginine, asparagine, glutamine, lysine; also tryptophan contains an aromatic heterocycle, although it is not basic.

Exercise 5.12.6

Draw D-alanine.

Answer



Exercise 5.12.7

One of the amino acids has a configuration (*R or S*) that is the opposite of all the others. Which one?

Answer

Cysteine

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5.13: Macromolecular Structures- Alpha-Helices

Amino acids are very important building blocks. They form larger structures such as polypeptides, oligopeptides and proteins. The first two cases are just terms for chains of amino acids bonded together; the third refers to extremely long chains, and sometimes several long chains wrapped together.

Peptides are formed via amide bonds between an amino group on one amino acid and a carboxylic acid group on another.

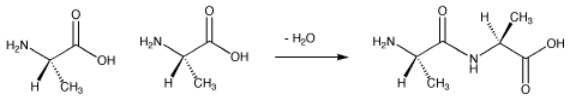


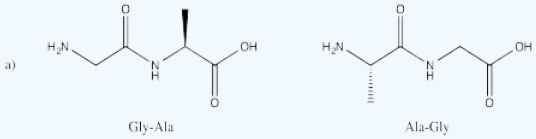
Figure 5.13.1: Formation of the peptide Ala-Ala.

Exercise 5.13.1

Sometimes more than one combination of amino acids is possible in a peptide.

a. Show the two possible combinations of alanine and glycine.
b. Would these compounds have identical properties? Why or why not?

Answer

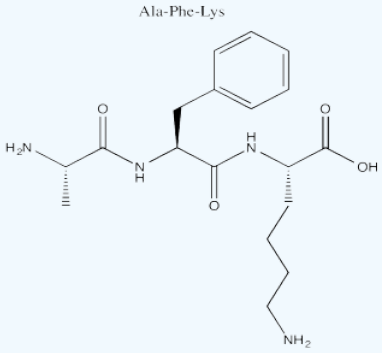


b) No. They are constitutional isomers of one another.

Exercise 5.13.2

Peptide names are written by describing the chain of amino acids from the amine end of the peptide to the carboxylic acid end. Draw the peptide Ala-Phe-Lys.

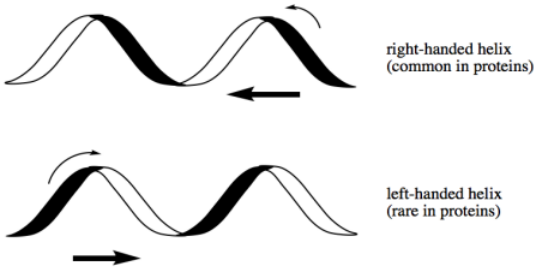
Answer



There are a number of possible "macromolecular structures" that peptides and proteins can adopt. One of them is an alpha helix, in which a long chain of peptides coils up like a phone cord (go to a museum if you don't know what a phone cord looks like).

- Alpha helices are a common structural motif in proteins.
- Alpha helices are chiral; a mirror-image form is possible.

- The shape of the alpha-helix is rooted in the shape of the L-amino acids that compose the protein.



- The determination of helical structures in proteins was a very recent discovery at the time that Rosalind Franklin obtained x-ray crystallography data on a DNA sample. It was during a visit to her lab that Francis Crick and James Watson began to think that DNA also had a helical structure. Franklin's unusual data resembled results for proteins that Watson and Crick had recently been shown by Linus Pauling. Watson and Crick correctly surmised that DNA had a similar structure. Pauling won the Nobel Prize, twice, Watson and Crick won the Nobel Prize for their work on DNA structure, but Rosalind Franklin unfortunately died very young, and the Nobel Prize is not awarded posthumously. Partly as a result, her name is very often not associated with this important work, despite her crucial contribution.

- Alpha helices are also found in DNA.
- The chiral component of DNA is a chiral carbohydrate.

In proteins, the alpha helix is chiral. It almost always adopts a right-handed curl. If you start at one end of the helix, with your right thumb pointing along the chain from the end, the fingers of your right hand will follow the direction of the chain as it curls along the helix. In a left-handed helix, the same thing is true with your left hand. Although the relationship is complicated, this overwhelming preference to adopt a right-handed helix is enforced by the configurations of the chiral centers in the individual amino acids.

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5.14: Optical Resolution

Optical resolution refers to the separation of two different enantiomers from each other. Very rarely, this has been done if the crystalline forms of two enantiomers are visibly different from each other. For example, Louis Pasteur was able to separate the two enantiomers of tartaric acid from each other because the two compounds just happened to crystallize separately. The crystals that formed had multifaceted habits that were visibly mirror images of each other. He painstakingly separated the two enantiomers using a pair of tweezers and a microscope.

Most of the time, we don't get so lucky. Two enantiomers are normally so similar to each other physically that we can't separate them.

However, there can be a pressing need to do so. That's because two enantiomers may have identical physical properties, but they may have very different biological properties. In the cell, they may encounter other chiral materials, including proteins and sugars. Their interactions with those chiral molecules may be strongly influenced by how they fit together. The result may be the difference between a compound relieving a child's athsma or making it worse.

Chiral compounds, of course, are often compared to hands. Two enantiomers are like a right hand and a left hand, mirror images of each other that look exactly the same but are instead completely opposite.

Figure 5.14.1: Handedness or chirality: a left and a right hand.

(You don't like hands with three fingers? Start reading the comics page. It's a well-established convention.)

The fact that the interaction of chiral compounds with other chiral compounds is influenced by their stereochemistry is often compared to the fit of your two hands to the same glove. Not surprisingly, one hand fits the glove better than the other one.

Figure 5.14.2: Handedness or chirality: a left and a right hand, and one glove.

One way to separate two enantiomers is through *chiral column chromatography*. Chiral column chromatography uses something like a hand-glove approach to separate two enantiomers from each other.

In case you aren't familiar with chromatography, we should take a look at it in general terms first. Chromatography describes the separation of compounds through their different physical interactions between two different phases as the compounds pass through a long column or tube.

The column is packed with one material, called the stationary phase, whose job it is to stick to the compounds and keep them from moving through the tube. The stationary phase could be simple alumina or silica (like very finely powdered sand) or it could be a complicated synthetic material protected by a patent.

Another material, called the mobile phase, flows through the column. The job of the mobile phase is to tug the compounds along and get them through the column. The mobile phase could be a gas, allowed to flow through the column from a compressed tank, or a liquid, pushed through with a pump.

A tug-of-war ensues between the mobile phase and the stationary phase. Different compounds will have different affinities for each phase. Compounds that are more strongly attracted to the mobile phase will move more quickly. Compounds that are held more firmly by the stationary phase will move more slowly.

Chiral column chromatography involves the use of one of those patented stationary phases. The stationary phase has a specific kind of chiral molecule (or a chiral moiety, just a piece of a molecule) bonded all over it. The differing interactions between the two enantiomers and the chiral elements of the stationary phase result in the two compounds moving through the column at different rates. The compound that fits together with the chiral stationary phase will slow down and take longer to come through the column.

A second major way of separating two enantiomers is through the use of a *chiral resolving agent*. A chiral resolving agent is a compound that already has a chiral center of its own. It is used in its pure form: only one enantiomer and not the other, having already been purified somehow (or selectively synthesized). This compound has to be able to react somehow with the target compound. When it does, it will form a third, new compound. The third compound should contain both chiral centers: the one from the target compound and the one from the chiral resolving agent.

That changes everything. The compound contains two chiral centers. One of these is identical among all the molecules in the sample; that's the one from the pure chiral resolving agent. The other one is present in either of two configurations; that's the one from the enantiomeric target compound. That means we now have a mixture of diastereomers.

- Two enantiomers have the same physical properties. They cannot be separated easily by standard laboratory techniques.
- Two diastereomers have different physical properties. they can often be separated via standard laboratory techniques.
- If an additional chiral center can be incorporated into a pair of enantiomers so that they become diastereomers, they can be separated.

The classic example of this method of obtaining one isomer of a compound involves the formation of a diastereomeric salt. The salt has multiple chiral centers, and so diastereomers are possible.

If a racemic mixture of phenylsuccinic acid is mixed with a pure sample of (-)-proline (a naturally available amino acid), a proton transfer (or Brønsted acid-base) reaction occurs. Two protons are transferred from the phenylsuccinic acid to the proline. One proline has a position available for one extra proton, so the two protons end up on two different prolines. Because protons have +1 charge, each proline is cationic. The phenylsuccinic acid gave up two positives, so it is a dianion. Together, these three ions form a salt.

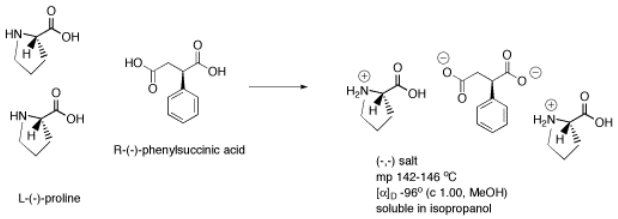


Figure 5.14.3: Formation of a salt containing three chiral centers.

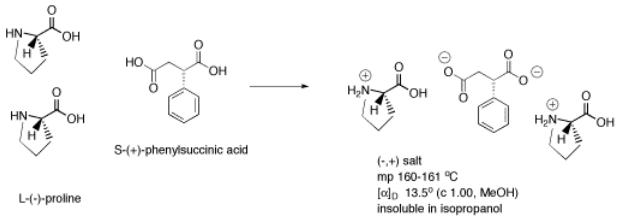
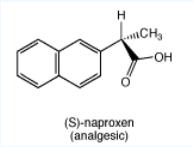


Figure 5.14.4: Formation of a salt containing three chiral centers. This one is a diastereomer of the salt in the previous picture.

If a racemic mixture of phenylsuccinic acid is used, but pure (-)-proline is added, two possible diastereomers result. One chiral center, in the proline, is always the same. The other chiral center, in the phenylsuccinic acid, can be in two different configurations. As a result, cations and anions may pack differently together in each case, so different melting points and solubilities result. One salt precipitates or forms a solid from the solution, but the other stays dissolved. The two diastereomers can be separated by filtration.

Exercise 5.14.1

Suppose you have a pure sample of L-phenylalanine. Write equations for reactions, using structures, that show how you could use it to obtain a sample of (*S*)-naproxen, an analgesic, from a racemic mixture of naproxen.



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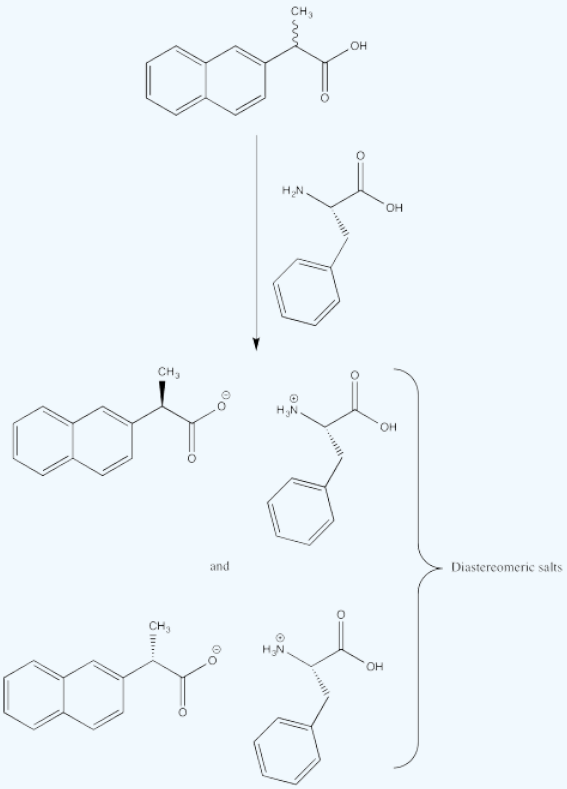
Answer



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5.15: Another Kind of Stereochemistry- Alkene Isomers

Isomers related by chirality are not the only kind of geometric isomers. One other example is cis-trans isomerism in alkenes; that is, different orientations around a carbon-carbon double bond (and other double bonds, in some cases).

In cis isomers, there is a non-hydrogen group at each end of the alkene, and they are on the same side of the double bond axis.

***cis*-2-butene**

Figure 5.15.1: A *cis*-isomer of an alkene.

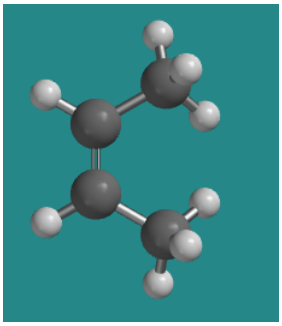
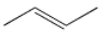


Figure 5.15.2: A ball-and-stick model of *cis*-2-butene.

Go to **Animation SC12.1.** A three-dimensional model of *cis*-2-butene.

In trans isomers, there is a non-hydrogen group at each end of the alkene, and they are on the opposite sides of the double bond axis.



***trans*-2-butene**

Figure 5.15.3: A *trans*-isomer of an alkene.

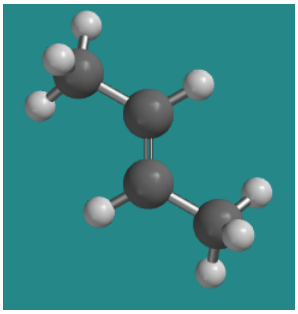


Figure 5.15.4: A ball-and-stick model of *cis*-2-butene.

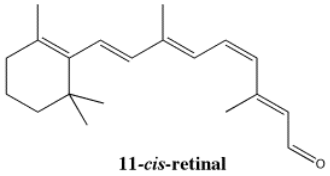
Go to **Animation SC12.1.** A three-dimensional model of *trans*-2-butene.

- In cis isomers, the non-hydrogen groups at each end of an alkene are on the same side.
- In trans isomers, the non-hydrogen groups at each end of an alkene are on opposite sides.

This kind of isomerism is different from the shape changes seen in saturated hydrocarbons such as butane; that is, compounds that have only single bonds, and not double bonds, don't have these specific isomers. (However, saturated ring structures can have cis and trans isomers; in that case, the terms describe whether two groups are on the same face of a ring or opposite faces). There is free rotation in butane, because the single bonds that hold the carbons together are not as sensitive to the orientation of the tetrahedral carbons at either end of the bond. In contrast, turning the trigonal planar carbon at one end of a double bond would disrupt the p orbital overlap that forms the pi bond. That would cost a lot of energy.

Cis and *trans* isomers do play important biological roles. For example, one of the proteins responsible for vision is rhodopsin. Rhodopsin has bound to it an organic compound called retinal (the oxygen in retinal is replaced by a nitrogen in an amino acid side chain in the protein to form active rhodopsin).

One of the bonds in the active form of retinal has a *cis* configuration. You may know from conformational analysis that there would be some crowding between the groups that are held close together on one side of the double bond. That crowding, sometimes called steric strain, causes an increase in energy.



11-*cis*-retinal

Figure 5.15.5: An isomer of retinal, important in vision.

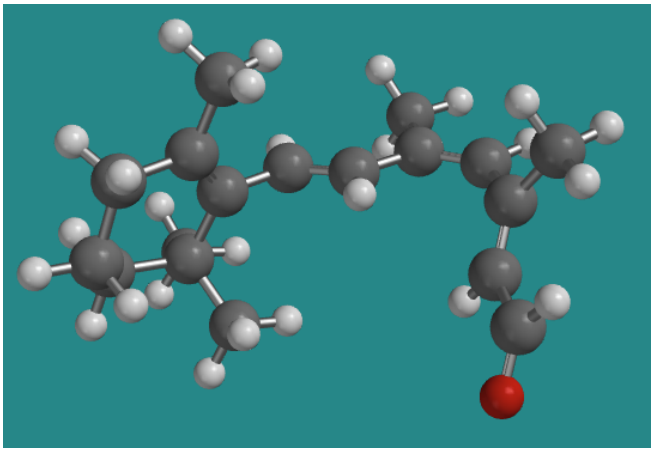
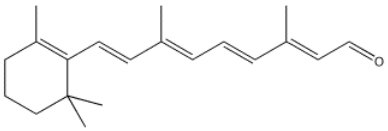


Figure 5.15.6: A ball-and-stick model of 11-*cis*-retinal.

Go to **Animation SC12.1.** A three-dimensional model of *cis*-retinal.

However, if a photon is absorbed by the molecule, an electron can be excited from a ground state level to an excited state level. This electron would then occupy a pi antibonding orbital, weakening the pi bonding in the system. That makes it easier for the molecule to rotate, and it does so.

Once free to rotate, the molecule more easily adopts a more ope n, less folded shape. It becomes the all-*trans* isomer.



***all-trans*-retinal**

Figure 5.15.7: An all- *trans*-isomer of retinal.

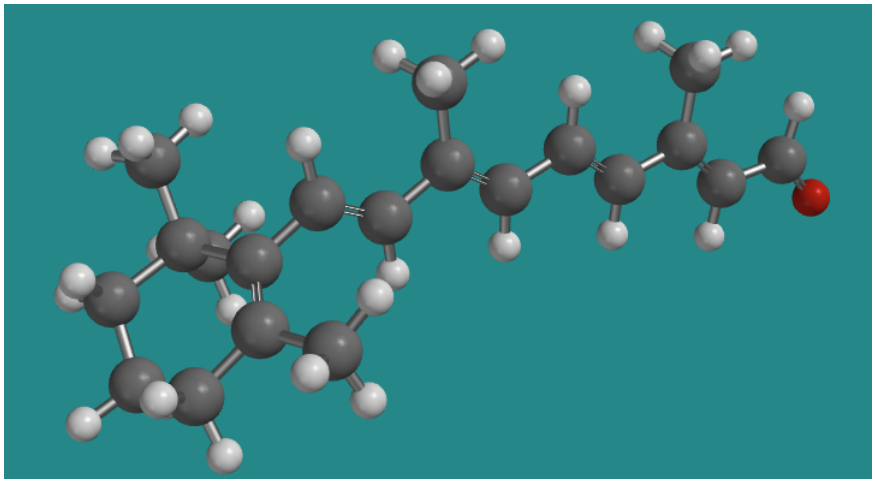


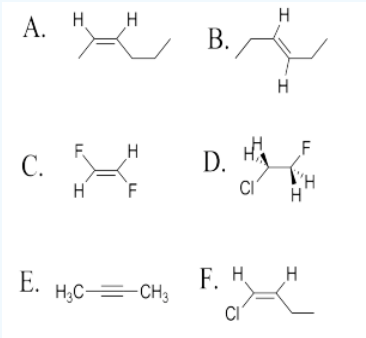
Figure 5.15.8: A ball-and-stick model of *trans*retinal.

Go to **Animation SC12.1.** A three-dimensional model of *trans*-retinal.

The shape change in retinal is important because it is bound to the rhodopsin protein. The protein is folded around the retinal, so that when the retinal portion changes shape, the protein has to undergo a conformational change in order to fit around the retinal. The resulting conformational change of the protein allows a signal to be sent telling the brain that light has been detected at a particular place in the eye.

Exercise 5.15.1

Determine whether the following molecules are cis, trans or neither.



Answer A.:

Cis

Answer B.:

Trans

Answer C.:

Trans

Answer D.:

Neither (There is free rotation around the C-C single bond.)

Answer E.:

Neither (C-C triple bonds have substituents at 180 degrees to each other (linear).)

Answer F.:

Cis

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5.16: E and Z Alkene Isomers

Double bonds can exhibit stereoisomerism if there is more than one way to arrange two groups at opposite ends of a double bond: either on the same side of the bond axis (commonly *cis*) or opposite sides of the double bond axis (commonly *trans*). There is a different way of denoting these two stereochemical configurations that is always used if the compound has a more complicated structure. Compounds that have more than one non-hydrogen group at either end of the double bond are **not** normally referred to as *cis* or *trans* isomers, but are instead called *E* or *Z* isomers.

- In Z isomers, the highest-priority groups at each end of an alkene are on the same side of the double bond axis. The double bond axis is a straight line drawn through the two atoms that are double bonded to each other.
- *Z* is from the German *zusammen* (together).
- In E isomers, the highest-priority groups at each end of an alkene are on opposite sides of the double bond axis.
- *E* is from the German *entgegen* (against).

Highest-priority is decided based on atomic number.

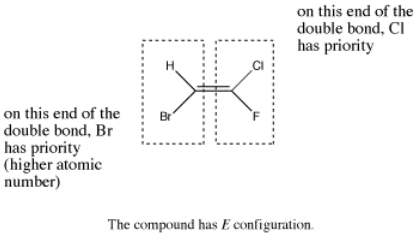


Figure 5.16.1a: An example of an *E* alkene.

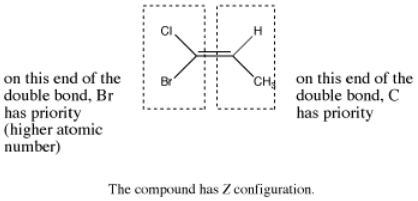


Figure 5.16.1b: An example of a *Z* alkene.

If the first atoms attached to one end of the double bond are the same, go **one bond further** on each chain and compare all the atoms that come next. If one of the chains at this point contains an atom with a higher atomic number than any of the atoms on the other chain, it is given higher priority.

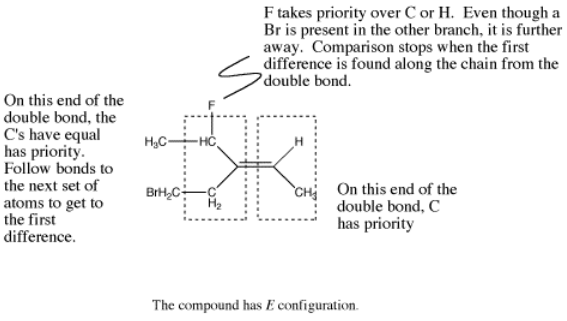


Figure 5.16.1c: A more complicated example of an *E* alkene.

Sometimes, going one bond further leads to the same set of atomic numbers along both branches, but there are more of the higher atomic numbered atom on one branch than the other.

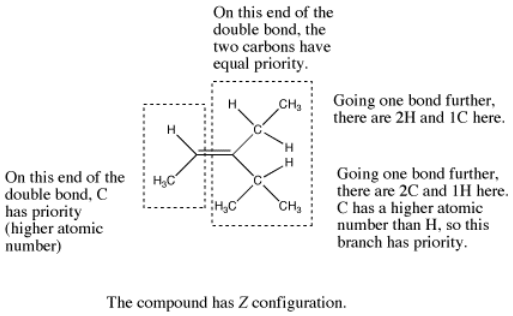
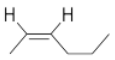


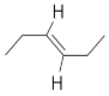
Figure 5.16.1d: Another complicated example, this time of a *Z* alkene.

Remember, this is an arbitrary set of rules that have been adopted to name these compounds so that people can refer to one isomer or the other. They may not be the rules that you would have come up with on your own.

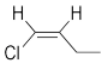
Exercise 5.16.1

Determine whether the following molecules are E or Z.

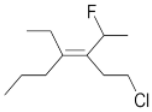
A. 

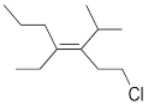
B. 

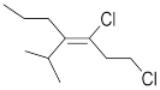
C.

D. 

E.

F. 

G. 

H. 

Answer A.:

Z

Answer B.:

E

Answer C.:

E

Answer D.:

Z

Answer E.:

E

Answer F.:

E

Answer G.:

Z

Answer H.:

E

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5.17: Stereoisomers in Other Geometries- Octahedra

Note

This page shows examples of coordination complexes, in which a number of groups called "ligands" bond to a central metal atom or ion. For more information about these complexes, see the brief introduction here.

Earlier we looked at cis- and trans-isomers in square planar platinum complexes. Other transition metal complexes display cis-trans isomerism. Octahedral complexes can also have two particular ligands adjacent to each other or on opposite sides of the metal atom. For example, the cation $[(NH_3)_4CoCl_2]^+$ has a cis-isomer and a trans-isomer.

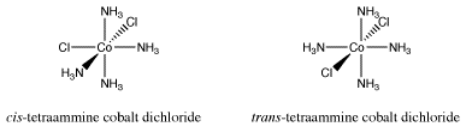


Figure 5.17.1: *Cis*- and *trans*-isomers of an octahedral cobalt compound.

Go to **Animation SC17.1.** A three-dimensional model of *cis*-$(NH_3)_4CoCl_2$.

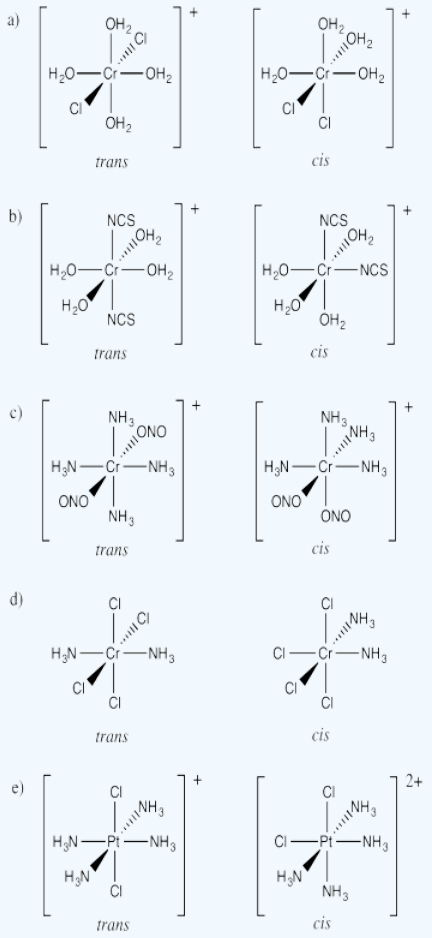
Go to **Animation SC17.2.** A three-dimensional model of *trans*-$(NH_3)_4CoCl_2$.

Exercise 5.17.1

Draw *cis* and *trans* isomers for the following compounds.

a) $[Cr(OH_2)_4Cl_2]^+$ b) $[Co(OH_2)_4(SCN)_2]^+$ c) $[Co(NH_3)_4(ONO)_2]^+$ d) $Pt(NH_3)_2Cl_4$ e) $[Pt(NH_3)_4Cl_2]^{2+}$

Answer



Cis and *trans* isomers are found when there are two ligands whose spatial relationship can be described easily as "beside each other" or "across from each other". What if there are more than two ligands that can adopt different geometric arrangements around a metal?

An example is found in the complex $Co(NH_3)_3Cl_3$. In that compound, which has an octahedral geometry, the three chlorines might be found all in a row, or they might be found clustered into a triangle. When three ligands are found in a row on an octahedron, the geometry is called "*meridional*" or simply "*mer*". When the three cluster together in a triangle, the geometric relationship is called "*facial*" or simply "*fac*".

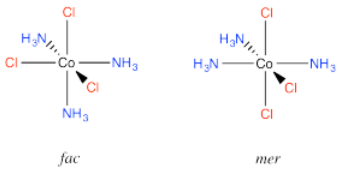
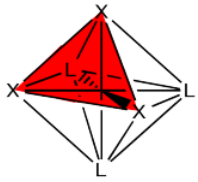


Figure 5.17.2: The *fac*- and *mer*- configurations of $(NH_3)_3CoCl_3$.

Go to **Animation SC17.3.** A three-dimensional model of *fac*-$(NH_3)_3CoCl_3$.

Go to **Animation SC17.4.** A three-dimensional model of *mer*-$(NH_3)_3CoCl_3$.

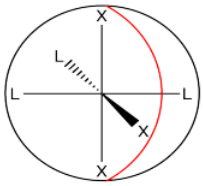
The *fac* designation is derived from the location of the three ligands whose positions are being compared: they are all found along one of the *faces* of an octahedron.



a facial relationship

Figure 5.17.3: Illustration of a facial relationship on an octahedron.

The mer designation comes from the fact that the three ligands are found along one meridian. A meridian is simply a line from one apex of the compound all the way to the opposite apex. It is like a meridian on the earth, from the north pole to the south pole.



a meridian

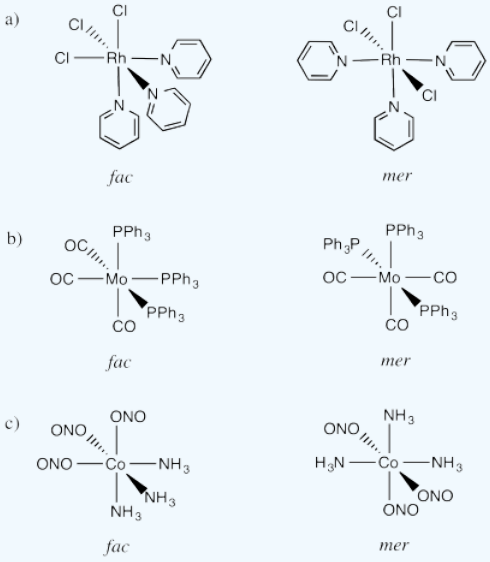
Figure 5.17.4: Illustration of a meridian along an octahedron.

Exercise 5.17.2

Draw *fac* and *mer* isomers of the following compounds.

a. $RhCl_3py_3$ (py is a six-membered ring with five carbons and a nitrogen)
b. $Mo(CO)_3(PPh_3)_3$
c. $Co(NH_3)_3(NO_2)_3$

Answer



Some of the compounds on this page demonstrate another type of isomerism. It is called "linkage isomerism" and it involves which of the atoms in the ligand is connected to the metal. For example, the atoms at either end of a thiocyanate ion, SCN^-, both have lone pairs. One or the other might bind to a metal under different circumstances. The sulfur might be attached to the metal, or else it could be the nitrogen. These two options form two different linkage isomers.

Often, to communicate which linkage isomer we are talking about, the desired isomer is indicated by placing the atom attached to the metal first in the formula of the compound. For example, writing the formula $[Co(OH_2)_4(SCN)_2]^+$ suggests the isomer in which

the sulfur is attached to the cobalt. Writing the formula $[Co(OH_2)_4(NCS)_2]^+$ suggests the nitrogen is attached to the cobalt.

Exercise 5.17.3

Draw structures for the following linkage isomers.

a. $[Co(NH_3)_4(NO_2)_2]^+$ and $[Co(NH_3)_4(ONO)_2]^+$
b. $[Co(OH_2)_4(SCN)_2]^+$ and $[Co(OH_2)_4(NCS)_2]^+$
c. $[Cr(OH_2)_5(CN)]^{2+}$ and $[Cr(OH_2)_5(NC)]^{2+}$

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5.18: Enantiomers in Octahedral Complexes

Enantiomers are another kind of isomer that occur in octahedral metal complexes. Like the square planar platinum complexes seen before, these compounds consist of metal ions with other atoms or groups bound to them. More information about the binding of ligands to metals is found in the section on Lewis acids and bases.

These groups that bind to metal ions are called ligands. One example of a type of octahedral compounds that can form enantiomers is bidentate complexes. In bidentate complexes (from the Greek *two teeth*) or chelating complexes (from the Greek *crab*), a ligand binds very tightly to the metal because it holds onto the metal via more than one atom. Ethylenediamine is one example of a bidentate ligand.

Figure 5.18.1: Ethylenediamine (sometimes abbreviated en).

- Bidentate ligands bind very tightly to a metal because they form two bonds with it, rather than just one.
- In an octahedral complex, the two donor atoms in a bidentate ligand bind cis to each other. They can't reach all the way around the molecule to bind trans to each other.

The spatial relationship between the metal and the two atoms connected to it from the same ligand forms a plane. If more than one bidentate ligand is connected to the metal, the relative orientation of one plane to another creates the possibility of mirror images. A complex containing three bidentate ligands can take on the shape of a left-handed propeller or a right-handed propeller.

Figure 5.18.2: A left-handed propeller shape (left) is seen in Λ isomers of octahedral enantiomers. A right-handed propeller (right) is seen in Δ isomers of octahedral enantiomers.

If you turned this propellor, in what direction would the air be pushed? Maybe it is an airplane propellor or maybe it is a fan blade. If you turned a lambda fan blade counter-clockwise, it would blow cool air on you. You would have to turn a delta fan clockwise to cool off.

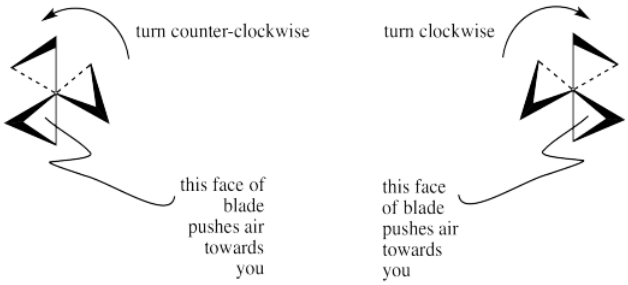


Figure 5.18.3: More details about that propellor analogy.

These shapes are alternatively described as a left-handed screw and a right handed screw. If you want to screw a right-handed screw into a floor, you turn the screwdriver clockwise. If you want to screw a right-handed screw into a floor, you turn the screwdriver counterclockwise. Screws are chiral in much the same way that a helix is chiral. The threads on the screw cycle either clockwise or counterclockwise as they run down the length of the screw.

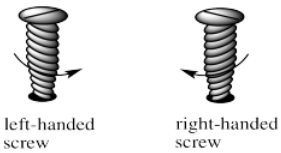


Figure 5.18.4: A left-handed screw shape (left) is seen in Λ isomers of octahedral enantiomers. A right-handed screw (right) is seen in Δ isomers of octahedral enantiomers.

If you can picture turning the "delta" or "lambda" propellor shape so that it screws into the page behind it, which direction would you turn it?

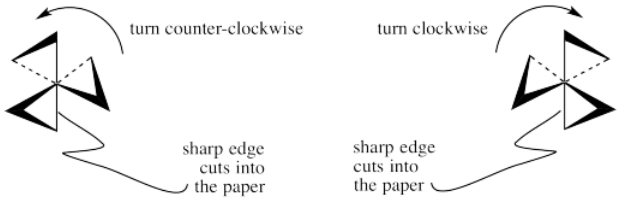


Figure 5.18.5: Another way of thinking about the propellor or screw shape.

You would turn the lambda screw counter-clockwise to send it into the page behind it. You would have to turn the delta screw the opposite way; turning it clockwise would send it into the page.

Examples of this enantiomeric relationship include cobalt complexes of bidentate ligands.

Go to **Animation SC17.3.** A three-dimensional model of Δ-$Co(en)_3$.

Go to **Animation SC17.3.** A three-dimensional model of Λ-$Co(en)_3$.

These relationships are also seen when there are just two bidentate ligands in the compound.

Go to **Animation SC17.3.** A three-dimensional model of $\Lambda Co(en)_2(NH_3Cl$.

Go to **Animation SC17.3.** A three-dimensional model of $\Delta Co(en)_2(NH_3Cl$.

What do we know about enantiomers?

- enantiomers have identical physical properties, except...
- enantiomers have opposite optical rotation.

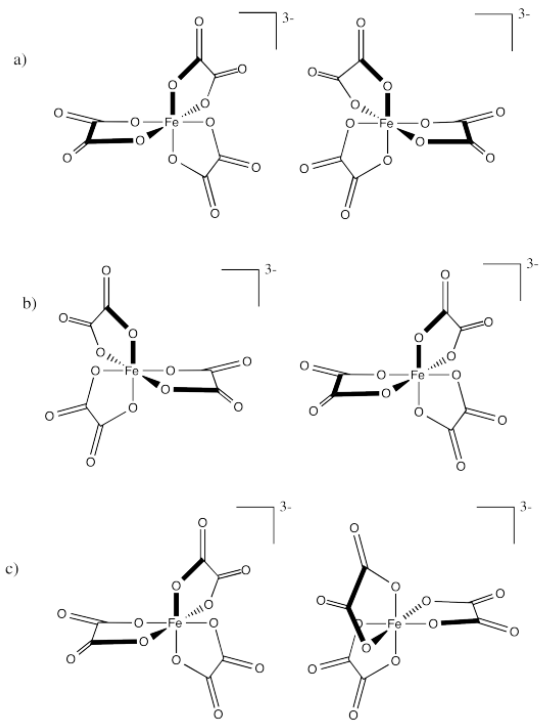
These kinds of complexes were historically important in demonstrating how small molecules and ions bound to metal cations. By showing that some metal complexes were chiral and displayed optical activity, early 20th century workers such as Alfred Werner were able to rule out some competing ideas about the structures of metal compounds.

Today, we know that metal complexes play important roles in enzymes in biology, and Werner's work on metal complexes laid the groundwork for how we think about these complexes.

In addition, stereochemistry in metal complexes became very important in the late 20th century, especially as pharmaceutical companies looked for catalysts that could aid in the production of one enantiomer of a drug, and not the other, in order to maximize pharmaceutical effectiveness and minimize side effects.

Exercise 5.18.1

Identify the relationships between the following pairs of iron(III) oxalate ions.



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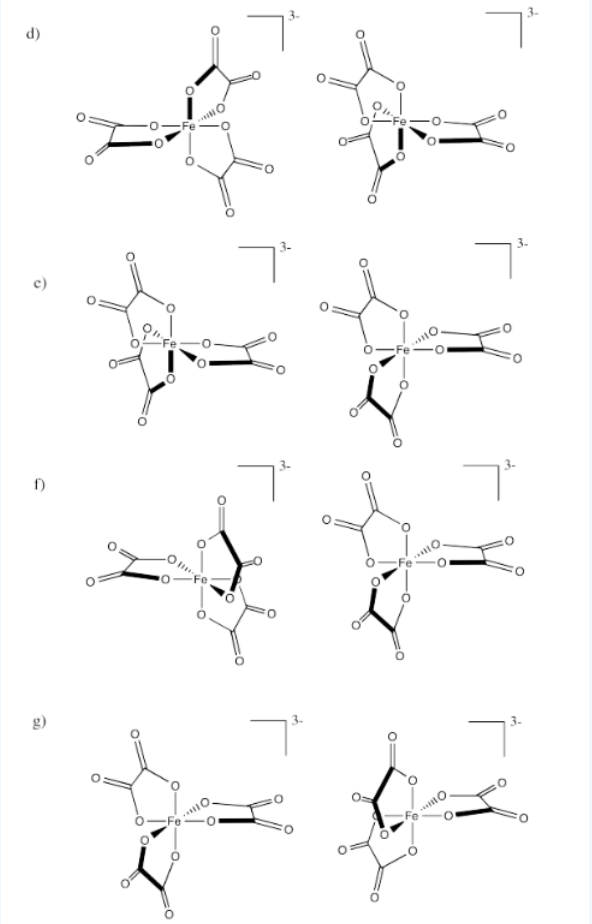


Answer a:

Enantiomers

Answer b:

Enantiomers

Answer c:

Identical

Answer d:

Identical

Answer e:

Enantiomers

Answer f:

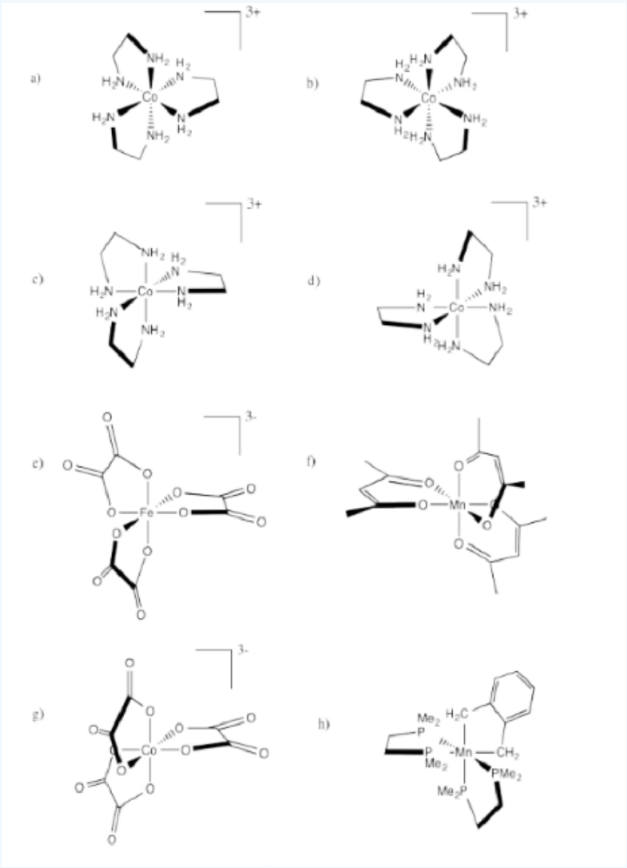
Identical

Answer g:

Enantiomers

Exercise 5.18.2

Indicate whether each of the following compounds is the Δ or Λ isomer and draw its enantiomer.



Answer a:

Δ

Answer b:

Λ

Answer c:

Δ

Answer d:

Λ

Answer e:

Δ

Answer f:

Δ

Answer g:

Λ

Answer h:

Λ

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5.19: Chiral Catalysts for Production of Enantiomerically Pure Compounds

Chiral metal complexes became very important over the last 30 years of the twentieth century, particularly as companies sought to synthesize rare and difficult-to-obtain natural products for use as pharmaceuticals.

One of the landmark developments in this area was the production of chiral metal phosphine complexes. Phosphines are molecules containing phosphorus that bind to metal ions and promote catalytic activity. Among other workers, William Knowles of Monsanto was able to isolate complexes with chiral phosphorus atoms and use them to catalyze reactions producing almost entirely one enantiomer. The resulting synthesis of the anti-Parkinson's drug L-DOPA produces 97% of the desired enantiomer and only 3% of the opposite enantiomer.

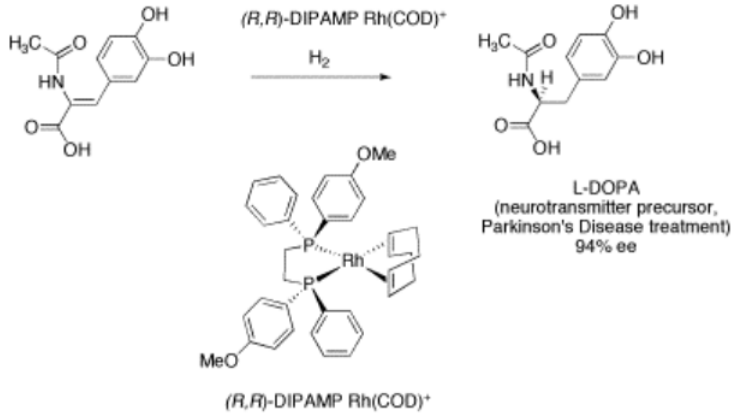

Figure 5.19.1: Knowles' catalyst in Monsanto's L-DOPA synthesis.

Go to **Animation SC19.1.** A three-dimensional model of Knowles' chiral catalyst.

Chiral catalysts work because metal-catalyzed reactions require the substrate to bind to the metal ion. If there is a chiral center at or very close to the metal ion, very often a substrate is forced to bind to the metal ion in a very specific way. In the case of the Monsanto L-DOPA synthesis, only one face of the C=C double bond can be presented to the metal atom (it won't fit together the other way), and the metal delivers two hydrogen atoms to that face of the double bond and not to the other.

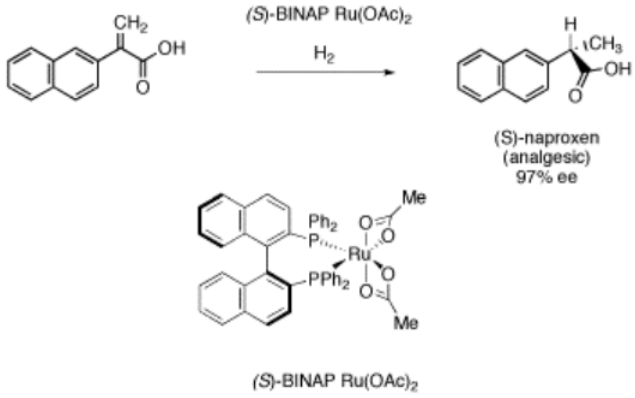

Figure 5.19.2: Noyori's catalyst in synthesis of (*S*)-naproxen.

Go to **Animation SC19.2.** A three-dimensional model of Noyori's chiral catalyst, (*R*)-configuration.

Go to **Animation SC19.3.** A three-dimensional model of Noyori's chiral catalyst, (*S*)-configuration.

Another pharmaceutical produced in highe enantiomeric excess employs a chiral metal complex that contains no chiral center. Ryoji Noyori is a professor at Nagoya University in Japan and also president of RIKEN, a major Japanese research institute involving about 3000 scientists. Among numerous other scientific contributions for which he is responsible, Noyori developed a number of complexes using BINAP ligands, which contain large, planar rings.

This case is roughly analogous to enantiomeric octahedral complexes like $Co(en)_3 3+$, in which the the planes of the BINAP can twist in either one direction or the other. The rings cannot twist past each other, so when the BINAP complexes to the ruthenium,

they get locked into either of two enantiomeric shapes, despite the fact that the compound does not really have a chiral center.

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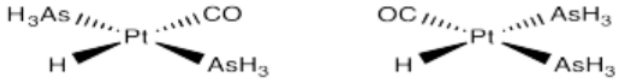
5.20: Solutions to Selected Problems

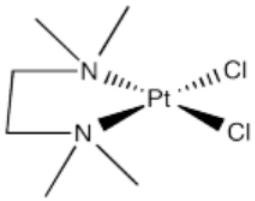
Exercise 5.2.1:

a)

b)

c) 

Exercise 5.2.2:



Needs to *cis*. The tmeda group is not long enough to reach the *trans* position

Exercise 5.3.1:

Clockwise.

Exercise 5.3.2:

Counter-clockwise.

Exercise 5.3.3:

Counter-clockwise.

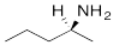
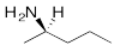
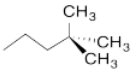
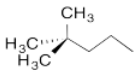
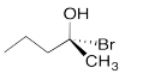
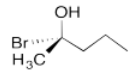
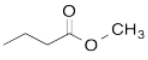
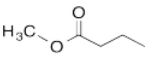
Exercise 5.3.4:

Clockwise.

Exercise 5.3.5:

Enantiomer B has a molecular weight of 126 g/mol, a density of 0.995 g/mL, an optical rotation of [α] = – 26°, a melting point of 65°C and a boiling point of 225°C.

Exercise 5.3.6:

	Mirror Image	Superimposable	Chiral?
		Yes	No
		No	Yes
		Yes	No
		Yes	No
		Yes	No
		No	Yes
		Yes	No

Exercise 5.3.7:

A. The plane of the page is a mirror plane. There is also one perpendicular to the page that reflects one H into the other.
B. The plane of the page contains one P-Cl bond and bisects the other Cl's.
C. The plane of the page is a mirror plane.
D. Mirror plane contains P-Br bond and bisects the Cl's.
E. There is no lone pair on the B. Therefore all atoms lie in a mirror plane.
F. No mirror planes--the molecule is therefore chiral.
G. There is a plane perpendicular to the page that contains the Br and Cl and bisects the cyclopropane ring.
H. No mirror planes--the molecule is therefore chiral.
I. There is a plane perpendicular to the page that contains the Br and Cl and bisects the cyclopropane ring.
J. The C-C bond can be rotated by 60 degrees so that there is a plane perpendicular to the C-C bond axis.
K. The C-C bond in one of the chlorine-containing arms can be rotated so that there is a mirror plane that goes through the ethyl group (with no Cl's) and the P, and one chlorine containing arm is the reflection of the other.
L. Since a double bond is planar, there is a mirror plane that contains all six atoms.
M. There is a mirror plane that contains two C's and bisects the two Cls.
N. No mirror planes--the molecule is therefore chiral. The rings are not in the same plane due to the CH3 and NH2 groups, which bump into each other. They also prevent rotation around the C-C bond between the rings.

Exercise 5.3.8

Picture (a)

Exercise 5.3.9:

Picture (b)

Exercise 5.3.10:

Picture (d)

Exercise 5.3.11:

Picture (c)

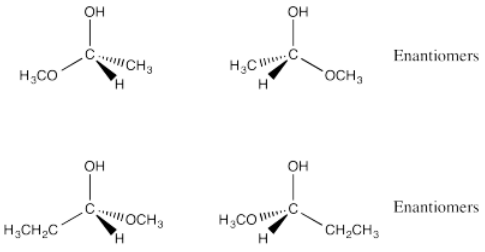
Exercise 5.4.1:

Priority of groups:
1 Br (red)
2 Cl (bright green)
3 F (pale green)
4 H (white)

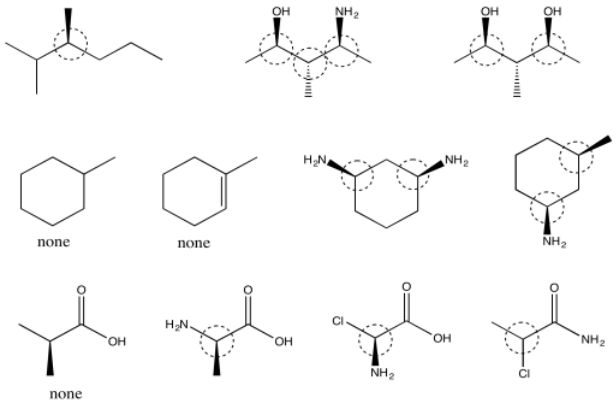
In the molecule in figure 5.4.2, with the low-priority hydrogen pointed away, bromine is at the top, chlorine is clockwise from the bromine, and fluorine is clockwise from the chlorine. It therefore has an assigned configuration of *R*.

In the molecule in figure 5.4.3, with the low-priority hydrogen pointed away, bromine is at the top, chlorine is counterclockwise from the bromine, and fluorine is counterclockwise from the chlorine. Thus, it has an assigned configuration of *S*.

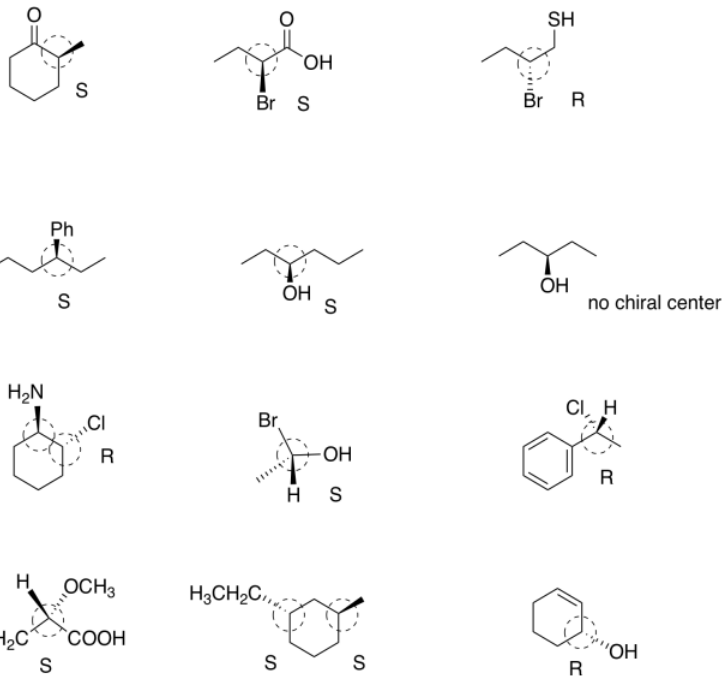
Exercise 5.4.2



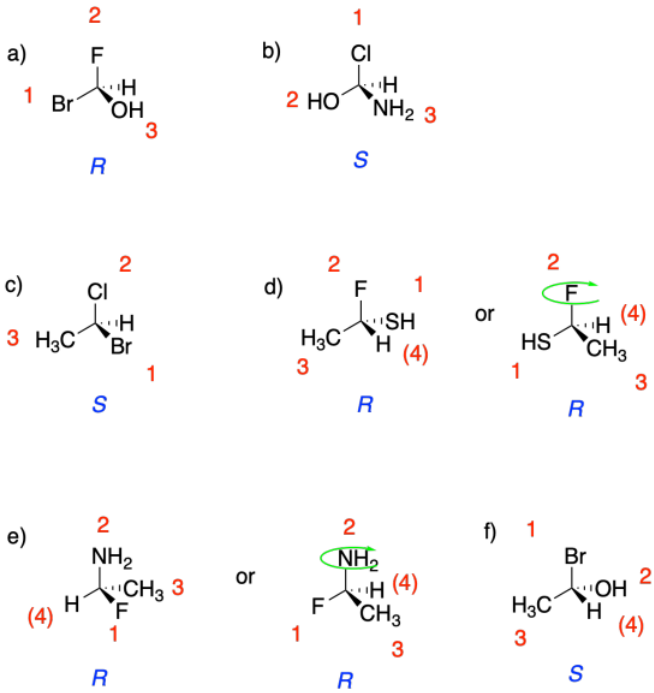
Exercise 5.4.3:



Exercise 5.4.4:



Exercise 5.4.5:



Exercise 5.4.6:

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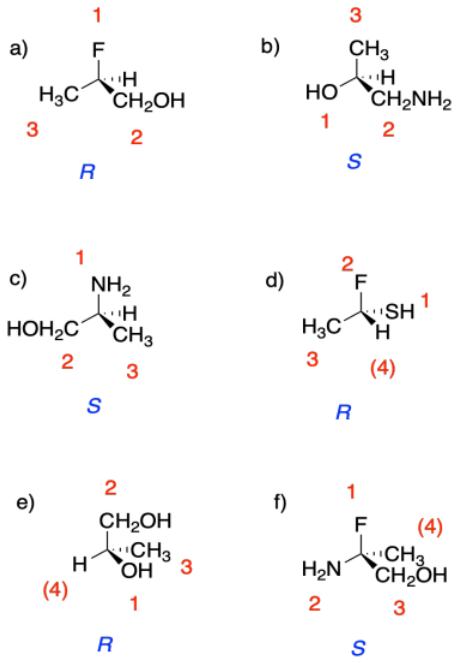
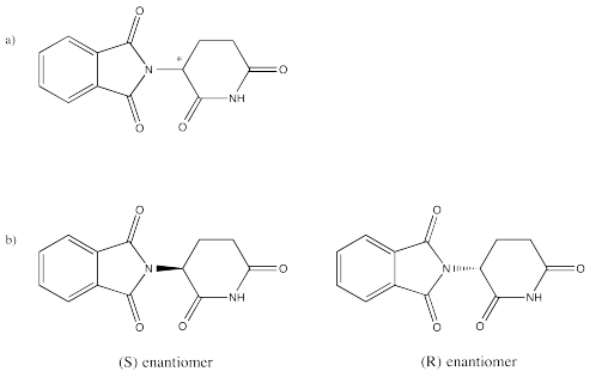


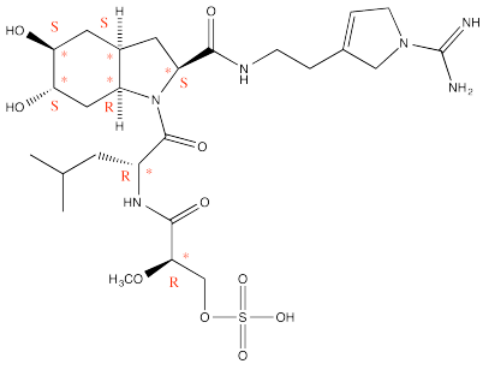
Exercise 5.5.1:

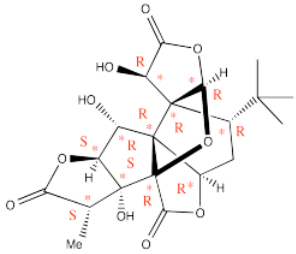


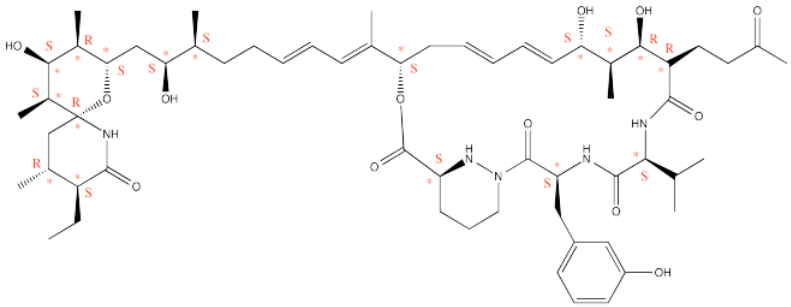
Exercise 5.5.2:

Exercise 5.5.3:

https://chem.libretexts.org/@go/page/191275







Exercise 5.6.1:

A pure sample of A would have $[\alpha] = 75^{\circ}$

Optical purity or enatiomeric excess = $\frac{50}{75} = 66\%$

% major enantiomer = $66 + \frac{34}{2} = 83\%$

% minor enantiomer = $100 - 83 = 17\%$

Exercise 5.6.2

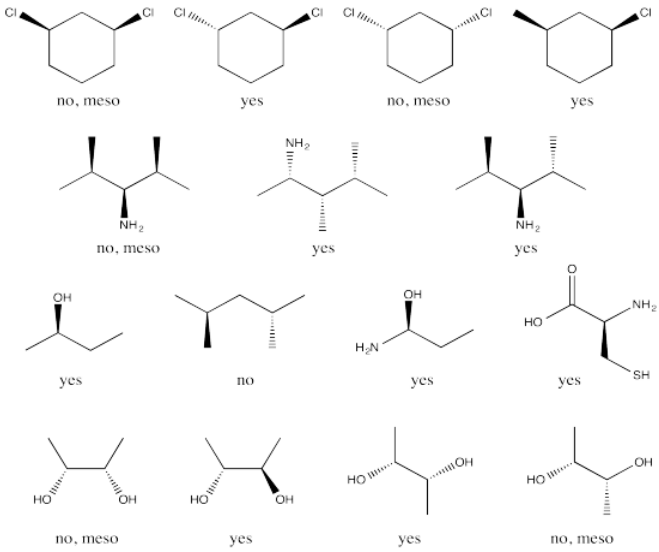
$$\%\, major\ = 90\%$$

$\%\, major\ = 10\%$

Optical purity or enantiomeric excess = $\frac{X}{-50} = 90 - 10 = 80\%$

Solve for X. $X = -40^{\circ}$

Exercise 5.6.4:



Exercise 5.7.1:

a) $[\alpha] = \frac{\alpha}{(c)(l)}$

$c = (\frac{0.250g}{2mL})(\frac{10mL}{1dL}) = 1.25\,\frac{g}{dL}$

$\alpha = \frac{(0.775^\circ + 0.806^\circ + 0.682^\circ)}{3} = 0.754^\circ$

$[\alpha] = \frac{\alpha}{(c)(l)} = \frac{(0.754^\circ)}{(1.25\,\frac{g}{dL})(0.5dm)} = +1.21^\circ$

b)

– 1.21°

Exercise 5.7.2:

$$[\alpha] = \frac{\alpha}{(c)(l)}$$

$[\alpha] = 32\circ$

$c = (\frac{0.150g}{1mL})(\frac{10mL}{1dL}) = 1.5\,\frac{g}{dL}$

c = (0.150g/ 1 mL)(10 mL/1 dL) = 1.5g/dL

$[\alpha] = \frac{\alpha}{(c)(l)} = 32^\circ = \frac{\alpha}{(1.5\,\frac{g}{dL})(0.5dm)}$

Solve for α. $\alpha = +24^\circ$

Exercise 5.8.1:

D-glyceraldehyde is R
L-glyceraldehyde is S

Exercise 5.8.2:

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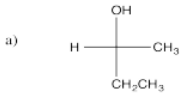
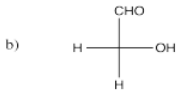
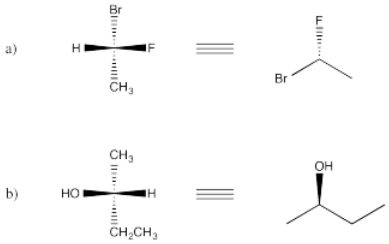




Exercise 5.8.3:



Exercise 5.9.1:

a) left b) right

Exercise 5.9.2:

a) right b) left

Exercise 5.9.1:

a) right b) right

Exercise 5.9.2:

a) left b) left

Exercise 5.9.5:

D-threose
2S, 3R

Exercise 5.9.6:

L-threose
2R, 3S

D- and L-threose are enantiomers of one another

Exercise 5.9.7:

L-erythrose
2S, 3S

L-erythrose and L-threose are diastereomers of one another.

Exercise 5.9.8:

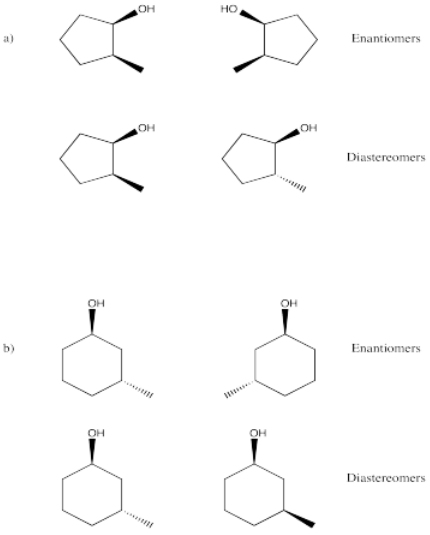
a) $(2)^3$ = 8 possible stereoisomers

RRR; SSS; RRS; SSR; RSS; SRR; SRS; RSR

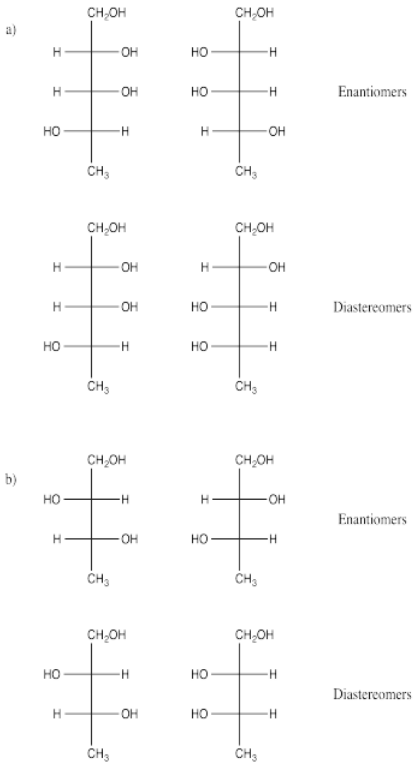
b) 4 pairs

c) 12 different possible pairs of diastereomers

Exercise 5.9.9:



Exercise 5.9.10:



Exercise 5.10.1:

a) D-threitol → 2R, 3S

b) L- threitol → 2S, 3S

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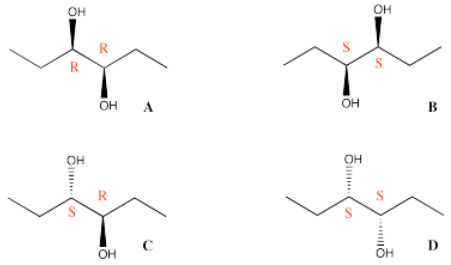
c) erythritol → 2S, 3R or 2R, 3S (a meso compound)

Exercise 5.10.2:

It does not matter which end you start counting from on these compounds since they are constituted the same.

Exercise 5.10.3:



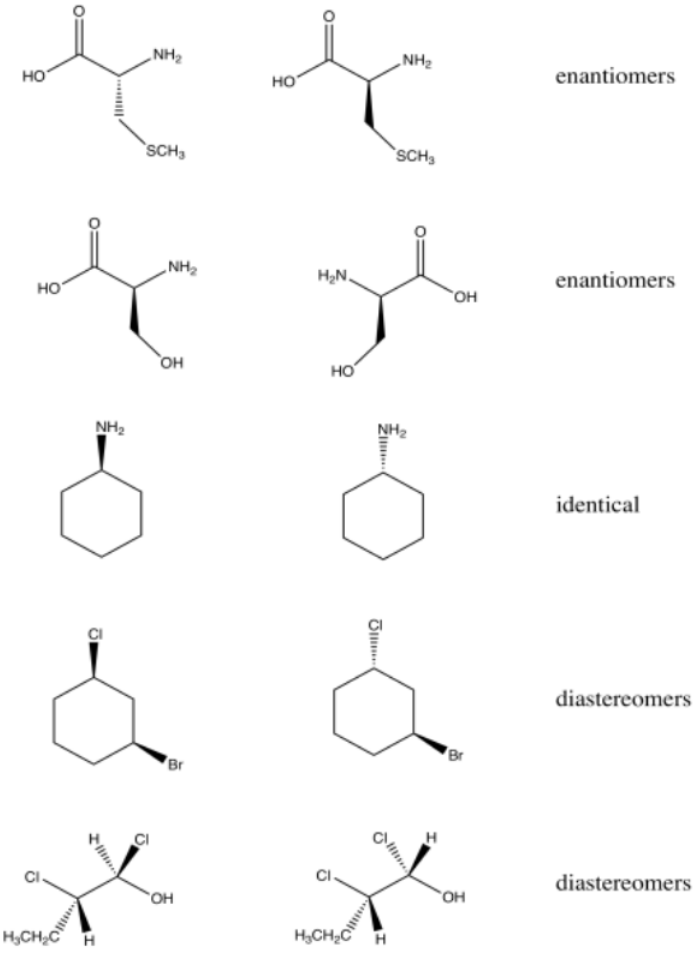
a) **B** and **D**

b) **A** and **D** or **A** and **B**

c) **A** and **C** or **B** and **C** or **D** and **C**

d) **C**

Exercise 5.10.4:



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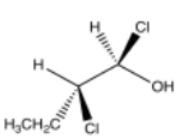
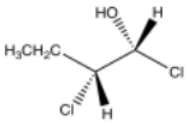
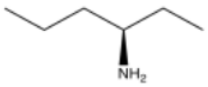
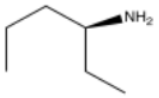
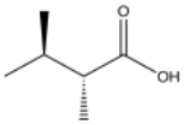
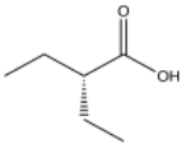
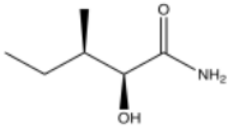
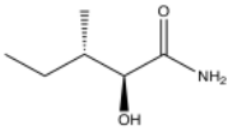
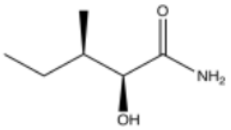
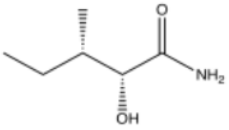
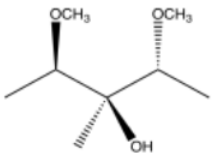
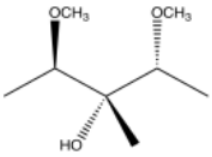


identical



enantiomers



constitutional isome

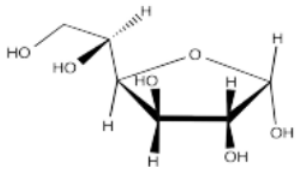
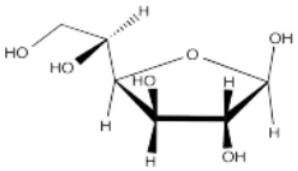


diastereomers



enantiomers

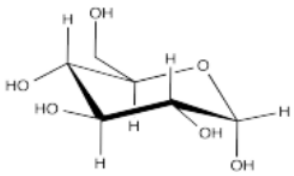
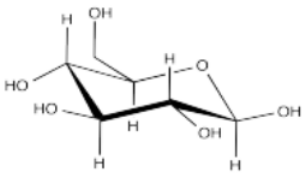


identical

Exercise 5.11.1:

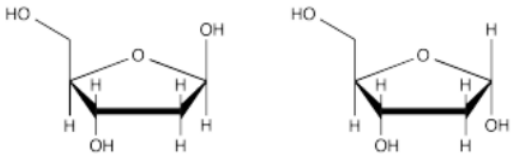
a)

b)

Exercise 5.11.2:



β-deoxyribofuranose α-deoxyribofuranose

a) Trans

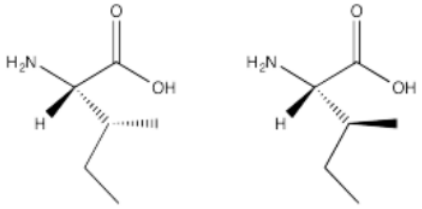
b) Cis

Exercise 5.12.1:

Glycine

Exercise 5.12.2:

Isoleucine



Exercise 5.12.3:

Proline

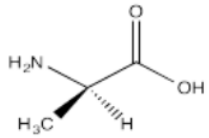
Exercise 5.12.4:

Glutamic acid and aspartic acid

Exercise 5.12.5:

Arginine, asparagine, glutamine, lysine; also tryptophan contains an aromatic heterocycle, although it is not basic.

Exercise 5.12.6:



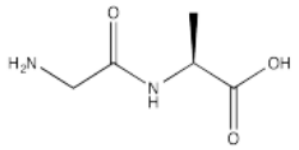
D-alanine

Exercise 5.12.7:

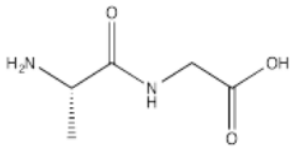
Cysteine

Exercise 5.13.1:

a)



Gly-Ala

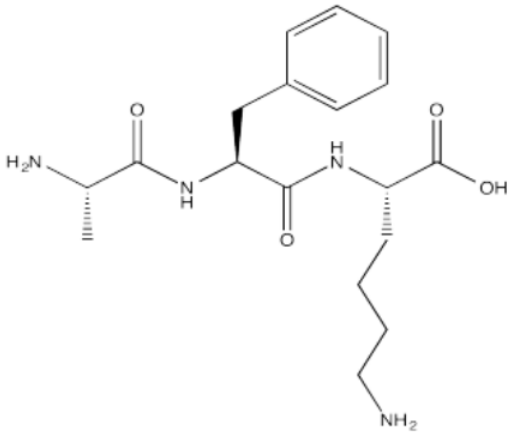


Ala-Gly

b) No. They are constitutional isomers of one another.

Exercise 5.13.2:

Ala-Phe-Lys



Exercise 5.14.1:

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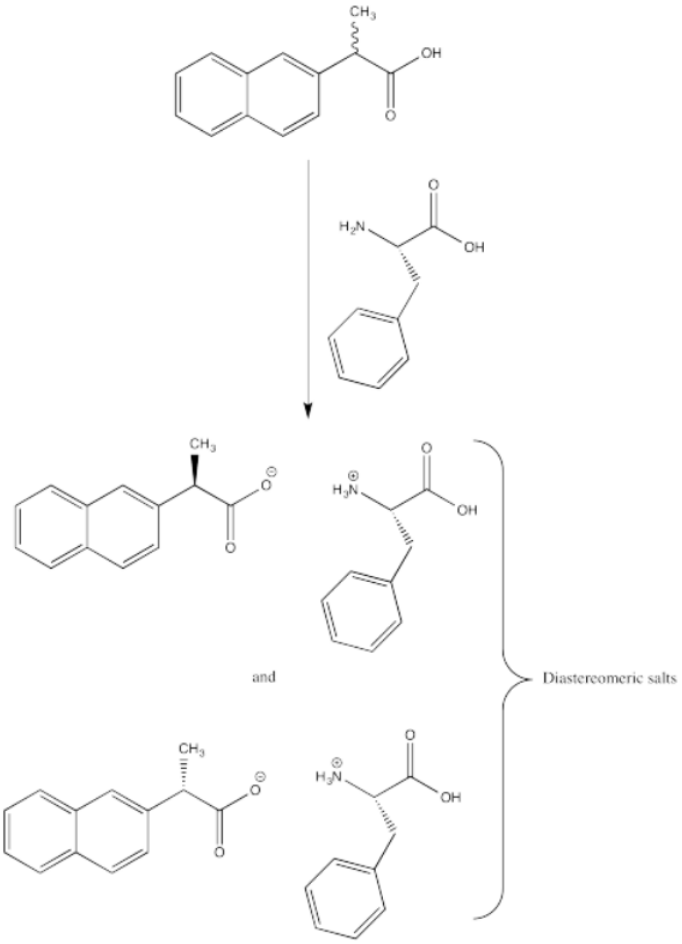


Exercise 5.15.1:

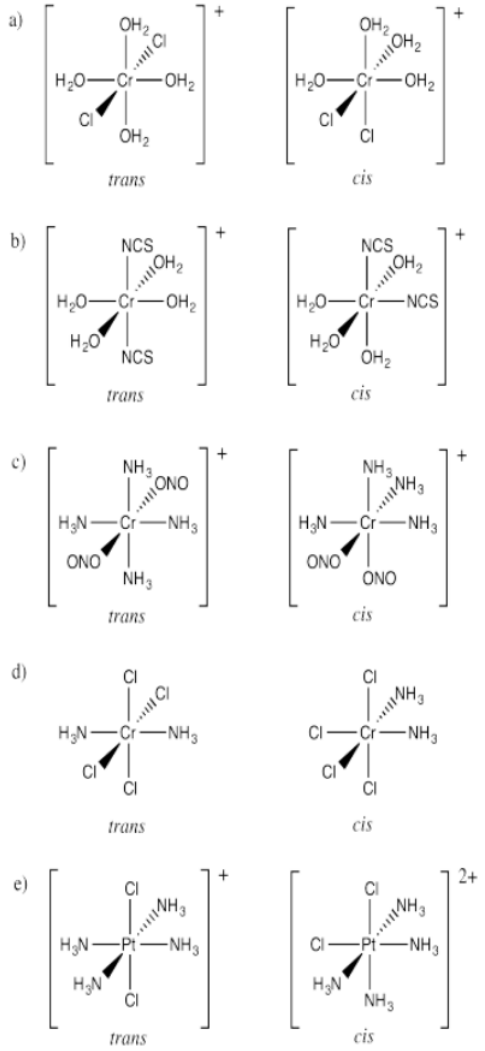
A. Cis
B. Trans
C. Trans
D. Neither (There is free rotation around the C-C single bond.)
E. Neither (C-C triple bonds have substituents at 180 degrees to each other (linear).
F. cis

Exercise 5.16.1:

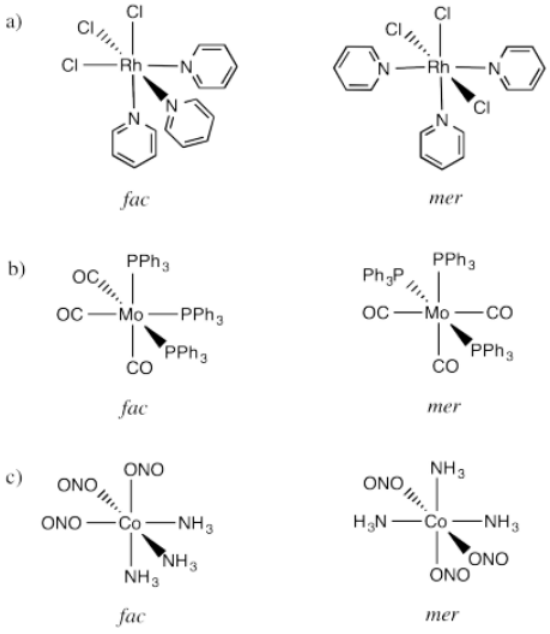
A. Z
B. E
C. E
D. Z
E. E
F. E
G. Z
H. E

Exercise 5.17.1:

https://chem.libretexts.org/@go/page/191275



Exercise 5.17.2:



https://chem.libretexts.org/@go/page/191275

Exercise 5.18.1:

a) Enantiomers

b) Enantiomers

c) Identical

d) Identical

e) Enantiomers

f) Identical

g) Enantiomers

Exercise 5.18.2:

a) Δ b) Λ c) Δ d) Λ e) Δ f) Δ g) Λ h) Λ

Exercise 5.20.1:

Pure = 125°

Optical purity = $\frac{100}{125} = 0.80$

$$\% \, Major = 80 + \frac{20}{2} = 90\%$$

$$\% \, Minor \, 100 - 90 = 10\%$$

Exercise 5.20.2

Pure = 100°

Optical purity = $\frac{95}{100} = 0.95$

$\% \, Major = 95 + \frac{5}{2} = 97.5\%$

$$\% \, Minor \, 100 - 97.5 = 2.5\%$$

Exercise 5.20.3

$$Pure = 18^{\circ}$$

$$\% \, Major = 60\%$$

$\% \, Minor = 40\%$

Optical purity = $\frac{X}{18} = 20\%$

Solve for X:

$$X = 3.6^{\circ}$$

Exercise 5.20.4:

$$Pure = 25^{\circ}$$

$$\%Major = 80\%$$

$\%Minor = 20\%$
Optical purity = $\frac{X}{25} = 80 - 20 = 60\%$

Solve for X:

$$X = 15^\circ$$

Exercise 5.20.5

$$[\alpha] = \frac{observed\ rotation}{(l)(c)}$$

$c = \frac{0.050g}{2.0mL} = 0.025\frac{g}{mL}$

Average observed rotation = $\frac{(0.625+0.706+0.682)}{3} = 0.671^\circ$

$$[\alpha] = \frac{0.671^\circ}{(0.025\frac{g}{mL})(0.5dm)} = 53.68^\circ$$

Exercise 5.20.6:

$$[\alpha] = \frac{observed\ rotation}{(l)(c)}$$

$c = \frac{0.540g}{2.0mL} = 0.27\frac{g}{mL}$

Average observed rotation = $\frac{(1.225+1.106+1.182)}{3} = 1.171^\circ$

$$[\alpha] = \frac{1.171^\circ}{(0.27\frac{g}{mL})(1.0dm)} = 4.34^\circ$$

Exercise 5.20.7:

$$[\alpha] = \frac{observed\ rotation}{(l)(c)}$$

$$c = \frac{0.250g}{2.0mL} = 0.125\frac{g}{mL}$$

$42^\circ = \frac{observed\ rotation}{(0.125\frac{g}{mL})(0.5dm)}$

observed rotation = 2.625°

Exercise 5.20.8

a) $[\alpha] = \frac{observed\ rotation}{(l)(c)}$

$$c = \frac{0.10g}{2.0mL} = 0.05\frac{g}{mL}$$

$c = \frac{0.10g}{2.0mL} = 0.05\frac{g}{mL}$

Average observed rotation = $\frac{(0.995+0.904+0.936)}{3} = 0.945\circ$

$[\alpha] = \frac{0.945^\circ}{(0.05\frac{g}{mL})(1.0dm)} = 18.9\circ$

b) % optical purity = $\frac{(100)(18.9)}{25} = 75.6\%$

c) enantiomeric excess = 75.6%

d) $\frac{(100-75.6)}{2} = 12.2\%$

12.2 % one enantiomer
87.8% other enantiomer

e) Enantiomers differ in how they interact with plane polarized light, but not in other physical analyses.

Exercise 5.20.9

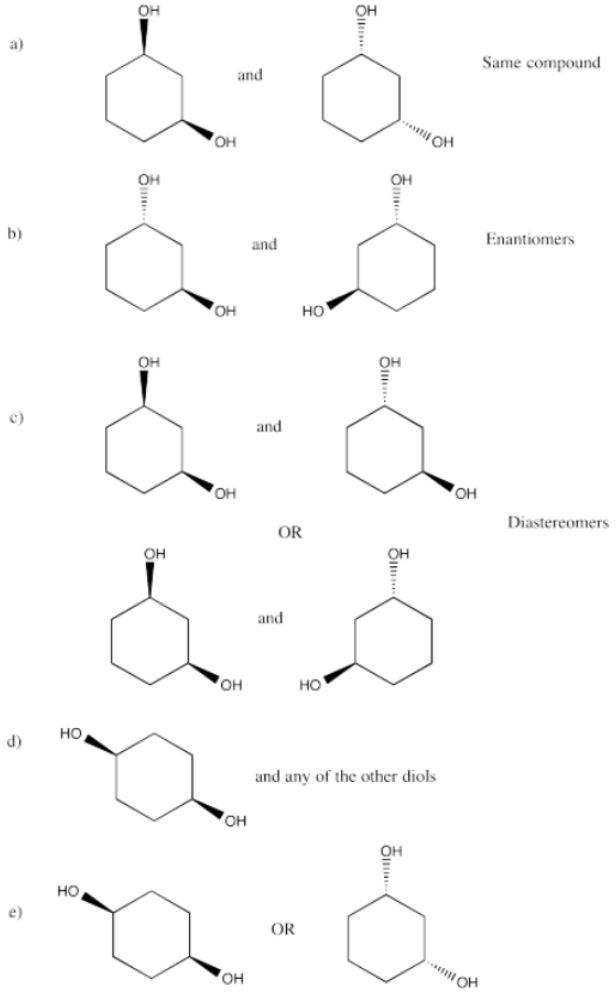
$$[\alpha] = \frac{observed\ rotation}{(l)(c)}$$

$$40\circ = \frac{observed\ rotation}{(l)(c)}$$

$40\circ = \frac{observed\ rotation}{(l)(1.1c)}$

Observed rotation = 44°

Exercise 5.20.10



Exercise 5.20.11:

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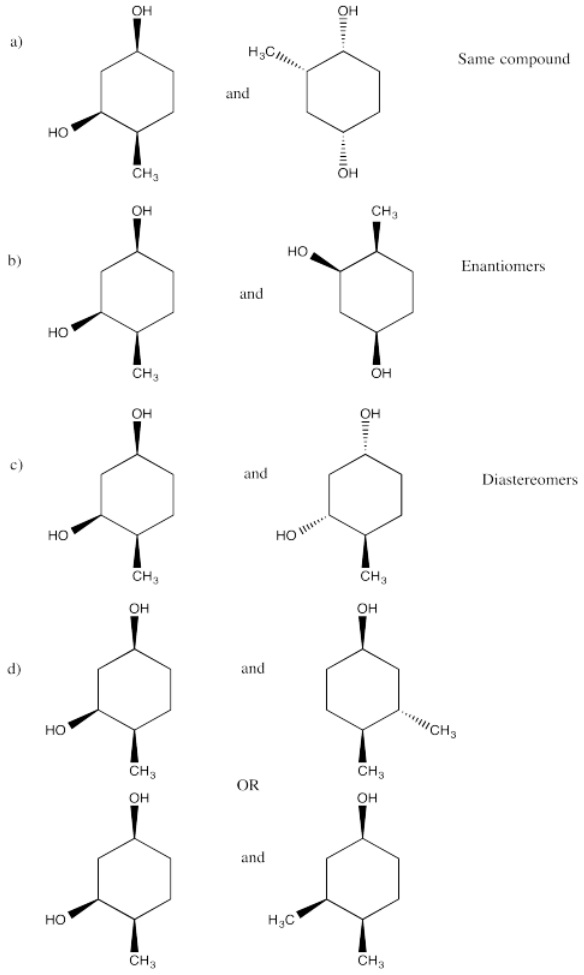

Exercise 5.20.12:

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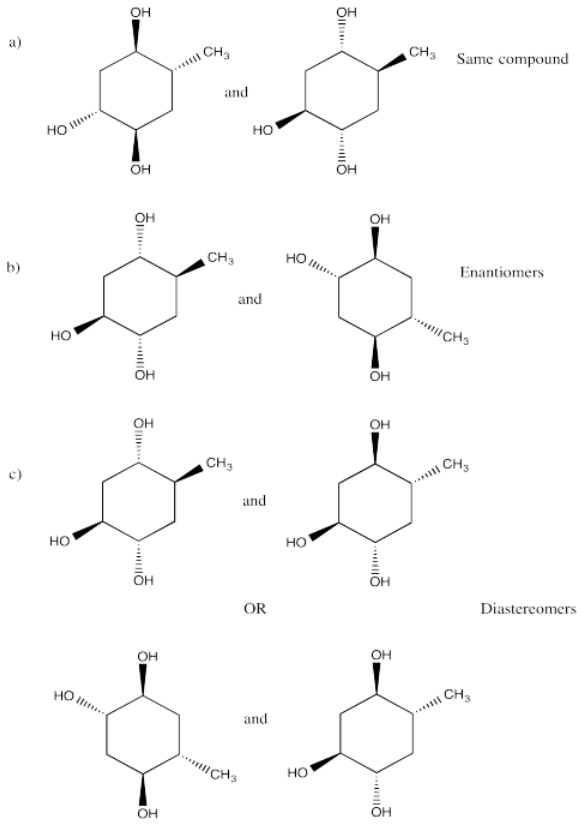

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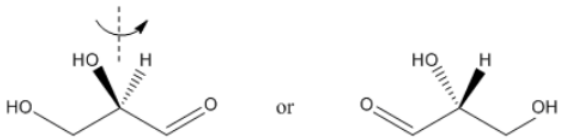
5.21: Biological Building Blocks- Carbohydrates

Carbohydrates are one of the major classes of biological molecules. Of course, they play an important role in energy storage and transport. They are also crucial parts of important structures such as DNA.

Carbohydrates, in general, are polyhydroxylated aldehydes and ketones. That means their structure can be thought of as having a carbonyl, C=O, for one of its carbons. All of the other carbons in the structure are attached to a hydroxyl group, OH. It's a little more complicated than that because carbohydrates are sort of shape-shifting molecules: they undergo very simple reactions that can slightly change their structure, and they can change back again.

The simplest carbohydrate is glyceraldehyde. It is a three-carbon chain with a carbonyl on one end and hydroxy groups on the other two atoms. The second carbon in the chain is chiral.



D-glyceraldehyde

Figure 5.21.1: D-glyceraldehye is one of two enantiomers of the simplest carbohydrate.

The naturally-occurring carbohydrates are chiral.

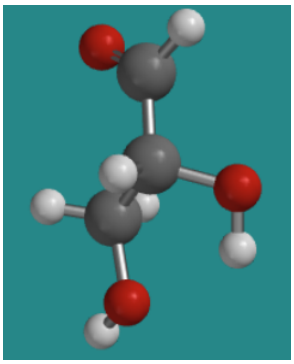
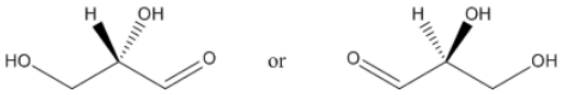


Figure 5.21.2: Ball-and-stick model of D-glyceraldehyde.

Go to **Animation SC8.1.** A three-dimensional model of D-glyceraldehyde.



L-glyceraldehyde

Figure 5.21.3: Ball-and-stick model of L-glyceraldehyde.

Go to **Animation SC8.2.** A three-dimensional model of L-glyceraldehyde.

Exercise 5.21.1

What is the absolute configuration of L-glyceraldehyde? What about D-glyceraldehyde?

Answer

D-glyceraldehyde is R

L-glyceraldehyde is S

Biological molecules are frequently homochiral. That means that we have one enantiomer of glyceraldehyde in most organisms, but not the other. The one we have is D-glyceraldehyde. There are always a few organisms that have figured out over the eons how

to make the other enantiomer of a naturally-occuring chiral molecule, but almost everything in nature shares our preference for D-glyceraldehyde.

Not only that, but all of the other carbohydrates share that same chiral center. You can think of the other carbohydrates as being based on glyceraldehyde. To make a bigger carbohydrate, additional carbons must be added into the glyceraldehyde chain. They are added to the carbonyl end, leaving the chiral center of glyceraldehyde unchanged. Just as the second-last carbon (really, the middle carbon) in glyceraldehyde is chiral and has a specific configuration, so do all of the others, and they all have the same configuration at that carbon.

- The "last" chiral center in other carbohydrates all have the same configuration as the chiral center in glyceraldehyde.

Most of the time, if you look in a biology or biochemistry textbook, you will see carbohydrates drawn in very particular ways. Now, carbohydrates can always take a couple of different forms (remember, they are shape-shifters). They usually have a ring form and a chain form, although very small carbohydrates only have a chain form. The chain form is usually drawn in a cross shape or tree shape, with a long vertical line crossed by horizontal lines. These drawings are called Fischer projections. If there is a chiral center in a Fischer projection, then it matters whether groups on the horizontal line are drawn on the right or on the left.

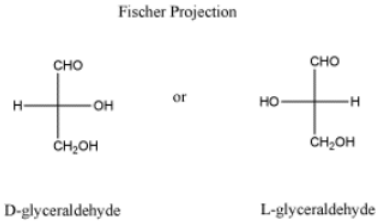


Figure 5.21.4: Fischer projections of glyceraldehyde.

- Fischer projections are drawings that are sometimes used to show stereochemistry in a different way.
- The groups to left and right of the Fischer projection are coming towards you.
- The groups on top and bottom are going away from you.
- The carbon chain is drawn vertically with attachments at the sides.
- Normally, the chain is oriented so that the "highest priority functional group" on the chain is at or near the top of the chain; that usually means the group with the most bonds to oxygen. In glyceraldehyde, the CH=O group is drawn at the top rather than at the bottom.

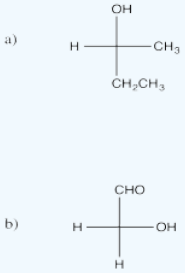
The big advantage of Fischer projections is that you can easily tell at a glance the relationship between two molecules, and the relationship between specific chiral centers along the chain. Are the molecule the same? Are they mirror images? Are the chiral centers the same? Are they opposite?

On the next page, we will see some slightly bigger carbohydrates.

Exercise 5.21.2

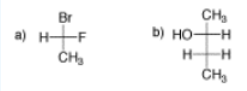
Draw the following molecules as Fischer projections.

Answer

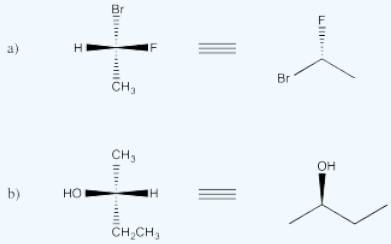


Exercise 5.21.3

Convert the following Fischer projections into wedge-dash drawings.



Answer



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CHAPTER OVERVIEW

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6.1: Introduction to Conformation

When we smell something, the information travels to us via molecules, and almost always these are organic molecules. These molecules can be detected by a variety of organs, including noses in dogs and antennae in crickets, but no matter what organ is sensing the smell, one of the crucial factors in determining how an organism reacts to a compound is the shape of the molecule. The sense of smell depends on thousands of different receptors in the organ, working conceptually on a lock-and-key basis: a molecule with a given shape can fit into a given receptor, and when it does, a signal is sent telling the nervous system that the organism has encountered that particular type of molecule, and the organism reacts appropriately.

What gives a molecule its shape? Given a structural formula, could you determine the shape of the corresponding molecule in three dimensions? Could you predict its biological activity, including not only its smell, but also a host of other behaviors linked to the shape of molecular messengers, such as anti-cancer activity or narcotic properties? These questions are at the cutting edge of biological chemistry. Although they are best answered through computer modeling, we can develop some of the qualitative ideas used in these models.

Computer modeling employs "basis sets", small sets of information that the computer could apply to any molecule in order to predict its properties. In order to understand computational conformational analysis, in this chapter we will develop a very simple basis set as an example.

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6.2: Simple Molecules

Ethene (CH_2=CH_2) contains two trigonal planar carbon atoms. Each carbon is bonded to two hydrogens as well as the other carbon.

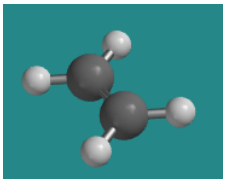

Figure 6.2.1: A ball-and-stick model of ethene.

This structure is illustrated in the Jmol animation linked below. These animations are completely manipulable with a mouse. (They are grabbable and movable. Use your mouse.)

Go to **Animation CA2.1.** A three-dimensional model of ethene.

From molecular orbital considerations, the two trigonal carbons must be coplanar with each other in order to maximize carbon-carbon pi bonding. As a result, the entire molecule must be planar.

Figure 6.2.2: Orbital pictures of ethene showing rotational freedom about the sigma bond (left) but lack of rotational freedom about the pi bond (right).

Ethane (CH_3-CH_3) is very similar to ethene, except that each carbon is tetrahedral and is bonded to three hydrogen atoms. There is no need to arrange the two carbon atoms with a certain orientation to each other because the sigma bond holding the two carbons together is symmetric about the C-C axis. As a result, there are a number of ways the two ends of the molecules could be oriented.

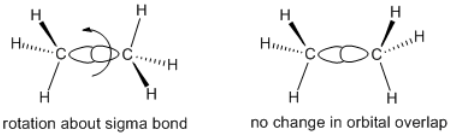

Figure 6.2.3: Ball-and-stick model of ethane in a "staggered conformation".

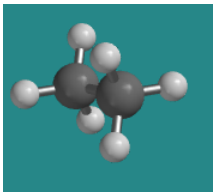

Figure 6.2.4: Ball-and-stick model of ethane in a "staggered conformation".

Go to **Animation CA2.2.** A three-dimensional model of ethane in staggered conformer.

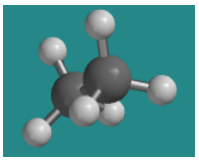

Figure 6.2.5: Ball-and-stick model of ethane in an "eclipsed conformation".

Go to **Animation CA2.3.** A three-dimensional model of ethane in eclipsed conformation.

Working with models often reflects reality quite well. While holding a model of ethane, you could grab one CH_3 group and twist it while holding the other one still, and as a result you could put the molecule into different poses. The ethane model is flexible via rotation around the C-C bond.

Ethane can adopt different shapes, because one end of the molecule can rotate with respect to the other. These different shapes are seen most dramatically while viewing ethane along the carbon-carbon bond. From this vantage point, rotation about the C-C bond

results in a changing shape that alternates between a six-pointed star and a three-pointed one. In the three-pointed star, some of the hydrogens are hidden or eclipsed behind the corresponding hydrogens on the carbon that is closest to the viewer; in the six pointed star they have come out into view again.

- A drawing that shows a molecule viewed along the axis of a rotating bond is called a Newman Projection.
- The different shapes obtained via bond rotation are called conformations.
- The angle between a specific C-H bond on one carbon and a specific C-H bond on another carbon, when viewed in a Newman projection, is called a dihedral angle.

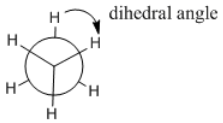

Figure 6.2.6: A view of ethane seen by looking along the C-C bond axis. This type of rendering is called a "Newman Projection".

- The conformation in which the Newman projection shows all six hydrogens of ethane in plain view is a staggered conformation.
- The conformation in which three of the hydrogens are hidden behind the others is an eclipsed conformation.
- In the eclipsed conformation, the dihedral angle could be 0, 120, 240 or 360 degrees; in a staggered conformer, the dihedral angle could be 60, 180, 300 degrees.

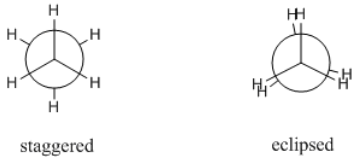

Figure 6.2.7: Newman projections showing staggered (left) and eclipsed conformations (right) of ethane.

Many conformations of ethane are possible, but not all of these conformations are equally likely. The most probable conformation is a staggered one.

- Staggered conformations are lower in energy than eclipsed ones.
- The term "conformer" is used for a stable conformation, one that has a practical chance of occurring.

The energy barrier to rotation about the C-C bond in an ethane molecule can be measured using microwave spectroscopy. This technique is similar to infrared spectroscopy but the molecular motion connected to microwaves is bond rotation rather than vibration. Experimentally, the barrier to rotation is about 3 kcal/mol. (Keep in mind that, in chemistry, the term "experimental" gives a finding more weight, not less, because it reflects reality.) This barrier is small enough that at room temperature an ethane molecule can freely rotate, but high enough that an ethane molecule would not be found sitting in the eclipsed state.

- The factor that destabilizes eclipsed conformations is called torsional strain.
- Torsional strain in ethane apparently arises from a molecular orbital interaction between a populated C-H σ bond and the empty C-H σ* orbital on the neighbouring carbon.

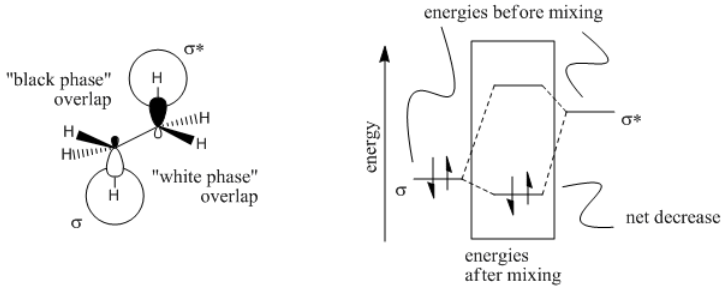

Figure 6.2.8: Orbital pictures of ethane showing a stabilizing interaction between a populated C-H σ bond and the empty C-H σ* orbital on the neighbouring carbon.

- When the two C-H bonds are in the same plane but pointing in opposite directions, the orbitals have proper symmetry to interact. This is called an antiperiplanar orientation, from anti, meaning "opposite", and periplanar, meaning "in the same

plane".

- This orientation is only possible when the neighbouring bonds are staggered.
- Eclipsed conformations lack this interaction and are higher in energy by about 3 kcal/mol (about 1 kcal/mol per C-H σ - σ* interaction.

Looking at a space filling model of ethane, it seems that the overall shape difference between staggered and eclipsed ethane is pretty small. The important point is that most organic structures are not static, but flexible. Also, torsional strain is found in all carbon-carbon bonds, so we will keep using the experimental result from ethane as we build a "basis set" for understanding conformation in larger molecules.

Still pictures of models obtained using Spartan 14 from Wavefunction, Inc., Irvine, California.

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6.3: Conformation of Butane

In the case of ethane, conformational changes are very subtle, but in others they are more obvious. Butane ($CH_3CH_2CH_2CH_3$) has four tetrahedral carbons and three carbon-carbon bonds connecting them together. Let's number the carbons along the chain C1, C2, C3 and C4. Rotating around the C-C bonds connected to the terminal carbons -- C1-C2 and C3-C4 -- only subtle changes in shape would be apparent. However, rotating about C2-C3 produces some pretty obvious shape changes.

Pay attention to where the two methyl groups are with respect to each other. If we call C1-C2-C3-C4 the dihedral angle, then at 0 degrees the molecule is in an eclipsed conformation, apparent when looking at the Newman projection. Looked at from other vantage points, the molecule is curled up into the shape of a letter C.

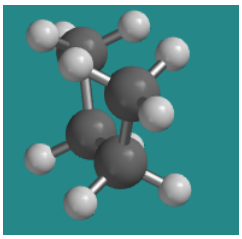


Figure 6.3.1: Ball-and-stick model of butane. The C-shape that it adopts here is called the "least-stable eclipsed" conformation.

Go to **Animation CA3.1.** A three-dimensional model of butane in an eclipsed conformation.

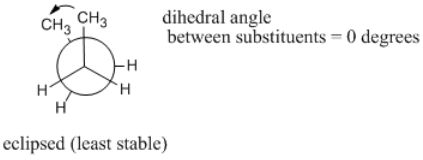


Figure 6.3.2: Newman projection of butane in the "least-stable eclipsed" conformation.

The "least stable eclipsed" conformation is described that way because there are two different eclipsed conformations; we will see the other one soon. Of the two eclipsed conformations, this one is less stable than the other one. In an eclipsed conformation, bonds coming from two neighbouring atoms are lined up with each other. The dihedral angle between these bonds -- the C1-C2 bond and the C3-C4 bond in the case of butane's least stable eclipsed conformation -- is 0 °. That situation introduces torsional strain. As a result, neither one of these eclipsed conformations is very stable.

At 60 degrees, the molecule is no longer eclipsed, and just as in ethane the energy is a little bit lower, but the overall shape when viewed from the side is still a sort of twisted C. This shape is one of two possible staggered conformations, in which there is no torsional strain.

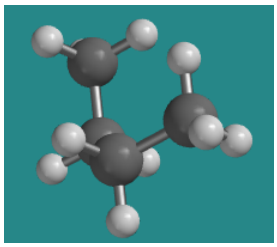


Figure 6.3.3: Ball-and-stick model of butane. This shape is called the "gauche conformation".

Go to **Animation CA3.2.** A three-dimensional model of butane in a gauche conformation.

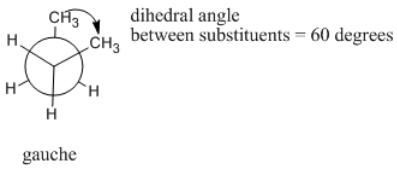


Figure 6.3.4: Newman projection of butane in the "gauche" conformation.

At 120 degrees the molecule is eclipsed again , but from the side it has now twisted almost into a shape like the letter Z. It is clearly different from the other eclipsed conformation. This one is a little more stable than the other eclipsed conformation, for reasons that we will look into shortly. It is called the "more stable eclipsed conformation".

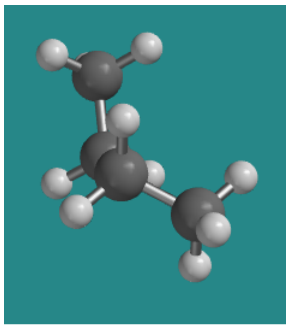


Figure 6.3.5: Ball-and-stick model of butane. This shape is called the "more stable eclipsed conformation".

Go to **Animation CA3.3.** A three-dimensional model of butane in an eclipsed conformation.

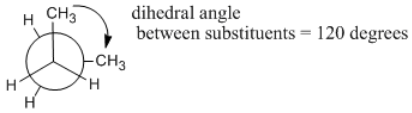


Figure 6.3.6: Newman projection of butane in the "more-stable eclipsed" conformation.

At 180 degrees, the molecule is staggered again and has settled into a regular, zig-zag, letter Z shape. There is no torsional strain, so this is one of the more stable shapes that the molecule can adopt. However, it is not the same shape as the other staggered conformer (the one we called "gauche"). This one is called the "anti" conformer.

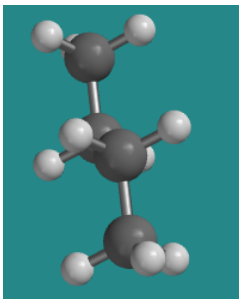


Figure 6.3.7: Ball-and-stick model of butane. This shape is called the "anti" conformation.

Go to **Animation CA3.4.** A three-dimensional model of butane in anti conformer.

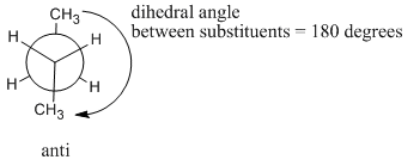


Figure 6.3.8: Newman projection of butane in the "anti" conformation.

These conformations of butane are really pretty different. Which shape would the molecule prefer? From what we learned about ethane, we could probably rule out the eclipsed conformations. Each of those would have 3 kcal/mol of torsional strain.

However, there is another factor that destabilizes the initial conformation at 0 degrees, in favor of the Z-shaped one with the methyl groups 180 degrees apart from each other. This factor is called "sterics" and it refers to the idea that molecules, or parts of molecules, take up space, and so two parts of the butane can't occupy the same place at the same time. Put more simply, sterics refers to crowdedness. When the two methyl groups in butane are too close together, they are too crowded, and they are at higher energy. When they get farther apart, crowding subsides and the energy in the molecule goes down.

- Torsional strain forces bonds on neighbouring carbons to be staggered.
- Steric strain forces groups away from each other to relieve crowding.

- Torsion and sterics both contribute to strain energy.
- Strain can be released by getting the molecule in a lower energy conformation.

For butane, that means getting those two methyl groups away from each other and keeping the bonds staggered.

There is some additional jargon that is used to describe these butane conformations:

- In an anti conformer, the largest groups are 180^0 from each other.
- In a gauche conformer, the bonds are staggered but the largest groups are 60^0 from each other.

Because of different steric interactions, the most stable conformer is the anti conformer. The second-most stable conformer is the gauche conformer. The other shapes we have looked at, the two eclipsed conformations, are not very stable at all. At room temperature, a bottle of butane gas has enough energy that the individual molecules can allow their bonds to spin around, sampling different shapes. However, at any given time, most of the molecules will be found in the anti conformer, because each of those molecules will spend most of its time in the most stable conformation. Some of the molecules will be found in the gauche conformer, because that is the second-most stable conformation. None of the molecules will be found in the eclipsed conformations, because those are points of maximum energy. The molecules have enough energy to rock back and forth a little bit, and sometimes they will not rotate all the way through an eclipsed conformation, but they won't stop there. Instead, they will keep rotating until they get to another staggered conformer.

- A butane molecule spends most of its time in the anti confrmer.
- A butane molecule spends some of its time in the gauche conformer.
- A butane molecule spends almost none of its time in eclipsed conformations.

Note that we have two very similar words: conformation and conformer. They are related, but not the same thing.

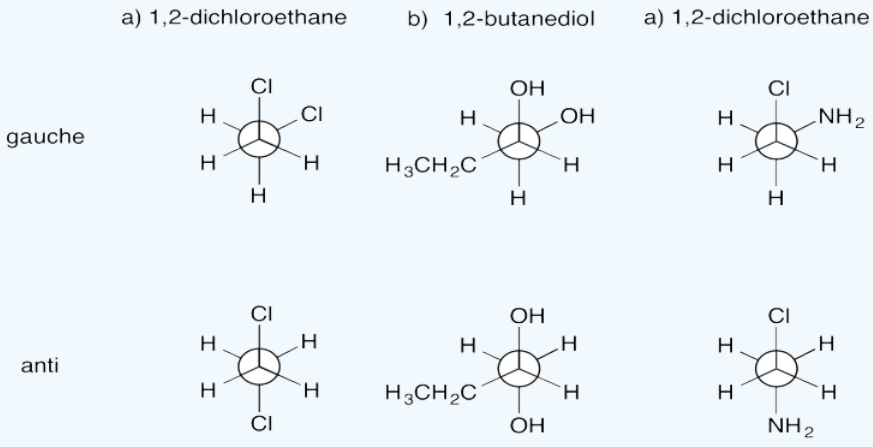
- A conformation is any shape that a molecule can adopt.
- A conformer is a conformation that is stable enough so that a molecule can adopt for significant amount of time.

Exercise 6.3.1

Draw Newman projections of the following compounds in a gauche and an anti conformation.

1. 1,2-dichloroethane ($ClCH_2CH_2Cl$)
2. 1,2-butanediol ($CH_3CH_2CH(OH)CH_2OH$)
3. 2-chloroethylamine ($ClCH_2CH_2NH_2$)

Answer



Still pictures of models obtained using Spartan 14 from Wavefunction, Inc., Irvine, California.

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6.4: The Basis Set

Using information on the rotational barrier of butane, which is about 4.5 kcal/mol, we can add more information to our basis set. We will also use information from other sources to build a more complete picture.

- In ethane, there is no steric strain, because the hydrogens are too far apart to crowd each other.
- In propane ($CH_3CH_2CH_3$), the hydrogens on the first and third carbon are close to each other, but hardly cause any crowding.
- In butane's anti conformer, there is no steric strain, because the methyl groups are far apart.
- In butane's least stable eclipsed conformer, with the methyls eclipsed, there is about 1.5 kcal/mol of steric strain. The 1.5 kcal sterics plus 3 kcal torsion equals the rotational barrier.
- In butane's gauche conformer, there is no torsion, but the amount of sterics appears to be only a little less than when the methyls are eclipsed.

One simple method of assessing steric strain, without memorizing a big table of information, is use an atom counting method. Count from one hydrogen, to the next atom, and so on to the other hydrogen that seems likely to interact with the first. In ethane, this distance is four atoms (H-C-C-H). In propane it is five. In butane it is six. The potential steric interaction in butane is accordingly called a six atom interaction. The basis set used in this method is given in the table below.

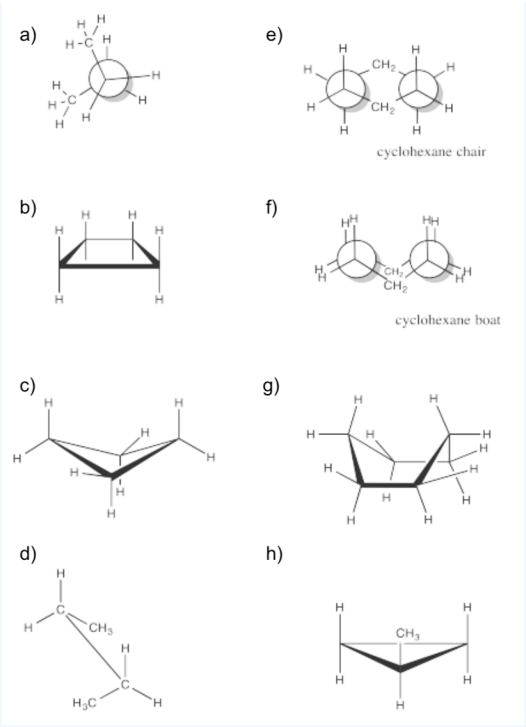
Table 6.4.1. Atom-Counting Basis Set for Estimating Strain Energy

Type of strain	Strain energy (kcal/mol)
torsion (three pairs of adjacent bonds eclipsed)	3
4-atom sterics	0
5-atom sterics	0.1
6-atom sterics, gauche	1
6-atom sterics, eclipsed	1.5
7-atom sterics, gauche	3

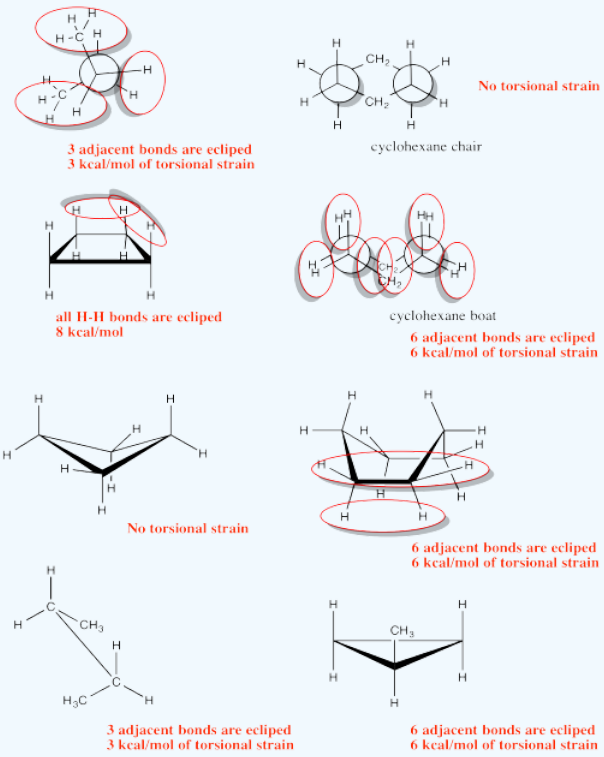
Note that a methyl (CH_3) group can always rotate, so multiple hydrogens on one methyl group could potentially interact with multiple hydrogens on another, but not at one time. We only need to take into account the full interactions that could happen simultaneously.

Exercise 6.4.1

Calculate the torsional strain in the following cases.

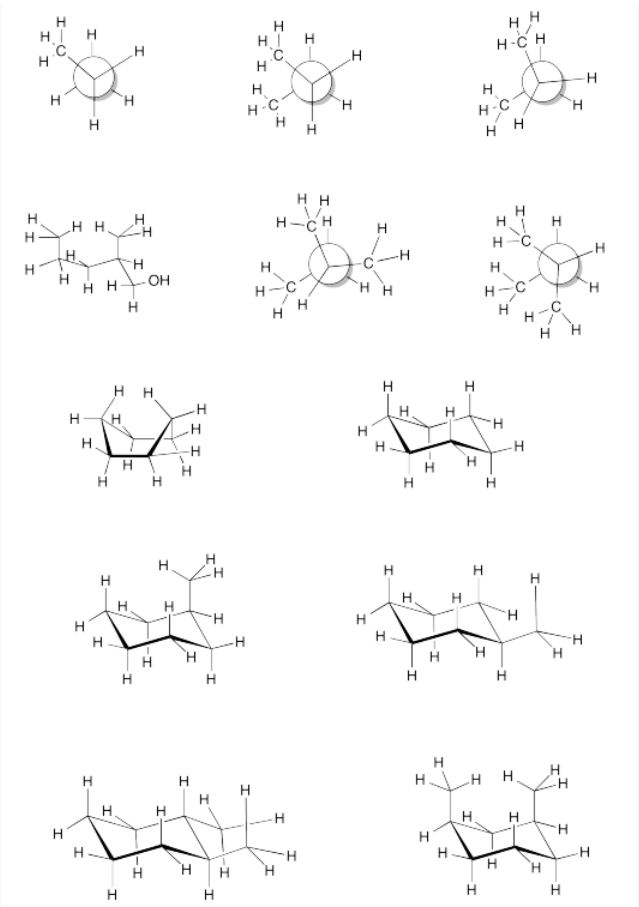


Answer



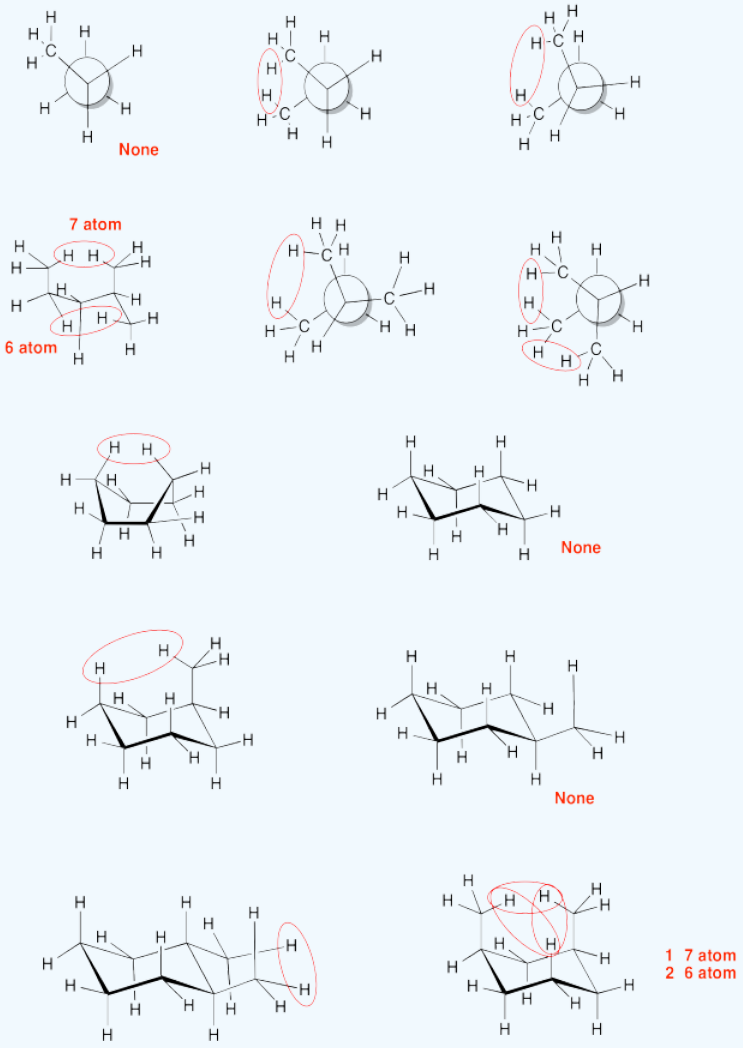
Exercise 6.4.2

Find all 6 atom interactions in the following pictures.



Answer

https://chem.libretexts.org/@go/page/189643

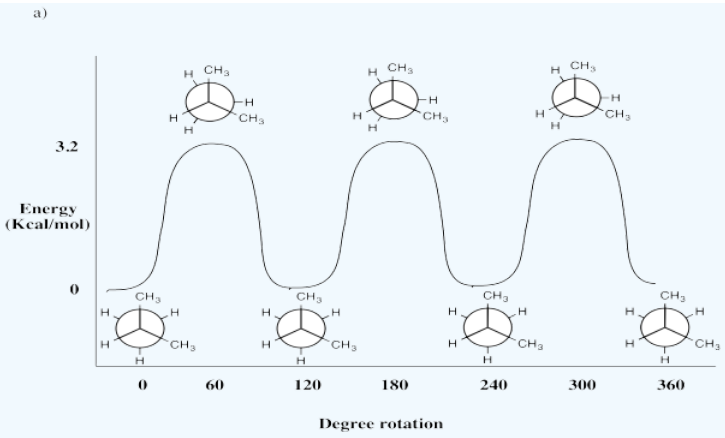


Exercise 6.4.3

Draw Newman Projections every 60° for the following molecules. Assess the strain energy for each Newman Projection found by rotating about the C2-C3 bond. Use the basis set in Table CA1. Plot strain energy vs. dihedral angle and label

a. 2-methylpropane ($CH_3CH(CH_3)CH_3$)
b. 2,3-dimethylbutane ($CH_3CH(CH_3)CH(CH_3)CH_3$)
c. pentane ($CH_3CH_2CH_2CH_2CH_3$)

Answer a:



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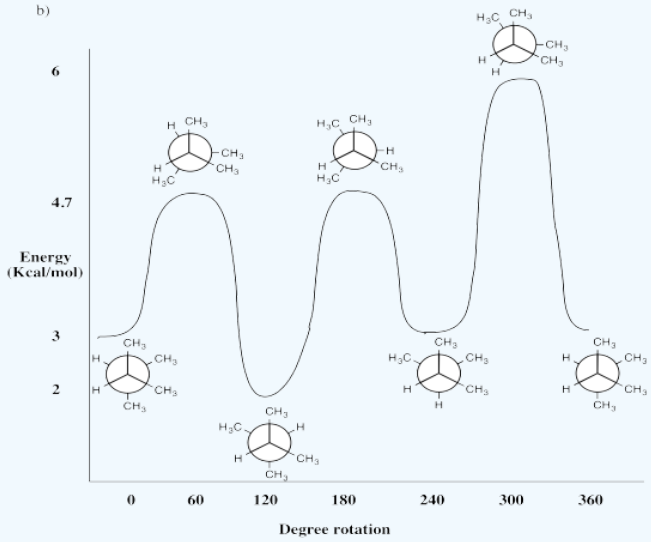

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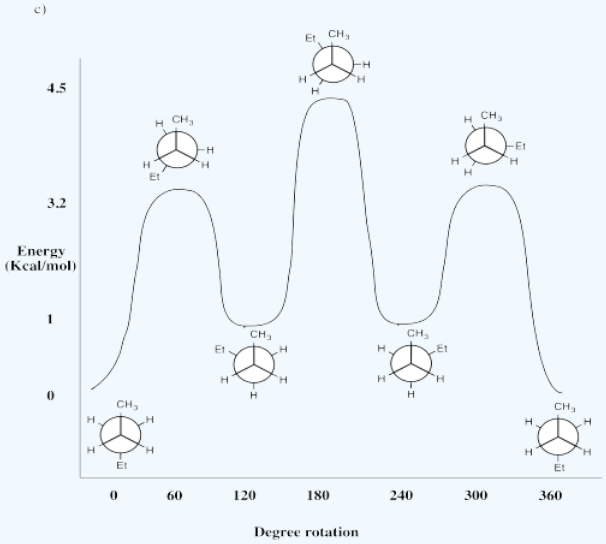

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6.5: Molecular Modeling

The shapes of molecules can be predicted by tallying up estimates of steric and torsional interactions. This task is referred to as a molecular mechanics calculation. The basis set used may vary from the one given here, but the idea is the same: a limited set of information is applied to molecules, no matter how large or complex, in order to measure the relative energy of different conformations. Typically a calculation is followed by a change in a dihedral angle somewhere, the calculation is repeated and so on, so that eventually the most stable conformation is found.

A calculation like this could take a very long time. Even on a computer, there is usually a need to speed things up. A common short cut for employs the following approach. If a change in dihedral angle results in a decrease in energy, the calculation continues with a new change in that dihedral angle. Eventually, if changes lead to increased energy, the program assumes the lowest energy has already been passed and it backtracks to that point again. It may then try another dihedral using the same method. In this way the computer does not waste time on calculations involving high energy eclipsed conformations or ones with steric problems. As a result, a molecular mechanics calculation can usually estimate the lowest energy conformer in a few seconds.

The limitation of that approach can be seen in a generic plot of energy vs. conformational change in which there is more than one low-energy conformer. How does the calculation determine that it has found the absolute lowest energy conformer, and not just a dip in the energy surface?

Figure 6.5.1: Plot of energy vs. conformational change for a fictional molecule.

For example, in a plot of butane's relative energy vs its dihedral angle around C2-C3. The gauche conformation occupies a "local energy minimum", meaning that the energy is lower here than when the dihedral angle is either greater or smaller, because in either direction the molecule would arrive at an eclipsed conformation with higher energy. In the approach described above, typically the default approach in most calculations, the computer could get stuck at the gauche conformation, because a change in either direction results in an increase in energy. However, if the computer would just push past those energy maxima then it would arrive at the anti conformation, which is the "global energy minimum", with the lowest energy of all.

- Beware of local minima when looking for the most stable conformer on a computer.
- Usually, you can tell whether the computer has the right answer based on your understanding of sterics.

Complete conformational analysis sometimes requires some method of "dihedral angle driving". In this kind of approach, the software user can tell the computer to calculate energies a given number of times around a given dihedral angle; for example, maybe a calculation would be done every sixty degrees for the dihedral around the C2-C3 bond in butane, or maybe every thirty degrees. That way, the computer is sure to find the global minimum for a particular dihedral angle.

More advanced methods may be required to arrive at correct low-energy structures for more complicated molecules. For example, hydrogen bonding is clearly a major factor controlling the structure of molecules such as DNA and proteins. We have looked only at steric and torsional strains because they are ubiquitous in molecular mechanics, but different basis sets, and different types of calculations, could take into account additional interactions such as hydrogen bonding or other electronic phenomena which would help correctly establish the shapes of more complex molecules.

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6.6: Cyclic System

Cyclic systems are a little different from open-chain systems. In an open chain, any bond can be rotated 360 degrees, going through many different conformations. That complete rotation isn't possible in a cyclic system, because the parts that you would be trying to twist away from each other would still be connected together. Cyclic systems have fewer "degrees of freedom" than aliphatic systems; they have "restricted rotation".

Because of the restricted rotation of cyclic systems, most of them have much more well-defined shapes than their aliphatic counterparts. Let's take a look at the basic shapes of some common rings.

- Many biologically important compounds are built around structures containing rings, so it's important that we become familiar with them.
- In nature, three- to six-membered rings are frequently encountered, so we'll focus on those.

A three membered ring has no rotational freedom whatsoever. A plane is defined by three points, so the three carbon atoms in cyclopropane are all constrained to lie in the same plane.

cyclopropane

Furthermore, if you look at a model you will find that the neighboring C-H bonds (C-C bonds, too) are all held in eclipsed conformations.

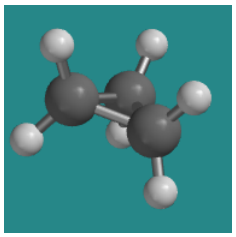


Figure 6.6.1: Ball-and-stick model of cyclopropane.

Go to **Animation CA6.1.** A three-dimensional model of cyclopropane.

Cyclopropane is always at maximum torsional strain. This strain can be illustrated in a line drawing of cyclopropane as shown from the side. In this oblique view, the dark lines mean that those sides of the ring are closer to you.

However, the ring isn't big enough to introduce any steric strain, which does not become a factor until we reach six membered rings. Until that point, rings are not flexible enough for two atoms to reach around and bump into each other.

The really big problem with cyclopropane is that the C-C-C bond angles are all too small.

- All the carbon atoms in cyclopropane appear to be tetrahedral.
- These bond angles ought to be 109 degrees.
- The angles in an equilateral triangle are actually 60 degrees, about half as large as the optimum angle.
- This factor introduces a huge amount of strain in the molecule, called ring strain.

Cyclobutane is a four membered ring. In two dimensions, it is a square, with 90 degree angles at each corner.

cyclobutane

However, in three dimensions, cyclobutane is flexible enough to buckle into a "butterfly" shape, relieving torsional strain a little bit. When it does that, the bond angles get a little worse, going from 90 degrees to 88 degrees.

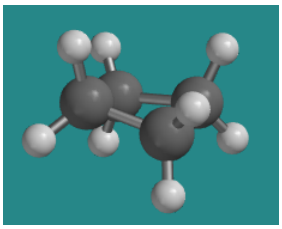
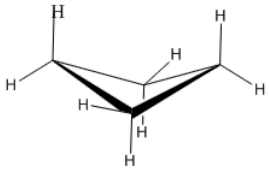


Figure 6.6.2: Ball-and-stick model of cyclobutane.

Go to **Animation CA6.2.** A three-dimensional model of cyclobutane.

In a line drawing, this butterfly shape is usually shown from the side, with the near edges drawn using darker lines.



- With bond angles of 88 rather than 109 degrees, cyclobutane has a lot of ring strain, but less than in cyclopropane.
- Torsional strain is still present, but the neighbouring bonds are not exactly eclipsed in the butterfly.
- Cyclobutane is still not large enough that the molecule can reach around to cause crowding. Steric strain is very low.
- Cyclobutanes are a little more stable than cyclopropanes and are also a little more common in nature.

Cyclopentanes are even more stable than cyclobutanes, and they are the second-most common paraffinic ring in nature, after cyclohexanes. In two dimensions, a cyclopentane appears to be a regular pentagon.

cyclopentane

In three dimensions, there is enough freedom of rotation to allow a slight twist out of this planar shape.

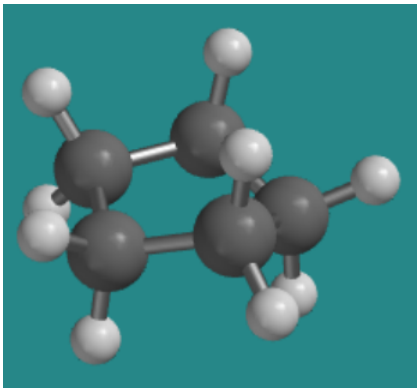
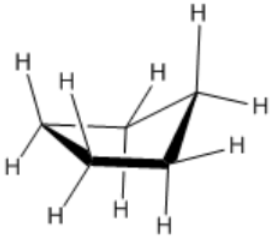


Figure 6.6.3: Ball-and-stick model of cyclopentane.

Go to **Animation CA6.3.** A three-dimensional model of cyclopentane

In a line drawing, this three-dimensional shape is drawn from an oblique view, just like cyclobutane.



- The ideal angle in a regular pentagon is about 107 degrees, very close to a tetrahedral bond angle.
- Cyclopentane distorts only very slightly into an "envelope" shape in which one corner of the pentagon is lifted up above the plane of the other four, and as a result, ring strain is entirely removed.
- The envelope removes torsional strain along the sides and flap of the envelope. However, the neighbouring carbons are eclipsed along the "bottom" of the envelope, away from the flap. There is still some torsional strain in cyclopentane.
- Again, there is no steric strain in this system.

Still pictures of models obtained using Spartan 14 from Wavefunction, Inc., Irvine, California.

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6.7: Cyclohexane

Finally, cyclohexane is the most common paraffinic ring of all, partly because it is possible to form a conformation of cyclohexane having very little strain energy. However, it has enough flexibility that things become more complicated than in the other rings we have looked at. If cyclohexane were flat, the C-C-C bond angles would be 120 degrees, like the corners of a regular hexagon. That's too big for a tetrahedral carbon, so the cyclohexane uses its flexibility to adopt a shape in which this strain energy is relieved.

cyclohexane

There are many shapes that a cyclohexane could adopt. We will look only at two of them and use our basis set to think about which one is more stable and more likely. One of these shapes is called a "boat" conformation. In this conformation, the opposite corners of the cyclohexane ring are pulled up above the plane of the other four carbons, forming the prow and stern of a boat.

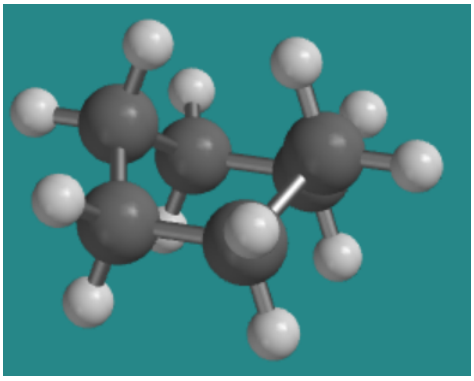


Figure 6.7.1: A highly strained conformation of cyclohexane.

Go to **Animation CA7.1.** A three-dimensional model of cyclohexane, in a strained conformation

The bond angles in the boat are 109 degrees. The boat has no ring strain.

There are torsional strains present along the two sides of the boat, although not at the prow and the stern.

The boat conformation suffers from steric strains. By pulling the carbons at the prow and stern up above the plane of the ring, the attached hydrogens get very close to each other.

In our basis set, this is a six atom interaction. We count the number of atoms to assess the potential steric interaction, we start at one of these crowded hydrogens, go through the first to fourth carbon, and then finish at another crowded hydrogen. That's a total of six atoms including the two atoms that appear to be leaning towards each other, so this is a significant steric interaction. If we then look along one of the sides of the boat in a Newman projection, we find that the stern and prow of the boat actually eclipse each other, so this six atom interaction is pretty strong, about 1.5 kcal/mol.

Add to that the 6 kcal/mol of torsional strain, from three pairs of eclipsed bonds on one side of the boat and three pairs on the other, and there is a total of 7.5 kcal/mol strain energy in the boat conformer of cyclohexane.

In reality, the boat conformation would not occur if there were another conformation significantly lower in energy.

- The boat conformation is an unstable conformation because of both torsional and steric strain.

A second shape is called the chair conformation. In a hand-held model, this shape can be obtained by grasping the prow of the boat and twisting it down below the boat, while keeping the stern in its same position above the boat.

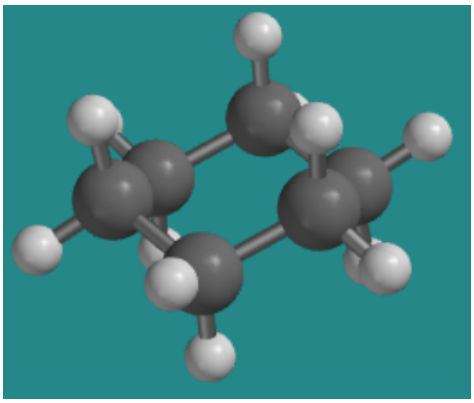


Figure 6.7.2: A low-energy conformer of cyclohexane.

Go to **Animation CA7.2.** A three-dimensional model of cyclohexane in its stable conformer

A thorough investigation of your model will show that there are no longer any torsional strains in this conformation.

There aren't any steric strains, either, because although you can identify pairs of hydrogens that are six atoms apart from each other, these pairs always seem to be pointing well away from each other.

In fact, if the model is viewed from above, so that it looks like a hexagon, six of the hydrogen atoms point directly outward away from the ring; they can't get much further apart than that. These atoms are all called equatorial hydrogens.

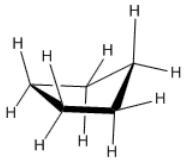
The only atoms that get close to each other at all are the three hydrogens above the ring, which are all roughly in the same area of space, and the three below the ring. These atoms are called axial hydrogens.

The worst steric strain in the chair is the 5-atom interaction between axial hydrogens. In our basis set, this interaction costs 0 kcal/mol. The chair is more stable than the boat by 7.5 kcal/mol.

This conformation of cyclohexane is the preferred conformer.

- Cyclohexane is always found in the chair conformer. This conformer has no torsional or steric strain.

The chair can be shown in a line drawing as shown below. Notice that three hydrogens point up from the chair and three point down. The other hydrogens are pointing outward from the center.



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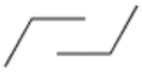
6.8: Diamond Lattice Drawings

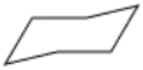
It will be helpful for you to be able to draw cyclohexane in the chair form because it is such a common structural element in natural compounds. Let's look at the way we would most easily draw cyclohexane: it's a six membered ring, a hexagon. Notice that the opposite sides of this ring are parallel. This feature is the key to drawing a chair.

Start by drawing two parallel lines of equal length, one slightly higher than the other and one slightly offset to the side. Most people find it easiest to make this first pair of lines horizontal.

A second pair of parallel lines will connect to these two at an angle, but at opposite ends of the original lines, and going in opposite directions: one upward, one downward.



At one end of the structure, we are beginning to draw the uplifted back of the chair, and at the other end is the downward footrest. Next, bridge the gaps at the two ends of the drawing with another pair of parallel lines.



That's the carbon skeleton of cyclohexane, but for careful conformational analysis we will also need to consider the positions of the hydrogens. Remember that there are three axial hydrogens above the ring and three below. Look at the ring you have drawn: three of the vertices are pointing downward and three are pointing upward. These vertices are pointing the way to the axial hydrogens. Extend these vertices with six parallel lines, three pointing up and three pointing down, from alternating corners.

You have just formed the axial C-H bonds.

Now, the useful thing to know about the drawing is that lines can only be drawn in four different directions. The remaining lines to the equatorial hydrogens will have to be chosen from among these directions. We already have lines in three directions on each carbon; we just need to add a fourth to each. To decide which direction is missing, skip one bond in either direction along the ring and you will find a parallel line.

Finally, remember that the equatorial hydrogens point outward, away from the ring, so keep these lines pointing away from the center of the chair.

This type of drawing is called a diamond lattice drawing, because the all-carbon structure of diamond can be constructed this way by extending the axial and equatorial lines into additional chairs. Diamond lattice drawings can also be used to depict staggered conformations of aliphatic hydrocarbons, but only if you are very careful. Taking a few minutes to practice these drawings now may be helpful before you proceed to the next section.

Exercise 6.8.1

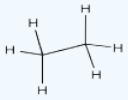
Using the cyclohexane chair as a template, draw diamond lattice representations of the following compounds in staggered conformations. If you have to, draw a whole chair and erase parts until you have only what you need.

a. ethane
b. propane
c. butane in a gauche conformation
d. butane in an anti conformation

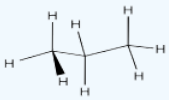
Answer

Template

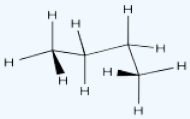
a) Ethane



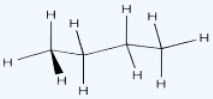
b) Propane



c) Butane in a gauche conformation



d) Butane in an anti conformation



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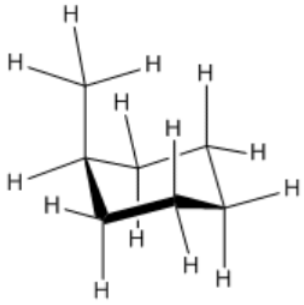
6.9: Substituted Cyclohexanes

Most rings found in nature are part of a larger structure, so understanding the shape of the ring is just the beginning of the question of conformation. How will substituents that are attached to the ring affect the shape? Let's look at substituted cyclohexanes, because they are very common and because their flexibility allows them to adopt very different shapes in order to accommodate attached groups.

Remember that in the chair form of cyclohexane, which has already been established as the most stable conformation by several kcal/mol, there are hydrogens in two distinct positions:

- axial positions
- equatorial positions.

Replacing one of these hydrogens with a methyl group would result in the methyl group sitting in either an axial or equatorial position. Let's assume it's in an axial position, which is above or below the ring rather than out to the sides.



- We know that there is no torsional strain in the chair, and we'll assume that the methyl group can be oriented such that it has no torsional strain either.
- We do need to look for steric strains. You will find that the methyl hydrogens are close to the two axial hydrogens on the same face of the ring. This is a six atom interaction in each case.
- We will assume that the methyl group is rotating freely such that only one of its hydrogens is close enough to these axial neighbors to cause steric strain, but there will be strain with both of those axial hydrogens.
- Sighting along the CH_2--C(H)Me bond on the edge of the ring, you can see that the interaction between the axial methyl and an axial hydrogen resembles the gauche interaction in butane. These two steric interactions will cause an increase in strain energy of about 2 kcal/mol.

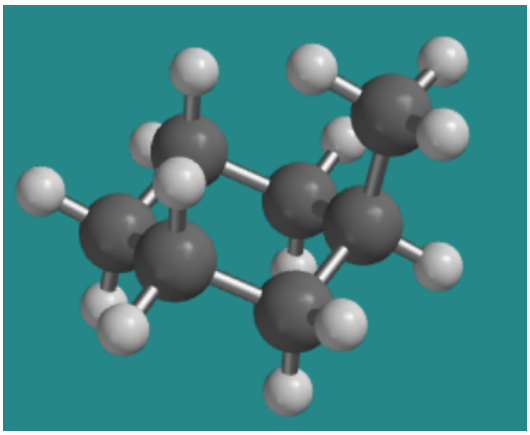


Figure 6.9.1: Methylcyclohexane in an axial methyl conformation.

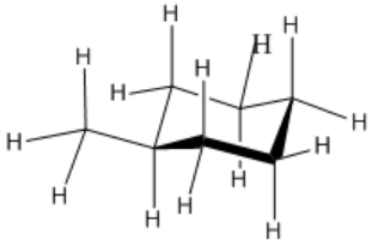
Go to **Animation CA9.1.** A three-dimensional model of methylcyclohexane, in an axial conformation

This chair conformation is undoubtedly somewhat stable; there is much less strain in this compound, for instance, than there was in the boat conformation of cyclohexane. However, it's possible that there is an even more stable conformation, and if so we should be able to find that conformation by twisting around some of the bonds in the molecule.

In cyclohexanes, there are usually two different chair conformations that can be accessed via a "ring flip". To see this, grasp a model of methylcyclohexane and identify two corners at opposite ends of the hexagon (the first and fourth carbons in the ring). One of these corners will be pointing down; push it up. The other corner will be pointing up; push it down. In doing so, all the other corners of the ring will change positions from down to up and from up to down as well, so that you end up with a new chair.

If you carry out a ring flip on methylcyclohexane, you will find that the methyl group moves between an axial position and an equatorial one depending on which form of the chair conformation it begins in. The actual compound can do this pretty easily at room temperature; although these two chairs occupy energy minima, the energy barrier between them is pretty low. It's possible that one of these conformations is a global minimum, however.

Take a look at the new conformation of methylcyclohexane, with the methyl group in an equatorial position.



- There need be no torsional strains.
- The methyl group is not very close to any neighbouring hydrogens. It is 5 atoms away from a couple of the other equatorial hydrogens, but 5 atom interactions are not large enough to worry about.
- As a result, there is no significant strain energy in this conformation. This is the most stable conformer of methylcyclohexane.

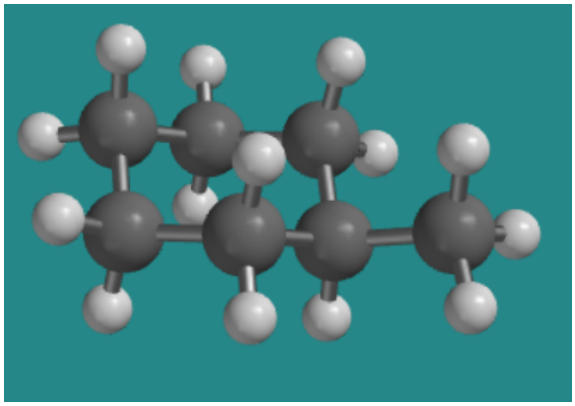


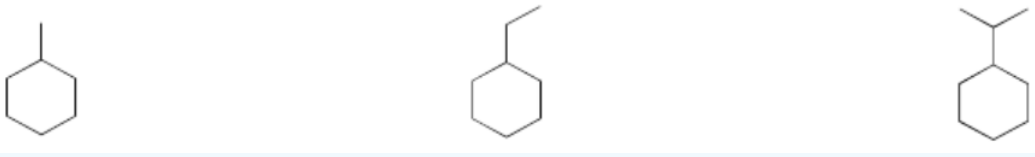
Figure 6.9.2: Methylcyclohexane in an equatorial methyl conformation.

Go to **Animation CA9.2.** A three-dimensional model of methylcyclohexane, in an equatorial conformation

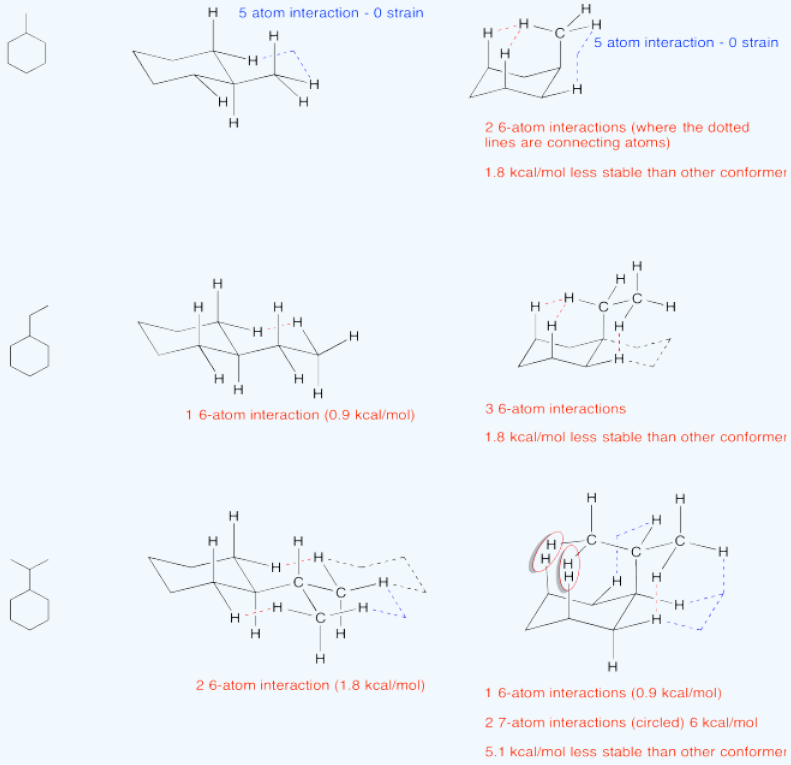
It is usually the case that when substituents are in equatorial positions, the conformation is more stable, for the same reasons that we saw with methylcyclohexane: it is pointing outward, away from the rest of the ring, rather than sharing the space above the ring with other atoms. However, it may not always be possible for substituents to be in that favored position.

Exercise 6.9.1

Practice drawing these monosubstituted cyclohexane structures in the chair forms.
a. Draw the compound on a diamond lattice.
b. Draw the other chair conformation.
c. Find all strain.
d. Determine which conformer is more stable.



Answer



Exercise 6.9.2

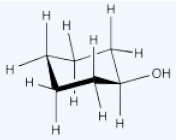
How will other substituents behave in axial vs. equatorial positions? Use a statistical assumption to estimate how much steric strain will be caused by a methyl group vs. an amino, a hydroxyl or a fluoro substituent. Apply your assumption to estimate the energy difference between axial and equatorial conformers of the following compounds:

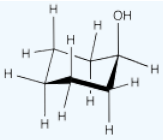
a) cyclohexanol (c-C6H11OH) b) cyclohexylamine (c-C6H11NH2)

c) fluorocyclohexane (c-C6H11F)

Answer

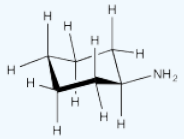
a)

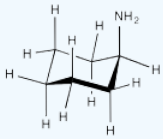




Estimate = (0.33)(2 kcal/mol) = 0.66 kcal/mol

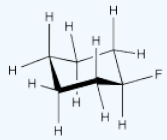
b)

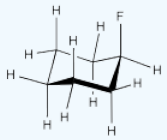




Estimate = (0.66)(2 kcal/mol) = 1.33 kcal/mol

c)

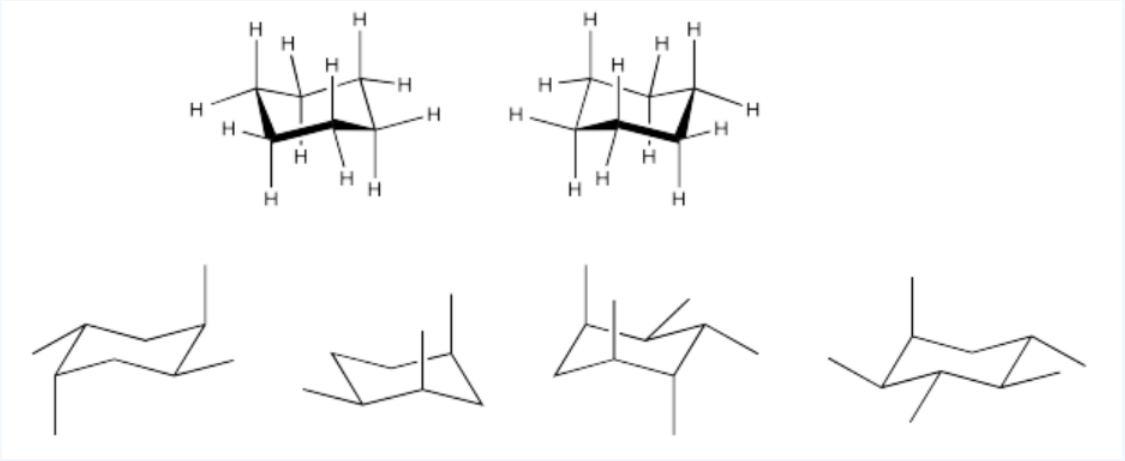




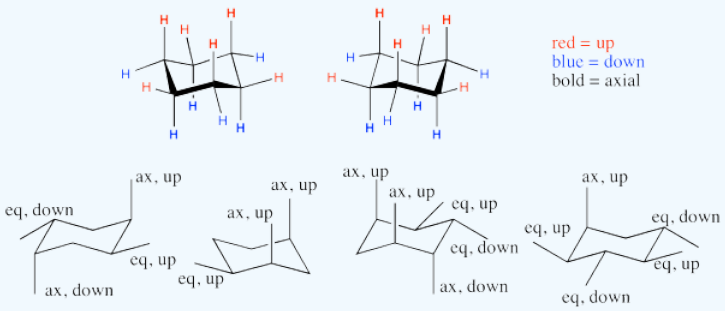
Estimate = 0 kcal/mol

Exercise 6.9.3

Label the substituents as axial or equatorial and as up or down.



Answer



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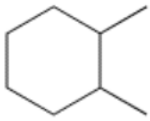
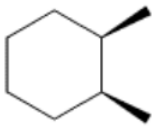
6.10: Disubstituted Cyclohexanes

Take a look at 1,2-dimethylcyclohexane. The two methyl (CH3) groups in this compound are on adjacent carbons.

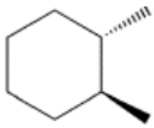


dimethylcyclohexane

There are two ways these methyl groups could be attached to the ring: they can either be on the same face, as they are in the *cis* isomer; or they can be on opposite faces, as they are in the *trans* isomer.



cis-dimethylcyclohexane



trans-dimethylcyclohexane

The difference between these two compounds is pretty clear from a regular hexagon view of the molecule, with wedges and dashes denoting the spatial relationship between the methyl groups. Wedges show things coming towards us, on the near face of the ring, and dashes show things away from us, on the far face of the ring.

The diamond lattice drawing can be a little confusing, in this case.

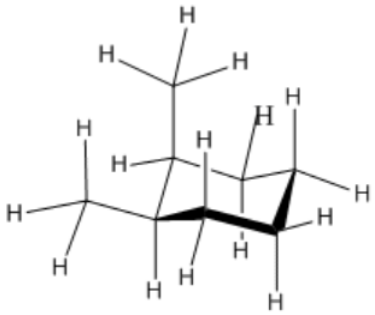


Figure 6.10.1: Line drawing of cis-1,2-dimethylcyclohexane. The methyl groups are both in the upper position of two possible positions.

- Remember that alternating corners of the ring point either up or down, and that each has an attached axial and equatorial position.
- The two methyl groups in cis-1,2-dimethylcyclohexane must occupy the axial position on one carbon and the equatorial position on the next.

That's because on a carbon that occupies a lower corner of the ring, the upper position that a methyl can occupy is equatorial, but for the next carbon, set in an upper corner of the chair, the upper position is an axial one. Viewed from the edge of the chair, two cis methyl groups would both be attached to either the upper face or the lower face of the chair, and so one would be axial and the other equatorial.

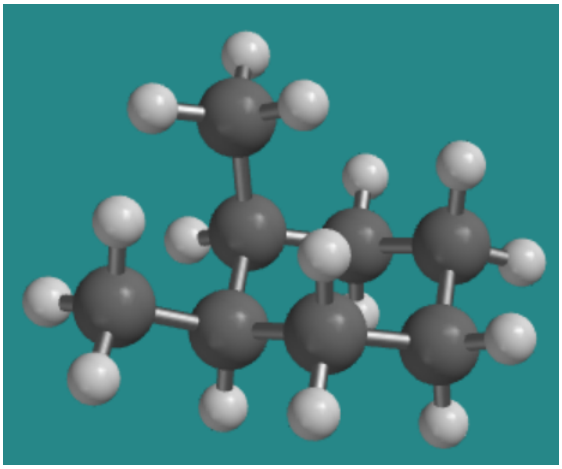


Figure 6.10.2: Ball-and-stick model of *cis*-1,2-dimethylcyclohexane.

Go to **Animation CA10.1.** A three-dimensional model of *cis*-dimethylcyclohexane.

In trans-1,2-dimethylcyclohexane, the two methyl groups would occupy opposite faces of the ring. The easiest way to view this relationship is in a conformation in which the two methyl groups are in axial positions on adjacent carbons, one pointing up and the other down.

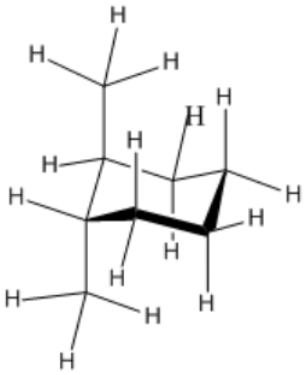


Figure 6.10.3: Line drawing of *trans*-1,2-dimethylcyclohexane. The methyl groups are in the upper and lower positions (one in each). The positions on opposite face are readily apparent.

This view can also be seen in a model.

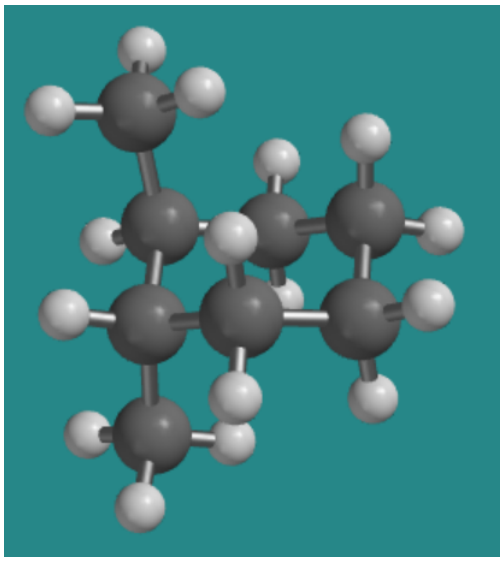


Figure 6.10.4: Ball-and-stick model of *trans*-1,2-dimethylcyclohexane.

Go to **Animation CA10.2.** A three-dimensional model of *trans*-dimethylcyclohexane, in a diaxial conformation.

However, a ring flip converts the same molecule into a different conformer, in which both these groups are equatorial. The methyl groups no longer appear to be trans to each other, but they must be, because we haven't broken any bonds and this is still the same molecule we were looking at in the diaxial conformation.

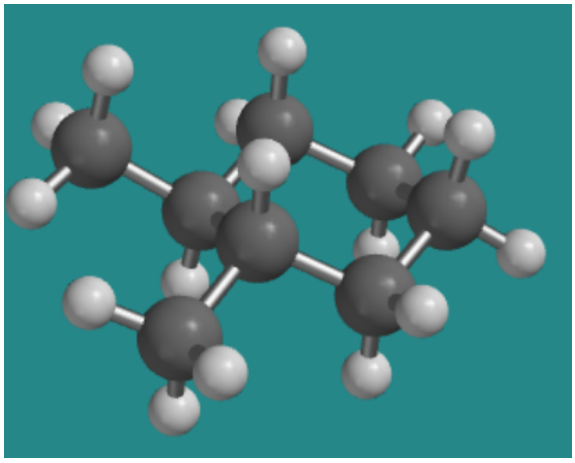


Figure 6.10.5: Ball-and-stick model of *trans*-1,2-dimethylcyclohexane in a diequatorial conformer.

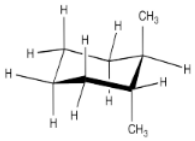
Go to **Animation CA10.3.** A three-dimensional model of *trans*-dimethylcyclohexane, in a diequatorial conformation.

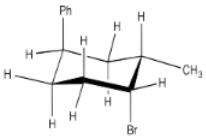
In fact, given the two positions available at each ring carbon, one of the methyls is always in the uppermost position, whether it is in an axial or equatorial orientation, and the other methyl is always in the lowermost position.

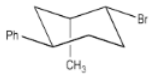
Figure 6.10.6: Line drawing of *trans*-1,2-dimethylcyclohexane in a diequatorial conformer; unlike the usual way of drawing structures, the bonds to the hydrogen atoms are shown. The methyl groups are in the upper and lower positions on their respective carbons (one in each).

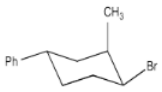
Exercise 6.10.1

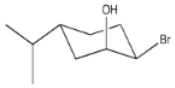
Convert the following chair structures to the wedge-dash projection.











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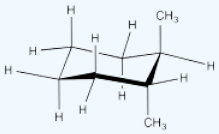

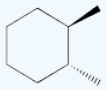

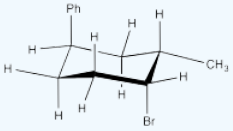

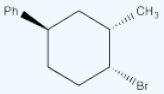

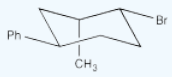

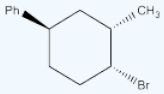

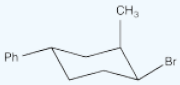

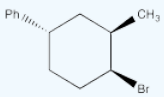

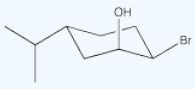

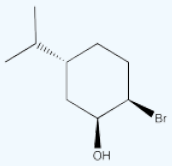

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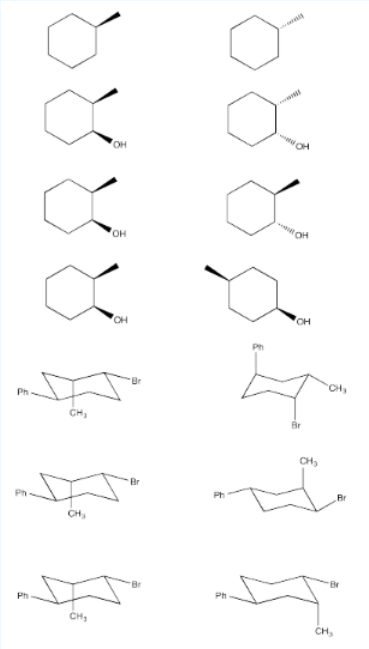
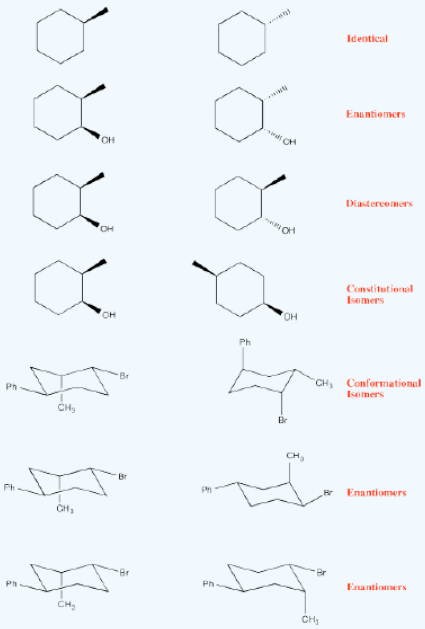
Exercise 6.10.2

Determine the stereochemical relationship between these pairs of compounds.

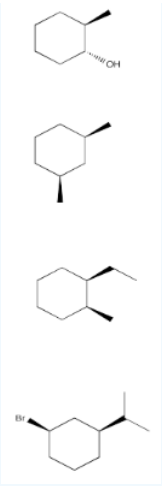


Answer



Exercise 6.10.3

3. For the following the disubstituted cyclohexane rings:
a. Circle all stereocenters and label them with the correct R/S designation.
b. Draw the two chair conformers on the diamond lattice. (Be careful not to draw the enantiomer).



Answer

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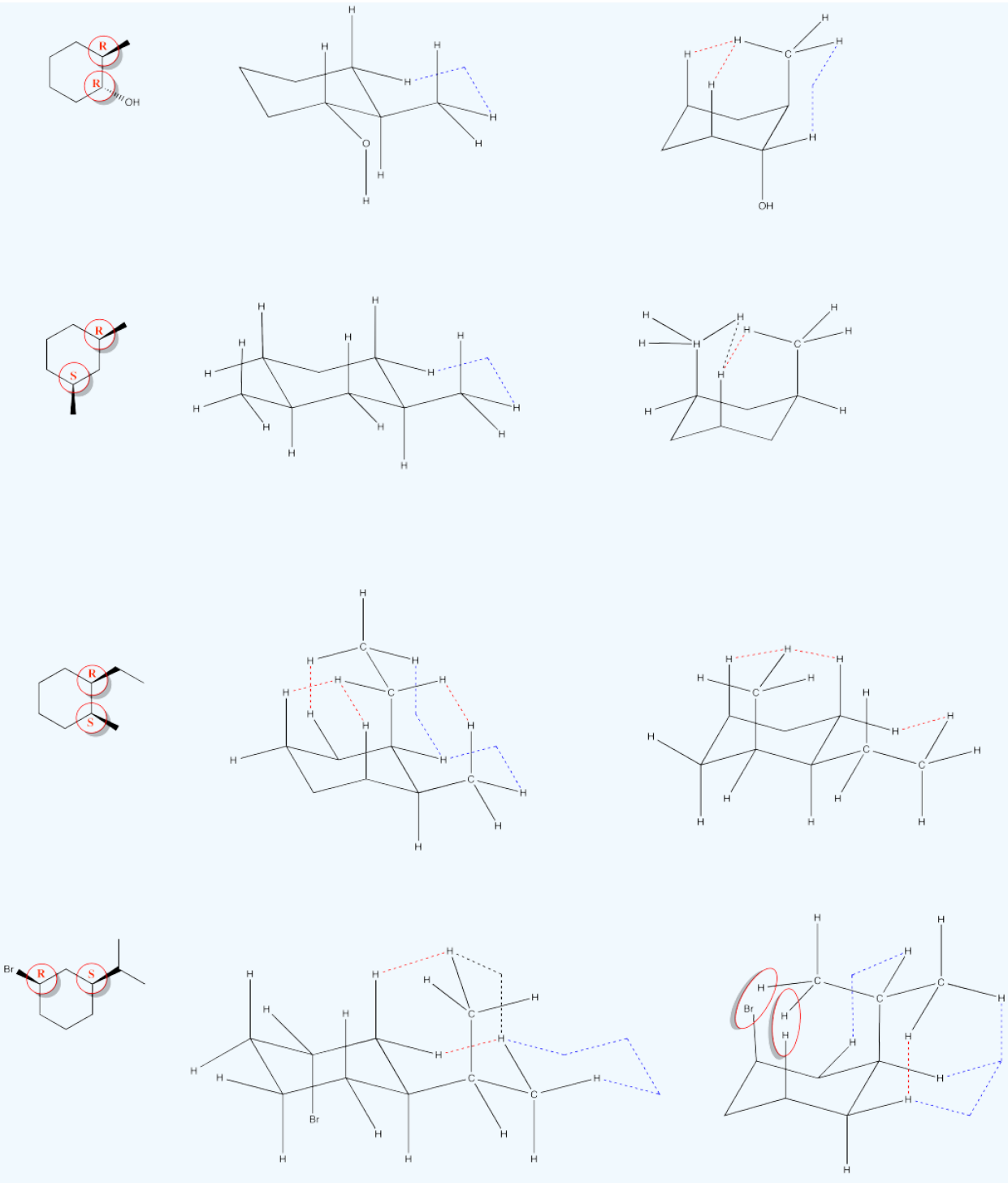

Exercise 6.10.4

Perform an analysis of steric interactions in the chair conformation of *trans*-1,2-dimethylcyclohexane. After a ring flip, perform this analysis again. Compare the energy of the two conformers.

Answer

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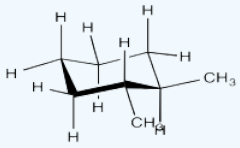
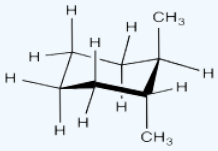
trans-1,2-dimethylcyclohexane



Estimate = 1 kcal/mol



Estimate = 4 kcal/mol

It's tempting when working with models to take a group off and snap it back on somewhere else in order to think about different conformations, but that isn't a good idea. Taking a group off the model requires breaking a bond, and that isn't what happens when molecules convert between conformers. Instead, molecules simply twist into new shapes without breaking any bonds. If you snap pieces on and off your model while trying to evaluate conformations, you may end up with a different isomer altogether; for instance, it would be easy to accidentally convert cis-1,2-dimethylcyclohexane into trans-1.2-dimethylcyclohexane.

Exercise 6.10.5

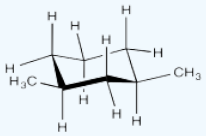
Perform an analysis of steric interactions in the two possible chair conformations of the following compounds.

a) *cis*-1,3-dimethylcyclohexane b) *trans*-1,3-dimethylcyclohexane

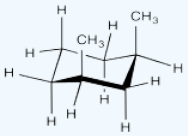
c) *cis*-1,4-dimethylcyclohexane d) *trans*-1,4-dimethylcyclohexane

Answer

a) *cis*-1,3-dimethylcyclohexane

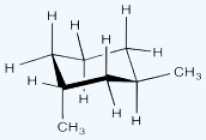


Estimate = 0 kcal/mol

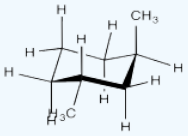


Estimate = 5 kcal/mol

b) *trans*-1,3-dimethylcyclohexane

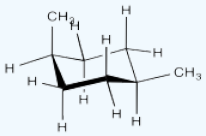


Estimate = 2 kcal/mol

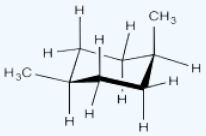


Estimate = 2 kcal/mol

c) *cis*-1,4-dimethylcyclohexane

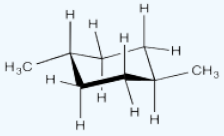


Estimate = 2 kcal/mol

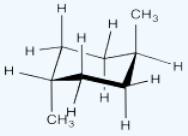


Estimate = 2 kcal/mol

d) *trans*-1,4-dimethylcyclohexane



Estimate = 0 kcal/mol



Estimate = 4 kcal/mol

Still pictures of models obtained using Spartan 14 from Wavefunction, Inc., Irvine, California.

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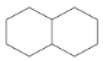
6.11: Other Rings

We have looked at some different six-membered rings, cyclohexanes, and have seen how substituents attached to these rings might influence the shape of the overall molecule. Cyclohexanes are particularly important because of they are quite common in nature. There are other variations of cyclic systems that are worth looking at, including different cyclohexane derivatives and other rings.

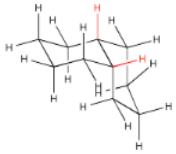
Bicyclics and Other Polycyclics

Decalins are examples of fused ring systems. In fused ring systems, two rings share an edge. Decalins contain ten carbons total, but the ten carbons are divided into two rings, each of which is six carbons around.



decalin

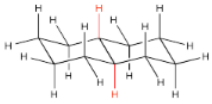
There are two possible isomers of decalin: *cis* and *trans*. The easiest way to distinguish the two isomers is to look for the two hydrogens on the shared edge between the two rings. Those two hydrogens are found on the same face of the *cis* decalin.



cis-decalin

Go to **Animation CA11.1.** A three-dimensional model of *cis*-decalin.

The two hydrogens along the junction are seen on the opposite faces in *trans* decalin.



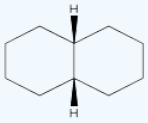
trans-decalin

Go to **Animation CA11.2.** A three-dimensional model of *trans*-decalin.

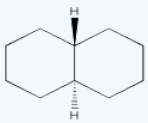
Exercise 6.11.1

Draw cis-decalin and trans-decalin using a wedge/dash picture.

Answer



cis-decalin

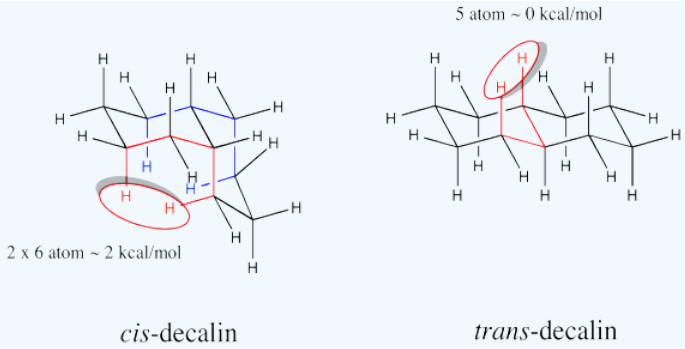


trans-decalin

Exercise 6.11.2

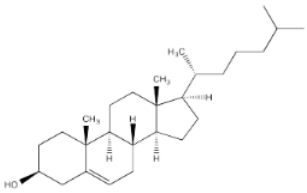
Calculate steric strains in *cis*-decalin and *trans*-decalin.

Answer



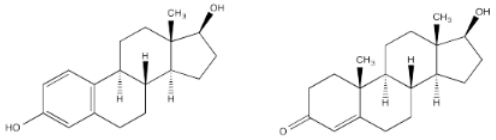
cis-decalin *trans*-decalin

Fused ring systems like decalin are very common. In fact, similar ring systems are found in steroids, which are an important class of lipids. Steroids generally have similar structures that include a series of fused rings as seen in the parent compound, cholesterol.



cholesterol

The similarity is striking between estradiol, a female sex hormone, and testosterone, a male sex hormone.



estradiol testosterone

Go to **Animation CA11.3.** A three-dimensional model of estradiol.

Go to **Animation CA11.4.** A three-dimensional model of testosterone.

Exercise 6.11.3

Consider a steroid structure such as cholesterol.

a. Based on the relationships along the fused edges between the ring, does the structure more closely resemble that of cis-decalin or that of trans-decalin?
b. The overall shape of the structure could probably best be described as (choose one: wide and wavy / compact and curled up / boxy like a cage).

Answer a:

The substituents are always *trans* along the junctions between each pair of rings. The steroids resemble a series of *trans*-decalin structures.

Answer b:

The overall structure would be more wide and wavy like a *trans*-decalin, rather than curled or boxy like a *cis*-decalin.

Polycyclic systems do not have to be fused along one edge like decalin. They can be connected in a variety of ways. Norbornane is an example of a bicyclic system in which the two rings actually share more than two carbons.

norbornane
bicyclo[2.2.1]heptane

Norbornane can be used to illustrate the systematic way to describe fused ring systems. The suffix describes the total number of carbons in the ring system. The prefix describes how many rings are fused together. The middle part, in brackets, indicates how many atoms form the "bridges" between the "bridgehead" atoms, where the system splits off into two different rings. One number is given to describe each bridge. In norbornane, there are two 2-carbon bridges and a single 1-carbon bridge.

Exercise 6.11.4

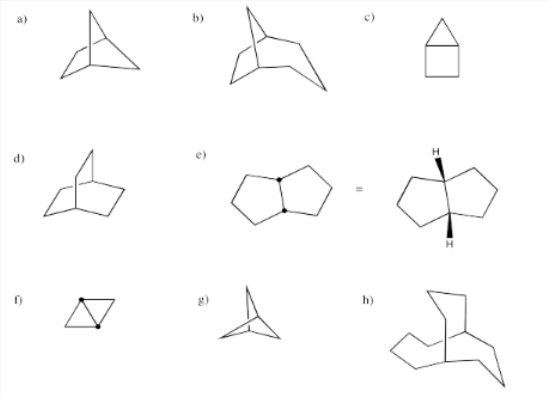
Write a systematic name for decalin.

Answer

Bicyclo[2.2.0]decane

Exercise 6.11.5

Provide systematic names for the following structures.



Answer a:

Bicyclo[2.1.1]hexane

Answer b:

Bicyclo[3.2.1]octane

Answer c:

Bicyclo[2.1.0]pentane (more commonly called "housane")

Answer d:

Bicyclo[2.2.2]octane

Answer e:

cis-Bicyclo[3.3.0]octane

Answer f:

cis-Bicyclo[1.1.0]butane

Answer g:

Bicyclo[1.1.1]pentane

Answer h:

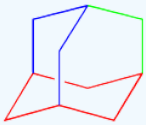
Bicyclo[4.3.3]dodecane

Exercise 6.11.6

How many different rings can you trace in the structure of adamantane?

adamantane

Answer

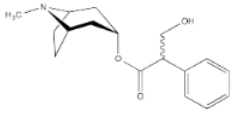


Although we could sketch out many rings using adamantane, just three rings are needed to include all the carbon atoms in the structure. Thus, adamantane is considered a tricyclic system. The systematic nomenclature of tricyclic systems gets a little more complicated, so we won't worry about that.

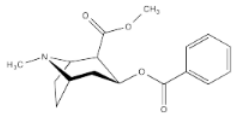
Bicyclic systems are common in nature. For example, the tropane alkaloids all contain a bicyclo[3.2.1] ring system. Alkaloids are a group of natural products that contain basic nitrogen atoms. The tropane alkaloids contain this nitrogen atom in the 1-atom bridge. Tropinone is a simple example.

tropinone

Common examples of natural products containing the tropinone structure include atropine and cocaine. Atropine, derived from deadly nightshade or belladonna, is a heart medication; it is used to increase heart rate if the rate gets too low. Atropine can also be fatal if used incorrectly, causing a wide range of physiological effects; in some dosages, it can even *decrease* the heart rate. Cocaine, of course, is a narcotic and a controlled substance.



atropine



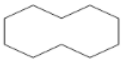
cocaine

These compounds have a special place in the history of organic and medicinal chemistry. During World War I there was a shortage of atropine, prompting Sir Robert Robinson to develop an efficient synthesis of tropinone as an inexpensive source of synthetic atropine.

Larger Rings

Larger rings of carbon atoms are possible, although they are not as common as five- and six-membered rings. Ring formation is thought to be easiest from a six-carbon chain, because the two ends of the chain can easily wrap around to connect together yet they are not so distant that such an encounter becomes unlikely.

Intermediate-sized rings, such as cyclodecane, become distorted to avoid steric interactions. Internal steric interactions are an added complication in the formation of some rings.



cyclodecane

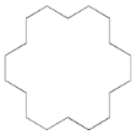
Exercise 6.11.7

Show the steric interactions within cyclodecane.

Answer

If cyclodecane adopted a regular diamond lattice conformation, there would be a whopping 8 atom interaction in the middle of the ring. That interaction isn't even included in our basis set. It would cost at least 6-7 kcal/mol. As a result, the cyclodecane adopts a twisted structure to avoid this interaction.

At some point, in very large rings, steric problems are not as severe. The hydrogens on the inside of the ring may be far enough away from each other to avoid interactions. Cyclooctadecane is an example of such a ring. Although interior 6-atom interactions are possible, the ring is flexible enough to twist in such a way as to avoid these problems.



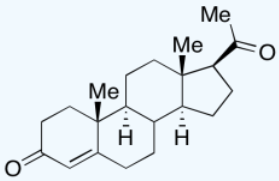
cyclooctadecane

Exercise 6.11.8

Look at the model for progesterone and make a line drawing of it.

Go to Animation CA11.5. A three-dimensional model of progesterone.

Answer

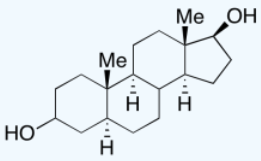


Exercise 6.11.9

Look at the model for androstanediol and make a line drawing of it.

Go to Animation CA11.6. A three-dimensional model of androstanediol.

Answer



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6.12: Rings with Heteroatoms

Rings often contain atoms other than carbon. In many cases, the same basic shape of the carbocyclic compound is still adopted. For example, replacing a carbon of cyclohexane with an oxygen, as in tetrahydropyran, preserves the same basic chair shape.

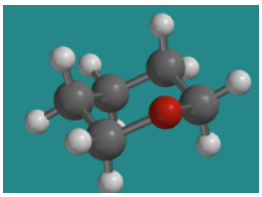


Figure 6.12.1: Ball-and-stick model of tetrahydropyran. Note the similarity to a cyclohexane structure.

Go to **Animation CA12.1.** A three-dimensional model of tetrahydropyran.

The tetrahydropyran structure is common in nature, showing up most frequently in the form of sugars such as glucose. Glucose has a number of different forms that exist in equilibrium. The predominant form in aqueous solution is β-D-glucopyranose.

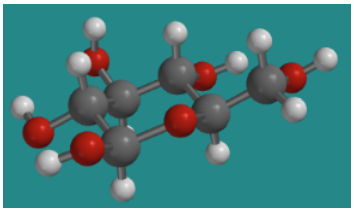


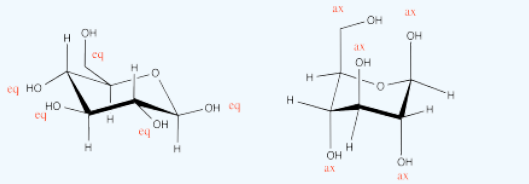
Figure 6.12.2: Ball-and-stick model of β-D-glucopyranose. Note the tetrahydropyran substructure.

Go to **Animation CA12.2.** A three-dimensional model of β-D-glucopyranose.

Exercise 6.12.1

Draw β-D-glucopyranose in a chair. Label each substituent axial or equatorial. Perform a ring flip and compare steric strain in the two conformers.

Answer



One of the other isomers in equilibrium with β-D-glucopyranose in solution is α-D-glucopyranose. The two isomers are almost identical to each other, except one hydroxyl group is pointing a different direction.

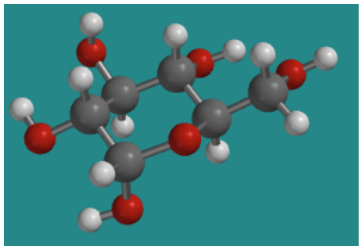


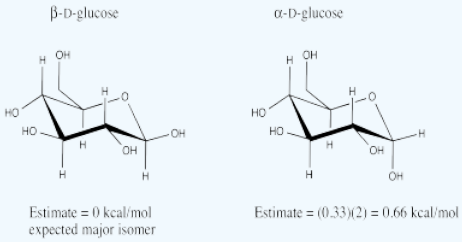
Figure 6.12.3: Ball-and-stick model of α-D-glucopyranose.

Go to **Animation CA12.3.** A three-dimensional model of α-D-glucopyranose.

Exercise 6.12.2

Compare steric strain in the two glocopyranose isomers. Which isomer should be the major one?

Answer



We can isolate that core tetrahydropyran structure of the sugar again, bringing with it the one hydroxyl group that differs between the two glucose isomers. In one of the glucose isomers, the hydroxyl group is in an axial position, as it is in this axial conformation of 1-hydroxytetrahydropyran.

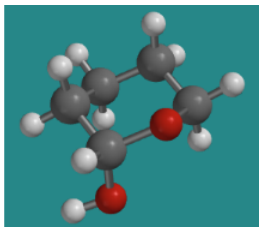


Figure 6.12.4: Axial conformer of 1-hydroxytetrahydropyran.

Go to **Animation CA12.4.** A three-dimensional model of 1-hydroxytetrahydropyran.

In the other glucose isomer, the hydroxy group is in an equatorial position, as it is in this equatorial conformation of 1-hydroxytetrahydropyran.

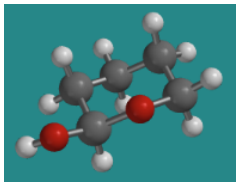


Figure 6.12.5: Equatorial conformer of 1-hydroxytetrahydropyran.

Go to **Animation CA12.5.** A three-dimensional model of 1-hydroxytetrahydropyran.

Exercise 6.12.3

An unusual effect is seen in cases in which an oxygen in a ring is attached to a carbon that also holds an OH group (see drawings above). This O-C-OH group is called a hemiacetal. In a six membered ring, the hemiacetal could be found in two different isomeric positions. In sugars, these are called alpha and beta positions.

a) Based on steric considerations, which of these two isomers should be more stable?

b) These two isomers exist in equilibrium with each other. Which isomer should be the major species present?

c) In solvents of modest polarity, such as dichloromethane, a factor other than sterics actually reverses this equilibrium; the sterically disfavored compound becomes more stable. What factor do you think is responsible for this phenomenon?

d) In solvents of high polarity, such as water, the factor in question (c) becomes less important, and sterics dominate the equilibrium. Why would a highly polar environment diminish the effect discussed in part (c)?

Answer a:

The β-D-glucose isomer should be the more stable isomer. The β-D-glucose isomer places the C1 hydroxyl group in the equatorial position.

Answer b:

The β-D-glucose isomer should be the more abundant isomer.

Answer c:

This is due to something called the anomeric effect. In solvents of modest polarity, such as dicholoromethane, the α-D-glucose isomer is not as polar as the β-D-glucose isomer. In the α-D-glucose isomer the dipoles of the ring oxygen and the C1 hydroxyl group opposing each other (therefore the overall effect is the molecule is less polar). In addition, the α-D-glucose isomer is stabilized by hyper conjugation of the ring oxygen and C1. For more information see http://en.Wikipedia.org/wiki/Anomeric_effect

Answer d:

A more polar environment would promote having more of the β-D-glucose isomer around. In the β-D-glucose isomer, the dipoles of the ring oxygen and the C1 hydroxyl group align each other (therefore the overall effect is the molecule is more polar).

Inflexible Rings

Many rings do not undergo conformational changes because they are not very flexible. Frequently these rings contain a number of double bonds; remember that rotation is not allowed around a double bond because the bond would break.

For example, cyclohexane is a six-membered carbon ring that has a chair structure. It is flexible and can undergo conformational changes. Benzene is also a six-membered carbon ring, but it does not have a chair structure. It is flat and rigid. It cannot undergo conformational changes, because none of its C-C bonds can rotate.

- Benzene does not undergo conformational changes because of delocalized bonding around the ring.
- This aromatic ring is completely flat, maximizing interaction between the p bonding orbitals.

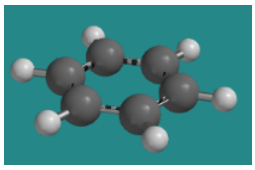


Figure 6.12.6: Ball-and-stick model of benzene.

Go to **Animation CA12.6.** A three-dimensional model of benzene.

Other rings also display aromatic delocalization in which heteroatoms also participate. In some cases, the heteroatom simply participates in a regular double bond. In others, the heteroatom donates a lone pair into the π system.

Furan is an example in which a lone pair from the oxygen is delocalized in order to reach aromatic stability.

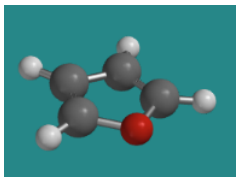


Figure 6.12.7: Ball-and-stick model of furan.

Go to **Animation CA12.7.** A three-dimensional model of furan.

Pyridine is an example in which the ring has aromatic delocalization, but the lone pair on the nitrogen does not participate. Because the nitrogen already has a p bond, the lone pair is orthogonal to that bond, and lies in the plane of the ring.

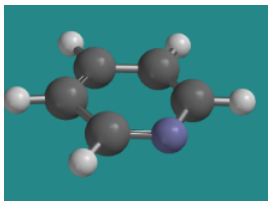


Figure 6.12.8: Ball-and-stick model of pyridine

Go to **Animation CA12.8.** A three-dimensional model of pyridine.

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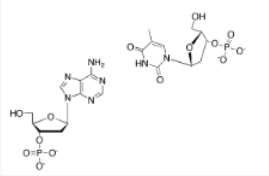
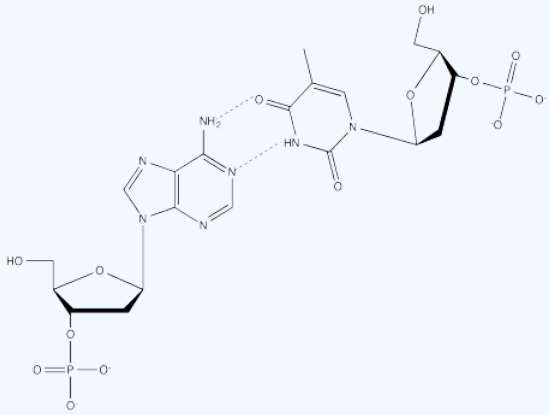
6.13: More Practice with Conformation

Exercise 6.13.1

Hydrogen bonding can have a strong influence on molecular shape. For example, it is a key factor in determining the shape of DNA. In DNA, "base pairs" in adjacent strands of DNA hydrogen bond to each other. Show how adenine and thymine, shown in the following drawing, hydrogen bond to each other.

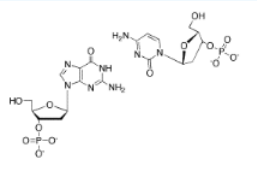


Answer

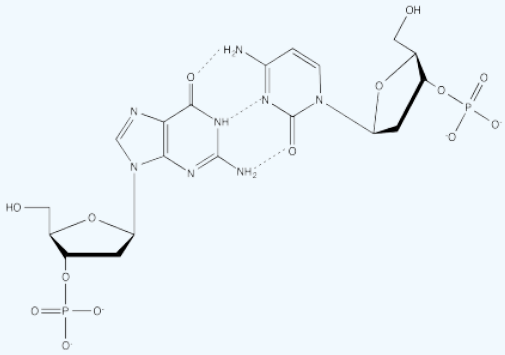


Exercise 6.13.2

Show how cytosine and guanine, shown in the following drawing, hydrogen bond to each other.

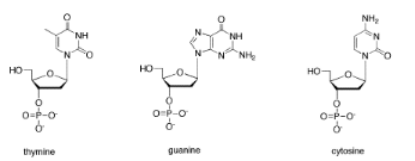


Answer

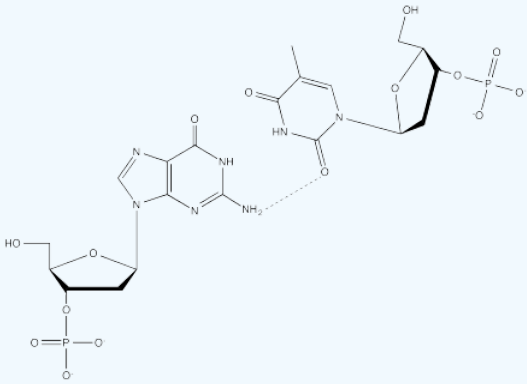


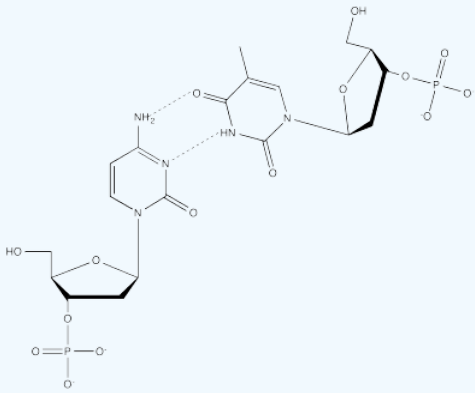
Exercise 6.13.3

Show why thymine is not well-suited to hydrogen bond to cytosine and guanine.



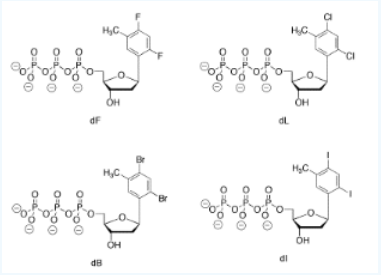
Answer





Exercise 6.13.4

Eric Kool at Stanford University has used "designer nucleotides" to study DNA polymerase and DNA repair mechanisms. He has been particularly interested in how sterics and hydrogen bonding affect these functions. The following set of nuleotides were designed to mimic a natural nucleotide. Perhaps surprisingly, these nucleotides are acceptable substrates as far as DNA polymerase is concerned, and they can be incorporated into the "correct" position in DNA.



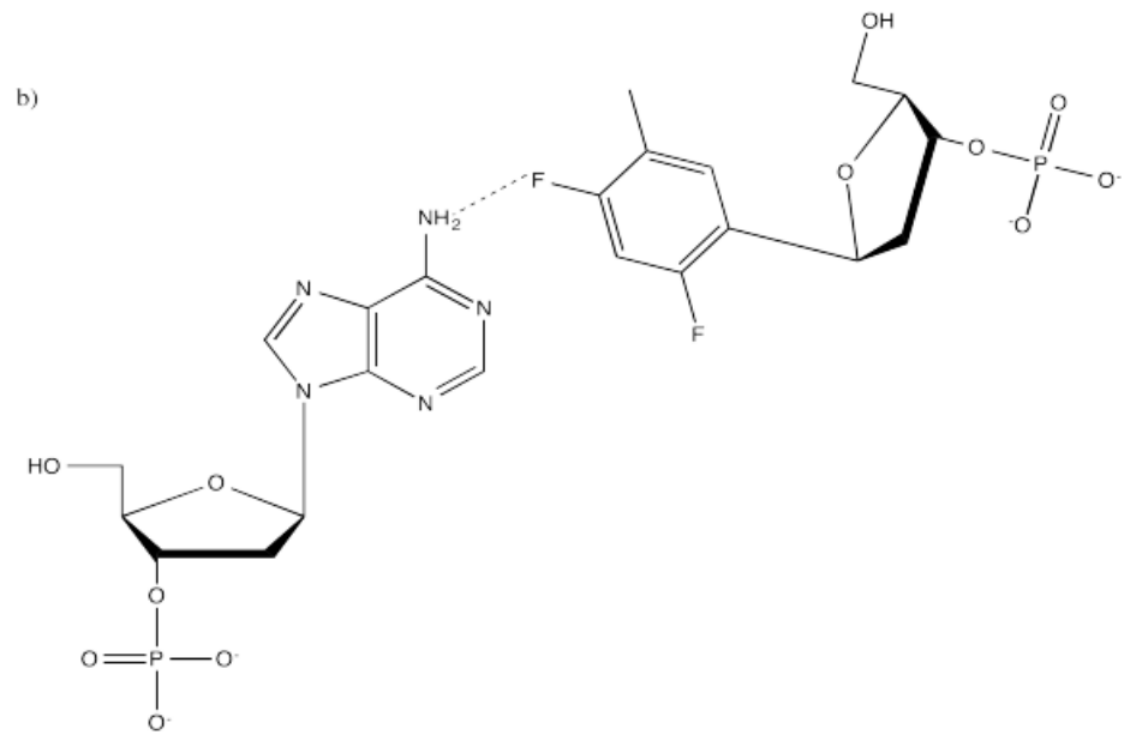
a. Which natural nucleotide do these designer molecules resemble most closely in shape?
b. Show how the designer nucleotide, dF, would fit together with the correct base pair partner for that natural nucleotide.

c. Compare and contrast these nucleotides with the natural one, in terms of their ability to hydrogen bond with the correct "base pair partner".
d. Compare and contrast these nucleotides with the natural one, in terms of their ability to fit together with the correct "base pair partner" in a DNA molecule.

Answer a:

Thymine 5'-triphosphate

Answer b:



Answer c:

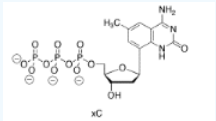
dF is only able to hydrogen bond with adinine in one position while thymine can hydrogen at two positions with thymine.

Answer d:

dF is similar in size and electronic nature to thymine. The fluorine groups on dF are somewhat smaller than oxygen on thymine, but present a comprable polar group that is able to act as a hydrogen bond acceptor. dF lacks the hydrogen bond donating ability as seen in thymine.

Exercise 6.13.5

Another one of Kool's "designer nucleotides" is shown below.

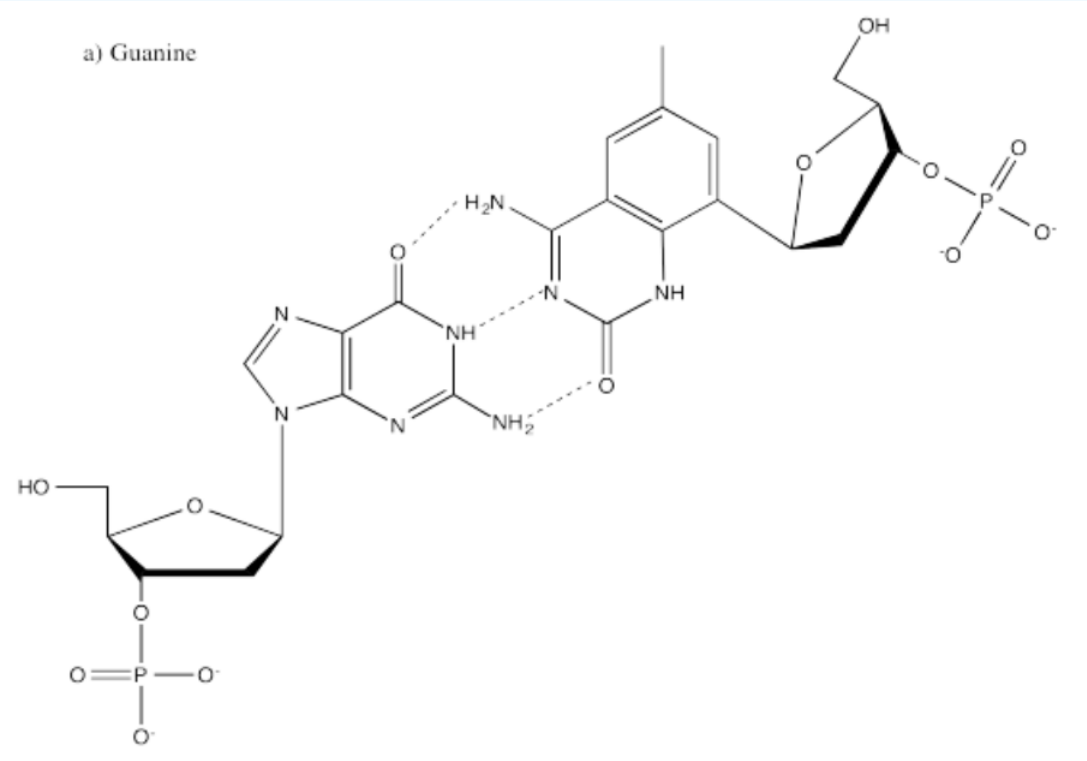


a) Which natural nucleotide would xC interact with most strongly? Show the interaction.

b) Compare and contrast xC with its natural analog, in terms of their ability to hydrogen bond with the correct "base pair partner".

c) Compare and contrast xC with its natural analog, in terms of their ability to fit together with the correct "base pair partner" in a DNA molecule.

Answer a:



Answer b:

xC is similar to cytosine. Both molecules present hydrogen bond donors and acceptors in the same positions.

Answer c:

While xC is similar to cytosine in terms of placement of hydrogen bond donors and acceptors, the additional ring creates steric problems in that the hydrogen bond donors and acceptors are placed too close to the correct "base pair partner".

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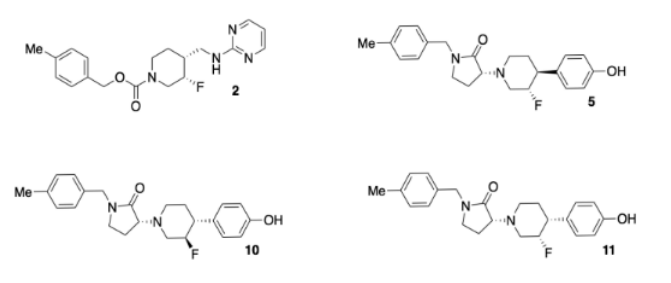
6.14: Application Problems

Exercise 6.14.1

Researchers at Bristol-Myers-Squibb developed a new antidepressant (compound **2**, below). The drug binds to GluN2B receptors, shutting down a central nervous system signal that has been linked to depression. Unfortunately, heart problems appeared as a side effect of the medication; the drug also binds to hERG receptors, interfering with potassium ion channels that are important for heart function.



The team designed a new set of compounds (including **5**, **10**, **11**, above. Adapted with permission from Lawrence R. Marcin, Jayakumar Warrier, Srinivasan Thangathirupathy, *et al*, *ACS Med. Chem. Lett*. **2018**, *9*, 472−477. Copyright 2018 American Chemical Society. Used with permission.).

They wanted to make sure the new compounds would still fit tightly in the GluN2B receptor, which is about 9-11 Ångstroms long.

a. On compound **5**, circle bonds that run roughly parallel to the length of the molecule (i.e. left-right; don't circle any that are more up-down).
b. Count up the number of these in a row. If each one is about 1 Å long, estimate the length of the molecule.
c. The functional groups are also important because they control interactions with the receptor. On compound **10**, circle and name four of the functional groups. Place an asterisk beside any functional groups found in both compounds **2** and **10**.
d. What other factor are the researchers clearly looking at between compounds **5**, **10**, **11**? Why would the researchers be interested in that factor?
e. State the relationships between compounds **5**, **10**, **11**.
f. Find three chiral centers in compound **10**. Draw enough of the structure around each chiral center to make it obvious which one you are considering. Rank the priority of the substituents. Assign the configuration (*R* or *S*) to each center.
g. Researchers added an extra ring in the new compounds. Circle the new ring in compound **10** that has no equivalent in compound **2**.
h. They incorporated this ring because were interested in adding "conformational rigidity". To illustrate this idea, draw a Newman projection looking down

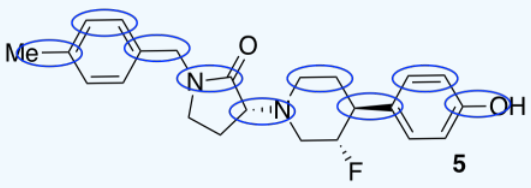
   i) the middle bond of butane ii) any bond of cyclobutane

   Explain why a ring introduces "conformational rigidity" or "conformational restrictions".

i. Why were the researchers interested in adding conformational rigidity?
j. Only one of the rings in compound **5** can adopt chair conformations (the others are flat). Draw the two possible chairs. Asses steric strains in each conformer. Indicate which conformer is more stable.

Compound **5** was the most promising candidate; it required the lowest dose for GluN2B but the highest dose to bind hERG.

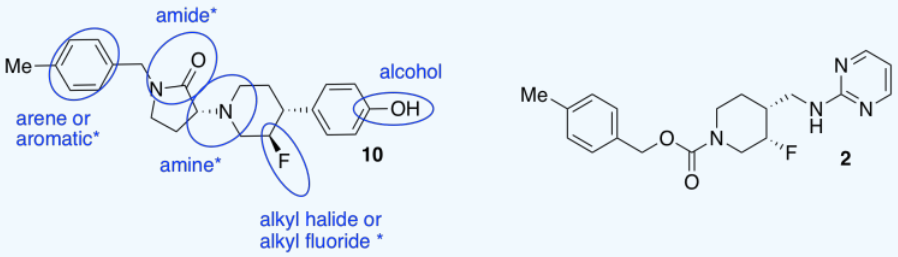
Answer a:



Answer b:

about 9 Å

Answer c:



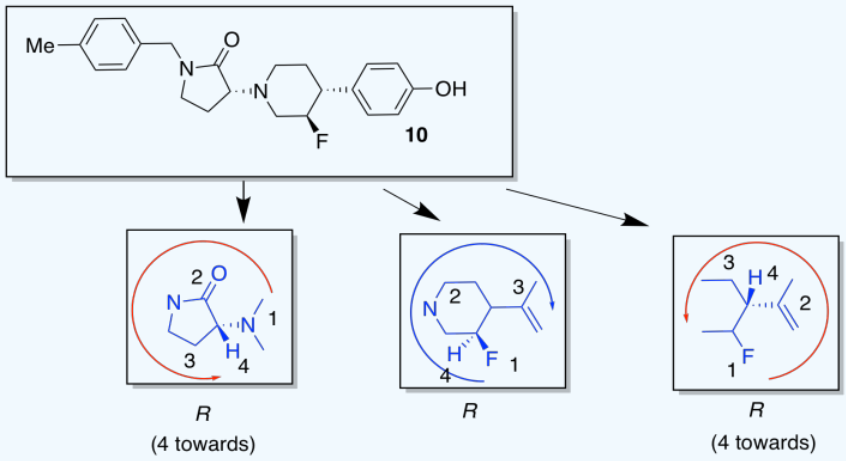
Answer d:

Stereochemistry. Because biological receptors are generally proteins containing unique, and chiral, binding sites, they hope to find a stereoisomer that fits the GluN2B receptor, but not the hERG receptor.

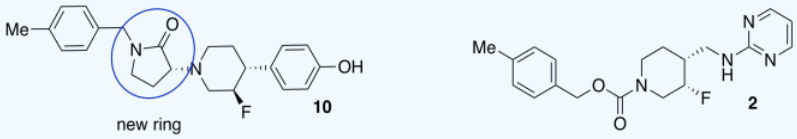
Answer e:

These compounds are diastereomers of each other.

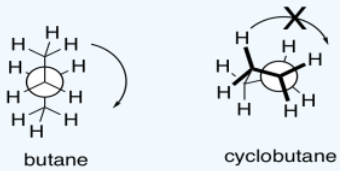
Answer f:



Answer g:



Answer h:



The ring introduces conformational rigidity by preventing the bond from undergoing complete rotation; it is tied back by the connection on the other side of the ring.

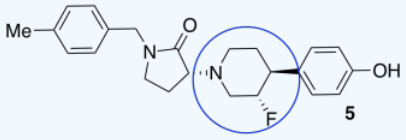
Answer i:

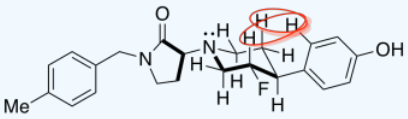
They were trying to decrease the number of possible conformations, or shapes, that the compound could adopt. That way, it would be less likely to bind in both the GluN2B receptor and the hERG receptor.

Answer j:

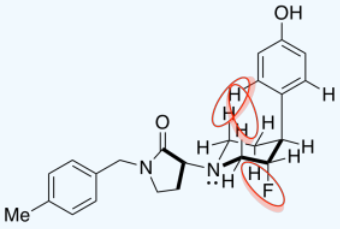
The substituents around the flexible six-membered ring could adopt a number of conformations. We will choose ways that minimize additional steric interactions so that we can focus on the most basic interactions.

Note that amines do not usually have fixed stereochemistry; the fourth substituent on an amine nitrogen is a lone pair, which does not occupy a fixed position in space. Unlike a carbon, the nitrogen can readily switch from one stereochemistry to another.





2 x 6-atom = 2 x 1 = 2 kcal/mol

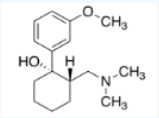


2 x 7-atom + 1 x 6-atom = 2(3) + 1 = 7 kcal/mol

The one on the left, with more equatorial substituents and thus fewer steric interactions, is the more stable one.

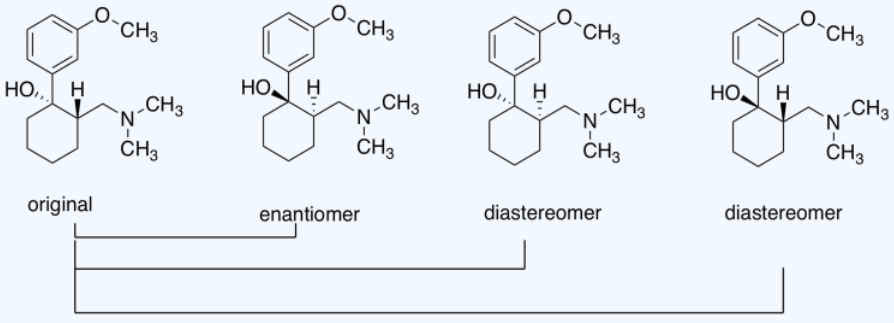
Exercise 6.14.2: Tramadol

Tramadol (below) is an opioid analgesic. It is used to treat chronic pain. It is administered as a racemic mixture; each compound targets a different pain receptor.



a. Draw the enantiomer and any diastereomer(s) of the molecule shown. Label the configurations at the chiral centers.
b. If the original molecule is part of the therapeutic tramadol mixture, which other compound is also administered?
c. The original compound contains a ring that could adopt different chair conformers. Draw both conformers and assess steric strain in each.
d. Which conformer is the more stable one?
e. The most stable conformer is not necessarily the medicinally active one. How would dosage need to be adjusted if the least stable conformer were actually the active form?

Answer a:



Answer b:

The original and its enantiomer; the first two above, from the left.

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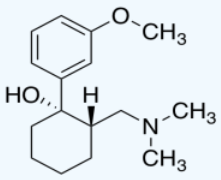
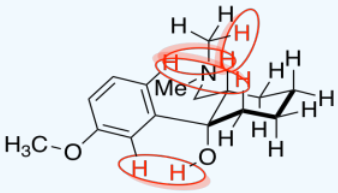
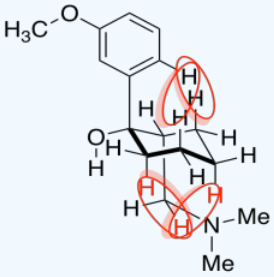
Answer c:





4 x 6-atom = 4 kcal/mol



2 x 7-atom + 2 x 6-atom =
2(3) + 2(1) = 8 kcal/mol

Answer d:

The one on the left, with both groups equatorial and less steric strain, is more stable.

Answer e:

If the one on the left is active, a lower dose can be used because it will spend more time in the active form and be able to bond more receptors. If the less stable one, on the right, is the active form, a higher dose will be needed because only a small fraction of the molecules will be ready to bind the receptor at any given time.

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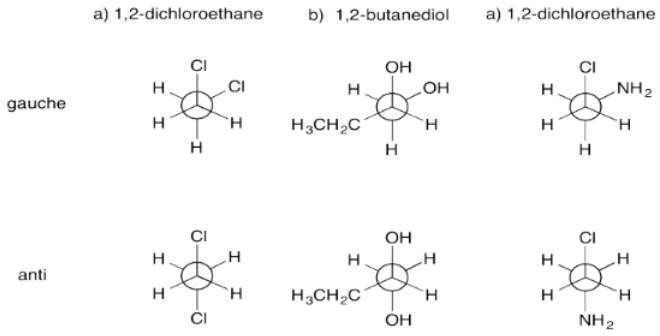
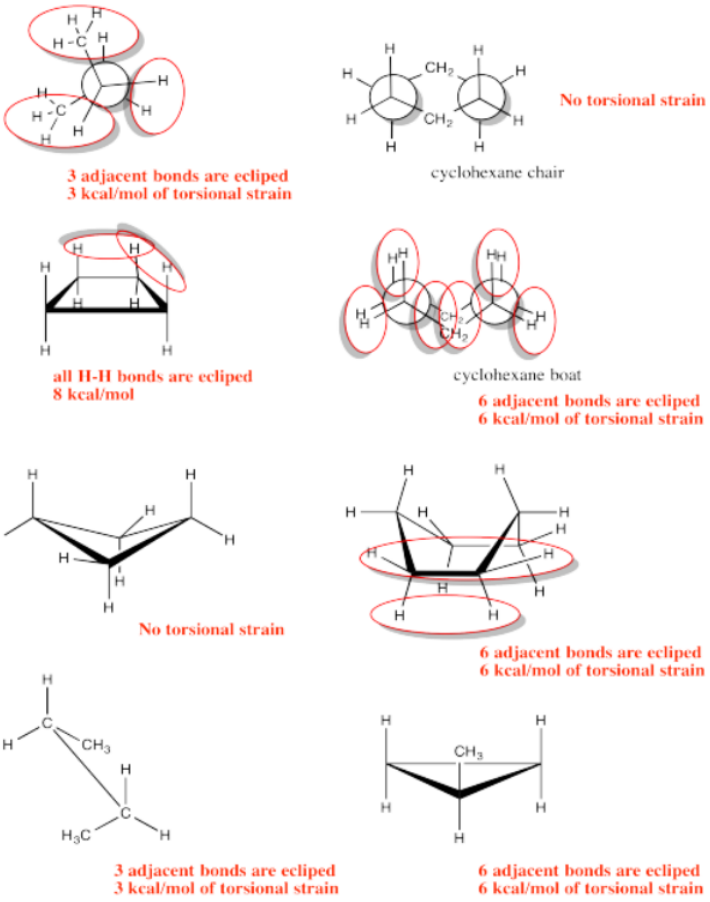
6.15: Solutions to Selected Problems

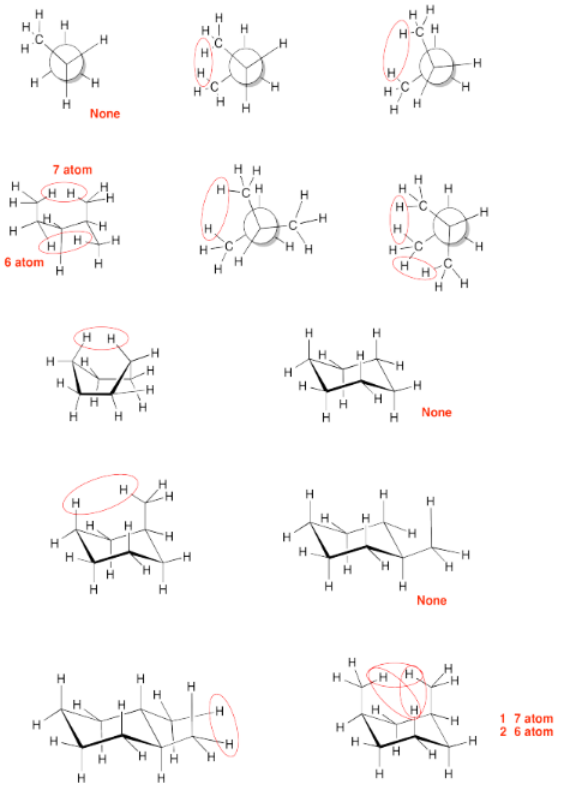
Exercise 6.3.1:



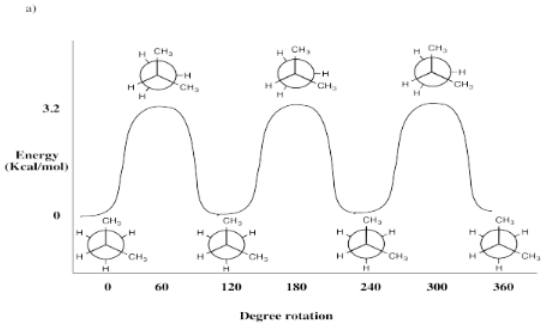
Exercise 6.4.1:



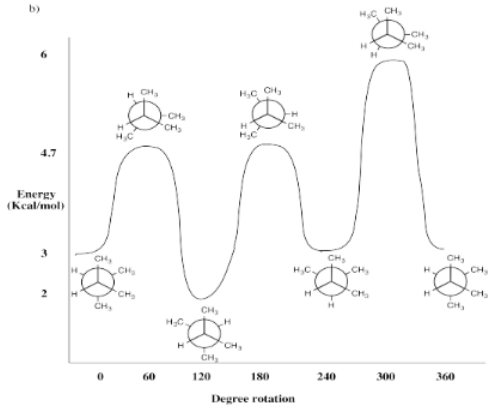
Exercise 6.4.2:



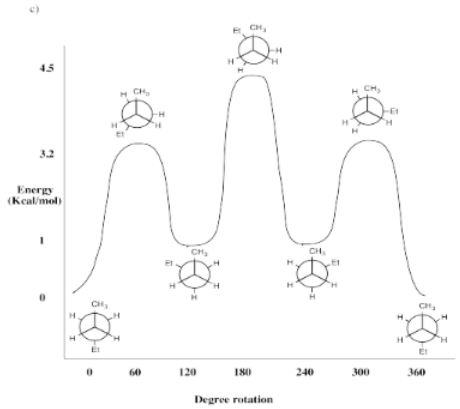
Exercise 6.4.3a:



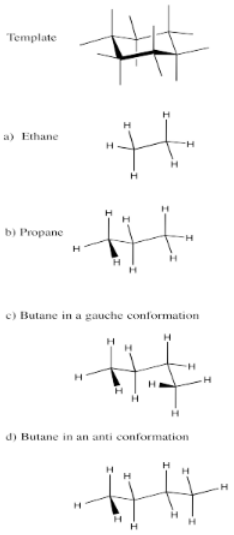
Exercise 6.4.3b:



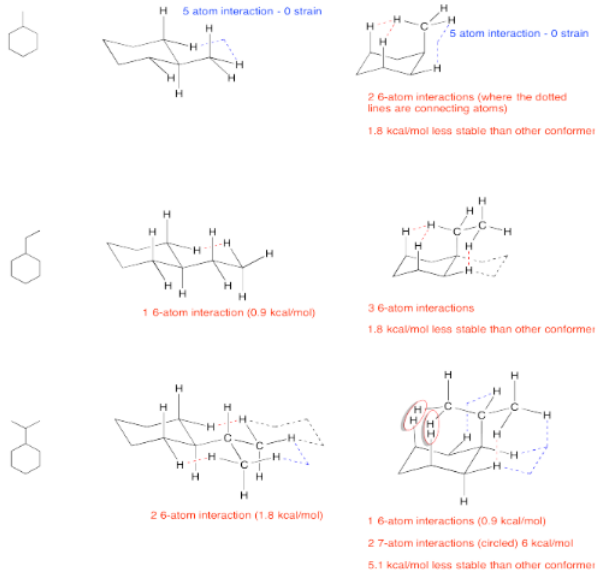
Exercise 6.4.3c:



Exercise 6.8.1:



Exercise 6.9.1



Exercise 6.9.2:

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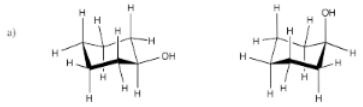
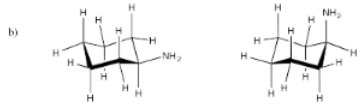
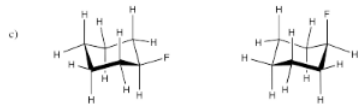


Estimate = (0.33)(2 kcal/mol) = 0.66 kcal/mol

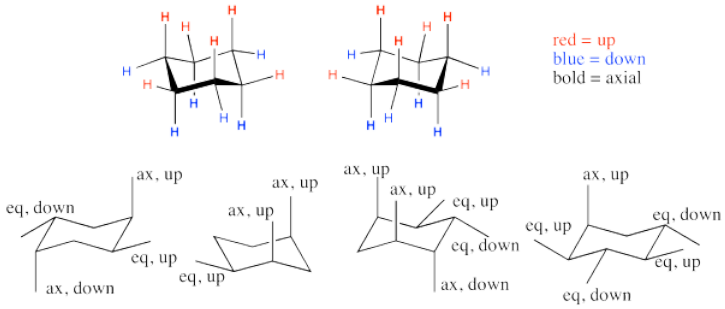


Estimate = (0.66)(2 kcal/mol) = 1.33 kcal/mol

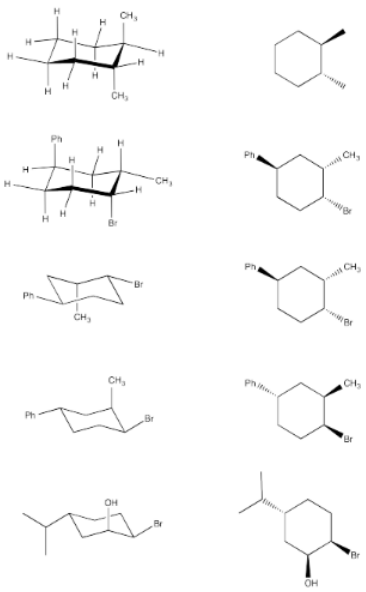


Estimate = 0 kcal/mol

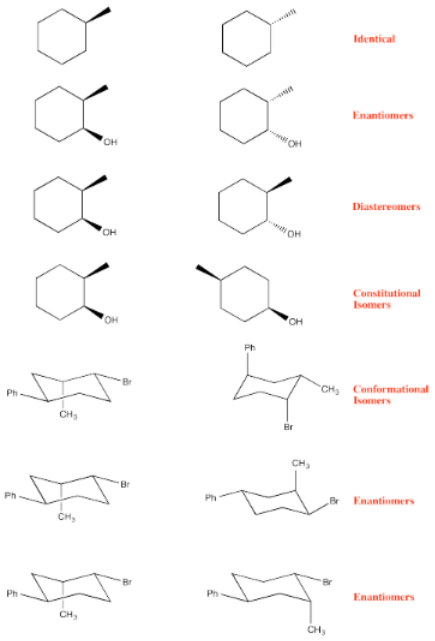
Exercise 6.9.3:



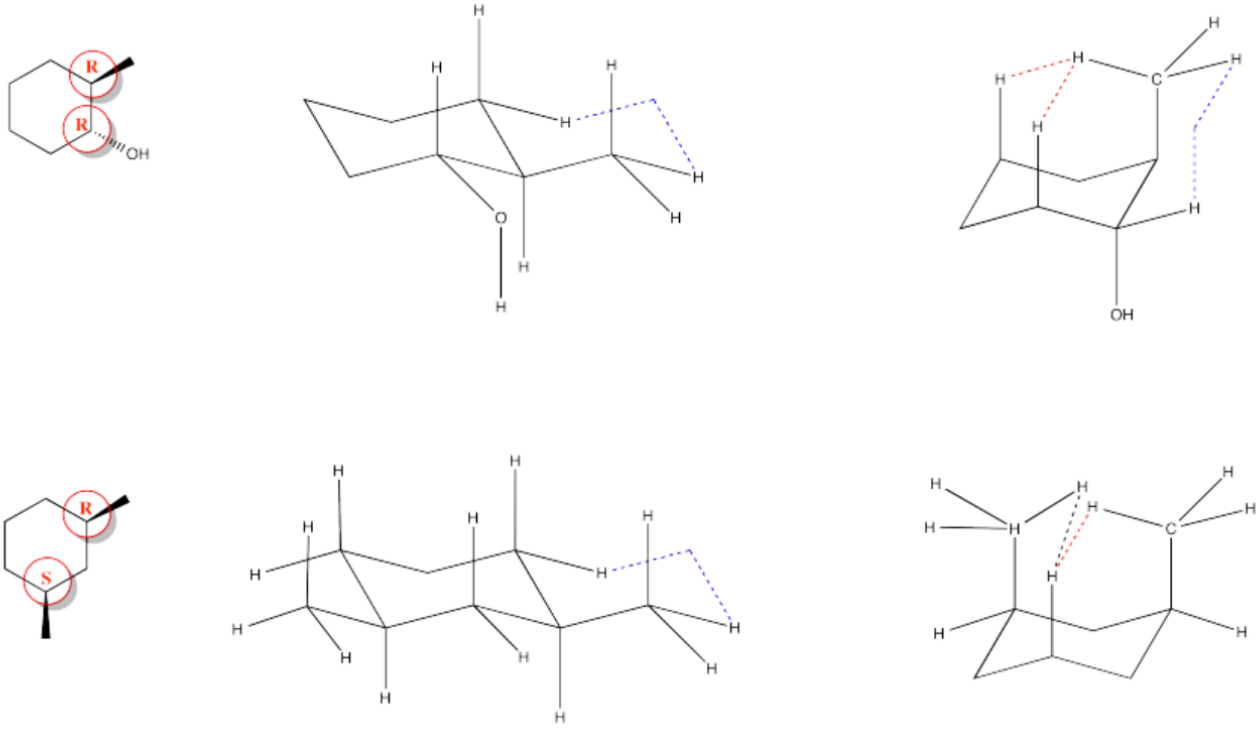
Exercise 6.10.1:



Exercise 6.10.2:

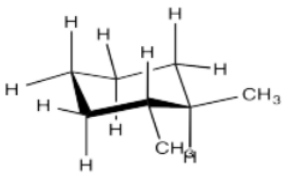


Exercise 6.10.3:

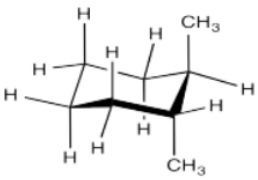


Exercise 6.10.4:

trans-1,2-dimethylcyclohexane



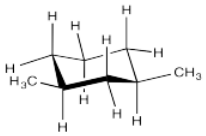
Estimate = 1 kcal/mol



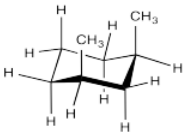
Estimate = 4 kcal/mol

Exercise 6.10.5:

a) *cis*-1,3-dimethylcyclohexane

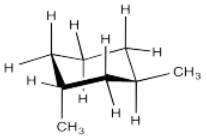


Estimate = 0 kcal/mol

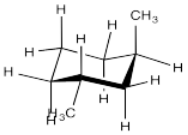


Estimate = 5 kcal/mol

b) *trans*-1,3-dimethylcyclohexane

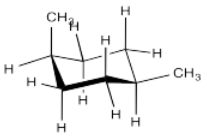


Estimate = 2 kcal/mol

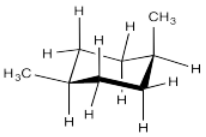


Estimate = 2 kcal/mol

c) *cis*-1,4-dimethylcyclohexane

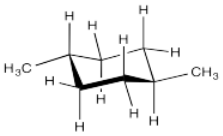


Estimate = 2 kcal/mol

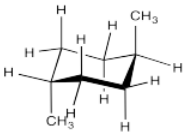


Estimate = 2 kcal/mol

d) *trans*-1,4-dimethylcyclohexane

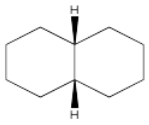


Estimate = 0 kcal/mol

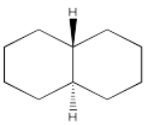


Estimate = 4 kcal/mol

Exercise 6.11.1:

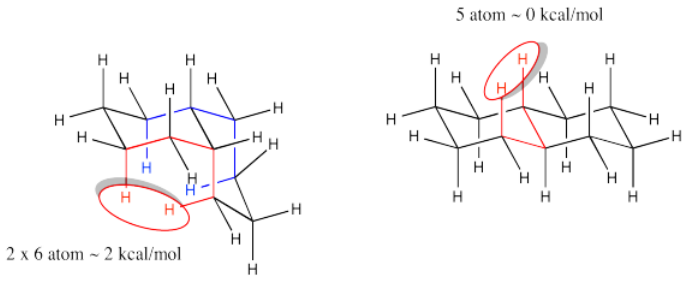


cis-decalin



trans-decalin

Exercise 6.11.2:



cis-decalin *trans*-decalin

Exercise 6.11.3:

a. The substituents are always *trans* along the junctions between each pair of rings. The steroids resemble a series of *trans*-decalin structures.
b. The overall structure would be more wide and wavy like a *trans*-decalin, rather than curled or boxy like a *cis*-decalin.

Exercise 6.11.4:

Bicyclo[2.2.0]decane

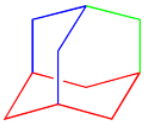
Exercise 6.11.5:

a) Bicyclo[2.1.1]hexane b) Bicyclo[3.2.1]octane c) Bicyclo[2.1.0]pentane (more commonly called "housane")

d) Bicyclo[2.2.2]octane e) *cis*-Bicyclo[3.3.0]octane

f) *cis*-Bicyclo[1.1.0]butane g) Bicyclo[1.1.1]pentane h) Bicyclo[4.3.3]dodecane

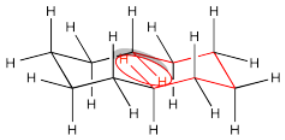
Exercise 6.11.6:



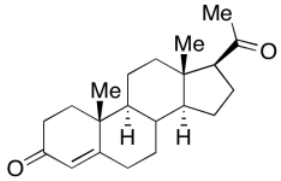
Although we could sketch out many rings using adamantane, just three rings are needed to include all the carbon atoms in the structure. Thus, adamantane is considered a tricyclic system. The systematic nomenclature of tricyclic systems gets a little more complicated, so we won't worry about that.

Exercise 6.11.7:

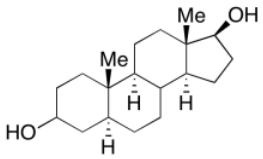
If cyclodecane adopted a regular diamond lattice conformation, there would be a whopping 8 atom interaction in the middle of the ring. That interaction isn't even included in our basis set. It would cost at least 6-7 kcal/mol. As a result, the cyclodecane adopts a twisted structure to avoid this interaction.



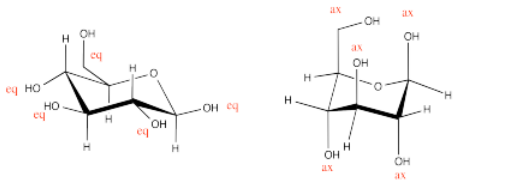
Exercise 6.11.8:



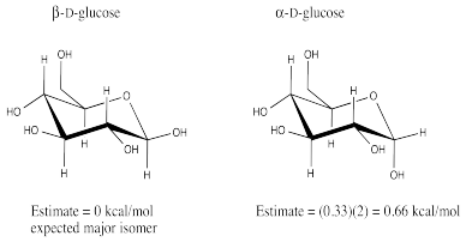
Exercise 6.11.9:



Exercise 6.12.1:



Exercise 6.12.2:



Exercise 6.12.3:

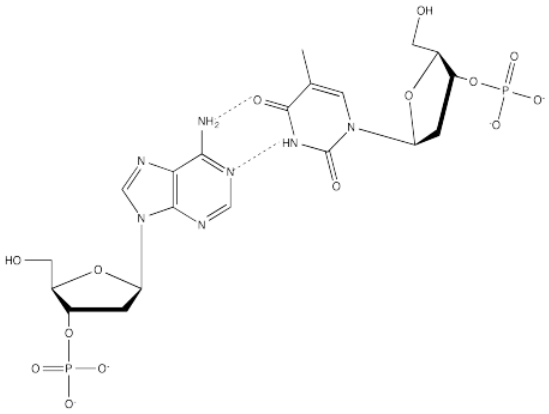
a) The β-D-glucose isomer should be the more stable isomer. The β-D-glucose isomer places the C1 hydroxyl group in the equatorial position.

b) The β-D-glucose isomer should be the more abundant isomer.

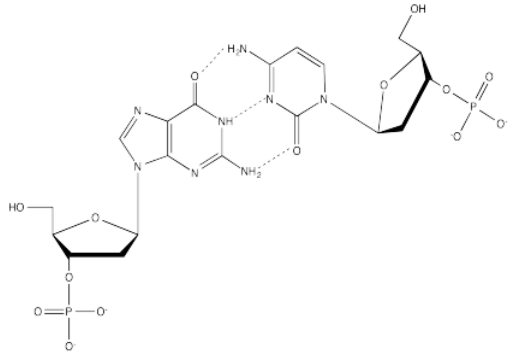
c) This is due to something called the anomeric effect. In solvents of modest polarity, such as dicholoromethane, the α-D-glucose isomer is not as polar as the β-D-glucose isomer. In the α-D-glucose isomer the dipoles of the ring oxygen and the C1 hydroxyl group opposing each other (therefore the overall effect is the molecule is less polar). In addition, the α-D-glucose isomer is stabilized by hyper conjugation of the ring oxygen and C1. For more information see http://en.Wikipedia.org/wiki/Anomeric_effect

d) A more polar environment would promote having more of the β-D-glucose isomer around. In the β-D-glucose isomer, the dipoles of the ring oxygen and the C1 hydroxyl group align each other (therefore the overall effect is the molecule is more polar).

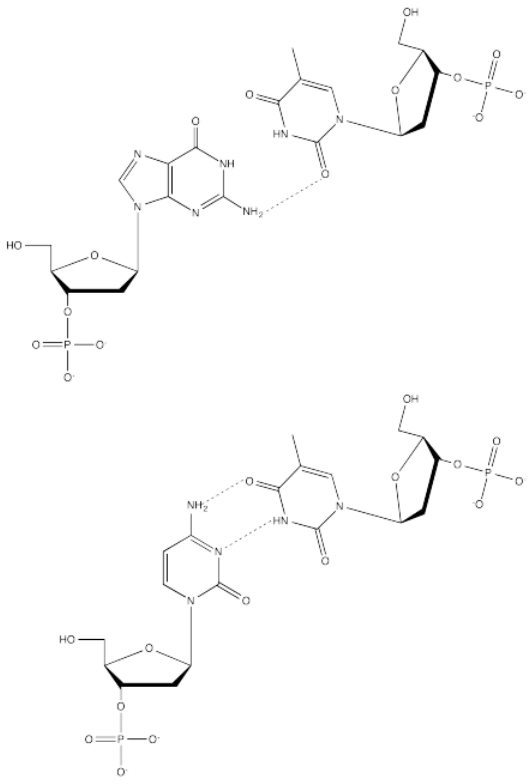
Exercise 6.13.1:



Exercise 6.13.2:



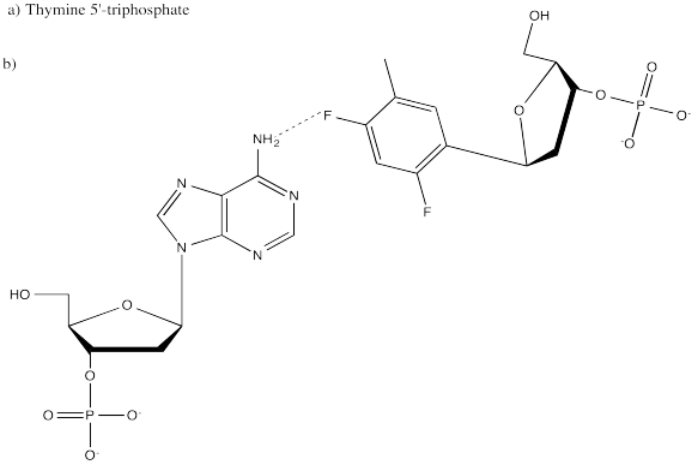
Exercise 6.13.3:



Exercise 6.13.4:

a) Thymine 5'-triphosphate

b)

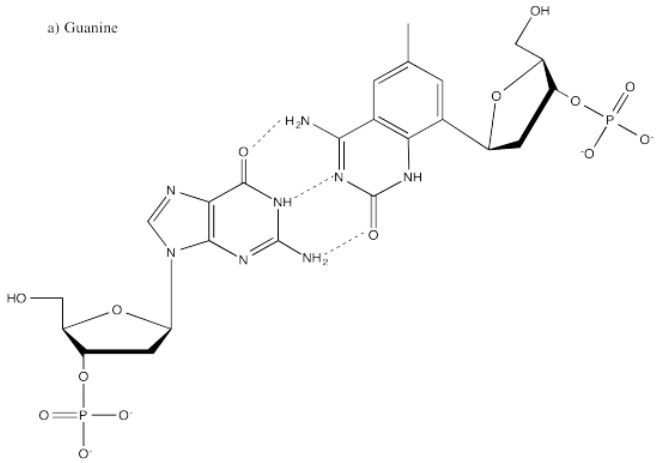


c) dF is only ably to hydrogen bond with adinine in one position while thymine can hydrogen at two positions with thymine.

d) dF is similar in size and electronic nature to thymine. The flourine groups on dF are somewhat smaller than oxygen on thymine, but present a comprabale polar group that is able to act as a hydroger bond acceptor. dF lacks the hydrogen bond donating ability as seen in thymine.

Exercise 6.13.5:

a) Guanine

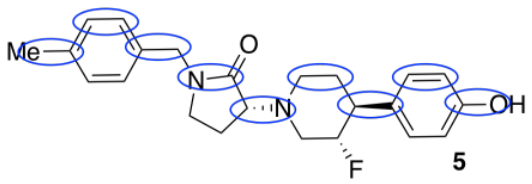


b) xC is similar to cytosine. Both molecules present hydrogen bond donors and acceptors in the same positions.

c) While xC is similar to cytosine in terms of placement of hydrogen bond donors and acceptors, the additional ring creates steric problems in that the hydrogen bond donors and acceptors are placed too close to the correct "base pair partner".

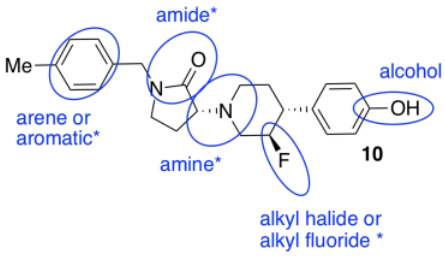
Exercise 6.14.1:

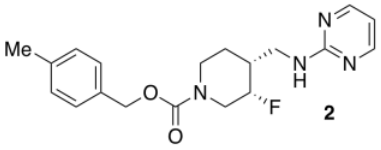
a)



b) about 9 Å

c)

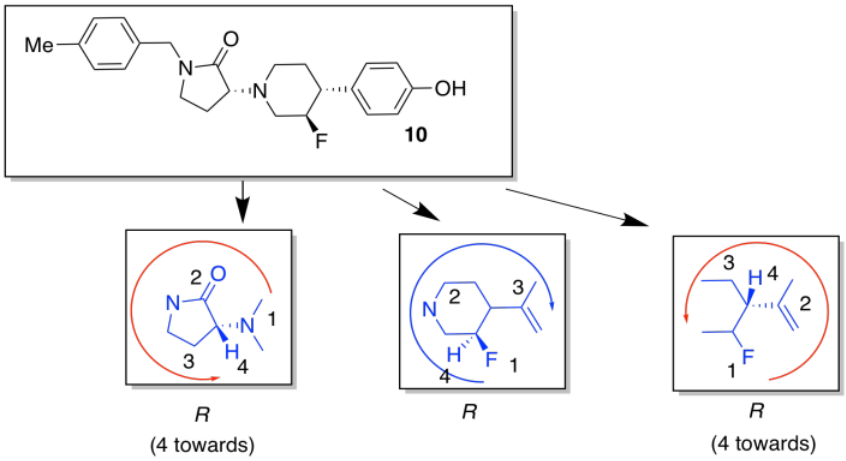




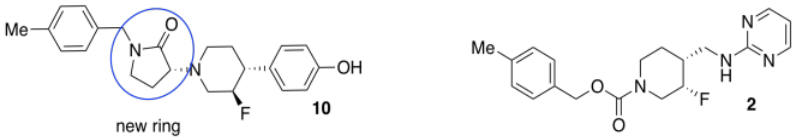
d) Stereochemistry. Because biological receptors are generally proteins containing unique, and chiral, binding sites, they hope to find a stereoisomer that fits the GluN2B receptor, but not the hERG receptor.

e) These compounds are diastereomers of each other.

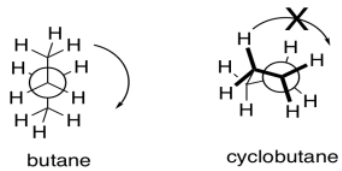
f)



g)



h)

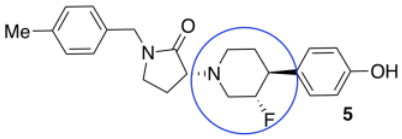


The ring introduces conformational rigidity by preventing the bond from undergoing complete rotation; it is tied back by the connection on the other side of the ring.

i) They were trying to decrease the number of possible conformations, or shapes, that the compound could adopt. That way, it would be less likely to bind in both the GluN2B receptor and the hERG receptor.

j) The substituents around the flexible six-membered ring could adopt a number of conformations. We will choose ways that minimize additional steric interactions so that we can focus on the most basic interactions.

Note that amines do not usually have fixed stereochemistry; the fourth substituent on an amine nitrogen is a lone pair, which does not occupy a fixed position in space. Unlike a carbon, the nitrogen can readily switch from one stereochemistry to another.



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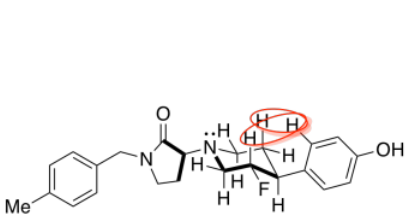
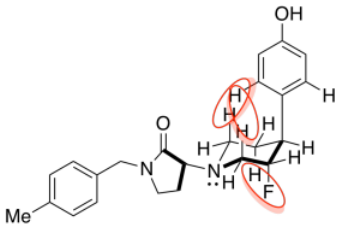


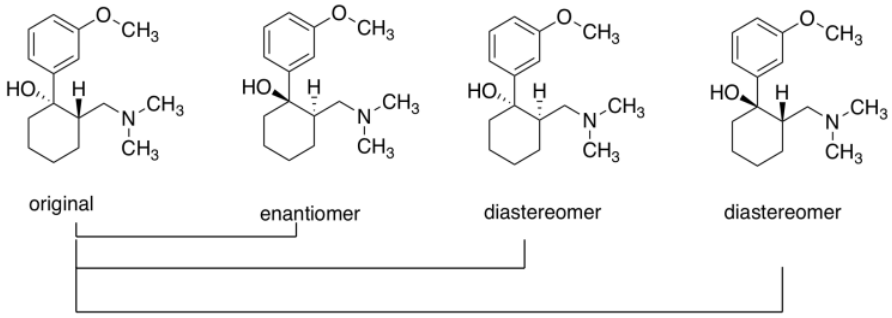
2 x 6-atom = 2 x 1 = 2 kcal/mol



2 x 7-atom + 1 x 6-atom = 2(3) + 1 = 7 kcal/mol

The one on the left, with more equatorial substituents and thus fewer steric interactions, is the more stable one.

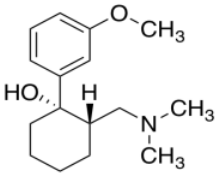
Exercise 6.14.2:

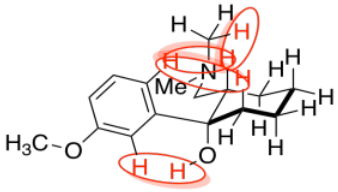


original enantiomer diastereomer diastereomer

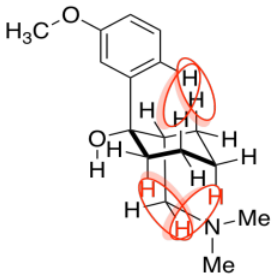
b) The original and its enantiomer; the first two above, from the left.

c)





4 x 6-atom = 4 kcal/mol



2 x 7-atom + 2 x 6-atom = 2(3) + 2(1) = 8 kcal/mol

d) The one on the left, with both groups equatorial and less steric strain, is more stable.

e) If the one on the left is active, a lower dose can be used because it will spend more time in the active form and be able to bond more receptors. If the less stable one, on the right, is the active form, a higher dose will be needed because only a small fraction of the molecules will be ready to bind the receptor at any given time.

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CHAPTER OVERVIEW

7: Structure-Property Relationships

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7.4: London Interactions
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7.13: Intermolecular Attractions and Protein Structure
7.14: Application Problems
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7.1: The Properties of Water

There is something very special about water, H_2O. For starters, it is essential for life. A human being can live for only three days without fresh water. Indeed, the cells in our bodies are made mostly of water.

For most organisms, it is important that cellular water remains in liquid form. Frostbite or death results if cells freeze.

Fortunately, we live on a remarkable planet. The median temperature on the surface of the earth is roughly 4 degrees celsius. That's a pretty good temperature for liquid water. Water is a liquid between 0 degrees celsius and 100 degrees celsius. If the earth were just a little colder -- if it were a few million miles farther from the sun, like Mars -- then it would be too cold for liquid water. Almost all the water on earth would be frozen. If the earth were a few million miles closer to the sun, like Venus, then the earth would be a little too hot for liquid water. Most of the water on earth would be water vapor in the atmosphere.

One of the reasons water is so special is the broad range of temperatures over which it stays in the liquid state. Molecules of similar size and complexity remain liquid over much narrower temperature ranges. For example, methane, CH_4, melts at -182 ^oC and boils at -164 ^oC. It is liquid only over a range of only 18 degrees celsius. On a summer day in Minnesota, the afternoon high may be 95 ^oF (35 ^oC) and the overnight low could drop to 60 ^oF (15 ^oC). That's a range of 20 ^oC. Methane goes all the way from a solid to a gas over a similar temperature span. If there were some methane-based organism subjected to a similar temperature change on a distant moon of Saturn, it could start its day as a popsicle, thaw out for a few productive hours of grazing in the morning, and float away like a balloon by lunchtime.

Not only is there a huge difference in the temperature range available to liquid water and liquid methane, but these two similar compounds freeze at very different temperatures. Other common small molecules like oxygen, O_2, nitrogen, N_2, carbon monoxide, CO, and hydrogen sulfide, H_2S, are gases at 25 C at atmospheric pressure. That is a comfortable room temperature. Water freezes at 0 ^oC: a cold day in Chicago. Methane freezes at -182 ^oC: a cold day on Saturn.

Exercise 7.1.1

Explain why water other small molecules like methane and dinitrogen are gases at room temperature, whereas water is a liquid.

Answer

One difference between water and these other molecules is that water is polar: there is a significant electronegativity difference between the oxygen and the hydrogen. The charges in one water molecule may be interacting with charges in other water molecules.

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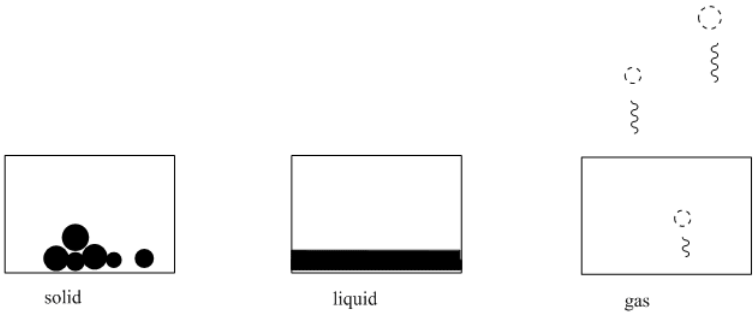
7.2: Changes of State

By now you are probably well aware that all the matter around you exists in one of three states: it is a solid, like the earth; a liquid, like the water; or a gas, like the air. In some places on earth, however, materials are not restricted to one particular state, but can change from one to another depending on the weather. On a winter day Yellowstone Park, you might walk past a hot spring and see frozen ice and snow, liquid water, and clouds of steam all at once.

There are several different ways in which you could describe these three phases of matter. Solids have a definite shape, regardless of the container in which they are placed. A marble is still a marble, whether it is rolling around in a bowl or a flowerpot. Liquids take up the shapes of their containers; a liter of water could get round like a fishbowl or square like a brownie pan. Gases are harder to see and more difficult to imagine. They expand to take up the spaces in which they are placed. A gas will even escape from a container that does not have a tight lid on it, much like the carbon dioxide bubbles rise out of a can of soda once it has been opened.



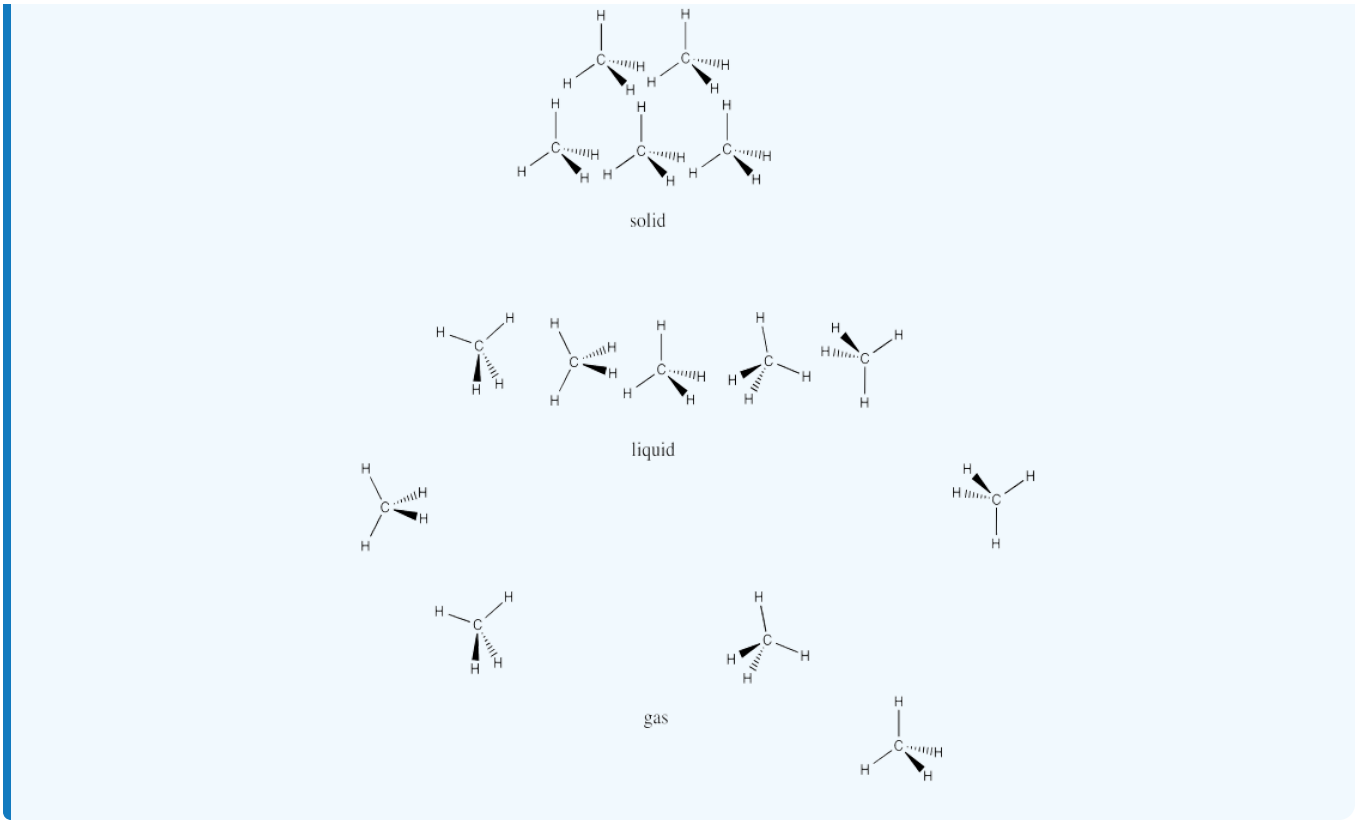
Another way of thinking about these states of matter has to do with the speed of the molecules in the matter, and how much energy those molecules contain. If you don't feel like you have much energy, you probably lay around a lot near the bottom of your container or dorm room, like a lump of coal on the bottom of a coal bin. If you have more energy, you might move around throughout your room, walking from place to place on the floor, but largely staying within its walls. If you have a great deal of energy, you may begin to dance or leap into the air or escape through the doorway to the outside.

Matter is a little bit like that, too. How much energy a group of molecules has -- and consequently how quickly they are moving on average -- strongly influences whether that material is in the solid, liquid or vapor phase. Solids tend to be composed of very slowly moving molecules while gases generally consist of speedier ones.

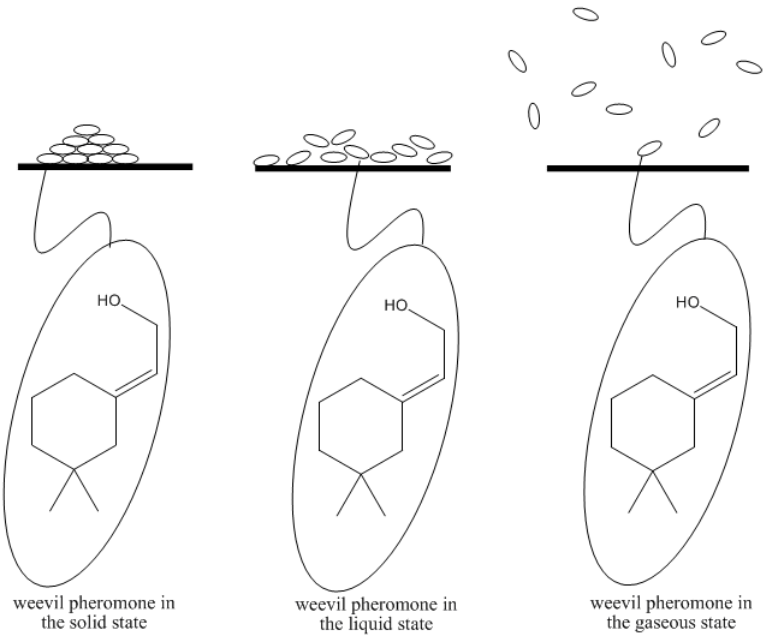
Exercise 7.2.1

Draw a picture of a group of methane (CH_4) molecules in the solid state, liquid state and phase.

Answer



Remember, each molecule has the same form whether it is in the gas phase, liquid phase or solid phase. The only thing that changes is the amount of energy the molecules have. As a result, the speed of the molecules and the ability of the molecules to attract each other also changes.



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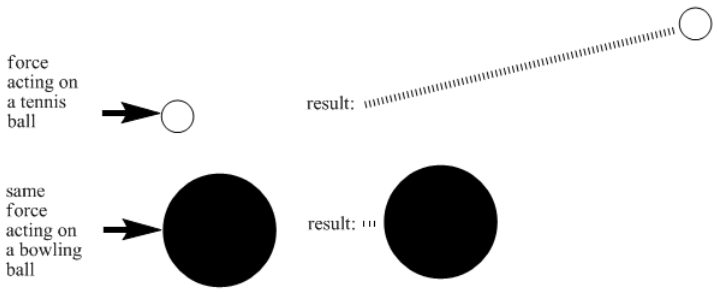
7.3: Kinetic-molecular Theory

Temperature is an indicator of how much energy is available in the surroundings. The higher the temperature, the more energy there is available, and the faster molecules can go. Different kinds of matter require different amounts of energy to get moving. That's why some compounds are gases at room temperature while others are solids.

There are many reasons for these differences. One factor is the mass of a molecule. If you hit a tennis ball with a tennis racket, you can be sure that it will sail through the air, but the same thing might not be true if you hit a bowling ball with a tennis racket. By putting an equal amount of energy into a tennis ball and a bowling ball, you would make the tennis ball move much faster than the bowling ball. Lighter objects need less energy to reach high speeds.



For a molecular example, let's look at halogens. All the elemental halogens are simple diatomic molecules. Their chemical properties have many similarities, but they have very different boiling points and melting points. Iodine, with the greatest mass, is a solid at room temperature, while fluorine has the lowest mass and is a gas at pretty much all the temperatures you are likely to encounter on Earth.

Name & formula	MW, g/mol	mp, ° C	bp, ° C
fluorine, F_2	**38.0**	**-219.6**	**-188.4**
chlorine, Cl_2	**70.9**	**-100.98**	**-34.6**
bromine, Br_2	**159.8**	**-7.2**	**58.8**
iodine, I_2	**253.8**	**113.5**	**184.3**

Clearly the mass of a molecules influences its state. Does the mass of a molecule alone allow us to predict its behavior? No. A much more important factor involves another difference between gases, liquids and solids: attraction between molecules. The molecules in solids are not just sitting still; they are sitting still *together*. Getting a crystal of iodine to evaporate requires coaxing molecules away from each other, and overcoming this attraction between them.

There are many different types of intermolecular attractions. The halogens in the table above cling to each other via the weakest type: London dispersion interactions. We will start by looking at those interactions, and then move to stronger kinds, such as dipole interactions and hydrogen bonding.

Exercise 7.3.1

Based on the data in the table above, what would you predict for the melting point and boiling point of nitrogen, N_2, and oxygen, O_2?

Answer

As far as we can tell from these data, the melting point of nitrogen and oxygen would be somewhere around -220°C, whereas the boiling point would be around -180°C. We would expect these numbers to be similar to fluorine, which has a similar mass. In fact, the melting and boiling points of oxygen are about -219°C and -183°C, respectively. The melting and boiling points of nitrogen are about -210°C and -196°C, respectively.

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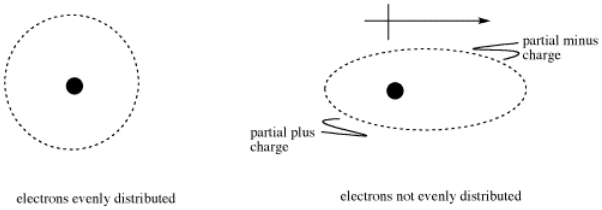
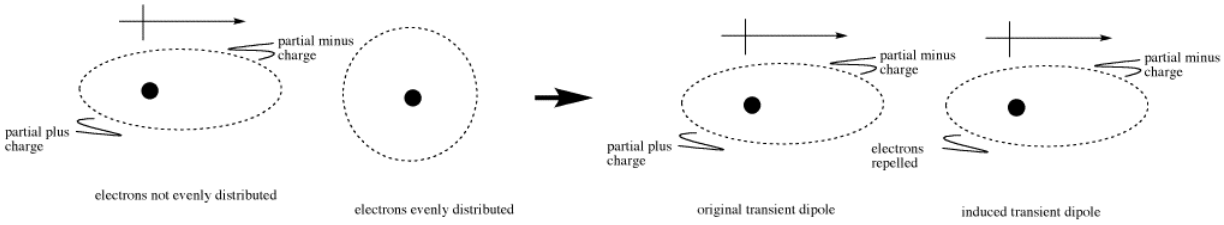
7.4: London Interactions

All molecules can experience London interactions or dispersion forces (sometimes called *van der Waals interactions*, although many people use this term to describe any kind of intermolecular attraction). These interactions are temporary electrostatic attractions caused by the random movement of electrons around a molecule. If at one moment more of the electrons are found on one side of the molecule than the other, then the molecule will develop a dipole.

A dipole is a separation of charge. If electrons slosh over to one side of the molecule, that end of the molecule becomes negatively charged, because electrons are negative. The other end of the molecule, however, becomes positively charged, because the negatively charged electrons that should be balancing the positive charge of the nucleus have drifted to the other end of the molecule. We symbolize this charge separation with a dipole arrow. One end of the arrow looks like a plus sign; that's the more positive end. The pointy end of the arrow represents the negative end.



This dipole is transient, meaning it does not last very long. However, in its short lifetime it could actually induce another dipole in a neighboring molecule. The electrons gathering on one side of one molecule could repel the electrons on the near side of the next molecule. This situation would leave the more negative end of one molecule next to the more positive end of its neighbor, and a weak attraction would result.



In most molecules, and especially relatively non-polar ones, these kinds of interactions last for tiny fractions of seconds. That means that if molecules rely entirely on London interactions to stick together, they probably don't stick together very well.

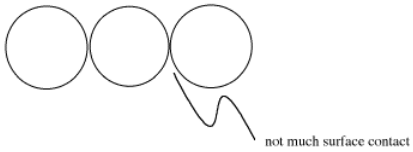
However, there are a couple of factors that can make these small interactions add up until they are pretty significant. First, molecules with many, loosely-held electrons would experience more London interactions than molecules with fewer, more tightly-held electrons. That's because the more electrons there are, and the more freely they are moving, the more likely they are to create that initial transient dipole. This factor is pretty significant when comparing the halogens, since fluorine has nine tightly-held electrons while iodine has fifty three, and most of them are so far from the nucleus that they are hard to keep track of.

In addition, this type of attraction does not work very well between two molecules that are far away from each other. Because it is such a weak attraction, it works best when the two molecules are very close to each other. The more contact there is between the surfaces of the two molecules, the more likely it is that one molecule can induce a dipole in its neighbor, and the stronger the attraction will be.

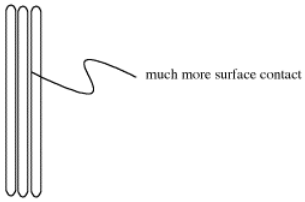
It's all a matter of surface area. The more surface contact between two molecules or two materials, the more likely they are to interact with each other. In fact, this sort of phenomenon can lead to some surprising results if taken to the extreme. Many researchers believe that the ability of geckos to walk on walls and ceilings, even if the surface is very smooth, is entirely due to van der Waals forces. Millions of tiny fibers (or setae) cover the bottoms of the lizard's feet, and each of these fibers is covered in hundreds of tinier pads (or spatulae). These structures ensure that there is enough surface contact for many, many weak interactions to add up to one strong grip. Some companies are even trying to use this idea to make very strong but removable adhesives based on this gecko model.

Now consider the difference between the attractive forces that would be found in two different shapes of molecules. In one case, the molecules are small and round, like ping-pong balls. In the other case, the molecules are long, and linear, like ribbons of spaghetti or lasagna.

You can arrange ping pong balls in any way you like (without squashing them flat), and they will never be able to do more than barely touch their neighbors.



Lasagna noodles stack very easily on top of each other, and have a good deal of contact with the other lasagna noodles.



If London interactions rely on temporary dipoles that are induced only if molecules can get very close to each other; it would be best if the two molecules could almost touch each other.

This factor results from the physical law that electric forces fall off very quickly with increasing distance. The farther apart the molecules, the less strongly they can have an effect on each other.

So, the long, ribbon-like molecules, having more surface area in contact with their neighbors, are more likely to induce dipoles in their neighbors, and are more likely to stick together. The spherical molecules, with less surface area in contact, will attract each other more weakly.

What sort of molecules are shaped like ping pong balls and spaghetti? Two very similar molecules, both with the formula C_5H_{12}, can serve as examples.

Normal pentane, or n-pentane, is a molecule in which all five carbons are arranged in a string, with the hydrogens completing the valence of each carbon. Neopentane, or 2,2-dimethylpropane, is a molecule in which one central carbon is bonded to each of the four other carbons, and each of those four carbons has three hydrogens on it. On paper, one might imagine pentane is spaghetti shaped, but neopentane looks more like a cross. You need to look at a space-filling model to see that neopentane is very much like a ball.

It turns out that pentane has a boiling point of 35 ^oC, while neopentane, with the exact same molecular formula, has a boiling point of -9 ^oC. That means that, at comfortable room temperature, pentane is a liquid, while neopentane is a gas even on a pretty cold day. The pentane molecules stick together more because there is more contact between them; the neopentane molecules don't, and they each go their own way, forming a gas.

Pentane and neopentane are isomers. They have the same formula but different structures. Isomers is from the Greek, meaning "same things", referring to their identical content. However, isomers often have very different physical and biological properties.

Exercise 7.4.1

Compare London forces in the following pairs of molecules, and predict the relative melting points of the two compounds.

a) $CH_3(CH_2)_6CH_3$ and $CH_3(CH_2)_{100}CH_3$

b) $CH_3(CH_2)_6CH_3$ and $CH_3(CH_2)_3C(CH_3)_3$

c) CH_3Br and CH_3Cl

Answer a:

A chain that is 8 carbons long would have much lower London interactions than a chain that is 102 atoms long. The greater the contact between molecules, the greater the chance for weak attractions due to small charges arising from random electron movement. The molecule with the longer chain would have the higher melting point, because more energy would have to be added in order to overcome those attractions and get the molecules moving.

Answer b:

The first chain is more linear whereas the second chain is more branched. The more linear molecules will pack together more easily, allowing greater surface contact for increased London interactions. The straighter chain would have a higher melting point.

Answer c:

Bromomethane has a lot more electrons than chloromethane. Based on London interactions alone, we would expect bromomethane to have a higher melting point. In fact, the melting point of bromomethane is about -94^{o}C, compared to about -97^{o}C for chloromethane; there must be another factor that compensates for the difference in numbers of electrons and makes these values so close.

Exercise 7.4.2

Predict the relative boiling points of 3,4-dibromohexane and 3,3-dimethylhexane.

Answer

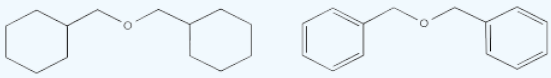
Because of the large numbers of electrons in bromine, we would expect a higher boiling point in 3,4-dibromohexane.

Exercise 7.4.3

What would you predict about the relative melting points of dibenzyl ether and bis(cyclohexylmethyl) ether. (Note: "bis" is often used instead of "di" as a prefix for more complicated groups.)

Answer

Remember benzyl refers to the group $C_6H_5CH_2$ (below right); cyclohexylmethyl suggests the superficially similar $C_6H_{12}CH_2$ (below left).



The benzyl group contains trigonal planar carbons, whereas the cyclohexylmethyl group contains only tetrahedral carbons. The benzyl groups, being flatter, could pack more easily together and interact more strongly. We would expect dibenzyl ether to have a higher melting point.

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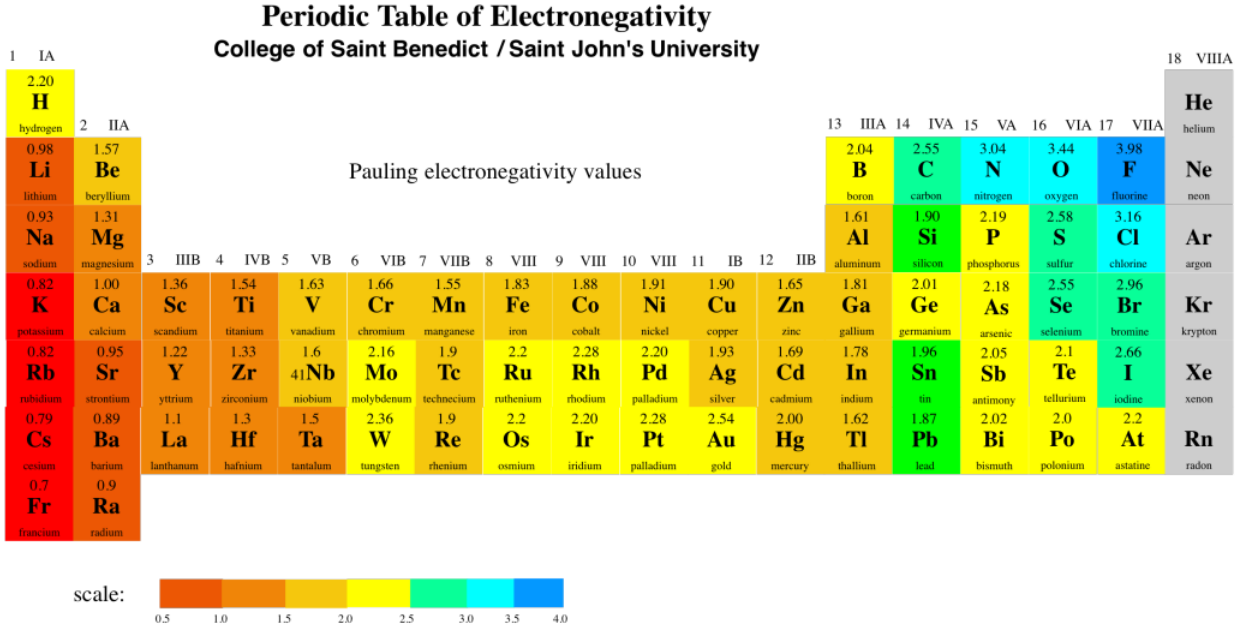
7.5: Dipole Interactions

When two different kinds of atoms are connected to each other, the electrons between them are typically not shared evenly. That's because in most cases, two different atoms would have two different electronegativity values. One atom would be more electronegative than the other. It would have a stronger attraction for the electrons in the shared bond, and the electrons would be a little bit more attracted to that atom than the other.

Remember, electronegativity is a periodic trend. As we move to the right in the periodic table, more and more protons are added to the nucleus, and so atoms on the right attract electrons more strongly that do the atoms on the left. Also, as we move from top to bottom of the periodic table, the valence shells of the atoms become larger; that means valence electrons are getting farther from the nucleus, so they are less tightly held. Those two factors, distance and amount of charge, control the strength of interaction between charged particles.



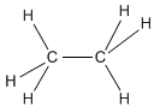
The periodic table above shows Pauling electronegativity values. There are different ways to calculate electronegativity, but the Pauling scale is very commonly used. Calculating the Pauling scale depends on being able to observe compounds, so the noble gases are not usually given a value in this scale, because they normally don't form any compounds.

For example, when a carbon atom is bonded to a fluorine atom, there is an electronegativity difference between the two atoms. There is a difference in electronegativity values of almost 1.5 units between these two atoms. Fluorine is more electronegative than carbon because it has more protons in the nucleus than carbon. The electrons are pulled closer to the fluorine than to the carbon. A carbon-fluorine bond is polarized towards the fluorine. A molecule like fluoromethane, CH_3F, has a permanent dipole.

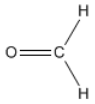
Note that there are also dipoles in C-H bonds, but they are so much smaller than the ones in the C-F bond that they do not matter. The overall dipole has a buildup of negative charge on the fluorine.

You can imagine that molecules with permanent dipoles would interact with each other much more strongly than molecules that rely on temporary dipoles in order to stick together. Molecules with no natural dipole will stick only loosely together, but molecules with permanent dipoles will stick to each other easily.

Ethane, C_2H_6 (sometimes written CH_3CH_3, suggesting two carbons are each connected to three hydrogens, and also to each other), and formaldehyde, CH_2O, have different formulae but the same molecular weight. Based on weight alone, it would take about the same amount of energy to move an ethane molecule and a molecule of formaldehyde.



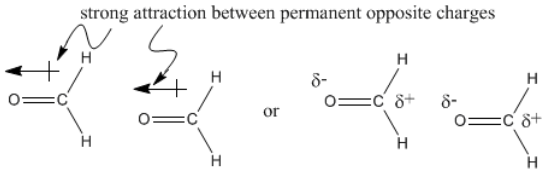
ethane



formaldehyde or methanal

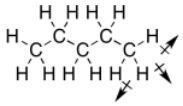
The two molecules also have somewhat similar shapes, unlike neopentane and pentane. At room temperature, ethane and formaldehyde are both gases. Nevertheless the two compounds have very different boiling points; formaldehyde becomes liquid around -20 ^{o}C, which would be a very cold winter day in, say, Chicago. Ethane does not become liquid unless it is cooled to around -90 ^{o}C, a cold winter day on Neptune, at which point formaldehyde is just about ready to freeze solid.

The difference between these two molecules must be due to the oxygen atom in formaldehyde. Oxygen, the second most electronegative element in the periodic table, can form some very polar bonds. The difference between carbon and oxygen is 0.89 units, almost a full electronegativity unit. The permanent dipole that results between the oxygen and carbon makes the formaldehyde molecules much stickier than the ethane molecules, which depend on fleeting London interactions if they are going to hold on to each other.



In contrast, the difference in electronegativity between carbon and hydrogen is actually pretty small (about 0.35 units, based on the Pauling scale). The tiny dipole in the C-H bond is so much smaller than the one in the C=O bond that it really isn't a factor here.

Taking that story a little further, hydrocarbons (molecules made up of hydrogen and carbon) are the most common example of non-polar compounds, because their bonds are either completely nonpolar C-C bonds or else C-H bonds with very low polarity. There is a tiny dipole in a C-H bond, but it isn't enough to make the molecules attract each other very well. Furthermore, there tend to be a lot of C-H bonds in a hydrocarbon pointing in all sorts of directions; an approaching molecule would be unlikely to encounter either a fully positive end or a fully negative end of the molecule. In the end, all those little dipoles in all those C-H bonds end up cancelling each other out.



There are other variations on dipole interactions that are pretty common. For example, you could imagine that a dipolar molecule would interact pretty strongly with an ion. We will take a look at that situation shortly when we think about how mixtures of different compounds interact with each other. However, perhaps the most important variation in organic chemistry is hydrogen bonding.

Exercise 7.5.1

Comment on dipole moments in the following compounds and predict their relative boiling points.

a) 1-chlorobutane vs. pentane

b) triethylamine vs. 3-ethylpentane

c) diethyl ether vs. pentane

Answer

These compounds all contains lots of non-polar C-C and C-H bonds, which would not have appreciable dipoles. However, in each pair, there is a compound that contains mroe polar bonds as well: C-Cl, C-N and C-O.

Sometimes a molecule that contains polar bonds is not really polar overall. Carbon dioxide is a good example. Polar molecules strongly attract each other because the more negative end of one molecule is attracted to the more positive end of the next molecule via electrostatics. Opposites attract. In carbon dioxide, however, both ends of the molecule are more negative. How can they attract each other?

There's more to it. Dipoles are "vector quantities". That means it isn't just the amount of charge separation that matters; it's also the direction of separation. In carbon dioxide, a linear molecule, there are two polar bonds. Those polar bonds point directly away from each other. The dipole of one bond balances out the dipole of the other bond. Overall, the molecule does not have a dipole.

Water, on the other hand, is a different case. Like carbon dioxide, water has two polar bonds. However, the bonds in water do not lie in a straight line like the ones in carbon dioxide. They are at an angle to each other instead. That means their dipoles are not quite pointing in opposite directions. As a result, water has an overall dipole moment.

At the extreme, a polar bond can get to the point that one atom is pulling the electrons so strongly toward itself that it pulls them completely away from the other atom. The first atom becomes an anion, and the second atom becomes a cation. At this point, we have an ionic bond, rather than a covalent one. How different must the electronegativity values be in order to have an ionic bond? The usual rule of thumb is a difference of about 1.6 electronegativity units. So, for example, all of the blue atoms in the periodic table above would form ionic bonds with all of the red atoms. The green atoms would form ionic bonds with most of the dark red atoms, but not with the light red ones.

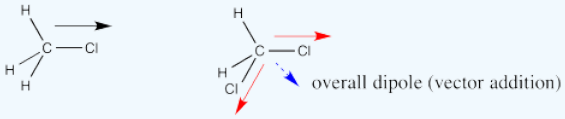
Exercise 7.5.2

The dipole moment of a molecule (essentially the size of its dipole) can be calculated from the dielectric constant of a material, which can be measured experimentally on a bulk quantity of the compound. The dipole moment of chloromethane, 12.9 D, is higher than that of dichloromethane, 9.08 D, even though dichloromethane has a greater number of polar bonds than chloromethane. Explain why.

Answer

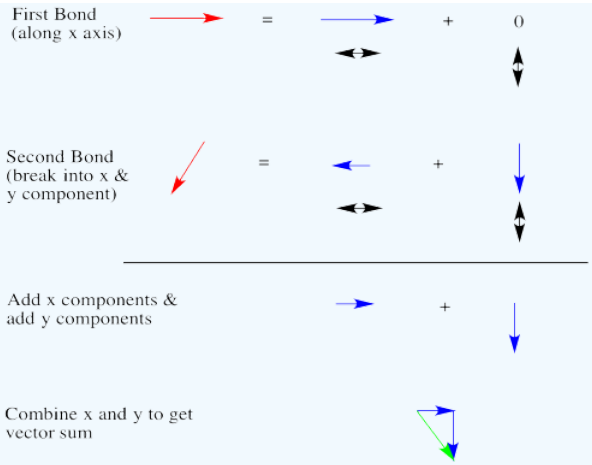
Dipoles are vectors. If we have two polar bonds, they will add together using vector addition. Any vector can be shown as the sum of two other vectors. Below, the red arrow points down and to the left. How far down and how far to the left? We can show how far using the blue arrows. The blue arrow down and the blue arrow to the left add up to give the red arrow that goes down and to the left.

In dichloromethane, there are two polar bonds. Both bonds are polarized towards the more electronegative chlorine. As drawn below, one bond has a dipole straight to the right. The other bond has a dipole that goes down and to the left. If the molecule has an *overall* dipole, with a positive end of the whole molecule and a negative end of the whole molecule, which end would be positive and which would be negative?



It seems reasonable that the positive end would be somewhere over on the hydrogen side and the negative end would be somewhere over on the chlorine side. The overall dipole, as opposed to the individual bond dipoles, would point somewhere in the direction of the blue, dashed arrow. But how big would it be? Surely it's bigger than either of the two individual dipoles, because they are adding together, right?

Let's take a very qualitative look. The first red arrow is just to the right. We'll break the second arrow into a smaller arrow down and an even smaller arrow to the left. The sum of the left/right arrows is a very small arrow to the right.



The sum of the up/down arrows is just a small arrow down. Overall, the sum is a green arrow going down and to the right. The result doesn't really seem any bigger than an individual bond dipole.

Exercise 7.5.3

Dichloromethane nonetheless has a higher boiling point (39 °C) than chloromethane (-24 °C). Explain why.

Answer

Despite the relatively similar dipole moments, dichloromethane's boiling point is much higher than chloromethane's. The difference probably lies in the much greater mass of dichloromethane.

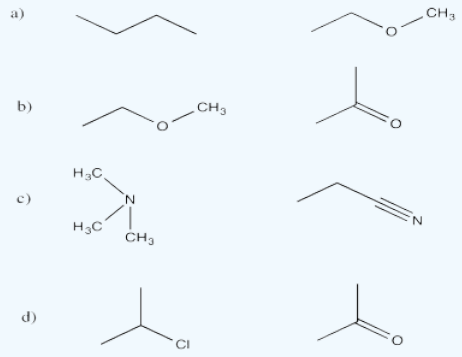
Exercise 7.5.4

Comment on dipole moments in the following compounds and predict their relative boiling points.

a. butane and ethyl methyl ether
b. ethyl methyl ether and 2-propanone
c. trimethylamine and propanenitrile
d. 2-propanone and 2-chloropropane

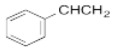
Answer

In each case, the one on the right has a larger dipole and a higher melting point.



Exercise 7.5.5

a. Draw the Lewis structure for each molecule with the correct electronic geometry.
b. Draw in dipole moments.

CBr_4	$CH_3(CO)CH_3$	CO_2
$CH_3CH_2CH_2CH_3$	BF_3	CH_3OH
$CH_3CH_2OCH_2CH_3$	$(CH_3CH_2)_3N$	XeF_6
CH_3CH_2CN		CH_3Cl

c. Decide if the molecule is polar.

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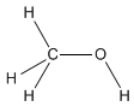
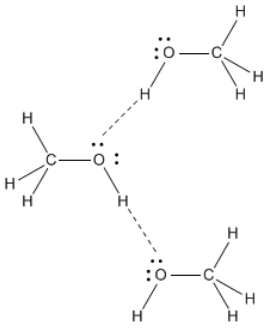
7.6: Hydrogen Bonding

Methanol, CH_4O (or CH_3OH, a CH_3 group attached to an OH), is another example of a molecule with a similar molecular weight to ethane. Like formaldehyde, methanol freezes somewhere around-90 ^oC, but it does not become a gas until it is heated to 65 ^oC. Methanol is certainly similar to formaldehyde in some ways. It contains oxygen and is very polar. The huge difference in their boiling points is due to the very strong hydrogen bonds in methanol.

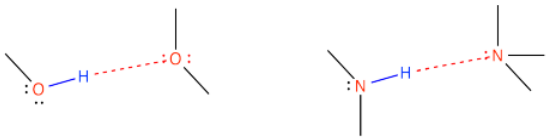


methanol

Hydrogen bonding occurs when there is a significant amount of positive charge building up on a hydrogen atom. That happens because the hydrogen is attached to an atom that is much more electronegative than the hydrogen. As a result of that positive charge, a lone pair on another molecule strongly interacts with the hydrogen.



Hydrogen bonds occur only when a hydrogen is attached to one of the few most electronegative elements in the periodic table: fluorine, oxygen or nitrogen. It is these strong hydrogen bonds that are responsible for the relatively high boiling point of methanol; there is so much positive charge on the hydrogen of the OH group that it can essentially form a real bond with the lone pair on another methanol molecule.



Water is an even better example of a hydrogen bonding compound; in fact, water molecules are so tightly bound to each other that this very small molecule freezes at 0 ^oC and does not boil until 100 ^oC (way, way hotter than an August day in Las Vegas). Water molecules are much less able to move around freely than are ethane molecules, even though ethane molecules weigh almost twice as much.

For practical purposes, hydrogen bonding usually involves compounds that contain N-H and O-H bonds. That's because oxygen and nitrogen are the second- and third-most electronegative elements in the periodic table, respectively. There are many, many examples of compounds like that. It also occurs in HF, of course, because fluorine is usually considered the most electronegative element, but there is really only one example of a compound with that bond, so you are much less likely to have to worry about that example. Slightly weaker hydrogen bonds have also been shown to occur involving other species, such as S-H bonds, but the most significant ones involve N-H and O-H bonds.

Exercise 7.6.1

Which of the following molecules are capable of strong hydrogen bonding?

a) ethanal, CH_3CHO b) ethylamine, $CH_3CH_2NH_2$ c) acetic or ethanoic acid, CH_3CO_2H d) dimethyl peroxide, CH_3OOCH_3

Answer

Only ethylamine and ethanoic acid have the N-H or O-H bonds that are polar enough for hydrogen bonding.

Exercise 7.6.2

Predict the relative order of melting points in the following amines:

hexylamine, $CH_3(CH_2)_4CH_2NH_2$; triethylamine, $(CH_3CH_2)_3N$; dipropylamine, $(CH_3CH_2CH_2)N$

Answer

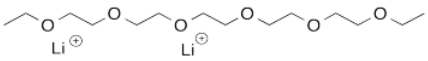
hexylamine > dipropylamine > triethylamine

The one with the greatest potential for hydrogen bonding will have the highest melting point.

Exercise 7.6.3

Identify the strongest IMF in each case.

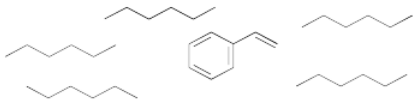
A.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

B.



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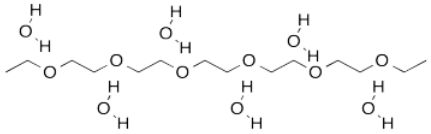
C.



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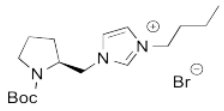
D.



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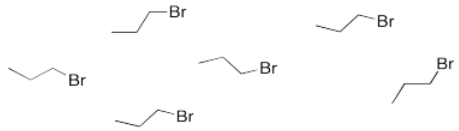
hydrogen bonding ion-ion dipole-induced dipole

E.



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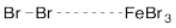
hydrogen bonding ion-ion dipole-induced dipole

F.



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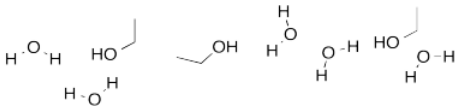
hydrogen bonding ion-ion dipole-induced dipole

G.



dipole-dipole induced dipole-induced dipole ion-dipole

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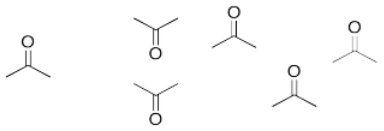
H.

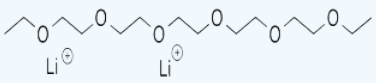


dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

Answer

A.



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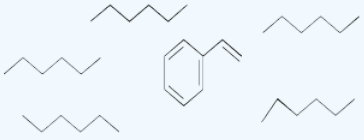
B.



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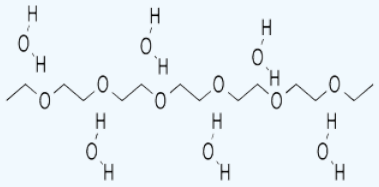
hydrogen bonding ion-ion dipole-induced dipole

C.



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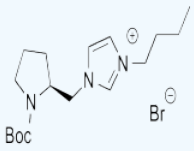
hydrogen bonding ion-ion dipole-induced dipole

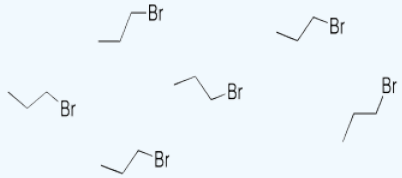
D.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

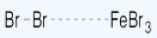
E.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

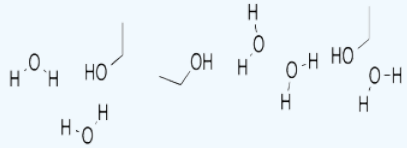
F.



dipole-dipole induced dipole-induced dipole ion-dipole

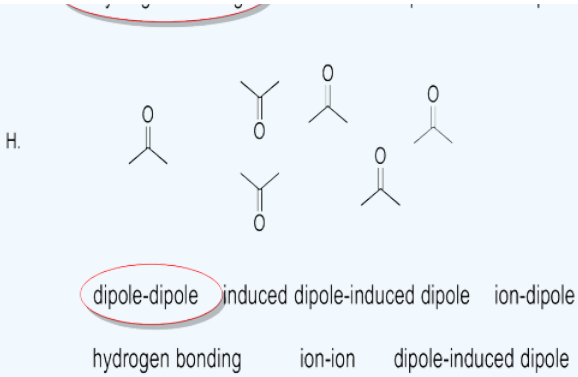
hydrogen bonding ion-ion dipole-induced dipole

G.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole



Biological Molecules and IMFs

Because compounds containing oxygen and nitrogen are so common in biology, hydrogen bonding is a fairly common feature in organic and biological chemistry.

Carbohydrates are one of the major classes of biomolecules. Carbohydrates are compounds that contain lots of OH groups, so they have lots of potential to form hydrogen bonds.

Proteins and peptides contain amide groups. Amides contain N-H bonds; hydrogen bonds involving amides are crucial influences in the structure of proteins.

Large biological molecules like proteins consists of 1000s of atoms, which interact through "intramolecular" ion-ion, London dispersion, dipole-dipole, and hydrogen bonding to create a unique 3D structure. Other molecules, both small and large, can bind to biological macromolecule using the same intermolecular interactions. An example of a protein, bovine low molecular weight protein tyrosyl phosphate, binding to inorganic phosphate, is shown below.

The displays above show three different ways to render the LMW-PTPase. You will recognize the spacefill and wireframe models, but note their complexity compared to the smaller molecules you have studied thus far. The cartoon molecules removes much of the detail by stripping away atoms and bonds, and replacing them with lines, ribbons (representing alpha helices) and block arrows (representing beta structure). ***[Not Available]***

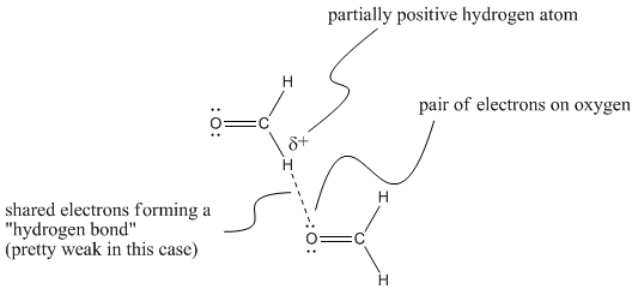
Inorganic phosphate, an inhibitor of this enzyme, binds to the enzyme through the intramolecular forces mentioned above. It is rendered in spacefill with the protein in cartoon and wireframe modes.

DNA may be the most well-known example of a compound that displays hydrogen bonding. In DNA, complementary "base pairs" hydrogen bond to each other to held two strands of DNA together.

Weak, "Secondary" Hydrogen Bonds

Hydrogen bonding is really a special case of dipole forces. It occurs under very particular circumstances: in the presence of O-H or N-H bonds, which provide both a very positive hydrogen and a lone pair, the two features necessary for a hydrogen bonding interaction.

In general, we think of a hydrogen bond as the electrostatic interaction between an electron pair on one atom and a hydrogen atom that has built up a partial positive charge. There are some examples where that might be happening, but that we would rather keep separate from the general idea of a hydrogen bond. For example, a lone pair on an oxygen atom in formaldehyde might be attracted to a hydrogen on another formaldehyde, which would be at the more positive end of the molecule. There is evidence from x-ray crystallography that such weak "hydrogen bonds" occur in the solid state in molecules containing aldehyde groups, similar to the one in formaldehyde.



However, these kinds of interactions are really very weak. They shouldn't be thought of in the same category as regular hydrogen bonds. For that reason, we will give them a separate term, "secondary" hydrogen bond. This type of interaction is fairly esoteric and you are not that likely to see it. We're looking at it here really to underscore the idea that there is something very special about the hydrogen bonds resulting from compounds that contain O-H and N-H bonds.

Later, you will see that whenever there is a case in which there is an opportunity for regular hydrogen bonding, the properties of the molecule are dramatically affected. That isn't true otherwise. Secondary hydrogen bonds may be responsible for some very subtle effects in the solid state, when molecules are already at pretty low energy and are not moving around much. However, they hardly change the properties of a molecule beyond what we would expect based on simple dipole-dipole interactions.

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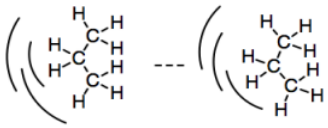
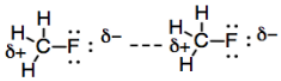
7.7: Ionic Attractions

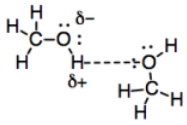
So far, we have seen that all molecules can potentially have weak attractions that make them cling to each other. Because the electrons in an atom or molecule are not stationary, but are always in motion, there is always a chance that a molecule will become lop-sided temporarily. Its electrons can lean a little to one side, leading to a small buildup of negative charge on that side. The molecule would be slightly low on electron density on the other side, leading to a small buildup of positive charge there. This temporary dipole can induce temporary dipoles in other molecules nearby. That slightly positive side can tug on the electrons on a molecule nearby. And so on; a chain of these events can cascade through a group of molecules. We get an induced dipole-induced dipole interaction.



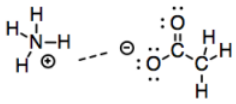
We have also seen that some molecules have permanent dipoles. If two atoms are bonded together and they have a sufficiently large difference in electronegativity, then there is a significant charge separation between the two atoms, and a permanent dipole results. The difference between these permanent dipoles and the ones we saw in London interactions is that the London interactions rise and fall in an instant. The London interactions typically don't last long enough to hold two molecules together very tightly, unless there are an awful lot of these interactions. Because a fixed dipole is permanent, there is little opportunity for two molecules with a dipole-dipole interaction to squirm away from each other.



Hydrogen bonds are a particularly strong example of dipole-dipole interactions because of the significant electronegativity difference between oxygen and hydrogen. The interaction is also strengthened by the availability of a lone pair on oxygen to facilitate the interaction with the partial positive charge on the hydrogen. Furthermore, they are really important when you live on such a watery planet.

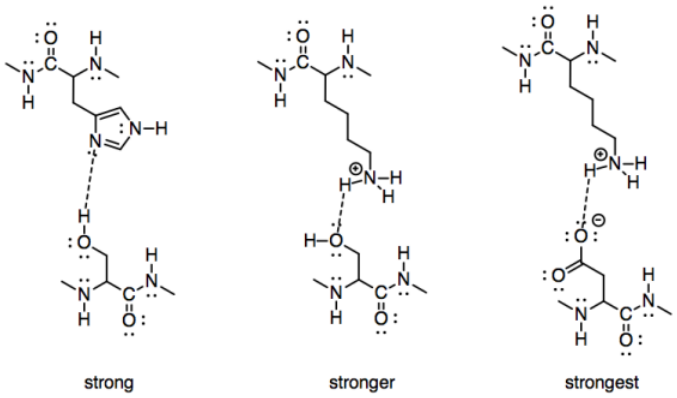


So, these interactions get progressively stronger based on the amount of charge separation in the bond. The logical conclusion to that progression is a bond that is completely ionized. What if one end of the bond has a full negative charge and the other end has a full positive charge? Obviously, ions should have even more electrostatic attraction for each other than mere dipoles.



Now, many treatments of intermolecular attractions don't even consider ionic attractions; they've got that covered under "ionic bonding". Nevertheless, it's useful to look at ionic attractions in the present context, as well, because they help to complete the picture of how two molecules might interact with each other.

To take a biological example, we might consider the strength of interaction of two amino acid side chains. A serine and histidine would have significant interactions with each other, because both contain side chains capable of hydrogen bonding. A serine would have a stronger interaction with the side chain of a positively charged lysine, however. To go one step further, a positively charged lysine would have an even stronger attraction to a negatively charged aspartate.



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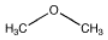
7.8: Comparing Properties of Isomers

Sometimes there is more than one way to connect a given group of atoms into a molecular structure. Given the formula C_2H_6O, two different isomers are possible: methyl ether and ethanol. They have the same formula but different structures. The word, "isomer", is from the Greek, meaning "same things", referring to their identical content. However, isomers often have very different physical and biological properties.

ethanol



dimethyl ether

These two compounds have different physical properties, as you can see in the table below.

compound	melting pt, ° C	boiling pt, ° C
dimethyl ether	**-138**	**-25**
ethanol	**-117**	**78**

Remember, typical room temperature is about 25 °C. That means that at room temperature, dimethyl ether is a gas, because it is above its boiling point. Ethanol, on the other hand, is a liquid at room temperature. Ethanol at that temperature is well above its freezing point but has not yet reached its boiling point.

Why is that? What is the origin for the differences in physical properties between these two, similar compounds, one of which is a gas at room temperature while the other is a liquid? Both contain carbon-hydrogen and carbon-oxygen bonds. The ethanol also contains a carbon-carbon bond and an oxygen-hydrogen bond.

Certain bonds, or groups of bonds, confer specific behaviors on the compounds in which they are found. For instance, when an OH group is found in an organic compound, it can make the compound moderately acidic. It also makes the compound a little more likely to be a solid or liquid rather than a gas. Why?

The dominant intermolecular attraction between ethanol molecules is hydrogen bonding. What we mean is, although two ethanol molecules may be attracted by London dispersion forces and even by dipoles, both of those factors pale in comparison to the attraction that arises from hydrogen bonding. Hydrogen bonding is the single most important factor holding two ethanol molecules together.

In dimethyl ether, on the other hand, hydrogen bonding is not a factor. In this molecule, the major intermolecular attraction involves regular dipole moments. Because hydrogen bonds are typically much stronger attractions than ordinary dipole moments, a group of ethanol molecules is much harder to separate from each other than a group of dimethyl ether molecules. The ethanol has a much higher boiling point.

Exercise 7.8.1

Compounds don't really have to be isomers in order to compare them in this way. They just have to be similar enough that we can reasonably compare them.

For example, propan-2-one or acetone, $CH_3(CO)CH_3$, has a boiling point of 56-57 °C whereas 2-propanol, $CH_3CH(OH)CH_3$, has a boiling point near 83 °C. Explain the difference.

Answer

The hydrogen bonding between 2-propanol molecules is a stronger interaction and is more difficult to overcome than the dipole-dipole interactions between 2-propanone molecules. Thus, 2-propanone molecules can more easily escape into the vapour phase.

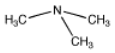
Different collections of bonds that are commonly found in organic compounds are referred to as functional groups. Functional groups influence the physical properties of the compounds in which they are found. They can also influence the biological activity

of a compound; that is, they can help determine whether a compound might be active as a specific type of drug, a hormone, or other types of compounds that regularly interact with organisms in nature.

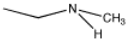
In the case we looked at above, we were comparing an alcohol to an ether. In an alcohol, there is an OH group attached to a carbon. In an ether, there is an O attached to two carbons. (There are exceptions to these definitions: if an OH group is attached to a carbonyl, a C=O group, it is not an alcohol but a carboxylic acid. If an oxygen is attached to a carbonyl and to another carbon, it is not an ether but an ester.) In general, we can say that, because of the difference in intermolecular attractions, an alcohol has a higher boiling point than a comparably-sized ether.

- Properties of materials are closely related to their structure
- Two isomeric compounds, composed of exactly the same elements in exactly the same ratio, may have very different properties because of the different ways that the atoms are connected within the compounds.

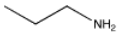
Another example of isomers is found by looking at the formula C_3H_9N. This time there are three different structures that can occur with the given formula. All three isomers contain the "amine" functional group. An amine is just a nitrogen connected to a mixture of carbons and hydrogens. Again, the three isomers have different properties, and these differences are not just restricted to melting points and boiling points. What factor do you think is responsible for these differences.



trimethylamine



N-methylethylamine



n-propylamine

compound	melting pt, ° C	boiling pt, ° C	density, g/mL
trimethylamine	**-117**	**3**	**0.6356**
N-methylethylamine	**not reported**	**37**	**0.688**
n-propylamine	**-83**	**48**	**0.7173**

The differences in melting points and boiling points are quite straightforward. The first example possesses no potential for hydrogen bonding. The second one does because it contains an N-H bond and the third even more so, because it contains two N-H bonds rather than one.

Unlike alcohols and ethers, whether or not an amine contains an N-H does not change the name of the functional group. It is still called an amine. That may be an unfortunate artifact of history, because clearly an amine that can hydrogen bond is a little different from an amine that cannot, in just the same way that an alcohol is different from an ether. To compensate for that lack of distinction between amines, an additional adjective is used to describe them. An amine in which the nitrogen is attached to only one carbon and two hydrogens is called a "primary amine" (primary means one, as in one carbon attachment). An amine in which the nitrogen is attached to two carbons and one hydrogens is called a "secondary amine" (secondary means attachment to two carbons). An amine in which the nitrogen is attached to three carbons and no hydrogens is called a "tertiary amine" (attachment to three carbons).

Isomers have a variety of properties that are different from the properties of other members of their group. Not all of these properties can be easily explained by looking at different structures, but some can. The **density** of a material is the ratio of its weight to its volume (in more "scientific" language: mass/volume). A material with a higher density than another can be thought of as having the same weight, but shrunken to a smaller volume. Alternatively, it could be thought of as having the same volume, but packed full of more mass.

Note that the isomers in the table above have different densities. The densities in the table refer to liquid densities. Despite their similarities, the three compounds in the liquid state pack together a little differently. That, too, is a result of structural differences.

Exercise 7.8.2

Explain the differences between the densities in the table above. The values in the table all refer to the materials in their liquid states.

Answer

There is hydrogen bonding between molecules of *N*-methylethylamine, but not between molecules of triethylamine, which are held together by relatively weak dipoles. Trimethylamine molecules are not held together as tightly as the *N*-methylethylamine molecules, which therefore pack more densely. On the other hand, *n*-propylamine contains two N-H bond, compared to only one in *N*-methylethylamine. Consequently, *n*-propylamine has a greater propensity to form hydrogen bonds, and it packs together even more densley than the *N*-methylethylamine.

Exercise 7.8.3

Although this information is not noted in the table above, density values are usually listed along with the temperature at which the value was measured. That's because density is actually a function of temperature. Most materials become more dense as they get colder and less dense as they get warmer. Explain why density varies with temperature.

Answer

Temperature is a measure of how much energy is available in the environment. As temperature increases, molecules obtain more energy and they transfer that energy into a variety of molecular motions. As they move around more, they are less able to remain densely packed. The density decreases as the temperature goes up. Conversely, things tend to shrink as they cool, because molecules slow down and begin to pack more tightly. They become more dense.

There are other properties that can be compared and explained based on the structures of compounds. **Vapour pressure** is closely related to boiling point. It refers to the pressure exerted by molecules escaping from a liquid into the vapour phase. The more easily molecules can get away from each other in the liquid and escape into the vapour phase above the liquid, the higher the vapour pressure. The higher the vapour pressure, the more easily the liquid reaches the boiling point. In a simple sense, we can think of strong attractions between molecules holding them in the liquid phase and lowering their vapour pressure.

Viscosity refers to the resistance to flow in a liquid. The higher the viscosity of a liquid, the more slowly it flows. Maple syrup is more viscous than water, but honey is more viscous than maple syrup. In a simplified way, we can think of molecules clinging to their neighbors as they flow past each other, hindering flow and increasing viscosity. Thus, the intermolecular attractions between molecules in a liquid affect its viscosity.

It's a little like a group of friends rushing down a crowded street in Manhattan. If they all hold hands, they don't make as rapid progress as they would individually. Individually, each member of the group is able to step aside, dart forward and get past the oncoming pedestrians. Clinging together, they all have to turn, come to a halt and wait for people to let them past.

Surface tension is a measure of how strongly a liquid resists external forces. You might think of it as how tightly the molecules in a material cling to each other when given the chance to cling to something else instead.

The most familiar picture of surface tension is a drop of water. Water forms drops because the molecules in the water cling to each other more strongly than they do to the molecules in the air. Those are mostly nitrogen molecules, N_2, with a significant fraction of oxygen molecules, O_2. The molecules in the air are quite non-polar, because they are made of the same kinds of atoms: two nitrogens, for instance. There is no electronegativity difference that would impart a dipole to the molecule. That's in stark contrast to a highly polar water molecule; it's hard to find molecules more polar than that. If a water molecule were to interact with a molecule of dinitrogen, it would be trading in some strong hydrogen bonds with other molecules. That wouldn't be worth it.

Exercise 7.8.4

Explain the differences in the vapour pressures of the following compounds (listed in hectoPascals, hPa).

a. acetic acid, CH_3CO_2H (15.3) vs. propan-2-one, $CH_3(CO)CH_3$ (240)
b. ethyl acetate, $CH_3CO_2CH_2CH_3$ (97) vs. diethyl ether, $CH_3CH_2OCH_2CH_3$ (587)
c. pentane, $CH_3CH_2CH_2CH_2CH_3$, (573) vs. heptane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ (48)

Answer a:

Acetic acid posesses hydrogen bonding capability, whereas 2-propanone has the ability to form only dipole-dipole interactions. Thus, 2-propanone molecules are not held in the liquid phase as strongly as acetic acid, and the former

compound has a higher vapour pressure.

Answer b:

The C=O bond of ethyl acetate has a substantial dipole, but the dipoles in ether don't add up to very much; they are smaller to begin with and they partially cancel out via vectorial addition. Ether molecules can escape the liquid more easily, resulting in a higher vapour pressure.

Answer c:

Both molecules are limited to relatively weak London dispersion interactions. Because heptane forms a longer chain than pentane, there will be a slightly greater interaction between heptane molecules than between pentane molecules. Pentane thus has the higher vapour pressure.

Exercise 7.8.5

Explain the differences in the viscosities of the following compounds (listed in centiPoise, cP, or milliPascal-seconds, mPa·s).

a. diethyl ether, $CH_3CH_2OCH_2CH_3$ (0.22) vs. 2-butanone, $CH_3(CO)CH_2CH_3$ (0.41)
b. decane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ (0.70) vs hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$ (0.26)
c. diethyl ether, $CH_3CH_2OCH_2CH_3$ (0.22) vs. 1-butanol, $CH_3CH_2CH_2CH_2OH$ (2.54)

Answer a:

The C=O bond 2-butanone has a substantial dipole, but the dipoles in ether don't add up to very much; they are smaller to begin with and they partially cancel out via vectorial addition. The 2-butanone molecules cling together more strongly, resulting in a higher viscosity.

Answer b:

Both molecules are limited to relatively weak London dispersion interactions. Because decane forms a longer chain than hexane, there will be a slightly greater interaction between decane molecules than between hexane molecules. Decane thus has the higher viscosity. Later, if you study macromolecules, you will see that in very, very long chains, "entanglement" becomes a factor as well. Just as the name implies, really long chains get tangled up together and have a difficult time moving past each other; that's why materials like cooking oil and motor oil are so viscous.

Answer c:

The 1-butanol can hydrogen bond together, but the ether only has weak dipole-dipole interactions. The 1-butanol is therefore more viscous.

Exercise 7.8.6

Explain the differences in the surface tensions of the following compounds (listed in dynes/cm).

a. 1-butanol, $CH_3CH_2CH_2CH_2OH$ (25) vs diethyl ether, $CH_3CH_2OCH_2CH_3$ (16)
b. 1-butanol, $CH_3CH_2CH_2CH_2OH$ (25) vs 1,3-butanediol, $HOCH_2CH_2CH(OH)CH_3$ (47)
c. formamide, $H(CO)NH_2$ (57) vs. nitromethane, CH_3NO_2 (36)

Answer a:

The 1-butanol can hydrogen bond together, but the ether only has weak dipole-dipole interactions. The 1-butanol therefore has greater surface tension.

Answer b:

The 1-butanol can hydrogen bond together, but the 1,3-butanediol has two OH groups and can form even more hydrogen bonds than 1-butanol can. The 1,3-butanediol therefore has greater surface tension.

Answer c:

The formamide has N-H bonds and so it is capable of hydrogen bonding. Despite having a pretty darned big dipole, the nitromethane can't really hydrogen bond together. The formamide therefore has greater surface tension.

You don't have to have data in front of you to compare two compounds' properties. At least to some extent, you may be able to look at two similar structures and make an educated guess about which one will melt or evaporate more readily than the other, provided they have different functional groups that you can compare. Knowing something about structure has explanatory value; you can explain differences based on structure. It also has predictive value: you can predict differences based on structure.

Exercise 7.8.7

In the following pairs of isomers, which one would be expected to have the highest boiling point?

a. 2-propenol, CH_2CHCH_2OH vs propanal, CH_3CH_2CHO
b. ethyl pentanoate, $CH_3CH_2O_2CCH_2CH_2CH_2CH_3$ vs heptanoic acid, $CH_3CH_2CH_2CH_2CH_2CH_2CO_2H$
c. 1-hexen-3-one, $CH_2CHCOCH_2CH_2CH_3$ vs diallyl ether, $(CH_2CHCH_2)_2O$

Answer a:

2-propenol. It has hydrogen bonding capability but propanal does not.

Answer b:

heptanoic acid. It has hydrogen bonding capability but ethyl pentanoate does not.

Answer c:

1-hexen-3-one. Its dipole is greater than that in the ether, because it comes from a C=O bond rather than C-O bonds.

Exercise 7.8.8

In the following pairs of isomers, which one would be expected to have the highest viscosity?

a. 2-butanone, $CH_3COCH_2CH_3$ vs. methyl allyl ether, $CH_3OCH_2CHCH_2$
b. pentane, $CH_3CH_2CH_2CH_2CH_3$ vs octane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
c. dimethoxyethane, $CH_3OCH_2CH_2OCH_3$ vs 1,3-butanediol, $HOCH_2CH_2CH(OH)CH_3$

Answer a:

2-butanone. Its dipole is greater than that in the ether, because it comes from a C=O bond rather than C-O bonds.

Answer b:

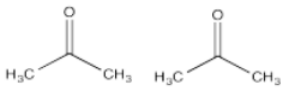
octane. It has greater London dispersion interactions that pentane because of the greater surface contact area in octane.

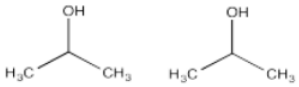
Answer c:

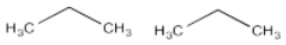
1,3-butanediol. It has hydrogen bonding but the DME does not.

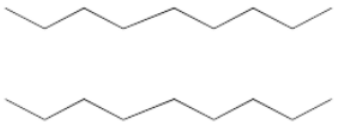
Exercise 7.8.9

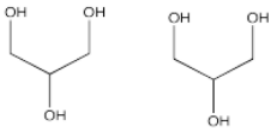
In each of the following questions, you have a choice between A and B. Choose which option in which stronger attractions are present.

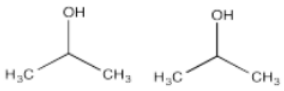
A. 

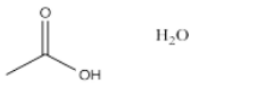
B. 

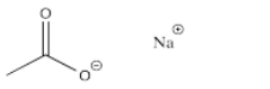
A. 

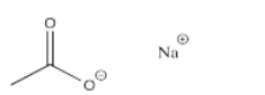
B. 

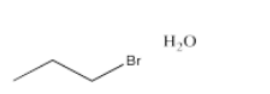
A. 

B. 

A. 

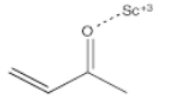
B. 

A. 

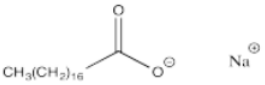
B. 

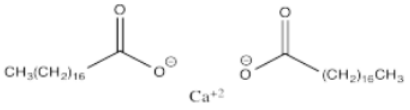
A.

B.

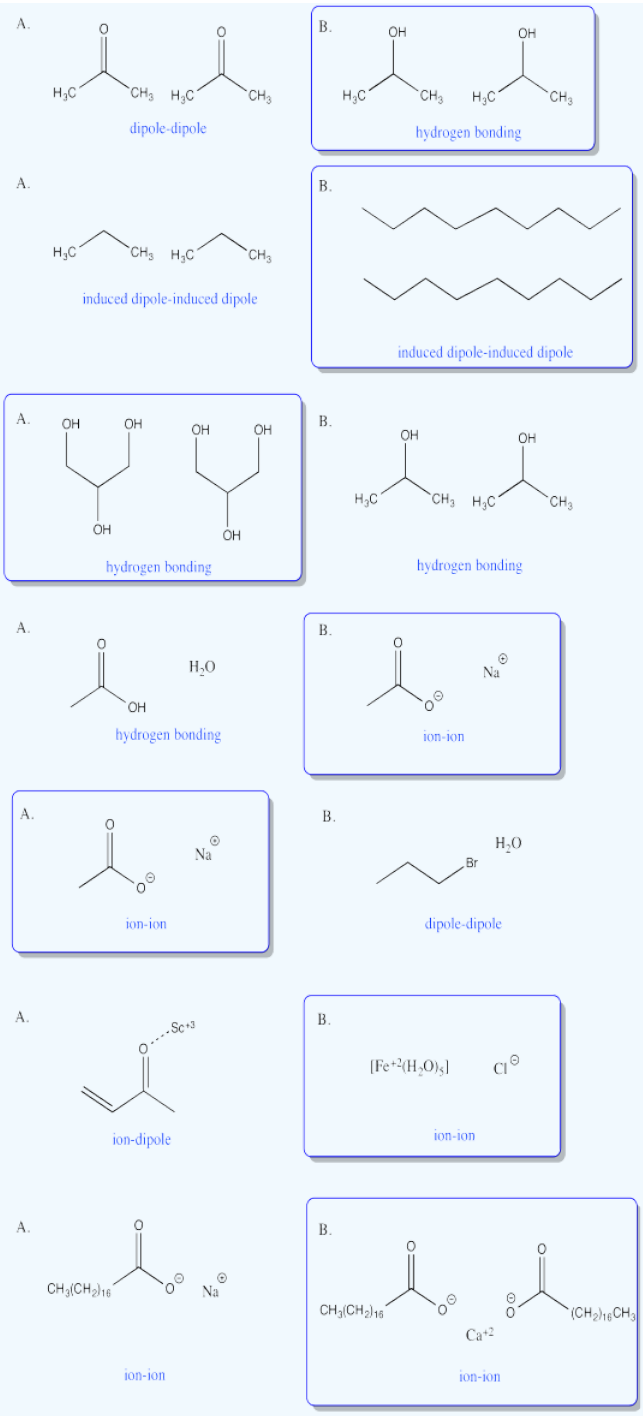
A. 

B.

A. 

B. 

Answer



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7.9: Miscibility

So far, we've been thinking about how one molecule could interact with another molecule of the same compound to form a liquid or a solid. What about two different compounds? It turns out that whether two different compounds interact with each other depends on the same kinds of interactions we have looked at so far.

Two liquids that do not really mix well together, such as oil and water, are described as immiscible. Two liquids that appear to mix completely together are said to be miscible. Water and ethanol are one example of a pair of miscible liquids, because you can take any amount of ethanol and mix it with any amount of water and you will always end up with a clear, colorless liquid just like the ones you started with.

Exercise 7.9.1

What kind of intermolecular attraction allows water and ethanol to mix together?

Answer

Hydrogen bonding.

Exercise 7.9.2

The following pairs of liquids are miscible. Identify the predominant type of intermolecular attraction between each pair.

a. 2-propanone and ethyl ethanoate (ethyl acetate)
b. pentane and octane
c. dichloromethane and 2-butanone
d. methanol and ethanoic acid

Answer a:

dipole interactions

Answer b:

London interactions

Answer c:

dipole interactions

Answer d:

hydrogen bonding

Exercise 7.9.3

Explain, in terms of intermolecular forces, why water and octane are not miscible.

Answer

Water molecules interact with each other mainly through hydrogen bonding, whereas octane molecules interact with each other via London interactions. The main problem here is the strong hydrogen bonding between the water molecules. All molecules, in principle, could interact with each other via London interactions. However, if octane molecules were introduced among the water molecules, they would take up space. Some of the water molecules would not be able to get close enough to each other to hydrogen bond anymore. The loss of that very stabilizing interaction would be too costly.

Exercise 7.9.4

Explain, in terms of intermolecular forces, why ethanenitrile and hexane are not miscible.

Answer

This problem is similar to the previous one, but in this case the attraction between the strong dipoles of the nitrile groups would be too much to overcome.

Sometimes, the attractions between molecules are a little more complicated. Two molecules may have different interactions on their own, but when placed together still manage to interact with each other. For example, dichloromethane and hexane mix together pretty well.

How can that be? Dichloromethane has dipole interactions. Hexane has nothing more than London interactions. Ethanenitrile and hexane didn't mix for that very reason. But the problem was not whether those two molecules could interact with each other; they could. The problem was that ethanenitrile would not give up its dipole-dipole interactions for the small amount it could gain by mixing with hexane.

In this case, the dipoles between dichloromethane are much smaller; they aren't held back from the hexane molecules as strongly. On the other hand, the interaction between the the hexane and dichloromethane is actually amplified a little bit. Whereas hexane molecules rely solely on weak, transient London interactions to cling to each other, dichloromethane has a permanent dipole. That permanent dipole is able to enhance the transient dipole in hexane.

This is called a dipole / induced dipole interaction. The slight tug dichloromethane exerts on hexane's electrons actually helps the two different molecules interact more strongly.

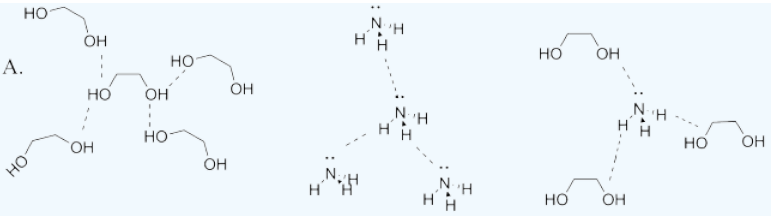
Exercise 7.9.5

Below are several solvents and some possible solutes. For each pair,

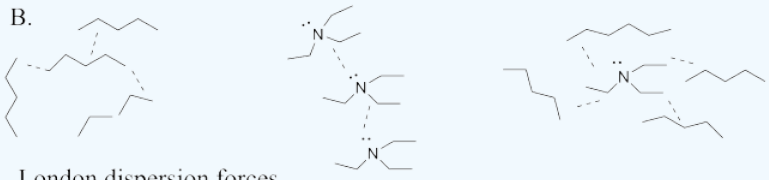
i. Draw a solvent molecule interacting with several other (identical) solvent molecules. Label the strongest intermolecular force holding them together.
ii. Draw a solute molecule interacting with several other (identical) solute molecules. Label the strongest intermolecular force holding them together.
iii. Draw one solute molecule interacting with several solvent molecules. Label the strongest intermolecular force holding them together. Predict whether the solvent will dissolve significant amounts of the solute.

A. Solvent = Ethylene glycol ($HOCH_2CH_2OH$); Solute = NH_3
B. Solvent = Pentane ($CH_3(CH_2)_2CH_3$); Solute = triethylamine, $[(CH_3CH_2)_3N]$
C. Solvent = CH_2Cl_2; Solute = NaCl

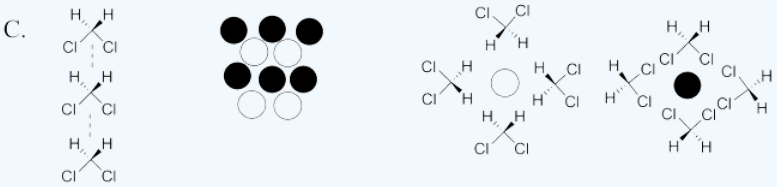
Answer



IMF's comparable; therefore solute is likely soluble.



Even though forces are different, the dipole in the amine is weak and there would also be significant LDF's between the pentane and the ethyl groups, so likely miscible.



Given that the dipole in CH_2Cl_2 is weak, NaCl will likely not dissolve.

Exercise 7.9.6

Describe the intermolecular interaction between each of the following pairs.

a) 2-propanone; benzene

b) 2-propanol; dichloromethane

c) ethanol; ethanoic acid

d) octanol; methylbenzene

Answer a:

dipole / induced dipole

Answer b:

dipole / dipole

Answer c:

hydrogen bonding

Answer d:

dipole / induce dipole

Solubility is conceptually similar to miscibility. If you can mix a solid with a liquid and the solid particle gets smaller and smaller until it disappears, it must have dissolved in the liquid. At that point it may look like you are left only with the original liquid, but really the individual molecules of the solid are just distributed throughout the liquid instead of all sitting together on the bottom. You can see this when blue kool-aid powder dissolves in water to give blue kool-aid. The blue substance has not disappeared; it has become intimately mixed with the water. Just as you cannot see an individual "chunk" of water, you cannot see an individual "chunk" of the original solid anymore -- it has separated into individual units (molecules) that are too small to be seen.

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7.10: Solubility

In order for two substances to be miscible, or in order for one substance to be soluble in another, the two kinds of molecules must interact with each other. Not only that, but there must be strong enough attraction of one type of molecule for the other so that they are willing to move away from their identical siblings. If the attractive forces between the unlike molecules are strong enough to overcome those forces between both sets of like molecules, dissolution results.

Table salt dissolves in water because the very polar water molecules attract both the positively charged sodium ions and the negatively charged chloride ions. This interaction is called an ion / dipole interaction.

In order to distribute the sodium cations and chloride ions throughout the solution, some of the water molecules may need to back away from each other to make room for the ions. Some of the strong hydrogen bonds may be lost, but the energy needed to overcome those interactions is compensated by the attraction between the dipole of the water and the sodium or chloride ions.

Other salts dissolve in water, too, but some of them dissolve more easily than others. You could easily dissolve about 360 g of table salt in a liter of water, but the solubility of calcium carbonate is only about 0.01 grams per liter. That's partly due to the fact that the ions in sodium chloride, Na^+ and Cl-, have lower charges than the ions in calcium carbonate, Ca^{2+} and CO_3^{2-}. The higher the charges on the ions, the stronger their electrostatic attraction for each other, and the harder it is for the water to pull them apart. It's a good thing, too; if the calcium carbonate in marble were to dissolve too easily, think of how many buildings and statues would dissolve in the rain.

Exercise 7.10.1

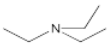
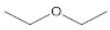
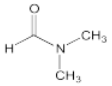
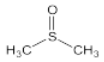
Rank the following salts from most easily to least easily dissolved in water: $MgSO_4$, LiCl, $AlPO_3$

Answer

The predicted order, from most soluble to least, would be LiCl > $MgSO_4$ > $AlPO_4$ because the ions increase in charge from 1+/- to 2+/- to 3+/-

The factors that control the solubility of ions can be complex, though. For example, the charges on the ions also affect the strength of the interaction with the water molecules. Highly charged ions interact more strongly with each other, but they also interact more strongly with water molecules.

There are other solvents that can dissolve salts via ion / dipole interactions. Typically they would have strong dipoles. However, not many solvents have dipoles as strong as that of water.

Name(s), Abbreviation	Structure	Dielectric Constant
triethylamine, TEA		2.43
ether, diethyl ether, Et_2O		4.3
tetrahydrofuran, THF		7.5
methylene chloride, dichloromethane, DCM		9.1
pyridine, py		12.5
methanol, MeOH		30
acetonitrile, ACN		37.5
N,N-dimethylformamide, DMF		38
dimethylsulfoxide, DMSO		46.7
water		80
formamide		38

Exercise 7.10.2

Which of the following solvents would be most capable of dissolving some LiCl? Rank from greatest solubility to least solubility.

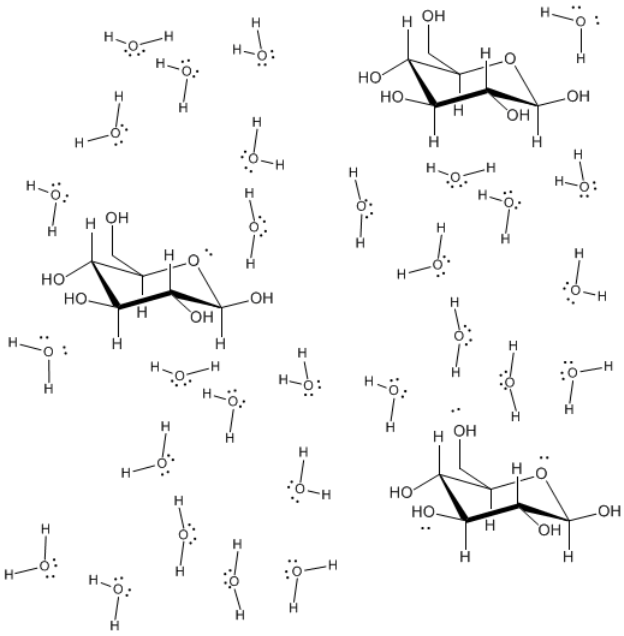
triethylamine, dimethylsulfoxide, dichloromethane, acetonitrile, pyridine.

Answer

The predicted order, from most soluble to least, would be

dimethylsulfoxide > acetonitrile > pyridine > dichloromethane > triethylamine.

Of course, it isn't just salts that can dissolve in solvents. Other solids can, too, if they can interact with solvent molecules strongly enough. Sugar also dissolves pretty well in water. Why do you think that is so?



sugar dissolved in water

Sugars, of course, can hydrogen bond easily with water, so they are usually pretty soluble.

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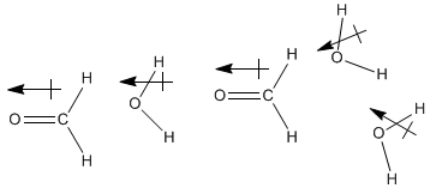
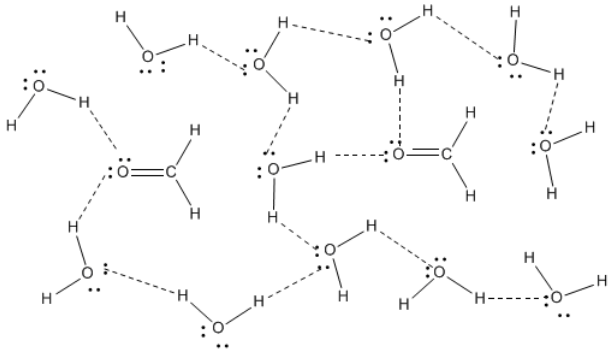
7.11: Hydrogen Bond Acceptors

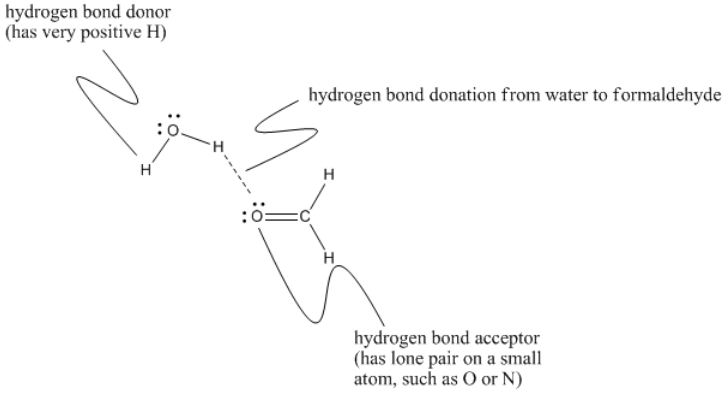
Formaldehyde is another example of a compound that dissolves well in water, and in fact the most common way to obtain formaldehyde is as an aqueous solution. You may have encountered such a solution in an anatomy or general biology lab, because formaldehyde solutions are used as preservatives for biological specimens. Of course, water and formaldehyde are both polar molecules, so it is easy to imagine their dipoles interacting together. However, formaldehyde does not have very strong hydrogen bonds like water does, so at first glance it seems as if formaldehyde might not interact with water molecules as strongly as water molecules interact with each other.



Actually, the interaction between these molecules may be stronger than it first seems. Although formaldehyde does not engage in strong hydrogen bonds by itself, in the presence of water or another protic compound -- one that contains a very positive hydrogen, such as H_2O, HF or NH_3 -- strong hydrogen bonds do form.



This occurs because formaldehyde has an oxygen atom with lone pairs and so it can act as a *hydrogen bond acceptor*. That means it can engage in hydrogen bonding with something that does have positive hydrogens that can interact with its lone pairs. The water in this case is acting as the *hydrogen bond donor* for formaldehyde. Hydrogen bond acceptors are often important in biological systems, where nearly everything takes place in the presence of water.



Exercise 7.11.1

Which of the following compounds are capable of hydrogen bonding? Which are hydrogen bond acceptors? Which are neither?

a) triethylamine

b) pentanal

c) ethylamine

d) diethyl ether

e) butanamide

f) hexene

Answer a:

H-bond acceptor

Answer b:

H-bond acceptor

Answer c:

Fully H-bonding

Answer d:

H-bond acceptor

Answer e:

Fully H-bonding

Answer f:

neither

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7.12: Heterogenous Mixtures

Why does not oil dissolve in water? Oil is composed, in part, of long chains of carbon atoms with hydrogens attached. These chains aren't very polar. It shouldn't be too hard to pull them apart, because they are held together only by London interactions. The chains really aren't long enough to create the strong London interactions that would prevent oil from mixing with water.

On the other hand, it is pretty difficult to pull water molecules away from each other, and the oil does not have the means to do so; it just isn't polar enough. If the water molecules don't move away from each other, there will be no room between them for the individual oil molecules to become dissolved. These two substances will not mix together very well.

Consequently, if placed in the same vessel, they will remain separate and form two different layers. The more dense layer (the water) will sink to the bottom while the lighter, less dense one (the oil) will float to the top.

The same situation is true for a number of other, non-polar organic compounds, such as benzene and toluene. These liquids are too non-polar to dissolve very well in water. Consequently if you mix benzene and water, the two liquids will form two separate layers. Benzene has a specific gravity or density of 0.874 g/mL, whereas the density of water is 1.0 g/mL. As a result, benzene would float on the top, while water would sink to the bttom. Mixing the two layers up as hard as you can may produce temporary mixing (the mixture would form a sort of cloudy, sparkly mess called schlieren), but once left alone the benzene and water would separate out again.

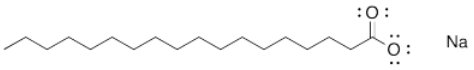
There's one more useful example we should look at. Suppose we have a molecule that is very polar on one end, but non-polar at the other. Soap, for instance, is an ionic compound, but while the cation is usually just a sodium ion, the anion is more complicated. This molecular anion most often contains a very polar "carboxylate group", composed of a carbon with two attached oxygens. It also contains a very long carbon chain, just like in the oil. So one part of the molecule should dissolve well in water, while the other does not. There is a trade-off, and a balance will be struck that determines exactly how soluble the soap is in the water. Interestingly, when placed in water, these soap molecules will arrange themselves in groups so that the polar ends face outward, towards the water, while the nonpolar ends are tucked on the inside. Think of the "circle the wagons" scene in a classic western movie.

There are two reasons why this phenomenon is useful. Micelle formation, as the behavior is called, allows nonpolar substances, such as dirt and oils, to be dissolved in the polar water. The dirt can interact perfectly well with the nonpolar soap tails, and so it will end up in the middle of the micelles, and something that could not be dissolved in plain water turns out to be perfectly soluble in soapy water. But at another level, micelle formation is a very good model for some of the phenomena of cell and molecular biology. For instance, cell membranes are composed of molecules that are somewhat similar to soap molecules. These molecules form groupings similar to large micelles, but with an additional layer of molecules on the inside of the circle, with their polar ends pointing inward. That leaves the nonpolar ends of both layers sandwiched together, out of the water. Proteins also have polar and non-polar regions, and getting the non-polar regions away from the water leads the protein to adopt a specific shape that, in turn, determines the behavior of the protein.

Exercise 7.12.1

The structure of soap is shown below.

a. Calculate the formal charge on the oxygens and the sodium.



b. The 'tail' of the soap is circled. Is it polar or non-polar?

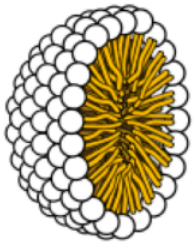
c. What type of IMF would you predict for:

tail-tail of 2 soap molecules: _____
head-tail of 2 soap molecules: _____
water-tail of a soap molecule: _____
water-head of a soap molecule:_____

d. Would you expect the tails to be soluble in water?

e. Which IMF interactions would be strongest?

f. Soap molecules form micelles (shown below) in water. Draw several water molecules in this picture. Where will they be (inside or outside) this micelle structure.



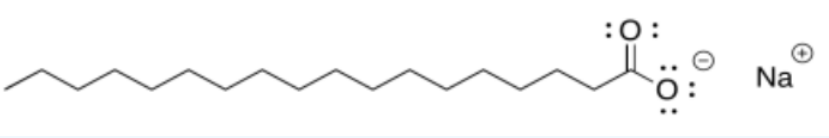
picture from wikipedia: http://en.wikipedia.org/wiki/Soap

f. Explain why soap forms this micelle structure in the presence of water. Use IMF.

g. Dirt is usually non-polar fats or other non-polar organic structures. Where would dirt be in this picture above?

h. How does soap clean dirt/grease off your hands?

Answer a:



Answer b:

Tail is nonpolar and hydrophobic. Head is polar and hydrophilic.

Answer c:

induced dipole - induced dipole

ion-induced dipole

dipole-induced dipole

ion-dipole

Answer d:

No. The dipole-induced dipole is too weak to overcome hydrogen bonding between waters.

Answer e:

Ion-dipole between water and the hydrophilic head of the soap.

Answer f:

outside

Answer f:

Water is attracted to the hydrophilic heads to form this strong ion-dipole interaction whereas the tails cannot overcome the strong hydrogen bonding of water-water interactions.

Answer g:

Hydrophobic dirt and grease will prefer to interact with the hydrophobic tails (inside micelles).

Answer h:

The grease will be encapsulated in the micelle and washed away in water.

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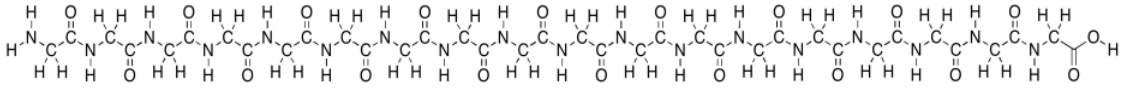
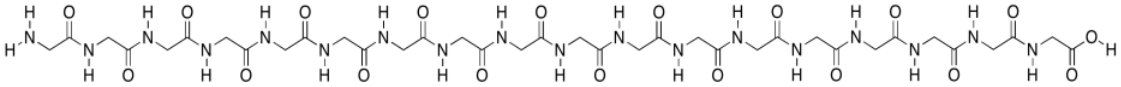
7.13: Intermolecular Attractions and Protein Structure

Intermolecular attractions contribute a crucial part to the behavior of everyday materials around us. In biology, attractions involving biomolecules are essential to their function. To get an idea of the role played by intermolecular attractions, such as hydrogen bonding, in biology, let's look at a common type of biomolecule: proteins.

Remember that proteins are polymers made up of lots of amino acids joined together ny peptide bonds. An explicit, atom-labeled structure is shown below. In addition, there is an abbreviated, skeletal structure below that. This line drawing does not label the carbon atoms explicitly; it does not even show where hydrogen atoms are if they are connected to carbons. You are just supposed to know that they are there. The trade-off is a much cleaner, simpler picture.

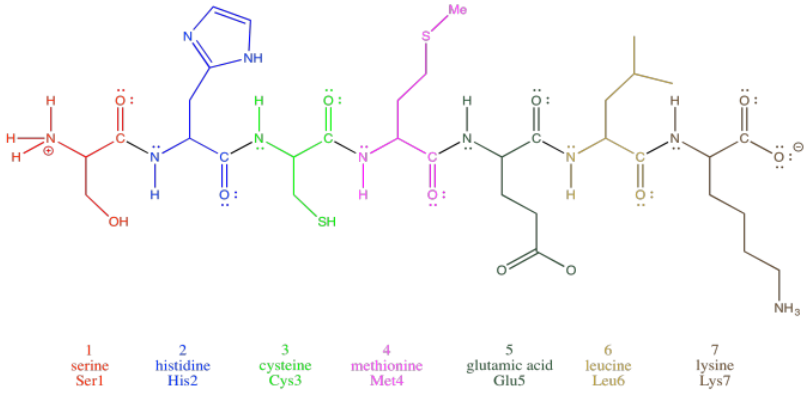




In the line structure, we can easily see the zig-zag backbone of the protein chain. Periodically along that chain we can see an amide bond (N-C=O). The amide bonds have been formed by joining the amino end of one amino acid to the carboxylic end of another.

This amino acid chain isn't very long; we probably wouldn't even call it a protein, because proteins are so much bigger than that. We would just call it a polypeptide or an oligopeptide -- the latter term means there are a bunch of amino acids in this chain, but not even enough to consider it a true polymer. The particular oligopeptide we are looking at is a poly(glycine) molecule. All of the amino acids are the same monomer: glycine.

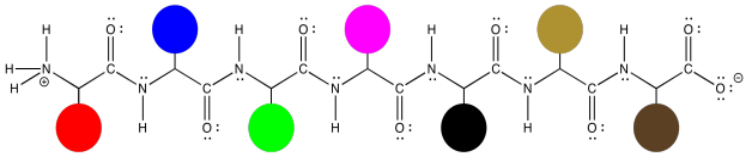
Oligopeptides, although not really proteins, are important in their own way. They are often used as signaling molecules because their small size allows them to travel relatively easily throughout an organism. Most proteins and oligopeptides are composed of different amino acids. Just to illustrate this idea, an example is shown below; it is a seven amino acid chain.



In order to help describe their structure, proteins and peptides are usually numbered, starting from the amino end of the chain (notice "oligopeptide" and "polypeptide" are a bit of a mouthful, so they often get shortened to the more general term "peptide"). Often, if a researcher wants to discuss a particular amino acid along the chain, they will list both its number and its amino acid identity. The amino acids differ from each other by their "side chain" or "residue"; that's the part hanging from the main backbone.If the water molecules don't move away from each other. For example, serine's side chain is a CH_2OH group; methionine's is a $CH_2CH_2SCH_3$ group. So, when you're reading the latest article in that issue of *Biochemistry* you've been waiting for all week, and they mention that Ser237 plays a crucial role in catalysing the formation of an important neurotransmitter, they are talking about a particular serine residue attached at the 237th position of the protein, counting from the nitrogen end.

Those protein structures can get a little bit complicated, simply because the molecules are so large. However, the basic idea of the structure is prettty simple. The same zig zag backbone runs throughout the entire molecule, and the residues are evenly spaced

along the backbone. Here, we can represent those different residues as colored dots. The structure starts to seem a little like a series of different balloons tied to a clothesline.

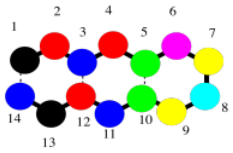


That isn't to see that the structures of those side chains are not important. They are very important, and we will get back to them a little later. Sometimes, though, you have to decide what you need to focus on right now, and it might be that we want to look at the backbone without the distraction of all of those side chain structures.

In fact, even the backbone might be too much detail. Maybe we just want to keep in mind that we are dealing with a polymer, a long chain of amino acids bound together. We might fall back to an even simpler drawing of colored beads on a string to signify that chain.

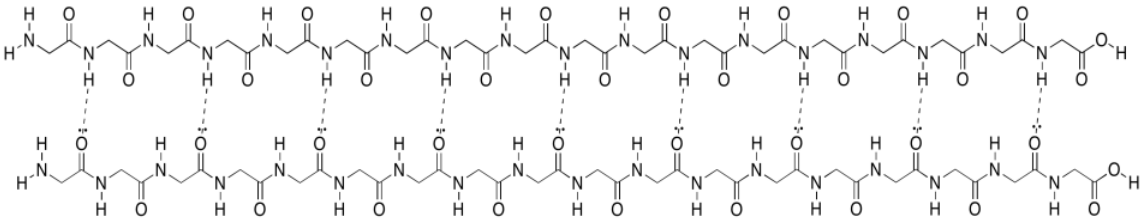
Now let's just stick with the simple beads on a string picture for a minute to think about protein structure. That simple order of amino acids -- which one is at the amino end of the chain, who comes after that, and who comes after that, all the way to the carboxylate end of the chain -- is called the primary structure of the protein. The **primary structure** is just what amino acids are found in the protein, and in what order.

The **secondary structure** is a second level of detail about the protein. It begins to describe the three-dimensional shape of the structure. That's where intermolecular attractions come in to the picture. A protein, being a very long chain, can usually reach back and interact with itself. Really, we should call these intramolecular attractions, since they are within the same molecule. The interactions could involve different side chains of the protein, but frequently they also involve the backbone. Remember, the backbone has lots of carbonyl oxygen capable of donating a lone pair, and lots of amide N-H bonds capable of donating a proton, so hydrogen bonding along the backbone is very important. The cartoon below tries to suggest a chain that has looped back alongside itself, and is held in place by some sort of interactions (the dashed lines).



That sort of motif, in which a protein can turn and run parallel to itself, and can be held in place by an interaction (specifically hydrogen bonds), is found in beta-sheets. Beta-sheets are very common in proteins.

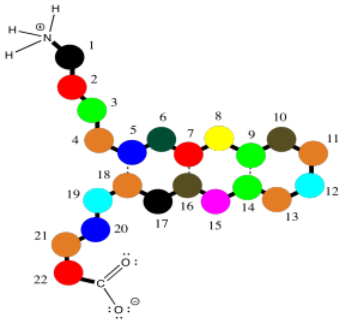
Unfortunately, the cartoon does not really convey any details about the intramolecular attractions that hold it in place. To see that, we should take a look at a more detailed example. Here we have that polyglycine oligomer again, and we are using it to illustrate hydrogen bonding between two chains to form a beta-sheet. In this case, we have drawn the two peptides as two separate molecules. However, as in the cartoon, we could also have one long peptide that turns back to run alongside itself.



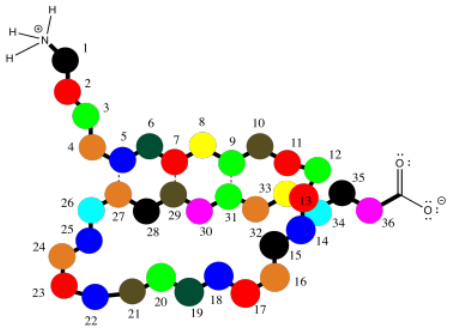
Note that, in the example above, the two chains are running in the same direction (the amino ends are on the left and the carboxylate ends are on the right). That's an example of what's called a parallel beta-sheet. You can also have an anti-parallel beta

sheet, in which the two chains are running in opposite directions. That is illustrated in the following diagram, using our simplified balloons-on-a-clothesline drawing.

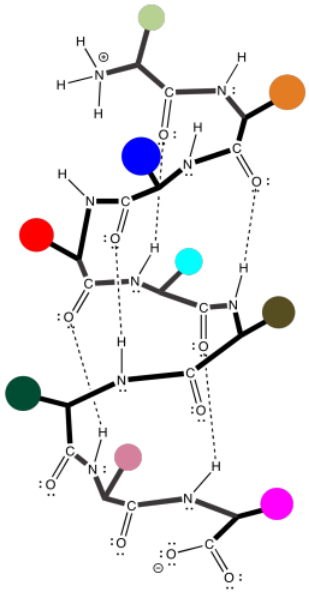
The hydrogen bonds are spaced slightly differently in these two cases. Once again, these might be two different peptide chains interacting with each other, but it is very common for one chain to undergo a turn and reach back to hydrogen bond with itself. That would put the two sections of chain running antiparallel to each other. This idea is illustrated in the simple cartoon below.



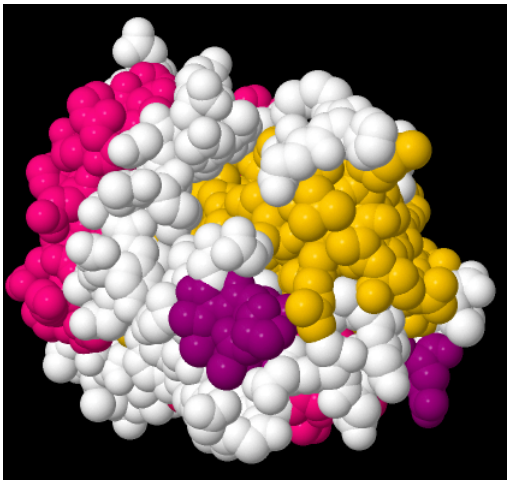
The earlier case, of a parallel beta-sheet, is also possible in a single chain; it simply involves a much longer turn, so that the chain loops around to run in the same direction as the original section. This case is illustrated in the cartoon below.



Beta sheets, of both kinds, are very common in proteins. So are alpha-helices, in which a peptide chain coils around like a spiral staircase. It is held in that shape, once again, by hydrogen bonding along the backbone of the protein.

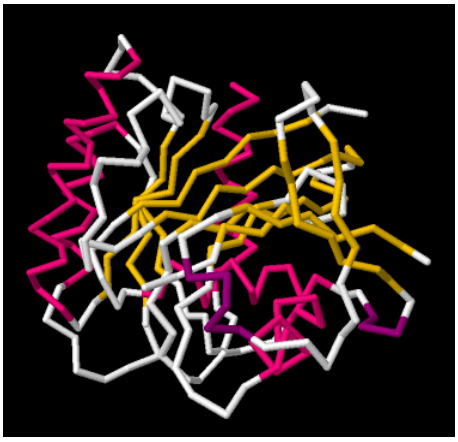


Beta-sheets and alpha-helices are two common examples of secondary structure. They are units of structural organization that frequently show up in protein structures. Look at the following example; it's a picture of a real crystal structure result for a protein. Researchers took this protein (in this case, it's called a GTP Binding Protein) and carefully got it into a crystalline form. Then they shone X-rays through the crystal. By analysing how the X-rays were scattered as they passed through the crystal, they could go back and determine where all of the atoms were. For that, they could get this "space-filling" picture, showing the positions of all the atoms.



That picture is a little complicated, but each round ball in that mass represents a carbon, oxygen, nitrogen, or sulfur (hydrogen atoms are usually too small to spot using X-rays). The colors were added by the researchers to keep track of parts of the structure they were interested in, and, you'll see in a minute, the secondary structures.

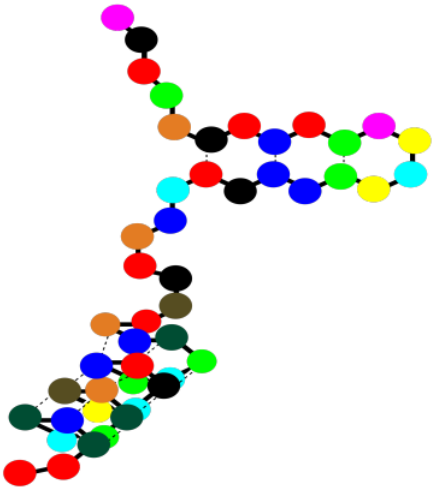
If we go to a simpler model, we will ignore individual atoms and just trace out that backbone chain of the protein. Things will suddenly look much less complicated.



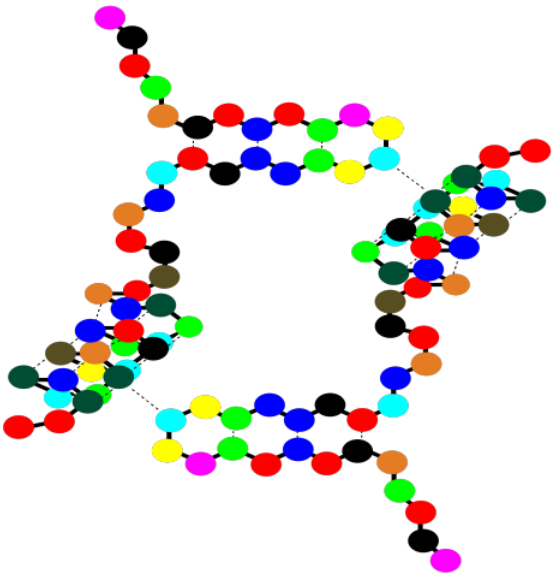
Now, if you take a look at the pink part on the left side, you can almost see how the backbone forms a coil, like a spiral staircase. That's an alpha helix. And those yellow zig-zags in the middle appear to be tracking each other. As one chain zigs up, so does its neighbour. When one chain zigs down, its neighbour follows. That's because they are connected. They are forming a beta sheet.

So the researchers simplify further, replacing part of the backbone with a pink helix. They replace other parts of the backbone with yellow ribbons; where the yellow ribbons run alongside each other, they are forming beta sheets. The arrows at the ends of the ribbons point towards the carboxylate end of the chain.

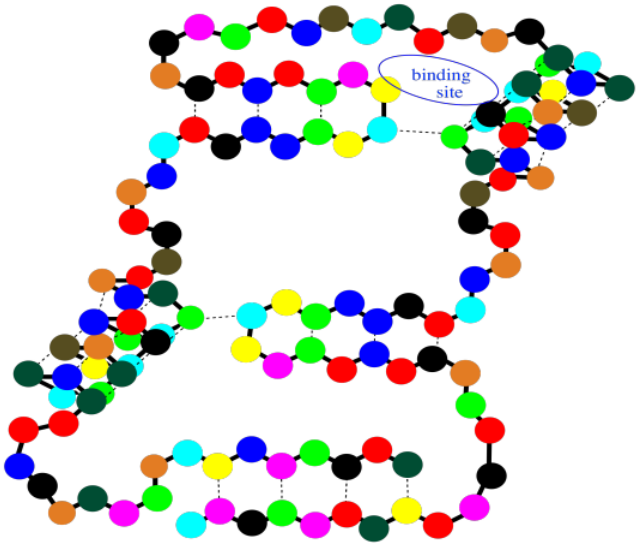
So a protein can contain both alpha helices and beta sheets. It can also contain less organized loops and turns. That higher level of structure -- how are the beta sheets and alpha helices and other things organized in space -- is called the **tertiary structure**. In a very simple cartoon, the protein might start with a length of chain, go into a beta sheet, run through another open length of chain or a loop, and finish with an alpha helix. The overall shape it forms is the tertiary structure.



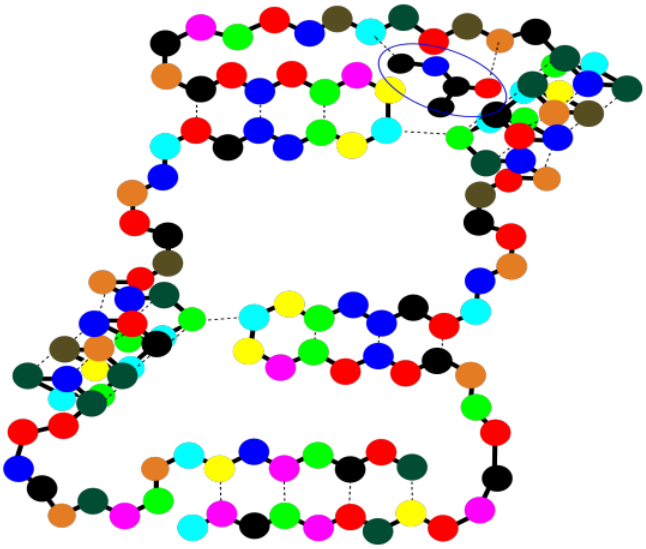
There is one more level of structure in a protein, although not all proteins have this feature. It is called the **quaternary structure**. A quaternary structure is really a cluster of more than one protein, stuck together. Below, the cartoon shows a dimer. Two identical tertiary structures are held together by intermolecular attractions. QUaternary structure is an example of what's called a "supramolecular assembly". That's when two or more molecules come together and hold on tightly, forming a bigger structure that's bigger than a molecule.



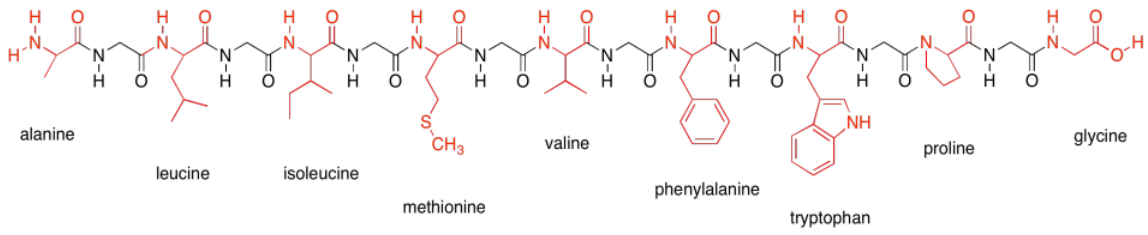
Notice that there are gaps within that cartoon structure. Those gaps can be very important. Usually a protein packs very tightly and does not leave many spaces; when a space is there, it is often for a specific reason. A gap in a protein can hold another molecule. The other molecule might be another protein that arrives and "docks" temporarily while some important task is performed. It might also be a small molecules that needs to bind with the protein to accomplish some goal.



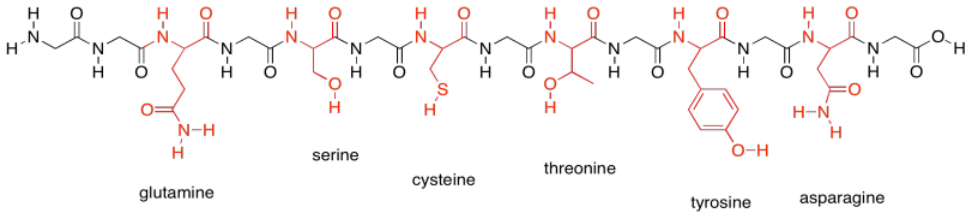
These binding sites are crucial for your survival as an organism. At the same time, they are also exploited by physicians when they prescribe a medication. The drug that the doctor gives you, more often than not, binds in a specific place in a specific protein, tweaking its activity a little. Usually it gets the protein to slow down and take a break, but in some cases it may pep the protein up a little bit and make it work harder. Of course, whatever the small molecule it, and whatever it's doing there, it binds into that "active site" through intermolecular attractions.



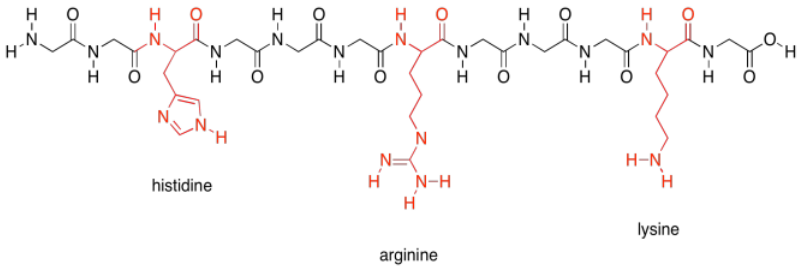
That's it for protein structures. Let's just take a minute, though, to get to know the amino acids that make up proteins. The amino acids are usually divided into four different categories, partly based on their potential for intermolecular attraction. Here are the **nonpolar amino acids**. They are sometimes called the hydrophobic amino acids, because they can't hydrogen bond with things like water. They are shown here connected into a peptide chain, so that you can see what they would look like in a protein.



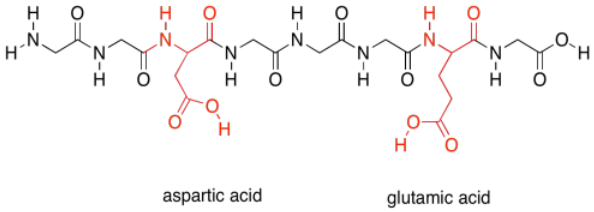
In contrast, the following group shows the members of the **polar amino acids**. They are much better at hydrogen bonding and other polar interaction, such as ion-dipole interactions.



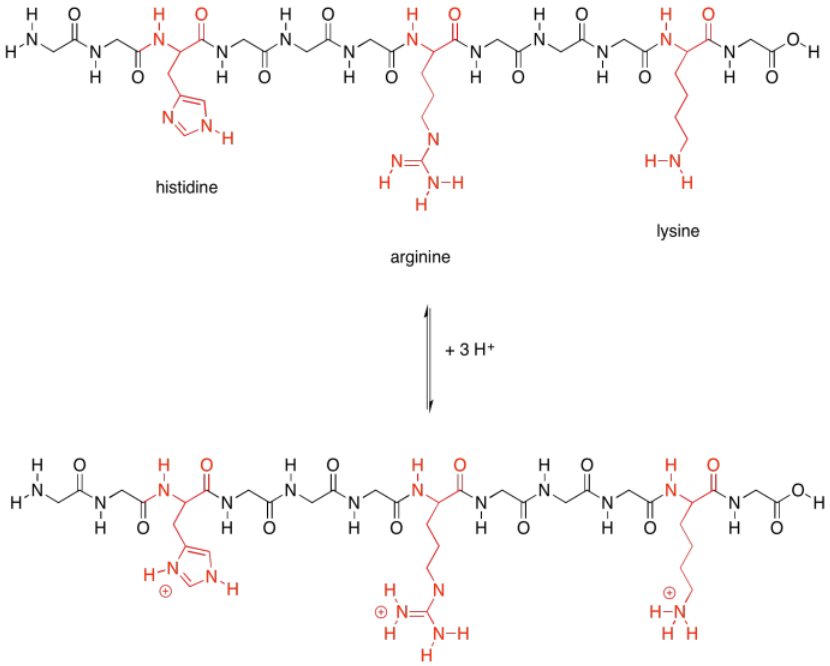
There are a few polar amino acids that were not included in that last group because they are special. These are the **basic amino acids**. There are just three of them.



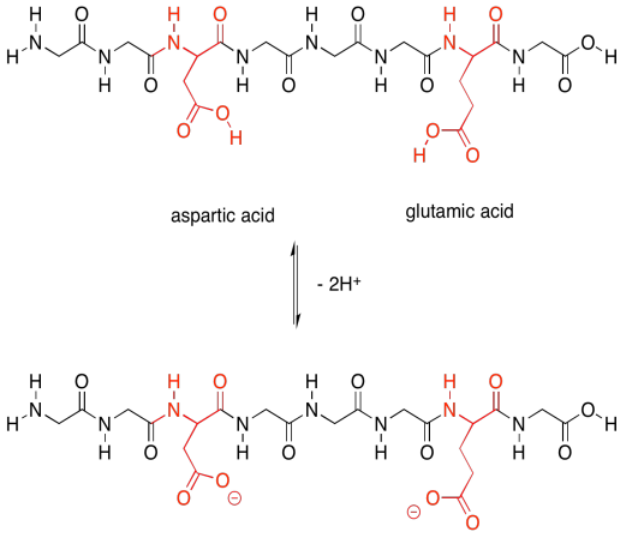
Finally, there are two more special polar ones. These are the **acidic amino acids**.



Those last two groups are special because each one actually has two possible structures. They will vary depending on their environment. The basic amino acids are each able to pick up an extra proton (an H^+ ion). That's very important; they help the protein carry out lots of important jobs by moving protons around.



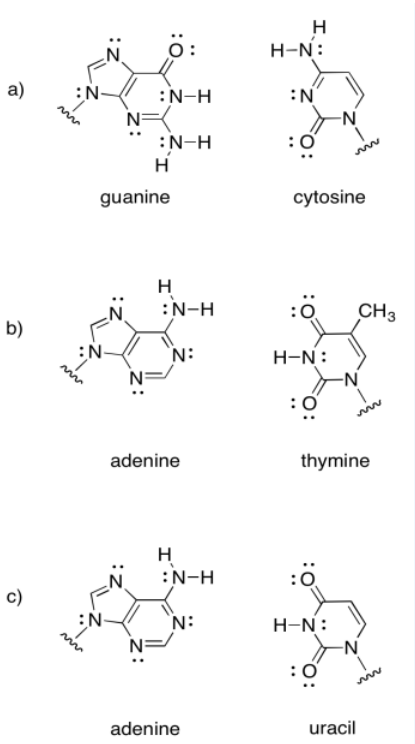
The acidic amino acids, on the other hand, can each give away a proton. They are also needed to carry out different tasks by the protein.



Not only that, but the acidic amino acids usually have a negative charge on their side chains, because usually they are in the state in which they have lost a proton. The basic amino acids often have positive charge on their side chains, for similar reasons: they are usually in the state with an extra proton. That means that these two sets of amino acids are capable of additional intermolecular attractions, both within the protein structure and with other molecules that may come along and bind to the protein.

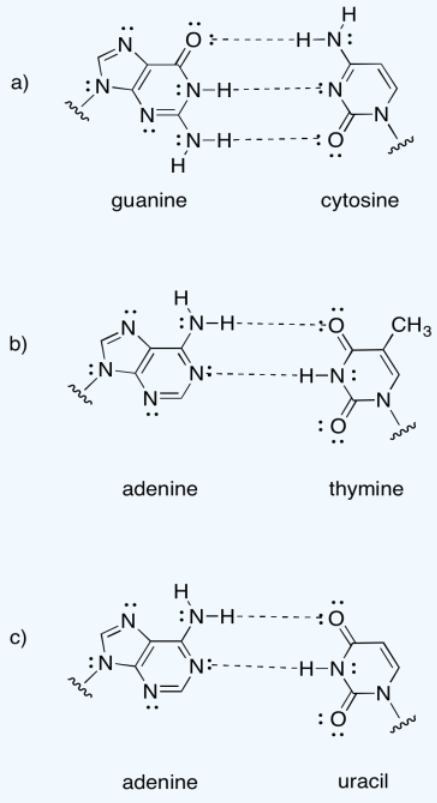
Exercise 7.13.1

Intermolecular attractions play a crucial role in other biomolecules, such as DNA. A DNA "molecule" is really a supramolecular assembly of two separate molecules. Show how the following DNA base pairs would hold onto each other.



Answer

Note that the last example is actually found in RNA, not DNA. RNA is found as a single strand, rather than a pair of strands. It hydrogen bonds to itself in a particular shape, not unlike the way a protein adopts a specific shape.



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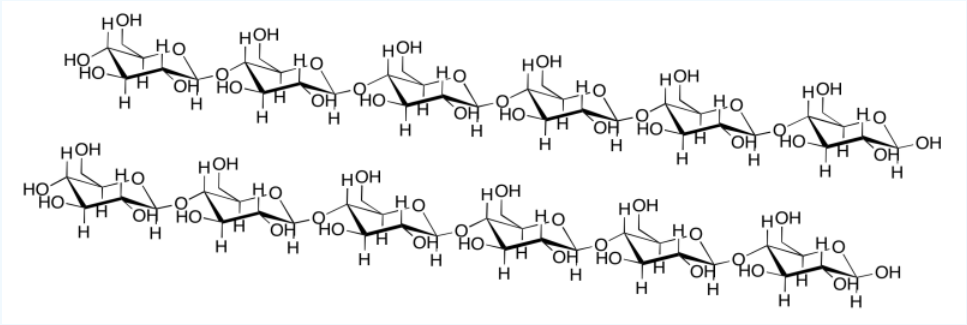
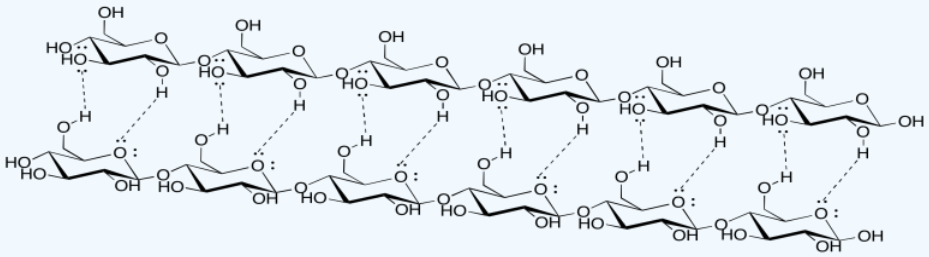
Exercise 7.13.2

Intermolecular attractions can be important in other biomolecules, such as cellulose. Show how the following cellulose chains could hold onto each other.

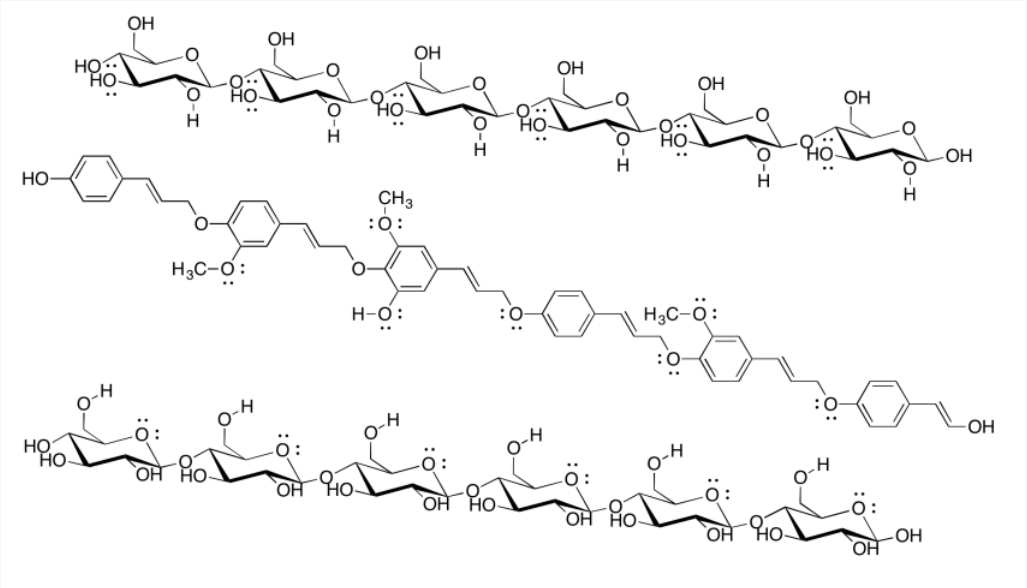


Answer



Exercise 7.13.3

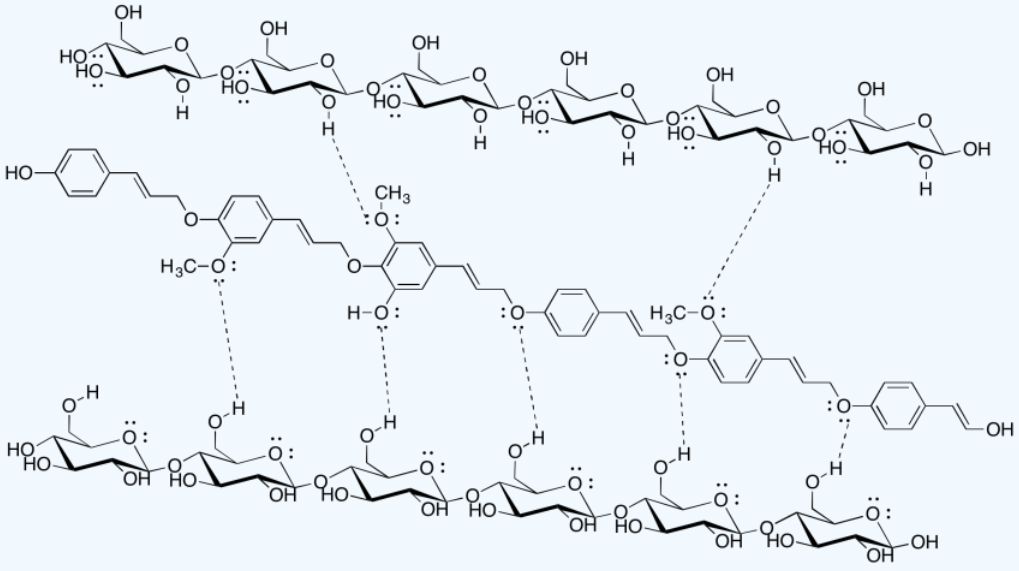
Cellulose is an industrially important commodity: we use it to make clothing and money (usually from cotton) as well as paper (usually from wood), for example. The pulp & paper industry expends a great deal of energy processing wood in order to make paper, with a major goal being the removal of lignin (which makes up about 15-30% of most woods, compared to about 30-50% cellulose content). The following drawing shows two chains of cellulose and a chain of lignin. Why would paper companies want to remove the lignin?



Answer

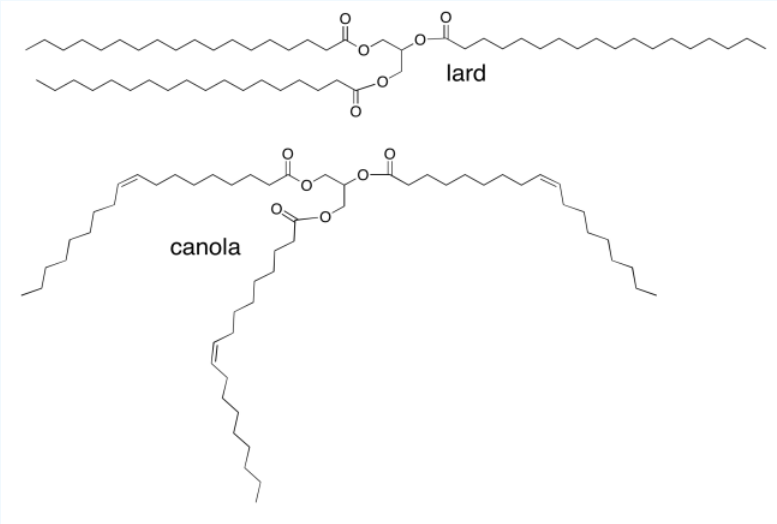
https://chem.libretexts.org/@go/page/191994

Although lignin is capable of some hydrogen bonding, it cannot make nearly as many hydrogen bonds as cellulose can. Paper containing lignin would be much weaker, and more likely to tear or to fall apart when it gets wet, because the cellulose molecules would not be able to bind each other as tightly with lignin mixed in. In fact, brown paper bags from the grocery store are made from *kraft*, which has not had lignin removed; they are much weaker than most paper, especially if they get wet.



Exercise 7.13.4

Vegetable oils, such as canola oil, are high in "unsaturated" fatty acids, in which the fatty acid chains in the triglyderides contain C=C double bonds. For example, canola oil contains about 60% oleic acid, an 18-carbon chain with a double bond in the middle. Animal fats, such as lard, contain mostly saturated fatty acids (with no C=C double bonds). Lard contains about 30% stearic acid; it's the same chain length as oleic acid but without the double bond. Why is canola an oil, whereas lard is a solid?



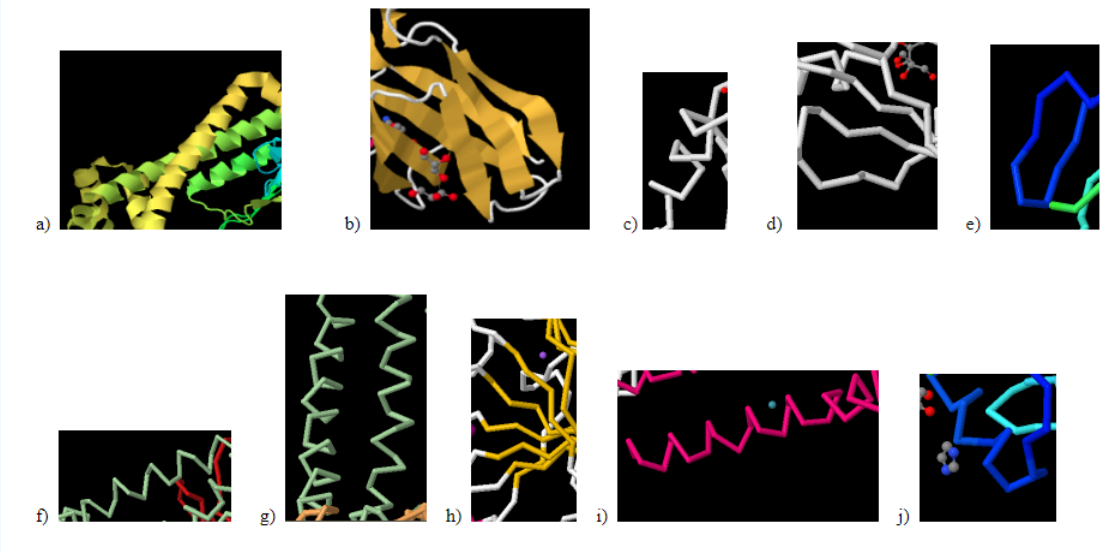
Answer

The dominant intermolecular attraction here is just London dispersion (or induced dipole only). London dispersion is very weak, so it depends strongly on lots of contact area between molecules in order to build up appreciable interaction. The stearic acid-containing triglycerides will be able to pack much more closely together than the more jumbled oleic acid-

containing ones, so they will have much more surface contact and much stronger attractions. They will hold together into a solid.

Exercise 7.13.5

Identify the following pictures as illustrations of either alpha helices or beta sheets.



Answer a:

alpha helix

Answer b:

beta sheet

Answer c:

alpha helix

Answer d:

beta sheet

Answer e:

beta sheet

Answer f:

alpha helix

Answer g:

alpha helix

Answer h:

beta sheet

Answer i:

alpha helix

Answer j:

alpha helix

X-ray crystal structures for space-filling, backbone, and cartoon illustrations: Filchtinski, D.; Sharabi, O.; Ruppel, A.; Vetter, I.R.; Herrmann, C.; Shifman, J.M. What makes Ras an efficient molecular switch: a computational, biophysical, and structural study of Ras-GDP interactions with mutants of Raf. m>J. Mol. Biol. **2010** *399*: 422-435. Images obtained via RCSB Protein Data Bank (3KUD).

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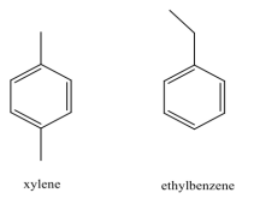
7.14: Application Problems

Exercise 7.14.1

The cleaner, Goof Off (the MIRACLE remover)®, is advertised to remove grease, oil and wax from surfaces. Goof Off is composed of a mixture of xylene and ethyl benzene. The structures of these compounds are shown below:



Grease, oil and wax are hydrocarbon compounds. Why does Goof Off® work better than water to remove these substances? To support your answer, use IMF tables to determine:

a) the strongest IMF between water and water;

b) Goof Off® and Goof Off;

c) Goof Off® and grease; and

d) strongest IMF between grease and water.

Why does Goof-off work better to dissolve grease and oil than if you just use water?

Answer a

a)

	water	**water**
ionic	no	no
H-bond acceptor	yes	yes
H-bond donor	yes	yes
dipole	yes	yes
induced dipole	yes	yes

Water hydrogen bonds with water.

Answer b

b)

	goof	**goof**
ionic	no	no
H-bond acceptor	no	no
H-bond donor	no	no
dipole	no	no
induced dipole	yes	yes

Goof-off forms induced dipole/induced dipole interactions (London dispersion forces) with itself.

Answer c

c)

	goof	grease
ionic	no	no
H-bond acceptor	no	no
H-bond donor	no	no
dipole	no	no
induced dipole	yes	yes

Goof-off forms induced dipole/induced dipole interactions (London dispersion forces) with grease.

Answer d

d)

	grease	water
ionic	no	no
H-bond acceptor	no	yes
H-bond donor	no	yes
dipole	no	yes
induced dipole	yes	yes

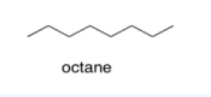
Water forms dipole/induced dipole interactions with grease.

The key to why goof-off works is that it engages in the same London dispersion interactions with the grease as the grease does itself. Water is good at dissolving many things, but not grease. That's mostly because the water would have to give up some of the strong hydrogen bonds with other water molecules in order to fit grease molecules among the water molecules.

Exercise 7.14.2

Often, a pint of gas-line antifreeze (commonly called "HEET", after a popular brand) is added to the gas tanks of cars, especially in the coldest days of winter, to prevent gas-line freeze-up. (Small amounts of water in gasoline can freeze when it is very cold. This blocks the fuel line and stops the engine.)

a) Assume that gasoline is pure octane (C_8H_{18}). What is the strongest IMF force between octane molecules in gasoline?



b) One type of gas-line antifreeze contains almost 100% isopropyl alcohol, shown below. What is the strongest IMF between two isopropyl alcohol molecules?

c) Isopropyl alcohol is completely soluble in both water and gasoline. Why? Consider the IMF involved when isopropyl alcohol is:

i) interacting with water
ii) Interacting with octane

d) When HEET is added to a tank of gas it tends to cause water to dissolve (or at least stay suspended) in gasoline. Show in a picture and explain how this happens, on the molecular level.

e) All gasoline in Minnesota is required to contain 10% ethanol (CH_3CH_2OH). Given this formulation, would a Minnesotan need to use HEET? Explain.

Answer a

a)

	octane	octane
ionic	no	no
H-bond acceptor	no	no
H-bond donor	no	no
dipole	no	no
induced dipole	yes	yes

That's going to be induced dipole-induced dipole interactions in octane.

Answer b

b)

	isopropanol	isopropanol
ionic	no	no
H-bond acceptor	yes	yes
H-bond donor	yes	yes
dipole	yes	yes
induced dipole	yes	yes

Hydrogen bonding in isopropanol.

Answer c

c)

i)

	isopropanol	water
ionic	no	no
H-bond acceptor	yes	yes
H-bond donor	yes	yes
dipole	yes	yes
induced dipole	yes	yes

Hydrogen bonding between isopropanol and water.

ii)

	octane	isopropanol
ionic	no	no
H-bond acceptor	no	yes
H-bond donor	no	yes
dipole	no	yes
induced dipole	yes	yes

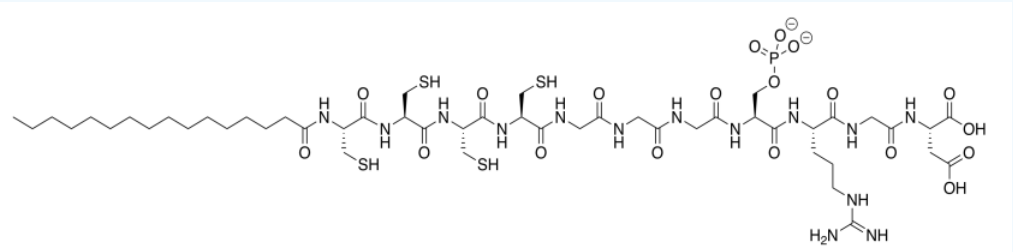
Dipole-induced dipole interactions between octane and isopropanol.

Answer e

No, the ethanol should do the same thing that the HEET does.

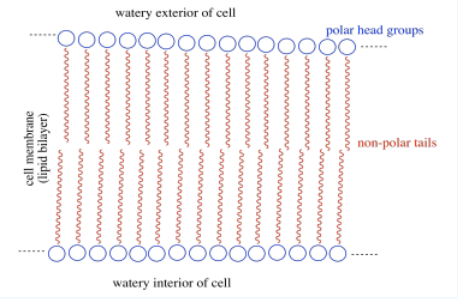
Exercise 7.14.3

The laboratory of Samuel Stupp at Northwestern designs molecules with potential biomedical applications. The compound below was made to promote bone regeneration at the cell surface. Bone is mostly composed of calcium phosphate, $Ca_3(PO_4)_2$ (Adapted with permission from Liam C. Palmer, Christina J. Newcomb, Stuart R. Kaltz, Erik D. Spoerke and Samuel I. Stupp, *Chem. Rev.* **2008**, *108*, 4754-4783. Copyright 2018 American Chemical Society.).



a) This molecule is a synthetic amphiphile; it has a polar end and a non-polar end. Put a rectangle around the polar part of this molecule. Circle the nonpolar part of the molecule.

b) The amphiphile inserts into the cell membrane. A cartoon of a portion of a cell membrane is shown below. Add a cartoon of the synthetic amphiphile to the membrane. What is the IMF through which it interacts with the membrane?



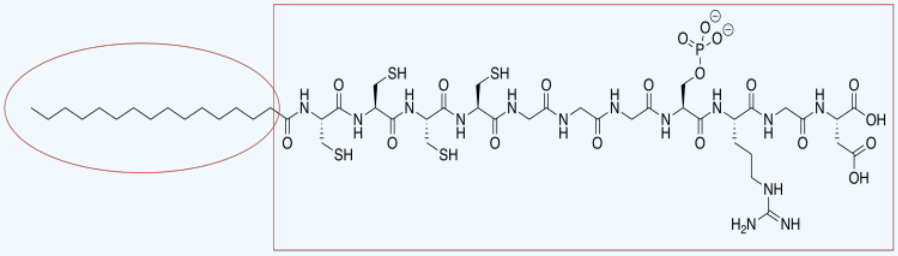
c) Based on its position in the periodic table, what is the charge on a calcium ion?

d) Based on the overall neutral charge of calcium phosphate, $Ca_3(PO_4)_2$, what is the charge on phosphate?

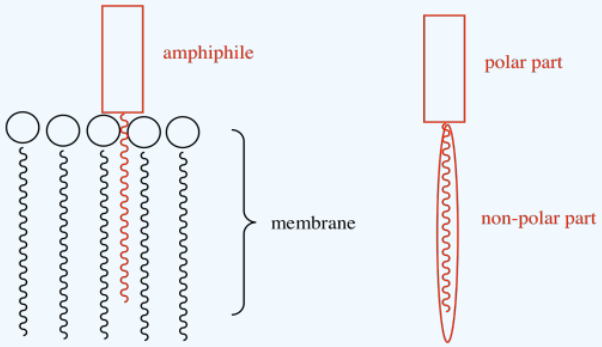
e) What is the advantage of bone being composed of calcium and phosphate rather than more common ions like sodium and chloride?

f) Show how this amphiphile would promote bone growth.

Answer a:



Answer b:



Answer c:

Ca^{2+} (two atoms from the left edge).

Answer d:

PO_4^{3-} because 3 x (2^+) + 2 x (3^-) = 0; neutral charge overall.

Answer e:

These high charges ($2^+/3^-$) bind much more tightly than the low charges ($1^+/1^-$) in sodium chloride.

Answer f:

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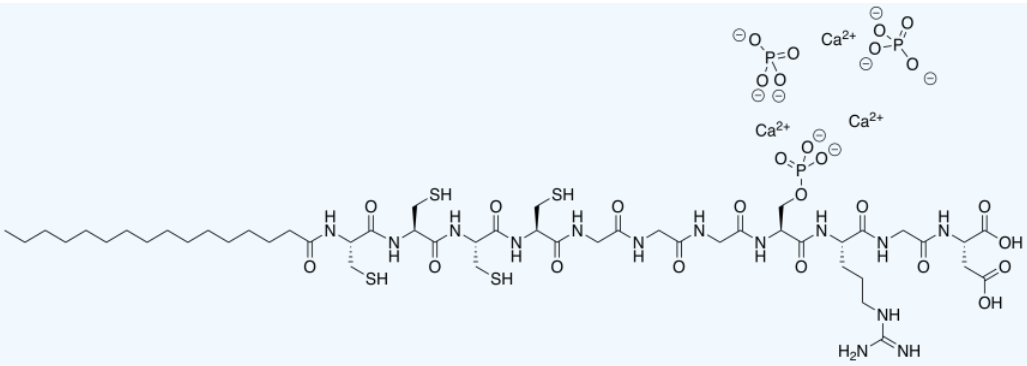
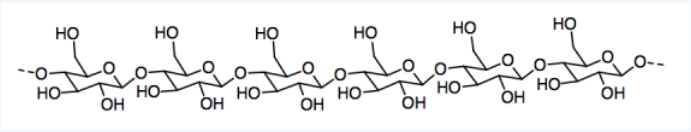


Exercise 7.14.4

Let's make some paper.

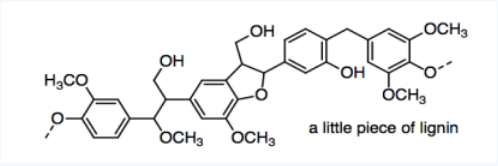
Paper is made from cellulose fibers that stick together to form a sheet. Cellulose, in turn, is a polymer made from individual glucose molecules bonded together in a chain.



a) Circle an individual glucose unit in the cellulose.

b) Name and draw the IMF that holds two cellulose chains together.

One of the problems in making paper is that the most important source of cellulose is generally wood pulp. Wood pulp differs from other plant materials in that it contains lignin.



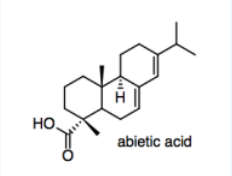
The lignin is pretty important in the plants -- it provides structural rigidity or stiffness that allows trees to grow a lot taller than other plants -- but it isn't useful in paper. It is left in brown paper bags (kraft paper), but those tear more easily than paper that has had lignin removed.

c) Show why lignin would weaken the interaction between cellulose molecules.

One of the problems with paper is that it can absorb water and swell; it can even dissolve if there is enough water.

d) Show why paper absorbs water so easily.

One way to combat moisture absorption is to add sizing to the paper. Sizing can be mixed in with the cellulose mash before it is rolled out into sheets ("internal sizing"), or it can be sprayed onto the paper sheet after it is rolled out ("surface sizing"). Rosin, also obtained from trees, is a common source of sizing; one of its major components is abietic acid.



e) In order to modify the properties of the paper, the rosin will have to stick to the paper. Explain how it does that.

f) How does rosin make the paper more water-resistant?

A very old source of sizing was rabbitskin glue; gelatin is a related material that is still used as sizing today (in addition to being the basis for a jiggly dessert). These materials are mostly proteins, rich in glycine, proline, alanine, phenylalanine, leucine and valine, among other amino acids.

g) How would a protein stick to the paper?

h) What kind of amino acid residues would make the paper water-resistant?

Raw paper is quite transparent, so opaquifiers are usually added. They make a more opaque material so that you can write on both sides. Titanium dioxide is a common opaquifier.

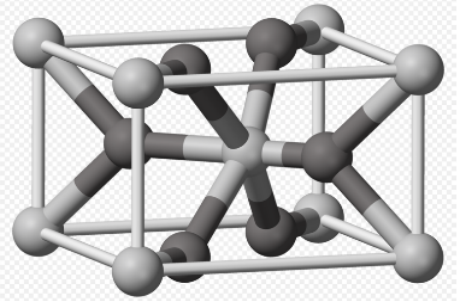
i) In order to get to a noble gas configuration, what would be the charge on a Ti ion? An O ion?

j) Therefore, what is the formula of titanium oxide (the ratio of the ions in the compound)?

k) Titanium oxide does not dissolve very well in water. Why not?

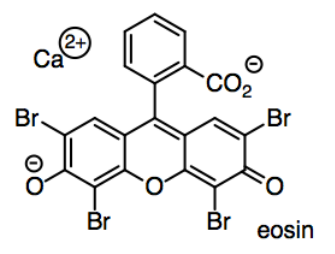
l) Titanium oxide does stick in the fabric of the paper. Name the IMF.

m) In the picture, the O is dark and the Ti light (picture credit: Ben Mills; public domain). Calculate the number of each atom in the unit cell.



n) Describe the type of unit cell formed by the Ti atoms alone.

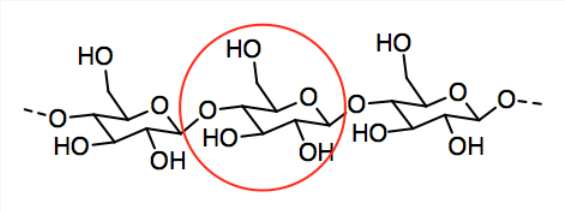
We will need to try out the paper by writing on it. In a ballpoint pen, the ink (such as eosin red, used to grade your compositions in English class) is suspended or dissolved in a light oil such as benzyl alcohol.



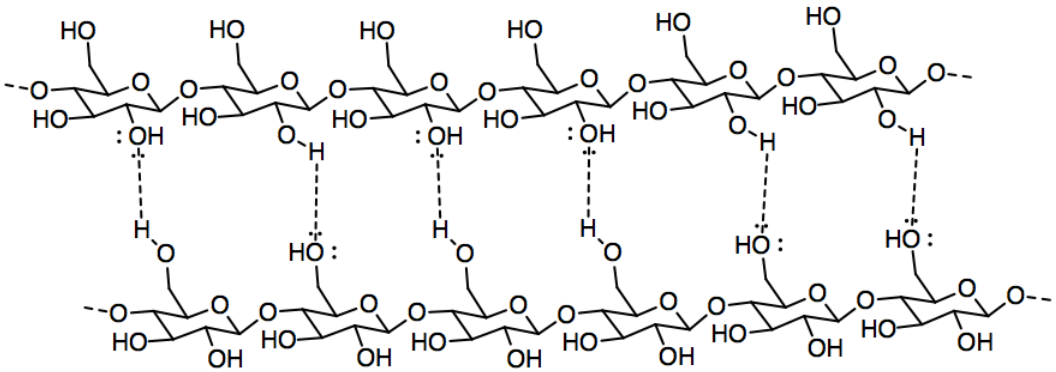
o) How does eosin dissolve in benzyl alcohol? Show and name one kind of IMF on the drawing.

p) Why will the eosin stick to the paper?

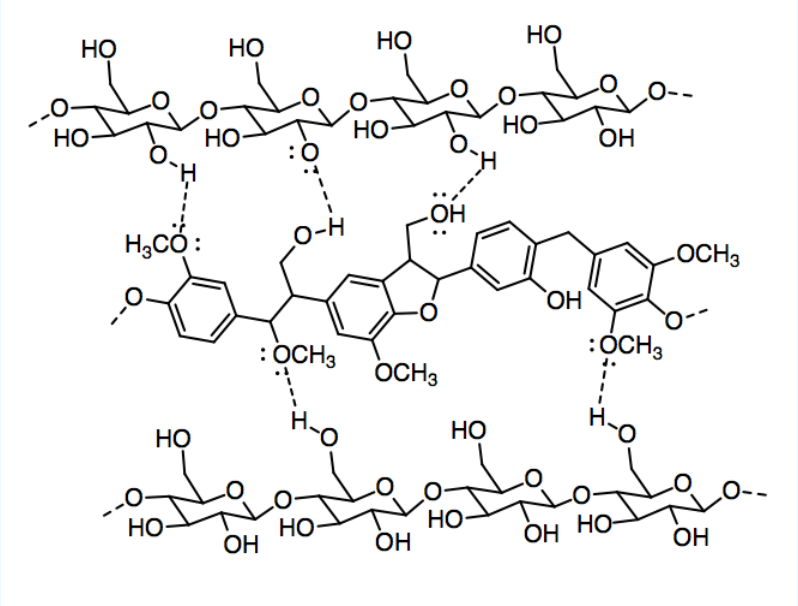
Answer a:



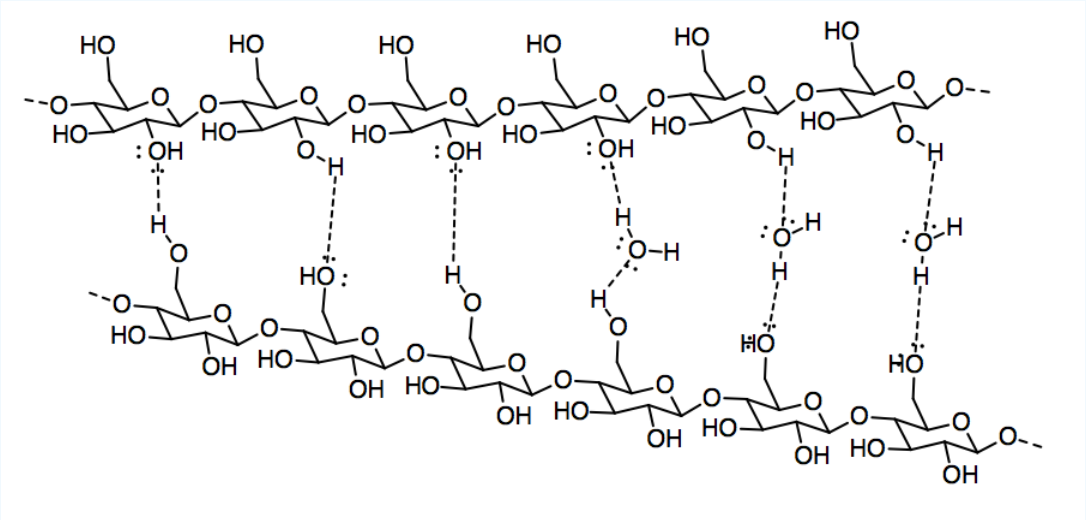
Answer b:



Answer c:



Answer d:



Answer e:

The carboxylic acid group provides sites for hydrogen bonding, including both a hydrogen bond donor in the OH group and an additional hydrogen bond acceptor in the C=O group.

Answer f:

It introduces a "hydrophobic" part in which the major intermolecular force with water would be a dipole-induced dipole interaction. If the water molecules keep to themselves, they will be able to maximize the amount of hydrogen bonding they can do with each other. The water is better off not mixing in with the paper.

Answer g:

All proteins have polar backbones formed by their amide bonds or peptide linkages (-NH-C=O). These portions can hydrogen bond with the cellulose in the paper. In addition, there may be polar side chains such as serine or threonine, for example, containing OH groups that can hydrogen bond with the paper.

Answer h:

Hydrophobic residues would add water resistance, for the same reason as the hydrophobic part of the abietic acid in rosin.

Answer i:

Ti^{4+} would have the same electronic configuration as argon. O^{2-} would have the same electronic configuration as neon.

Answer j:

The formula is TiO_2, so that the positive charges (4^+) and the negative charges ($2 \times 2^- = 4^-$) are balanced.

Answer k:

The 4^+ and 2^- charges are pretty large. Highly charged ions are difficult to dissolve, because the ion-dipole attraction of the ion with the water cannot compete with the very strong ionic attractions between the ions.

Answer l:

Ion-dipole. You can imagine the partially negative oxygen atoms of cellulose interacting with the titanium cations and the partially positive hydrogens of the OH groups in the cellulose interacting with the oxide anions.

Answer m:

Ti: one full atom in the center and eight in the corners, so 1 + 8x(1/8) = 2 Ti atoms.

O: two full atoms (towards the left and right ends of the picture) plus four half atoms (on the upper and lower faces of the cell), so 2 + 4x(1/2) = 4 O atoms.

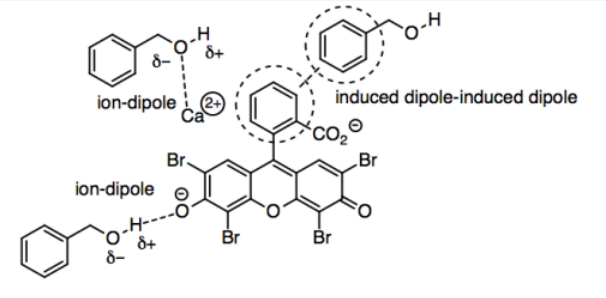
ratio: 1 Ti : 2 O or TiO_2 in formula notation.

Answer n:

The Ti are packed in a cell that resembles a body-centered cubic cell. However, the cell is not really cubic, because it is stretched out a little. Sometimes we call that shape "tetragonal".

Answer o:

The benzyl alcohol could interact with the eosin in a number of ways, because eosin is a fairly large, complicated molecule (at least at this stage in your studies). We could imagine ion-dipole interactions, in which the partially positive hydrogens on the OH groups in the benzyl alcohol interact with the anionic oxygens of the eosin, or the partially negative oxygens in the benzyl alcohol interact with the positive calcium ion.



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However, the polar part of benzyl alcohol is really the smaller part of the molecule. The bigger part of the molecules is the benzene, a six-membered carbon ring with three double bonds. The carbons at the ends of those double bonds are trigonal planar, so because the benzene is built up from planar atoms, it is completely flat. C-C bonds are not polar, and C-H bonds are hardly polar at all, so the dominant IMF in this part of the molecule is London dispersion or induced dipole-induced dipole interaction. That's a pretty weak interaction generally, but it can get a little stronger between large molecules, or between flat ones, because two flat molecules can have more surface area in contact with each other. That means the benzenes in benzyl alcohol and the benzenes in eosin have appreciable London forces that allow them to interact with each other.

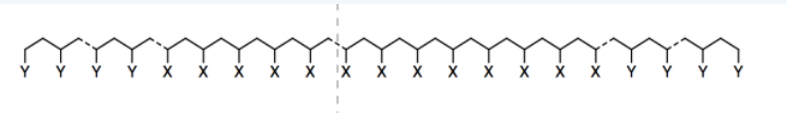
Answer p:

With the cellulose, covered in OH groups, the polar interactions outlined above will become more prominent.

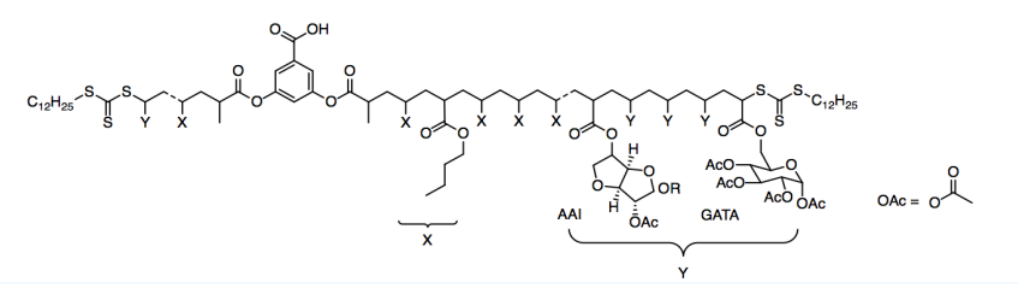
Exercise 7.14.5

Let's make a Post-It Note©. Post-It Notes are basically sticky pieces of paper. If we are going to make one, we will need some paper. Once you have the paper, we will need an adhesive to make it sticky.

Researchers in Teresa Reineke's lab at University of Minnesota have developed new adhesives based on sugars, a renewable resource (Nasiri, M.; Saxon, D. L.; Reineke, T. M. *Macromolecules* **2018**, *51*, 2456-2465. Copyright 2018, American Chemical Society. Used with permission.). The adhesives are long polymer chains containing about 800 X groups in a row, with between 12 and 90 Y groups at each end.



They tried two different kinds of Y groups: AAI and GATA.



a) What kind of functional group is OAc?

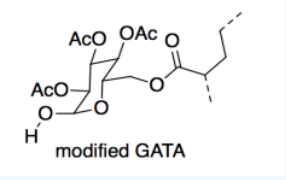
b) How many chiral centers are found in the AAI group? In the GATA group?

A good glue has a balance between adhesion – sticking to something else – and cohesion – sticking together. If there are lots of these chains in the adhesive (like strands of spaghetti), they can stick to each other via intermolecular forces.

c) Show and name the IMFs that would occur between (i) two alkyl chains on group X; (ii) the ester groups on GATA.

d) What IMF leads to good adhesion of the polymer to paper?

In a static shear test, a 1-pound weight is stuck on a vertical surface with the adhesive, and the time it takes to fall off is measured. The AAI version outperformed the GATA version (6000 vs. 800 minutes). However, the lab made a slight alteration to the GATA and the adhesion time doubled (to 1600 minutes).



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Thinking only of cohesion, why did the strength of the material improve?

e) Show and name the IMF on a drawing of the modified GATA. Compare its strength to the IMF it replaces in the original GATA.

The lab also performed a peel adhesion test. They measured the force required to peel the “post-it note” from a surface. Both GATA and AAI versions out-performed Scotch© Tape, duct tape, and genuine Post-It© Notes.

Answer a:

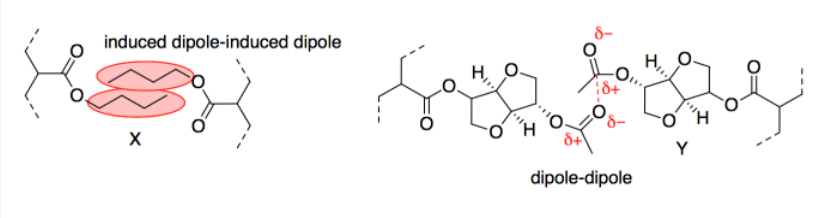
OAc is an ester.

Answer b:

AAI has three chiral centres; GATA has five.

Answer c:

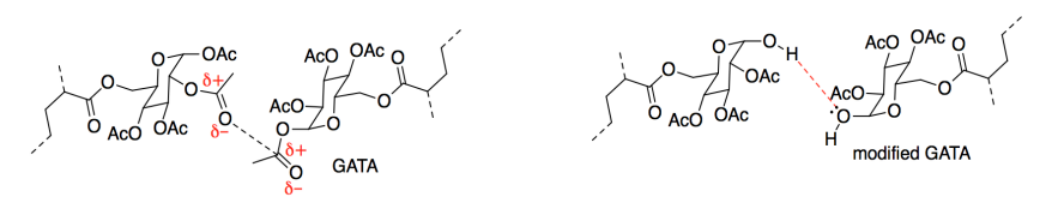
The chains in the adhesive would stick to each other via intermolecular attractions. Dipole-dipole attractions would be the strongest. However, induced dipole-induced dipole or London dispersion forces would actually be significant because there would be hundreds of such interactions along the chains.



Answer d:

The most significant interaction with the paper would be hydrogen bonding. The cellulose in the paper would provide hydrogen bond donors (the OH groups) and the side groups in the adhesive chains would provide hydrogen bond acceptors (all those oxygens). However, if the paper contains a lot of sizing, induced dipole-induced dipole or London dispersion forces may form a significant part of the interaction. As with cohesion, this would not be a significant factor except that there are so many alkyl chains involved, so these tiny attractions would add up.

Answer e:



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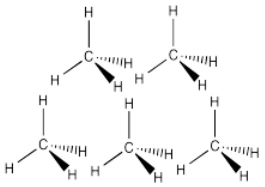
7.15: Solutions to Selected Problems

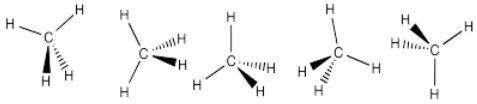
Exercise 7.1.1:

One difference between water and these other molecules is that water is polar: there is a significant electronegativity difference between the oxygen and the hydrogen. The charges in one water molecule may be interacting with charges in other water molecules.

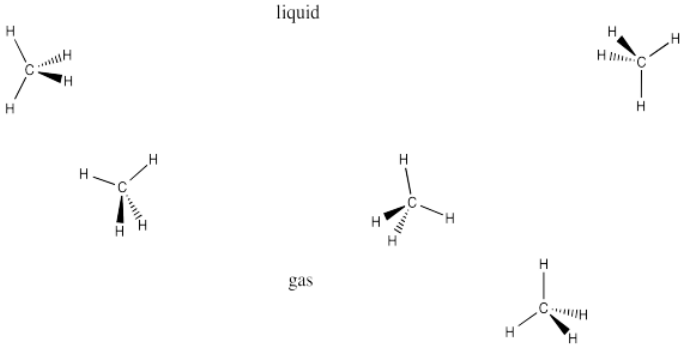
Exercise 7.2.1:



solid



liquid



gas

Exercise 7.3.1:

As far as we can tell from these data, the melting point of nitrogen and oxygen would be somewhere around -220°C, whereas the boiling point would be around -180°C. We would expect these numbers to be similar to fluorine, which has a similar mass. In fact, the melting and boiling points of oxygen are about -219°C and -183°C, respectively. The melting and boiling points of nitrogen are about -210°C and -196°C, respectively.

Exercise 7.4.1:

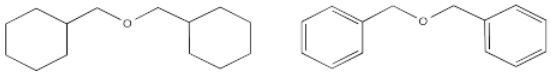
a. A chain that is 8 carbons long would have much lower London interactions than a chain that is 102 atoms long. The greater the contact between molecules, the greater the chance for weak attractions due to small charges arising from random electron movement. The molecule with the longer chain would have the higher melting point, because more energy would have to be added in order to overcome those attractions and get the molecules moving.
b. The first chain is more linear whereas the second chain is more branched. The more linear molecules will pack together more easily, allowing greater surface contact for increased London interactions. The straighter chain would have a higher melting point.
c. Bromomethane has a lot more electrons than chloromethane. Based on London interactions alone, we would expect bromomethane to have a higher melting point. In fact, the melting point of bromomethane is about -94°C, compared to about -97°C for chloromethane; there must be another factor that compensates for the difference in numbers of electrons and makes these values so close.

Exercise 7.4.2:

Because of the large numbers of electrons in bromine, we would expect a higher boiling point in 3,4-dibromohexane.

Exercise 7.4.3:

Remember benzyl refers to the group $C_6H_5CH_2$ (below right); cyclohexylmethyl suggests the superficially similar $C_6H_{12}CH_2$ (below left).



The benzyl group contains trigonal planar carbons, whereas the cyclohexylmethyl group contains only tetrahedral carbons. The benzyl groups,being flatter, could pack more easily together and interact more strongly. We would expect dibenzyl ether to have a higher melting point.

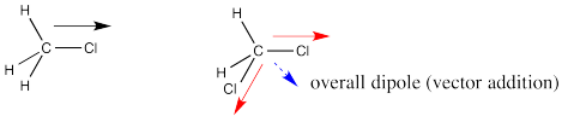
Exercise 7.5.1:

These compounds all contains lots of non-polar C-C and C-H bonds, which would not have appreciable dipoles. However, in each pair, there is a compound that contains more polar bonds as well: C-Cl, C-N and C-O.

Exercise 7.5.2:

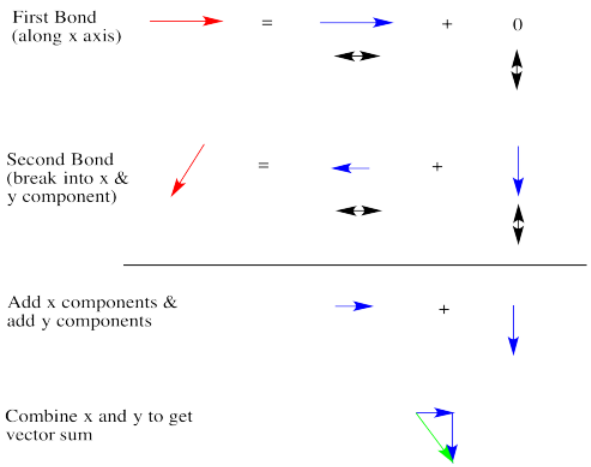
Dipoles are vectors. If we have two polar bonds, they will add together using vector addition. Any vector can be shown as the sum of two other vectors. Below, the red arrow points down and to the left. How far down and how far to the left? We can show how far using the blue arrows. The blue arrow down and the blue arrow to the left add up to give the red arrow that goes down and to the left.

In dichloromethane, there are two polar bonds. Both bonds are polarized towards the more electronegative chlorine. As drawn below, one bond has a dipole straight to the right. The other bond has a dipole that goes down and to the left. If the molecule has an *overall* dipole, with a positive end of the whole molecule and a negative end of the whole molecule, which end would be positive and which would be negative?



It seems reasonable that the positive end would be somewhere over on the hydrogen side and the negative end would be somewhere over on the chlorine side. The overall dipole, as opposed to the individual bond dipoles, would point somewhere in the direction of the blue, dashed arrow. But how big would it be? Surely it's bigger than either of the two individual dipoles, because they are adding together, right?

Let's take a very qualitative look. The first red arrow is just to the right. We'll break the second arrow into a smaller arrow down and an even smaller arrow to the left. The sum of the left/right arrows is a very small arrow to the right.



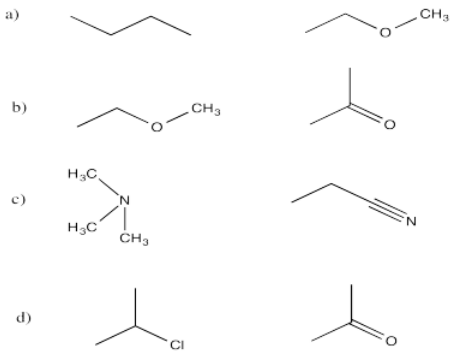
The sum of the up/down arrows is just a small arrow down. Overall, the sum is a green arrow going down and to the right. The result does not really seem any bigger than an individual bond dipole.

Exercise 7.5.3:

Despite the relatively similar dipole moments, dichloromethane's boiling point is much higher than chloromethane's. The difference probably lies in the much greater mass of dichloromethane.

Exercise 7.5.4:

In each case, the one on the right has a larger dipole and a higher melting point.



Exercise 7.6.1:

Only ethylamine and ethanoic acid have the N-H or O-H bonds that are polar enough for hydrogen bonding.

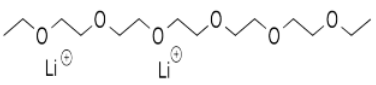
Exercise 7.6.2:

hexylamine > dipropylamine > triethylamine

The one with the greatest potential for hydrogen bonding will have the highest melting point.

Exercise 7.6.3:

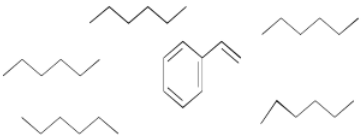
A.



dipole-dipole induced dipole-induced dipole **ion-dipole**

hydrogen bonding ion-ion dipole-induced dipole

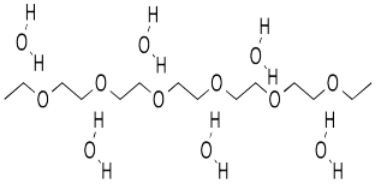
B.



dipole-dipole **induced dipole-induced dipole** ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

C.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

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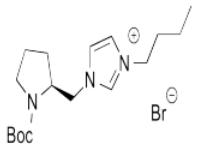
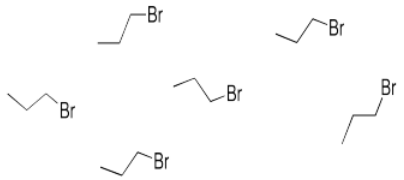
D.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding **ion-ion** dipole-induced dipole

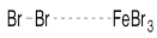
E.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

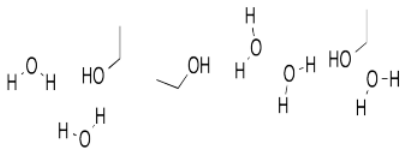
F.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion **dipole-induced dipole**

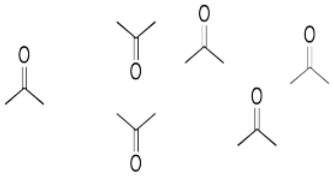
G.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

H.



dipole-dipole induced dipole-induced dipole ion-dipole

hydrogen bonding ion-ion dipole-induced dipole

Exercise 7.8.1:

The hydrogen bonding between 2-propanol molecules is a stronger interaction and is more difficult to overcome than the dipole-dipole interactions between 2-propanone molecules. Thus, 2-propanone molecules can more easily escape into the vapour phase.

Exercise 7.8.2:

There is hydrogen bonding between molecules of *N*-methylethylamine, but not between molecules of triethylamine, which are held together by relatively weak dipoles. Trimethylamine molecules are not held together as tightly as the *N*-methylethylamine molecules, which therefore pack more densely. On the other hand, *n*-propylamine contains two N-H bond, compared to only one in *N*-methylethylamine. Consequently, *n*-propylamine has a greater propensity to form hydrogen bonds, and it packs together even more densley than the *N*-methylethylamine..

Exercise 7.8.3:

Temperature is a measure of how much energy is available in the environment. As temperature increases, molecules obtain more energy and they transfer that energy into a variety of molecular motions. As they move around more, they are less able to remain densely packed. The density decreases as the temperature goes up. Conversely, things tend to shrink as they cool, because molecules slow down and begin to pack more tightly. They become more dense.

Exercise 7.8.4:

a. Acetic acid posesses hydrogen bonding capability, whereas 2-propanone has the ability to form only dipole-dipole interactions. Thus, 2-propanone molecules are not held in the liquid phase as strongly as acetic acid, and the former compound has a higher vapour pressure.
b. The C=O bond of ethyl acetate has a substantial dipole, but the dipoles in ether don't add up to very much; they are smaller to begin with and they partially cancel out via vectorial addition. Ether molecules can escape the liquid more easily, resulting in a higher vapour pressure.
c. Both molecules are limited to relatively weak London dispersion interactions. Because heptane forms a longer chain than pentane, there will be a slightly greater interaction between heptane molecules than between pentane molecules. Pentane thus has the higher vapour pressure.

Exercise 7.8.5:

a. The C=O bond 2-butanone has a substantial dipole, but the dipoles in ether don't add up to very much; they are smaller to begin with and they partially cancel out via vectorial addition. The 2-butanone molecules cling together more strongly, resulting in a higher viscosity.
b. Both molecules are limited to relatively weak London dispersion interactions. Because decane forms a longer chain than hexane, there will be a slightly greater interaction between decane molecules than between hexane molecules. Decane thus has the higher viscosity. Later, if you study macromolecules, you will see that in very, very long chains, "entanglement" becomes a factor as well. Just as the name implies, really long chains get tangled up together and have a difficult time moving past each other; that's why materials like cooking oil and motor oil are so viscous.
c. The 1-butanol can hydrogen bond together, but the ether only has weak dipole-dipole interactions. The 1-butanol is therefore more viscous.

Exercise 7.8.6:

a. The 1-butanol can hydrogen bond together, but the ether only has weak dipole-dipole interactions. The 1-butanol therefore has greater surface tension.
b. The 1-butanol can hydrogen bond together, but the 1,3-butanediol has two OH groups and can form even more hydrogen bonds than 1-butanol can. The 1,3-butanediol therefore has greater surface tension.
c. The formamide has N-H bonds and so it is capable of hydrogen bonding. Despite having a pretty darned big dipole, the nitromethane can't really hydrogen bond together. The formamide therefore has greater surface tension.

Exercise 7.8.7:

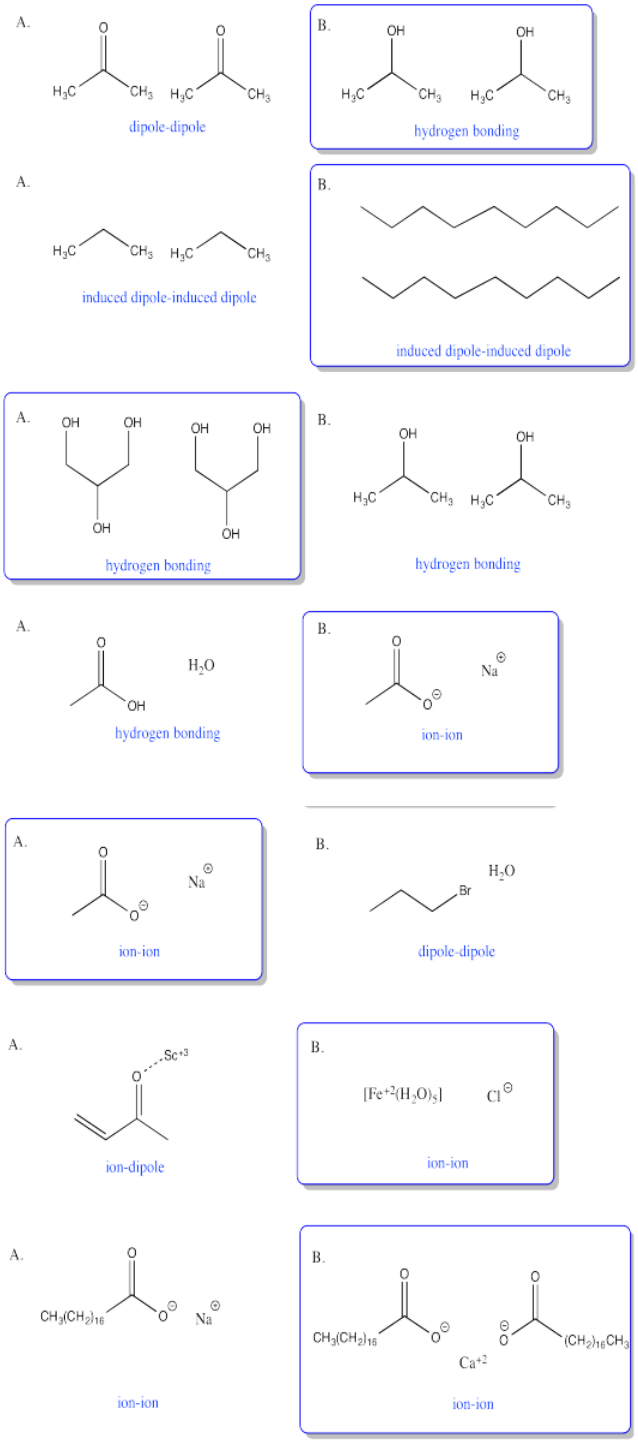
a. 2-propenol. It has hydrogen bonding capability but propanal does not.
b. heptanoic acid. It has hydrogen bonding capability but ethyl pentanoate does not.
c. 1-hexen-3-one. Its dipole is greater than that in the ether, because it comes from a C=O bond rather than C-O bonds.

Exercise 7.8.8:

a. 2-butanone. Its dipole is greater than that in the ether, because it comes from a C=O bond rather than C-O bonds.

b. octane. It has greater London dispersion interactions that pentane because of the greater surface contact area in octane.
c. 1,3-butanediol. It has hydrogen bonding but the DME does not.

Exercise 7.8.9:



Exercise 6.9.1:

Hydrogen bonding.

Exercise 6.9.2:

a) dipole interactions b) London interactions c) dipole interactions d) hydrogen bonding

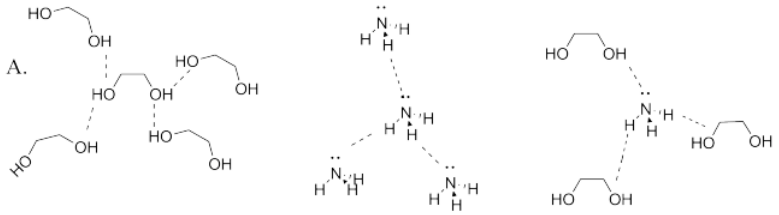
Exercise 6.9.3:

Water molecules interact with each other mainly through hydrogen bonding, whereas octane molecules interact with each other via London interactions. The main problem here is the strong hydrogen bonding between the water molecules. All molecules, in principle, could interact with each other via London interactions. However, if octane molecules were introduced among the water molecules, they would take up space. Some of the water molecules would not be able to get close enough to each other to hydrogen bond anymore. The loss of that very stabilizing interaction would be too costly.

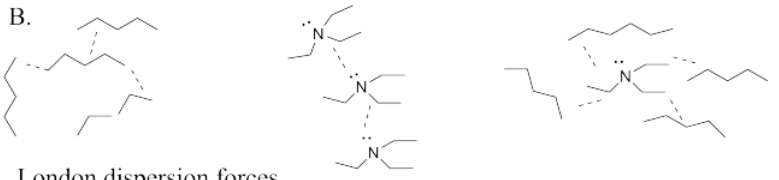
Exercise 6.9.4:

This problem is similar to the previous one, but in this case the attraction between the strong dipoles of the nitrile groups would be too much to overcome.

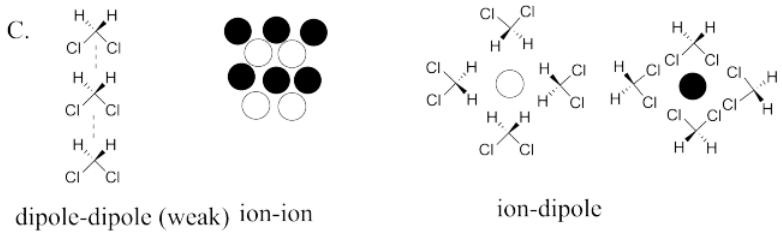
Exercise 6.9.5:



IMF's comparable; therefore solute is likely soluble.



Even though forces are different, the dipole in the amine is weak and there would also be significant LDF's between the pentane and the ethyl groups, so likely miscible.



Given that the dipole in CH_2Cl_2 is weak, NaCl will likely not dissolve.

Exercise 7.9.6:

a) dipole / induced dipole b) dipole / dipole c) hydrogen bonding d) dipole / induced dipole

Exercise 7.10.1

The predicted order, from most soluble to least, would be LiCl > $MgSO_4$ > $AlPO_4$ because the ions increase in charge from 1+/- to 2+/- to 3+/-

Exercise 7.10.2:

The predicted order, from most soluble to least, would be dimethylsulfoxide > acetonitrile > pyridine > dichloromethane > triethylamine.

Exercise 7.11.1:

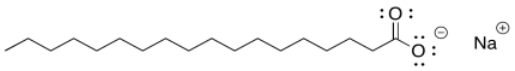
a) H-bond acceptor b) H-bond acceptor c) fully H-bonding d) H-bond acceptor e) fully H-bonding f) neither

Exercise 7.12.1:

SP11

1. The structure of soap is shown below.

a. Calculate the formal charge on the oxygens and the sodium.



b. The 'tail' of the soap is circled. Is it polar or non-polar?

tail is nonpolar& hydrophobic

head is polar & hydrophilic

c. What type of IMF would you predict for:

tail-tail of 2 soap molecules: _____ induced dipole - induced dipole
head-tail of 2 soap molecules: _____ ion - induced dipole
water-tail of a soap molecule: _____ dipole-induced dipole
water-head of a soap molecule:_____ ion-dipole

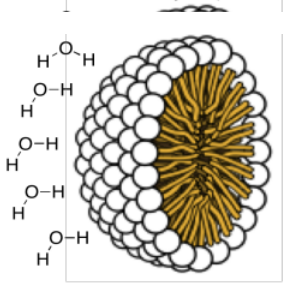
d. Would you expect the tails to be soluble in water?

No The dipole-induced dipole is too weak to overcome hydrogen bonding between waters.

e. Which IMF interactions would be strongest?

Ion-dipole between water and the hydrophilic head of the soap.

f. Soap molecules form micelles (shown below) in water. Draw several water molecules in this picture. Where will they be (inside or outside) this micelle structure.



picture from wikipedia: http://en.wikipedia.org/wiki/Soap

f. Explain why soap forms this micelle structure in the presence of water. Use IMF.

Water is attracted to the hydrophilic heads to form this strong ion-dipole interaction whereas the tails cannot overcome the strong hydrogen bonding of water-water interactions.

g. Dirt is usually non-polar fats or other non-polar organic structures. Where would dirt be in this picture above?

Hydrophobic dirt & grease will prefer to interact with the hydrophobic tails (inside micelle).

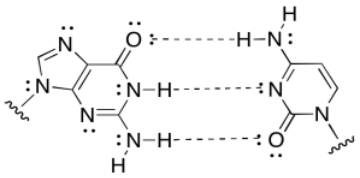
h. How does soap clean dirt/grease off your hands?

The grease will be encapsulated in the micelle and washed away in water.

Exercise 7.13.1:

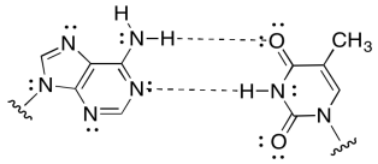
Note that the last example is actually found in RNA, not DNA. RNA is found as a single strand, rather than a pair of strands. It hydrogen bonds to itself in a particular shape, not unlike the way a protein adopts a specific shape.

a)



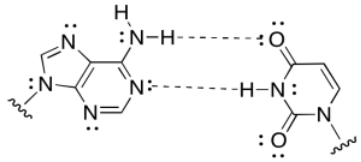
guanine cytosine

b)



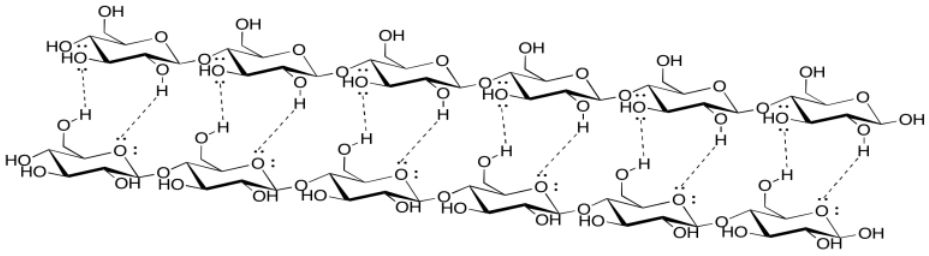
adenine thymine

c)



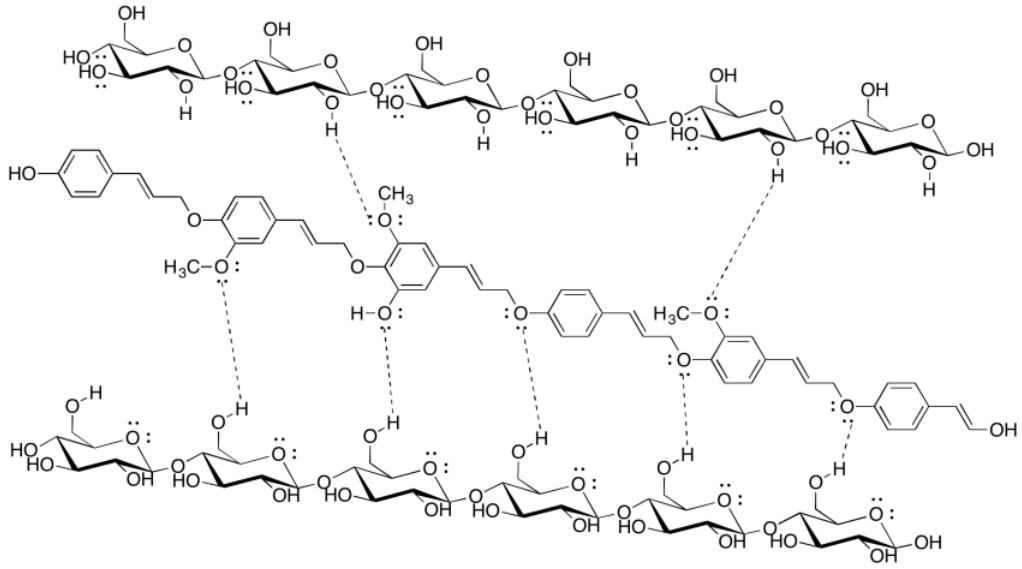
adenine uracil

Exercise 7.13.2:



Exercise 7.13.3:

Although lignin is capable of some hydrogen bonding, it cannot make nearly as many hydrogen bonds as cellulose can. Paper containing lignin would be much weaker, and more likely to tear or to fall apart when it gets wet, because the cellulose molecules would not be able to bind each other as tightly with lignin mixed in. In fact, brown paper bags from the grocery store are made from *kraft*, which has not had lignin removed; they are much weaker than most paper, especially if they get wet.



Exercise 7.13.4:

The dominant intermolecular attraction here is just London dispersion (or induced dipole only). London dispersion is very weak, so it depends strongly on lots of contact area between molecules in order to build up appreciable interaction. The stearic acid-containing triglycerides will be able to pack much more closely together than the more jumbled oleic acid-containing ones, so they will have much more surface contact and much stronger attractions. they will hold together into a solid.

Exercise 7.13.5:

a) alpha helix b) beta sheet c) alpha helix d) beta sheet e) beta sheet

f) alpha helix g) alpha helix h) beta sheet i) alpha helix j) alpha helix

Exercise 7.14.1:

a)

	water	**water**
ionic	no	no
H-bond acceptor	yes	yes
H-bond donor	yes	yes
dipole	yes	yes
induced dipole	yes	yes

Water hydrogen bonds with water.

b)

	goof	**goof**
ionic	no	no
H-bond acceptor	no	no
H-bond donor	no	no
dipole	no	no
induced dipole	yes	yes

Goof-off forms induced dipole/induced dipole interactions (London dispersion forces) with itself.

c)

	goof	grease
ionic	no	no
H-bond acceptor	no	no
H-bond donor	no	no
dipole	no	no
induced dipole	yes	yes

Goof-off forms induced dipole/induced dipole interactions (London dispersion forces) with grease.

d)

	grease	water
ionic	no	no
H-bond acceptor	no	yes
H-bond donor	no	yes
dipole	no	yes
induced dipole	yes	yes

Water forms dipole/induced dipole interactions with grease.

The key to why goof-off works is that it engages in the same London dispersion interactions with the grease as the grease does itself. Water is good at dissolvng many things, but not grease. That's mostly because the water would have to give up some of the strong hydrogen bonds with other water molecules in order to fit grease molecules among the water molecules.

Exercise 7.14.2:

a)

	octane	octane
ionic	no	no
H-bond acceptor	no	no
H-bond donor	no	no
dipole	no	no
induced dipole	yes	yes

That's going to be induced dipole-induced dipole interactions in octane.

b)

	isopropanol	isopropanol
ionic	no	no
H-bond acceptor	yes	yes
H-bond donor	yes	yes
dipole	yes	yes

induced dipole	yes	yes

Hydrogen bonding in isopropanol.

c)

i)

	isopropanol	**water**
ionic	no	no
H-bond acceptor	yes	yes
H-bond donor	yes	yes
dipole	yes	yes
induced dipole	yes	yes

Hydrogen bonding between isopropanol and water.

ii)

	octane	**isopropanol**
ionic	no	no
H-bond acceptor	no	yes
H-bond donor	no	yes
dipole	no	yes
induced dipole	yes	yes

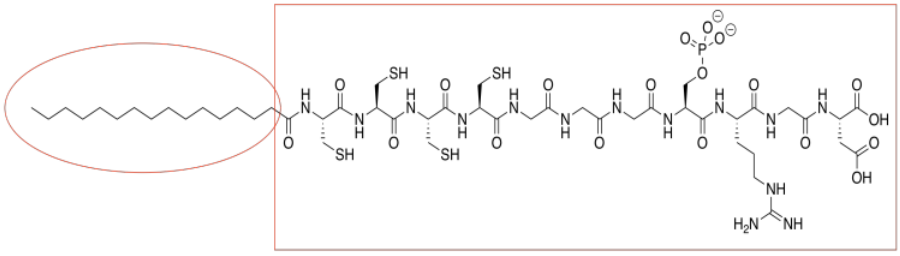
Dipole-induced dipole interactions between octane and isopropanol.

d)

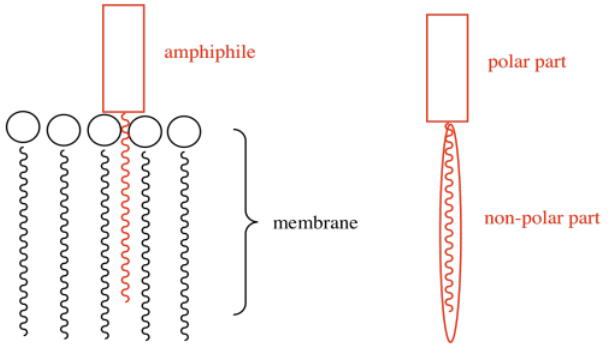
e) No, the ethanol should do the same thing that the HEET does.

Exercise 7.14.3:

a)



b) The amphiphile inserts into the cell membrane. Draw a cartoon of a portion of a cell membrane. Add a cartoon of the synthetic amphiphile to the membrane. What is the IMF through which it interacts with the membrane?

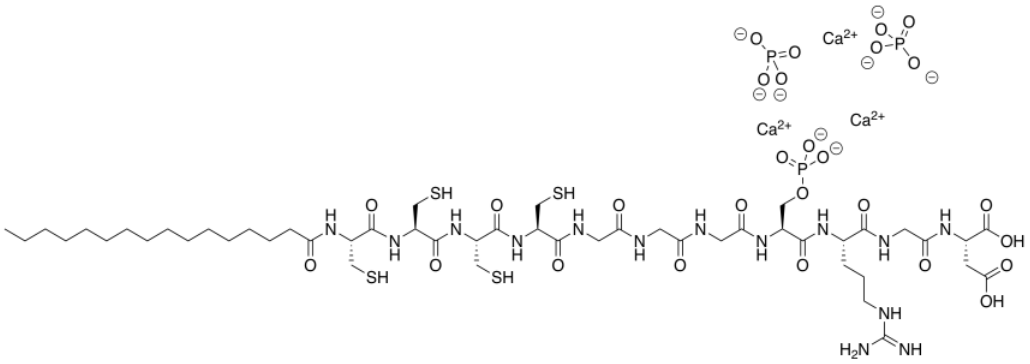


c) Ca^{2+} (two atoms from the left edge).

d) PO_4^{3-} because $3 \times (2^+) + 2 \times (3^-) = 0$; neutral charge overall.

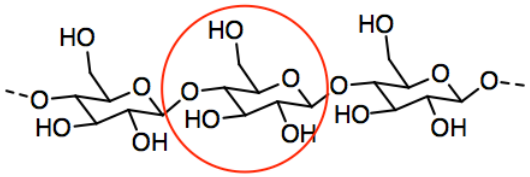
e) These high charges ($2^+/3^-$) bind much more tightly than the low charges ($1^+/1^-$) in sodium chloride.

f)

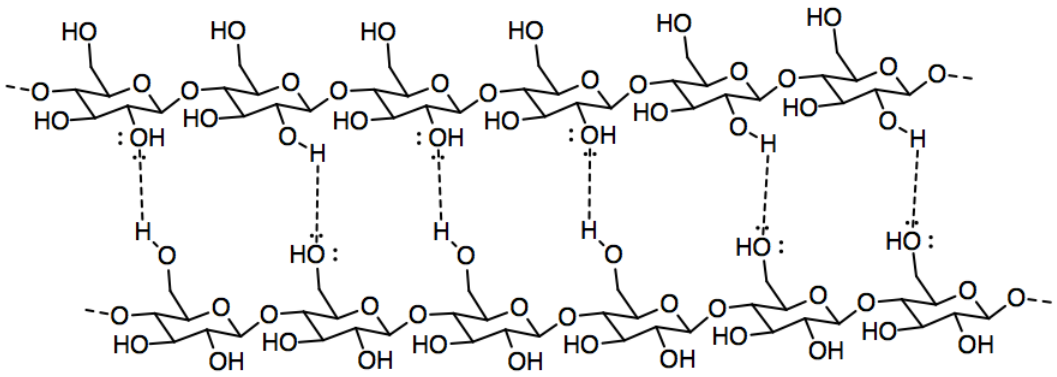


Exercise 7.14.4:

a)



b)



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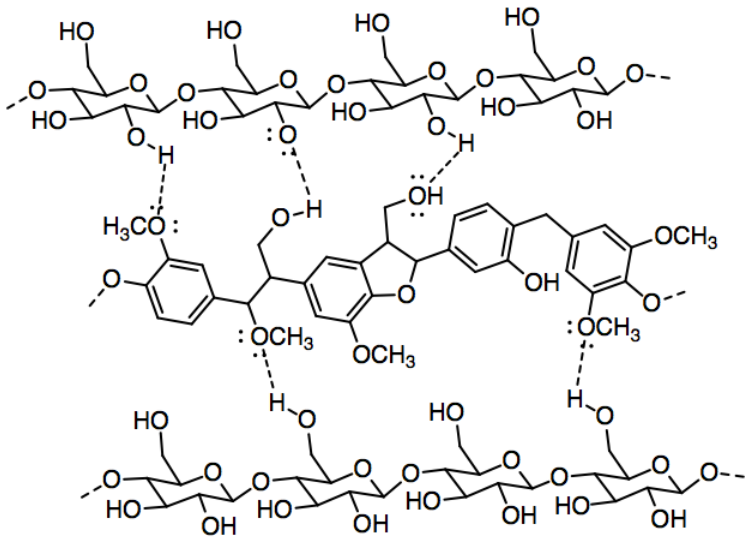
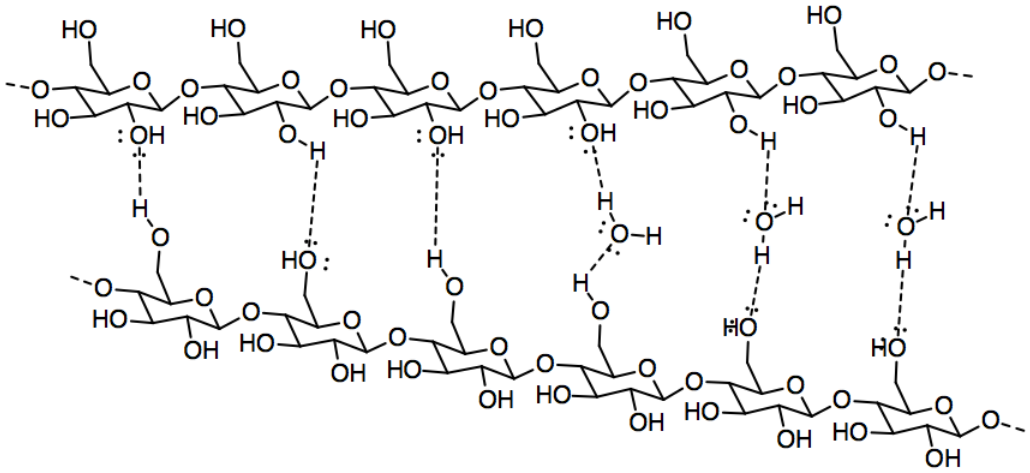
c)



d)



e) The carboxylic acid group provides sites for hydrogen bonding, including both a hydrogen bond donor in the OH group and an additional hydrogen bond acceptor in the C=O group.

f) It introduces a "hydrophobic" part in which the major intermolecular force with water would be a dipole-induced dipole interaction. If the water molecules keep to themselves, they will be able to maximize the amount of hydrogen bonding they can do with each other. The water is better off not mixing in with the paper.

g) All proteins have polar backbones formed by their amide bonds or peptide linkages (-NH-C=O). These portions can hydrogen bond with the cellulose in the paper. In addition, there may be polar side chains such as serine or threonine, for example, containing OH groups that can hydrogen bond with the paper.

h) Hydrophobic residues would add water resistance, for the same reason as the hydrophobic part of the abietic acid in rosin.

i) Ti^{4+} would have the same electronic configuration as argon. O^{2-} would have the same electronic configuration as neon.

j) The formula is TiO_2, so that the positive charges (4^+) and the negative charges ($2 \times 2^- = 4^-$) are balanced.

k) The 4^+ and 2^- charges are pretty large. Highly charged ions are difficult to dissolve, because the ion-dipole attraction of the ion with the water cannot compete with the very strong ionic attractions between the ions.

l) Ion-dipole. You can imagine the partially negative oxygen atoms of cellulose interacting with the titanium cations and the partially positive hydrogens of the OH groups in the cellulose interacting with the oxide anions.

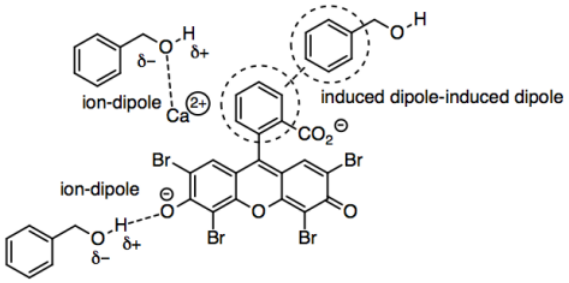
m) Ti: one full atom in the center and eight in the corners, so 1 + 8x(1/8) = 2 Ti atoms.

O: two full atoms (towards the left and right ends of the picture) plus four half atoms (on the upper and lower faces of the cell), so 2 + 4x(1/2) = 4 O atoms.

ratio: 1 Ti : 2 O or TiO_2 in formula notation.

n) The Ti are packed in a cell that resembles a body-centered cubic cell. However, the cell is not really cubic, because it is stretched out a little. Sometimes we call that shape "tetragonal".

o) The benzyl alcohol could interact with the eosin in a number of ways, because eosin is a fairly large, complicated molecule (at least at this stage in your studies). We could imagine ion-dipole interactions, in which the partially positive hydrogens on the OH groups in the benzyl alcohol interact with the anionic oxygens of the eosin, or the partially negative oxygens in the benzyl alcohol interact with the positive calcium ion.

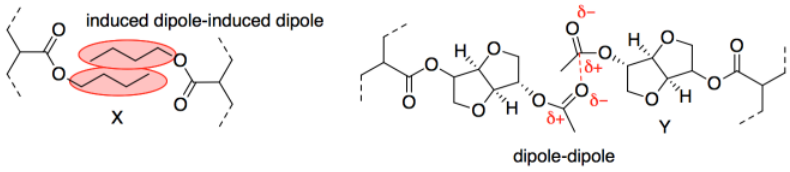


However, the polar part of benzyl alcohol is really the smaller part of the molecule. The bigger part of the molecules is the benzene, a six-membered carbon ring with three double bonds. The carbons at the ends of those double bonds are trigonal planar, so because the benzene is built up from planar atoms, it is completely flat. C-C bonds are not polar, and C-H bonds are hardly polar at all, so the dominant IMF in this part of the molecule is London dispersion or induced dipole-induced dipole interaction. That's a pretty weak interaction generally, but it can get a little stronger between large molecules, or between flat ones, because two flat molecules can have more surface area in contact with each other. That means the benzenes in benzyl alcohol and the benzenes in eosin have appreciable London forces that allow them to interact with each other.

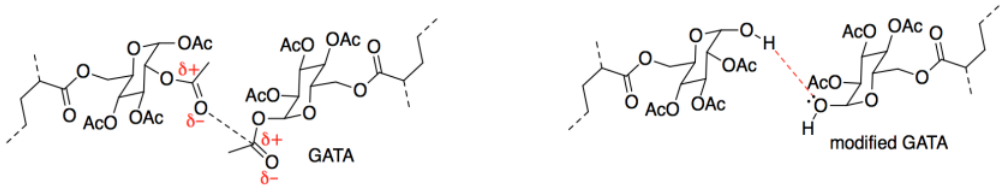
p) With the cellulose, covered in OH groups, the polar interactions outlined above will become more prominent.

Exercise 7.14.5:

a. OAc is an ester.
b. AAI has three chiral centers; GATA has five.
c. The chains in the adhesive would stick to each other via intermolecular attractions. Dipole-dipole attractions would be the strongest. However, induced dipole-induced dipole or London dispersion forces would actually be significant because there would be hundreds of such interactions along the chains.



d. The most significant interaction with the paper would be hydrogen bonding. The cellulose in the paper would provide hydrogen bond donors (the OH groups) and the side groups in the adhesive chains would provide hydrogen bond acceptors (all those oxygens). However, if the paper contains a lot of sizing, induced dipole-induced dipole or London dispersion forces may form a significant part of the interaction. As with cohesion, this would not be a significant factor except that there are so many alkyl chains involved, so these tiny attractions would add up.



e.

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CHAPTER OVERVIEW

8: Introduction to Biomolecules

8.1: Lipids
8.2: Proteins
8.3: Nucleic Acids
8.4: Carbohydrates
8.5: Biomolecule Application Problems

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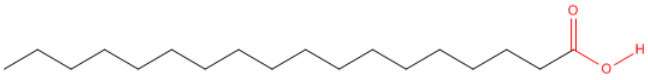
8.1: Lipids

Fatty Acids: Single Chain Amphiphiles

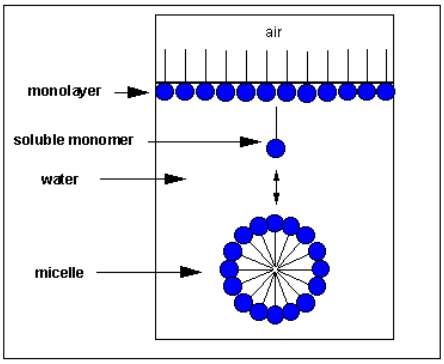
Consider stearic acid, a type of lipid known as a fatty acid. It has an 18 C atom chain with a carboxylic acid group (RCO_2H) at one end.



The carboxyl end (shown in red) containing the two oxygens is polar, but the rest of the molecule is completely nonpolar. We can draw a "cartoon" model of this molecule as a circle representing the carboxyl polar end or "head group" with a single connecting line representing the long, nonpolar "tail".

A molecule that contains a distinct polar region and a distinct single chain nonpolar region is called a **single chain amphiphile**.

How would this fatty acid interact with water? A small number of these molecules might be soluble in water (remember even insoluble salts dissociate to a small degree to form some ions). The nonpolar tail is not stable in water, but the polar head is. Some of the molecules migrate to the surface of the water, with the nonpolar tails protruding into the air and away from water, forming a monolayer on the surface. Others will self-aggregate through IMFs to form a spherical structure in which the nonpolar tails are sequestered from water and the polar heads are facing the water. This structure is called a **micelle**. In the figure below, the polar head groups are shown in blue.



Which IMFs are involved? First consider attractive IMFs. The buried nonpolar chains can interact and be stabilized through London forces. Buried inside of the micelle, the nonpolar chains are sequestered from water. This view fits our simple axiom of "like-dissolves like". The polar head groups can be stabilized by ion-dipole interactions between charged head groups and water. Likewise H-bonds between water and the head group stabilize the exposed head groups in water. Repulsive forces are also involved. Head groups can repel each other through steric factors, or ion-ion repulsion from like-charged head groups. The attractive forces must be greater than the repulsive forces, leading to micelle formation.

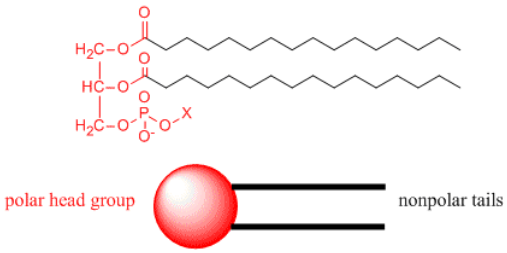
Jmol
: Micelle
Jmol14
(Java) |
JSMol
(HTML5)

Detergents are molecules, like fatty acids, that have distinct and separate polar and nonpolar regions. They form micelles in water. Grease from clothes or foods, normally not soluble in water, can "dive" into the middle of the micelle and be carried off by this

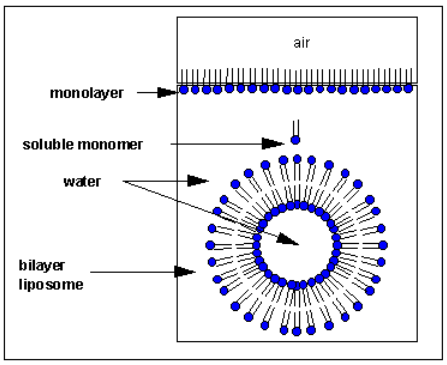
structure. This effectively "solubilizes" the nonpolar molecule. **Notice that there is no water inside the micelle** as you can see in the figure and Jmol computer model above.

Phospholipids: Double Chain Amphipiles

Now consider another lipid, a phospholipid, the example shown below. X represents a polar group containing a charged phosphate.



Note that it has a polar end (shown in red), but in contrast to stearic acid, it has two long nonpolar tails shown in black. We can draw a "cartoon" model of this as a circle representing the polar end or "head group" with two connecting lines representing the two long nonpolar "tails". It is a double chain **amphiphile**. Phospholipids are the major component of biological membranes. Again, in the figure below, the polar head groups are shown in blue.



How would this phospholipid interact with water? Again, as with single chain detergents, there are several possible ways. A small number of these molecules might be soluble in water. Nonpolar tails are unstable in water, while the polar head are stable in water. As in the case of single chain detergents, some of the molecules migrate to the surface of the water, with the nonpolar tails sticking out into air, away from water, to form a monolayer on the top of the water. Others will self- aggregate through IMFs to form a bilayer or membrane instead of a micelle, which only contains single chain amphiphiles. The polar head groups in a double chain amphiphile can get closer together than in a micelle since there are extra stabilizing interactions among the side chains. The result is the formation of a membrane **bilayer** which affords less space for each head group than in a micelle. Imagine the bilayer membrane curving around and eventually meeting itself. A structure like this would look like a small biological cell. In contrast to a micelle, the interior of this multimolecular lipid aggregate, called a **liposome or vesicle**, is filled with water which can interact through IMFs with the head groups of the inner leaflet of this membrane. The head groups of the outer leaflet of the membrane interact through IMFs with the bulk water.

Jmol
: Nonhydrated Bilayer
Jmol14 (Java) | JSMol (HTML5)

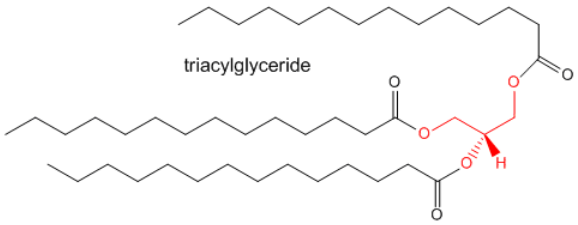
Liposomes are useful since they are simple models of actual biological membranes. In addition, they can be used therapeutically. Toxic drugs, like those used in chemotherapy, can be incorporated into the aqueous volume inside a liposome where they can be targeted to specific tumor cells.

Liposomes and micelles seem to be complicated structures. However their formation and structure can be predicted from the simple solubility properties of these molecules and through an understanding of IMFs.

Ever wonder why a solution of sodium hydroxide (a base) feels slippery on your skin? The hydroxide base cleaves the bond between fatty acids connected to more complex skin phospholipids. The free fatty acids then aggregate spontaneously to form micelles which act like detergents which as you know feel slippery as well.

Triacylglycerides

We've seen the structures of a single fatty acid and of a phospholipid which contains two fatty acids linked to glycerol. Another very abundant lipid contains three fatty acids connected to glycerol to form a triacylglyeride, as shown below.



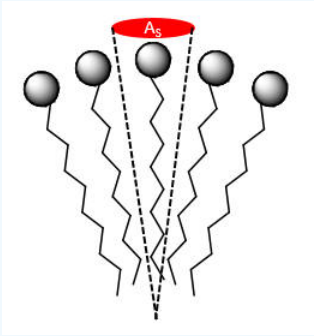
This molecule overall is so nonpolar that it self-associates to form lipid drops which are stored predominantly in fat or adipose tissue in the body. Instead of having a structural role, it functions mainly as a source of energy.

Exercise 8.1.1

We've discussed how lipids can form aggregates in aqueous solution. Now let's reverse the scenario. Draw a diagram showing what might happen if lots of stearic acid molecules were added to the solvent hexane, C_6H_{14}.

Exercise 8.1.2

An important property of a micelle is the surface area/head group (A_S/HG). This is equal to the total surface area of the micelle divided by the number of single chain amphiphiles in the micelle, A_{tot}/#amphiphiles.



What kind of repulsive forces exist between head groups? What happens to A_S/HG if the total charge on the head group increases? Decreases? How would IMFs between the nonpolar chains affect micelle stability?

Exercise 8.1.3

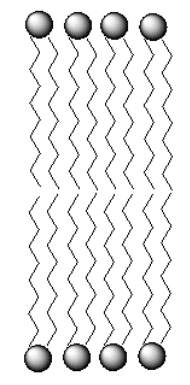
Imagine now that you squish the spherical micelle into a bilayer. Think of this as flattening a tennis ball. What would happen to the (A_S/HG)? (Hint: Think of pencils sticking out radially from the tennis ball, with the erasers representing head groups. What happens to the eraser spacing as it the tennis ball distorts to a bilayer?. How does this explain why charge single chain amphiphile don't form bilayers?

Exercise 8.1.4

Now try a different thought experiment. Add more and more of the same single chain amphiphile to a spherical micelle. The shape must deviate from a sphere. Why? Draw a cartoon diagram to illustrate your point. In this case the lipid aggregate can grow if it adopts a cylindrical shape. Compare the (A_S/HG) for the spherical, cylindrical and bilayer shapes. Which of these shapes are more likely to form

Exercise 8.1.5

Now lets consider a bilayer made of **double** chain amphiphiles (shown below). Compare the A_S/HG for a bilayer to a scenario where the double chain amphiphile forms a micelle? Now draw a cartoon diagram to explain the observation that double chain amphiphiles don't form **micelles** (note the bilayer shown).

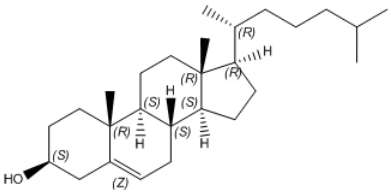


Exercise 8.1.6

Now explain how the double chain amphiphiles can tolerate the close packing of head groups found in the bilayer while single chain amphiphiles usually can't.

Exercise 8.1.7

There are many other different types of lipids. An example, cholesterol, is shown below. This molecule has many biological functions. It is often found in lipid bilayers. Draw a cartoon showing how cholesterol might fit into a bilayer.



cholesterol

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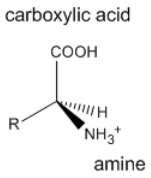
8.2: Proteins

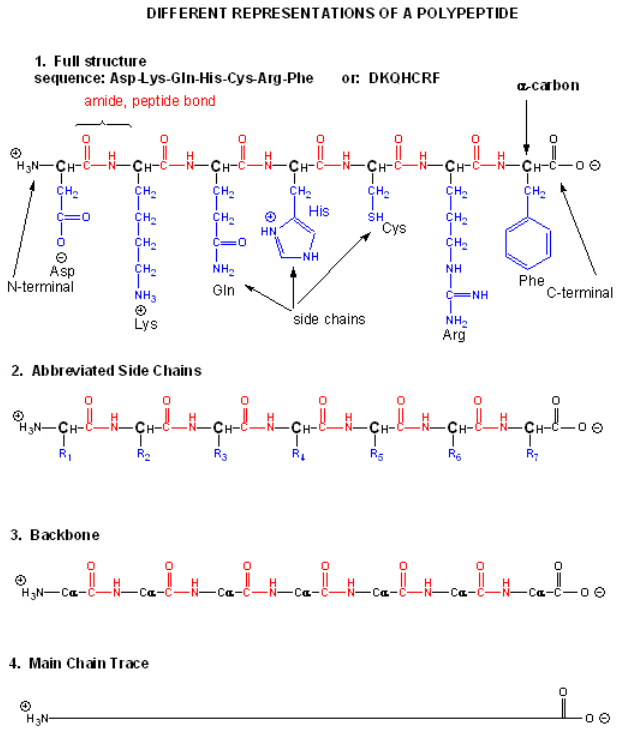
Proteins are large biological molecules that have molecular weights ranging from the thousand to the millions. Humans have about 24,000 different proteins which catalyze chemical reactions, recognize foreign molecules and pathogens, allow cellular and organism movement, and regulate cell response, including cell division and death.

Proteins are polymers consisting of monomers called **amino acids**. There are twenty different naturally occurring amino acids that differ in one of the four groups connected to a central carbon atom. In an amino acid, the central (alpha) carbon has an **amine** group (RNH_2, RNH_3^+), a **carboxylic acid** group (RCOOH, $RCOO^-$), a hydrogen (H), and one of twenty different R groups (also called **side chains**) attached to it.



The R groups are classified as generally nonpolar, polar charged, or polar uncharged. The smallest amino acid is glycine (Gly) which has a hydrogen atom as its R group. All of the other 19 naturally-occurring amino acids have one stereocenter (at the carbon containing the amine and carboxyl groups) and can exist as two possible enantiomers; only the L-enantiomer occurs in proteins. All amino acids in proteins have the absolute configuration shown above. With the exception of the amino acid cysteine (Cys) with a -CH_2SH for an R group (which happens to have an R stereocenter), all of the remaining amino acids found in proteins have an S stereocenter.

Amino acids form polymers when an amino group of an amino acid is covalently attached to the **carbonyl** carbon (C=O) of the carboxyl group of the next amino acid. The resulting link between the amino acids is an **amide** bond which biochemists call a **peptide bond.** In this reaction, water is released (condensation). In a reverse reaction, the peptide bond can be cleaved by water (hydrolysis). When two amino acids link together to form an amide link, the resulting structure is called a dipeptide. Likewise, we can have tripeptides, tetrapeptides, and other polypeptides. At some point, when the structure is long enough, it is called a protein. There are many different ways to represent the structure of a polypeptide or protein. Each shows differing amounts of information. A heptapeptide, Aspartic Acid-Lysine-Glutamine-Histidine-Cysteine-Arginine-Phenylalanine is shown below. Each amino acid is denoted by a three letter code (Asp-Lys-Gln-His-Cys-Arg-Phe).



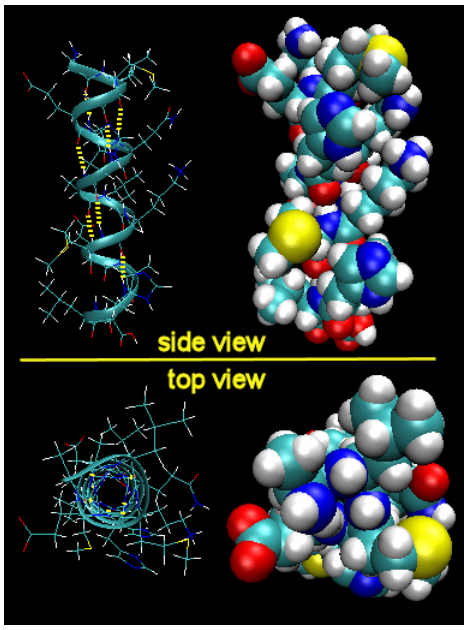
Notice that the protein chain has a beginning (an **N-terminus** with a amino group) and an end (a **C-terminus** with a carboxyl group). Also note that every atom in the backbone has a slight charge arising from the presence of the electronegative atoms O and N. Hence the **backbone is polar**. The R groups on each amino acid in the peptide are also called **side chains**.

The actual linear sequence of amino acids that make up a protein is called its **primary (1^o) structure.** Both the sequence of a amino acids and total chain length differ from one protein to another. Just for an octapeptide, there are over 25 billion different possible arrangements of amino acids. Hence the diversity of possible proteins is enormous.

Most proteins do not form an elongated structure as implied by the extended structures shown above. Rather they collapse on themselves to form compact, mostly globular (roughly spherical) structures. They do so as groups local and distant on the chain attract each other through IMFs which are now exerted within the large protein and not between different proteins. What kinds of IMFs are involved?

To simplify the process, lets consider first just the polar backbone without the side chains. The main chain can clearly form hydrogen bonds with itself and to water. If the hydrogen bonds are between the amide H (a hydrogen bond "donor" and a carbonyl O (a hydrogen bond "acceptor") a fixed number of amino acids distant from the amide H, a regular, repetitive **secondary (2^o) structures** called a helix can form. One especially prevalent helix, the **alpha helix,** forms within a short stretch of amino acids when the amide H of an amino acid (given the number i^{th}) in the backbone forms a hydrogen bond to the carbonyl C four amino acids in the protein sequence (i^{th} + 4). There are 3.6 amino acids/turn of the alpha helix.

Alpha Helix (dotted yellow lines represent hydrogen bonds)

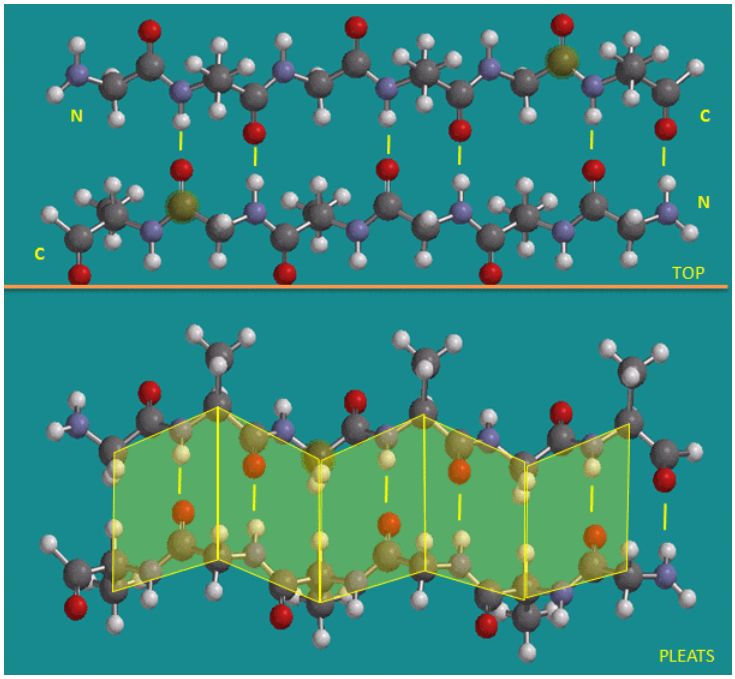


Note that all the side chains (R groups) are pointing away from the helix axis. Evident from the space-filling model, there is no opening in the helix as you look down the axis because the actual atoms are densely packed. The trace of an alpha helix in a protein is usually represented by a red or purple curly ribbon.

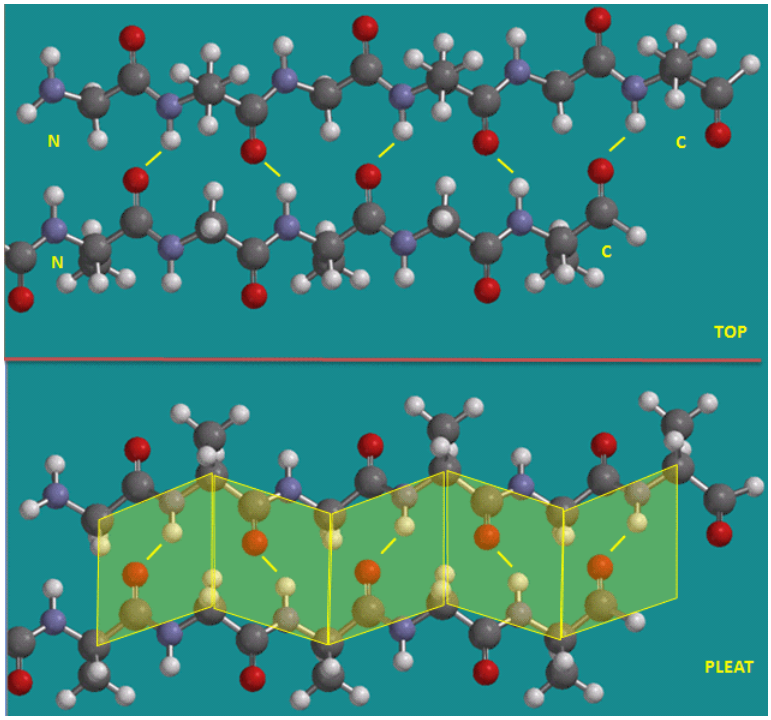
Jmol:
An isolated helix from an Antifreeze Protein
Jmol14
(Java) |
JSMol
(HTML5)

Beta strands/sheets, another type of secondary structure, also occur when H bonds form between adjacent short stretches of amino acids in which the backbone of the short stretches are running either in the same N-C direction (**parallel beta strands**) or in opposite directions (**antiparallel beta strands**). The hydrogen bonds in secondary structures are all among main chain atoms in the backbone, not among side chains. Beta structure is usually represented in "cartoon" form by yellow flat ribbons with an arrow showing the direction of the protein backbone from the N-terminus to C terminus direction.

Antiparallel Beta Strands (yellow lines represent hydrogen bonds)



Parallel Beta Strands (yellow lines represent hydrogen bonds)



The side chains in the beta sheet are perpendicular to the plane of the sheet, extending out from the plane on alternating sides. Parallel sheets characteristically distribute nonpolar (or hydrophobic) side chains on both side of the sheet, while antiparallel sheets are usually arranged with all the hydrophobic residues on one side. This requires an alternation of hydrophilic and hydrophobic side chains in the primary sequence. Antiparallel sheets are found in silk with the sheets running parallel to the silk fibers. The following repeat is found in the primary sequence: (Ser-Gly-Ala-Gly)n), with Gly pointing out from one face and Ser or Ala from the other.

Jmol:
Twisted beta sheet from Arabinose Binding Protein Jmol14 (Java) | JSMol (HTML5)

Protein folding is determined by much more than the formation of hydrogen bonds between backbone donors and acceptors. We must consider the effects of the 20 different R groups (side chains) which complicate the folding process. A protein ultimately folds in space to form a unique 3D shape, which usually contains some alpha helices and beta sheets. The overall 3 D structure is called the **tertiary (3^0) structure** of the protein. The 3D structure of a protein determines the function of the protein. Protein shape and surface charge characteristics determine which molecules, both small and large, bind to the protein.

Here are some models of proteins showing secondary and tertiary structures.

Jmol:
M
et-Myoglobin
- predominantly alpha-helical protein Jmol14 (Java) | JSMol (HTML5)

Jmol:
Superoxide Dismutase - predominantly beta structure
Jmol14 (Java) | JSMol (HTML5)

Jmol:
Triose Phosphate Isomerase - has both alpha and beta secondary structure
Jmol14 (Java) | JSMol (HTML5)

The structure of proteins is much more complicated than micelles and bilayers. To a first approximation, a protein consists of a polar main chain/backbone from which amino acid side chains of varying polarity and charge hang. These side chains can be polar uncharged, polar charged, or nonpolar. In general the nonpolar side chains are more stable buried in the center of the protein, where they are surrounded by other nonpolar side chains and are oriented away from polar water. Compare this to the structure of a micelle. Given the greater complexity of protein primary and tertiary structure, however, not all nonpolar side groups can be buried. Some are on the surface exposed to solvent. Likewise, polar and charged polar side chains like to be on the surface exposed to water, but some will find themselves buried. If they are, they will be surrounded by polar side chains or interact with buried hydrogen bond donors and acceptors on the backbone that stabilize the buried polar group. Here are some findings about proteins derived from the known 3D structure of thousands of different proteins:

- On average, about **50%** of the amino acids in a protein are in secondary structure with an average of about **27%** alpha helix and **23%** beta structure.
- The side chain location varies with polarity. **83%** of nonpolar side chains (such as Val, Leu, Ile, Met, and Phe) are in the interior in the folded protein.
- Charged polar side chains are almost equally partitioned between being buried or exposed on the surface.
- Uncharged polar groups such as Asn, Gln, Ser, Thr, and Tyr are mostly **(63%)** buried, and not on the surface.
- Globular (spherical) proteins are quite compact, with water excluded. The packing density (V_{vdw}/V_{tot}) is about 0.74, which is like the NaCl crystal and equals the closest packing density of 0.74. This compares to organic liquids, whose density is about 0.6-0.7.

The packing around a buried nonpolar side chain of the amino acid phenylalanine (Phe) is shown in the Jmol below. It shows the structure of a small protein (protein tyrosine phosphatase) and the amino acids groups surrounding the buried Phe.

Jmol:
Buried Phe in low molecular weight protein tyrosine phosphatase (bovine)
Jmol14 (Java) | JSMol (HTML5)

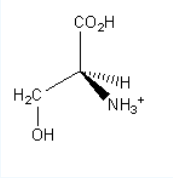
Exercise 8.2.1

Secondary structure in proteins involves

a. hydrogen bonds between side chain atoms and backbone atoms
b. hydrogen bonds between side chain atoms and other side chain atoms
c. London dispersion forces among side chain atoms
d. hydrogen bond between backbone atoms and other backbone atoms.

Exercise 8.2.2

The structure of the amino acid Ser is shown below:

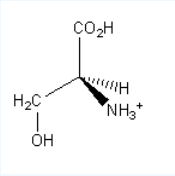


Which groups are involved in forming covalent bonds to other amino acids in a protein?

a. $-CH_2OH$ and $-CO_2H$
b. $-CH_2OH$ and $-NH_3^+$
c. $-CO_2H$ and $-NH_3^+$
d. -H and $-CH_2OH$

Exercise 8.2.3

The structure of the amino acid Ser is shown below:



If Ser was in an alpha helix, which group would most likely be projecting away from the helix axis?

a. $-CH_2OH$
b. $-NH_3^+$
c. $-CO_2H^+$
d. -H

Exercise 8.2.4

If Ser were part of a protein, which of the following would most likely **NOT** describe the environment around the side chain?

a. it could be buried in the protein surrounded by nonpolar amino acid side chains
b. it could be on the surface surrounded by water
c. it would buried adjacent to a glutamine side chain
d. it is polar so it could not be buried in the protein

Exercise 8.2.5

Molecules of a given protein have the following trait(s):

a. a defined amino acid sequence
b. an invariant molecular weight

c. a fixed amino acid composition
d. all of the above

Exercise 8.2.6

_____ between tightly packed amino acid side chains in the interior of a protein are a major contribution to the stability of the native state.

a. Dipole-dipole interactions
b. Ion - ion interactions
c. Covalent bonds
d. London dispersion forces

Exercise 8.2.7

If the following section of a polypeptide is folded into an alpha helix, to which amino acid is the carbonyl group of Ala H-bonded?

N term Ala-Leu-Ser-Asp-Glu-Val C term

a. Leu
b. Ser
c. Asp
d. Glu
e. Val

Exercise 8.2.8

Which form of a 10 amino acid peptide would most likely have the shortest length?

a. the peptide is in solution and not part of a proteins structure
b. the peptide is part of a protein and in a antiparallel beta sheet
c. the peptide is part of a protein and in a parallel beta sheet
d. the peptide is part of a protein and in an alpha helix

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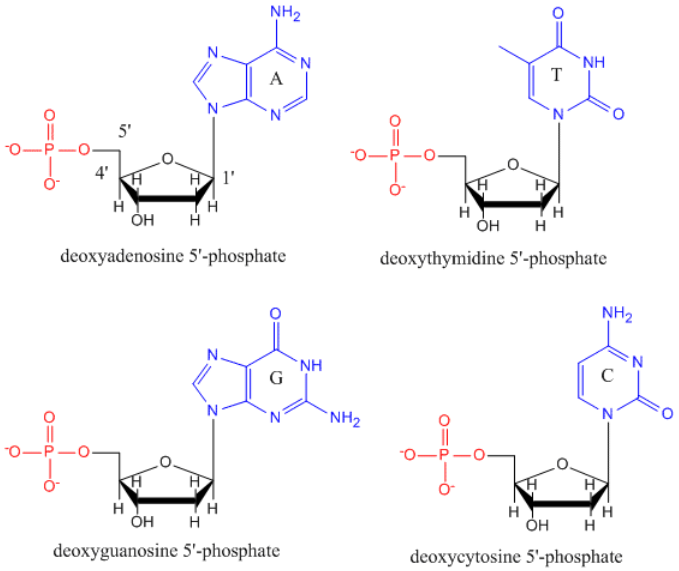
8.3: Nucleic Acids

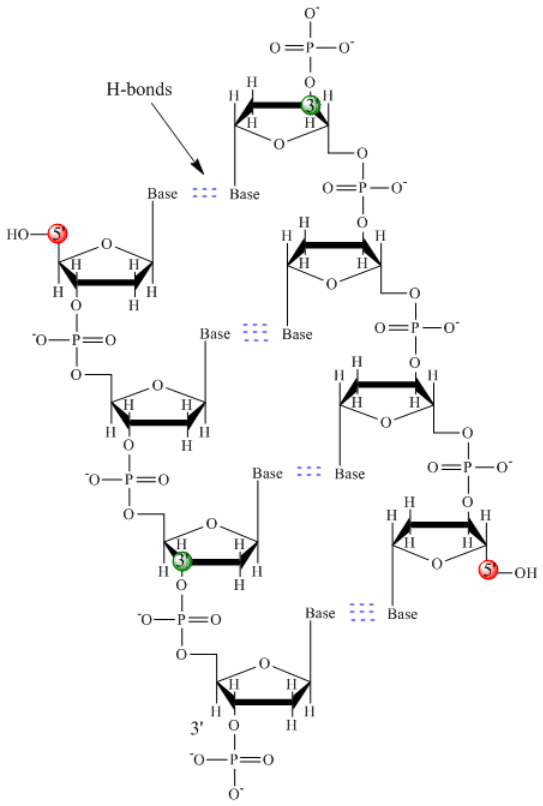
The nucleic acids RNA and DNA are involved in the storage and expression of genetic information in a cell. Both are polymers of monomeric nucleotides. DNA exists in the cell as double-stranded helices while RNA typically is a single-stranded molecule which can fold in 3D space to form complex secondary (double-stranded helices) and tertiary structures in a fashion similar to proteins. The complex 3D structures formed by RNA allow it to perform functions other than simple genetic information storage, such as catalysis. Hence most scientists believe that RNA preceded both DNA and proteins in evolution as it can both store genetic information and catalyze chemical reactions.

DNA

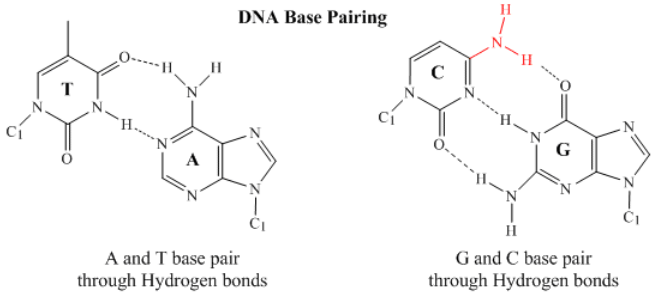
DNA is a polymer, consisting of monomers call **deoxynucleotides**. The monomer contains a simple sugar (deoxyribose, shown in black below), a phosphate group (in red), and a cyclic organic R group (in blue) that is analogous to the side chain of an amino acid.



Only **four** bases are used in DNA (in contrast to the 20 different side chains in proteins) which we will abbreviate, for simplicity, as A, G, C and T. They are bases since they contain amine groups that can accept protons. The polymer consists of a sugar - phosphate - sugar - phosphate backbone, with one base attached to each sugar molecule. As with proteins, the DNA backbone is polar but also charged. It is a polyanion. The bases, analogous to the side chains of amino acids, are predominately polar. Given the charged nature of the backbone, you might expect that DNA does not fold to a compact globular (spherical) shape, even if positively charged cations like Mg bind to and stabilize the charge on the polymer. Instead, DNA exists usually as a double-stranded (ds) structure with the sugar-phosphate backbones of the two different strands running in opposite directions (5'-3' and the other 3'-5'). The strands are held together by hydrogen bonds between bases on complementary strands. Hence like proteins, DNA has secondary structure; but in this case, rather than being within the backbone, hydrogen bonds are between the "side chain" bases on opposing strands. It is actually a misnomer to call dsDNA a molecule, since it really consists of two different, complementary strands held together by hydrogen bonds. A structure of ds-DNA showing the opposite polarity of the strands is included below.



In double-stranded DNA, the guanine (G) base on one strand can form three H-bonds with a cytosine (C) base on another strand (this is called a GC base pair). The thymine (T) base on one strand can form two H-bonds with an adenine (A) base on the other strand (this is called an AT base pair). Double-stranded DNA has a regular geometric structure with a fixed distance between the two backbones. This requires the base pairs to consists of one base with a two-ring (bicyclic) structure (these bases are called purines) and one with a single ring structure (these bases are called pyrimidines). Hence a G and A or a T and C are not possible base pair partners.



A and T base pair through Hydrogen bonds

G and C base pair through Hydrogen bonds

Double-stranded DNA varies in length (number of sugar-phosphate units connected), base composition (how many of each base set) and sequence (the order of the bases in the backbone). The following links provide interactive Jmol models of dsDNA made by Angel Herráez, Univ. de Alcalá (Spain) and Eric Martz.

External JSmol

:

- ds-DNA with base pairs and H-bonds
- Strands and helical backbone
- Ends, Parallelism

Chromosomes consist of one dsDNA with many different bound proteins. The human genome has about 3 billion base pairs of DNA. Therefore, on average, each single chromosome of a pair has about 150 million base pairs and lots of proteins bound to it. dsDNA is a highly charged molecule, and can be viewed, to a first approximation, as a long rod-like molecule with a large negative charge. It is a polyanion. This very large molecule must somehow be packed into a small nucleus of a tiny cell. In complex (eukaryotic) cells, this packing problem is solved by coiling DNA around a core complex of four different pairs (eight proteins total) of histone proteins (H2A, H2B, H3, and H4) which have net positive charges. The histone core complex with dsDNA wound around approximately 2.5 times is called the **nucleosome**.

Jmol
: Nucleosome
Jmol14
(Java) |
JSMol
(HTML5)

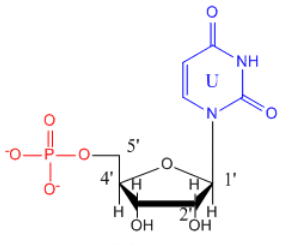
DNA can adopt two other types of double-helical forms. The one discovered by Watson and Crick and found in most textbooks is called B-DNA. Depending on the actual DNA sequence and the hydration state of the DNA, it can be coaxed to form two other types of double-stranded helices, Z and A DNA. The A form is much more open then the B form.

The 3.2 billion base pairs of DNA in humans contain about 24,000 short stretches (genes) that encode different proteins. These genes are interspersed among DNA that helps determining if the gene is decoded into RNA molecules (see below) and ultimately into proteins. For a particular gene to be activated (or "turned on"), specific proteins must bind to the region of a particular gene. How can binding proteins find specific binding targets among the vast number of base pairs that to a first approximation have a repetitive sugar-phosphate-base repeat? The Jmol below shows how specificity can be achieved. When DNA winds into a double helix through base-pairs between AT and GC, hydrogen bond donors (amide H's) and acceptors (O's) on the bases that are not used in intrastrand base pairing are still available in the major and minor grove of the ds-DNA helix (see Jmol below). Unique base pair sequences will display unique patterns of H bond donors and acceptors in the major grove. These donors/acceptors can be recognized by specific DNA binding proteins which can lead to gene activation upon binding.

Jmol
: dsDNA showing unique H bond donors and acceptors in the major grove
Jmol14 (Java) | JSMol (HTML5)

RNA

The monomers that make up RNA are identical to those for DNA with two differences. The 2'C of the ribose ring has an OH instead of H (as is found in deoxyribose). In addition, the thymine (T) base found in DNA is replaced with uracil (U). The structure of uridine-5-monophosphate is shown below.



uridine 5-phosphate

Based on analogy with DNA, you might expect RNA to adopt a double-stranded helical conformation. It can do this in short stretches, but instead, even in the presence of positively charged divalent cations, it is found predominantly in a single-stranded form. This single strand folds to form regions of secondary structure (double-stranded helices) imbedded in a complex tertiary structures (not unlike a protein).

The addition of the 2'OH on the ribose ring or RNA alters the pucker of the ribose ring and destabilizes ds-RNA in comparison to ss-RNA through steric interference. The five-membered ribose or deoxyribose ring can adopt an **envelope**-like structure in which one ring atom, representing the tip of the envelope, is above, or **endo**, to the other four coplanar atoms. In deoxyribose, the 2' ring carbon atom prefers the endo position; in ribose, the 3' C is endo (see Jmol model below). When double-stranded RNA forms, it is actually very similar in structure to the more open (and less abundantly found) A-DNA form.

Jmol

:

Jmol model showing puckering of ribose ring of RNA and deoxyribose ring of DNA

(updated to HTML5 asap)

Jmol

:

Jmol model comparing dsDNA and dsRNA

(updated to HTML5 asap)

Here are some examples of complex tertiary structures formed from single-stranded RNA which folds to form a compact 3D structure with some double-stranded A-type helices stabilized by intramolecular H bonds between G/C and A/U base pairs. .

Jmol

: Jmol model of tRNA (note the regions of secondary structure - A type dsRNA) (updated to HTML5 asap)

Jmol

:

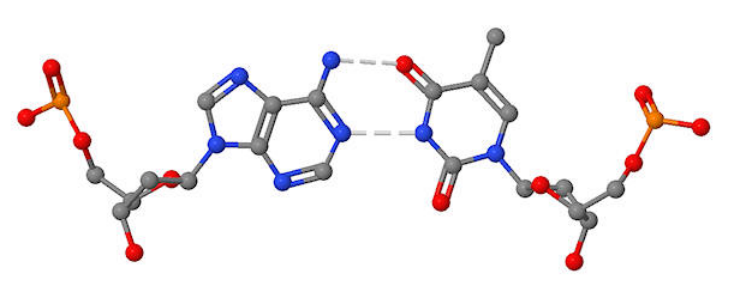
Jmol model of 70 S Ribosome from T. Thermophilus showing mRNA and tRNA interactions

(updated to HTML5 asap)

Exercise 8.3.1

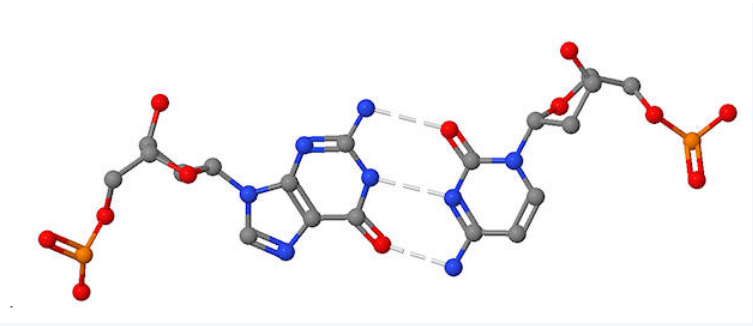
The figure below shows an actual base pair in a dsDNA.

- identify the base pair and the deoxyribose sugars
- place a negative charge on any atom with a negative charge
- label atoms other than those between the bases that could form H bonds with other DNA binding molecules



Exercise 8.3.2

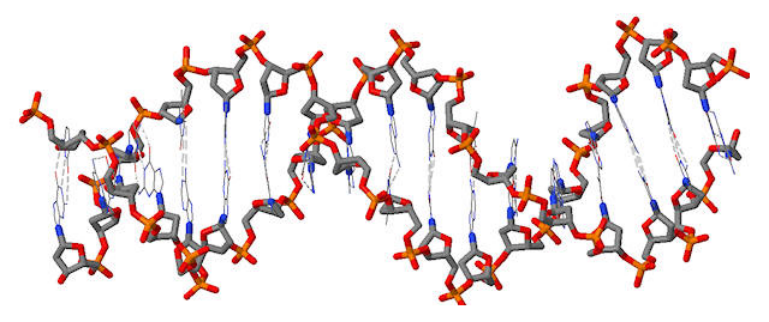
Do the same for the following base pair



- identify the base pair and the deoxyribose sugars
- place a negative charge on any atom with a negative charge
- label atoms other than those between the bases that could form H bonds with other DNA binding molecules

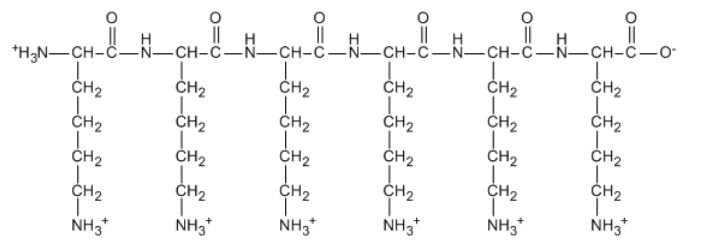
Exercise 8.3.3

The backbone of dsDNA is highlighted below. Place a circle on every atoms with a negative charge.

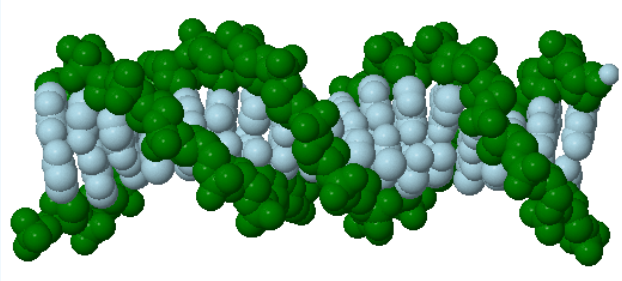


Exercise 8.3.4

The structure of a fully protonated peptide, poly-Lys, composed just of the amino acid lysine, is shown below.



Representing this molecule in cartoon form as an elongated ellipse, show how it might interact with on the DNA helix



Exercise 8.3.5

Based on your answer to the above question, what general feature might be present in DNA binding proteins?

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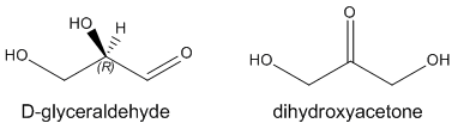
8.4: Carbohydrates

Carbohydrates (CHOs) are among the most complex of biological molecules. If you have ever "counted" your carbs, you know that one biological function of CHOs is to store and provide energy (upon oxidation) to the body for required functions. Instead of concentrating on how CHOs are used for energy production, we will focus predominantly on their structures, which allows them to elicit their main function to provide binding interactions with other biomolecules, either in solution or on cell membranes. Binding, promoted through IMFs, initiates and modulates all biological interactions and processes. First, we will consider the structure of simple and more complex carbohydrates.

Monosaccharides

The simplest carbohydrates are **monosaccharides**, small organic molecules that contain more than one OH (alcohol) group and a single aldehyde (RCOH) or ketone (RCOR). Hence the simplest monosaccharides, glyceraldehyde and dihydroxyacetone, contain three carbons. In contrast to the alkane hydrocarbons which have the generic formula C_nH_{2n+2}, simple monosaccharides have the generic formula $C_n(H_2O)_n$ which corresponds to their designation as carbo(hydrates).

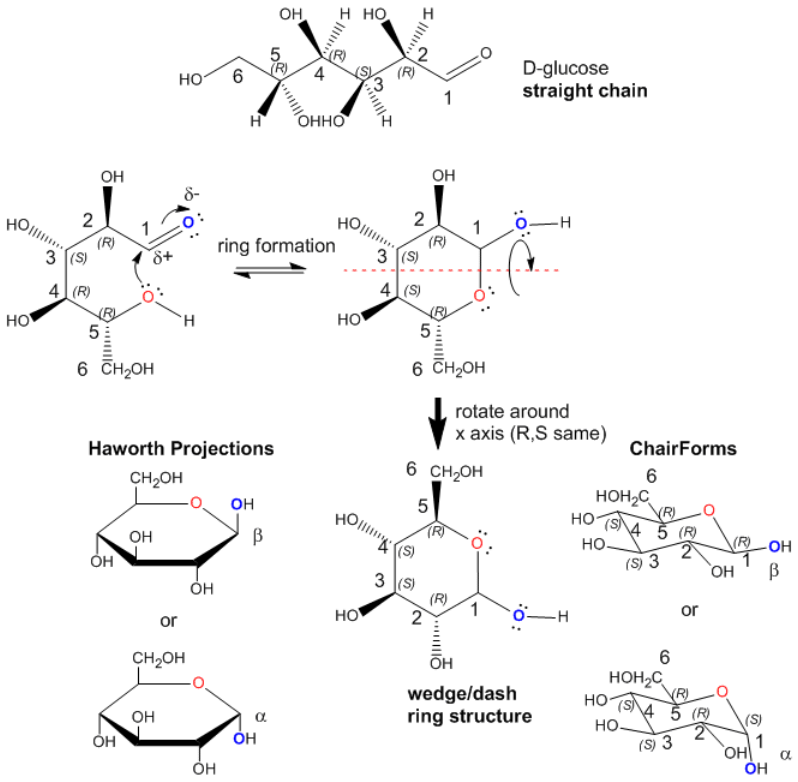


D-glyceraldehyde dihydroxyacetone

Glyceraldehyde has one stereocenter. The naturally occurring isomer shown above is R-glyceraldehyde. Instead of using the R/S systems to denote the absolute configuration of specific stereocenters in sugars (as well as amino acids), biochemists often use the D/L system. The D designation on sugars refers to any monosaccharide whose last stereocenter (or in the case of glyceraldehyde, the only stereocenter) has the same absolute configuration as R-glyceraldehyde. All naturally occurring amino acids have the L configuration as they have the same absolute configuration when compared to L-glyceraldehyde.

Monosaccharides can exist in solution in an equilibrium mixture of a straight chain and cyclic form. An example is shown below for the common sugar D-glucose (Glc). The R/S designation for each stereocenter is included to make it easier to see the orientation of each OH group as the straight chain form cyclizes. In the process of forming the 6-membered ring, a lone pair on the slightly negative OH on C5 forms a bond to the slightly positive C1. This process requires rotation around the various C-C bonds to allow the OH on C5 to approach C1. Since the carbon can only have 4 bonds, bond formation to C1 from the OH on C5 causes the C=O (an aldehyde) to become C-OH (an alcohol). The chair, wedge/dash and "Haworth" projections of the resulting ring are shown. Note that the OH on C1 can point up (beta form, remembered by the phrase butterflies UP) or down (alpha form, remembered by ants DOWN). In the beta form, all ring substituents are in the equatorial position (in the chair form) and in alternating up and down forms in the wedge structure, making the beta form the most stable of all possible 6-membered cyclic forms of 6C sugars.

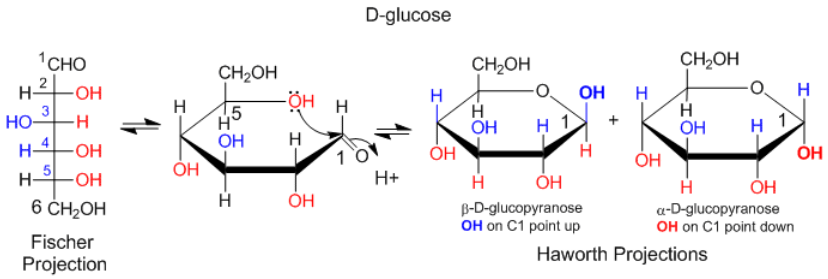
D-Glucose: Open chain and Cyclic (6 membered ring) Forms



Since there are 4 stereocenters in a 6C sugar aldehyde, there are 2^4 or 16 possible stereoisomers. Most 6C sugars are D sugars which are defined to have the same R,S designation as D-glyceraldehyde at the last stereocenter in the sugar. Common 6C sugars are D-mannose (Man) and D-galactose (Gal). D-glucose, D-mannose, and D-galactose, all of which have the R configuration at C5, differ in the orientation of the OH groups in the ring structures at C2, C3, and C4. Hence they are diastereomers. The most common 6C sugar containing a ketone (RCOR) at C2 is fructose.

Since sugars are polyhydroxy aldehydes or ketones, can the OH's on C2, C3, and C4 also form a bond to C1 (as illustrated for the C5 OH above) and form rings. They can but the most common form is the 6-membered ring form shown above for D-glucose. How many atoms would be in the rings if the other OH's were involved in ring formation? Why is the 6-membered ring most abundant in nature?

Another type of structural representation, the Fisher projection, is often used in biology texts. In this form, the structure is written in a vertical direction with vertical and horizontal lines (not wedges or dashes). It is simple to translate a Fisher project for simple sugars into a Haworth projection, then to a wedge/dash ring structure, and then to a chair form. An example of how to convert a Fisher projection to a Haworth for D-glucose is shown below. If the OH group points to the right in the Fisher projection, it points down in the Haworth projections. If the OH points to the left, it points up in the Haworth projection.



External JSmol (HTML5):
glucose
:

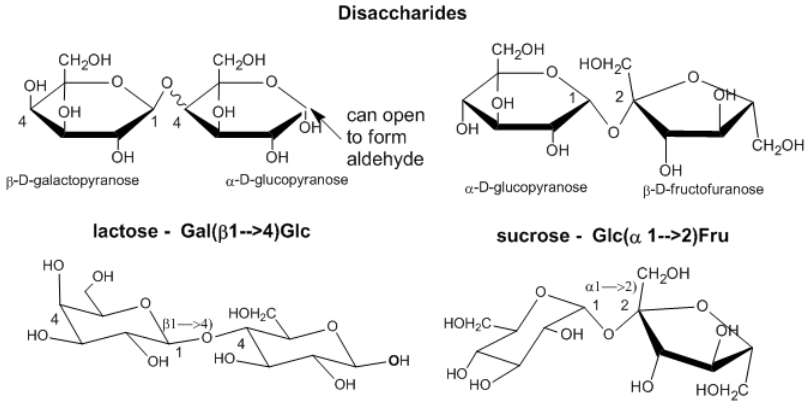
Chemical Derivatives of Monosaccharides

Many derivatives of monosaccharides are found in nature. These include:

- oxidized forms in which the aldehyde and/or alcohol functional groups are converted to carboxylic acids
- phosphorylated forms in which phosphate is added by ATP to form phosphoester derivatives
- amine derivatives such as glucosamine or galactosamine
- acetylated amine derivatives such as N-Acetyl-GlcNAc (GlcNAc) or GalNAc
- more complex condensation products of sugar derivatives with lactate ($CH_3CHOHCO_2^-$) and pyruvate, ($CH_3COCO_2^-$) to form muramic acid and neuraminic acids, (also called sialic acids), respectively.

Di- and Polysaccharides

As with proteins, which are polymers of amino acid monomers, covalent bonds can form between different sugar monomers to form disaccharides, trisaccharides, and ultimately polysaccharides, as shown below for two disaccharides, lactose and sucrose..



External JSmol (HTML5):
sucrose
:

Longer polysaccharides can be quite simple in structure, but given the diversity of monosaccharides that each have multiple OH groups available to connect two monosaccharides in a polymer, the complexity of polysaccharide structure can be overwhelming to study and understand. Compare this to a protein, a polymer of amino acids that, with the exception of the side chains, each have only two functional groups involved in the linkages between the amino acids.

Homopolysaccharides

The simplest polysaccharides consist of only one monosaccharide repeating unit. Three examples of homopolysaccharides, glycogen/starch, cellulose, and chitin are shown below. The monomer in glycogen/starch and cellulose is glucose. The differences between them is the linkage between the glucose monomers. In starch and glycogen, which are energy storage polysaccharides, the linkage is alpha 1-4. In cellulose, the most abundant biomolecule, the linkage is beta 1-4. The beta linkage ensures that all bulky groups on the glucose chairs are in the more stable, equatorial position. This is yet another example of the fact that structure can account for properties and function of molecules. A small covalent change to glucose, the substitution of a CH_3CONH- for a OH group on C2 of glucose gives the monosaccharide N-acetylglucosamine. This polymerizes, like cellulose, with a beta 1-4 linkage, to form a new polysaccharide, chitin, with markedly different properties than cellulose. Chitin, is the main component of the exoskeleton of arthropods.

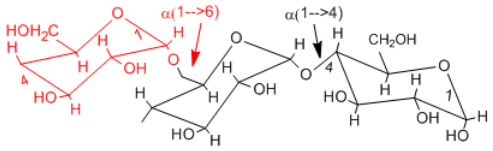
Starch consist of 20-30 % amylose, an unbranched alpha 1-4 polymer of D-glucose, and 70-80% amylopectin, which consists of alpha 1-4 links with alpha 1-6 links every 25-30 glucose residues. Glycogen is similar to amylopectin and also has a protein, glycogenin, at the core of the glycogen particle.

Homopolysaccharides

Energy Storage, Production

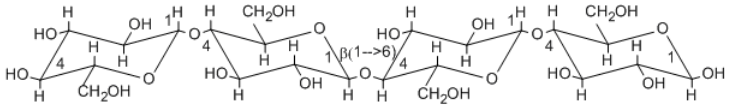
STARCH $\alpha(1\text{-->}4)$ glycosidic links main chain with many $\alpha(1\text{-->}6)$ branches

GLYCOGEN $\alpha(1\text{-->}4)$ glycosidic links main chain with fewer $\alpha(1\text{-->}6)$ branches

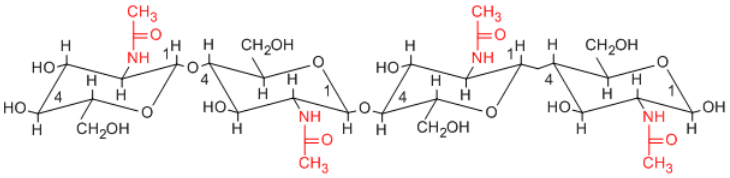


Sturctural Polysacchaides

CELLULOSE $\beta(1\text{-->}4)$ glycosidic links main chain; held together by intra/inter chan H-bonds



CHITIN $\beta(1\text{-->}4)$ glycosidic links main chain; major component in exoskeletons of arthropods.



External JSmol (HTML5):
amylose
:
amylose-Iodine
complex

External JSmol (HTML5):
amylopectin
:

External JSmol (HTML5):
amylopectin
:

External JSmol (HTML5):
model of glycogen

(similar to starch): Note that the the main chain twists (as indicated by the black chair forms in the figure above showing the main chain alpha 1-4 links), and thus forming a long helix. Triodiide, I_3^-, can fit into the opening of the helix, causing a solution of starch/glycogen to turn purple in this well known test for starch.

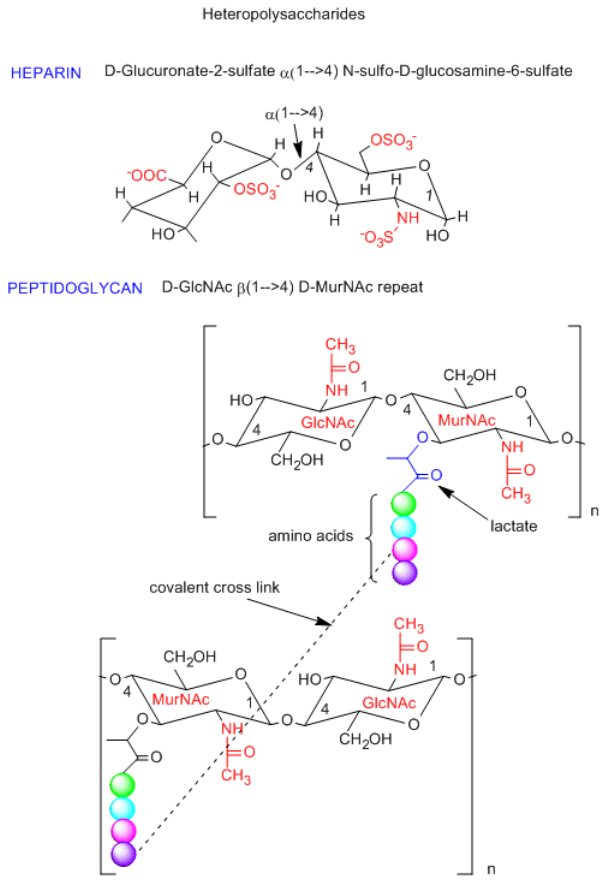
External JSmol (HTML5):

model of cellulose:

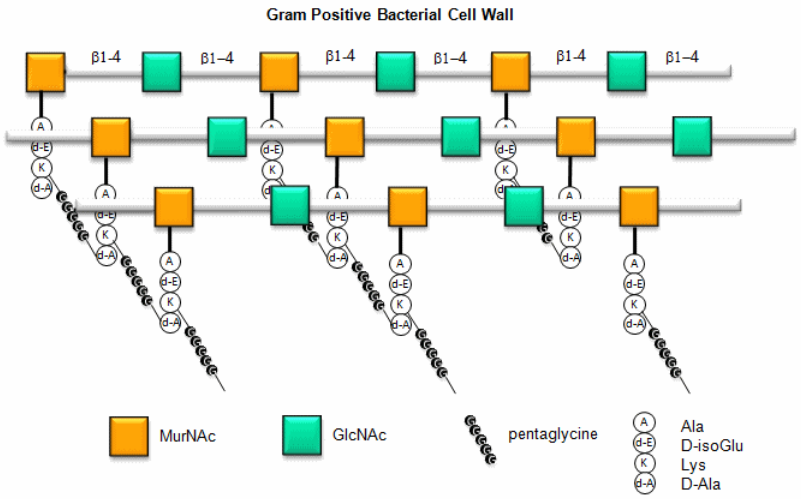
Note the extended, non-helical structure of the polymer

Heteropolysaccharides with disaccharide repeat

Polysaccharides can also be made of a repeating disaccharide unit, instead of repeating monosaccharides in the homopolysaccharides shown above. One example is a glycosoaminoglycan called heparin (an anticoagulant, shown in the figure below) that is composed repeating units of the disaccharide, D-glucuronate-2-sulfate (alpha 1,4) GlcNSulfo-6-sulfate. This disaccharides consists of two glucoses that have been chemically modified. Note the charges on this repeat unit. Another example is the disaccharide repeat in the peptidoglycan (contains both CHO and amino acids) cell walls of bacteria (see figure below). The repeat again consists of chemically modified glucose units. Compare the repeat with the main component of the cytoskeleton, chitin. Nature has chosen variants of this repeat to create a rigid and protective exoskeleton and cell wall for arthropods and bacteria.



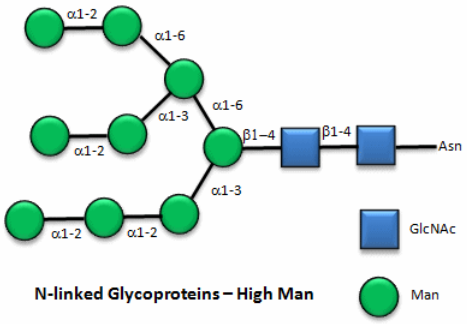
Here is a figure that provides a better view of the overall cell wall of Gram-positive bacteria.



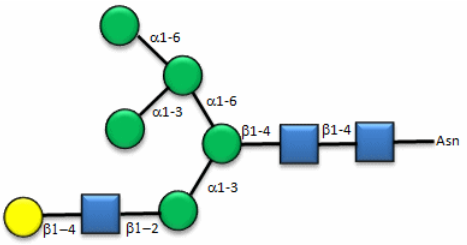
Carbohydrates in biomolecule recognition

Carbohydrates are covalently attached to many different biomolecules, including lipids, to form glycolipids, and proteins, to form glycoproteins. Glycoproteins and glycolipids are often found in biological membranes, to which they are anchored by nonpolar interactions. A special kind of glycoprotein, a proteoglycan, actually has more carbohydrate mass than protein. What is the function of these carbohydrates? Two are apparent. First, glycosylation of proteins helps protect the protein from degradation by enzyme catalysts within the body. However, a second main function arises from the facilitation of biomolecule recognition. Covalently attached carbohydrates that "decorate" the surface of glycoproteins or glycolipids provide new binding sites for interactions with other biomolecules. Hence glycosylation allows for cell:cell, cell:protein, or protein:protein interactions. Unfortunately, bacteria and viruses often recognize glycosylated molecules on cell membranes, allowing for their import into the cell.

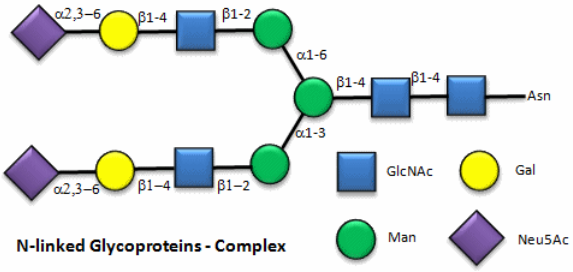
Here are some "cartoon" examples of carbohydrates covalently linked to the amino acid asparagine (Asn) on a glycoprotein.



N-linked Glycoproteins – High Man



N-linked Glycoproteins – Mixed (Hybrid)

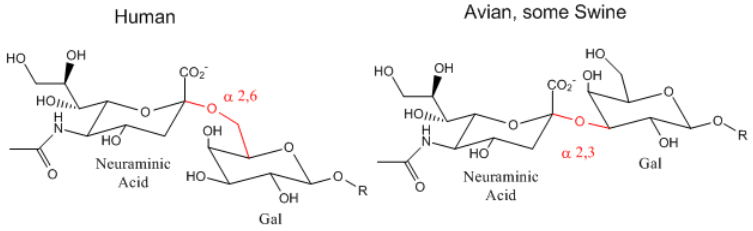


N-linked Glycoproteins - Complex

Here are some examples of biomolecular interactions promoted by IMFs involving carbohydrates.

Influenza Virus binding to Cell Surface Glycoproteins with Neu5Ac - A protein on the surface of influenza virus, hemagluttinin, binds to **sialic acid (Sia)**, which is covalently attached to many cell membrane glycoproteins on host cells. The sialic acid is usually connected through an alpha (2,3) or alpha (2,6) link to galactose on N-linked glycoproteins. The subtypes found in **avian** (and equine) influenza isolates bind preferentially to Sia (alpha 2,3) Gal which predominates in avian GI tract where viruses replicate. Human virus of H1, H2, and H3 subtype (cause of the 1918, 1957, and 1968 pandemics) recognize Sia (alpha 2,6) Gal, the major form in human respiratory tract. The swine influenza HA bind to Sia (alpha 2,6) Gal and some Sia (alpha 2,3)both of which found in swine.

Binding Site for Influenza Hemagluttinin Protein



- Jmol model of viral hemagluttinin bound to antiviral drugs and sialic (neuraminic acid) from Proteopedia

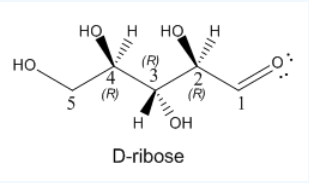
Leukocyte: Cell Wall binding - During inflammation, circulating leukocytes (a type of white blood cell) tether and roll on the walls of blood vessels where they become active. E-, L- and P-selectin proteins are the primary proteins responsible for the tethering and

rolling of these leukocytes. P-selectin binds, in part, to a tetrasaccharide, sialyl-Lewis^x (SLEX) on the cell surface.. The interaction between P-selectin and the cell mediates the initial binding/rolling of the leukocyte on the vessel wall.

- Jmol model of P-selectin binding to tetrasaccharide

Exercise 8.4.1

Draw a Haworth and wedge/dash ring structure for the five carbon sugar D-ribose, whose straight chain form is shown below. D-ribose is extremely important in the biological world since its 5-membered ring form is found in RNA. A variant, deoxyribose, in which the OH on C2 is replaced with an H atom, is part of the main chain of DNA.



D-ribose

Exercise 8.4.2

Humans utilize two kinds of energy storage molecules: glycogen and triacylglycerides. (Review the structure of triacyglycerides from Chapter 8.1). Given intermolecular forces between these different types of molecules and water, predict which one might be biologically advantageous from a weight/mass perspective for an organism who must support this storage mass.

Exercise 8.4.3

Using geometric figures to represent monomers, draw cartoon figures of the following

a. a straight chain homopolymer

b. a highly branched chain homopolymer

c. a linear heteropolymer with a repeat unit consisting of two different monomers

d. a highly branch polymer containing 4 different monomers

Exercise 8.4.4

Nature uses all of these motifs in the biological world of carbohydrates. There must be advantages of these varying structure. Offer a possible reason for the following types of polysaccharide structures being adopted by nature.

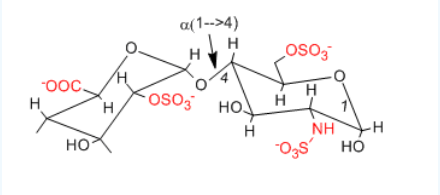
a. straight chain and elongated polymer of glucose which can form fibrils in cellulose

b. a highly branched polymer of glycogen which must be broken down by enzymes to form glucose in times of urgent energy need

c. a highly branched polymer of diverse monomers and chemically-modified monomers attached to proteins.

Exercise 8.4.5

The repeating disaccharide motif of heparin (discussed above) is shown below once more.



https://chem.libretexts.org/@go/page/189657

a. Would you expect this molecule to collapse into a compact spherical structure or have a more open and extended structure? Explain.

b. Heparin is used widely as an anticoagulant. It affects the properties of thrombin, an enzyme that causes the blood to clot. Thrombin is a globular (spherical) protein. For heparin to have a direct effect on thrombin, it must interact with it. What structural features of thrombin might be involved in this interaction? Draw a cartoon model showing the interaction.

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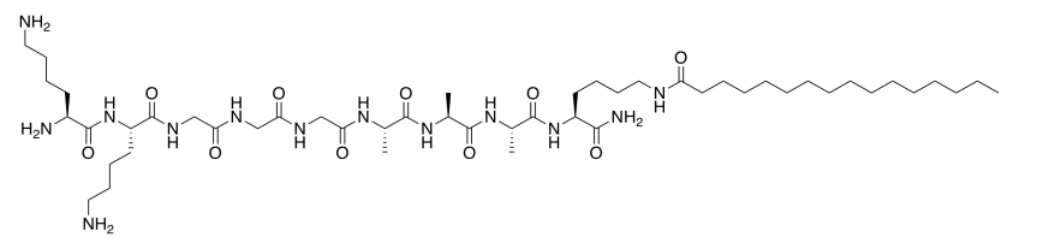
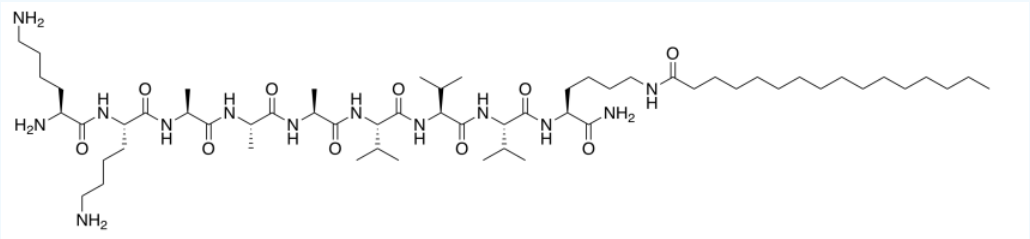
8.5: Biomolecule Application Problems

Exercise 8.5.1

The laboratory of Samuel Stupp at Northwestern designs molecules with potential biomedical applications. The molecule below helps recruit growth factor to the cell (Christina J. Newcomb, Shantanu Sur, Sungsoo S. Lee, Jeong Min Yu, Yan Zhou, Malcolm L. Snead, and Samuel I. Stupp, *Nano. Lett.* **2016**, *16*, 3042-3050. Copyright 2016 American Chemical Society).

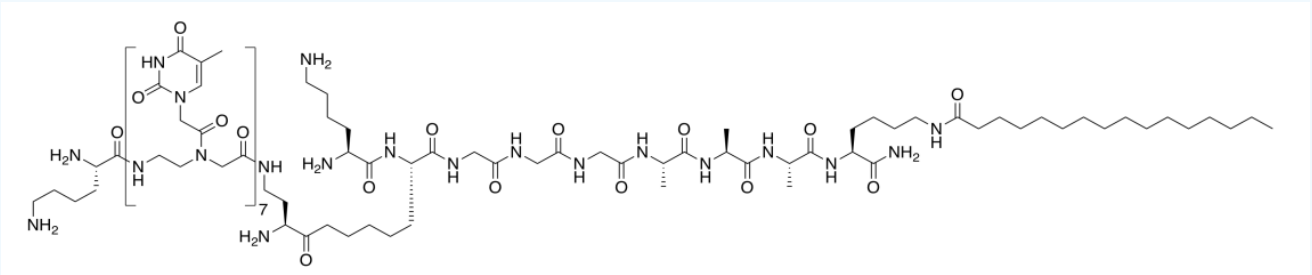


a. This molecule is a synthetic amphiphile. Put a rectangle around the polar part of this molecule. Circle the nonpolar part of the molecule.
b. The amphiphile inserts into the cell membrane. Draw a cartoon of a portion of a cell membrane. Add a cartoon of the synthetic amphiphile to the membrane. What is the IMF through which it interacts with the membrane?
c. How would the amphiphile attract / bind growth factor and other proteins?
d. This effect might be amplified if several of the amphiphiles bind to the membrane and cluster together. Use an abbreviated drawing (not the whole molecule) to show how two synthetic amphiphiles would interact with each other.
e. This drawing is reminiscent of a specific structural type seen in proteins. Which one?
f. The first amphiphile is not very good at interacting with others because it tends to spiral into a corkscrew shape. The amphiphile below is better at interacting with others because it keeps a flatter shape. Propose a reason why.



Exercise 8.5.2

Here is a second type of amphiphile from the Stupp lab. This molecule was designed to bind a DNA strand (Adapted with permission from Mustafo Guler, Jonathan K. Pokorski, Daniel H. Appella, and Samuel I. Stupp, *Bioconjugate Chem.*. **2005**, *16*, 501-503. Copyright 2018 American Chemical Society).



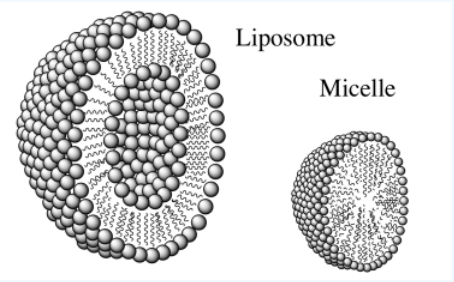
a. Circle the part of the molecule that would bind to a DNA base.
b. The base in the amphiphile binds to another DNA base. Draw the three other options.
c. Which DNA base would the amphiphile bind best? Show how with a drawing.

d. The melting point of DNA increases by 2°C for every AT pair; 4°C for every CG pair. Assuming all of the bases in the amphiphile bind to DNA, predict the melting point of the adduct.
e. DNA actually binds more tightly to this amphiphile than to another DNA strand. Propose a reason why.

Exercise 8.5.3

Problem IB5.3.

Liposomes are artificially prepared vesicles made of lipid bilayers. A drawing of a liposome is shown below along with its structural relative, a micelle.

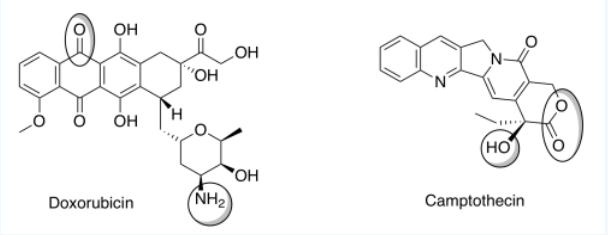


a. Compare and contrast a liposome with a micelle.
b. What type of molecules would be contained in the center of a liposome?
c. What type of molecules would be contained in the center of a micelle?

1. Liposomes are used for drug delivery due to their unique properties. A liposome encapsulates a drug that cannot easily pass through the lipid bilayer.
2. A liposome can carry both hydrophobic molecules and/or hydrophilic molecules:

d. [Hydrophobic / Hydrophilic] chemicals can be dissolved into the membrane. (Choose one.)
e. [Hydrophobic / Hydrophilic] chemicals can be dissolved into the liposome's center. (Choose one.)

Another interesting property of liposomes is their ability to target cancer. Tumors do not have tight junctions between cells and are leaky. Liposomes of certain sizes, typically less than 200 nm, can rapidly enter tumor sites from the blood, but are kept out of healthy tissue by the endothelial wall. Anti-cancer drugs such as Doxorubicin and Camptothecin (shown below) are currently being marketed in liposome delivery systems.



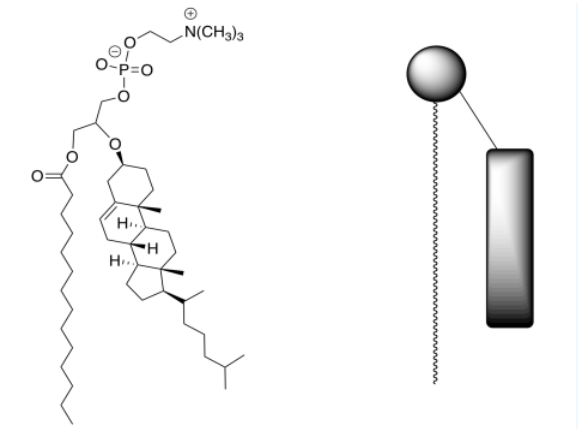
f) Identify each of the circled functional groups.

g) To encapsulate these drugs in liposomes, you will need to predict whether they are water soluble or not. Choose the best attribute for each compound.

Doxorubicin [water-soluble / insoluble in water]
Camptothecin [water-soluble / insoluble in water]

To deliver the molecules to sites of action, the lipid bilayer can fuse with other bilayers such as a cell membrane, thus delivering the liposome contents.

Since cholesterol can improve the stability of lipid bilayers, some researchers designed and synthesized a category of phospholipids that incorporate cholesterol covalently linked to the glycerol backbone of phosphatidylcholine (shown below).



h) On the structure of the phosphatidylcholine, put a circle around the polar head, a rectangle around the cholesterol group, and a dashed ellipse around the fatty acid group.

i) Draw a picture of the lipid bilayer formed with this phospholipid (use the cartoon on the right) vs a regular phospholipid with cholesterol added in.

Data on animal models suggest that liposomes formed with the sterol modified phospholipid are very effective for delivery of anti-cancer agents.

j) Suggest at least two advantages to the sterol modified liposomes.

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CHAPTER OVERVIEW

9: Cell Tutorial

9.1: The Cell- An Overview
9.2: The Cell- Lipids
9.3: The Cell - Proteins
9.4: The Cell- Nucleic Acids
9.5: The Cell- Carbohydrates

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9.1: The Cell- An Overview

You have probably studied the cell many times, either in high school, or in college biology classes. There are many websites available that review both prokaryotic (bacterial), archeal and eukaryotic cells (see links at bottom). This tutorial is designed specifically from the viewpoint of chemistry. It explores four classes of biomolecules (lipids, proteins, nucleic acids and carbohydrates) and describes in a simplified pictorial manner where they are found, made, and degraded in the cell (i.e. their history). It focuses on eukaryotic cells, which in contrast to simpler prokaryotic cells, have internal organelles surrounded by membranes that compartmentalize chemical reactions. First a general overview of the cell is presented. Subsequent chapters will concentrate on specific biomolecules.

Let's think of a cell as a chemical factory which designs, imports, synthesizes, uses, exports and degrades a variety of chemicals (in the case of cell, these include lipids, proteins, nucleic acids and carbohydrates). It also must determine or sense the amount of raw and finished chemicals it has available and respond to its own and external needs by ramping up or shutting off production. The figure of the cell below and in other linked sites based on it was made available with the kind permission of Liliana Torres.

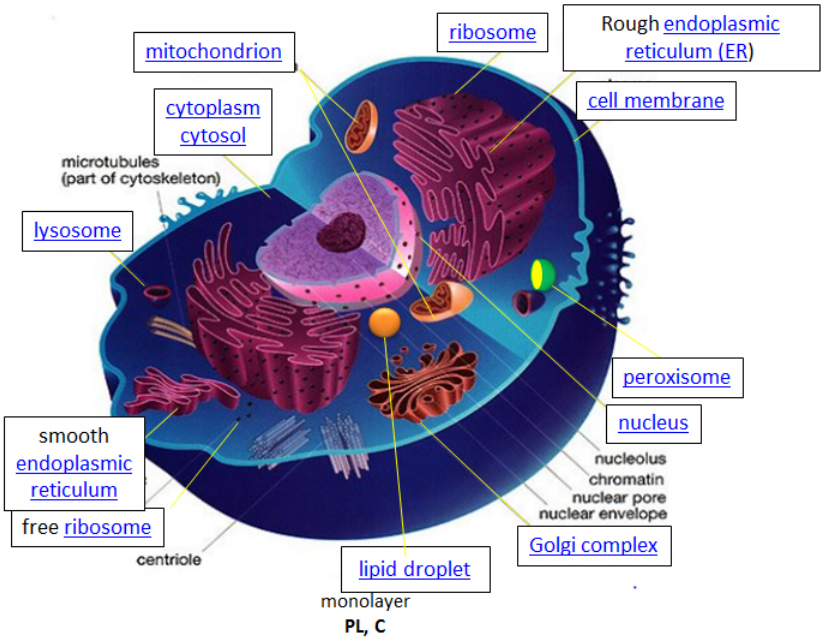


Figure 9.1.1: A Eukaryotic Cell

http://torresbioclan.pbworks.com/w/page/22377234/Spikefish%20About%20Cells

Use with permission from Liliana Torres. Also at www.animalport.com/animal-cells.html

Design - The design for a cell mostly resides in the blueprint for the cell, the genetic code, which is comprised of the DNA in the cell nucleus and a small amount in the mitochondria. Of course, the DNA blueprint must be read out (transcribed) by protein enzymes which themselves were encoded by the DNA. The genetic code has the master plan that determines the sequence of all cellular proteins, which then catalyze almost all other activities in the cell, including catalysis, motility, architectural structure, etc. In contrast to DNA, RNA and protein polymers, the length and sequence of a polysaccharide polymer is not driven by a template but rather by the enzymes that catalyzes the polymerization.

Import/Export: Many of the chemical constituents of the cell arise not from direct synthesis but from import of both small and large molecules. The imported molecules must pass through the cell membrane and in some cases through additional membranes if they need to reside inside membrane-bound organelles. Molecules can move into the cell by passive diffusion across the membrane but usually their movement is "facilitated" by a membrane receptor. Molecules can also move up a concentration gradient in a process called "active transport". Given the amphiphilic nature of the bilayer (polar head group exterior, nonpolar interior), you would expect that polar molecule like glucose would have difficulty in moving across the membrane. In fact membrane transport proteins are involved in the movement of both nonpolar and polar molecules.

- *transporters, carrier proteins and permeases*: These membrane proteins move specific ligand molecules across a membrane, typically down a concentration gradient. Computer simulations of the facilitated diffusion of lactose across the membrane is shown in the following link. Animation of lactose diffusion through the LacY receptor

(The link above and immediately below are from the Theoretical and Computational Biophysics group at the Beckman Institute, University of Illinois at Urbana-Champaign. These molecular dynamic simulations were made with VMD/NAMD/BioCoRE/JMV/other software support developed by the Group with NIH support.)

- *ion channels* - These membrane proteins allow the flow of ions across membranes. Some are permanently open (nongated) while others are gated open or closed depending on the presence of ligands that bind the protein channel and the local environment of the protein in the membrane. Flow of ions through the channel proceeds in a thermodynamically favored direction, which depends on their concentration and voltage gradients across the membrane.

- *pores*: Some membranes (nuclear, mitochondria) assemble proteins (such as porins) to form large, but regulated pores. Porins are found in mitochondrial membranes while nucleoporins are found in the nuclear membrane. Small molecules can generally pass through these membrane pores while large one are selected based on their tendency to form transient intermolecular attractive forces with the pore proteins. The following link shows the diffusion of water through aquaporin. animation of water diffusion through the aquaporin channel,

- *endocytosis*: Very large particles (for example, LDL or Low Density Lipoproteins or viruses) can enter a cell through a process called endocytosis. Initially the LDL or virus binds to a receptor on the surface of the cell. This triggers a series of events which leads to the invagination of the cell membrane at that point. This eventually pinches off to form an **endosomal** vesicle which is surrounded by a protein called clathrin. "Early" endosomes can pick up new proteins and other constituents as well as shed them as they move and mature through the cell. During this maturation process, protein pumps in the endosome lead to a decrease in the endosomal pH which can lead to conformation changes in protein structure and shedding of proteins. Eventually the "late" endosome reaches and fuses with the lysosome, an internal organelle which contains degradative enzymes. Undegraded components like viral nucleic acids or cholesterol, are delivered to the cell. This transport can also go in the reverse direction and recycle receptors to the cell membrane. Likewise vesicles pinched off from the Golgi complex can fuse with endosomes, with some components surviving the process to reenter the Golgi.

Synthesize/Degrade: Cells have to both synthesize and degrade small molecules as well as larger polymeric protein, carbohydrates and nucleic acids. The anabolic (synthetic) and catabolic (degradative) pathways are often compartmentalized in time and space within a cell. For example fatty acid synthesis is carried out in the cytoplasm but fatty acid oxidation is carried out in the mitochondria. Proteins are synthesized in the cytoplasm or completed in the endoplasmic reticulum (for membrane and exported proteins) while they are degraded in the lysosome or more importantly in a large multimolecular structure in the cell called the proteasome.

Let's consider some key characteristics of a cell before we get into the details.

Cells and their internal compartments have regulated concentrations of ions and hydronium ion.

As expected the pH of the cytosol (the aqueous substance surrounding all the organelles within the cell) varies from about 7.0-7.4, depending on the metabolic state of the cell. Some organelles have proton transporters that can significantly alter the pH inside an organelle. For example the pH inside the lysosome, a degradative organelle, is about 4.8. The collapse of the pH gradient across the inner mitochondrial membrane is sufficient to drive the thermodynamically unfavored synthesis of ATP.

Compared to the extracellular fluid, the concentration of potassium ion is higher inside the cell, while concentrations of sodium, chloride and calcium ions are higher on the outside of the cell (see table below). These concentration gradients are maintained by ion transporters and channels and require energy expenditure ultimately in the form of ATP hydrolysis. Changes in these concentrations are integral to the signaling system used by the cell to sense and respond to changes in its external and internal environments.

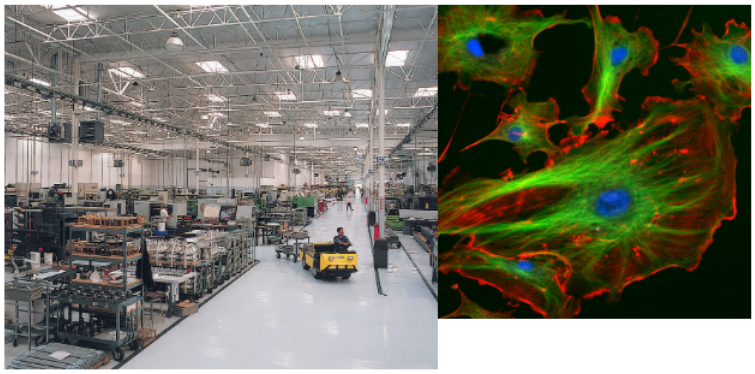
Water is found in bulk form as well as bound to macromolecules like proteins and polysaccharides. These waters would be expected to have different properties. The table below show approximate ion concentrations in the cell.

Ion	Inside (mM)	Outside (mM)
Na^+	140	5
K^+	12	140

Cl-	4	15
Ca^{2+}	1 uM	2

Cells have an internal framework that provides architectural and internal structural support.

The "cytoskeletal" architecture of a (with molecular "cables"- and "girder-like" structures) is not dissimilar from a factory.



http://www.cybercom.net/~copters/trips/pictures/factory_inside.jpg http://en.Wikipedia.org/wiki/File:FluorescentCells.jpg

The internal framework or **cytoskeleton** of a cell, is composed of microfilaments, intermediate filaments, and microtubules. These are comprised of monomeric proteins which self assemble to form the internal architecture. Parts of the cytoskeleton can be seen in the photo above (taken from Wikipedia).

Microfilaments of actin monomers (which are stained with a red/orange fluorophore) and microtubules which offer more structural support made of tubulin monomers (stained green) along with the blue-stained nucleus, are shown in the image. Organelles are supported and organized by the cytoskeleton (primarily microtubules). Even the cell membrane is supported underneath the inner leaflet by actin (stained orange) and spectrin microfilaments. Motor proteins like myosin (that moves along actin microfilaments) and dynein and kinesin (that move along tubulin microtubules) carry cargo (vesicles, organelles) in a directional fashion. The cell is not a disorganized collection of molecules and organelles. Rather is a highly organized for optimal chemical production, use and degradation.

Cell have a variety of shapes. Some circulating immune cells must slip through the cells that line capillary walls to migrate to sites of infection. The same process occurs when tumor cells metastasize and escape to other sites in the body. In order to do so, the cell must drastically change shape, a response that requires dissociation of the cytoskeleton polymers into monomers which are available later for repolymerization.

The cell is an amazingly crowded place.

In chemistry labs, we typically work with dilute solutions of solute molecules in a solvent. You have probably heard that the body is comprised of 68% water, but the water concentration is obviously dependent on the cellular environment. Solute molecules like protein and carbohydrates are densely packed. Cells are so crowded that the space between larger molecules like protein is less than the size of protein. Studies have shown that the stability of a protein is increased in such condition, which would help keep the protein in the folded, native state. Another consequence of high concentrations is that it would promote the binding or self aggregation of like molecules as well as dislike ones which from an equilibrium perspective would not occur in dilute solutions. Hence the study of biomolecules in dilute solutions in the lab may not reveal the actual complexities of interactions and activities of the same molecule *in vivo*. Recently investigators have added a neutral copolymer of sucrose and epichlorhydrine to cells *in vitro*. These particles induced organization of extracellular molecules secreted by cell, forming an organized extracellular "matrix" which induced the organization of the microfilaments on the inside of the cell as well as inducing changes in cell activity.[1] *In vitro* enzyme activity of a key enzyme in glycolysis dramatically increases under crowded conditions.[2] Another result of crowding may be the spatial and temporal association of key enzymes in specific metabolic pathways, allowing easier diffusion of substrates and products within the colocalized enzymes.

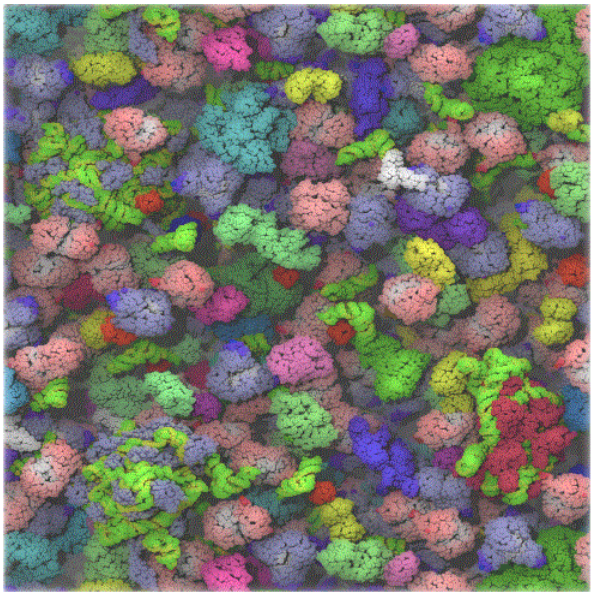


Figure 9.1.2: The crowded cytoplasm of E. Coli - Ufrom McGuffee SR, Elcock AH (2010) PLoS Comput Biol 6(3): e1000694. doi:10.1371/journal.pcbi.1000694 (open source journal)

The computer simulation used 50 different types of the most abundant macromolecules of the E. coli cytoplasm and 1008 individual molecules. Rendering of the cytoplasm model at the end of a dynamics simulation. RNA is shown as green and yellow. This figure was prepared with VMD

Cell components undergo phase transitions to form substructures within the cell.

A perplexing question is how do substructures form within a cell. This includes not only the biogenesis of organelles like mitochondria but also smaller particle such as polysaacharide granules, lipid droplets, protein/RNA particles (including the ribosome) as well as the nucleolus of the cell nucleus. It might be easiest to consider this problem using two examples from the lipid world, lipid droplets and membrane rafts. You are very familiar with phase transitions that occur when a sparing soluble nonpolar liquid is added to water. At a high enough concentration, the solubility of the nonpolar liquid is exceeded and a phase transition occur as evidenced by the appearance of two separate liquid phases. The same process occurs when triglycerides coalesce into lipid droplets with proteins associated on their outside. Another example occurs within a cell membrane when lipids with saturated alkyl chains self associate with membrane cholesterol (which contains a rigid planar ring system) to form a lipid raft characterized by greater packing efficiency, rigidity and thickness that other parts of the membrane. These lipid rafts often recruit protein involved in signaling processes within the cell membranes. This process of phase separation is also called liquid/liquid demixing as two "liquid-like" substances separate.

It appears that proteins that interact with RNA are composed of less diverse amino acid and have more flexible ("more liquid-like) structures allowing their preferential interaction with RNA to form large RNA-protein particles (like the ribosome and other RNA processing structures) in a fashion that mimics liquid/liquid demixing. All of these interactions are just manifestations of the various intermolecular forces you studied in earlier chemistry classes.

You have studied lipid, protein, nucleic acid and carbohydrate structure in introductory biology and/or chemistry classes.

A list of web sites and applets on eukaryotic cell structure:

- Cell Tutorial from UCLA
- Plant and animal cell simulation (requires Java)
- Download Apple Store Applet for IPad, Itouch, IPhone: 3D Cell

References:

1. Zeiger AS, Loe FC, Li R, Raghunath M, Van Vliet KJ (2012) Macromolecular Crowding Directs Extracellular Matrix Organization and Mesenchymal Stem Cell Behavior. PLoS ONE 7(5): e37904. doi:10.1371/journal.pone.0037904 .

2. Apratim Dhara, Antonios Samiotakisb, Simon Ebbinghausa, Lea Nienhausa, Dirar Homouzb, Martin Gruebelea, and Margaret S. Cheungb. Structure, function, and folding of phosphoglycerate kinase are strongly perturbed by macromolecular crowding. Proc. Natl Acad Sci. www.pnas.org/cgi/doi/10.1073/pnas.1006760107

3. Anthony A. Hyman and Kai Simons. Beyond Oil and Water--Phase Transitions in Cells. Science 337, 1047 (2012); DOI: 10.1126/science.1223728

4. McGuffee SR, Elcock AH (2010) Diffusion, Crowding & Protein Stability in a Dynamic Molecular Model of the Bacterial Cytoplasm. PLoS Comput Biol 6(3): e1000694. doi:10.1371/journal.pcbi.1000694

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9.2: The Cell- Lipids

French Translation √ by Anna Chekovsky

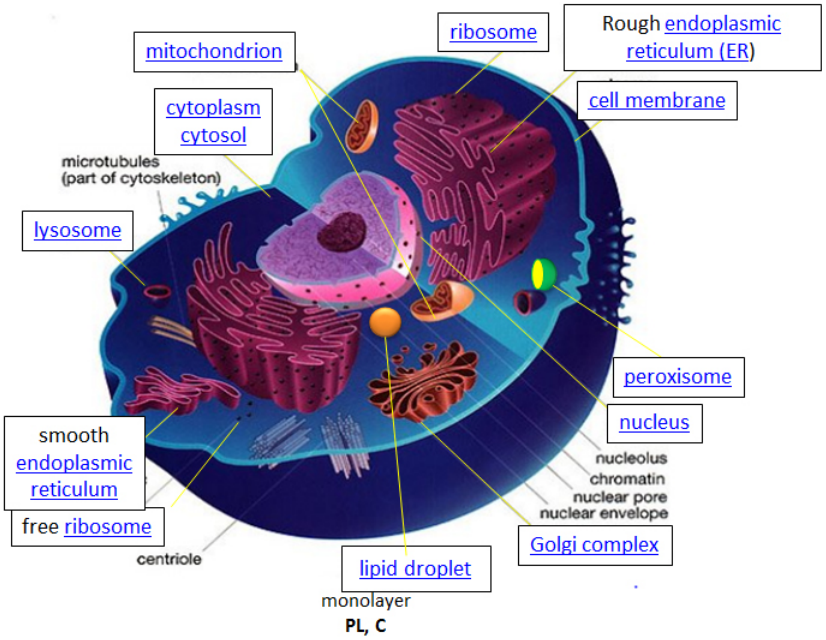

Figure 9.2.1: A Eukaryotic Cell

http://torresbioclan.pbworks.com/w/page/22377234/Spikefish%20About%20Cells

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Lipids are small biological molecules which are soluble in organic solvents, such as chloroform/methanol, and are sparingly soluble in aqueous solutions. The simple classification of lipids belies the complexity of possible lipid structures as over 1000 different lipids are found in eukaryotic cells. This complexity has led to the development of a comprehensive classification system for lipids. In this system, lipids are given a very detailed as well as all-encompassing definition: "hydrophobic or amphipathic small molecules that may originate entirely or in part by carbanion-based condensations of thioesters (fatty acyl, glycerolipids, glycerophospholipids, sphingolipds, saccharolipds and polyketides) and/or by carbocation-based condensations of isoprene units (prenol lipids and sterol lipids)."

The following site will show you the "life" history of lipids in cells.

- Lipids and Cells: an animated PowerPoint
- Lipids and Cells: PDF

The sites linked above are written and maintained by Henry V. Jakubowski, Ph.D., College of Saint Benedict / Saint John's University. These materials are available for educational use.

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9.3: The Cell - Proteins

Henry Jakubowski

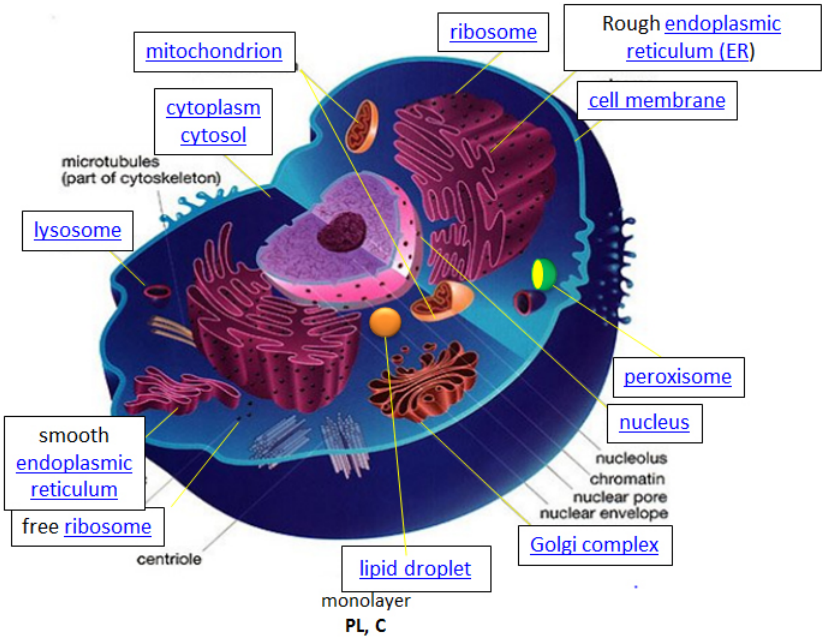

Figure 9.3.1: A Eukaryotic Cell

http://torresbioclan.pbworks.com/w/page/22377234/Spikefish%20About%20Cells

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Proteins are polymers of bifunctional alpha-amino acids each containing a different R group at the alpha carbon. Encoded by the DNA genome, proteins are involved in all cellular activities including recognition, catalysis, movement, and signalling.

The following site will show you the "life" history of proteins in cells.

- Proteins and Cells: an animated PowerPoint
- Proteins and Cells: PDF

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9.4: The Cell- Nucleic Acids

Henry Jakubowski

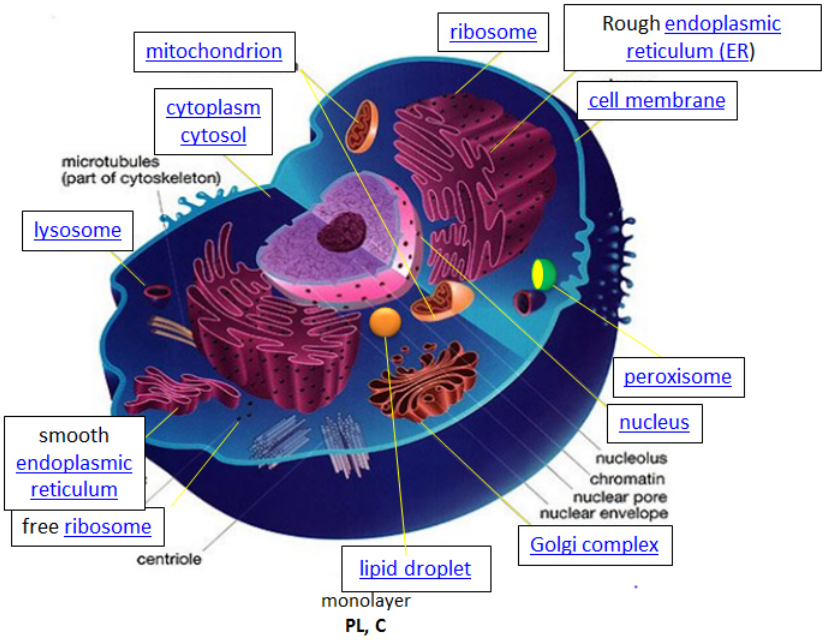

Figure 9.4.1: A Eukaryotic Cell

http://torresbioclan.pbworks.com/w/page/22377234/Spikefish%20About%20Cells

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Nucleic acids are polymers of deoxyribonucleotides (DNA) or ribonucleotides (RNA). DNA contains the genetic code that when transcribed into RNA followed by translation of the RNA for around 22,000 protein. Only about 2% of the 3.2 billion base pairs of DNA encodes protein. The function of 80% of the remaining genome has recently been found to regulate the transcription of DNA, mostly through various types of RNA transcribed from the DNA.

The following site will show you the "life" history of nucleic acids in cells.

- Nucleic Acids: PowerPoint
- Nucleic Acids: PDF

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9.5: The Cell- Carbohydrates

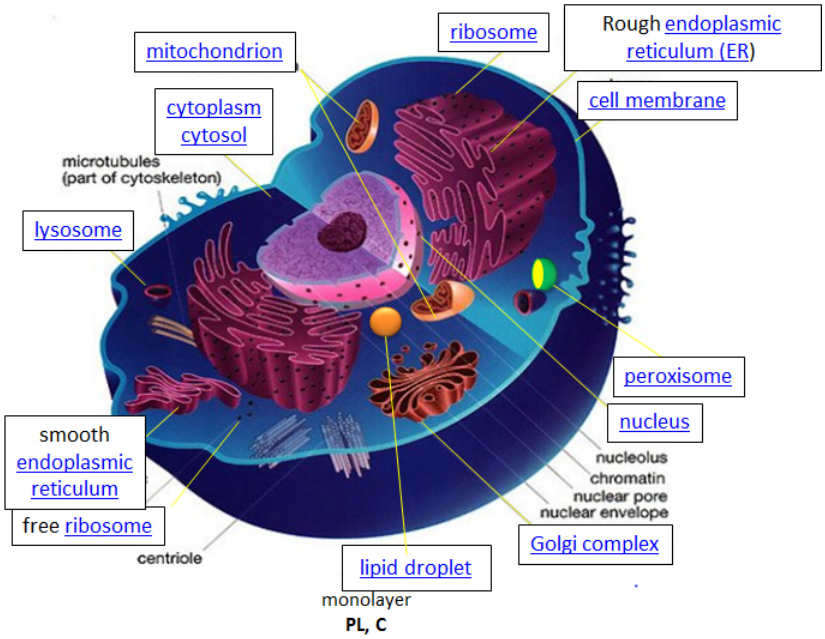

Figure 9.5.1

http://torresbioclan.pbworks.com/w/page/22377234/Spikefish%20About%20Cells

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Carbohydrates are A.

The following site will show you the "life" history of nucleic acids in cells.

- Carbohydrates: animated PowerPoint
- Carbohydrates: PDF

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CHAPTER OVERVIEW

10: Network Solids

10.1: A Network Solid - Diamond
10.2: Other Forms of Carbon
10.3: Silicates and Silica
10.4: Aluminosilicates
10.5: Solutions to Selected Problems

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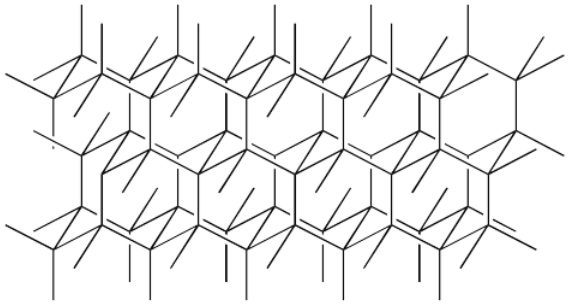
10.1: A Network Solid - Diamond

Some materials don't fall into any of the categories that we have seen so far. They are not metals, so they can't be described as lattices of identical ions surrounded by delocalized electrons. They are not ionic solids, so they can't be thought of as arrays of one type of ion with the counterions packed into the interstitial holes to balance the charge. They are not molecules, so we wouldn't draw them as discrete, self-contained collections of connected atoms.

Diamond, for example, is a **network solid**. Diamond is an allotrope of carbon - it is one of several forms of elemental carbon found in nature. It looks something like this, on an atomic scale. The lines are bonds between the carbon atoms. Each carbon atom makes four bonds, one to each of four different neighbors.



Diamond is composed entirely of carbon atoms, but carbon is too electronegative to allow its electrons to completely delocalize into an electron sea, like metallic elements do. It forms a crystalline, solid structure, but it does not dissolve even a tiny bit in water like ionic compounds would, because it has no ions to form ion-dipole interactions with the water molecules. It forms covalent bonds with its neighboring atoms, sharing these electrons rather than exchanging them, but it forms an extended solid rather than individual units.

- Network solids are like molecules because they have covalent bonds connecting their atoms.
- Network solids are unlike molecules because they don't have a limited or specific size; their structures can extend "seemingly forever" on the atomic scale.

What do most people know about diamonds? They are very expensive, of course. They are very shiny. They are very, very hard. In fact, there is a scale used by minerologists to describe the hardness of materials called "Mohs scale of hardness". The scale was developed by German geologist Friedrich Mohs in the early 1800's. It simply places ten different minerals in order from softest to hardest and assigns each of them a number. Diamond is a 10, meaning it is the hardest material on the scale. Diamond is, in fact, the hardest naturally-ocurring substance in the world.

Table 10.1.1: Mohs scale of hardness.

Mineral	Hardness
talc	1
gypsum	2
calcite	3
fluorite	4
apatite	5
orthoclase	6
quartz	7
topaz	8
corundum	9
diamond	10

Mohs scale is qualitative, not quantitative; each mineral in the scale is harder than the one before it. Mohs scale has been widely used by field geologists because of its simplicity. If you pick up a mineral and can scratch it with that diamond you keep in your toolbox, but the corundum does not leave a mark, then the hardness of the new sample is around 9.

Exercise 10.1.1

Rank the following minerals using Mohs scale.

a. graphite, which scratches talc but is itself scratched by gypsum
b. stishovite, which can scratch corundum but not diamond; diamond scratches stishovite
c. opal, which scratches orthoclase and fluorite but not quartz or topaz
d. obsidian, which can be scratched by quartz and orthoclase but not apatite; obsidian does not scratch apatite, either
e. ruby, which is scratched by diamond; however, neither corundum nor ruby can scratch each other.
f. emerald, which can be scratched by ruby and topaz but scratches quartz

Answer a:

graphite is between 1 & 2

Answer b:

stishovite is between 9 & 10

Answer c:

opal is between 6 & 7

Answer d:

obsidian is about 5

Answer e:

ruby is about 9

Answer f:

emerald is between 7 & 8

Exercise 10.1.2

"Absolute hardness" can be measured in a number of ways. For example, a sample can be scored by a diamond needle using carefully controlled pressure, and the width or depth of the score can be measured to get a quantitative comparison of the hardness of different materials.

Plot the hardness of each material according to Mohs scale on the x axis and the hardness determined by a sclerometer test to see the relationship between Mohs scale and absolute hardness.

material	hardness
talc	1
gypsum	3
calcite	9
fluorite	21
apatite	48
orthoclase	72
quartz	100
topaz	200
corundum	400

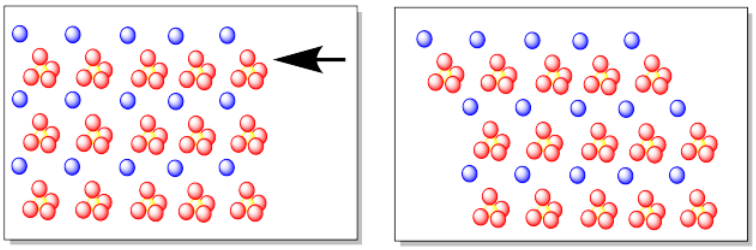
material	hardness
diamond	1600

What makes diamond so hard? Let's compare it to a few of the softer minerals in the scale. Gypsum is a crystalline hydrate of calcium sulfate: $CaSO_4 \cdot 2H_2O$. Calcite is a mineral form of calcium carbonate: $CaCO_3$. Fluorite is composed of calcium fluoride: CaF_2.

These materials are all ionic solids. Gypsum contains calcium cations and sulfate anions, as well as bound water. Calcite contains calcium ions and carbonate ions. Fluorite contains calcium ions and fluoride ions. Surely the ionic bonds that hold these ions together are very strong. Why can they be deformed and scratched?

An ionic bond is not directional. It does not matter whether a sulfate ion is above or below a calcium ion, or to the left or the right of it. The attraction between the ions is still the same.

If we imagine a shearing force on a crystal of calcium sulfate, meaning that we are pushing against only one layer of the crystalline material, then we might see that layer slide in response to the force. As the ions in that layer slide, they begin to lose their attraction to the ions in the layer beneath them, but then they become attracted to new ions that are sliding towards. When we are finished, we still have an ionic solid in which ions are atracted to counterions around them, but the partners have changed.



We can't do that in diamond because the carbon atoms are all covalently bonded to each other. The electrons in those bonds appear to be localized in particular regions of space around the carbon atoms, making a framework of tetrahedra. That strong framework holds each carbon atom in place with four bonds, so that it is difficult to displace any one atom or layer of atoms.

Silicon: an analog of carbon

Silicon is found below carbon in the periodic table. Consequently, it has some chemical similarities with its neighbor. For example, pure silicon adopts a structure that is very similar to that of diamond.

Elemental silicon, Si, is indispensable for modern electronics because, in the presence of trace impurities, it has semiconducting properties. However, elemental silicon really does not exist in nature. It must go through chemical reduction from silica, SiO_2, in an electric arc furnace:

$$\mathrm{SiO_2 + 2\,C \longrightarrow Si + 2\,CO} \tag{10.1.1}$$

The resulting silicon is painstakingly purified by a number of chemical processes. For example, it can be converted to SiCl4, which is then purified repeatedly via distillation to remove trace impurities, then turned back into silicon by reduction with zinc:

$$\mathrm{SiCl_4 + 2\,Zn \longrightarrow Si + 2\,ZnCl_2} \tag{10.1.2}$$

One of the final steps is recrystallization of the silicon from its molten phase. A rod with a small "seed" of pure silicon is dipped into the molten silicon and slowly drawn upwards. As the molten silicon cools against the cooler surface of the rod, it recrystallizes. The rod is pulled slowly upward, and pure silicon continues to grow on the cooler, crystalline silicon being pulled from the melt, forming a long crystal.

Exercise 10.1.3

Draw the structure of elemental silicon.

Exercise 10.1.4

Silicone is not the same thing as silicon. Silicone is a class of polymer. It exists as long, flexible chains in which the same group of atoms is repeated over and over. There are lots of kinds of silicone, but one example of a silicone formula is $((CH_3)_2SiO)_n$. The subscript *n* means the unit in parentheses is repeated over and over in a chain.

a. Draw a section of silicone several units long.
b. Explain how the structures of silicon and silicone might give them very different physical properties.

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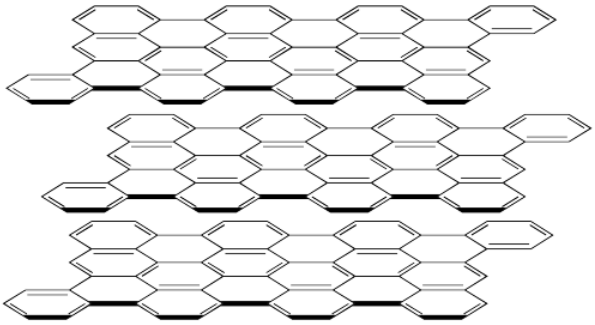
10.2: Other Forms of Carbon

Diamond is just one form in which elemental carbon can be found. Other forms include graphite, lonsdaleite and fullerenes.

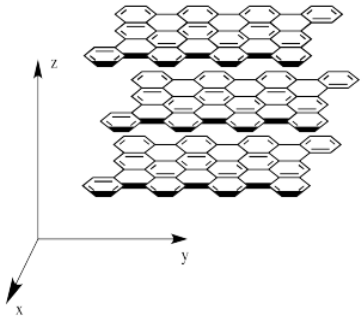
Graphite

Graphite is a mineral that, like diamond, is composed of carbon. However, the carbon atoms in graphite are arranged in a different way than they are in diamond. There are significant consequences for the relative properties of diamond and graphite.



Graphite is not nearly so hard as diamond. It has a hardness of about 1.5 on the Mohs scale, compared to diamond's 10 rating. That difference is related to the fact that graphite is composed of separate sheets, called graphene sheets, whereas diamond is firmly bonded in three dimensions. A force exerted on graphite can easily displace one layer away from its neighbors.

However, graphite isn't equally hard in all directions. If a force is exerted parallel to the graphene sheets, one sheet can be moved with respect to the next one. That isn't true perpendicular to the sheets. On the picture, the sheets could slide on the x and y directions but not in the z direction.

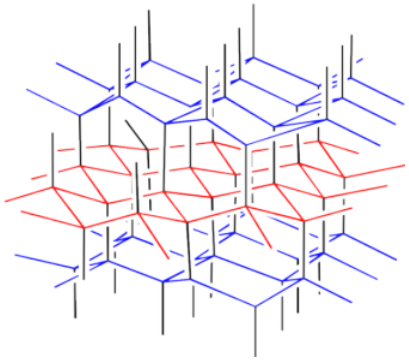


That general idea is true in other materials. Even diamond is not equally hard on all surfaces. Minerals often have typical shapes because they are cleaved more easily along specific planes, but are harder to break along others.

Other properties also depend on the plane of the crystal in network solids. For example, graphite is also a conductor of electricity along its graphene planes, but not perpendicular to them.

Lonsdaleite

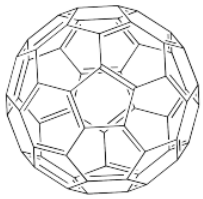
Lonsdaleite is named in honour of Kathleen Lonsdale, the Irish crystallographer who first demonstrated the planar structure of benzene via X-ray diffraction. It is a very rare form of carbon generated during the impact of meteors that contain graphite. In the high energy of impact, layers of graphite fuse together to form a structure that at first glance looks a lot like diamond. A rough sketch of the lonsdaleite structure is depicted below.



Lonsdaleite formed in nature is much softer than diamond, probably because the chaotic nature of its origin leaves lots of graphite-like domains embedded in the lonsdaleite. Instead of having bonds regularly spaced throughout the material, there are probably flawed portions in which part of one layer is still unconnected from the next. It has a hardness of about 8 on the Mohs scale.

Fullerenes

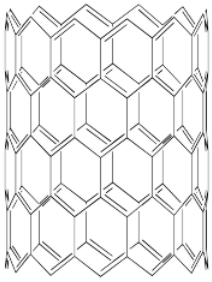
The fullerenes are a form of elemental carbon that really does not fall completely under the category of network solids. They are a little like network solids but they do form discrete units, and so they are really molecules. A fullerene is a little bit like a small sheet of graphite that has been curved into a ball. The shapes of the spherical ones resemble the Geodesic Domes designed by architect Buckminster Fuller in the 1960's; that's where they get their name. Spherical fullerenes are also called buckyballs.



example of a fullerene

Fullerenes were first discovered in the 1990's by Harold Kroto. There was an ensuing rush to develop new applications for the materials. For example, people have proposed using buckyballs as lubricants (like little ball bearings, they would roll between two surfaces). Much of the interest in this area, however, has focussed on potential electronic properties of these materials.

Carbon nanotubes are conceptually similar to fullerenes. Instead of being spherical, they are tube-shaped. They can also be though of as graphite sheets that have been curved into a new shape.



section of a carbon nanotube

Coal and Other Forms of Carbon

Many other forms of carbon that are commonly found on earth are not pure carbon. We often think of coal as being equivalent to carbon, a notion that is reinforced by the common knowledge that diamonds are a result of immense geological pressures and high temperatures acting on coal seams over long periods of time. Coal actually comes in many different grades containing varying amounts of carbon.

Lignite or "brown coal" can contain as little as 60% carbon. The rest of it is composed of varying amounts of hydrogen, oxygen, nitrogen and sulfur -- all of which are common elements found in living or "organic" things. The most valuable grade of coal, anthracite, contains over 90% carbon. There are varying grades in between.

Why does coal contain all of those elements found in living things? Coal forms from the compression of organic material over geological time scales. Most of the atoms present in that organic material are still present in the coal.

Other non-living but organic materials are important ecologically and agriculturally. As plant and animal matter decays, it turns eventually into "humus" (hyoo-muss) or the organic material of the soil. Humus comes from those portions of organic material that are not easily broken down. Humus contains a significant amount of carbon, as well hydrogen and oxygen. Different kinds of soils contain different levels of humus, which confers varying properties on the soil such as moisture- and nutrient-retention.

Coal and humus are not exactly network solids. What fullerenes have in common with network solids is a regular, crystalline pattern of covalent bonds extended across the solid, but they are limited in size. Coal and humus demonstrate an opposite case: they do not have a limited size and their bonded networks can extend seemingly endlessly, but there is nothing regular or repeating about their structure. Instead, these materials are "amorphous" extended solids.

- Crystalline materials display regularly repeating patterns in three dimensions
- Amorphous materials do not display regular patterns in any direction; they are arranged seemingly at random

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10.3: Silicates and Silica

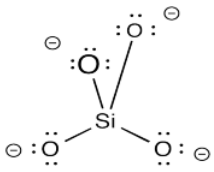
About 90% of the earth's crust is composed of silicate minerals. Silicates are compounds composed of silicon and oxygen; these compounds have negative charges on them. That means there are positive counterions found together with these anions. The variety of possible cations, ranging from sodium and potassium to copper and iron, is one of the factors that leads to a dazzling array of silicate minerals.

In addition to having a wide range of possible cations, silicate anions themselves have a breadth of available structures. These structures range from individual silicate anions (SiO_4^{4-}) to three dimensional networks of tetrahedra.

Silicates are not necessarily network solids, but we will see that their structures range from straightforward ionic solids at one extreme to something that looks more and more like an extended network at the other. By looking at these materials we can learn a little bit more about the related network solids.

Nesosilicates

Nesosilicates (meaning "island" silicates) are individual silicate anions arranged in crystalline ionic solids with their counterions. Those individual ions mean that nesosilicates are not network solids at all. They represent the extreme, other end of the silicate spectrum of structures.



The nesosilicate anion forms a tetrahedral shape. The silicon atom is at the center and the oxygen atoms are at the four corners. That tetrahedral shape is often illustrated in structural drawings rather than drawing the atoms explicitly. Instead of showing the SiO_4^{4-} anion with labelled atoms on the left, the tetrahedron on the right is shown to represent it.

Silicates can have lots of different cations. Frequently, several different cations may be found in one material. For example, olivine is a pretty common nesosilicate with magnesium and iron cations (Mg^{2+} and Fe^{2+}). If the olivine is of very high quality, it can be a gemstone, called peridot.

There are two limiting forms of olivine, called "endmembers". At one end is forsterite, Mg_2SiO_4. At the other end is fayalite, Fe_2SiO_4. In between is every possible combination of magnesium and iron. There could be equal amounts of magnesium and iron, or there could be just a few magnesium ions and many, many iron ions in a sample.

- Minerals frequently occur in families, in which one, similar ion can be substituted for another.
- Frequently, both ions can be present in varying amounts, but the properties of the material (such as color) change with changing ratios of these ions.
- The minerals that have just one of the possible ions but not the other are called the endmembers of the family.

Another common nesosilicate is garnet. Garnets are used as gems as well as abrasives -- they are sometimes used in sandpaper. There are many kinds of garnet, but a common one is almandine, the red-brown color of which we usually think of as "garnet". Garnets always contain two different cations. One of them is a M^{2+} ion and the other is a M^{3+} ion (M here just stands for "metal"). These two counterions are always present in a 3:2 ratio in garnet.

Exercise 10.3.1

Show that forsterite and fayalite are overall neutral.

Answer a:

forsterite: Mg_2SiO_4: If each nesosilicate unit has a charge of 4^- because of the formal charges on the four oxygens, then the two magnesiums must combine to balance that charge with a 4^+ charge. Each magnesium must have a 2^+ charge of its own. That seems reasonable, since magnesium is two atoms from the left edge of the periodic table; it would have a 2^+ charge in a noble gas configuration.

Answer b:

fayalite: Fe_2SiO_4: In order for this to work, each iron would have to have a 2^+ charge. Transition metal charges are harder to predict than alkali and alkaline earth metals because they are farther from the edge of the periodic table, but it turns out that the two most common charges on an iron ion are 2^+ and 3^+, so this charge seems reasonable.

Exercise 10.3.2

Suppose an olivine has 100 nesosilicate anions for every 25 magnesium ions.

a. How many iron ions (assume Fe^{3+}) would there be in the neutral olivine?
b. What would be the values of x and y in $Mg_xFe_ySiO_4$?

Answer a:

If each nesosilicate has a charge of 4^-, then the total negative charge is 100 x 4^- = 400^-. If there are 25 magnesium ions, each with a 2^+ charge, the total positive charge is 25 x 2^+ = 50^+. That leaves a net negative charge of 400^- + 50^+ = 350^-. The irons would balance that charge with an equal positive charge. The number of iron ions would be 350+/3+ = 150.

Answer b:

If we divide these ratios by 100 to arrive at the one nesosilicate in the formula, we get $Mg_{0.25}Fe_{1.5}SiO_4$. It doesn't mean there is a quarter of a magnesium ion anywhere; this formula is just the overall ratio of atoms.

Exercise 10.3.3

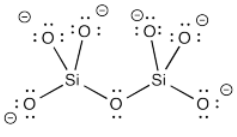
Almandine is a nesosilicate. It contains aluminum (which is almost always Al^{3+} in nature) and iron (in this case Fe^{2+}) in a 2:3 ratio. What is its formula?

Answer

So far we have Al_2Fe_3. The positive charge = 2 x 3^+ + 3 x 2^+ = 12^+. That charge must be balanced by the nesosilicate anions, which are each 4^-. So the number of silicates is $12^-/4^-$ = 3. The formula is $Al_2Fe_3(SiO_4)_3$.

Sorosilicates

Sorosilicates ("sister" silicates) are silicate anion dimers. The two silicate units share an oxygen atom. In the polyhedral depiction, the two tetrahedra share a corner. Sorosilicates clearly aren't network solids, either. They just contain slightly bigger anions than nesosilicates.



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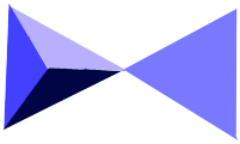
Sorosilicates are not nearly as common as nesosilicates. Where they exist, sorosilicates are found in the presence of other anions, as well as cations. In some minerals, they are even found in combination with nesosilicates. For example, epidote is a more common form of sorosilicate-containing mineral. It could be a number of colors but is usually green. It contains nesosilicate, sorosilicate, oxide and hydroxide anions, as well as calcium, iron and aluminum cations.

The sorosilicate anion can actually adopt different shapes in different cases. It contains two units that can twist relative to each other. The different shapes that result are called "conformations". A different conformation is shown below. In the picture on the left, we are looking at it from the same angle as the orosilicate shown above. In the picture on the right we are looking at it from a different angle to emphasize that the two tetrahedra are pointing in opposite directions. We are looking at the top of one tetrahedron but the bottom of the other one.

angle 1



angle 2

Exercise 10.3.4

Epidote contains just one of each of its four different anions in its formula.

a. Write the formula, with appropriate charge, for each of its anions. Note that the oxygen atoms in the hydroxide (OH) and oxide (O) ions each have an octet.
b. Epidote also contains two Ca^{2+} ions in its formula, but varying amounts of Fe^{3+} and Al^{3+}. How much iron and aluminum, total, does it have in its formula?

Answer a:

The anions are nesosilicate (4^-) + sorosilicate (6^-) + oxide (2^-) + hydroxide (1^-). The total charge is 13^-.

Answer b:

Calcium is an alkaline earth metal, two atoms from the left edge of the periodic table. The two calciums would partially balance that charge with 2 x $2^+ = 4^+$ charge; the net charge is now $13^- + 4^+ = 9^-$.

If each Al or Fe has charge 3^+, then the number needed to balance the charge is $9^+/3^+ = 3$ Fe/Al ions.

Exercise 10.3.5

Use your three-dimensional drawing tools (lines, wedges and dashes) to show the two different conformations of sorosilicate via Lewis structures.

Neither nesosilicates not sorosilicates are network solids. They are really just families of ionic solids. However, by looking at the relationship between the nesosilicate ion and the sorosilicate ion, we can see why many silicates do start to look more like network solids. If one oxygen atoms can be shared between two silicate units, maybe more can, too.

Inosilicates

If two silicate units can share an oxygen, more can, too. In fact, long chain silicates can form. To do so, two of the oxygens in a silicate unit have to be shared with two other silicate units. The same is true in the next unit, and so on, forming a long chain. Materials containing these long chain silicates are called inosilicates ("sinew" or "string" silicates). The polyhedral drawing of a section of inosilicate ion is shown below.

Inosilicates are not exactly network solids because they do not form three-dimensional networks. However, at least in one direction, they are covalently bonded and can extend indefinitely. There could be hundreds of silicate units in a row. In a sense, inosilicates could also be described as polymers. They contain individual units that keep repeating all along the chain. In the polyhedral drawing, the repeating units are simply tetrahedra.

The inosilicate chain drawn above does illustrate an important consideration that it has in common with network solids. All network solids are different on the inside than they are on the outside. We can illustrate that difference in the inosilicate chain because it is a relatively simple structure. In the inosilicate chain, each tetrahedron along the chain looks just like the next, but the ones on the end are different. They are only attached to one neighbor, not two. Compared to the other repeating units, these ones will have an extra oxygen with a negative charge.

Extending that idea to network solids, in which the covalent bonds extend in three directions, we will encounter a similar problem as we move out from the center of the solid and we reach the surface. The structure at the surface will be different from the structure in the interior of the solid, because we will run out atoms to keep connecting to.

- Network solids have different structures at the surface of the material than they do in the interior of the material.
- The surface of the material must have slightly different groups present because the network has come to an end.

One of the most important inosilicates is wollastonite, which is used in a number of industries. Wollastonite is a bright white mineral in which the counterion for the inosilicate is calcium ion, Ca^{2+}. It is added to ceramic tiles, paints and plastics, partly because it increases their durability and strength. It is sometimes used to make brake pads for cars; it provides friction when pressed against the rotor, slowing down the wheels on your car, but because of its durability it does not wear out too quickly.

Exercise 10.3.6

Convert the polyhedral drawing of inosilicate ion into a Lewis structure. You can stop after five repeating units.

Exercise 10.3.7

Looking at the Lewis structure for inosilicate ion, how many calcium ions would accompany each repeating unit in Wollastonite?

Exercise 10.3.8

In your Lewis structure for inosilicate ion, circle the repeat units. Propose a formula for Wollastonite.

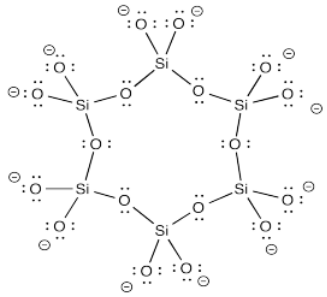
Exercise 10.3.9

Suggest a reason why Wollastonite might confer strength on ceramics and other materials.

Cyclosilicates

If silicate units can form chains, it shouldn't be a surprise that they can form other shapes, too. For example, the silicate units can wrap around to form rings. They come in a veriety of different sizes. These types of silicates are called cyclosilicates ("wheel" silicates).

On of the most familar cyclosilicate mineral groups is the beryl family. The most prominent member of the family is emerald. It contains the cyclic anion shown below.



The polyhedral form is a gorgeous star.

All beryls have the same cyclosilicate anion. They even have the same counterions, with the general formula $Be_3Al_2(Si_6O_{18})$. However, beryls come in different colors because of small amounts of cation impurities. In emerald, a tiny amount of chromium ion provides the green color. In the closely related aquamarine, a tiny amount of Fe^{2+} results in a pale blue; however, when Fe^{3+} is present, the mineral is yellow, instead.

Exercise 10.3.10

The California state gem, benitoite, contains a cyclosilicate anion with just three silicon atoms in it.

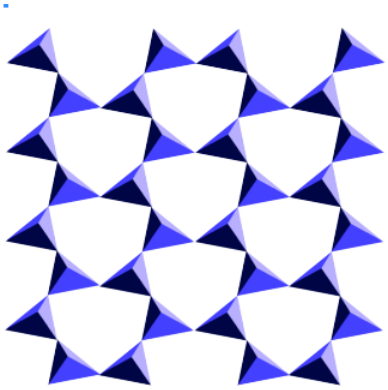
a. Draw the Lewis structure of this cyclosilicate.
b. Draw the polyhedral depiction of this cyclosilicate.
c. This anion is accompanied by a barium and a titanium ion. Given their places in the periodic table, what is the likely charge on each cation?

Clearly we have turned back from the edge of network solids again. These anions may be large, but they certainly don't extend on and on in any direction. However, previously, we looked at single unit silicates and extended them to doubles, then linked them together to make longer chains. What would happen if we could link some cyclosilicates together?

Instead of getting a one-dimensional chain, we would get a two-dimensional network.

Phyllosilicates

The name "phyllosilicates" means, roughly, "leaf"-silicates. These anions are sheets or leaves in which silicates link together to make two-dimensional networks. The structure shown below would extend on and on through the top, bottom and sides of the page (or the screen).



The most familiar examples of phyllosilicates are the mica family. If you have ever seen mica, with its thin sheets, you can easily imagine how it would be composed of two-dimensional networks like the one above. One of the most interesting applications of mica was its use as "Muscovy glass" in the old days in Russia. Its thin, transparent layers made very good windows.

Micas are a slightly more complicated example of phyllosilicates because they are also aluminosilicates. That is, they contain aluminum as well as silicon within their extended oxide network.

Another familiar example is chrysotile, which is one of many minerals that we think of as "asbestos". It is commonly called "white asbestos" and it accounts for the vast majority of asbestos mining in the world. Chrysotile has the formula $Mg_3(Si_2O_5)(OH)_4$.

Exercise 10.3.11

Consider the formula for chrysotile.

a. What is the usual charge on a magnesium ion, given its place in the periodic table?
b. What is the charge on hydroxide ion?
c. The phyllosilicate ion is written as Si_2O_5, representing the overall ratio of those two atoms in the structure, but of course it does not come in units of that size. What is the total negative charge per Si_2O_5 unit?
d. What does that translate into in terms of negative charge per individual silicate unit (i.e. one individual silicate unit per silicon atom)? Explain whether that makes sense in terms of the polyhedral structure for a phyllosilicate shown above.

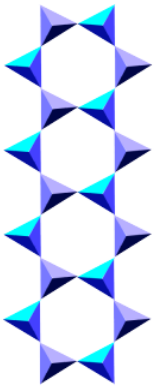
For decades, chrysotile was prized for its naturally insulating and fire-resistant qualities. It was commonly used in homes and other buildings until we realized that it produces a carcinogenic dust. Typically, the danger from this dust only arises from repeated exposure during the mining of asbestos and manufacture of asbestos-containing products. However, it could also be a long-term problem because of dust produced during building renovation projects.

Other, less common forms of asbestos include "blue asbestos" or crocidolite, with formula $Na_2Fe^{II}_3Fe^{III}_2Si_8O_{22}(OH)_2$, and grey-to-brown amosite, $(Mg,Fe)_7Si_8O_{22}(OH)_2$.

Note that there are some complications in the way these formulae are written. There are two different kinds of iron ion in crocidolite. One is an Fe^{2+} ion and the other is an Fe^{3+} ion. Often, in structures and formulae, the charges on metal ions are denoted by the "oxidation state", a number written using Roman numerals. Hence, Fe^{II} means Fe^{2+} in this context and Fe^{III} means Fe^{3+}.

The formula for amosite is actually suggesting something that we have seen before. In amosite, iron and magnesium ions can easily replace each other in the structure. In this case, the ions are Mg^{2+} and Fe^{2+}. The (Mg,Fe) just means we need some combination of these ions for a total of seven ions.

However, crocidolite and amosite are actually examples of inosilicates rather than phyllosilicates. They are a little bit different from the inosilicates that we saw before, however. Rather than containing single polysilicate chains, these materials contain double polysilicate ribbons.



In the picture, the inosilicate ribbon extends through the top and bottom of the page (or the screen) but not to the sides.

If you have ever seen asbestos, which is a fibrous mineral (a little like a clump of long hair), you may be able to imagine a connection between these structures and the physical appearance of the mineral.

Exercise 10.3.12

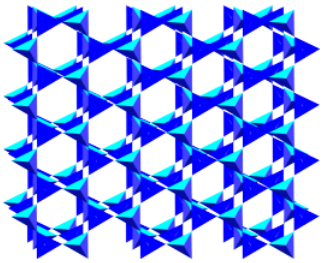
Provide formulae for the endmembers of the amosite family.

Tectosilicates ("building" silicates) form three-dimensional frameworks.

In sorosilicates, individual silicate unit share oxygens with their neighbors via *one* of the corners of their tetrahedra. In inosilicates, individual silicate unit share oxygens with their neighbors via *two* of the corners of their tetrahedra. In phyllosilicates, individual silicate unit share oxygens with their neighbors via *three* of the corners of their tetrahedra.

In tectosilicates, individual silicate unit share oxygens with their neighbors via *four* of the corners of their tetrahedra.

These structures are pretty complicated and generally include aluminum as well as silicon oxides. However, an idealized drawing of such a network is shown below.



The idea of the drawing is that the silicate structure extends in two dimensions like the phyllosilicates, but also in a third direction, bonding to additional tetrahedra above and below the plane of the drawing.

Silica

Silica is truly a covalent network solid. Its formula is SiO_2. Unlike silicates, which are anions, it is a neutral compound, so it does not need counterions to balance a charge. Like the tectosilicates, it forms a three-dimensional network, with one individual silicate unit sharing an an oxygen with its neghbours via all four corners of the tetrahedron.

Although it is a three-dimensional extended solid, it is useful to look for sub-structures within the network, just as it is useful to identify unit cells of ionic solids. In silica, a pattern arises by following "chains" of silica tetrahedra through the network. As we follow along from one tetrahedron to the next, we find a spiral pattern in which each tetrahedron is twisted relative to the one before it. Eventually, every fourth (or in some cases, seventh) tetrahedron echoes the original and the pattern repeats itself.

This spiral shape is reminiscent of DNA. Like DNA, the chains within the three-dimensional structure form helices. They could form right-handed helices or left handed helices. As a result, silica is a "chiral" material and it is "optically active", topics that are covered in stereochemistry.

As in other network solids, silica must have a different structure on its surface than in the interior. On the surface, there are no more individual silicate units with which to form links.

Instead, dangling oxygen atoms may form covalent bonds to hydrogen, so that the surface is covered with OH groups. They may also remain as siloxide ions just as they do in silicates; in that case, they might have counterions such as sodium or potassium.

However, compared to the bulk interior of the solid, the surface contributes very little to the overall mass of the material. As a result, these extra hydrogens and sodiums are not included in the formula of silica. In reality, the true formula of a sample of silica might be something like this (just a fictional example to emphasize the idea):

$$\mathrm{Si}_{1,022,000,000,000,000,000,000}\mathrm{O}_{2,044,000,000,000,000,000,000}\mathrm{H}_{36}\mathrm{Na}_{42}$$

but nobody would ever write that. The material is one millionth of a percent hydrogen, one millionth of a percent sodium, about 66.7% oxygen and approximately 33.3% silicon. It's pretty darned close to SiO_2.

Silica is a very common material. Its most familiar pure form is quartz. In addition to being found as large crystals, microcrystalline particles of quartz is found in a wide rage of other minerals. It's also the major component of sand.

Exercise 10.3.13

Zircon is a nesosilicate containing Zr^{4+} ion. What is its formula?

Exercise 10.3.14

Propose a formula for a simple, single-chain inosite containing only sodium counterions.

Exercise 10.3.15

Jadeite is beautiful green mineral; high quality stones are one of the forms of the gemstone, jade. Jadeite is a simple, single-chain inosite containing equal numbers of Na^+ and Al^{3+} counterions. Propose a formula for this mineral.

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10.4: Aluminosilicates

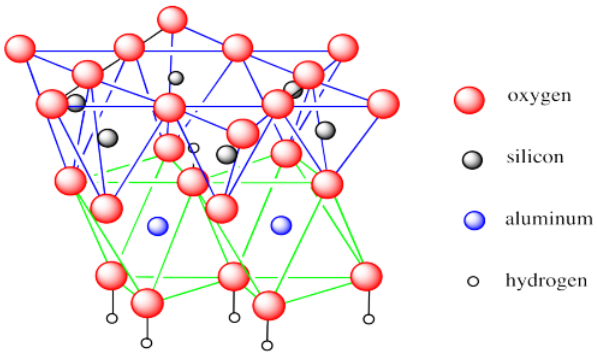
Aluminosilicates are compounds containing oxides of both silicon and aluminum. These compounds are quite common in the earth's crust, so it is worth taking a look at a few examples. Two of the most prevalent types are phyllosilicates, with extended layered structures, and tectosilicates, with structures that extend through a three dimensional network of covalent bonds.

Phyllosilicates

The clay minerals are a class of layered aluminosilicates formed by weathering of other silicate minerals. You are probably familiar with clay in some form or other. It is much finer-grained than sand, which is another product of weathering that is commonly found in the soil or exposed at beaches. Unlike sand,clay can sometimes be formed into shapes. We will take a look at two important examples.

The first example, kaolinite, is the major component of kaolin, a clay that is heavily used in making "china" and other ceramics. It is usually white but small amounts of iron can make it pink, yellow or orange. Kaolin contains hexagonally arrayed layers of silicate tetrahedra, as we have seen in other phyllosilicates. The difference is that this layer sits on top of a layer of aluminate octahedra, with some of the oxygens shared between the two layers.

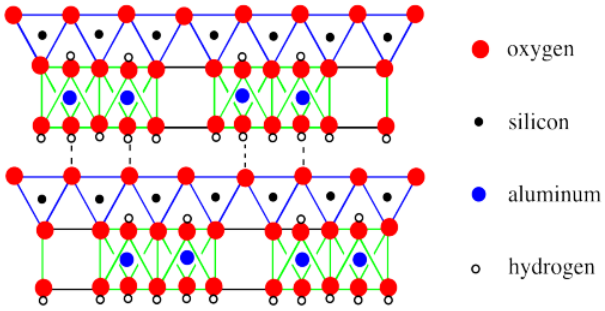
In the picture below, the lines are meant to reinforce the idea of the geometries involved: tetrahedra are outlined in blue and octahedra are outlined in green. The bonds between silicon and oxygen are not shown, nor are the bonds between aluminum and oxygen. We have shown the tetrahedra on top and the octahedra below but there really is no top or bottom to the layer, so it can just as easily be drawn the other way around.



Kaolinite is an example of what is sometimes called a 1:1 clay mineral or a T-O clay mineral. These designations convey the idea that there is one tetrahedral layer and one octahedral layer bonded together by shared oxygen atoms.

If you take a look at the structure, you will see that some of the oxygen atoms are bonded to hydrogens; they are hydroxides. These hydroxides play an important role in the long-range structure of kaolin.

In the picture below, we have simplified the structural drawing to a cartoon. We have also expanded the view to see cross sections of two phyllosilicate sheets and to see a little bit further down each sheet.



In the drawing, the basal layer of hydroxides (that's the layer of OH groups on the bottom face of a sheet) interacts with the basal layer of oxides on the next sheet (that's the layer of oxides on the top of the sheet). These sheets are held together via hydrogen

bonding. Of course, there are more sheets than that. You could easily picture a third layer above the ones that are shown, with its basal hydroxides hydrogen bonding with the oxygens of the tetrahedral layer on top of the drawing.

The other feature that is apparent in this drawing is that the long-range structure of the layer varies a little bit. Some of the octahedra are missing. Only 2/3 of the possible sites in the octahedral are actually occupied, although they are not necessarily spaced out evenly like in the drawing. There are other clay minerals that don't have these absences, although we aren't going to look at any here.

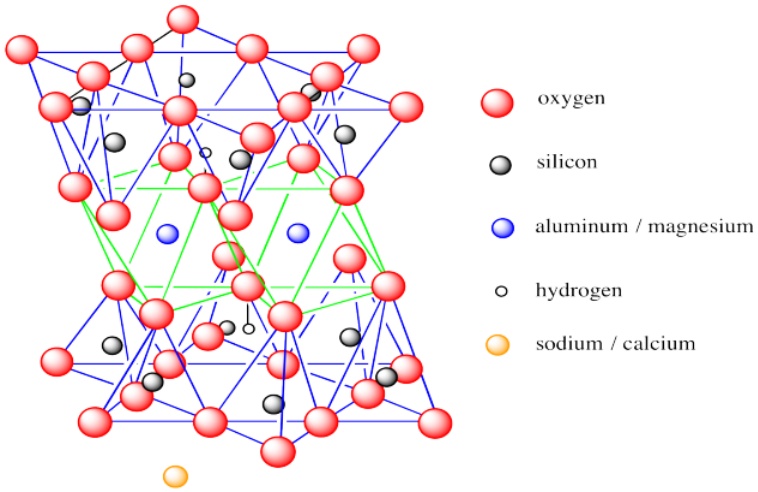
One of the unique features in kaolinite is an electrically neutral layer. If we were to consider all of the oxygens to be O^{2-}, with the cations Si^{4+}, Al^{3+} or H^{+} based on the positions of these atoms in the perioidc table, then the positive and negative charges would exactly balance each other. That contrasts with what we will see in the other cases that we will look at.

Exercise 10.4.1

Kaolinite has a general formula $Al_2Si_2O_5(OH)_4$. Show that kaolinite is electronically neutral overall.

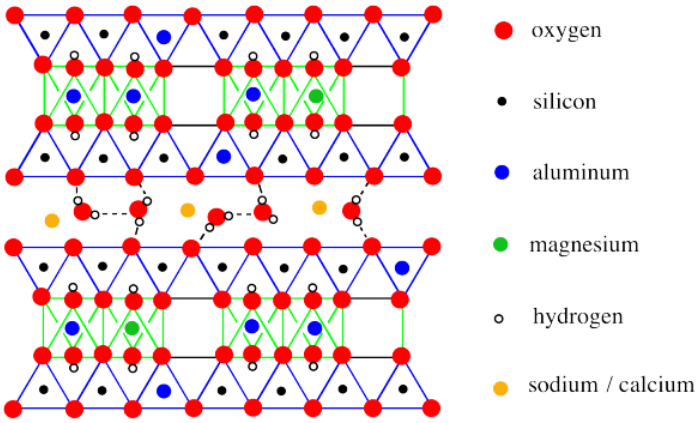
Montmorillonite is an example of another type of clay mineral. It is important as a soil additive in gardens because it helps with moisture retention. It is also used in the petroleum industry when drilling for oil; a slurry of montmorillonite in water helps keep the drill bit cool.

The structure, shown below, has a lot in common with kaolinite.



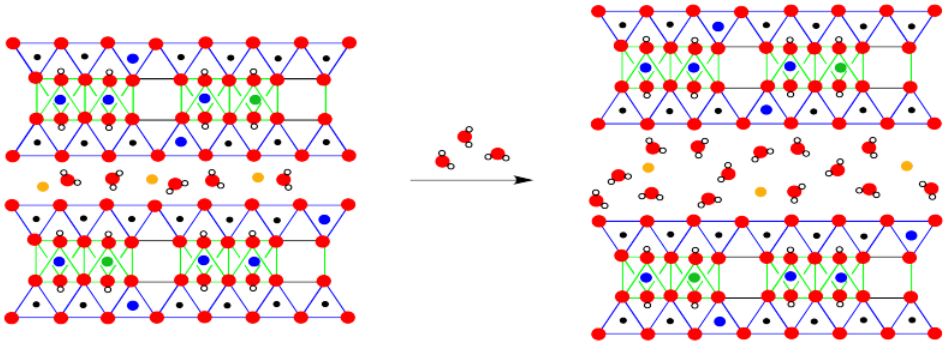
However, there are some key differences. Monmorillonite is a 2:1 clay mineral or a T-O-T clay mineral. Its octahedral layer is sandwiched between two tetrahedral layers. Also, there are fewer hydroxide groups in monmorillonite than in kaolinite; both basal layers are oxides, with hydroxides being found only in the interior of the layer. Finally, montmorillonite does not form electrically neutral layers. The layer is overall anionic, requiring counterions to balance out the charge. These ions are usually Na^{+}, but also include Ca^{2+}.

A more extended view of monmorillonite once again reveals the absence of a third of the aluminate octahedra, as well as some other, subtle differences.



The most obvious difference is the presence of water molecules between the layers. That difference is a key feature of montmorillonite's properties. However, the long-term structure also reveals occasional substitutions, in which a magnesium has replaced an aluminum in an octahedral site, or an aluminum has replaced a silicon in a tetrahedral site.

The moisture-retaining ability of montmorillonite is related to the cushion of water molecules between the layers of the material. More water can always be allowed in.



Exercise 10.4.2

Predict the effect of the following substitutions on the charge of a montmorillonite sheet.

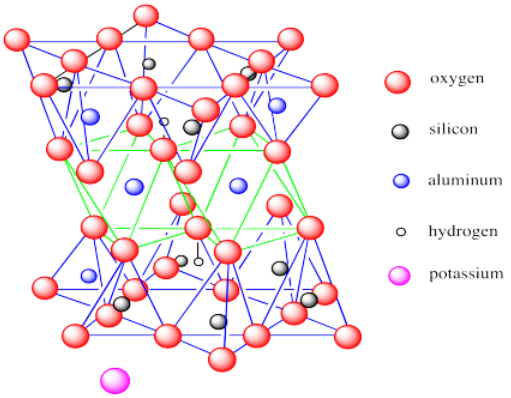
a. A silicon is replaced by an aluminum.
b. An aluminum is replaced by a magnesium.

Exercise 10.4.3

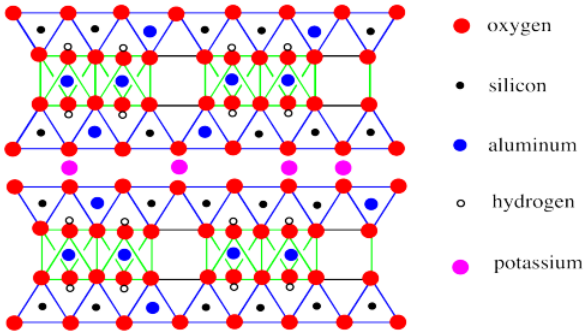
Potters and ceramicists typically wouldn't use montmorillonite clay in their work. Explain why.

Micas provide additional examples of phllosilicates. The most common form of mica is muscovite, which at one time was used in Russian windows. It has a very distinctive appearance, forming blocks that can be peeled apart into thin, solid sheets of transparent material.

Muscovite is not a clay mineral. It does not form from weathering of other rocks. However, it clearly has some structural similarities to clay minerals, especially to montmorillonite.



Like montmorillonite, muscovite sheets contain octahedral layers sandwiched between tetrahedral layers. Also, there are some substitutions of aluminum for silicon in the tetrahedral layer.



A striking difference between montmorillonite and muscovite is the absence of water molecules between layers in the mica. Instead, the space between the sheets is occupied only by potassium ions.

Exercise 10.4.4

What interaction holds the sheets of muscovite together?

Exercise 10.4.5

How is the structure of muscovite related to the physical appearance of the mineral?

Tectosilicates

Once again, tectosilicate structures get very complicated and we will only look at them briefly.

One of the most common groups of aluminosilicates is the feldspars. They are thought to make up about 50% of the earth's crust. Feldspars, like silica, have extended three-dimensional structures. However, like silica, we can see some patterns emerging by following individual chains of tetrahedra through the structure. In silica, we saw spirals or helices; in feldspars, we see zig-zags instead.

Feldspars are significantly different from silica because of frequent substitution of aluminum for silicon and because their structures contain counterions. These counterions are frequently potassium, sodium or calcium.

Exercise 10.4.6

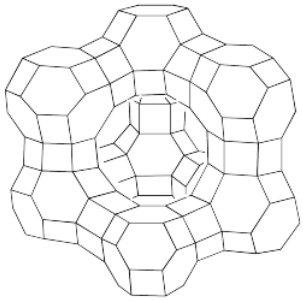
The feldspar endmembers are potassium feldspar, albite and anorthite. Potassium feldspar is the potassium endmember of the group, $KAlSi_3O_8$. Determine the formulae for:

a. albite, the sodium endmember.
b. anorthite, the calcium endmember.

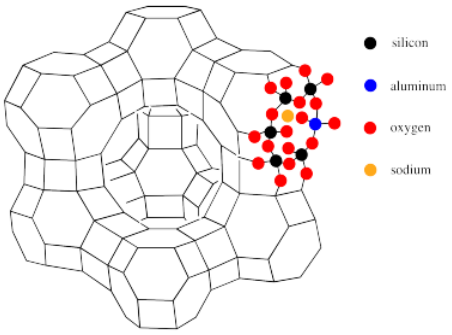
Feldspars are the most common class of tectosilicates, but one of the most interesting classes is the zeolites. Zeolites are tremendously unique and useful materials. They are characterized by a great capacity for storing gases and small molecules. In fact, the name zeolite translates from the Greek to mean "boiling stones", because they may give off steam when heated. Zeolites are also used in catalysis in the petroleum industry, helping to convert petroleum distillates into more useful forms.

The reason zeolites are able to store small molecules is directly tied to their very porous, cage-like structure. In order to emphasize that feature, zeolites are frequently drawn as octahedral line drawings. The following sketch shows the structure of a faujasite, a naturally-occurring zeolite that is also made synthetically for industrial purposes.

The structure is truncated; it would extend further through the attachment of similar units in different directions. However, this view lets us see some key features. A large cavity is clearly seen in the middle of the structure. In addition, there are smaller cavities inside the hexagonal "globes" on the corners, as well as tunnels through the hexagonal "drums" connecting the globes. The hexagons themselves are really pore-like openings into the interior of the zeolite.



The connection between this polyhedral structure and the atomic makeup of faujasite is illustrated below. There, the atoms around one of the hexagonal pores have been filled in.



Each vertex or corner of the structure represents a silicon. However, aluminum can substitute in for silicon to varying degrees. along each line in the polyhedral drawing there is an oxygen atom. Thus, the hexagonal pores in the drawing are really rings formed by twelve atoms, not six: six silicons (or aluminums) and six oxygens. Also illustrated in this picture is the anionic nature of the zeolite framework, necessitating the presence of counterions such as sodium.

Zeolites are useful because molecules can be stored inside of them. Also, molecules can be made to react with each other while trapped inside a zeolite at high temperature. Researchers are very interested in making new architectures of zeolites, and in modifing them to contain catalytic sites that will carry out important reactions.

The structures of zeolites can have a kind of architectural beauty. However, there is one zeolite that has been used in art since ancient times. Ultramarine is a deep blue pigment obtained by grinding lapis lazuli. The characteristic color comes from deep blue thiozonide anions (S_3^-) trapped within the zeolite structure.

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10.5: Solutions to Selected Problems

a) graphite is between 1 & 2 b) stishovite is between 9 & 10 c) opal is between 6 & 7

d) obsidian is about 5 e) ruby is about 9 f) emerald is between 7 & 8

a. forsterite: Mg_2SiO_4: If each nesosilicate unit has a charge of 4^- because of the formal charges on the four oxygens, then the two magnesiums must combine to balance that charge with a 4^+ charge. Each magnesium must have a 2^+ charge of its own. That seems reasonable, since magnesium is two atoms from the left edge of the periodic table; it would have a 2^+ charge in a noble gas configuration.
b. fayalite: Fe_2SiO_4: In order for this to work, each iron would have to have a 2^+ charge. Transition metal charges are harder to predict than alkali and alkaline earth metals because they are farther from the edge of the periodic table, but it turns out that the two most common charges on an iron ion are 2^+ and 3^+, so this charge seems reasonable.

a. If each nesosilicate has a charge of 4^-, then the total negative charge is 100 x 4^- = 400^-. If there are 25 magnesium ions, each with a 2^+ charge, the total positive charge is 25 x 2^+ = 50^+. That leaves a net negative charge of 400^- + 50^+ = 350^-. The irons would balance that charge with an equal positive charge. The number of iron ions would be 350+/3+ = 150.
b. If we divide these ratios by 100 to arrive at the one nesosilicate in the formula, we get $Mg_{0.25}Fe_{1.5}SiO_4$. It does not mean there is a quarter of a magnesium ion anywhere; this formula is just the overall ratio of atoms.

So far we have Al_2Fe_3. The positive charge = 2 x 3^+ + 3 x 2^+ = 12^+. That charge must be balanced by the nesosilicate anions, which are each 4^-. So the number of silicates is $12^-/4^-$ = 3. The formula is $Al_2Fe_3(SiO_4)_3$.

The anions are nesosilicate (4^-) + sorosilicate (6^-) + oxide (2^-) + hydroxide (1^-). The total charge is 13^-.

Calcium is an alkaline earth metal, two atoms from the left edge of the periodic table. The two calciums would partially balance that charge with 2 x 2^+ = 4^+ charge; the net charge is now 13^- + 4^+ = 9^-.

If each Al or Fe has charge 3^+, then the number needed to balance the charge is $9^+/3^+$ = 3 Fe/Al ions.

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CHAPTER OVERVIEW

11: Transition Metal Complexes

11.1: Introduction
11.2: Building Blocks- Metal Ions and Ligands in Transition Metal Complexes
11.3: Electron Counting
11.4: Chelation
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11.8: Solutions for Selected Problems

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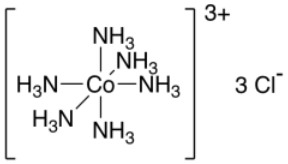
11.1: Introduction

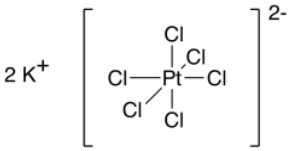
Transition metals are found in the middle of the periodic table. In addition to being found in the metallic state, they also form a range of compounds with different properties. Many of these compounds are ionic or network solids, but there are also some molecular compounds, in which different atoms are arranged around a metal ion. These compounds are called *transition metal complexes* or *coordination complexes*. They are often brightly-colored compounds and they sometimes play very useful roles as catalysts or even as pharmaceuticals.

Because of their relatively low electronegativity, transition metals are frequently found as positively-charged ions, or cations. These metal ions are not found by themselves, instead, they attract other ions or molecules to themselves. These species bind to the metal ions, forming coordination complexes.

Hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$, is an example of a coordination complex. It is a yellow compound. The "complex" part refers to the fact that the compound has a bunch of different pieces. There is a cationic part, which itself is a moderately complicated structure, plus three chloride anions.



Potassium hexachloroplatinate, $K_2[PtCl_6]$, is another good example. It is another bright yellow compound. This time, the anion is the more complex part, and there are two potassium ions as well.

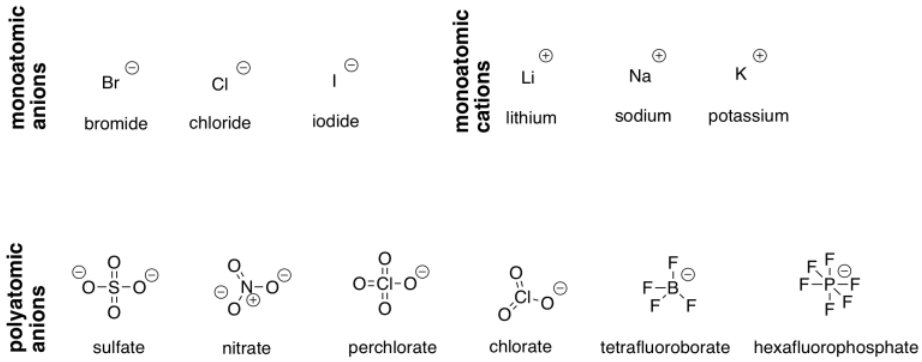


The formulae for coordination complexes always give you hints about the structures. The stuff inside the square brackets always makes up one of the ions. In that part, there are a number of things attached to the transition metal. Those things attached to the transition metal are called ligands; we'll take a closer look at them later. The part outside the square brackets tells you what the counterions are; those are there to balance out the charge of the ion inside the square brackets.

Very often, the counterions are individual atomic ions, like chloride anions (Cl^-) or potassium cations (K^+). So, when you see the K_2 within the formula, the potassium atoms are not connected together; they are two separate potassium ions: 2 K^+. Likewise, the Cl_3 at the end of a formula does not really mean a group of three chlorine atoms clustered together; they are three separate chloride ions, 3 x Cl^-.

Sometimes, polyatomic ions that act as counterions to these complexes; this is especially common in the case of anions. Most often, they are oxoanions, in which an atom has some number of oxygens attached to it. A couple of the most common examples are nitrate (NO_3^-) and sulfate (SO_4^{2-}); these ions have been known for hundreds of years. Tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) are a couple of twentieth-century anions.

A number of common ions are listed in the table below. Most of them have a +1 or -1 charge. Sulfate is the only common example listed with a 2- charge.

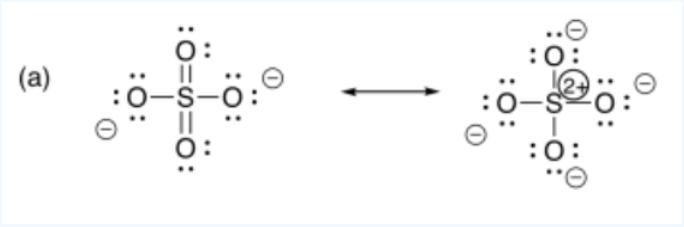


Note that some of these structures use a charge-minimised Lewis structure. In third-row elements, these structures may contain additional bonds to the central atom, going past the octet, in order to lower the number of + and - charges. Sulfate and perchlorate can also be drawn as octet-obedient structures, in which the sulfur and chlorine have true octets, and charge separation occurs. However, hexafluorophosphate has no octet-obedient Lewis structure; regardless of how you draw it, the phosphorus has six bonds.

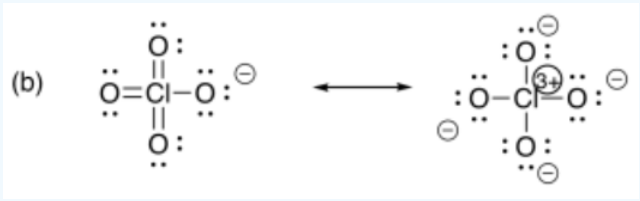
Exercise 11.1.1

Draw the octet-obedient structures for (a) sulfate and (b) perchlorate.

Answer a



Answer b

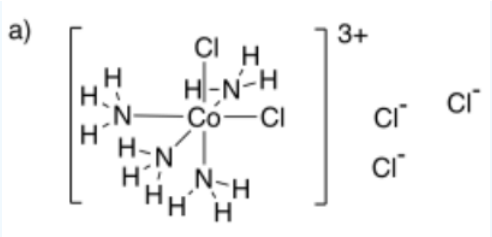


Exercise 11.1.2

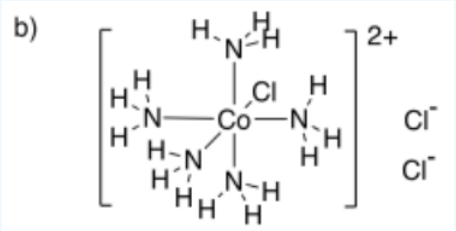
Indicate the individual ions in the following complexes.

a. $[Co(NH_3)_4Cl_2]Cl$
b. $[Co(NH_3)_5Cl]Cl_2$
c. $[Co(NH_3)_5NO_2]Cl_2$
d. $[Co(NH_3)_5OH_2]Cl_3$
e. $K_2[PtCl_4]$
f. $Na_2[Co(SCN)_4]$
g. $[Pt(NH_3)_2(OH_2)_2](NO_3)_2$
h. $[Co(NH_3)_4(OH_2)_2]_2(SO_4)_3$

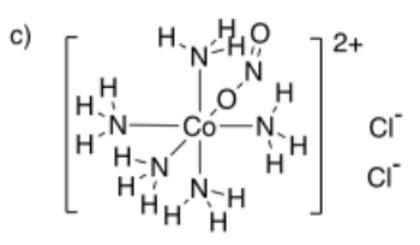
Answer a



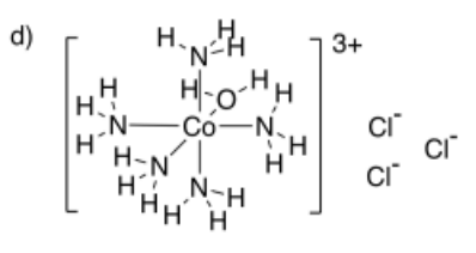
Answer b



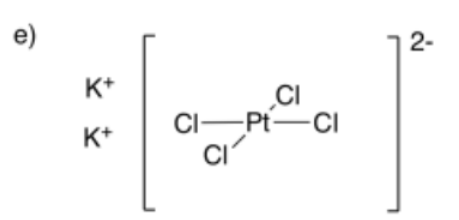
Answer c



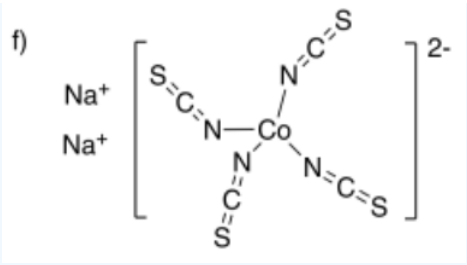
Answer d



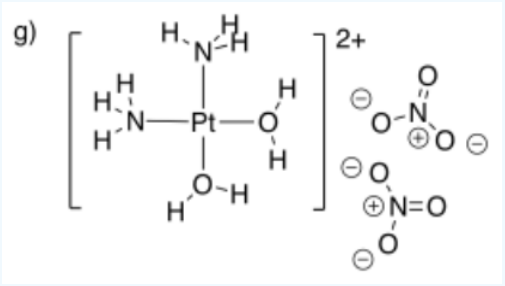
Answer e



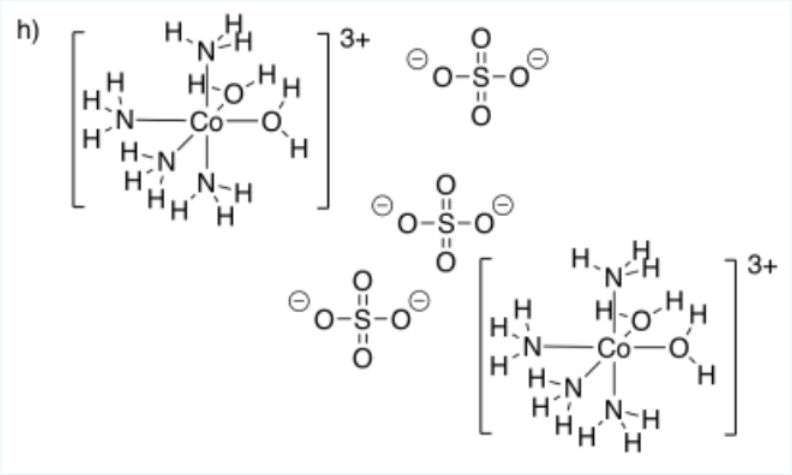
Answer f



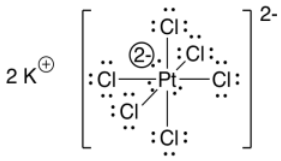
Answer g



Answer h



We haven't drawn proper Lewis structures for these coordination complexes so far. For the hexachloroplatinate complex, the Lewis structure is shown below:



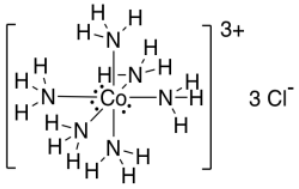
The electron accounting looks like this:

atom	electrons
Pt	10 e^-
Cl	6 x 7 e^-
charge	add 2 e^-
total	54 e^-

Two electrons for each bond takes up 12 electrons. That leaves 42 more. If each chlorine gets three lone pairs, that uses up another 36 electrons. There are six left, and they could be left on the platinum.

That is a lot of electrons. But remember where platinum sits in the periodic table: it's a transition metal. How many electrons does the next noble gas have? Eighteen: that's radon. This structure works out perfectly in terms of reaching a noble gas configuration.

For another example, let's take a look at the cobalt complex.



This time, the electron counting looks like:

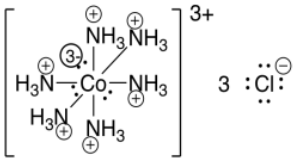
atom	electrons
Co	9 e^-
N	6 x 5 e^-
H	18 x 1 e^-
charge	lose 3 e^-
total	54 e^-

A dozen of those electrons get used for the six Co-N bonds, leaving 42 more. We need another 36 for the eighteen N-H bonds; that leaves six electrons. We can just put those on the cobalt, like last time.

Each nitrogen ends up with its octet (eight electrons in four bonds). Each hydrogen has its "octet" (two electrons in a bond, corresponding to helium's noble gas configuration. Cobalt also gets its "octet" (eighteen electrons corresponding to krypton's noble gas configuration).

These are still really big, unwieldy numbers. We need a simplification. We won't really count up all of the electrons in coordination complexes because they tend to be assembled from pre-existing parts (the "ligands") that already have their octets. The ligands are just donating their electrons to the metal in the center. Instead, we focus on that metal, and see how many electrons it has once all of the ligands have been attached.

Also, notice that in the Lewis structure of the cobalt complex, we neglected the formal charges. That's actually common practice with transition metal complexes. The reason for that is simply that the structure is getting pretty crowded with all the lone pairs and formal charges. Normally, in order to simplify an already complicated structure, the lone pairs on the transition metal and the formal charges are not shown.



On the next page, we will practice electron counting some more. We will also take a look at some common ligands: the pieces that are directly attached to the transition metal ions.

See a more in-depth discussion of coordination complexes in a later course.

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11.2: Building Blocks- Metal Ions and Ligands in Transition Metal Complexes

Transition metal complexes or coordination complexes are molecules that contain groups arranged around a central metal ion. In a way, these are like "lego-molecules", easily assembled from smaller parts, and sometimes they are easily transformed into new molecules by switching out old parts for new ones. That rapid assembly and disassembly is part of what makes these compounds very useful in both industrial and biological catalysis.

What are the building blocks that go into a coordination complex? The key, central part is usually a transition metal ion (although cations from other parts of the periodic table are also seen in some cases). The following table shows some common examples of ions formed by each of the transition metals.

Table 11.2.1: Some common transition metal ions.

Sc^{3+}	**Ti^{4+}** Ti^{3+}	**V^{5+}** V^{4+}	**Cr^{3+}** Cr^{6+} Cr^{2+}	**Mn^{2+}** Mn^{4+} Mn^{7+}	**Fe^{3+}** Fe^{2+}	**Co^{2+}** Co^{3+}	**Ni^{2+}**	**Cu^{2+}** Cu^{+}	**Zn^{2+}**
Y^{3+}	**Zr^{4+}**	**Nb^{5+}** Nb^{3+}	**Mo^{6+}** Mo^{4+} Mo^{5+}	**(Tc^{7+})*** (Tc^{4+})*	**Ru^{3+}** Ru^{4+} Ru^{2+}	**Rh^{3+}** Rh^{+}	**Pd^{2+}** Pd^{4+}	**Ag^{+}** Ag^{2+}	**Cd^{2+}**
La^{3+}	**Hf^{4+}**	**Ta^{5+}**	**W^{6+}** W^{4+} W^{5+}	**Re^{4+}** Re^{6+} Re^{7+}	**Os^{4+}** Os^{3+}	**Ir^{4+}** Ir^{3+}	**Pt^{2+}** Pt^{4+}	**Au^{3+}** Au^{+}	**Hg^{2+}** Hg^{1+}

For each transition metal, the most common form of ion is listed first. For example, iron is often found in compounds as Fe^{3+}. Other common ions are also shown below that; iron is seen pretty frequently as Fe^{2+}. Other charges are possible; iron has been reported with charges all the way from Fe^{0} to Fe^{6+}, but these cases are less common.

Also, it's worth noting that the top row of transition metals is generally much more common than the next two rows. That does not mean that the others are less important; gold (Au), silver (Ag) and platinum (Pt) are certainly important economically. However, you may be more likely to encounter examples of complexes from the first row. That's especially true in biological chemistry, because organisms have evolved to make use of those metal ions that are most readily available to them.

Exercise 11.2.1

a. The metals on the left hand side of the table tend to have relatively high charges compared to the metals on the right. What do ions such as Sc^{3+}, Zr^{4+}, and Ta^{5+} have in common that would explain this trend?
b. The metals on the right side of the table have relatively low charges. In nature, metals such as copper (Cu), silver (Ag), and gold (Au) are frequently found as native metals (e.g. Cu^{0}, with no charge at all) rather than as compounds. Explain this preference for low charges in this part of the transition metals.
c. The metals in the middle, on the other hand, have very wide ranges of charges (that's why the table lists three common charges for those, although even more exist). Why?

Answer a:

All of these ions have the electronic configuration of the preceding noble gas, Ar. These metals have just started filling the next energy levels; these electrons are relatively high in energy, with relatively few protons attracting them (compared to later elements in the row). The valence electrons are relatively easy to use, although not the core electrons.

Answer b:

These metals have relatively high numbers of protons compared to the elements to their left in the same row. They have relatively high electronegativity, so they do not lose many electrons.

Answer c:

These metals in the middle display a mixture of behaviours: they are electronegative enough to stabilize relatively low charges, but far enough to the left that they can become fully oxidised to reach a noble gas configuration.

The charge on the metal ion is sometimes called the *oxidation state*. This term refers to the fact that metals that are exposed to the elements sometimes become positively charged, forming compounds such as metal oxides. The oxygen from the air provides the oxide or hydroxide ion to counter the charge when the metal atom loses electrons and becomes a metal cation. Familiar examples include the oxidation of aluminum metal to form silvery-white aluminum oxide; you may have seen aluminum screen doors that are actually covered in a coating of aluminum oxide. The Statue of Liberty was originally covered in copper metal, but quickly became coated in money-green copper oxide.

Sometimes, within a complex, the charge or oxidation state of the metal is denoted using Roman numerals. For example, Co^{3+} is sometimes writted Co(III); Mn^{2+} might be written Mn(II).

So, if you need to brush up on Roman numerals:

1 = I; 2 = II; 3 = III; 4 = IV; 5 = V; 6 = VI; 7 = VII; 8 = VIII; 9 = IX

After that, we won't need to worry about it. Sometimes osmium is found as Os(VIII), for example, but we don't see a 9+ charge very often.

The metal ion is the first building block. The second building block is the ligand. The ligands are the pieces that are arranged around the metal ion. On the last page, we saw chloride anions (Cl^-) and ammonia (NH_3) act as ligands in different transition metal complexes. It is easy to imagine how a positively charged metal ion would attract a negatively charge anion such as chloride. As it happens, neutral ligands are just as common. The main requirement for sticking to a metal ion is a non-bonding pair of electrons, or a lone pair (at least, that's the case at this stage of your education).

The following table illustrates a variety of ligands for transition metal complexes.

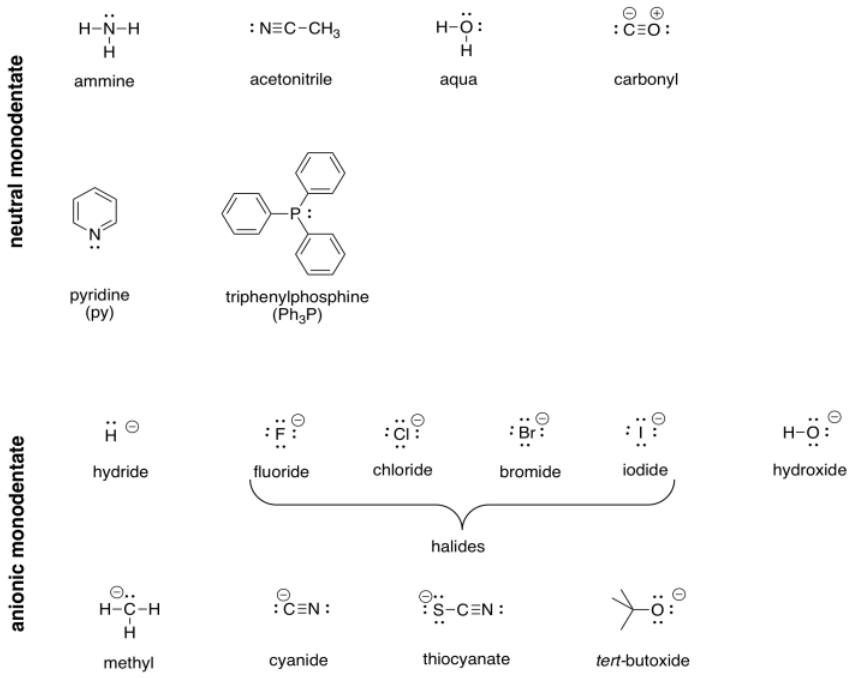

Figure 11.2.1: Some common ligands.

Exercise 11.2.2

Calculate the overall charge on the following complexes, if any.

a) $[Fe(II)(OH_2)_6]$ b) $[Cr(III)(NH_3)_5Cl]$ c) $[(py)_4Mn(II)(SCN)_2]$

d) $[Fe(II)(CN)_6]$ e) $[Co(III)(CN)_5CO]$ f) $[Fe(II)(CN)_5NH_3]$

Answer a:

H_2O = 0 charge; Fe(II) = 2+ charge; total = 2+

Answer b:

H_3N = 0 charge; Cl = 1- charge; Cr(III) = 3+ charge; total = 2+

Answer c:

py = 0 charge; SCN = 1- charge; Mn(II) = 2+ charge; total = 0

Answer d:

CN = 1- charge; Fe(II) = 2+ charge; total = 4-

Answer e:

CN = 1- charge; CO = 0 charge; Co(III) = 3+ charge; total = 2-

Answer f:

CN = 1- charge; NH_3 = 0 charge; Fe(II) = 2+ charge; total = 3-

A coordination complex has a central metal ion with a number of ligands arranged around it. The last piece is the counterions, which would balance out the charge of the transition metal complex ion. We saw examples of common counterions on the introduction page.

Exercise 11.2.3

Calculate the charge or oxidation state on the metal ion in each of the following complexes.

a) $[Cr(OH_2)_6](NO_3)_3$ b) $K_3[FeF_6]$ c) $[Cr(SCN)(NH_3)_5]SO_4$

d) $K_4[Mn(CN)_6]$ e) $[Au(NCCH_3)_2]ClO_4$ f) $[(Ph_3P)Ag(CN)]$

Answer a:

Overall charge = 3+; ligands charge = 0; charge on Cr = 3+

Answer b:

Overall charge = 3-; ligands charge = 6-; charge on Fe = 3+

Answer c:

Overall charge = 2+; ligands charge = 1-; charge on Cr = 3+

Answer d:

Overall charge = 4-; ligands charge = 6-; charge on Mn = 2+

Answer e:

Overall charge = 1+; ligands charge = 0; charge on Au = 1+

Answer f:

Overall charge = 0; ligands charge = 1-; charge on Ag = 1+

On the next page, we will see how some ligands can bind to a metal more than once. That helps them hold on more tightly.

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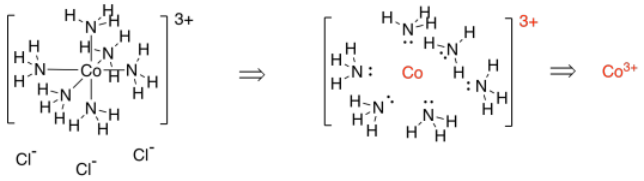
11.3: Electron Counting

Transition metals bind to ligands in order to edge closer to electronic saturation. In other words, the electrons donated by the ligands to form the bonds to the metal help that metal get to the next noble gas configuration. It does not always get there, and sometimes it overshoots, but that's a rough guide.

Consider the coordination complex below. $[Co(NH_3)_6]Cl_3$ contains a cobalt complex ion and three chloride counterions; the counterions just there to balance the charge. We could think of that complex as being assembled from a cobalt ion and six ammonia molecules. The six ammonia molecules each lend a lone pair to help the cobalt towards its octet. If we go backwards, and disassemble the complex into its components, we see that each of those ammonia molecules was neutral. There is no formal charge on any of those nitrogens. If they are all neutral, but the complex has a positive charge, then where did the positive charge come from?



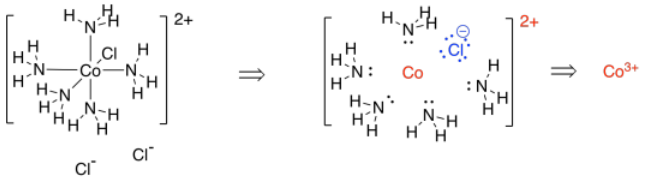
The answer has to be the cobalt ion. The cobalt has a 3+ charge (or "oxidation state"). Knowing that, we can figure out how many electrons cobalt has in its valence shell within the complex.

In the periodic table, cobalt has nine valence electrons. However, if the overall complex has a charge of 3+, then the cobalt also had a charge of 3+. It has lost three electrons, so it only has six left. Once it forms the complex, each ammonia donates a pair of electrons; that's twelve total. The valence shell around cobalt includes its own d electrons plus that twelve donated by the ligands, for a total of eighteen.

We can summarise in a table:

metal valence e^- (or d e^-)	9 e^-
charge on complex	3+
charge on ligands	0
charge on metal	3+
metal ion d e-	6 e^-
e^- donated by ligands	6 x 2 = 12 e^-
total	18 e^-

$[Co(NH_3)_5Cl]Cl_2$ is a very similar example. This time, when we dissect the complex, we find a chlorine that would have a formal charge of 1- (we always assume the ligands all had octets before they joined the metal). The overall complex has a 2- charge; taking into account that there is a charge of -1 on the chloride within that complex, then the cobalt ion must have a charge of 3+ in order to arrive at that overall 2+ charge.



Again,we can use a table to count the electrons on cobalt in the complex.

metal valence e^- (or d e^-)	9 e^-

charge on complex	2+
charge on ligands	1-
charge on metal	3+
metal ion d e-	6 e^-
e^- donated by ligands	12 e^-
total	18 e^-

Exercise 11.3.1

Confirm the electron count on the metal is 18 electrons in each of the following complexes.

a) $Pd(PPh_3)_4$ b) $Cr(CO)_6$ c) $[Cu(NCCH_3)_4]ClO_4$

d) $Fe(CO)_5$ e) $K_4[Fe(CN)_6]$

Answer a:

Pd valence e^-	10 e^-
charge on complex	0
charge on ligands	0
charge on Pd	0
revised Pd e^-	10 e^-
e^- donated by ligands	4 x 2 = 8 e^-
total	18 e^-

Answer b:

Cr valence e^-	6 e^-
charge on complex	0
charge on ligands	0
charge on Cr	0
revised Cr e^-	6 e^-
e^- donated by ligands	6 x 2 = 12 e^-
total	18 e^-

Answer c:

Cu valence e^-	11 e^-
charge on complex	+1
charge on ligands	0
charge on Cu	+1
revised Cu e^-	10 e^-
e^- donated by ligands	4 x 2 = 8 e^-
total	18 e^-

Answer d:

Fe valence e^-	8 e^-
charge on complex	0
charge on ligands	0
charge on Fe	0
revised Fe e^-	8 e^-
e^- donated by ligands	5 x 2 = 10 e^-
total	18 e^-

Answer e:

Fe valence e^-	8 e^-
charge on complex	-4
charge on ligands	-6
charge on Fe	+2
revised Fe e^-	6 e^-
e^- donated by ligands	6 x 2 = 12 e^-
total	18 e^-

Exercise 11.3.2

Determine the electron count on the metal in each of the following complexes.

a) $RhClH_2(PPh_3)_2$ b) $[Ni(OH_2)_4](ClO_4)_2$ c) $[Cu(NH_3)_4](BF_4)_2$ d) $K_2[PtCl_6]$

Answer a:

a)

Rh valence e^-	9 e^-
charge on complex	0
charge on ligands	-3
charge on Rh	+3
revised Rh e^-	6 e^-
e^- donated by ligands	5 x 2 = 10 e^-
total	16 e^-

Answer b:

b)

Ni valence e^-	10 e^-
charge on complex	2+
charge on ligands	0
charge on Ni	2+
revised Ni e^-	8 e^-
e^- donated by ligands	4 x 2 = 8 e^-
total	16 e^-

Answer c:

c)

Cu valence e^-	11 e^-
charge on complex	2+
charge on ligands	0
charge on Cu	2+
revised Cu e^-	9 e^-
e^- donated by ligands	4 x 2 = 8 e^-
total	17 e^-

Answer d:

d)

Pt valence e^-	10 e^-
charge on complex	2-
charge on ligands	6-
charge on Pt	4+
revised Pt e^-	6 e^-
e^- donated by ligands	6 x 2 = 12 e^-
total	16 e^-

On the next page, we will see how some ligands can bind to a metal more than once. That helps them hold on more tightly.

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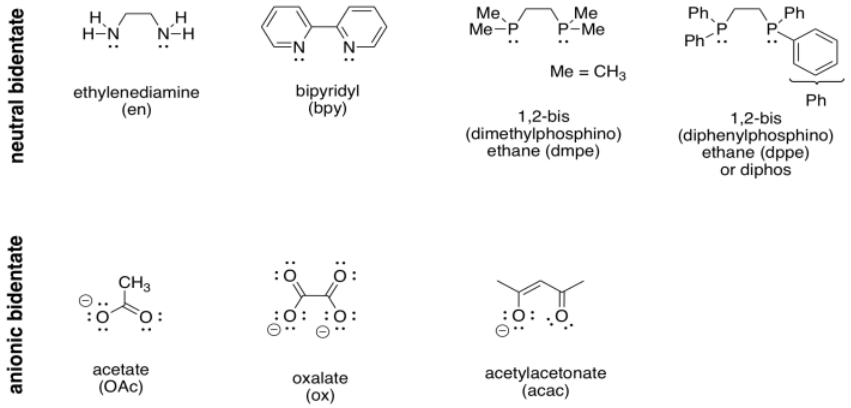
11.4: Chelation

Each ligand that binds to a transition metal donates a pair of its electrons to the metal, sharing those electrons in a metal-ligand bond. Counting the total number of electrons in the metal's valence shell is fairly easy when you know that each ligand contributes two electrons.

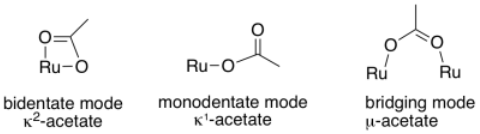
But what if a ligand could contribute more than two electrons? Take a look at the following table. Each of the ligands shown here can bind to a metal twice. The ligand forms two bonds to the metal, donating two pairs of electrons. It might seem obvious, but forming two bonds to the metal means the ligand binds more tightly to the metal. Remember the lego-like nature of transition metal complexes: ligands can come and go, but these ligands are less likely to go; they hold on.



These ligands are called bidentate ligands. That means, literally, that they have two teeth. That does not sound like much, but the ligands we have seen previously are described as monodentate; they have only one tooth. Bidentate ligands can bite into the metal, and hold onto it, more strongly than monodentate ones.

Another term used for these kinds of ligands is derived from the Greek *chele*, for claw. These ligands grab onto the metal like the claw of a lobster or crab; they *chelate*. The "chelate effect" is the tendency of these ligands to bind firmly to a metal, whereas monodentate ligands might come off more easily.

Now, just because a ligand could be bidentate does not mean that it always binds that way. That's often true with the acetate ligand, for example, because the four-membered ring that forms when it binds through both oxygens is a little too strained. Consequently, there are examples binding through both oxygen atoms, and there are also examples of binding through only one. Sometimes, acetate uses one oxygen to bind to one metal atom and the other oxygen to bind to a second metal atom, forming a bridge.



Usually, if a ligand is capable of chelation, assume it binds that way. However, there may be cases in which you are asked specifically to draw it binding in one way or another.

Exercise 11.4.1

Determine the denticity of each ligand in the following complexes.

a) $[Cu(en)_2(OH)_2]$ b) $[RuCl_2(dmpe)(bpy)]$ c) $[Ni(acac)_2(OH_2)_2]$ d) $K_2[Cu(ox)_2(OH_2)_2]$

e) $[FeH_2(dmpe)_2]$ f) $[RuH(OAc)(PPh_3)_3]$ g) $[Co(en)_2Cl_2]BF_4$ h) $[Ru(bpy)_2(HOCH_2CH_3)_2](ClO_4)_2$

Answer a:

en = bidentate; OH = monodentate

Answer b:

dmpe = bidentate; bpy = bidentate; Cl = monodentate

Answer c:

acac = bidentate; H_2O = monodentate

Answer d:

ox = bidentate; H_2O = monodentate

Answer e:

dmpe = bidentate; H = monodentate

Answer f:

H = monodentate; PPh3 = monodentate; OAc = bidentate. In this case, the acetate gets the complex to 18 electrons by binding twice.

Answer g:

en = bidentate; Cl = monodentate

Answer h:

bpy = bidentate; $HOCH_2CH_3$ = monodentate

Exercise 11.4.2

Determine the charges (or oxidation states) on the metals in the following complexes:

a) $K[Cr(ox)_2(OH_2)_2]$ b) $K[Mn(acac)_3]$ c) $[Cr(en)_2Cl_2]PF_6$ d) $[Co(en)_2(OH)Cl]ClO_4$

e) $Na_3[Mn(ox)_3]$ f) $K_3[Cr(ox)_3]$ g) $Na[Au(bpy)(CN)_2]$

Answer a:

Overall charge = 1-; ligands charge = 4-; charge on Cr = 3+

Answer b:

Overall charge = 1-; ligands charge = 3-; charge on Mn = 2+

Answer c:

Overall charge = 1+; ligands charge = 2-; charge on Cr = 3+

Answer d:

Overall charge = 1+; ligands charge = 2-; charge on Co = 3+

Answer e:

Overall charge = 3-; ligands charge = 6-; charge on Mn = 3+

Answer f:

Overall charge = 3-; ligands charge = 6-; charge on Cr = 3+

Answer g:

Overall charge = 1-; ligands charge = 2-; charge on Au = 1+

Exercise 11.4.3

Determine the electron count on the metal in each of the complexes from the previous problem.

Answer a:

Cr = d^6; Cr^{3+} = d^3; ox = 2 x $4e^-$ = 8 e^-; water = 2 x $2e^-$ = 4 e-; total = 15 e^-

Answer b:

Mn = d^7; Mn^{2+} = d^5; acac = 3 x $4e^-$ = 12 e^-; total = 17 e^-

Answer c:

Cr = d^6; Cr^{3+} = d^3; en = 2 x $4e^-$ = 8 e^-; Cl = 2 x $2e^-$ = 4 e-; total = 15 e^-

Answer d:

Co = d^9; Co^{3+} = d^6; en = 2 x $4e^-$ = 8 e^-; OH = $2e^-$; Cl = 2 e-; total = 15 e^-

Answer e:

Mn = d^7; Mn^{3+} = d^4; ox = 3 x $4e^-$ = 12 e^-; total = 16 e^-

Answer f:

Cr = d^6; Cr^{3+} = d^3; ox = 3 x $4e^-$ = 12 e^-; total = 15 e^-

Answer g:

Au = s^1d^{10}; Au^{1+} = d^{10}; bpy = 2 x $2e^-$ = 4 e^-; cyanide = 2 x $2e^-$ = 4 e-; total = 18 e^-

See a more in-depth discussion of coordination complexes in a later course.

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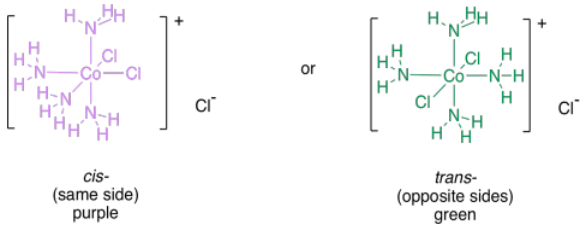
11.5: Isomers

Sometimes, two compounds can have the same molecular formula but different structures. In transition metal complexes, that can happen if the same ligands are arranged around the metal in different ways.

For example, the complex ion $[CoCl_2(NH_3)_4]^+$ contains two chlorine ligands that can be placed in two different ways around the cobalt. The cobalt in this complex has octahedral geometry. Every ligand in the complex is 90 degrees away from four other ligands, and 180 degrees away from a fifth. If there are two chloride ligands, then they might be found 90 degreed away from each other, or they might be found 180 degrees away from each other. The former case exists, and it is called the *cis*-isomer; the latter case also exists, and is called the *trans*-isomer (*cis* means same, as in same side, as opposed to *trans*, which means opposite).



cis-
(same side)
purple

trans-
(opposite sides)
green

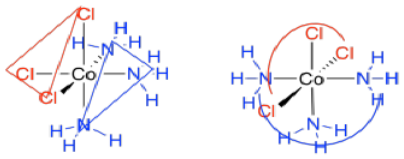
In this case, the two compounds have different physical properties, most readily seen in the two different colors of the complexes: one is purple and the other is green. The exact reasons for the colors are subtle; you're not expected to know why one is green and the other is purple at this stage.

Exercise 11.5.1

Draw structures for the following compounds:

a. *trans*-$Fe(py)_4Cl_2$
b. *trans*-$Mn(OH_2)_4F_2$
c. *cis*-(bpy)V(acac)Cl_2
d. cis-$Mo(CO)_4(PMe_3)_2$

A group of three ligands can also adopt two different geometries in an octahedron. The three ligands can be found clustered together on one side of the complex. They occupy one face of the octahedron, in what is called the *fac*-geometry. Alternatively, they could lie all in a row. Sitting along a meridian of the octahedron, they adopt a *mer*-geometry.



fac *mer*

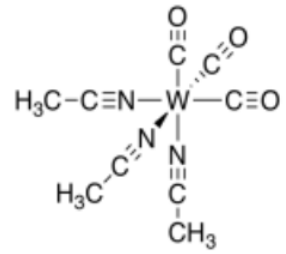
Exercise 11.5.2

Draw structures of the following complexes:

a. *fac*-$W(CO)_3(NCCH_3)_3$
b. *mer*-$Mo(CO)_3(PMe_3)_3$
c. *fac*-$Mo(CO)_3(PF_3)_3$
d. *mer*-$Mo(CO)_3(PCl_3)_3$
e. *fac*-$Na[Mn(CO)_3(CN)_3]$

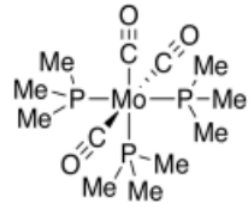
Answer a:

a)



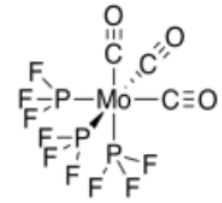
Answer b:

b)



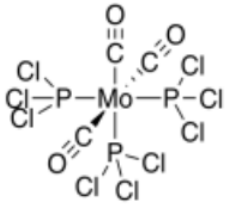
Answer c:

c)



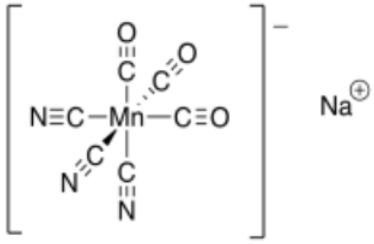
Answer d:

d)



Answer e:

e)



See a more in-depth discussion of coordination complexes in a later course.

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11.6: Naming Transition Metal Complexes

It's sometimes useful to be able to be able to read the name of a compound and understand what that means. The names of coordination compounds tend to be pretty long because of the number of pieces involved, but they usually follow a trend.

- Coordination compounds often contain a "complex" ion, with ligands attached to the metal ion, as well as a counterion, to balance charge. If there is a cation and an anion, the cation is named first.

$[Ni(OH_2)_6]Cl_2$, **hexaaquanickel(II) chloride** (nickel cation before chloride anion)

In the formula, you can always tell one ion from the other because the complex ion (metal plus ligands) is always enclosed in square brackets. Anything outside of brackets is the counterion or counterions.

- Ligands are listed in front of the metal.

$[Cu(NH_3)_6]Br_2$, hexa**ammine**copper(II) bromide (ammine ligand before copper metal)

Note that anionic ligands generally end in "o" in the name of a coordination compound. Chloride becomes chloro. Acetate becomes acetato. Neutral ligands keep their regular names, but the two common molecules H_2O and NH_3 are called "aqua" and "ammine", respectively.

If two different ligands are found in the complex, they are listed alphabetically.

$[Co(OH_2)_5Cl](NO_3)_2$, penta**aqua***chloro*cobalt(III) nitrate (aqua before chloro)

- If there is more than one ligand of the same kind, then the number of ligands is indicated as follows:

ligands	prefix
2	di
3	tri
4	tetra
5	penta
6	hexa

In the examples above, there were six waters, "hexaaqua", six ammines, "hexaammine", and five waters, "pentaaqua".

Sometimes ligand names are complicated. For example, they may already contain prefixes denoting a number, such as ethylene**di**amine, $NH_2CH_2CH_2NH_2$. The di means that there are two amino groups in the ligand. We avoid saying "di" to describe something that already contains a "di". Instead, for more complicated ligands like this, we use the following system:

ligands	prefix
2	bis
3	tris
4	tetrakis
5	pentakis
6	hexakis

For example, $[(Ph_3P)_4Pd]$ is **tetrakis**(triphenylphosphine)palladium(0).

If you need to stress that only one ligand of a certain type is present, you could use the numbering adjective "mono". For example, if you are comparing a compound with two CO ligands to another that has only one, you might call them "the dicarbonyl compound" and "the monocarbonyl compound", respectively.

- The metal is named following the ligands, and its charge or oxidation state is listed using Roman numerals.

$[Co(en)_2Cl_2]ClO_4$, dichlorobis(ethylenediamine)**cobalt(III)** perchlorate.

However, if the complex ion containing the metal is an anion, the metal is given the suffix "-ate", sometimes replacing its normal ending.

$K_2[PtCl_6]$, potassium hexachloroplatin**ate**(IV)

If the complex ion is an anion and the element's symbol does not match its name in English, the Latin name of the metal is usually used rather than the English one. For example, an iron-containing anion would contain the term "ferrate" instead of "iron"; a copper-containing one would be called a "cuprate", one with gold would be called an "aurate" and so on.

- There is no need to describe the number of counterions, because that information can be worked out given the charge on the metal and the charges on the ligands.

$Na_2[CuF_4]$, sodium tetrachlorocuprate(II) (no need to say there are two sodium ions).

Exercise 11.6.1

Provide names for the following complexes:

a) $K[Cr(ox)_2(OH_2)_2]$ b) $[Co(NH_3)_5Br](NO_3)_2$ c) $[Cr(en)_2Cl_2]PF_6$ d) $[Co(bpy)_2(OH)Cl]ClO_4$

e) $[TiCl_3(OH_2)_3]$ f) $K_3[Fe(CN)_6]$ g) $Na[Au(bpy)(CN)_2]$

Answer a:

potassium diaquabis(oxalato)chromate(III)

Answer b:

pentaamminebromocobalt(III) nitrate

Answer c:

dichlorobis(ethylenediamine)chromium(III) hexafluorophosphate

Answer d:

bis(bipyridine)chlorohydroxocobalt(III) perchlorate

Answer e:

triaquatrichlorotitanium(III)

Answer f:

potassium hexacyanoferrate(III)

Answer g:

sodium bipyridinedicyanoaurate(I)

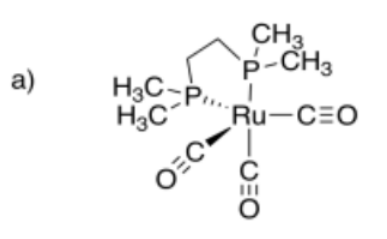
Bipyridine is sometimes called "bipyridyl".

Exercise 11.6.2

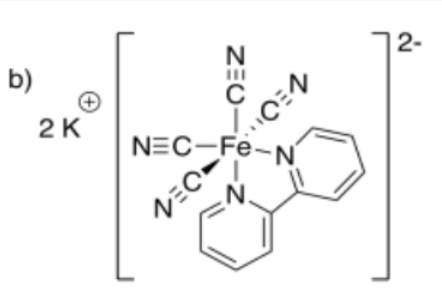
Draw the following structures:

a. dicarbonylbis(1,2-dimethylphosphino)ethaneruthenium (0)
b. potassium bipyridyltetracyanoferrate(II)
c. pentaamminechlorochromium(III) perchlorate
d. tetraacetonitrilecopper(I) tetrafluoroborate
e. sodium ethylenediaminebis(oxalato)cobalt(III)
f. chlorotris(triphenylphosphine)rhodium(I)

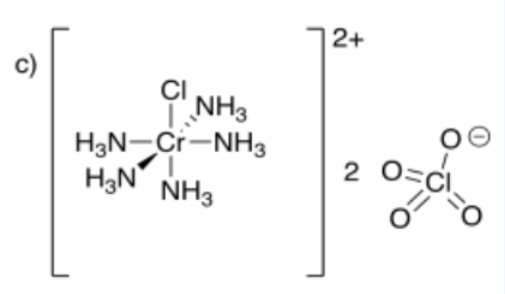
Answer a:



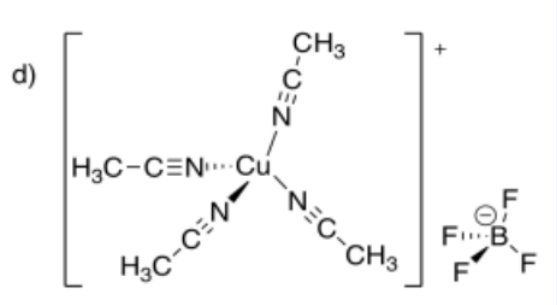
Answer b:



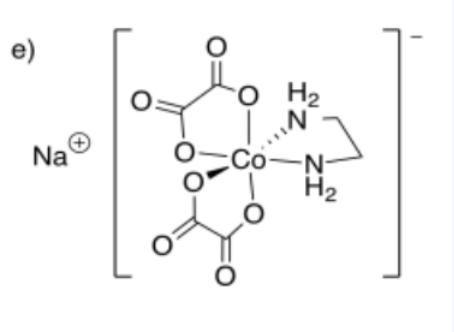
Answer c:



Answer d:



Answer e:



Answer f:

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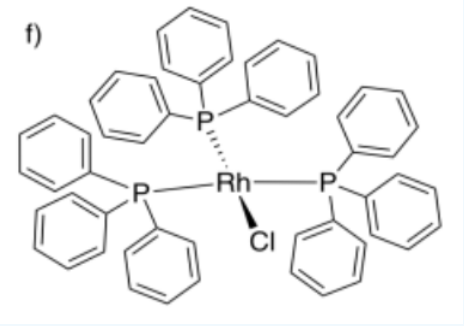

See a more in-depth discussion of coordination complexes in a later course.

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11.7: Geometry in Transition Metal Complexes

If you have studied Lewis structures, then you know that the number of lone pairs and atoms around a specific atoms tells you the geometry at that specific atom. Something very similar is true in coordination complexes, but it's slightly simpler. In transition metal complexes, the lone pairs on the metal do not contribute to the metal complex's overall geometry. All that matters is the number of ligands attached to the metal.

- In coordination complexes, the number of ligands determines the geometry.

As a result, there is a pretty straightforward correlation between coordination number (the number of ligands) and geometry.

# ligands	**geometry**
2	linear
3	trigonal planar
4	tetrahedral; sometimes square planar
5	trigonal bipyramidal; sometimes square pyramidal
6	octahedral

There are two exceptions to that straightforward rule. Coordination number four and coordination number five both have two possible geometries. How do we know which will happen?

For coordination number five, we really can't make an easy prediction. In terms of the angles between ligands, these two possible geometries are really pretty close to each other, so the distinction is subtle. If you call everything that's five-coordinate a trigonal bipyramidal geometry, you will be in the right ballpark.

Coordination number four is a different story; we do have some predictive ability here. However, there are two different factors that come into play, so there are still some subtle cases.

The first factor is sterics or crowding. In a tetrahedron, the four ligands are 109 degrees away from each other. In square planar geometry, the four ligands are only 90 degrees away from each other. Since a tetrahedral geometry is less crowded, sterics makes this geometry more favorable and common.

To form a square planar geometry, there has to be some factor that offsets the steric preference for tetrahedral geometry. Electronic destabilization can occur in tetrahedral geometry. The same goes for square planar geometry; however, destabilization occurs to a lesser extent when there are eight electrons on the metal in this geometry. As a result, square planar geometry is most common when the metal has eight electrons.

See a more in-depth discussion of coordination complexes in a later course.

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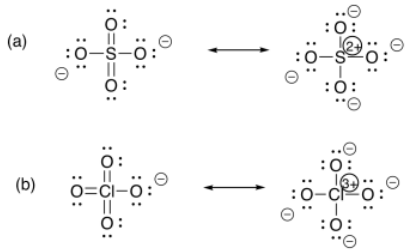
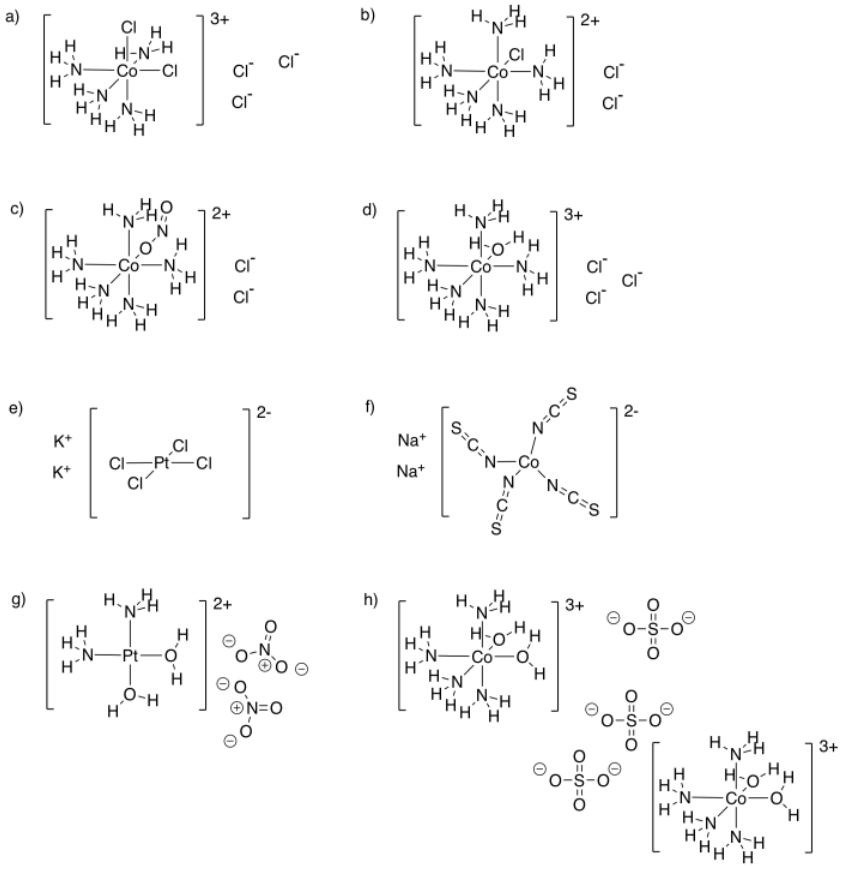
11.8: Solutions for Selected Problems

Exercise 11.1.1:



Exercise 11.1.2:



Exercise 11.2.1:

a. All of these ions have the electronic configuration of the preceding noble gas, Ar. These metals have just started filling the next energy levels; these electrons are relatively high in energy, with relatively few protons attracting them (compared to later elements in the row). The valence electrons are relatively easy to use, although not the core electrons.
b. These metals have relatively high numbers of protons compared to the elements to their left in the same row. They have relatively high electronegativity, so they do not lose many electrons.
c. These metals in the middle display a mixture of behaviors: they are electronegative enough to stabilize relatively low charges, but far enough to the left that they can become fully oxidised to reach a noble gas configuration.

Exercise 11.2.2:

a. H_2O = 0 charge; Fe(II) = 2+ charge; total = 2+
b. H_3N = 0 charge; Cl = 1- charge; Cr(III) = 3+ charge; total = 2+

c. py = 0 charge; SCN = 1- charge; Mn(II) = 2+ charge; total = 0
d. CN = 1- charge; Fe(II) = 2+ charge; total = 4-
e. CN = 1- charge; CO = 0 charge; Co(III) = 3+ charge; total = 2-
f. CN = 1- charge; NH_3 = 0 charge; Fe(II) = 2+ charge; total = 3-

Exercise 11.2.3:

a. Overall charge = 3+; ligands charge = 0; charge on Cr = 3+
b. Overall charge = 3-; ligands charge = 6-; charge on Fe = 3+
c. Overall charge = 2+; ligands charge = 1-; charge on Cr = 3+
d. Overall charge = 4-; ligands charge = 6-; charge on Mn = 2+
e. Overall charge = 1+; ligands charge = 0; charge on Au = 1+
f. Overall charge = 0; ligands charge = 1-; charge on Ag = 1+

Exercise 11.3.1:

a)

Pd valence e^-	10 e^-
charge on complex	0
charge on ligands	0
charge on Pd	0
revised Pd e^-	10 e^-
e^- donated by ligands	4 x 2 = 8 e^-
total	18 e^-

b)

Cr valence e^-	6 e^-
charge on complex	0
charge on ligands	0
charge on Cr	0
revised Cr e^-	6 e^-
e^- donated by ligands	6 x 2 = 12 e^-
total	18 e^-

c)

Cu valence e^-	11 e^-
charge on complex	+1
charge on ligands	0
charge on Cu	+1
revised Cu e^-	10 e^-
e^- donated by ligands	4 x 2 = 8 e^-
total	18 e^-

d)

Fe valence e^-	8 e^-
charge on complex	0
charge on ligands	0
charge on Fe	0
revised Fe e^-	8 e^-
e^- donated by ligands	5 x 2 = 10 e^-
total	18 e^-

e)

Fe valence e^-	8 e^-
charge on complex	-4
charge on ligands	-6
charge on Fe	+2
revised Fe e^-	6 e^-
e^- donated by ligands	6 x 2 = 12 e^-
total	18 e^-

Exercise 11.3.2:

a)

Rh valence e^-	9 e^-
charge on complex	0
charge on ligands	-3
charge on Rh	+3
revised Rh e^-	6 e^-
e^- donated by ligands	5 x 2 = 10 e^-
total	16 e^-

b)

Ni valence e^-	10 e^-
charge on complex	2+
charge on ligands	0
charge on Ni	2+
revised Ni e^-	8 e^-
e^- donated by ligands	4 x 2 = 8 e^-
total	16 e^-

c)

Cu valence e^-	11 e^-
charge on complex	2+
charge on ligands	0
charge on Cu	2+
revised Cu e^-	9 e^-
e^- donated by ligands	4 x 2 = 8 e^-
total	17 e^-

d)

Pt valence e^-	10 e^-
charge on complex	2-
charge on ligands	6-
charge on Pt	4+
revised Pt e^-	6 e^-
e^- donated by ligands	6 x 2 = 12 e^-
total	16 e^-

Exercise 11.4.1:

a. en = bidentate; OH = monodentate
b. dmpe = bidentate; bpy = bidentate; Cl = monodentate
c. acac = bidentate; H_2O = monodentate
d. ox = bidentate; H_20 = monodentate
e. dmpe = bidentate; H = monodentate
f. H = monodentate; PPh3 = monodentate; OAc = bidentate. In this case, the acetate gets the complex to 18 electrons by binding twice.
g. en = bidentate; Cl = monodentate
h. bpy = bidentate; $HOCH_2CH_3$ = monodentate

Exercise 11.4.2:

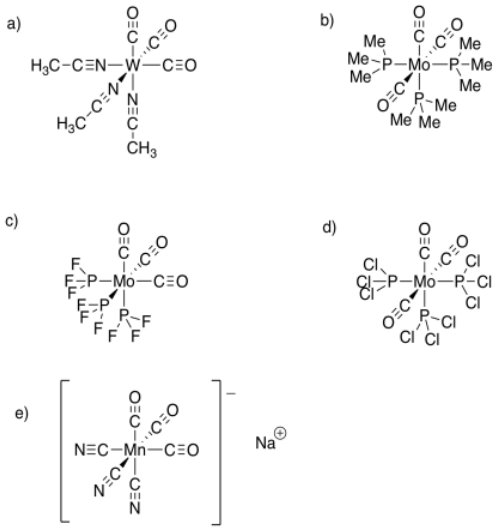
a. Overall charge = 1-; ligands charge = 4-; charge on Cr = 3+
b. Overall charge = 1-; ligands charge = 3-; charge on Mn = 2+
c. Overall charge = 1+; ligands charge = 2-; charge on Cr = 3+
d. Overall charge = 1+; ligands charge = 2-; charge on Co = 3+
e. Overall charge = 3-; ligands charge = 6-; charge on Mn = 3+
f. Overall charge = 3-; ligands charge = 6-; charge on Cr = 3+
g. Overall charge = 1-; ligands charge = 2-; charge on Au = 1+

Exercise 11.4.3:

a. Cr = d^6; Cr^{3+} = d^3; ox = 2 x $4e^-$ = 8 e^-; water = 2 x $2e^-$ = 4 e-; total = 15 e^-
b. Mn = d^7; Mn^{2+} = d^5; acac = 3 x $4e^-$ = 12 e^-; total = 17 e^-
c. Cr = d^6; Cr^{3+} = d^3; en = 2 x $4e^-$ = 8 e^-; Cl = 2 x $2e^-$ = 4 e-; total = 15 e^-
d. Co = d^9; Co^{3+} = d^6; en = 2 x $4e^-$ = 8 e^-; OH = $2e^-$; Cl = 2 e-; total = 15 e^-
e. Mn = d^7; Mn^{3+} = d^4; ox = 3 x $4e^-$ = 12 e^-; total = 16 e^-
f. Cr = d^6; Cr^{3+} = d^3; ox = 3 x $4e^-$ = 12 e^-; total = 15 e^-
g. Au = s^1d^{10}; Au^{1+} = d^{10}; bpy = 2 x $2e^-$ = 4 e^-; cyanide = 2 x $2e^-$ = 4 e-; total = 18 e^-

Exercise 11.5.1:

Exercise 11.5.2:



Exercise 11.6.1:

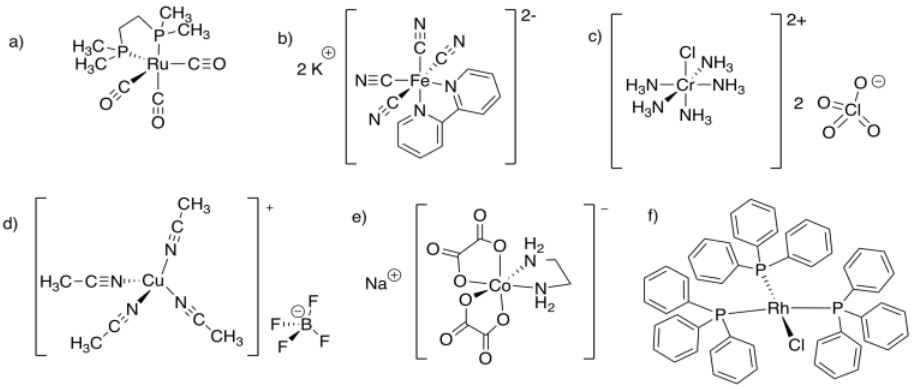
a) potassium diaquabis(oxalato)chromate(III) b) pentaamminebromocobalt(III) nitrate c) dichlorobis(ethylenediamine)chromium(III) hexafluorophosphate

d) bis(bipyridine)chlorohydroxocobalt(III) perchlorate e) triaquatrichlorotitanium(III) f) potassium hexacyanoferrate(III)

g) sodium bipyridinedicyanoaurate(I)

Bipyridine is sometimes called "bipyridyl".

Exercise 11.6.2:



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CHAPTER OVERVIEW

12: Macromolecules and Supramolecular Assemblies

12.1: What are Macromolecules?
12.2: Viscosity
12.3: Glass Transition
12.4: Polymer Architecture
12.5: Morphology and Microphase Separation
12.6: Polymer Synthesis
12.7: Molecular Weight
12.8: Supramolecular Assemblies
12.9: Solutions for Selected Problems

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12.1: What are Macromolecules?

Macromolecules are very large molecules. Their molecular weights can range from the thousands to the millions. They can have very different shapes, although the most common structure involves a long chain. Typically they are constructed from small, repeating units linked together to form this long chain.

These macromolecules are also called "polymers". Polymers are made of many small molecules linked together. These molecules are linked or "enchained" by covalent bonds. The small molecules that come together to form polymers are called "monomers". Sometimes small numbers of monomers can come together to form medium-sized molecules; there might be two repeating units, forming a dimer, or three repeating units, forming a trimer, and so on. These mini-polymers are often called oligomers in general.

The most common, naturally-occurring polymer in the world is cellulose. Cellulose is found in plants, where it plays an important structural role, lending strength to cell walls. We use cellulose fibers in a variety of applications. Cellulose from wood is the major component of paper and cardboard. Cellulose is also obtained from cotton fibers and is used to make fabric, usually for clothing. Paper currency is made of cellulose, too; usually the source is cotton, as well as some amount of linen.

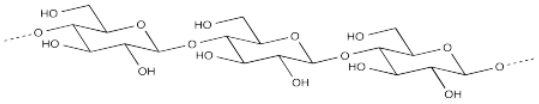


Figure 12.1.1:

Cellulose is made of a long chain of sugar units strung together in a chain. In the picture, the dashed lines indicate that the chain is continuing on. The individual sugar units are all D-glucose. These polyhydroxylated rings are all enchained in exactly the same way, forming a repeating pattern from one end of the molecule to the other.

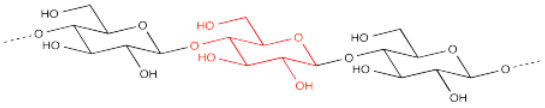


Figure 12.1.2:

It is very common to depict polymers with this repeating unit shown in parentheses. A subscript number after the parentheses indicates how many times this unit is repeated. If the number isn't known, this variable is indicated with the letter n.

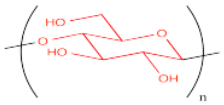


Figure 12.1.3:

The polymer is formed by enchaining a number of glucose monomers together. The particular form of glucose is α-D-glucopyranose. At the ends of the polymer chain, there are two hydroxyl end groups.

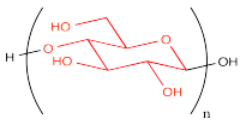


Figure 12.1.4:

When drawn this way, the etching of the polymer hardly differs from how we would depict the monomer.

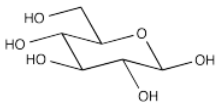


Figure 12.1.5:

The world's second-most common, naturally-occurring polymer is lignin. Like cellulose, lignin is found in the cell walls of plants, where it provides strength and structural support. However, lignin is generally associated with woody plants, and it is much

stronger, less flexible and more durable than cellulose. In fact,because of this durability, the removal of lignin from wood pulp poses a significant obstacle during the paper manufacturing process.

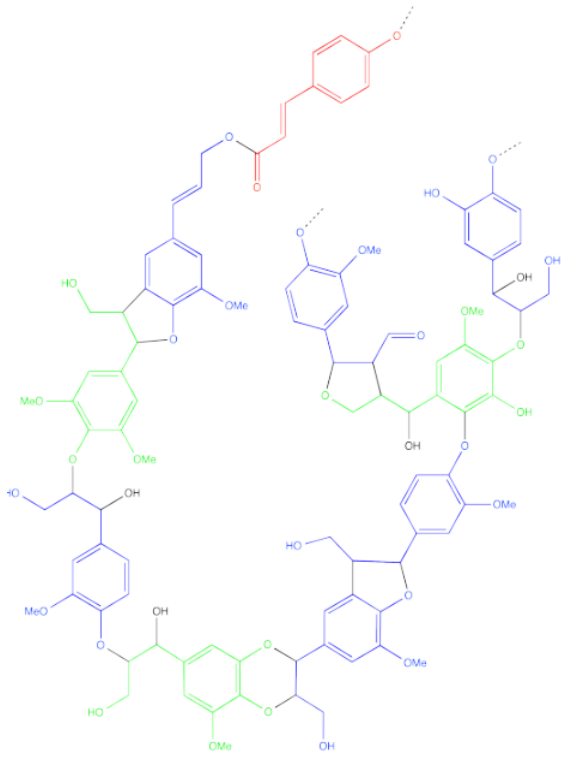


Figure 12.1.6:

Lignin has a more complicated structure than cellulose. It is also formed from monomers, but the structures of those monomers are less regular than in cellulose. Furthermore, they are put together in more complicated ways, rather than all being joined together in an identical fashion.

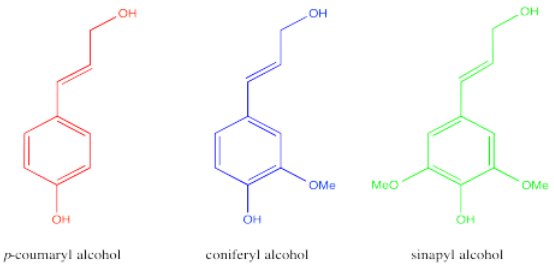


Figure 12.1.7:

Like lignin, proteins are also formed from multiple types of monomers. However, these monomers are all enchained in exactly the same way. Proteins have a perfectly repeating "backbone", although the "pendant" groups attached to this backbone vary from one unit to another.

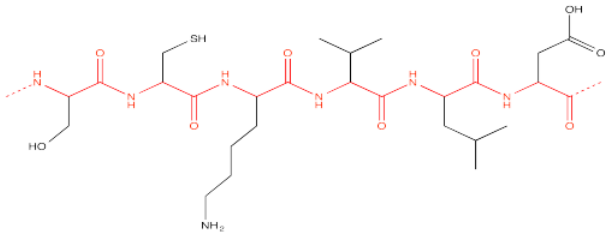


Figure 12.1.8:

In the picture, this backbone is shown in red. We can simplify the drawing by denoting all of the black, variable pendant groups as "R".

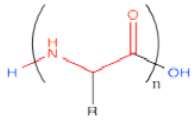


Figure 12.1.9:

As with cellulose, the picture of the polymer, when drawn this way, looks very much like a picture of the monomer. In either case, there is an acid-base equilibrium involving the amine group and carboxylic acid group in the monomer, or what are termed the N-terminus and C-terminus in the polymer.

Figure 12.1.10:

Commercial polymers are used in almost all aspects of daily life. Like the common biopolymers, they are constructed of small monomers assembled into long chains. Many common polymers are familiar to us from the recycling codes on the bottom of bottles and other packaging.

Polymer	Recycling Code	Example Uses
polyethylene terephthalate (PETE)	1	drink bottles
high density polyethylene (HDPE)	2	bottles for food and household cleaners
polyvinyl chloride (PVC)	3	plumbing, siding, window frames, shampoo bottles
low density polyethylene (LDPE)	4	carpet, fabric, squeezable bottles
polypropylene (PP)	5	bottle caps, straws, medicine bottles
polystyrene (PS)	6	CDs, disposable cups & plates
everything else (PLA, PC, ABS, etc.)	7	food packaging, electronics casing, signs

Drawings of these polymers (see problems below) illustrate that most of them have a long "backbone" with "pendant groups" attached periodically along that chain. Mcuh of the properties of commercial properties arise from that long chain structure. The different properties of these structures stem from the differences in those pandant groups, as well as alteartions in the backbone structure from one polymer to another.

Exercise 12.1.1

Revise the following drawings to show the repeating unit in parentheses.

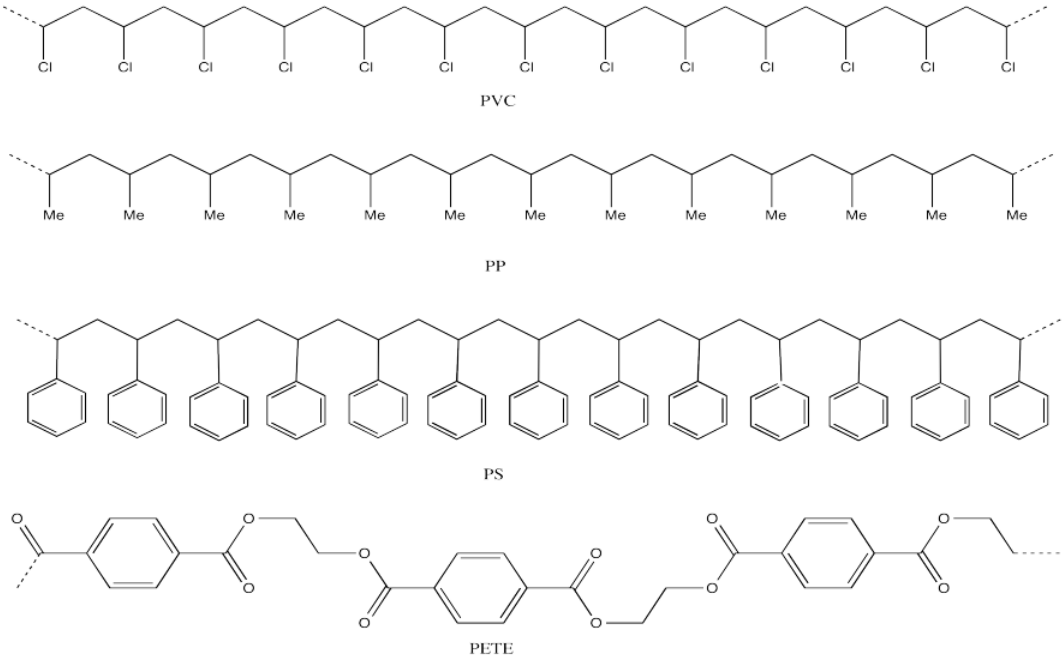
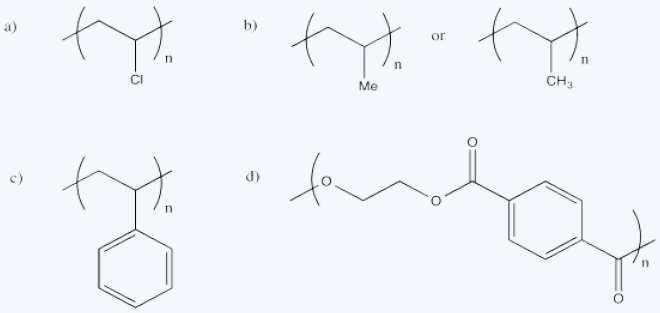


Figure 12.1.11:

Answer



Exercise 12.1.2

Expand the following polymer structures to show at least three repeating units.

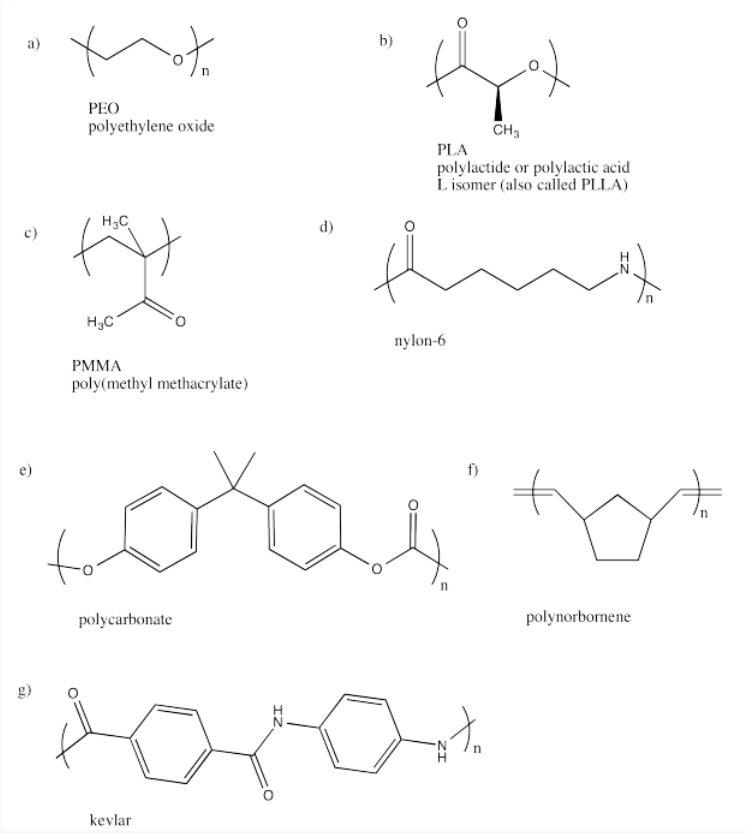


Figure 12.1.12:

Answer

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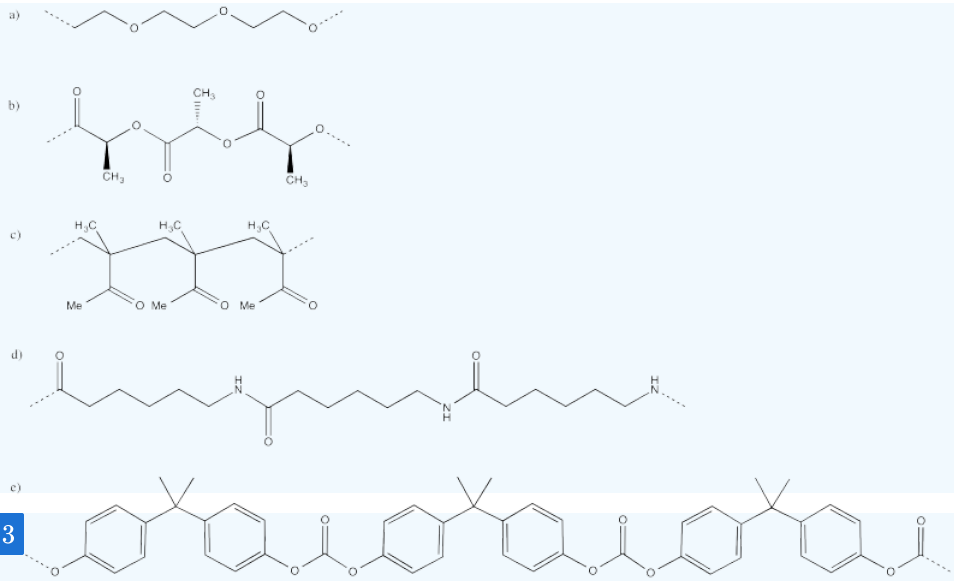

Exercise 12.1.3

Find an application for each of the polymers in the previous question.

Exercise 12.1.4

HDPE and LDPE have very similar structures. Like several other common polymers, such as PVC, PP and PS, they are olefin polymers in which the monomer makes a two-carbon repeating unit that appears in the backbone.

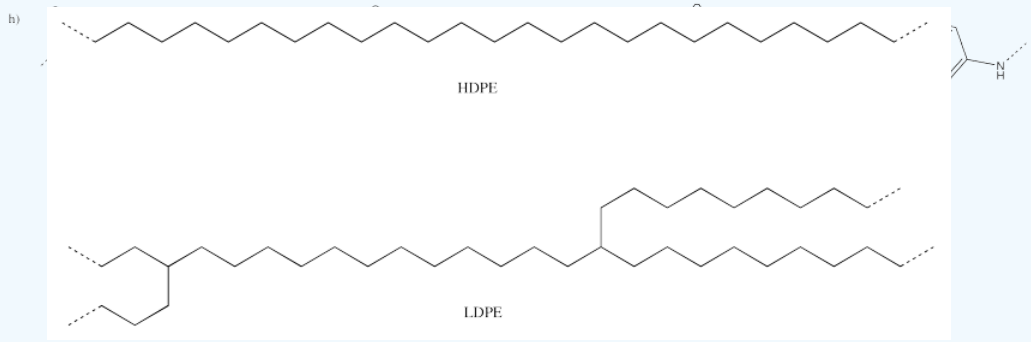

Figure 12.1.13:

a. Looking at the structures of both polymers, provide a structural picture in which the repeating unit is shown in parentheses.
b. LDPE has a slightly lower density than HDPE. Explain why.

Answer a

Answer b

Chains of HDPE are able to pack more tightly together than LDPE, in which the branches prevent tight packing of the backbone. That difference makes LDPE less dense than HDPE.

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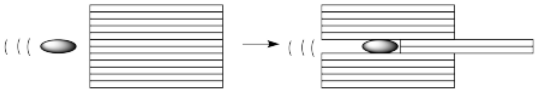
12.2: Viscosity

In their liquid state, polymers seem thicker than regular liquids. They are more like honey than tea. They are difficult to stir, vexing to pour, and impossible to draw up into a pipette. With tea, it's much easier to do all of these things. We describe this property of "thickness" as "viscosity".

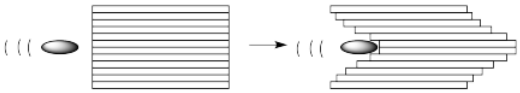
- Those tea-like liquids have low viscosity.
- Those honey-like liquids have high viscosity.

One way to think about motion through liquids is to imagine the liquid divided into layers. Of course it isn't, really. The reason we are thinking of it this way is to imagine what will happen when an object passes through the liquid, parallel to these layers. Maybe we're looking at a bullet being fired from a gun into a test chamber on CSI.

In a low-viscosity liquid, as the bullet moves through the liquid, it pushes a couple of layers out of the way. It does not have much effect on the surounding layers.

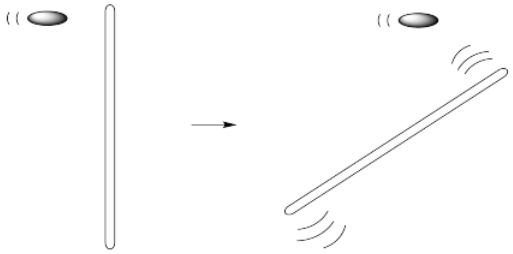


As the bullet moves through a high-viscosity liquid, it still displaces the layers in front of them, but those layers drags the surrounding layers along, too. Those surrounding layers, in turn, drag along the layers next to them.



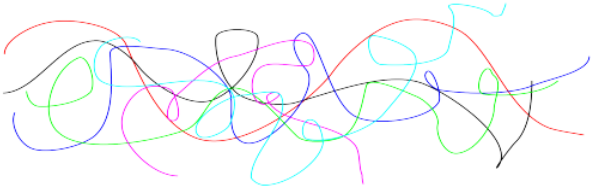
What is the difference between these two scenarios? On the molecular level, it has to do with the interaction between the molecules in one layer and the next. If the molecules are completely isolated, they don't interact with each other at all. The bullet just pushes the molecules ahead of it forward without disturbing the ones on either side.

A macromolecule is different from regular molecules because a force on one part of the molecule will be transmitted very far away. We can imagine a macromolecule spanning many layers, so that when the bullet hits one end of the molecule, the other end of the molecule transmits this force to its neighbors.



Viscosity is not a phenomenon limited to macromolecules. In fact, liquids don't really exhibit the no-viscosity case outlined above, because the molecules do interact with each other. However, different liquids do exhibit different viscosities, and macromolecules are on the high-viscosity end of the spectrum.

In reality, macromolecules are not like long sticks tumbling over each other. They are floppy and can change shape because of bond rotations; they can undergo "conformational change". As a result, macromolecules become "entangled" with each other.



Entanglement is a very important feature in polymer behavior. It influences the viscosity of a polyer in its melted state, which affects how easily the polymer can be molded into different shapes for different applications. Not only that, but it strongly influences the physical strength of a plastic in its regular, room-temperature state. The more entangled the polymer chains, the stronger the material.

- Entanglement increases viscosity of a polymer in the melt phase.
- Entanglement increases the strength of a polymer in the "solid" phase.

Exercise 12.2.1

Using water as a comparison point, explain the relative values of viscosity (η) of the following liquids, recorded near ambient temperature, 25 °C). Water: η =1.00 mPa s. (e.g. this one is a little lower than water because...)

a. ethylene glycol or 1,2-hydroxyethane: η = 16.1 mPa s.
b. olive oil: η = 84 mPa s.
c. methanol: η = 0.58 mPa s.
d. 2-propanone: η = 0.34 mPa s.
e. hexane: η = 0.294 mPa s.

Answer a:

Water can in principle form four hydrogen bonds: it can donate two and accept two. Ethylene glycol has two OH groups, so it can donate two H bonds and accept four. That enhanced clinginess is responsible for its higher viscosity.

Answer b:

Olive oil does not hydrogen bond; it isn't even very polar. However, it is a triglyceride and its fatty acid chains are about 80% oleic acid and linoleic acid, which are both 18-carbon chains. So the average olive oil molecule contains three 18 carbon branches, leading to a modest level of entanglement. Its viscosity is much higher than water's.

Answer c:

Methanol has only one OH bond, so it has a little less hydrogen bonding than water, but not enough of anything else to form other interactions. ts viscosity is a little lower than water's.

Answer d:

2-propanone has no hydrogen bonding at all, although it does have a dipole moment to hold different molecules together. Its viscosity is a little lower than methanol's.

Answer e:

Hexane has no dipole and no hydrogen bonding. It is really too short to become entangled. Molecules only attract each other through weak London dispersion interactions. Its viscosity is a little lower than 2-propanone's.

Exercise 12.2.2

Explain why the viscosity of a melted sample of polyethylene, $(CH_2CH_2)_n$, depends on the molecular weight of the polymers in the sample.

Answer

The greater the number of repeating units, the higher the molecular weight. Also, the greater the number of repeating units, the greater the entanglement and the higher the viscosity.

A curious example of a very high-viscosity liquid is illustrated by the pitch-drop experiment currently being performed at the University of Queensland, Australia. In this experiment, bitumen was poured into a glass funnel and the rate at which the bitumen drips through the funnel has been monitored subsequently. The experiment was set up in 1927. Ten drops have fallen so far.

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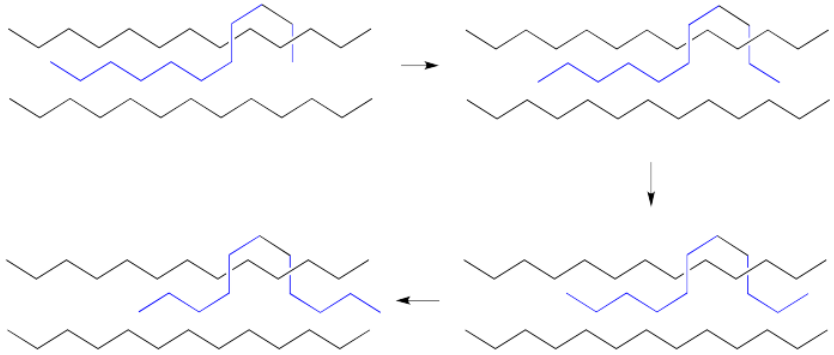
12.3: Glass Transition

Note

comprehension of this section may be aided by an understanding of conformational analysis.

Even though it appears to be a solid, a plastic bottle that you might throw into your recycling bin has some things in common with liquids. We think of the molecules in a solid as mostly static; maybe they rock back and forth a little bit, but they mostly stay put. The long chains in a polymer are constantly in motion, however.

These chains slide over each other like snakes in a process called "reptation" or "creep". This flowing motion of the chains is responsible for the flexibility of many plastics, which can often be bent easily even when they are solids.



When we exert a force upon a polypropylene bottle, it changes shape. Rather than being locked together, the polypropylene chains give way and move past each other. When we let go, the chains may just slide back to their original position, or close to it, returning the bottle to its original shape.

The chains slide back because they were originally in a stable conformation. Rapidly deforming the plastic twists the chains into less favorable positions. Left alone, they twist back into positions that are energetically more favorable.

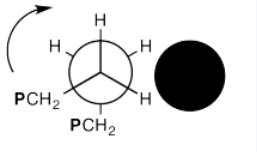
Of course, it is always possible that the plastic is deformed a little too far and does not bounce back to its original shape. In that case, the chains have become stretched out in such a way that they have become stuck. They may have become tangled in new ways. New obstacles have appeared that make it difficult for them to slide back again.

Sometimes, a force is exerted on a plastic material over a long period of time, causing the chains to slowly slide away from their original positions. The chains adopt a new equilibrium distribution. When the force is removed, the plastic has adopted a new shape. A formerly straight bar might become bowed under a weight, for example.

Exercise 12.3.1

In the drawing below, we are looking down a C-C bond in a polymer chain (left). We can see hydrogens attached to the carbon in front and the carbon behind, although the carbons are not labelled. We can see the where the polymer chain is attached, labelled "CH_2P". A cross-section of the neighbouring chain is also shown (in black).

Show, with the help of drawings, how a 360° rotation about that bond will cause the polymer chain on the left to creep over the one on the right.

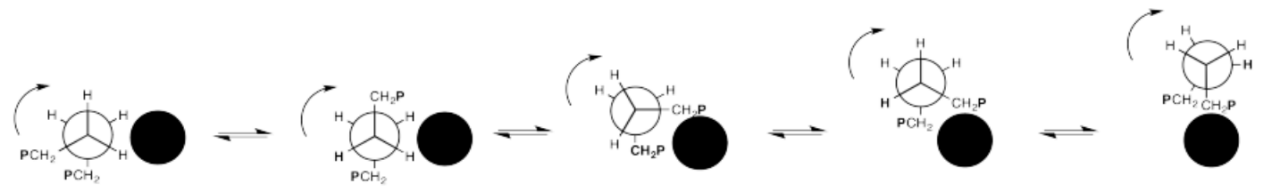


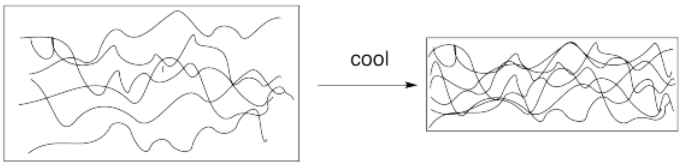
One of the most commonly-used diagnostic tests for a polymer is the measurement of the glass transition temperature (T_g). The glass transition temperature is related to the ease of chain flow in the material.

The glass transition represents a phase change. As a polymeric material is cooled, it changes from a more flexible, rubbery state to a more rigid, glassy state. This transition occurs because of the change in volume with temperature. Generally, solids shrink as they are cooled. At some point, the volume of a polymer decreases to the point at which the chains can no longer move past each other; there just isn't enough room.

Answer

You can think about a length of chain flopping over a neighbouring strand like a grappling hook, then pulling itself along as the bond continues to rotate, vaulting over the other chain.





The glass transition temperatures of a number of common polymers are listed below. These data indicate whether a given polymer will exist in a rubbery state or a glassy state at a particular temperature.

Name	Abbreviation	Approx. T_g, °C
low-density polyethylene	LDPE	-120
polyethylene oxide	PEO	-50
polypropylene	PP	-10
nylon-6	-	45
polylactide	PLA	65 (L isomer)
poly(ethylene terephthalate)	PETE	70
polyvinylchloride	PVC or V	90
polystyrene	PS or S	100
poly(methyl methacrylate)	PMMA	110
polycarbonate	PC	145
polynorbonene	-	215
kevlar	-	240

These values are only approximate. The glass transition temperature actually depends on a number of factors, including the average molecular weight of the polymer and how the data is measured.

Exercise 12.3.2

Explain why glass transition temperature would depend on molecular weight.

Exercise 12.3.3

Glass transition temperature is influenced by several factors, including the following ones.

a. sterics (crowdedness, or physical interference between groups as they move through space)
b. polarity
c. backbone rigidity (ability for bond rotation along backbone)

Answer a:

The greater the number of repeating units, the greater the entanglement. Entanglement acts as an impediment of the movement of chains, increasing the temperature at which chain motion becomes restricted (in other words, increasing the minimum volume needed to get the chains moving again). For example, polypropylene has a higher T_g than polyethylene, and that of polystyrene is even higher (although additional factors influencethe T_g of PS).

Answer b:

Increased polarity increases the attraction between chains and can even lead to formation of physical crosslinks between chains. This increased interaction hinders chains from moving freely and raises the glass transition temperature. For example, polylactide, poly(vinyl chloride) and poly(methyl methacrylate) all have much higher values of T_g than polypropylene.

Answer c:

If the backbone is rigid, reptation is hindered because the chain can't adopt different conformations. Chain flow is restricted more easily and the T_g is higher. Kevlar and polynorbornene both have stiff backbones because of the aromatics and aliphatic rings, respectively, that form part of the backbone. Both polymers have much higher values of T_g than polystyrene, in which the aromatics hang from a flexible chain.

In each case, explain how the factor would influence the glass transition temperature, and choose some examples from the table to support your claim.

Exercise 12.3.4

Polymers also undergo other phase transitions. For example, the melting point of polystyrene is around 240 °C. Explain, with the help of drawings, the difference between the glass transition temperature and the melting temperature.

Exercise 12.3.5

Indicate whether the following materials would be found in a rubbery state or a glassy state at a comfortable room temperature, about 25°C.

a) LDPE b) PS c) PVC d) PP

Answer a:

rubbery

Answer b:

glassy

Answer c:

glassy

Answer d:

rubbery

Exercise 12.3.6

Indicate whether the following materials would be found in a rubbery state or a glassy state at the boiling point of water, about 100°C.

a) PEO b) PETE c) PMMA d) PC

Exercise 12.3.7

Why do you think PVC is used in household plumbing, rather than other materials such as PLA or PEO?

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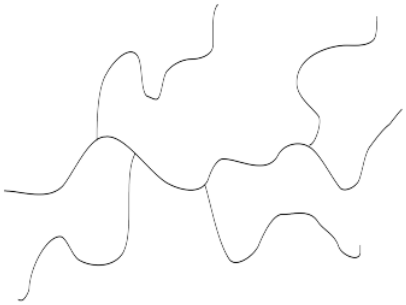
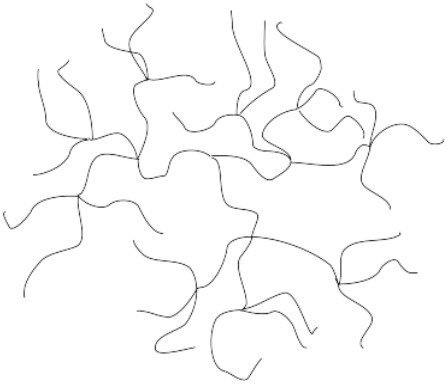
12.4: Polymer Architecture

The basic structure of a polymer is a chain. The chain is formed by the backbone of the polymer. It may be decorated with pendant groups, such as methyls in polypropylene, chlorines in polyvinyl chloride or phenyls in polystyrene, but the basic structure is like a long string.

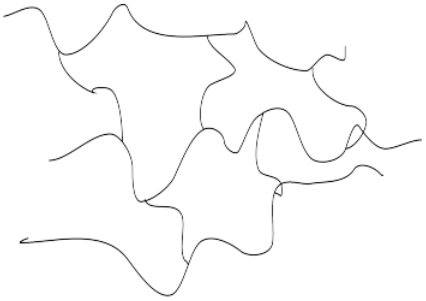
Sometimes, the architecture of a polymer can be more complex than that. For example, low-density polyethylene has branches coming off the main chain. Consequently, it is described as a branched polymer.



In some cases, branching is so extensive that the polymer does not resemble a chain at all. Some of these highly-branched polymers are called dendrimers. Dendrimers are tree-like structures that branch out in all directions from a central point. Viewed from a distance, a dendrimer would have an overall shape that is more like a fuzzy ball than like a coiled chain.



If the branches on one branched chain connect directly to other chains, then the polymer is said to be crosslinked. Crosslinked polymers can have extra strength and rigidity because they are less flexible than polymers in which the chains are able to move independently. However, just the right amount of crosslinking can make a polymer more elastic, making it bounce back to its original form after it is flexed.



Crosslinking can actually be of two different types: "chemical" or "physical". Chemical crosslinks are permanent covalent bonds between the chains. Physical crosslinks are more temporary; they are formed by strong intermolecular attractions, such as hydrogen bonds, between chains.

Exercise 12.4.1

Choose an architecture that would work well for each of the following applications, and explain your choice.

a. a thread for weaving into fabric
b. a rubber band
c. a "drug delivery device" that would slowly release trapped pharmaceuticals into the body
d. a plastic film to protect a surface

Answer a:

A regular chain structure could be wound into a thread easily. There would be enough entanglement to held the threed together.

Answer b:

A cross-linked structure would help a rubber band snap back to its original shape. However, too much cross-linking would make it too difficult to stretch the rubber band.

Answer c:

A dendrimer has lots of nooks and crannies that might be used to sponge up pharmaceuticals and slowly release them later.

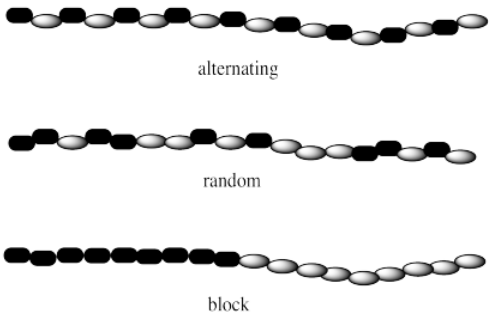
Answer d:

A branched or cross-linked structure might form a good two-dimensional network to provide a protective coating.

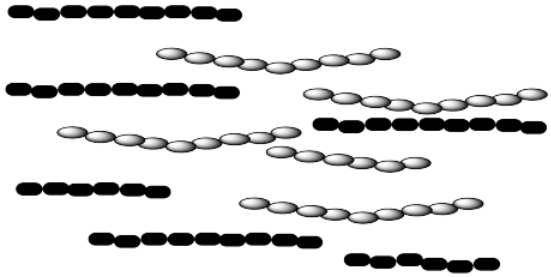
Copolymers

The structure of polymers can vary in how their chains are arranged. Additional structural complexity arises if the polymer is a copolymer. Regular polymers are made from one kind of monomer. Copolymers are formed from two different monomers.

If there are two different monomers, they may be arranged in different ways along the chain. Maybe the two monomers simply alternate, one after the other: that's called an alternating copolymer. Maybe they are distributed at random: that's a random or statistical copolymer. Maybe they are clustered in two separate groups: that's called a block copolymer.

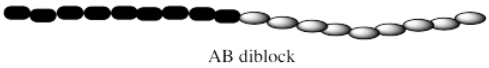


These copolymers are different from polymer blends. Polymer blends are just mixtures of two different kinds of polymers. Both polymer blends and copolymers are important. Either one might allow different properties of each polymer, such as strength and flexibility, to be brought together in one material.

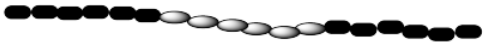


polymer blend

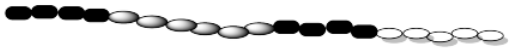
There are different kinds of block copolymers, depending on how the blocks of each monomer are arranged in the chain. The simplest kind of chain would contain one long block of the first monomer followed by one long block of the other. That's called a diblock (or AB diblock) copolymer . If two blocks of the same polymer are found on the ends, with a different one in the middle, that would be called an ABA triblock copolymer. If there were three different blocks from three different monomers, we would have an ABC triblock copolymer instead. There are lots of possible variations.



AB diblock

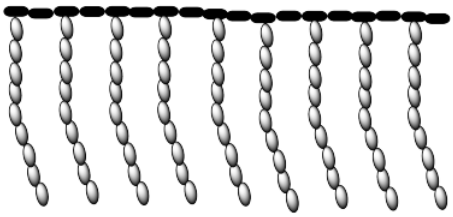


ABA triblock



ABA tetrablock

Sometimes, the blocks in a block copolymer are not found along the chain. For example, in some cases, the entire backbone may be composed of one monomer, with pendant chains attached to the backbone. A material with this type of architecture is called a graft copolymer, or sometimes a comb or a brush copolymer.



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12.5: Morphology and Microphase Separation

Morphology is the study of shapes. In the context of polymeric materials, morphology describes the distribution of phases within the material.

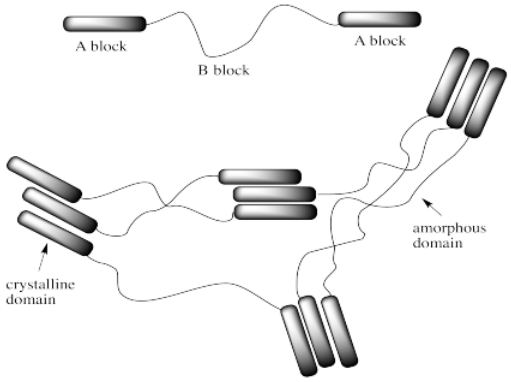
In general, polymers tend to exist as amorphous solids. Unlike metals or ionic solids, their components are not found in ordered layers or rows; those long chains don't line up nicely, but they get all tangled up instead. Whether in the glassy state or the rubbery state, the polymer chains aren't organized.

Oligomers -- smaller molecules made of just a few monomers -- crystallize more easily because their chains are too short to really get tangled up. If they are cooled down from the liquid phase, they can get arranged into orderly rows and form crystals.

Well, in reality, short sections of polymer chains can act like oligomers. If a polymer is cooled down from the melt, several parallel lengths of chain might actually settle into a crystalline pattern together. However, at some point one or more of the chains will get twisted up, bringing this ordered section to a halt as it trails off into an amorphous mess.

Frequently, polymers contain small "microcrystalline domains" surrounded by "amorphous domains." Most of the chains are tangled up, but little sections of them are crystalline. This type of phenomenon is called "microphase separation"; the material is not actually in the same phase all the way through.

Microphase separation is particularly important in copolymers. Sometimes, two different blocks don't completely mix together in the solid state, especially when doing so would disrupt strong interactions between the chains within one of the blocks. Maybe one of the blocks is actually more crystalline than the other. In that case, the different blocks might microphase separate into crystalline and amorphous domains.



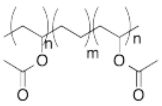
That kind of behavior can be very useful. The amorphous domains are very flexible. Those chains can be stretched and twisted without much problem. The crystalline domains, on the other hand, are very strong. They are like anchor points within the structure. Together, these two structures combine to make something that can be stretched, but only so far before it will snap back. They could make an elastic material, or an elastomer.

In many cases, the phase separation isn't between a completely crystalline and amorphous domains, but between a glassy domain and a rubbery domain. In that case, it's the same concept: parts of the material flow easily, whereas other parts do not. The latter segments hold the material firmly in place and help snap it back to its original shape after stretching.

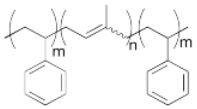
Exercise 12.5.1

The following ABA triblock copolymers can be used to make chewing gum. In each case, identify the part that would form the more amorphous microphase and the part that would form the more crystalline microphase, and explain your reasoning.

Poly(ethylene-co-vinyl acetate)



Poly(isoprene-co-styrene)



Answer

The polar vinyl acetate block of the first polymer contains carbonyl groups that would attract each other by dipole-dipole interactions. It is easy to imagine these segments forming physical crosslinks. The hydrocarbon chain in the middle block would prvide flexibility.

Although nonpolar, the benzene groups in styrene are flat and can stack together with relatively strong London dispersion forces. The higher Tg of polystyrene would make these blocks much stiffer than the more flexible polyisoprene block in the middle.

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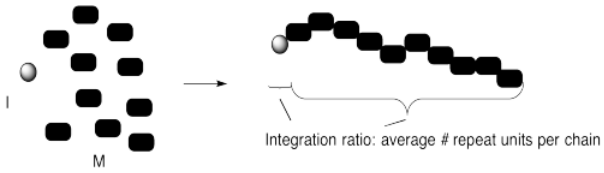
12.6: Polymer Synthesis

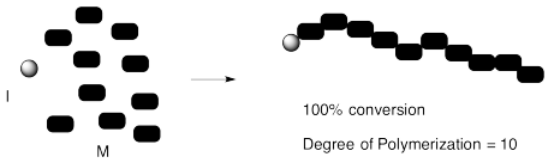
Macromolecules are very large molecules. Their molecular weights can range from the thousands to the millions. Typically they are constructed from small, repeating units linked together in some way.

How many repeating units are there in a chain? Because of the way synthetic polymers are made, we may be able to predict how long the chain is by the conditions we choose when we make it. Polymers are frequently made through the action of an initiator, which gets the monomer units to start attaching to each other. Without the initiator, the monomers just sit there. (There are exceptions; nylon 6-6 and other condensation polymers are sometimes made just by mixing two different kinds of monomers together, without an initiator.)

If each initiator in the process starts its own chain growing, then the ratio of monomers to intiators that we start with may tell us the chain length we will end up with.

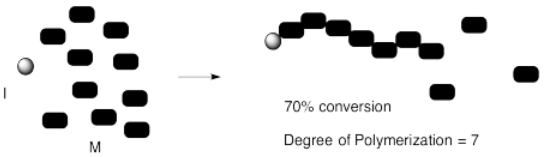


We can confirm that outcome experimentally by measuring the ratio of monomer to initiator in the polymer that is produced. That evidence is sometimes obtained by integration of a ^{1}H NMR spectrum. The "degree of polymerization" is the measured number of repeating units in the chain. In the case below, we started with 10 monomers per initiator and ended up with DP = 10.

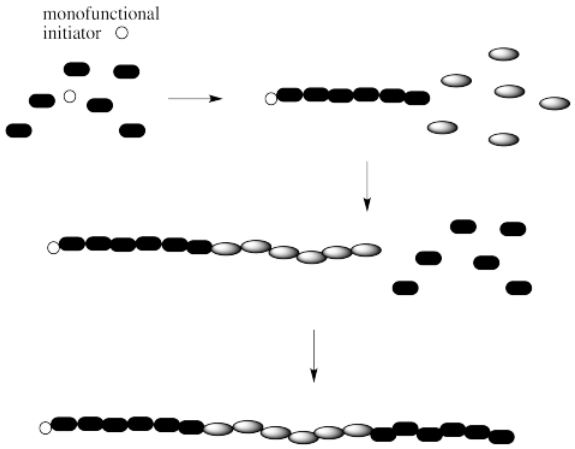


Things don't always work out that way. Maybe for some reason the chain stops growing unexpectedly (an event that is often called "chain death"). Maybe we stopped the reaction a little too early, before all the monomers had time to react. Maybe there is a reverse reaction, in which a polymer can break down into monomers again, and we end up at some balance between polymer formation and polymer breakdown (an "equilibrium").

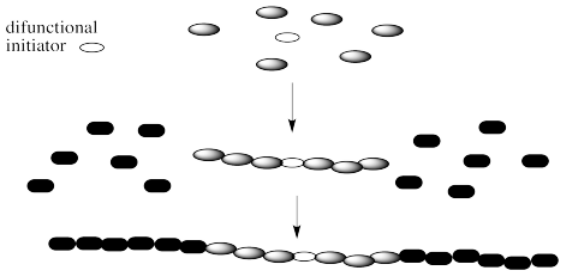
In that case, the degree of polymerization might not reflect the original monomer to initiator ratio. It might also depend upon the percent conversion -- that is, how much of the original monomers were converted into polymer. If we start with 10 monomers per initiator, but only 70% of the monomers are enchained in the reaction, then the degree of polymerization will be 7, not 10.



If we are dealing with a block copolymer, we may be interested in more than just the total number of monomers in the chain. We may instead be interested in the ratio of one monomer to the other (for example, A:B:A = 6:6:6 in the example below).



Note that there are a couple of different ways of making block copolymers. We can simply start growing the chain from one end, as shown above. Alternatively, we might start with a difunctional initiator. That's an initiator that starts gorwing the chain in two directions at once. The result is called a "telechelic polymer". This method of growth can be more efficient in some cases.



Exercise 12.6.1

Explain why a telechelic polymer might grow more quickly than a regular one.

Answer

The telechelic polymer has two growing ends per chain, so it grows twice as fast as a normal chain.

Exercise 12.6.2

If a polymerization is performed using a 500:1 ratio of initiators to monomers and the reaction reaches 85% conversion, what is the degree of polymerization?

Answer

If this chain reached 100% conversion, then the degree of polymerization would be 500. At 85% conversion, DP = 425.

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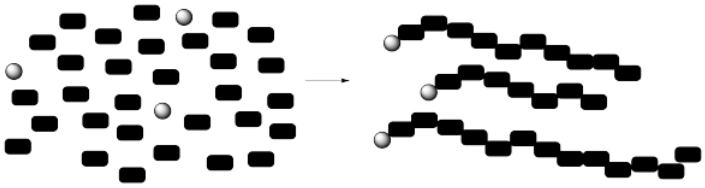
12.7: Molecular Weight

Macromolecules are very large molecules. Their molecular weights can range from the thousands to the millions. Typically they are constructed from small, repeating units linked together in some way.

Describing the molecular weight of a polymer is not as straightforward as it is in a small molecule. The fact that each macromolecule is built by joining together a large number of monomers complicates things. Exactly how many monomers are there in one polymer molecule? Twenty? Twenty-five? Thirty? Each of those possibilities would have a very different molecular weight.



This is generally the case in macromolecules, whether we are dealing with commercial or biological samples. Polymers are grown, often through the action of some "initiator" that picks up a monomer and starts knitting together a chain. What if one of the initiators starts a little later than the others? What if one of the chains grows a little faster than the others? What if something goes wrong and one chain stops growing?

As a result of a number of factors, polymers generally display a distribution of molecular weights representing a distribution of chain lengths. There is no exact molecular weight. Instead, an average must be determined.

Exercise 12.7.1

Explain the general relationship between degree of polymerization and molecular weight of the chain.

Answer

As the number of repeat units increases, the molecular weight increases.

Exercise 12.7.2

Calculate the molecular weight of each of the following polymer chains. For simplicity, assume the end groups are just hydrogen atoms in each case.

a. polystyrene (PS) with DP = 1,000
b. polylactide (PLA) with DP = 200
c. poly(ethylene oxide) (PEO) with DP = 50
d. polypropylene (PP) with DP = 100,000

Answer a:

The molecular weight is the sum of the weights of all the repeat units plus the weight of the end groups.

MW = 1,000 units x 104.15 Da/unit + 2 Da = 104,152 Da

Answer b:

MW = 200 units x 72.06 Da/unit + 2 Da = 14,412 Da (based on 200 simple repeating units, but this is a complicated case. In common practice, PLA is made from a dimeric monomer, with each monomer forming two repeat units in the chain, so a degree of polymerization of 200 really corresponds to 400 repeat units in the chain, which would have twice the molecular weight.)

Answer c:

MW = 50 units x 44.05 Da/unit + 2 Da = 2,202 Da

Answer d:

MW = 100,000 units x 42.08 Da/unit + 2 Da = 4,208,002 Da

Note that, in this case, the end groups make no appreciable difference in the weight because they are so small.

There are many different ways of estimating the average molecular weight of a polymer. These methods fall into two categories, giving rise to two different estimates of the average molecular weight.

In some techniques, the total weight of a sample is measured followed by a determination of the number of molecules present. The molecular weight is just the total weight divided by the number of molecules. This quantity is called the number average molecular weight, or M_n

Exercise 12.7.3

a. A sample weighing 3.205 g is determined to contain 5.50 x 10^{-4} moles. What is M_n?
b. A sample weighing 1.315 g is determined to contain 1.25 x 10^{-3} moles. What is M_n?
c. A sample weighing 0.225 g is determined to contain 3.20 x 10^{-7} moles. What is M_n?

Answer a:

MW = weight (in g) / moles

5827 Da

Answer b:

1052 Da

Answer c:

703,000 Da or 703 kDa

A classic example of this type of measurement is a freezing point depression. A pure liquid freezes at a specific temperature, but impurities in the liquid tend to interfere with crystal formation, lowering the freezing point. The change in freezing point depends on the number of molecules present in the impurity. In this approach, a measured amount of polymer would be dissolved in a specific quantity of toluene and the freezing point would be measured very carefully. The polymer in this context is acting as an impurity. The change in freezing point would indicate the number of molecules (or moles) of the impurity. The average molecular weight could then be calculated.

Other techniques rely on measurements that depend on the relative size of the macromolecules, rather than the number of them. The quantity determined this way is called the weight average molecular weight, or M_w.

A classic example of this type of measurement is a light-scatterring experiment. A beam of laser light is shone into a solution of polymer. Some of the light is scattered when it encounters polymer molecules, and the interference patterns in the scattered light can be decoded to give information about the particle size.

Typically, techniques that depend on particle size are more heavily influenced by the larger particles, and so $M_w > M_n$. The closer these numbers are to each other, the more uniform the partciles must be. The more different they are, the broader the distribution present. Consequently, the ratio M_w/M_n, historically called the polydispersity index (PDI), is an important indicator of how uniform the molecules are in size. "Polydisperse" as an adjective means that there is a wide distribution of sizes, as opposed to "monodisperse", meaning everything is the same size.

IUPAC has recently decided that the term "polydispersity index" should be abandoned in favor of the more concise term, dispersity (Đ).

Exercise 12.7.4

Determine the polydispersity in each of the following cases.

a. M_n = 2,105; M_w = 2,408
b. M_n = 102,365; M_w = 124,710
c. M_n = 56,300; M_w = 87,530
d. M_n = 8,105; M_w = 14,220
e. M_n = 1,170,000; M_w = 1,899,000

Answer a:

Đ = M_w / M_n

1.14

Answer b:

1.22

Answer c:

1.56

Answer d:

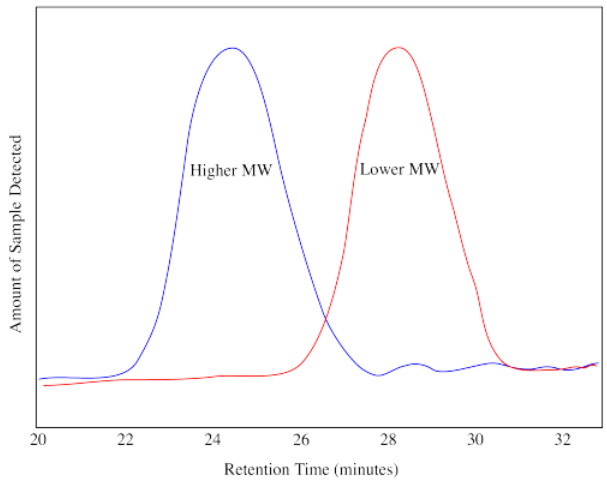
1.76

Answer e:

1.62

These days, two of the most common techniques for estimating molecular weight are ^{1}H NMR spectroscopy and size exclusion chromatography (although other techniques such as light scattering are still used). We'll take a closer look at NMR analysis in a minute. First we'll start with a simplified view of size exclusion chromatography (SEC) or, as it is sometimes called, gel permeation chromatography (GPC).

In SEC, a sample is sent through a column containing a porous gel. Generally, smaller molecules that wander into the pores within the gel take longer to get through the column. Larger molecules that can't fit into the pores emerge sooner. The effluent from the column is monitored by a technique such as UV-Vis spectroscopy or refractive index. The response from this detector changes over time, with a stronger response indicating more molecules are being detected as they come out of the column. The output from the instrument shows a distribution, not unlike a bell curve, indicating the distribution of molecular weights by comparison with a standard sample.



The drawing above shows you what a chromatogram or trace would look like for two different samples, one of higher molecular weight and one of lower molecular weight. The retention time in a GPC trace does not directly indicate the molecular weight of the polymer. A calibration has to be run. In a calibration, polymers of known molecular weight are run through the GPC and their chromatograms are obtained. The GPC trace of an unknown polymer, run on the same instrument under the same conditions, is then compared to the standard ones. Software is used to estimate the molecular weight and the polydispersity.

Exercise 12.7.5

Suppose the following drawing shows calibration traces for the chromatogram shown above (D stands for Daltons, another name for the units "g/mol"). Estimate the molecular weight of

a. the low molecular weight unknown.

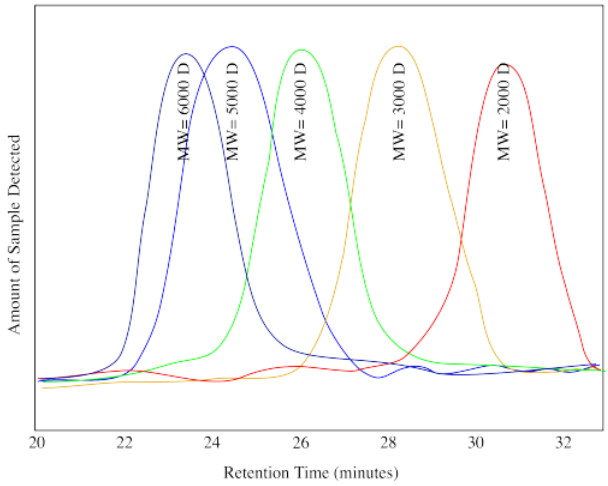
b. the high molecular weight unknown.

Answer a:

3,000 D

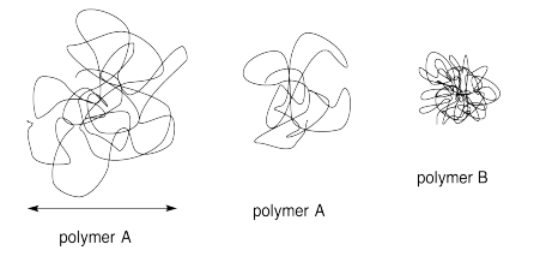
Answer b:

5,000 D



Exercise 12.7.6

SEC, which is based on the size of a coiled polymer molecule, can sometimes give misleading estimates of the molecular weight. Explain why with the help of the following diagram.



Answer

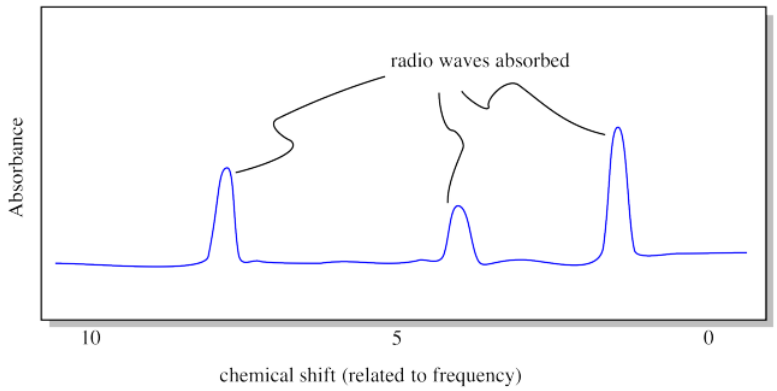
The longer the chain in polymer A, the bigger the sphere it coils into. There isn't much problem comparing samples of polymer A to each other, provided we have some way of calibrating sphere size to chain length.

However, polymer B appears to be more tightly coiled than A. A relatively small sphere could pack a lot more chain. We would have to be cautious about comparing the sphere size of B to that of A and drawing any conclusions about chain length or molecular weight.

NMR spectroscopy is a method that uses magnetic fields and radio waves to detect different kinds of atoms in a sample. ^{1}H NMR detects the hydrogen atoms in a sample. It is conceptually very similar to MRI used in hospitals and clinics. In the experiment, the sample is placed in a very strong magnetic field (somewhere on the order of a hundred thousand times greater than the earth's magnetic field on the planet's surface). Radio waves are sent through the sample. Most of them pass straight through, but some of them are absorbed by the hydrogen atoms.

The result of the NMR experiment is an NMR spectrum. A spectrum is really just a graph. On the x axis, it shows all the possible frequencies of the radio waves that were sent through the sample. On the y axis, it shows the absorption level: in other words, how much of the radio waves at each frequency that were absorbed by the sample. Did a particular frequency of radio waves just pass

right through the sample? The absorbance at that frequency would be zero. If a particular frequency is absorbed, there will be a "peak" on the graph (a high point) at that frequency.

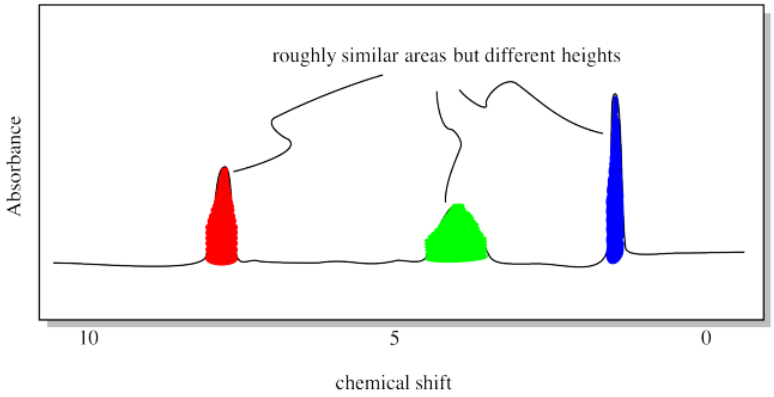


Each peak in the NMR spectrum corresponds to a hydrogen in a different environment. Maybe the hydrogen is attached to an oxygen atom, or a carbon atom, and so on. In the drawing shown above, the spectrum indicates three different locations for hydrogen atoms in the molecule. Note that "frequency" in NMR is called "chemical shift", for historical reasons. The units of chemical shift are parts per million, or ppm, for reasons that have to do with the mechanics of the experiment.

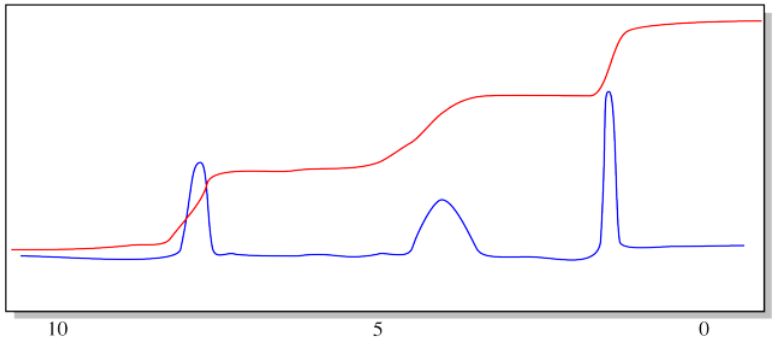
But how does that help us with molecular weight? We're getting there.

^{1}H NMR spectroscopy also allows us to measure how many hydrogens we have of each type, at least in a relative sense. It could tell us we have equal amounts of hydrogens in these three locations, or maybe twice as many in one location as there are in the other two. The relationship is pretty simple: the more hydrogens there are in a particular location, the bigger the peak associated with them. That's because if one hydrogen atom absorbs one radio frequency photon, two hydrogen atoms would absorb two radio frequency photons. That's twice as much. The peak should be twice as big for two hydrogens as it would be for one hydrogen.

What do we mean by "bigger", though? It turns out that the *height* of the peak does not really tell us anything. What matters is the *area* of the peak. That's because even for two seemingly identical protons in a sample, there are lots of factors that mess with the radio frequency absorbed, ever so slightly. So, if a specific hydrogen in one molecule absorbs a radio photon at 1.7005 ppm, a hydrogen in the exact same position in a second molecule might absorb at 1.7007 ppm. There are lots of complicated reasons for that. The result, however, is that NMR peaks get smeared out a little bit, so that it isn't the height that matters, but the area, which is the sum of a whole lot of very similar radio frequencies absorbed by those identical hydrogens in different molecules.

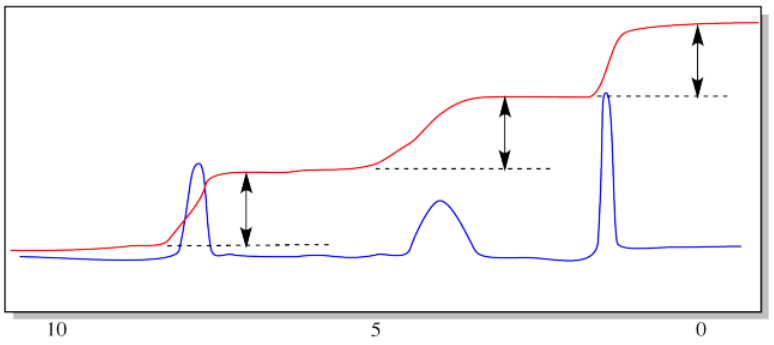


So we need to measure the areas of those peaks. Fortunately, NMR spectrometers are equipped with software that can do this. Classically, the instrument would print a red line across the spectrum. The red line would hop up every time it passed over a peak. The amount of each hop corresponded to the relative area of the peak.



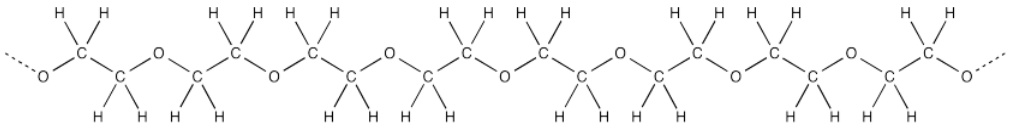
Notice that we don't even bother to label the y axis anymore. It does not tell us anything, anyway.

The drawing below emphasizes what we are measuring with the integral line. It is the vertical distance that the integral line hops up as it passes a peak. That distance is called the "integral". In this case, the integrals of the three peaks are all about equal.

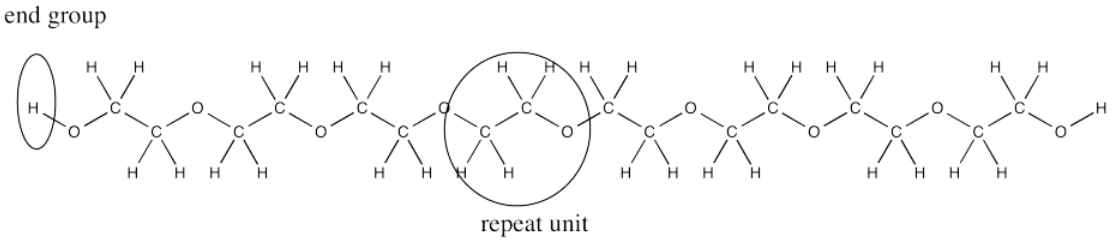


Now it's time to see how ^{1}H NMR spectroscopy can reveal molecular weight through a measurement called "end group analysis".

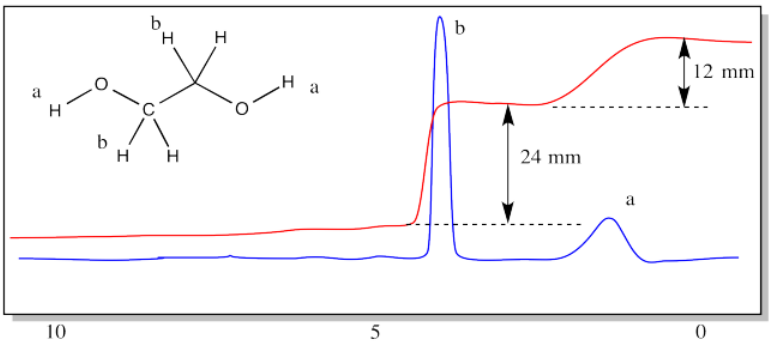
Consider the polymer poly(ethylene glycol), or PEG. PEG is commonly used in medicine. By itself it can be used as a laxative, depending on its molecular weight. It can also be mixed with pharmaceuticals; it helps control side effects and spreads the medicinal effect over a longer time, so you don't have to take the medicine as often.



Frequently, there is an OH group at both ends of the chain. In the middle, the polymer is made of CH_2CH_2O repeating units.

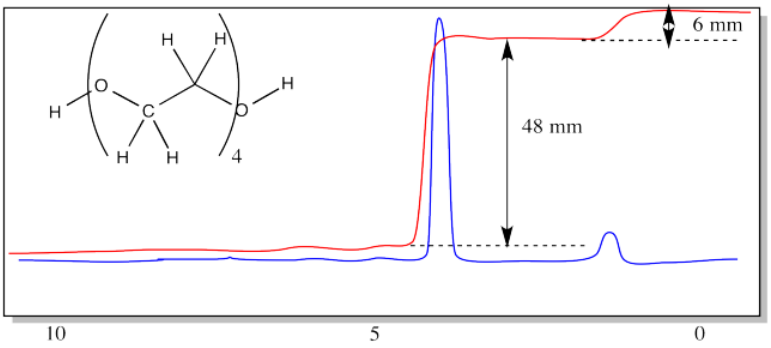


PEG can be thought of as a polymer of ethylene glycol (or ethane-1,2-diol). The structure of ethylene glycol is provided below. The structure of ethylene glycol shows two different kinds of hydrogens. There are the hydrogens along the chain, attached to carbons, and there are hydrogens at the ends of the chain, attached to oxygens. The ^{1}H NMR spectrum of ethylene would show a different peak for each of those types of hydrogens. There would be two peaks.



The spectrum also shows an integration line. We have measured the integral for each peak. It looks like a 2:1 ratio, because the vertical distance in one case is 24 mm and in the other case it is only 12 mm. Even if you don't know anything else about NMR spectroscopy, you can see that the peak around 4 ppm must correspond to the hydrogens on the carbons, whereas the peak around 1 ppm must correspond to the hydrogens on the oxygens. That's because there are four hydrogens on the carbons and only two on the oxygens. The ratio is 2:1.

The structure of PEG is pretty similar to that of ethylene glycol, except that it has a bunch of units strung in a row. The NMR spectrum of PEG is pretty similar to that of ethylene glycol, too.



In end group analysis, we compare the integral of a hydrogen found at the end of the chain to the integral of one found along the chain, in the repeating unit. In PEG, the end group is the OH group at either end. The repeat unit corresponds to the hydrogens on the carbons.

In the case above, there are two hydrogen in the end groups (one at each end). The four repeat units have four hydrogens each, for a total of sixteen. The integration ratio should be 16:2, or 8:1. The measured ratio is 48:6, or 8:1.

Contrast that result with the case of ethylene glycol, in which there isbasically just one repeat unit. The ratio in the oligomer (short polymer) is four times greater than the ratio in the monomer. That's because there are four times as many repeat units in the oligomer. We sometimes call the number of repeat units in the chain the "degree of polymerization".

Exercise 12.7.7

Expand the above structure of the 4-unit PEG oligomer to show the whole chain, rather than just the repeat unit in parentheses.

Exercise 12.7.8

What would be the integration ratio in the following oligomer?

Answer

16:1

To estimate chain length in NMR, a peak must be found from one of the repeating units along the chain as well as a peak from an end group, found only at the end of the chain. The integration of the repeating unit to the end group indicates the average number of repeating units per polymer. This technique essentially provides M_n.

Exercise 12.7.9

What is the molecular weight of the 4-unit PEG oligomer, the NMR spectrum of which was shown above?

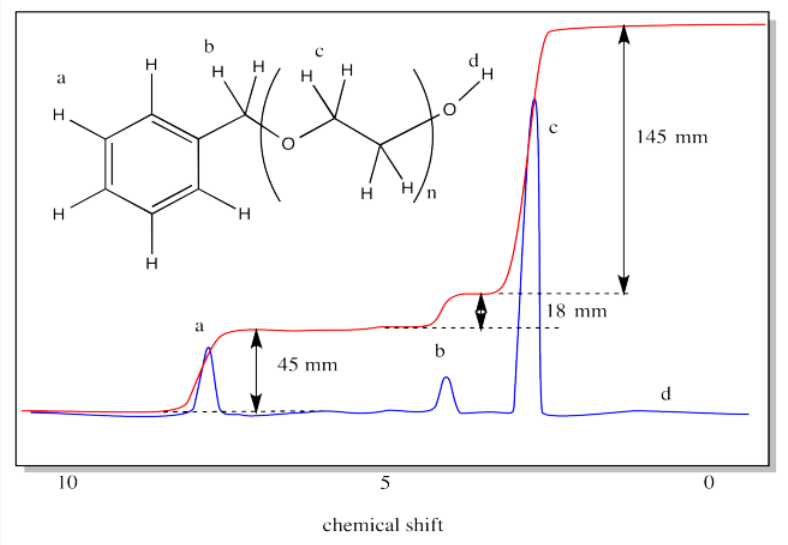
Answer

It's OH + 4 x (CH_2CH_2O) + H. That's 17 + (4 x 44) + 1 = 18 + 176 = 194 D.

In the next example, you are going to see a peculiar fact of life. The truth is, OH groups often don't show up well in ^1H NMR spectroscopy (for complicated reasons). That can complicate things. To get around that problem, people often make polymers in such a way that there is a different end group, other than an OH, so that the integration ratio can be measured more easily.

Exercise 12.7.10

Use the integration ratio in the following spectrum to estimate the degree of polymerization.



Answer

The ratio of c to b is 145:18 = 8:1. However, the number of hydrogens in the repeat unit c is 4; the number of hydrogens in the end group b is 2. That ratio is 2:1. That means the comparison we need is (145/4)/(18:2) = 4:1. The degree of polymerization is 4.

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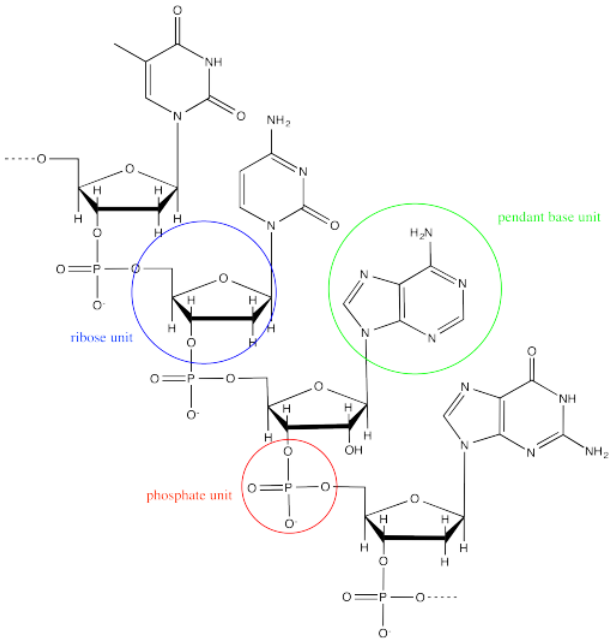
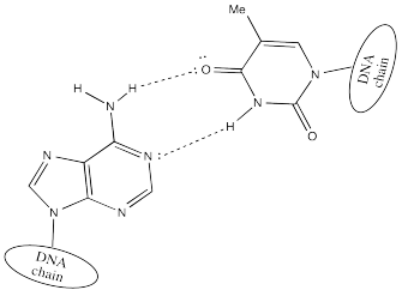
12.8: Supramolecular Assemblies

Supramolecular assemblies are a different type of large structure, related to macromolecules. In a supermolecular assembly, parts of the structure are held together by very strong interactions, but not necessarily by covalent bonds. For example, a polymer in which chains are held together by physical crosslinks such as hydrogen bonds may be considered to form a supermolecular assembly.

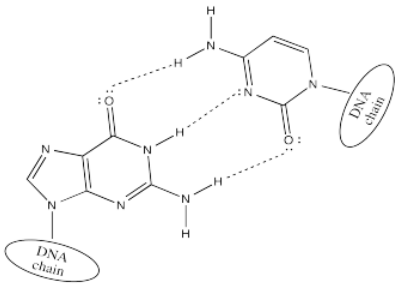
DNA is an example of a supramolecular assembly. Each strand of DNA is an alternating sugar-phosphate copolymer. Along this backbone, there are pendant "base" units, adenine, cytosine, guanine or thymine.



Two DNA strands form a helical supramolecular assembly through hydrogen bonding interactions that form between the bases. Thymine can hydrogen bond preferentially with adenine.



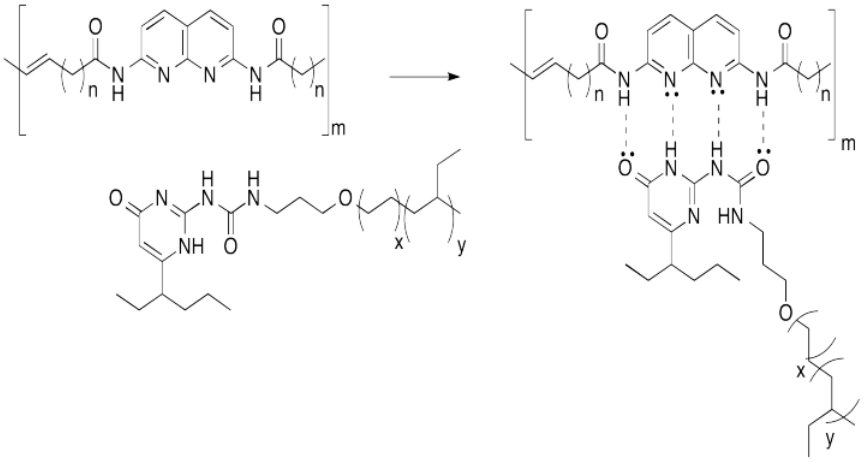
Cytosine hydrogen bonds preferentially with guanine.



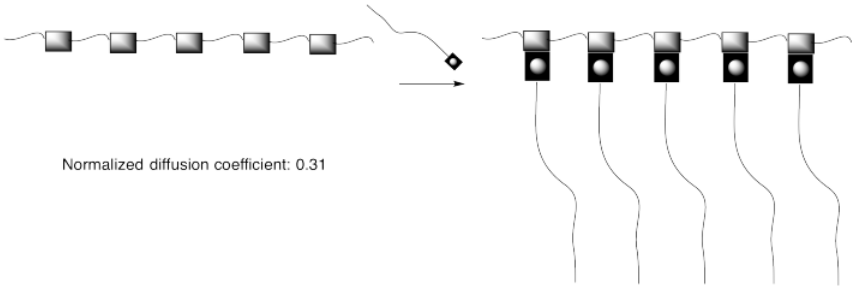
There are a number of different ways in which synthetic supramolecular assemblies can be formed. These kinds of structures have been getting increased attention in recent years as researchers try to develop new materials with useful properties. There are a few common methods through which the assemblies are formed. We will look at hydrogen bonding, host-guest chemistry and coordination chemistry.

Hydrogen Bonding

Hydrogen bonding is a common way to build supramoleucular assemblies. Bert Meijer at Eindhoven Technical University in the Netherlands has developed a number of systems that use this approach. For example, graft copolymers have been assembled in his lab by hanging pendant chains onto a polymer backbone via hydrogen bonds.



This approach can be pictured in cartoon, below, in which the hydrogen bonding elements are boxes and the lines are flexible chains or tails.



Exercise 12.8.1

The diffusion coefficients cited in the picture above are related to how easily compounds can move through a solution. The higher the diffusion coefficient, the more easily the compound moves through solution.

a. How is the diffusion coefficient related to viscosity?
b. Explain the difference between the diffusion coefficients of the two compounds above.

Answer a:

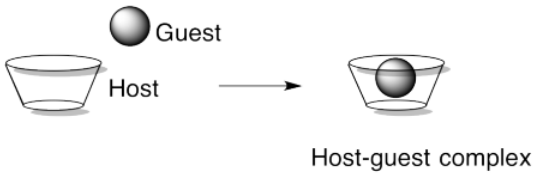
Viscosity is related to the amount of drag in the fluid. The more drag, the slower solutes will be able to move, so the diffusion coefficient is inversely related to viscosity (i.e. higher diffusion coefficientshould correlate with lower viscosity).

Answer b:

The regular chain polymer diffuses more easily than the graft copolymer / supramolecular assembly because the pendant chains in the latter lead to increased entanglement.

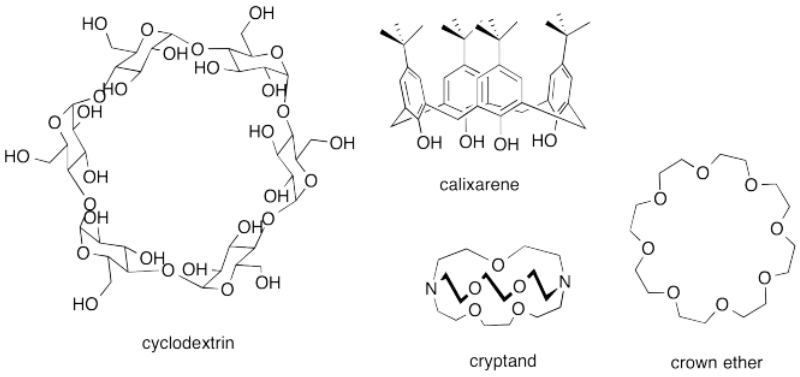
Host-Guest Complexes

Another approach to supramolecular assemblies is to exploit host-guest interactions to bring different parts of the assembly together. Host-guest complexes act a little bit like enzymes and their substrates in biology, or like materials bound inside zeolites. The idea is that one molecule has a cavity or opening big enough for another molecule to fit inside. It's a little like a basketball fitting into a peach basket.



There might be a physical attraction (an intermolecular force) between a host and a guest, but there does not have to be. Julius Rebek at the Scripps Institute has developed host complexes that will hold normally aloof guests such as N_2. Part of the reason guests can become comfortably ensconced without intermolecular attractions involves the fact that the molecule inside would have to take a very particular path in order to escape.

A number of host compounds are shown below. Each of them is designed to have an enclosed space of some kind. In some cases it's no more than a ring, but that is enough to keep the guest from escaping on those sides.



Exercise 12.8.2

The following host-guest system was designed in the lab of Taichi Ikeda at the National Institute for Materials Science in Japan. In the polymer notation, "x" and "n-x" are just numbers of repeating units. When solutions of the two polymers are mixed together, an elastic gel is formed.

a. Draw a cartoon of each of the polymers and of the host-guest linked assembly.
b. What makes this host and guest especially attractive for each other?
c. Describe the structure of this assembly, in terms of polymer architectures seen previously.
d. Why is the gel elastic?
e. This gel is "self-healing": it can be cut with a knife, but the pieces can then be stuck back together again. Explain how this re-attachment occurs.

Answer b:

The lone pairs on the oxygens in the host would be attracted to the positively charged nitrogens in the guest. The N-H groups in the guest would even act as hydrogen bond donors to the oxygens.

Answer c:

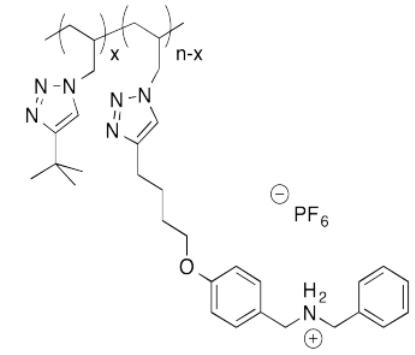
This supramolecular assembly forms a cross-linked architecture.

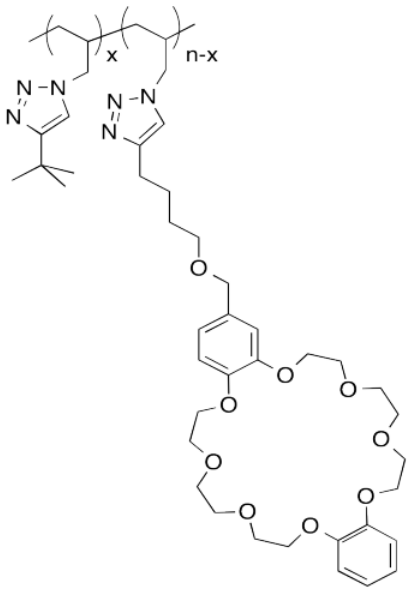
Answer d:

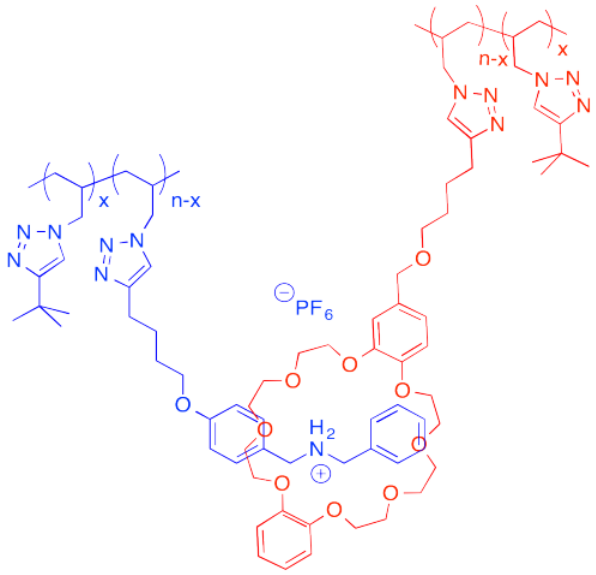
The gel is elastic because, although it contains flexible chains and can be distorted up to a point, at some point the crosslinks pull it back to its original position.

Answer e:

When the gel is cut, probably some guests are pulled away from their hosts along the surface of the cut. WHen the edges are placed back together, the guests can find new hosts and form the cross-linked structure again.



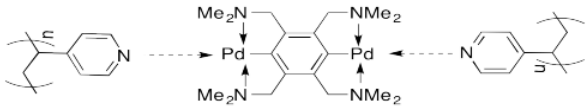




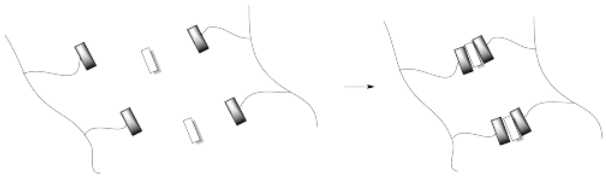
Coordination Compounds

If you don't know about coordination compounds, you might want to start with Lewis acid-base complexes.

A number of such assemblies have been reported from the lab of Stephen Craig at Duke University. For example, mixing a solution of certain palladium compounds into a solution of poly(vinylpyridine) (PVP) produces a thickening of the liquid into a honey-like consistency.



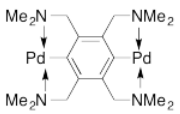
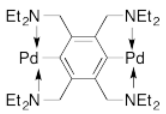
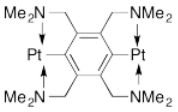
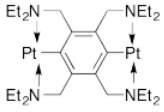
As a cartoon, this system can be represented as shown below. The palladium complexes form physical crosslinks between the pendant pyridine units on the polymer chains.



Exercise 12.8.3

This is a challenge problem for students of Chem 251.

Craig's lab reported the following kinetic data for the poly(vinylpyridine) / ML_n system in DMSO (dimethylsulfoxide) solvent. Remember, ML_n just means "coordination complex".

PVP/MLn complex				
k_d (s^{-1})	1450	17	0.026	0.0006
$K_b = k_a/k_d$ (M^{-1})	29	33	8000	4000

a. The rate constant k_d refers to the dissociation of a PVP/ML_n linkage. Show a likely mechanism for that reaction.

b. Explain why the reaction is faster with the methyl-substituted ligand than the ethyl-substituted one.
c. Is K_b the equilibrium constant for formation of the PVP/ML_n linkage or for dissociation of the linkage?
d. Explain the large difference in values of K_b between the palladium complexes and the platinum complexes.

Answer a:

The palladium in the complex is Pd(II), so it is d8 and the structure of the crosslink is square planar at palladium. Ligand exchange likely occurs through an associative process. That means that before the PVP dissociates, a new ligand would bind; this ligand is probably a solvent molecule, DMSO.

Answer b:

The increased crowding in the ethyl-substituted ligand, compared to the methyl, would hinder the approach of DMSO during substitution, slowing down the reaction.

Answer c:

K_b is defined as k_a/k_d, the rate constant for the association step over the rate constant for the dissociation step. It is the binding constant for PVP-Pd formation.

Answer d:

Palladium is a second row transition metal whereas platinum is a third row transition metal. Third row metals have greater ligand field splitting energies than second row metals and are generally less labile.

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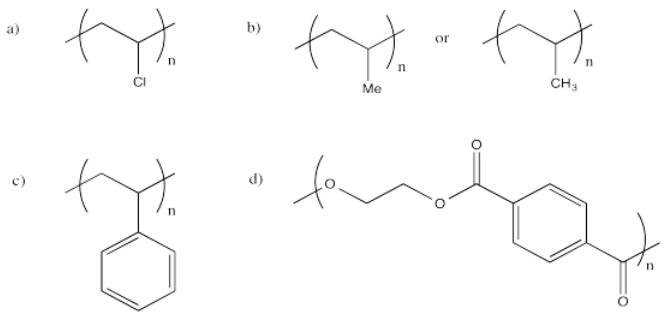
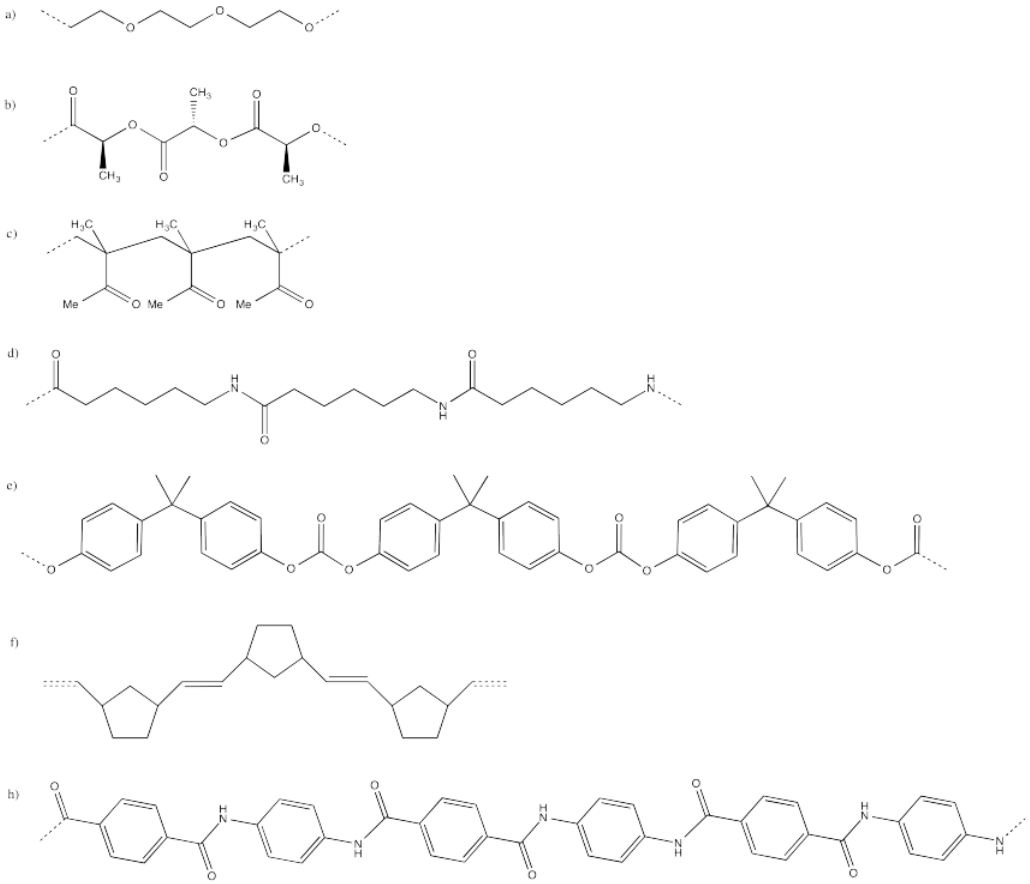
12.9: Solutions for Selected Problems

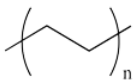
Exercise 12.1.1:



Exercise 12.1.2:



Exercise 12.1.4:



b) Chains of HDPE are able to pack more tightly together than LDPE, in which the branches prevent tight packing of the backbone. That difference makes LDPE less dense than HDPE.

Exercise 12.2.1:

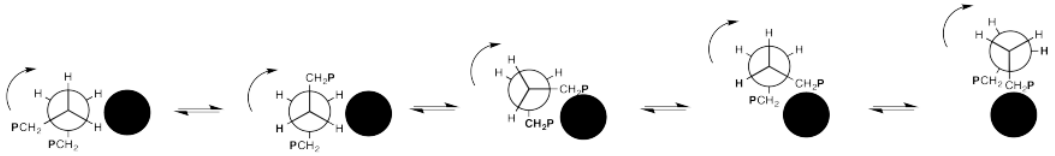
a. Water can in principle form four hydrogen bonds: it can donate two and accept two. Ethylene glycol has two OH groups, so it can donate two H bonds and accept four. That enhanced clinginess is responsible for its higher viscosity.
b. Olive oil does not hydrogen bond; it isn't even very polar. However, it is a triglyceride and its fatty acid chains are about 80% oleic acid and linoleic acid, which are both 18-carbon chains. So the average olive oil molecule contains three 18 carbon branches, leading to a modest level of entanglement. Its viscosit is much higher than water's.
c. Methanol has only one OH bond, so it has a little less hydrogen bonding than water, but not enough of anything else to form other interactions. Its viscosity is a little lower than water's.
d. 2-propanone has no hydrogen bonding at all, although it does have a dipole moment to hold different molecules together. Its viscosity is a little lower than methanol's.
e. Hexane has no dipole and no hydrogen bonding. It is really too short to become entangled. Molecules only attract each other through weak London dispersion interactions. Its viscosity is a little lower than 2-propanone's.

Exercise 12.2.2:

The greater the number of repeating units, the higher the molecular weight. Also, the greater the number of repeating units, the greater the entanglement and the higher the viscosity.

Exercise 12.3.1:

You can think about a length of chain flopping over a neighbouring strand like a grappling hook, then pulling itself along as the bond continues to rotate, vaulting over the other chain.



Exercise 12.3.2:

a. The greater the number of repeating units, the greater the entanglement. Entanglement acts as an impediment of the movement of chains, increasing the temperature at which chain motion becomes restricted (in other words, increasing the minimum volume needed to get the chains moving again). For example, polypropylene has a higher T_g than polyethylene, and that of polystyrene is even higher (although additional factors influencethe T_g of PS).
b. Increased polarity increases the attraction between chains and can even lead to formation of physical crosslinks between chains. This increased interaction hinders chains from moving freely and raises the glass transition temperature. For example, polylactide, poly(vinyl chloride) and poly(methyl methacrylate all have much higher values of T_g than polypropylene.
c. If the backbone is rigid, reptation is hindered because the chain can't adopt different conformations. Chain flow is restricted more easily and the T_g is higher. Kevlar and polynorbornene both have stiff backbones because of the aromatics and aliphatic rings, respectively, that form part of the backbone. Both polymers have much higher values of T_g than polystyrene, in which the aromatics hang from a flexible chain.

Exercise 12.3.5:

a) rubbery b) glassy c) glassy d) rubbery

Exercise 12.4.1:

There may be different architectures that lend themselves to the same applications.

a. A regular chain structure could be wound into a thread easily. There would be enough entanglement to held the threed together.
b. Across-linked structure would help a rubber band snap back to its original shape. However, too much cross-linking would make it too difficult to stretch the rubber band.
c. A dendrimer has lots of nooks and crannies that might be used to sponge up pharmaceuticals and slowly release them later.
d. A branched or cross-linked structure might form a good two-dimensional network to provide a protective coating.

Exercise 12.5.1:

The polar vinyl acetate block of the first polymer contains carbonyl groups that would attract each other by dipole-dipole interactions. It is easy to imagine these segments forming physical crosslinks. The hydrocarbon chain in the middle block would prvide flexibility.

Although nonpolar, the benzene groups in styrene are flat and can stack together with relatively strong London dispersion forces. The higher Tg of polystyrene would make these blocks much stiffer than the more flexible polyisoprene block in the middle.

Exercise 12.6.1:

The telechelic polymer has two growing ends per chain, so it grows twice as fast as a normal chain.

Exercise 12.6.2:

If this chain reached 100% conversion, then the degree of polymerization would be 500. At 85% conversion, DP = 425.

Exercise 12.6.3:

As the number of repeat units increases, the molecular weight increases.

Exercise 12.7.2:

The molecular weight is the sum of the weights of all the repeat units plus the weight of the end groups.

a. $MW = 1000 units \times 104.15 \frac{Da}{unit} + 2Da = 104152 Da$
b. $MW = 200 units \times 72.06 \frac{Da}{unit} + 2Da = 14412 Da$ (based on 200 simple repeating units, but this is a complicated case. In common practice, PLA is made from a dimeric monomer, with each monomer forming two repeat units in the chain, so a degree of polymerization of 200 really corresponds to 400 repeat units in the chain, which would have twice the molecular weight.)
c. $MW = 50 units \times 44.05 \frac{Da}{unit} + 2Da = 2202 Da$
d. $MW = 100000 units \times 42.08 \frac{Da}{unit} + 2Da = 4208002 Da$

Note that, in this case, the end groups make no appreciable difference in the weight because they are so small.

Exercise 12.7.3:

MW = weight (in g) / moles

a. 5827 Da
b. 1052 Da
c. 703,000 Da or 703 kDa

Exercise 12.7.4:

Đ = M_w / M_n

a. 1.14
b. 1.22
c. 1.56
d. 1.76
e. 1.62

Exercise 12.7.5:

a. 3,000 D
b. 5,000 D

Exercise 12.7.6:

The longer the chain in polymer A, the bigger the sphere it coils into. There isn't much problem comparing samples of polymer A to each other, provided we have some way of calibrating sphere size to chain length.

However, polymer B appears to be more tightly coiled than A. A relatively small sphere could pack a lot more chain. We would have to be cautious about comparing the sphere size of B to that of A and drawing any conclusions about chain length or molecular weight.

Exercise 12.7.7:

Exercise 12.7.8:

16:1.

Exercise 12.7.9:

It's $OH + 4 \times (CH_2CH_2O) + H$. That's $17 + (4 \times 44) + 1 = 18 + 176 = 194D$

Exercise 12.7.10:

The ratio of c to b is 145:18 = 8:1. However, the number of hydrogens in the repeat unit c is 4; the number of hydrogens in the end group b is 2. That ratio is 2:1. That means the comparison we need is (145/4)/(18:2) = 4:1. The degree of polymerization is 4.

Exercise 12.8.1:

a) Viscosity is related to the amount of drag in the fluid. The more drag, the slower solutes will be able to move, so the diffusion coefficient is inversely related to viscosity (i.e. higher diffusion coefficientshould correlate with lower viscosity).

b) The regular chain polymer diffuses more easily than the graft copolymer / supramolecular assembly because the pendant chains in the latter lead to increased entanglement.

Exercise 12.8.2:

b) The lone pairs on the oxygens in the host would be attracted to the positively charged nitrogens in the guest. The N-H groups in the guest would even act as hydrogen bond donors to the oxygens.

c) This supramolecular assembly forms a cross-linked architecture.

d) The gel is elastic because, although it contains flexible chains and can be distorted up to a point, at some point the crosslinks pull it back to its original position.

e) When the gel is cut, probably some guests are pulled away from their hosts along the surface of the cut. WHen the edges are placed back together, the guests can find new hosts and form the cross-linked structure again.

Exercise 12.8.3:

a. The palladium in the complex is Pd(II), so it is d8 and the structure of the crosslink is square planar at palladium. Ligand exchange likely occurs through an associative process. That means that before the PVP dissociates, a new ligand would bind; this ligand is probably a solvent molecule, DMSO.
b. The increased crowding in the ethyl-substituted ligand, compared to the methyl, would hinder the approach of DMSO during substitution, slowing down the reaction.
c. K_b is defined as k_a/k_d, the rate constant for the association step over the rate constant for the dissociation step. It is the binding constant for PVP-Pd formation.
d. Palladium is a second row transition metal whereas platinum is a third row transition metal. Third row metals have greater ligand field splitting energies than second row metals and are generally less labile.

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CHAPTER OVERVIEW

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13.1: Introductions

The nature of the chemical bond

At an elementary level, we can think about atoms being held together by simple electrostatic attraction. It is a fundamental principal that opposite charges attract. A positively charged ion and a negatively charged ion are held together by this force of attraction.

- This idea works well for ionic compounds, such as sodium chloride.
- It does not work well for compounds in which similar atoms are connected, such as ethane, C_2H_6.

Maybe the carbons are negatively charged and the hydrogens are positively charged, but what is holding the two carbons together if they have like charges?

A similar problem is encountered in diatomic molecules such as H_2. Is one of these hydrogen atoms negative while the other hydrogen atom is positive?

In the early twentieth century, G. N. Lewis noticed a trend in the characteristics of compounds that he called "the rule of two". If you were to count up the total number of electrons in any stable compound, you would always come up with an even number -- that is, some number that is divisible by two. Perhaps, Lewis reasoned, this predominance of even numbers arises because electrons need to be in pairs.

What does an element do if it has an odd number of electrons? One solution is to steal an electron from another element, or to allow one to be stolen away; these arrangements lead to ionic bonds. However, those elements not adept at stealing electrons may have a problem; they may need to share them instead. In order to share electrons, elements will have to form close associations with each other. They will become bonded together.

- An "ionic bond" is an electrostatic interaction between an anion and a cation.
- A "covalent bond" is one pair of electrons shared between two atoms.

Lewis took this idea further. If you count up the valence shell electrons around each of the atoms in stable compounds, not only are there even numbers, but there are almost always the same number of electrons as there are in one of the noble gases: He, Ne, Ar, Kr (2, 8, 8, or 18). This observation is sometimes called the Lewis octet rule because so many common atoms that form stable compounds obtain 8 electrons in their outermost shell as a result. Neon is the nearest noble gas to carbon, oxygen and nitrogen, and all of these atoms adopt 8-electron configurations in stable compounds.

Lewis structures illustrate how atoms can maintain these numbers of electrons by sharing with other atoms. These simple structural drawings are used to convey most of our ideas about molecular chemistry. However, additional information can often be found through quantum mechanics and a molecular orbital approach to bonding.

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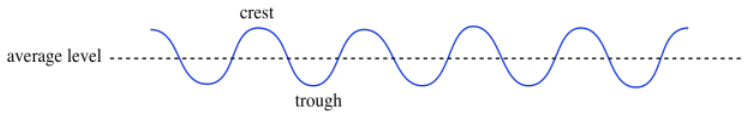
13.2: Wave Behavior and Bonding in the Hydrogren Molecule

In the early 20th Century, our understanding of light and matter was progressing very quickly, but some things still didn't make sense to people. Things really started to click when a number of physicists started thinking about things in a different way. One of the revolutionary things they did was to treat seriously, with mathematical equations, the wave nature of light and matter.

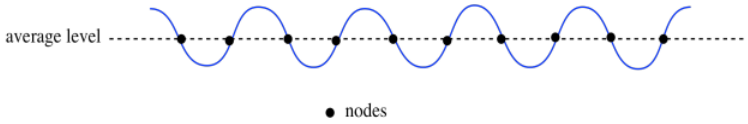
In the case of light, the idea actually dates back to the mid-17th Century. Christiaan Huygens, a Dutch clockmaker and astronomer, believed that light traveled in waves because he could see evidence of interference patterns in light, much like the way ripples on a pond can interfere with each other to produce new patterns. Other scientists, such as Newton, really thought light was made of small particles. In a sense, both were right, and we now think of particles of light, or photons, as having some of the properties of waves.

What do we know about waves? Waves on the surface of a lake or an ocean are good examples. You probably took a detailed look at them around 6th grade, although you may have forgotten some of the details. So, let's take another look.

Maybe you have stood beside a wave tank at a science museum and seen something that looks like this. The surface of the water undulates up and down. There are *crests* where the water mounds up in hills and *troughs* where the water slips away into valleys. Somewhere in between, there is an average water level, where the surface would settle if things were calm and there were no waves at all.

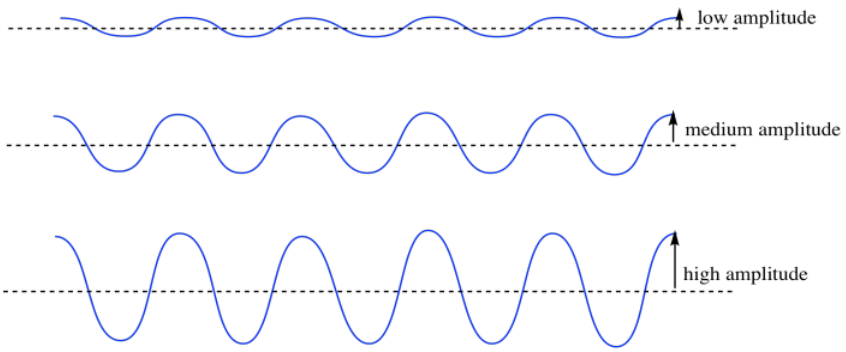


We can also think of waves as having null points or nodes; those are the positions halfway in between the crest and the trough.



Max Planck and Albert Einstein each took a closer look at that idea in the early 1900's when they were trying to determine the relationships between electrons in materials and their interaction with electromagnetic radiation. Electromagnetic radiation includes things like ultraviolet and visible light.

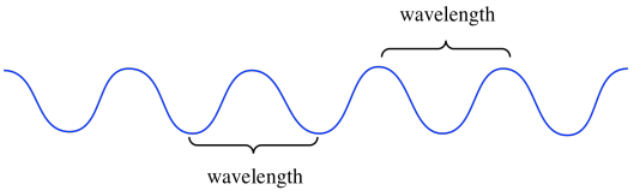
If we are standing at the seaside, one of the first things we notice about the waves is how tall they are. Maybe it's a really calm day and the waves are almost flat. Maybe it's a really rough day and the waves are really tall. The feature of waves that you are noticing is called the amplitude. That's the height of the wave from the average water level to the crest, or, conversely, the depth down to the trough. In the macroscopic world, the amplitude of the waves is really important. You need to know whether it's OK to stand and watch the waves, or whether it's getting too rough and you should seek higher ground. If you aren't careful, a really high amplitude wave could come crashing down on you.



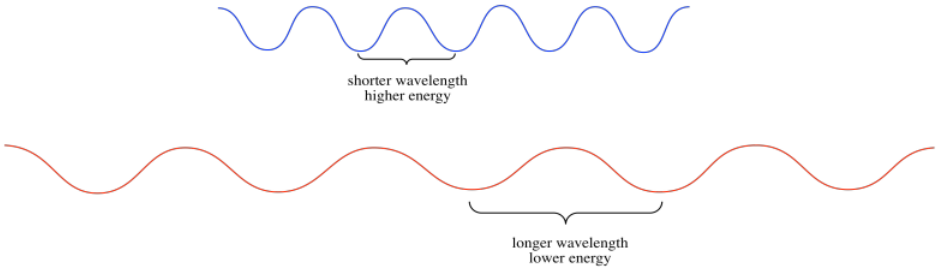
Waves on the ocean can have high amplitude or low amplitude, and there is a physical consequence. Sound waves can also have high amplitude (those are the loud ones) or low amplitude (those are the quiet ones). Of course, if the amplitude were really, really

low, we would almost have no wave at all (when that person is whispering a secret but you can't even hear them).

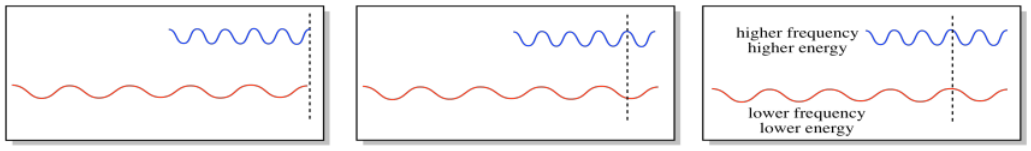
In the nanoscale world, the world of photons and electrons, the amplitude of a wave is a much more subtle thing. It isn't our first consideration. What's much more important is the wavelength. The wavelength is just the distance from one crest to the next, or from one trough to the next.



The wavelength is really important because, according to Planck and Einstein's analysis of experimental data, it's what determines the energy of an individual photon, or the energy of an individual electron. The shorter the wavelength of a photon or electron, the higher its energy. The longer the wavelength of a photon or electron, the lower its energy. This relationship is an example of inverse proportionality: when one gets bigger, the other gets smaller.



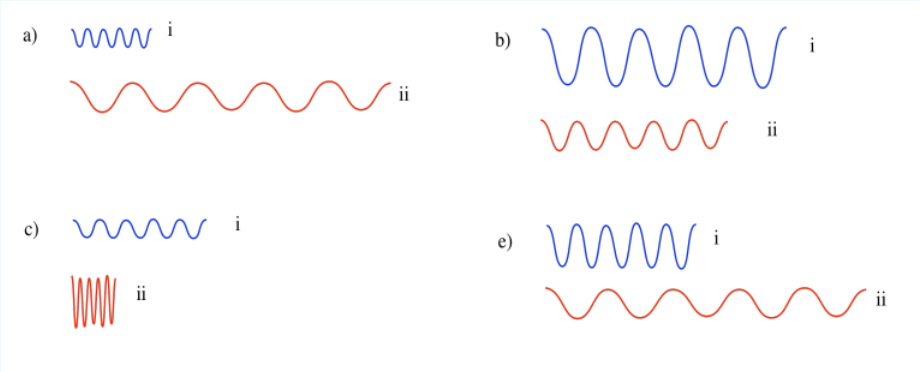
There is a complementary attribute of waves, and that is frequency. We can think of frequency as how often a wave crests. Alternatively, if we picture an electromagnetic wave passing a stationary object, the frequency would describe how often a crest passes the object. (All light travels at the same speed, about 3 x 10^8 m s^{-1}, so we don't have to worry about that being a factor.)



Frequency is inversely proportional to wavelength: the longer the wavelength, the lower the frequency. Consequently, frequency is directly proportional to the energy of the photon or electron. The higher the frequency, the higher the energy.

Exercise 13.2.1

Between each pair, which wave has greater energy?

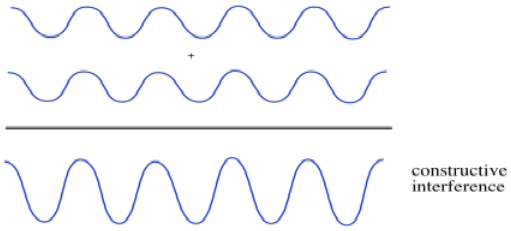


Answer

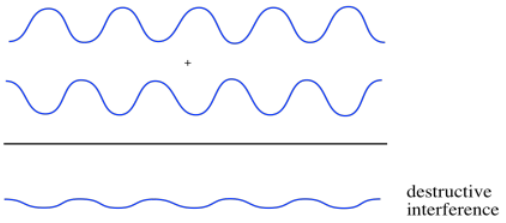
In each case, the wave with the higher frequency and shorter wavelength would have the higher energy. a) i; b) ii; c, ii; e) i.

Let's return to Christiaan Huygens' original observation of interference patterns in light. What does that mean?

Suppose two waves come together. We'll think about two different cases. In the first case, the two waves are in-phase with each other. That means that they both crest at the same time and their troughs are always aligned, too. What happens then? You can imagine the crests will just build on each other, getting taller, and the troughs will fall into each other, getting deeper. The amplitude of the waves, together, increases. This is constructive interference.



Now suppose that the two waves are out-of-phase. When one crests, the other bottoms out. In that case, the crest of one wave falls into the trough of the other. Everything levels out. This is destructive interference.



Constructive interference and destructive interference also occurs with waves on the water. That leads to lots of ripple patterns if you toss two stones into a still pond. Photons can also produce those kinds of patterns, and so can electrons.

Lewis suggests that two atoms with unpaired electrons may share their electrons to form a bond. In a Lewis structure, we can draw those two electrons between the symbols for the two atoms to show that a bond has formed. Quantum mechanics offers a quantitative mathematical view of molecules, and is considered to give an accurate picture of the behavior of atoms and molecules. Now, instead of putting two atoms beside each other and letting two dots get together to form a bond, like in a Lewis structure, we'll think about bonding in quantum mechanical terms.

- Two hydrogen atoms are placed next to each other.
- The two atoms are surrounded by the waves formed by their electrons.
- If the two atoms are close together, these two waves overlap in between the two atoms.

What happens when waves overlap? Interference patterns develop. Think of a flat, calm pond, into which you and a friend throw two small stones, a few feet apart. The resulting ripples move out in circles from the two points where the stones fell in, and when the two sets of waves meet each other, new patterns result. The circular sets of waves combine to form new waves with new shapes.

When waves meet, there are two basic combinations that result. These combinations depend on whether the two waves are in-phase or out-of-phase with each other.

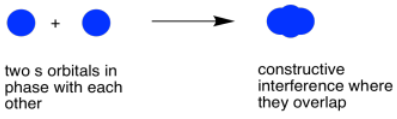
- If the waves are in-phase, so that the peak of one wave lands on top of the peak of another, and the trough of one wave coincides with the trough on the other, constructive interference occurs. The waves add up, and get bigger where they overlap.
- If the waves are exactly out-of-phase, the peak of one falls into the trough of another, and where they overlap the two waves are canceled out. This is destructive interference.

We can apply these ideas to the electrons in atoms that come together to make a bond. In Lewis structures, individual electrons on two different atoms are paired up in a bond between the two atoms. The electrons have to be combined to make a bond. If electrons have wave properties, then there will be interference patterns that result when these atoms come together.

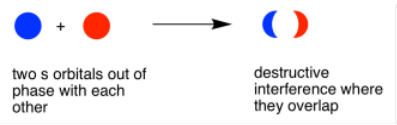
Before we start, note that the waves that we will be dealing with look a little different from the standing waves we looked at before. These waves will be three-dimensional and will occupy different regions of space. Instead of drawing phase information as peaks and troughs, we are going to use a common convention of shading to signify whether we are looking at the positive part (in terms of phase) or the negative part of a wave. For example, we might show the crests in blue and the troughs in red, or we might show one in black and the other in white. In a standing wave, the phases would look like this:

In a hydrogen atom, the electron is found in a spherical area around the nucleus. We won't be able to see two distinct phases - a crest and a trough - in this wave at one time. However, we could look at two different hydrogen atoms and illustrate whether their electrons are in-phase or out-of-phase with each other.

When those two electrons come together and they are in-phase with each other, constructive interference occurs. They won't overlap completely; these are atoms and they take up space. However, they will be able to sit pretty close to each other, sort of smushing their electrons together. That constructive interference will happen in the middles, between the atoms.



When the two electrons come together and they are out-of-phase, destructive interference occurs. Again, that will happen in the middle, between the atoms.



So, in the pair of hydrogen atoms, two waves can combine to produce two possible outcomes.

- In one, the height of the combined wave is highest between the two atoms, where they are overlapping and in-phase. The amplitude of the wave is greater here.
- In the other case, the combined wave is composed of two halves that are out-of-phase, and there is no wave at all between the two atoms, where they have canceled out; the amplitude of this wave is zero between the two nuclei.

Those two possible combinations produce two different results. We keep track of these outcomes using a molecular orbital interaction diagram. The diagram says that the two orbitals can combine in two different ways: in-phase or out-of-phase. The diagram also tells us that the in-phase combination results in a decrease in energy when the two atoms come together. The out-of-phase combination results in an increase in energy when the atoms come together.

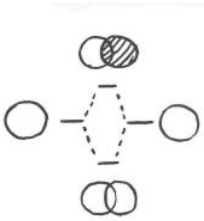


Figure 13.2.1: A molecular orbital interaction diagram for H_2. A hydrogen atom 1s orbital is shown on the **left** with its accompanying energy level. The same is shown on the **right**. In the **middle** of the diagram, the two hydrogen 1s orbitals can combine in two ways: in-phase and out-of-phase. These combinations produce two new orbitals (or electron waveforms) with two new energy levels.

Why does the in-phase combination go down in energy, whereas the out-of-phase combination goes up?

Consider the idea that these waves each have a wavelength, and that this wavelength is related to kinetic energy. For the 1s electron on a hydrogen atom, we can really only visualize half the wave; this half-wave is basically the size of a hydrogen atom, so the total wavelength would be two hydrogen atoms long (for lack of a better yardstick).

For the out-of-phase combination, we can visualize the entire wave, both its "peak" on one side and the "trough" on the other. The two hydrogen atoms are not merely sitting beside each other, they are actually overlapping, so that the distance from one end of the wave to the next is actually somewhat less than two hydrogen atoms. Let's say it's one and a half hydrogen atoms long. This wave has a shorter wavelength than the waves on either individual hydrogen atom, and so it is at higher energy.

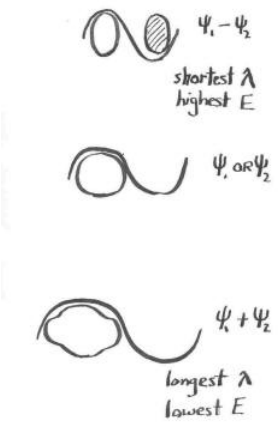


Figure 13.2.2: A comparison of wavelengths as seen along the bond axis in dihydrogen.

For the in-phase case, again, the two hydrogen atoms are overlapping. But this time we can only visualize half the wave; so the total wavelength would be longer than two hydrogen atoms. Maybe it's three hydrogen atoms long. This wave has a longer wavelength than the electron in an individual hydrogen atom, so it is at lower energy.

- The combination of atomic orbitals results in new, molecular orbitals.
- The number of atomic orbitals combined = the number of molecular orbitals produced.
- In-phase (low energy) and out-of-phase (high energy) combinations are possible.

And now for the weird part:

- According to quantum mechanics, the in-phase and out-of-phase combinations occur *simultaneously*.

Where would the two electrons actually go? The aufbau process used for atomic electron configurations holds true here. Two electrons can be found in the same space provided they are spin-paired; one would have spin "up" and the other one spin "down". Both electrons could be found in the lower energy orbital. That means both hydrogen electrons go down in energy when H_2 forms; the formation of a hydrogen molecule from two hydrogen atoms is thus exothermic.

- The occupied orbital is called a bonding orbital; it is responsible for the bond energy in H_2.
- Bond energy refers to the amount of energy given off when a bond forms.

What would happen if each hydrogen atom brought two electrons with it? Would two hydride ions form a bond?

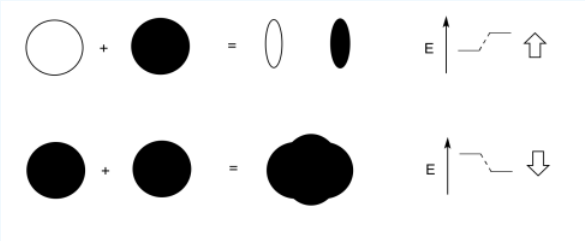
- There would be four electrons in an H_2^{2-} molecule.
- The first two electrons would occupy the lower, bonding orbital.
- The next two electrons would occupy the upper orbital
- Overall, there would be no net loss of energy, so a bond would not form.
- The out-of-phase combination is called an antibonding orbital, because its increase in energy offsets the decrease in energy that occurs when electrons go into a bonding orbital.
- Placing electrons in an antibonding orbital weakens or breaks a bond.

What does quantum mechanics tell us about bonding that we can't learn from Lewis structures? We learn that electrons can sometimes lower their kinetic energy by forming bonds. If that is the case, the bond will form. On the other hand, if kinetic energy cannot be lowered, the bond won't form at all.

- Covalent bonds form because electrons can adopt longer wavelengths.
- Electrons with longer wavelengths have lower kinetic energy.

Exercise 13.2.2

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



Answer

When two s orbitals combine out-of-phase, destructive interference occurs.

There is a node between the atoms.

The energy of the electrons increases.

When two s orbitals combine in-phase, constructive interference occurs.

There is no node between the atoms; the electrons are found between the atoms.

The energy of the electrons decreases.

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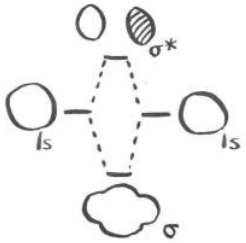
13.3: Molecular Orbitals- Lessons from Dihydrogen

In the case of the hydrogen molecule, we took two atomic orbitals and combined them to form two molecular orbitals. These new molecular orbitals had different wavelengths than the two atomic orbitals: one had a longer wavelength and was a little lower in energy, while the other had a shorter wavelength and was a little higher in energy. If we take into account the energy of the two original atomic waves, and compare them to the total energy of the two new molecular waves, there is no change overall.

We started with two atomic orbitals, and by combining them we produced two molecular orbitals. Both of these ideas are useful in considering the formation of more complex molecules from individual atoms.

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



Of course, from the point of view of the two real electrons, some remarkable changes have occurred. Both of these electrons have adopted a longer wavelength and a lower energy and that has made all the difference. There is an occupied molecular orbital and an unoccupied molecular orbital; only the occupied orbital makes a real energetic contribution to the overall stability of the molecule. The unoccupied orbital is completely imaginary.

A bonding picture of He_2 would look exactly the same, because it would also involve the overlap of 1s electrons on one atom with 1s electrons on the other atom. There would be a different electronic energy, however. That difference would affect the prospects of helium-helium bond formation.

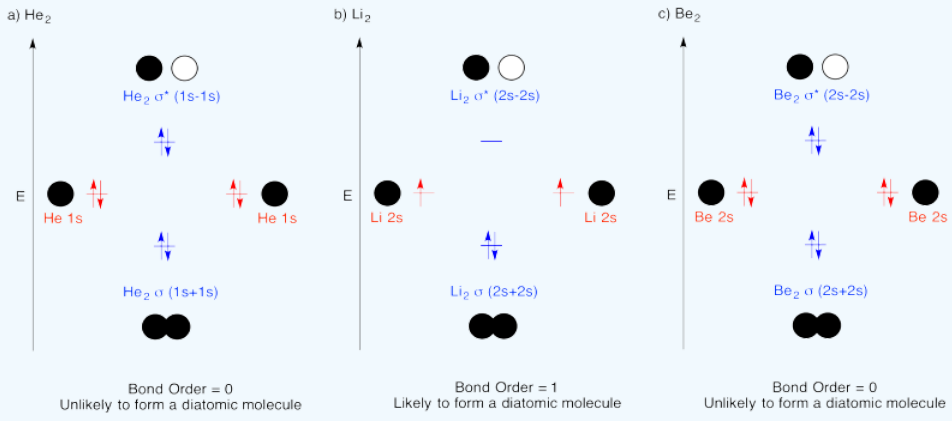
- The electrons have lower kinetic energy in the bond than they had before bonding.
- Electronic energy has decreased. A stable bond has formed.

Exercise 13.3.1

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

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

Answer



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13.4: Sigma Bonding with p Orbitals

Other diatomic molecules in the upper right corner of the periodic table can be constructed in a similar way. Look at dinitrogen, N_2. We can think about how dinitrogen would form if two nitrogen atoms were placed close enough together to share electrons. Nitrogen has more electrons than hydrogen, so this interaction is more complicated.

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

Nitrogen has five valence electrons, and these electrons are found in the 2s and 2p levels. There are three possible atomic orbitals in the 2p level where some of these electrons could be found: p_x, p_y and p_z. We need to look at the interaction between the s and p_x, p_y and p_z orbitals on one nitrogen atom with the s and p_x, p_y and p_z orbitals on the other nitrogen. That process could be extremely complicated, but:

- Orbital interactions are governed by symmetry.

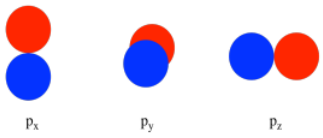
Orbitals interact most easily with other orbitals that have the same element of symmetry. For now, we can simplify and say that orbitals on one atom only interact with the same type of orbitals on the other atom.

- s orbitals interact with s orbitals. We can already see how that will work out in dinitrogen, because that is what happened in dihydrogen.
- p_x orbitals interact with p_x orbitals.
- p_y orbitals interact with p_y orbitals.
- p_z orbitals interact with p_z orbitals.

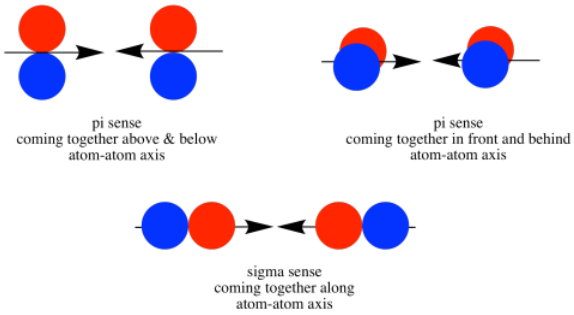
Another complication here is that the s and p orbitals do not start out at the same energy level. When the orbitals mix, one combination goes up in energy and one goes down. Does the s antibonding combination go higher in energy than the combinations from p orbitals? Do the p bonding combinations go lower in energy than the combinations from s orbitals? We will **simplify** and **assume** that the s and p levels remain completely separate from each other. This is not always true, but the situation varies depending on what atoms we are dealing with.

- The combination of one s orbital with another is just like in hydrogen. Two old orbitals will combine and rearrange to produce two new orbitals.
- There is a bonding combination in which the orbitals are in phase. The new orbital produced has longer wavelength than the original orbital. It is lower in energy.
- There is an antibonding combination in which the orbitals are out of phase. The new orbital produced has shorter wavelength than the original orbital. It is higher in energy.

In considering the interaction of two p orbitals, we have to keep in mind that p orbitals are directional. A p orbital lies along a particular axis: x, y or z. The three p orbitals on nitrogen are all mutually perpendicular or orthogonal to each other. That situation is in contrast to s orbitals, which are spherical and thus look the same from any direction.

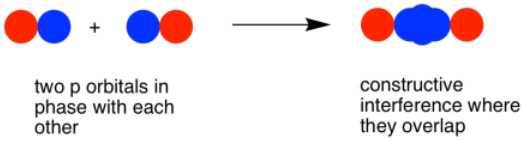


We first need to define one axis as lying along the N-N bond. It does not really matter which one. We arbitrarily say the N-N bond lies along the z axis. The p_z orbitals have a different spatial relationship to each other compared to the p_y and p_x. The p_z orbitals lie along the bond axis, whereas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

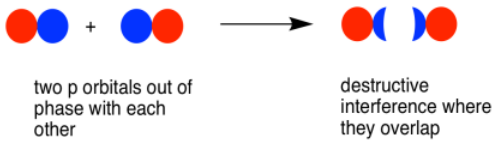


As the nitrogen atoms are brought together, one lobe on one p_z orbital overlaps strongly with one lobe on the other p_z orbital. The other lobes point away from each other and do not interact in any obvious way.

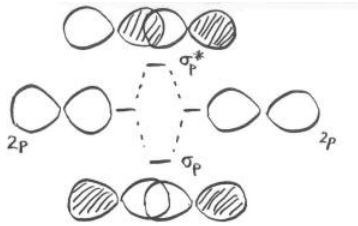
As with the s orbital, the p_z orbitals can be in phase or out of phase. The in-phase combination results in constructive interference. (By "in-phase" here we mean the lobes that overlap are in-phase; for that to happen the two p orbitals are actually completely out of phase with each other mathematically, so that one orbital is the mirror image of the other.) This combination is at longer wavelength than the original orbital. It is a lower energy combination.



The out-of-phase combination (meaning in this case that the overlapping lobes are out of phase) results in destructive interference. This combination is at shorter wavelength than the original orbital. It is a higher energy combination.



As a result, we have two different combinations stemming from two different p orbitals coming together in two different ways. We get a low-energy, in-phase, bonding combination and a high-energy, out-of-phase, antibonding combination.

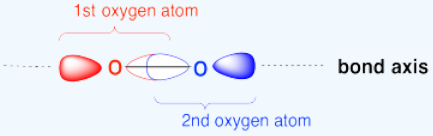


What about those other p orbitals, the ones that do not lie along the bond axis? We'll take a look at that problem on the next page.

Exercise 13.4.1

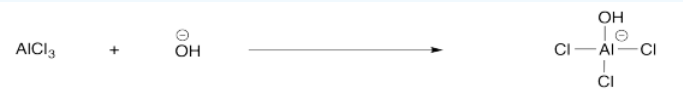
Draw an MO cartoon of a sigma bonding orbital formed by the overlap of two p orbitals between two oxygen atoms. Label the positions of the oxygen nuclei with the symbol "O". Label the O-O bond axis.

Answer



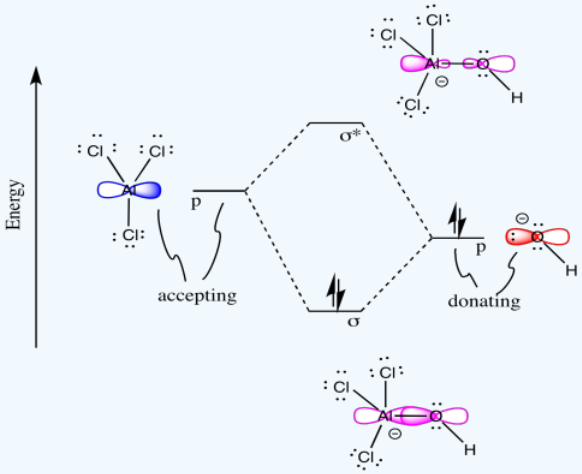
Exercise 13.4.2

Consider the following reaction.



- Draw an MO mixing diagram for the reaction above.
- Draw the orbital from the base that is likely to donate its electrons.
- Draw the orbital from the acid that is likely to accept electrons.
- Complete the MO mixing diagram of these two orbitals:
  - Label the electron donating orbital
  - Label the electron accepting orbital
  - Populate the MO mixing diagram with electrons
- Draw a cartoon showing the mixing of these orbitals.

Answer



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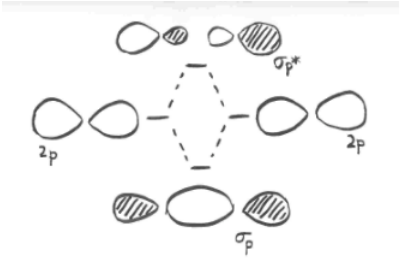
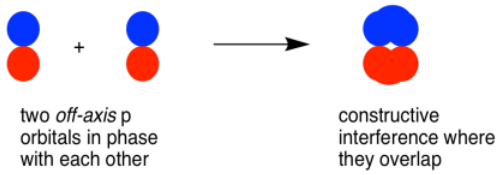
13.5: Pi Bonding with p Orbitals

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



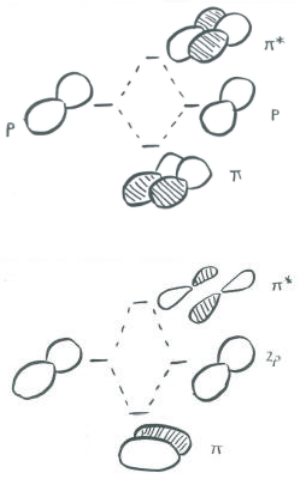
Parallel, but not collinear, p orbitals can also interact with each other. They would approach each other side by side, above and below the bond axis between the two atoms. They can be close enough to each other to overlap, although they do not overlap as strongly as orbitals lying along the bond axis.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



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

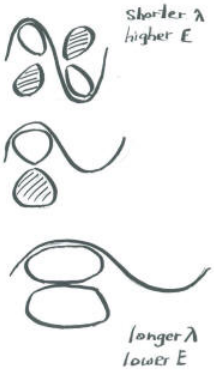
- parallel p orbitals can overlap to produce bonding and antibonding combinations.
- the resulting orbitals contain nodes along the bond axis.
- the electron density is found above and below the bond axis.
- this is called a p (pi) bond.

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

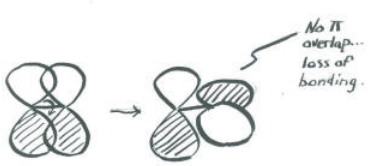


In a main group diatomic species like dinitrogen, one p orbital lying along the bond axis can engage in s bonding. The two p orbitals orthogonal to the bond axis can engage in p bonding. There will be both bonding and antibonding combinations.

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



An important consequence of the spatial distribution or "shape" of a p orbital is that it is not symmetric with respect to the bond axis. A s orbital is not affected when the atom at one end of the bond is rotated with respect to the other. A p orbital is affected by rotation. If one atom turns with respect to the other, the p orbital would have to stretch to maintain the connection. The orbitals would not be able to overlap, so the connection between the atoms would be lost.



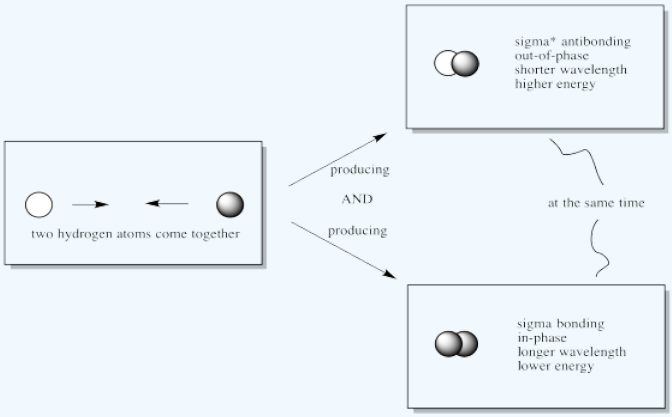
Exercise 13.5.1

When the 1s orbitals of two hydrogen atoms combine to form a hydrogen molecule, which molecular orbitals are formed?

Draw a picture.

Answer

When 2 atomic orbitals are combined, 2 molecular orbitals are formed: one in-phase bonding orbital and one out-of-phase antibonding orbital.



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Exercise 13.5.2

In-phase combinations of atomic orbitals give _____ orbitals.

Draw a picture

Answer

AIn-phase combinations of atomic orbitals give ***bonding*** orbitals.

Exercise 13.5.3

Out-of-phase combinations of atomic orbitals give _____ orbitals.

Draw a picture.

Answer

Out-of-phase combinations of atomic orbitals give ***antibonding*** orbitals.

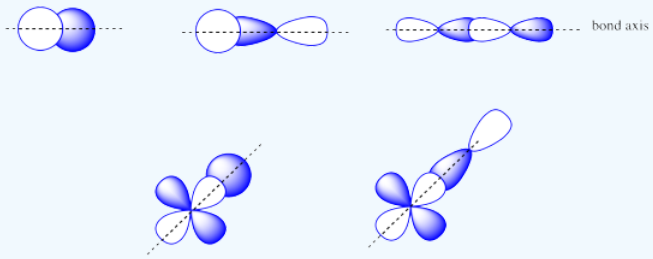
Exercise 13.5.4

The combinations of _____ atomic orbitals leads to σ orbitals.

Draw pictures.

Answer

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



Exercise 13.5.5

The combinations of _____ atomic orbitals leads to π orbitals.

Draw pictures.

Answer

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

Exercise 13.5.6

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

d. π
e. σ*

Answer

e) σ*

Exercise 13.5.7

Why can 1s orbital not interact with a 2s orbital?

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

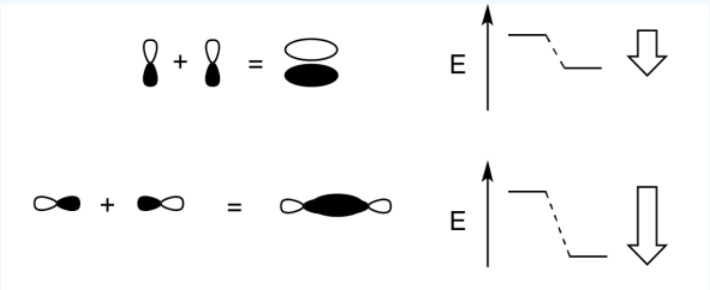
Answer

Li^+ and O^{2-} are more similar in size than K^+ and O^{2-}, so the bond between Li^+ and O^{2-} is stronger.

The energy difference between the 1s orbitals and 2s orbitals is too large, so they cannot interact. In order for orbitals to interact, the orbitals need to have the same symmetry, be in the same plane, and be similar in energy.

Exercise 13.5.8

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



Answer

When two parallel p orbitals combine out-of-phase, destructive intereference occurs.

There is a node between the atoms.

The energy of the electrons increases.

When two parallel p orbitals combine in-phase, constructive interference occurs.

There is no node between the atoms; the electrons are found above and below the axis connecting the atoms.

The energy of the electrons decreases.

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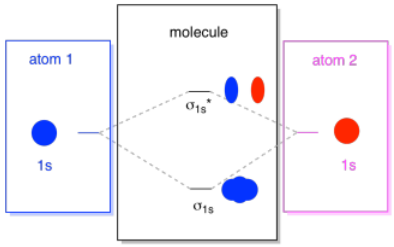
13.6: Assembling the Complete Diagram and Electron Population

So far, we have looked at the ways in which pairs of atomic orbitals could combine to form molecular orbitals -- to form bonds. Just as we think of there being a progression of atomic orbitals from lowest energy to highest (1s, 2s, 2p, 3s...), we can organize these molecular orbitals by order of their energy.

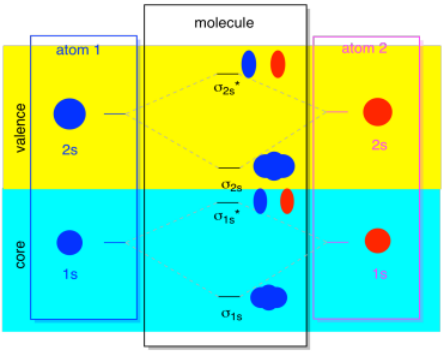
To a great extent, the order of molecular orbitals in energy can be considered to follow from the order of the atomic orbitals from which they are constructed. There are some departures from that rule, sometimes, but that's the simplest place to start. So, in a molecule, the lowest-energy molecular orbitals would be the ones formed from the lowest-energy atomic orbitals, the 1s orbitals.



What we see here is a molecular orbital interaction diagram. The middle of the diagram is just the molecular orbital energy diagram. It is analogous to the atomic orbital energy diagram (which goes 1s, 2s, 2p, 3s...). The order of energy so far is σ_{1s}, σ_{1s}*. The sides of the diagram just refer back to where those molecular orbitals came from, with dotted lines to guide you from one place to another. Altogether, the picture says that the 1s orbital on one atom and the 1s orbital on the other atom can combine in two different ways, producing the lower-energy, bonding σ_{1s} and the higher-energy, antibonding σ_{1s}*.

Note that we have not added any electrons to that molecular orbital energy diagram yet, but when we do, we will just fill them in from the bottom up, just like we would an atomic orbital energy diagram.

The next lowest set of atomic orbitals is the 2s level. These spherical orbitals would combine very much like 1s orbitals, and we would get a similar diagram, only at a slightly higher energy level.



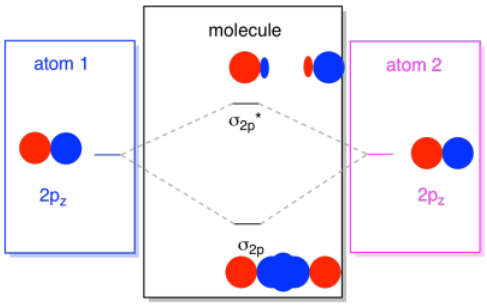
Most of the time, we aren't going to see both the σ_{1s} and the σ_{2s} displayed in the diagram. That's because if there are any 2s electrons, then those 1s electrons are really core electrons, not valence. They are buried a little deeper in the atom, and they don't play a very important role in bonding. Ignoring the core electrons is pretty common; if you recall, in atomic electron configurations we might write [He]$2s^2 2p^4$ instead of $1s^2 2s^2 2p^4$ for oxygen; we were ignoring the core. When we drew Lewis structures, we gave oxygen six electrons, rather than eight; we were ignoring the core.

In the context of MO, suppose we do have 2s electrons. That must mean that each atom has two 1s electrons of its own, for a total of four. When those four electrons are filled into the MO diagram from the bottom up, they will occupy both the bonding σ_{1s} and the antibonding σ_{1s}*. The effect of both those combinations being occupied is to cancel out the bonding; those two pairs of electrons remain non-bonding. So we can ignore them and we aren't really missing anything.

The 2s orbitals aren't the only ones in the second shell. There are also 2p orbitals. Remember, there are a couple of very different ways in which p orbitals can combine with each other, depending upon which axis they lie. If they do not lie parallel to each other -

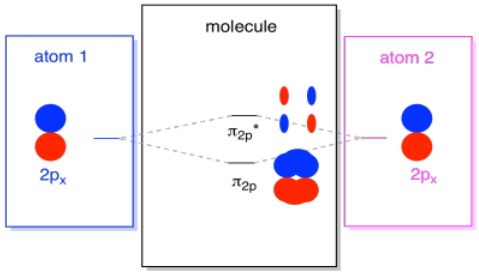
- that is, if they are perpendicular to each other, such as a p_x and a p_y -- then they cannot interact with each other at all. The p_z on one atom could interact with the p_z on the other atom, however, because they are parallel to each other.

Usually, we define the z axis as lying along the line between the two atoms we are looking at. Two p_z orbitals would lie along that axis, each with a lobe extending into the space between the atoms, and each with another lobe extending away, in the other direction



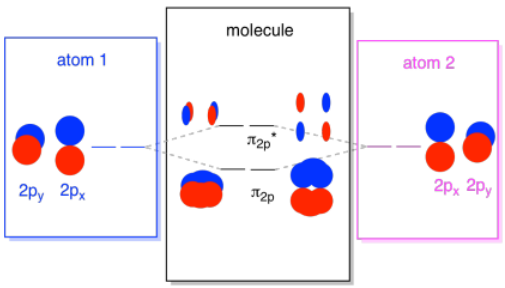
The resulting combinations are called σ because they do lie along the axis between the atoms (that's exactly what σ means, in terms of bonding). There is a σ combination, if the overlapping lobes are in phase with each other, and σ* combination, if those lobes are out of phase with each other. Because these new orbitals arise from the atomic 2p orbitals, we call them σ_{2p} and σ_{2p}*.

There are also those p orbitals that do not lie along the bond axis, or the axis between the two atoms. The p_x orbitals are perpendicular to the p_z orbitals we just looked at, and therefore perpendicular to the axis between the bonds. However, they are still parallel to each other, and they can still form combinations. These two orbitals would form an in-phase combination and an out-of-phase combination.

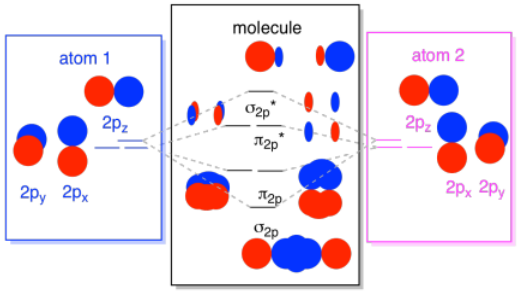


Note that the energetic separation between these two combinations is a little smaller that the gap between the σ_{2p} and σ_{2p}* levels. The difference is related to the degree of overlap between the atomic orbitals. The on-axis orbitals project strongly into the same space; they overlap a lot, and they interact strongly. The off-axis orbitals brush against each other, interacting less strongly, and resulting in smaller energetic changes. The gap between the π_{2p} orbital and π_{2p}* orbital is therefore much smaller than the one between the σ_{2p} and σ_{2p}* orbitals.

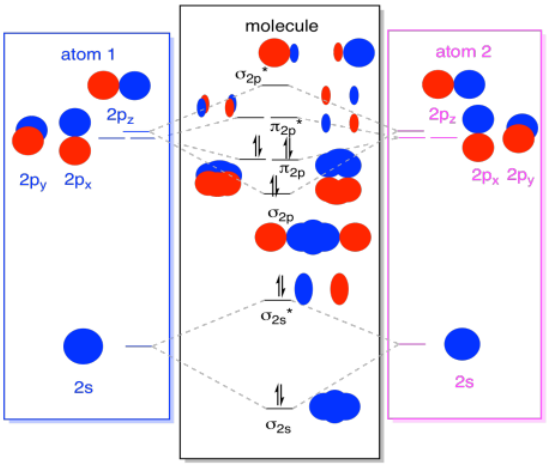
There are actually two of those off-axis p orbitals. In addition to the p_x set, we would have a p_y set. If the p_x set is in the plane of the screen, the p_y set has one orbital sticking out in front and one hidden behind. Nevertheless, the combinations between the two p_y orbitals are exactly the same as what we saw between the two p_x orbitals. They are just rotated into a perpendicular plane with respect to the p_x combinations.



We can put all of those 2p-based orbitals together in one diagram. It's starting to get a little more crowded, but this diagram is just a combination of the pieces we have already seen. Note that the p_x, p_y, and p_z atomic orbitals all start out at the same energy (we have stacked them here so that you can still see the correlation between the atomic and molecular orbitals). That means that the π_{2p} & π_{2p}^* orbitals will be "nested" between the σ_{2p} & σ_{2p}^* orbitals.



Finally, keeping in mind that the 2p orbitals are higher in energy than the 2s orbitals, we can combine those pictures into one diagram. Again, we have seen these individual pieces before; we are just assembling them now.

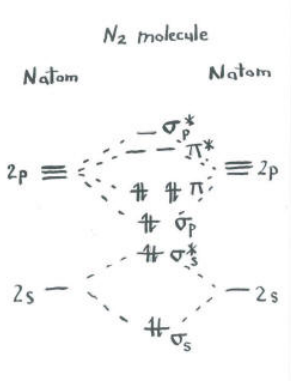


While we are at it, we can can add in the electrons. How? It's just the total number of valence electrons. For an example, we have used N_2. Each nitrogen has five valence electrons, for a total of ten, so we have just filled in ten electrons, starting at the bottom of the molecular orbital energy level diagram. If this were another molecule, such as F_2 or O_2, we would construct the overall diagram in a similar way, but just use a different number of electrons.

The orbital picture we have described above is really just a potential picture of the electronic structure of dinitrogen (and any other main group or p-block diatomic). We won't get a real picture of dinitrogen's structure until we populate these potential levels with electrons.

- Only the energy levels with electrons have an effect on the energy (and behavior) of the molecule.

In other words, the energy of the electrons determines the behavior of the molecule. The other energy levels are only possibilities that remain unfulfilled.



Think about the picture of dinitrogen.

- Each nitrogen has five valence electrons.
- There are a total of ten electrons.
- Two each go into the s_s bonding and s_s^* antibonding levels. Remember, we kept these separate from the p set as a simplification.
- Two each go into the s_p bonding and each of the p bonding levels.

The remaining orbitals (s_p^* antibonding and each of the p^* antibonding levels) are unoccupied. These are imaginary levels that do not play a role in determining the energy of dinitrogen. In a real molecular orbital calculation, the electrons in these levels would contribute to the overall energy of the molecule.

We get additional information from this picture. For example, we can see the bond order in dinitrogen.

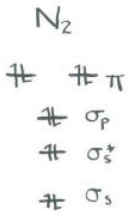
- Bond order is just the number of bonds between a pair of atoms.
- The bond order is one of several factors that influences the strength of the covalent bond.
- The higher the bond order, the more electrons are shared between the atoms, and the stronger the bond.

In dinitrogen, the s_s bonding s_s^* antibonding levels cancel each other out. One pair is lower in energy than it was in the atom, but the other is higher. There is no net lowering of energy. These electrons do not contribute to a nitrogen-nitrogen bond. These are non-bonding electron pairs.

The six electrons in the s_p bonding and the p bonding levels, however, represent a decrease in energy from the energy levels in the free nitrogen atoms. These three, low-energy pairs of electrons indicate three bonds between the nitrogen atoms.

Remember, we have made some short-cuts in this picture, and a real molecular orbital calculation could give slightly different results. Nevertheless, it would still reveal a bond order of three as well as two non-bonding electron pairs.

In addition, sometimes molecular orbital pictures are shown in different ways. A molecular orbital interaction diagram shows how atomic or molecular orbitals combine together to make new orbitals. Sometimes, we may be interested in only the molecular orbital energy levels themselves, and not where they came from. A molecular orbital energy level diagram just shows the energy levels in the molecule. Frequently, but not always, energy level diagrams are shown without any pictures of the orbitals, in order to focus attention on the energy levels, which in a fundamental way are the most important part of the picture. Furthermore, because only the occupied energy levels actually contribute to the energy of the molecule, sometimes the higher-energy, unoccupied orbitals are left out of the picture.



Very often the results of molecular orbital calculations reinforce what we would predict from Lewis structures. If you draw a Lewis structure of dinitrogen, you will also predict a triple nitrogen-nitrogen bond. The chief advantage of molecular orbital theory is that

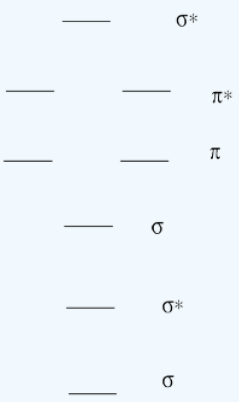
it allows quantitative prediction of energy when we do a real calculation on a computer. In addition, it is important to realize that there is no real reason for the octet rule unless we consider quantum mechanics. Lewis structures are founded on an empirical observation that electrons form pairs and octets, without attempting to explain why. Molecular orbital theory takes some fundamental relationships from physics and applies them to very complicated molecules with very good success. Just by knowing the number of electrons in the molecule, and by knowing approximately where the nuclei are located in the structure, molecular orbital calculations give very useful information about energy. In addition, in more complicated cases than N_2, these calculations can even correct our first guess about molecular geometry and where the bonds are located.

Exercise 13.6.1

A Molecular Orbital Diagram for a diatomic molecule (two atoms) always has the same basic pattern.

- Draw a picture of the levels.
- Label each level with σ, σ*, π, π*

Answer



Exercise 13.6.2

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

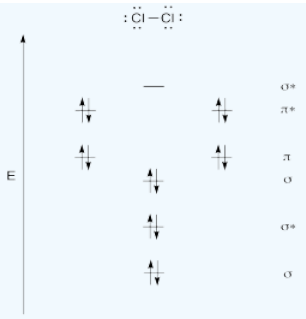
Answer

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

Exercise 13.6.3

Construct a qualitative molecular orbital diagram for chlorine, Cl_2. Compare the bond order to that seen in the Lewis structure (remember that an electron in an antibonding orbital cancels the stabilization due to bonding of an electron in a bonding orbital).

Answer

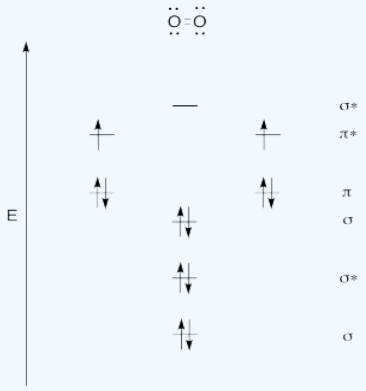


Bond Order = 1
MO diagram matches the Lewis structure

Exercise 13.6.4

a. Construct a qualitative molecular orbital diagram for oxygen, O_2.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?
d. Compounds that have all of their electrons paired are referred to as diamagnetic. Those with unpaired electrons are referred to as paramagnetic. Paramagnetic materials are attracted by a magnetic field, but diamagnetic things are not. How would you expect molecular oxygen to behave?

Answer

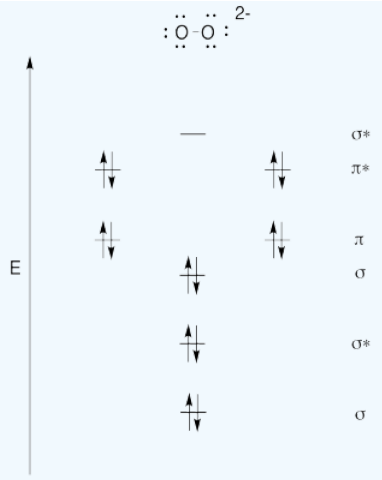


Bond Order = 2
MO diagram indicates two unpaired electrons and therefore does not match the Lewis structure. Based on the MO diagram oxygen would be paramagnetic and would be attracted to a magnetic field

Exercise 13.6.5

a. Construct a qualitative molecular orbital diagram for peroxide anion, O_2^{2-}.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?
d. Based on molecular orbital pictures, how easily do you think dioxygen could be reduced to peroxide (through the addition of two electrons)?

Answer

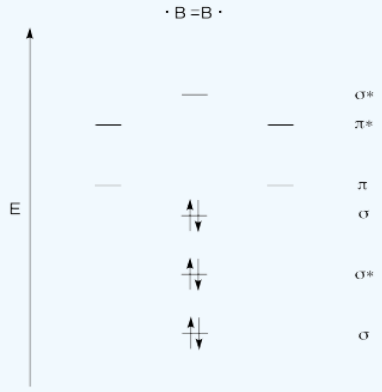


Bond Order = 1
MO diagram matches the Lewis structure. Both predict a Bond Order of 1 and 6 lone pairs of electrons. The addition of two electrons to O_2 to O_2^{2-} would be possible.

Exercise 13.6.6

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

Answer

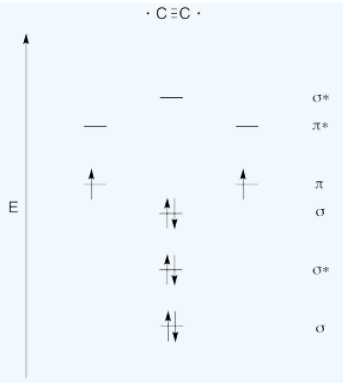


Bond Order = 1
Boron-Boron bonding should be possible

Exercise 13.6.7

a. Construct a qualitative molecular orbital diagram for dicarbon, C_2.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?

Answer

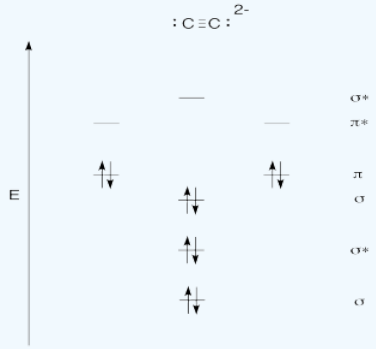


Bond Order = 2
MO diagram does not match the Lewis structure.
However, the MO diagram does concur about the
2 unpaired electrons.

Exercise 13.6.8

a. Construct a qualitative molecular orbital diagram for acetylide anion, C_2^{2-}.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?
d. Based on molecular orbital pictures, how easily do you think dicarbon could be reduced to acetylide (through the addition of two electrons)?

Answer



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

Exercise 13.6.9

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

Answer

Exercise 13.6.10

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

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

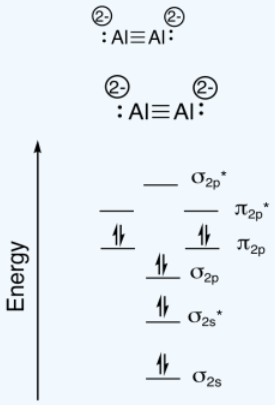
Answer

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

b) Al

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

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



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

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13.7: Experimental Evidence for Molecular Orbital Results

The molecular orbital picture of dioxygen differs from the Lewis picture. Both models predict an oxygen-oxygen double bond, but one model suggests unpaired electrons whereas the other indicates an electron-paired system. Often, there is experimental evidence available to check the reliability of predictions about structure. These data include measurements of bond lengths and bond strengths as well as magnetic properties.

Bond dissociation energy data tells us how difficult it is to separate one atom from another in a molecule. Bond order is one of the factors that influences bond strength. Thus, measuring a bond dissociation energy is one way to confirm that dioxygen really does contain an oxygen-oxygen double bond.

First, we need something to compare it to. Peroxides (such as hydrogen peroxide, H_2O_2, or sodium peroxide, Na_2O_2) probably contain oxygen-oxygen single bonds, according to their Lewis structures. These bonds are relatively weak, costing about 35 kcal/mol to break. In contrast, the bond in dioxygen costs about 70 kcal/mol to break. Its bond is about twice as strong; it is a double bond.

- Bond dissociation energies can be used to determine how many bonds there are between two atoms.

Bond dissociation energies can be complicated to measure. They require a comparison of energy changes in numerous chemical reactions so that the energy change resulting from cleavage of a specific bond can be inferred. In contrast, infrared absorption frequencies are easy to measure. They simply require shining infrared light through a sample and measuring what frequencies of the light are absorbed by the material. (A related technique, Raman spectroscopy, gives similar information by measuring subtle changes in the frequency of laser light that is scattered off a sample). The frequencies absorbed depend on what bonds are present in the material. These frequencies vary according to two basic factors: the weights of the atoms at the ends of the bond and the strength of the bond between them. The stronger the bond, the higher the absorption frequency.

Peroxides absorb infrared light at around 800 cm^{-1} (this unusual frequency unit is usually pronounced "wavenumbers"). Dioxygen absorbs infrared light around 1300 cm^{-1}. Since the atoms at the ends of the bond in both peroxide and dioxygen are oxygens, we can be sure that this difference in frequency is not due to a difference in mass. It is due to a difference in bond strength. The bond in dioxygen is much stronger than the O-O bond in peroxide, because the former is a double bond and the latter is a single bond.

- Vibrational spectroscopies (IR and Raman spectroscopy) can give information about the bond order between two atoms.

A third measure of bond order is found in bond length measurements. The more strongly bound two atoms are, the closer they are together. An O=O bond should be shorter than an O-O bond. Bond lengths can be measured by microwave spectroscopy (usually for gas-phase molecules), in which frequencies absorbed depend on the distance between the molecules. Alternatively, bond lengths can be measured by x-ray crystallography. X-rays can be diffracted through crystals of solid materials. The interference pattern that is produced can be mathematically decoded to produce a three-dimensional map of where all the atoms are in the material. The distances between these atoms can be measured very accurately.

The O-O bond in peroxides are about 1.49 Angstroms long (an Angstrom is $10^{-10}\,m$; this unit is often used for bond lengths because it is a convenient size for this task. Covalent bonds are generally one to three Angstroms long). The O-O bond in dioxygen is about 1.21 A long. The O-O bond in dioxygen is shorter and stronger than in a peroxide.

- Bond length data provides insight into the bond order.

In addition to bond order, there is the question of electron pairing in dioxygen. The Lewis structure suggests electrons are paired in dioxygen. The molecular orbital picture suggests two unpaired electrons.

Compounds with paired electrons are referred to as diamagnetic. Those with unpaired electrons are called **paramagnetic**. Paramagnetic substances interact strongly with magnetic fields.

It turns out that oxygen does interact with a magnetic fields. A sample of liquid-phase oxygen can be held between the poles of a magnet. Oxygen has unpaired electrons. This finding is consistent with molecular orbital theory, but not with simple Lewis structures. Thus, MO theory tells us something that the Lewis picture cannot.

- Magnetic information, and measurements of magnetism, give us experimental evidence of spin states. We can tell if electrons are paired, unpaired, and how many unpaired spins there are.

A final important source of experimental data is photoelectron spectroscopy. Photoelectron spectroscopy gives information about the electron energy levels in an atom or compound. In this technique, gas-phase molecules are subjected to high-energy

electromagnetic radiation, such as ultraviolet light or X-rays. Electrons are ejected from various energy levels in the molecule, and the binding energies of electrons in those levels is determined. Thus, photoelectron spectroscopy provides verification for exactly the sort of information that quantitative molecular orbital calculations are designed to deliver.

- Photoelectron spectroscopy tells how much energy is needed to remove electrons from various energy levels in a molecule. This technique gives us an accurate experimental picture of the energy levels that we predict with molecular orbital calculations.

Exercise 13.7.1

In the previous section, you were asked to draw MO diagrams for some molecules. Determine whether the molecules in problems MO 6.3-6.8 are paramagnetic or diamagnetic.

Answer

From MO6: 3. Diamagnetic (no unpaired electrons); 4. Paramagnetic; 5. Diamagnetic; 6. Diamagnetic; 7. Paramagnetic; 8. Diamagnetic

Exercise 13.7.2

Use a MO diagram to determine which species in the following pairs will have the longer bond. Give an explanation for your choice.

a. N_2 or N_2^+
b. N_2 or N_2^-

Answer a:

N_2^+. From the MO diagrams, N_2^+ has one less bonding electron. Thus, the bond order will be lower and the bond will be longer than in N_2.

Answer b:

N_2^-. From the MO diagrams, N_2^- has one more antibonding electron. Thus the bond order will be lower and the bond will be longer than N_2.

Exercise 13.7.3

Use a MO diagram to determine which species in the following pairs will have the stronger bond. Give an explanation for your choice.

a. O_2 or O_2^+
b. O_2 or O_2^-

Answer a:

O_2^+ . From the MO diagram, O_2^+ has one less antibonding electron. Thus the bond order will be higher and the bond will be stronger than in O_2.

Answer b:

O_2. From the MO diagram, O_2 has one less antibonding electron. Thus the bond order will be higher and the bond will be stronger than in O_2^-.

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13.8: Symmetry and Mixing

At first, we approximated and said that only orbitals of the same kind can interact with each other: s orbitals with s orbitals, p_x orbitals with p_x orbitals, and so on. One of the qualitative differences between a real MO calculation and our scrap-paper approach is that mixing does occur between different kinds of orbitals. However, restrictions still apply.

Orbital interactions are governed by symmetry. Without taking an entire course in Group Theory (the branch of mathematics that deals with symmetry), we can learn a little bit about symmetry as we need it.

One of the most basic aspects of molecular symmetry applies to diatomic molecules. That element is symmetry about the bond axis. If a molecule is spun around its bond axis -- as if the two atoms are the two wheels on an axle of a wagon or a car -- does the orbital change its orientation?

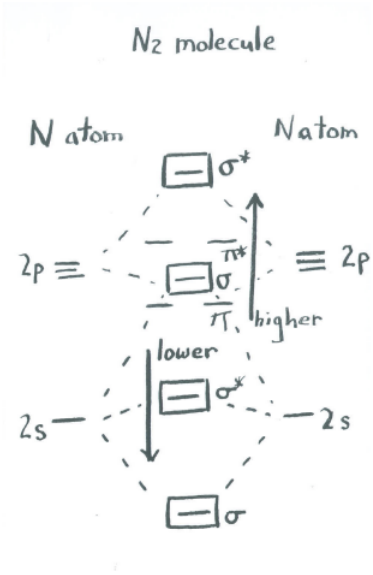
- An s orbital is so symmetric that it looks the same from any direction. No matter how you spin it, it looks the same. In a diatomic molecule, an s orbital is symmetric with respect to rotation about the bond axis.

- What about p orbitals? Suppose the bond axis is the z axis. Rotation about the z axis produces no change in orientation of a p_z orbital. The orbital spins but does not move through space.
- Rotation about the z axis does produce a visible change in orientation of a p_x orbital. The orbital spins like a propeller around the axis.

Rotation about the z axis does produce a visible change in orientation of a p_y orbital. The orbital spins like a propeller around the axis.

Our picture of main group diatomics changes slightly with this news. The p bonding orbitals remain unchanged. However, the s bonding orbitals share axial symmetry. That means that the s bonding orbitals, far from keeping completely separate from each other, actually mix together in some cases. That means there can be an orbital that is composed of an s and p_z orbital from one atom as well as an s and p_z orbital from the other. The only restriction is that, because four atomic orbitals are allowed to mix, four new molecular orbitals must be produced.

- As a result, in diatomics, an s orbital shares an element of symmetry with one p orbital, but not with the others.
- The rules of mathematics and quantum mechanics allow s orbitals in diatomics to interact with one p orbital with which it shares symmetry, but not with the other two.



Another way of thinking about this mixing effect is to take the molecular orbital picture we already made for dinitrogen and then say that the sigma bonding orbitals can interact with each other. That means they can push each other up or down in energy, mixing together to create new combinations with new energies. The extent of this mixing varies across the periodic table.

For main group diatomics like N_2, the effect is to lower the energy of the lower sigma orbitals (related to the atomic s levels) and raise the energy of the higher sigma orbitals (related to the atomic p levels). The result is that the second-highest sigma orbital is shifted slightly above the energy of the pi levels, rather than being slightly below them. This does not change the overall conclusions very much, but it is a favorable interaction because the lower-lying sigma levels, which are occupied by electrons, move to lower energy.

Attribution

- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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13.9: When Different Atoms Bond Together

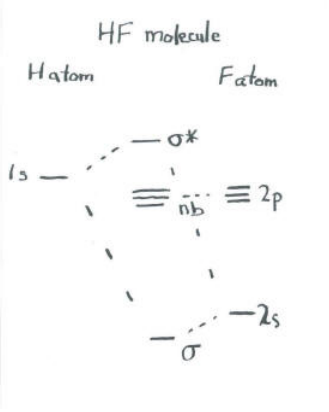
Two different atoms from the main group often bond together to make diatomic molecules. In most cases, the molecular orbital picture does not change very much from what we have already seen.

From a Lewis point of view, some very simple compounds include the hydrogen halides. For example, HF contains a hydrogen bonded to a fluorine.

A molecular orbital picture of HF could involve an s orbital on hydrogen interacting with an s orbital on fluorine. It may be that the three p orbitals on fluorine stay out of the way, do not interact with the hydrogen, and remain unchanged in the molecule. In that case, we are dealing with a picture of two s orbitals combining, as in dihydrogen.

The only difference is in the starting energy levels of the atomic electrons. The electrons in fluorine are at lower energy than the electron in hydrogen. Thus, the molecular orbital picture is skewed, with one side of the diagram at lower energy than the other.

- The energetic differences of the two atoms are shown in the molecular orbital interaction diagram.



There is a physical interpretation for this lopsidedness. Notice that the bonding orbital is closer in energy to fluorine than it is to hydrogen. Often, energetic similarity correlates with structural similarity. We think of these bonding electrons as being physically closer to the fluorine as well. In other words, the electrons in this bond are not equally shared, but are held more closely by fluorine.

- More energetic similarity to one atom implies electrons are found closer to that atom.

This idea is consistent with our ideas about bonding between dissimilar atoms. We would think of the H-F bond as a polar, covalent one.

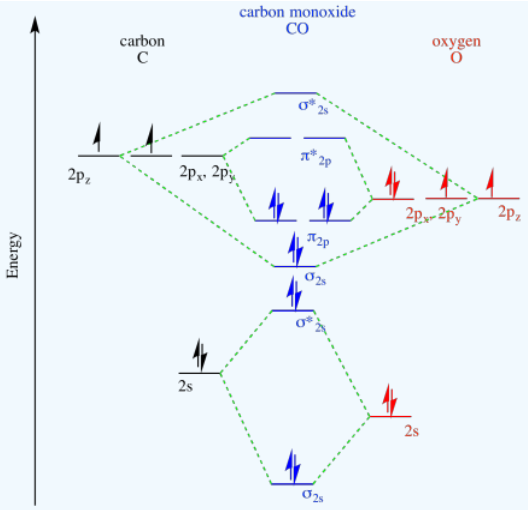
The idea that fluorine's electrons are at lower energy may be confusing. A 1s electron in fluorine is certainly at lower energy than a 2s or 2p electron in fluorine. However, a 1s electron in hydrogen is not necessarily at a lower energy than a 2s or 2p electron in fluorine. All the electrons in fluorine are at lower energy than the electron in hydrogen because fluorine has a much higher nuclear charge, with relatively little shielding from its own 1s electrons. Fluorine has a high Z_{eff}, as evinced by its high electron affinity (high attraction for more electrons) and high ionization potential (large amount of energy needed to strip an electron away).

Exercise 13.9.1

Construct molecular orbital interaction diagrams for the following diatomic molecules. In each case, what is the bond order? Is the compound diamagnetic or paramagnetic?

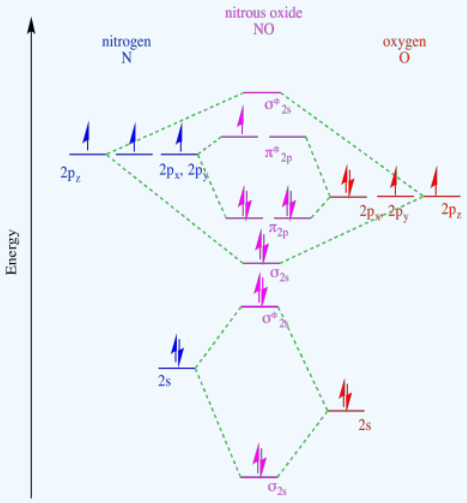
a. carbon monoxide, CO.
b. nitrous oxide, NO.
c. hypochlorite ion, ClO^-.

Answer a



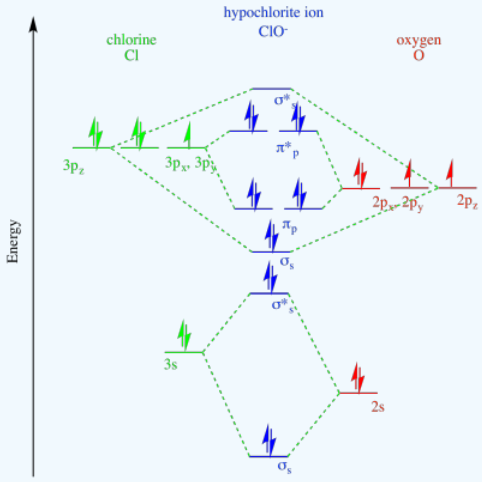
diamagnetic; bond order = 3 (3 net pairs bonding)

Answer b



paramagnetic (one electron unpaired);
bond order = 2.5 (2 net pairs bonding; third bonding pair offset by one electron antibonding)

Answer c



Note that the hypochlorite anion has one additional electron to make it negative.
diamagnetic; bond order = 1 (1 net pair bonding)

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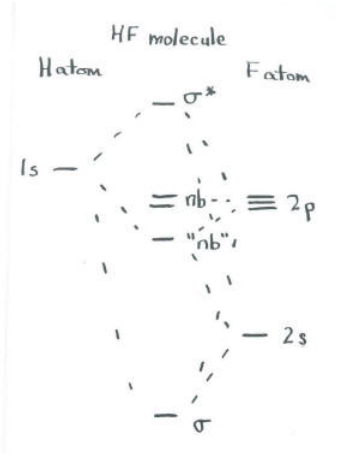
13.10: Another Complication in HF- Orbital Mixing

Earlier, we talked about the fact that axially symmetric orbitals can mix together to produce new combinations. In HF, we looked at the overlap of the 2s orbital on fluorine with the 1s orbital on hydrogen. However, one of the 2p orbitals can lie along the bond axis and share axial symmetry with the hydrogen 1s orbital.

We will call this fluorine orbital the $2p_z$ orbital. We could just as well label it p_x or p_y, but many people refer to the p orbital along the bond axis as the p_z. Note that the 2p orbitals that are perpendicular to the bond axis can't interact with the hydrogen 1s orbital. Because the bond axis crosses the p orbital at a node, where the p orbital changes phase, the hydrogen atom can't form either an in-phase or out-of-phase combination with this p orbital. It would actually be in-phase with one part of the orbital and out-of-phase with the other. Instead, these orbitals simply do not interact.

- The hydrogen 1s can combine with the fluorine 2s and the fluorine $2p_z$.
- Now there are three orbitals that may combine. They will produce three new orbitals.
- We should consider these three orbitals together. What different combinations can they make?
- The orbitals could all be in-phase -- that is, the 1s of hydrogen is in-phase with the 2s of fluorine, and also in-phase with the part of the $2p_z$ that overlaps with it.
- This will be a low-energy, bonding combination.
- The orbitals could be completely out-of-phase. The 1s of hydrogen is out-of-phase with the 2s of fluorine, and also out-of-phase with the part of the $2p_z$ that overlaps with it.
- This will be a high-energy, antibonding combination.
- 

The third combination is a little more subtle. The other possibility is that the 1s orbital of hydrogen is in-phase with one orbital of fluorine, but out-of-phase with the other. However, that means it could be in-phase with the 2s but out-of-phase with the $2p_z$, or vice versa. That means there are two more combinations, for a total of four. However, since we are using only three atomic orbitals, we can produce only three molecular orbitals. These two possible combinations must somehow be mathematically reduced to one.

Once again, mixing that occurs based on symmetry has some quantitative effects on the energies of the electrons, but in this case the qualitative effect is a subtle change in the ordering of energy levels.

- A third combination will be partially bonding and partially antibonding.
- This combination will be somewhat like a non-bonding orbital (although its exact energy may be slightly stabilized or destabilized with respect to the original atoms).

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13.11: Geometry and Orbital Contribution to Bonding

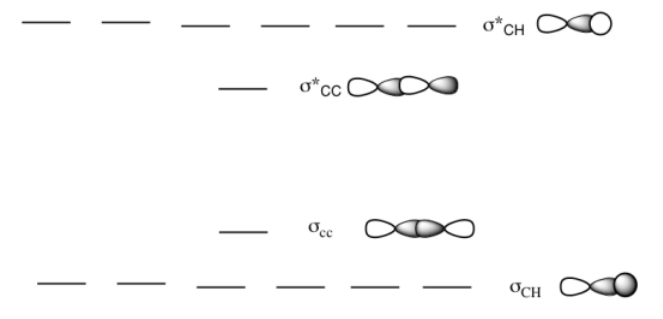
What if a molecule had three or more atoms in it? We can no longer draw a simple molecular orbital interaction diagram, in which we show on atom on each side and the molecular results in the middle, because we don't have two atoms coming together to share electrons.

Instead, we look at slightly simplified MO diagrams in which we keep track of the result all those atomic orbitals coming together to make new orbitals. At a very simple level, the qualitative result is always the same and can be roughly predicted based on the Lewis structure.

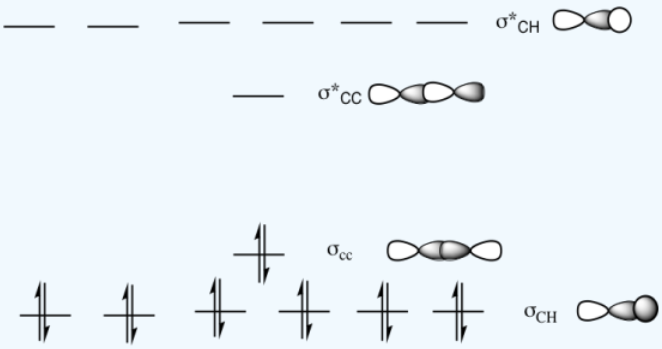
- There is a bonding MO for every bond you see in the Lewis structure. These levels are low on the diagram.
- Every bonding MO has a corresponding antibonding MO. These levels are high on the diagram.
- Lone pairs in Lewis structure correspond to non-bonding orbitals. These levels are intermediate on the diagram.
- The diagram is populated by the same number of electrons that you see in the Lewis structure.

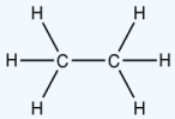
Exercise 13.11.1

a) This is the MO diagram for ethane.
Draw a Lewis structure of ethane.
Populate the electrons into the MO diagram.

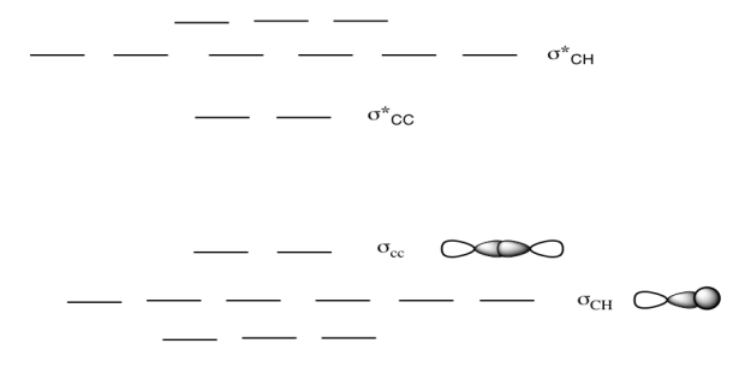


Answer a

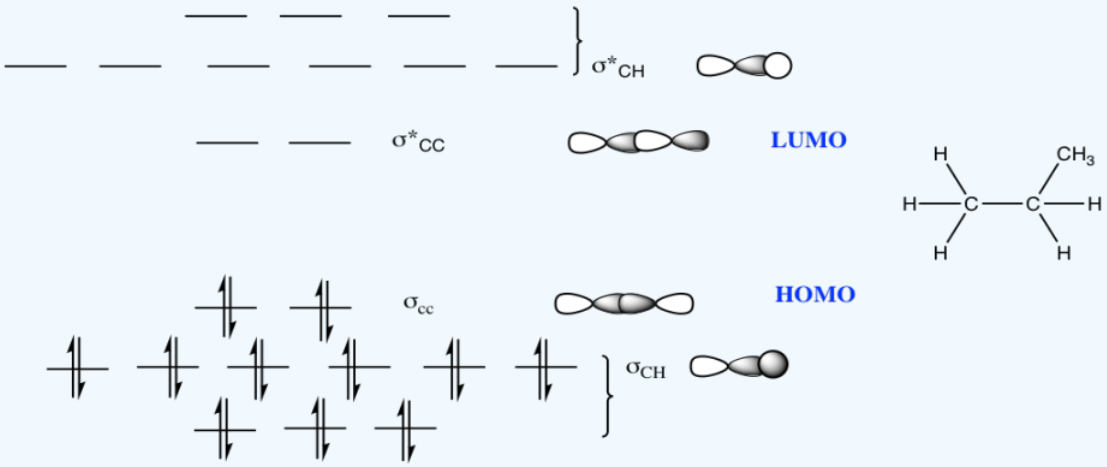




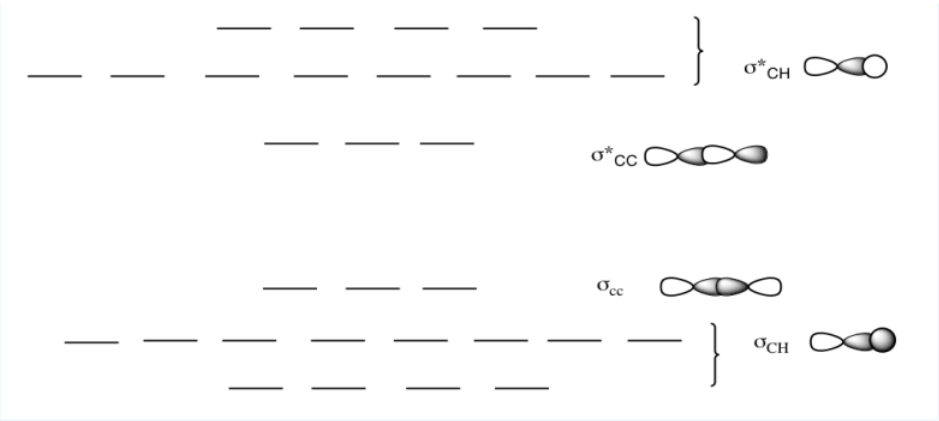
b) This is the MO diagram for propane.
Draw a Lewis structure of propane.
Populate the electrons into the MO diagram.
Add in the missing MO cartoons for the different levels.
Label the HOMO and LUMO.



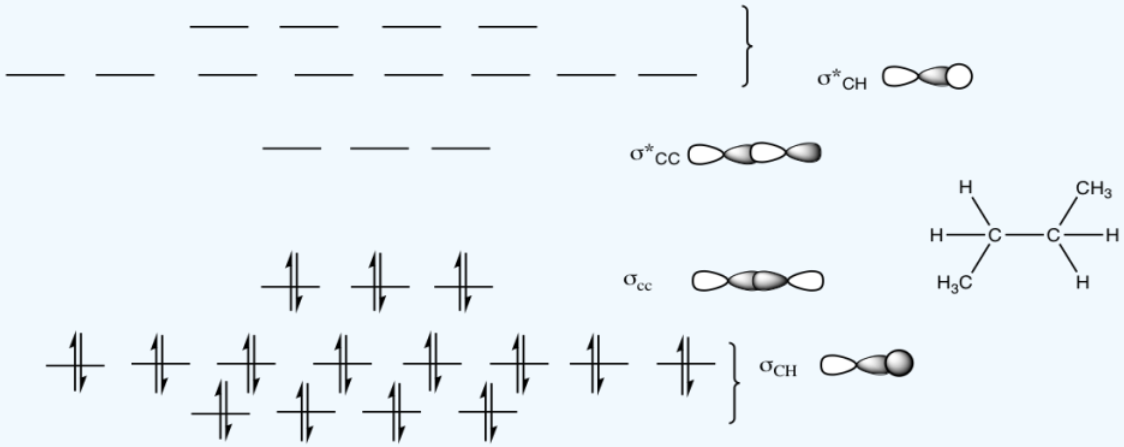
Answer b



c) This is the MO diagram for butane.
Draw a Lewis structure of butane.
Populate the electrons into the MO diagram.
What happpens to the MO diagram as the alkane chain length increases?



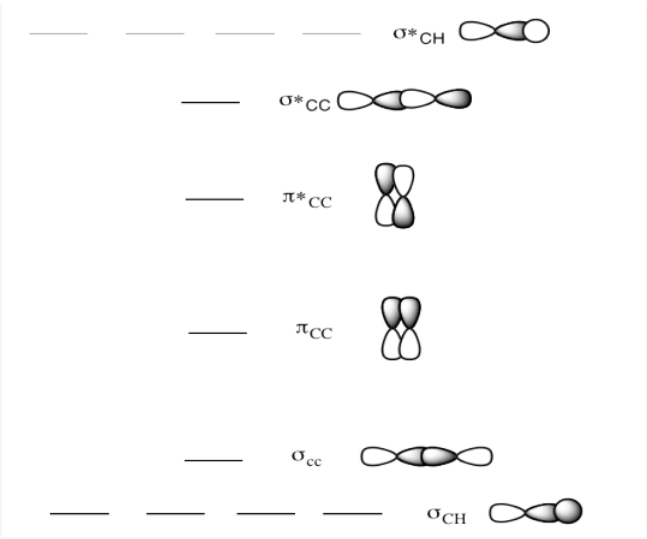
Answer c



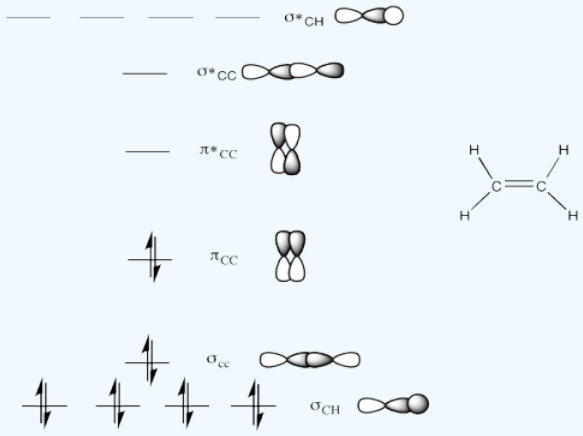
The number of orbitals = the number of bonds and the number of antibonds (thus twice as many orbitals as you would draw in a lewis structure.

Exercise 13.11.2

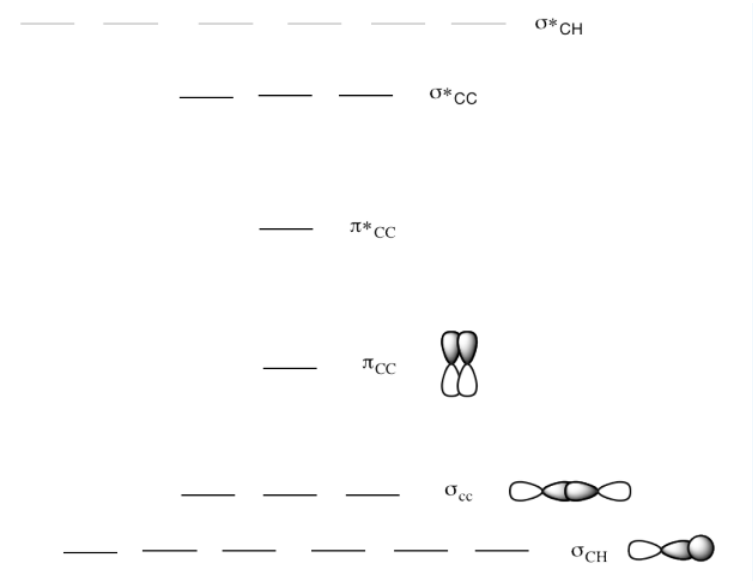
a) This is the MO diagram for ethene.
Draw a Lewis structure of ethene.
Populate the electrons into the MO diagram.



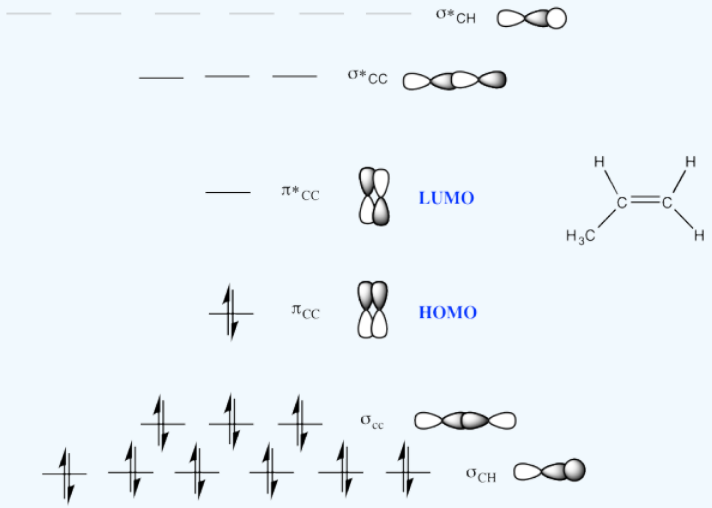
Answer a



b) This is the MO diagram for propene.
Draw a Lewis structure of propene.
Populate the electrons into the MO diagram.
Add in the missing MO cartoons for the different levels.
Label the HOMO and LUMO.



Answer b



c) This is the MO diagram for 1-butene.
Draw a Lewis structure of 1-butene.

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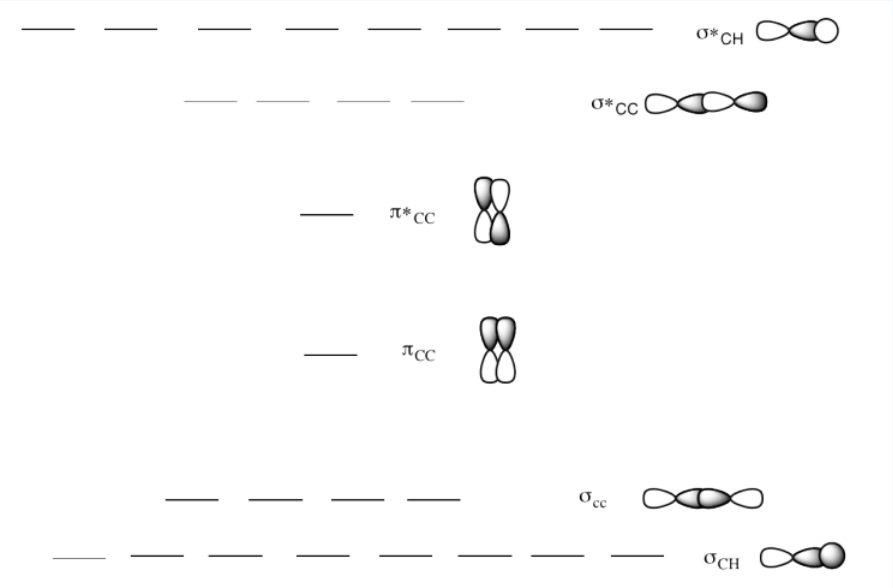
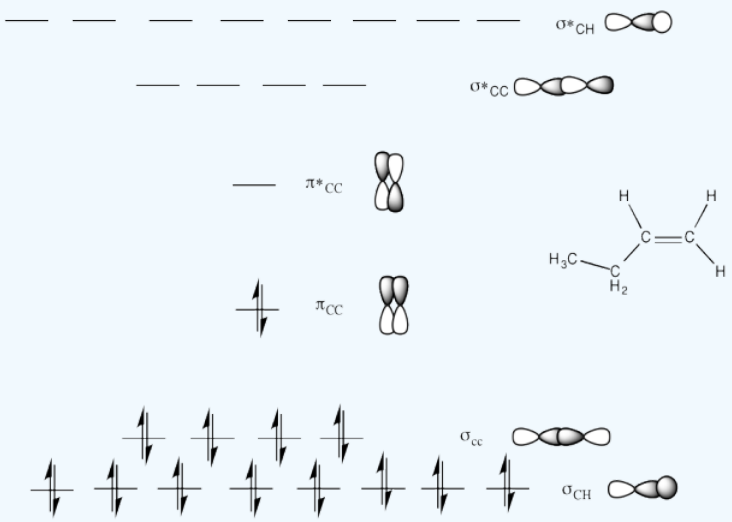
Populate the electrons into the MO diagram.
What happpens to the MO diagram as the alkane chain length increases?

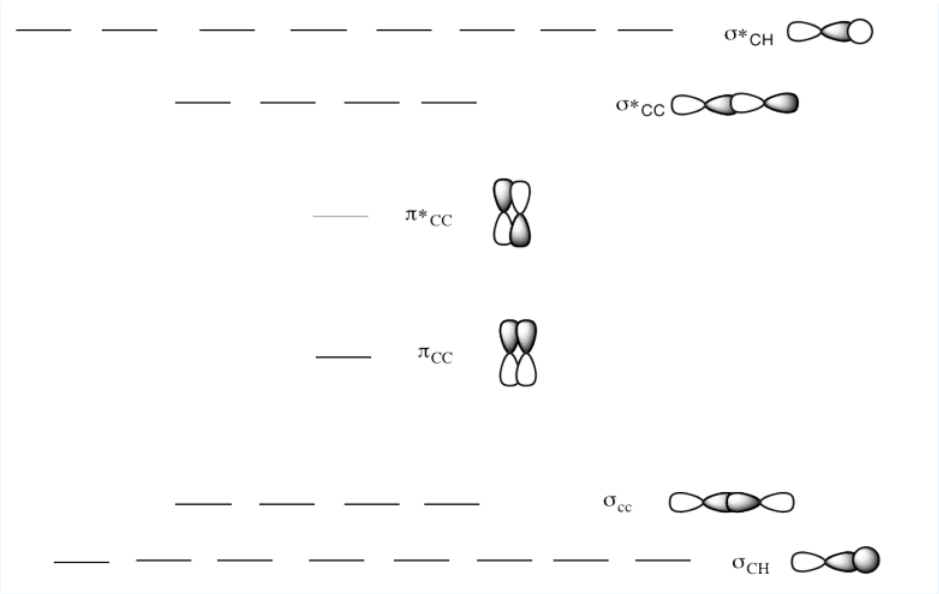


Answer c

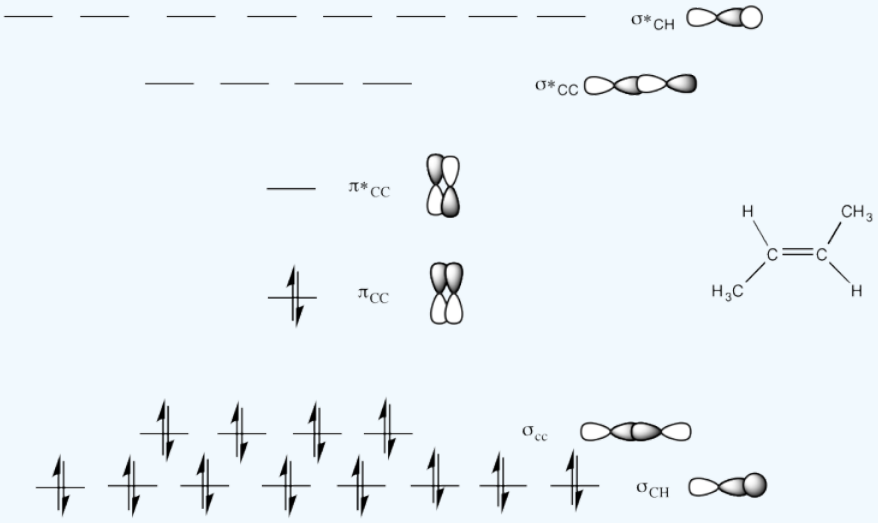


The number of orbitals = the number of bonds and the number of antibonds (thus twice as many orbitals as you would draw in a lewis structure.

d) This is the MO diagram for 2-butene.
Draw a Lewis structure of 2-butene.
Populate the electrons into the MO diagram.
Does the location of the pi bond change the MO diagram?

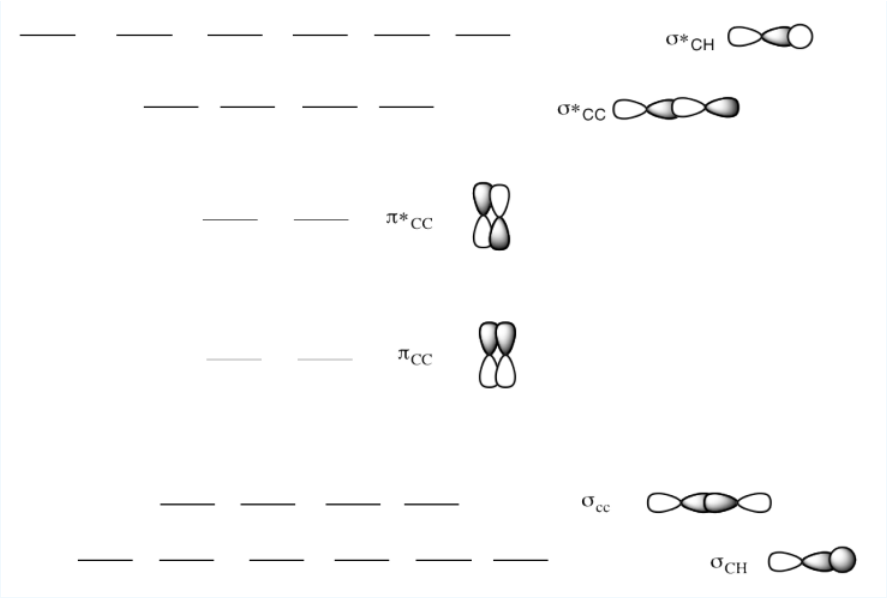


Answer d

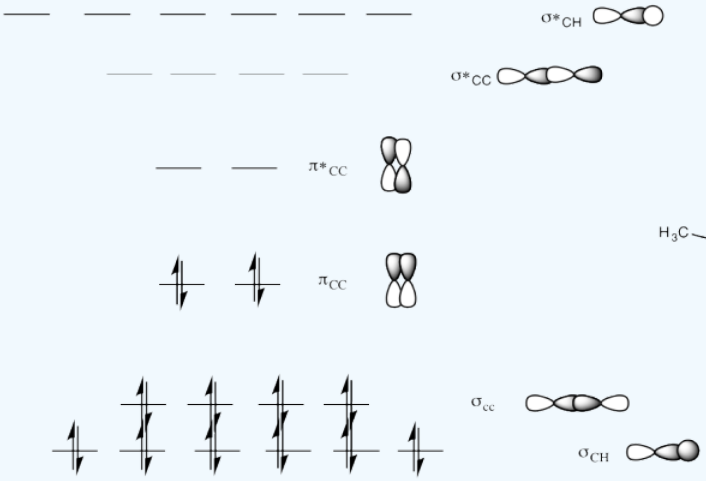


Location of pi bond makes little to no difference to the MO pattern.

e) This is the MO diagram for 1-butyne.
Draw a Lewis structure of 1-butyne.
Populate the electrons into the MO diagram.
How does an alkyne change the MO diagram?



Answer e

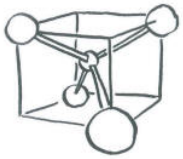


It results in the addition of another pi bond with approximately the same energy level.

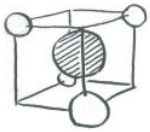
Methane is a moderately small molecule. Its Lewis structure is pretty easy to draw, with a carbon in the middle bonded to four hydrogens. Trying to find the interactions of the hydrogen 1s orbitals with the orbitals on carbon could be challenging. However, molecular orbital calculations generally start with a good guess at the geometry of the structure.

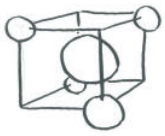
In quantitative calculations, that starting geometry is often modified after the energy of the molecule has been calculated. A long series of iterative calculations are done, changing bond lengths or bond angles each time, until the geometry with the lowest possible energy has been found. If this geometry has the lowest energy, then it is probably the shape that the molecule would really adopt in nature. In fact, it is assumed in quantum chemistry that if a lower energy structure can be found, it is always a more accurate picture of the real molecule (assuming no mistakes have been made in the calculation).

Since the carbon in methane has four groups attached to it, we can be pretty sure that the carbon is tetrahedral.



We will assume the four hydrogens are arranged at the corners of a tetrahedron around the central carbon. Overlap with the carbon 2s orbital is easy to see, because the s orbital can overlap with neighbors in all directions. Of course, there could be an in-phase combination and an out-of-phase combination.

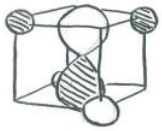


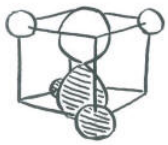


The complicated part arises when we want to introduce the carbon electrons and have them interact with the hydrogens. There is no universal orientation of p orbitals. Which way should they point?

In principle, it does not matter too much what direction we choose for the p orbitals. We should eventually end up with the same conclusions in the end. However, things may get extremely complicated and mistakes are likely to occur if we don't choose an orientation that makes the interactions simple to see. Since it does not matter which way the p orbitals are pointing, we should choose a direction that makes the calculation easiest.

- In a tetrahedron, the four corners point to alternating corners of a cube.
- The hydrogen atoms are in alternating corners of an imaginary cube around the carbon atom.
- The simplest way to align the p orbitals is to have them pointing at the faces of the cube.





Orienting the p orbitals this way simplifies things a lot. It means each lobe of each p orbital is directed at a space (on the face of a cube) in between two hydrogen atoms (on the opposite corners of the face). The other lobe of the same p orbital is directed at a space (on the opposite face of the cube) in between the other two hydrogen atoms (on the opposite corners of that face). The same is true for each p orbital, but they point at different faces and they interact with different combinations of the same four hydrogens.

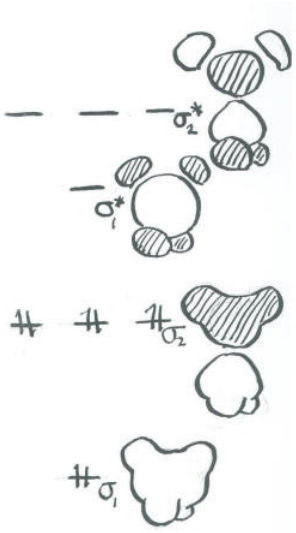
As a result of this choice, there are really only a few interactions to consider in methane.

- The carbon 2s orbital can be either in phase or out of phase with the entire group of hydrogen orbitals. That makes two combinations.
- The carbon 2p orbitals can be either in phase or out of phase with their adjacent hydrogen atoms. With three p orbitals, that makes six more combinations.
- Eight atomic orbitals combine to make eight molecular orbital combinations.

Note that here the hydrogen atoms are often treated as being in phase with each other, or at least pairs of them are. This assumption simplifies the calculation and cuts down on the number of non-allowed combinations (i.e. combinations that produce the total number of orbitals over eight).

Organizing these combinations in terms of energy:

- The carbon 2s + H in-phase combination is entirely bonding. It is very low in energy.
- The carbon 2s - H out-of-phase combination is entirely antibonding. It is very high in energy.
- The carbon 2p + H in-phase combinations are mostly bonding. However, there is a node through the middle of the molecule owing to the node in the p orbital. As a result, the two hydrogens adjacent to one lobe are out of phase with the two hydrogens on the other. This combination is medium-low in energy.
- The carbon 2p - H out-of-phase combinations is highly antibonding. There is a node through the middle of the molecule owing to the node in the p orbital. There are also nodes between the p orbitals and the hydrogen s orbitals. This orbital has the most nodes through the structure and therefore corresponds to the shortest wavelength and highest energy.



In general, this idea that the geometry around an atom determines what atomic orbitals are needed to form direct (sigma) bonds with its neighbors is closely tied to hybridization. That's the idea that s and p orbitals in the same shell will need to work together to bond to neighbouring atoms. In molecules, we sometimes blur the distinction between the ones that are needed to form this set of bonds, and refer to them instead as "hybrids". Hybridization is closely tied to the geometry of the central atom, so much so that the terms, geometry and hybridization, are occasionally used interchangeably.

- linear geometry corresponds to sp hybridization
- trigonal planar geometry correxponds to sp^2 hybridization
- tetrahedral geometry corresponds to sp^3 hybridization

Exercise 13.11.3

Construct a molecular orbital picture for borohydride anion, BH_4^-.

a) Use the geometry for BH_4^- that you would predict from its Lewis structure.

b) Select an orientation for the p orbitals on boron.

c) What interaction are possible between the set of hydrogens and the boron 2s orbital?

d) What interactions are possible between the set of hydrogens and one boron 2p orbital?

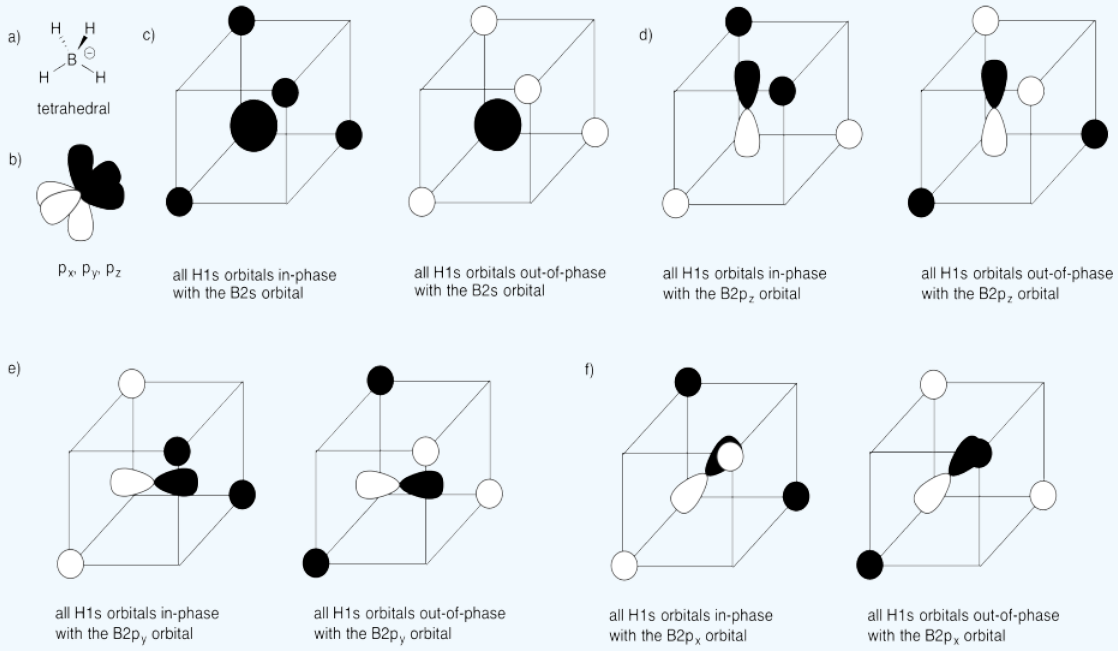
e) What interactions are possible between the set of hydrogens and the second boron 2p orbital?

f) What interactions are possible between the set of hydrogens and the third boron 2p orbital?

g) Can all the hydrogen orbitals interact in each case? If not, why not?

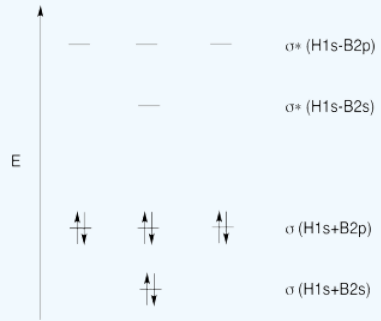
h) Order the resulting combinations in energy, show the resulting energy levels and populate them with the correct number of electrons.

Answer



g) In each case all four H1s orbitals interact with each boron orbital.

h) The constructive overlap of the four H1s orbitals and the B2s orbital results in the lowest energy combination as is contains no nodes. (LOWEST ENERGY)
The constructive overlap of the four H1s orbtials with the three B2p orbitals results in bonding orbitals containing a single node. (MEDIUM-LOW ENERGY)
The destructive overlap of the four H1s orbitals with the B2s orbital results in an anti-bonding orbital. (HIGH ENERGY)
The destructive overlap fo the four H1s orbital with the three B2p orbitals results in anti-bonding orbitals. (HIGHEST ENERGY)



Exercise 13.11.4

Construct a molecular orbital picture for borane, BH_3.

a) Use the geometry for BH_3 that you would predict from its Lewis structure.

b) Select an orientation for the p orbitals on boron.

c) What interaction are possible between the set of hydrogens and the boron 2s orbital?

d) What interactions are possible between the set of hydrogens and one boron 2p orbital?

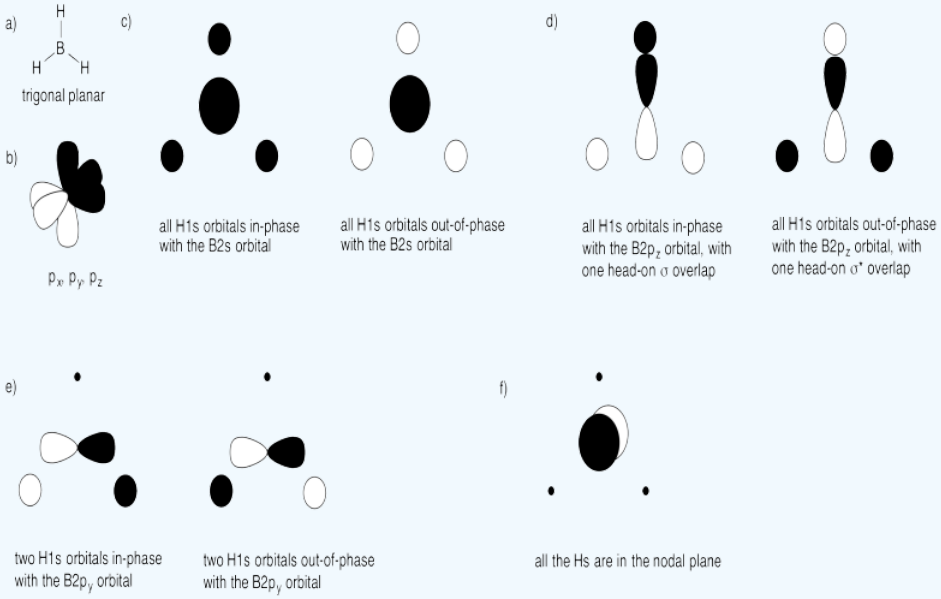
e) What interactions are possible between the set of hydrogens and the second boron 2p orbital?

f) What interactions are possible between the set of hydrogens and the third boron 2p orbital?

g) Can all the hydrogen orbitals interact in each case? If not, why not?

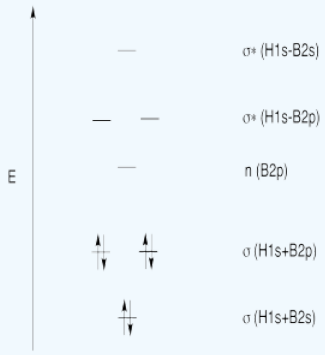
h) Order the resulting combinations in energy, show the resulting energy levels and populate them with the correct number of electrons.

Answer



g) In some of the cases the one or more Hs may be in a nodal plane.

h) The constructive overlap of the three H1s orbitals and the B2s orbital results in the lowest energy combination. (LOWEST ENERGY)
The constructive overlap of the three H1s orbtials with the B2p orbital results in a bonding orbital. (MEDIUM-LOW ENERGY)
The constructive overlap of the two H1s orbtials with the B2p orbital results in a bonding orbital. (MEDIUM-LOW ENERGY)
The B2p orbital that is perpendicular to the plane of hydrogen atoms results in a non-bonding orbital. (MEDIUM ENERGY)
The destructive overlap of the two H1s orbitals with the B2p orbital results in an anti-bonding orbital. (HIGH ENERGY)
The destructive overlap of the three H1s orbitals with the B2p orbital results in an anti-bonding orbital. (HIGH ENERGY)
The destructive overlap fo the three H1s orbitals with the B2p orbital results in an anti-bonding orbital. (HIGHEST ENERGY)



Exercise 13.11.5

Based upon your results of the previous two questions about borane and borohydride, comment on the energetics involved in the addition of a hydride ion (H^-) to borane to produce borohydride. For this question, just assume the hydride electrons start out at a similar energy to the 2p electrons of boron.

Exercise 13.11.6

Construct a molecular orbital picture for carbene, CH_2, in two different ways.

a) In one approach, assume the H-C-H forms a 180 degree angle (linear geometry). Only one of the p orbitals lies along this line.

b) In a second approach, assume the H-C-H form a 120 degree angle (angular geometry). These three atoms define a plane. Two of the p orbitals can lie in the plane of these three atoms.

c) Based on your molecular orbital energy level diagrams, which of these two possibilities do you think is most favorable?

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13.12: Approximations in More Complicated Structures

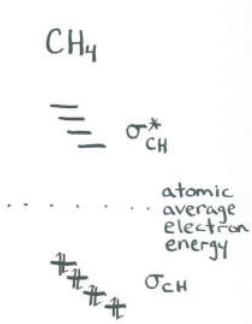
Very often, in qualitative discussions of molecular orbital theory, approximations are made to greatly simplify the view of the molecule. Information is lost whenever we approximate, so this is not as good as a more careful approach. However, there are cases in which we want to focus on one aspect of the molecule and don't want a complicated picture to distract from that focus.

For example, a common approximation of the structure of methane involves making two realizations:

- This structure requires that the carbon form bonds with hydrogens arranged in three dimensions around it. An s orbital could do this easily, because it is symmetric in all directions and can overlap with neighbors in any direction.
- In order to bond with hydrogens in three dimensions, all three p orbitals will be required, since together their axes define three dimensional space.

In an approximate approach, we don't worry about the specific interactions between specific pairs of orbitals. We simply say that the carbon 2s and 2p orbitals will all act together to bond with the four neighbouring hydrogens.

- - This structure requires that the carbon form bonds with hydrogens arranged in three dimensions around it. An s orbital could do this easily, because it is symmetric in all directions and can overlap with neighbors in any direction.
  - In order to bond with hydrogens in three dimensions, all three p orbitals will be required, since together their axes define three dimensional space.
  - The result is four bonding orbitals and four antibonding orbitals.
  - We don't worry about the relative energies of the four bonding orbitals; we assume they are all similar.



This result is not consistent with photoelectron spectroscopy. Our more rigorous approach to methane is more consistent with experimental data. However, this shortcut, which is sometimes referred to as a "hybridization" approach, is often used to discuss more complicated molecules.

- A tetrahedral atom can use an s orbital and three p orbitals to bond with its neighbors.
- When using a hybridization model, a tetrahedral atom. It is sometimes referred to by the label "sp^3 hybrid".

Exercise 13.12.1

Suppose you wanted to use a hybridization approach to show a rough molecular orbital diagram for borane, BH_3.

a) What is the expected geometry at boron in borane?

b) Could the s orbital bond with the hydrogens?

c) Given the geometry of boron, could all of the p orbitals bond with the hydrogens?

d) Are any orbitals not properly oriented to bond with the hydrogens? If so, they would be non-bonding and would not go up or down in energy upon formation of the molecule.

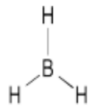
e) Show the resulting molecular orbital energy level diagram for borane.

f) Tetrahedral atoms are referred to as sp^3. What hybrid label would you give your boron with this geometry?

Answer

12.1

a) trigonal planar

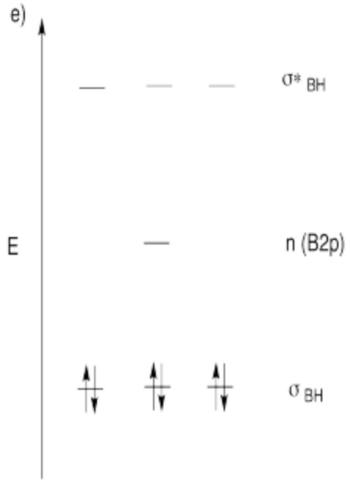


b) yes

c) no

d) one B2p orbital will be perpendicular to the plane of Hs

e)



f) sp^2

Exercise 13.12.2

Suppose you wanted to use a hybridization approach to show a rough molecular orbital diagram for beryllium hydride, BeH_2.

a) What is the expected geometry at beryllium?

b) Could the s orbital bond with the hydrogens?

c) Given the geometry of beryllium, could all of the p orbitals bond with the hydrogens?

d) Are any orbitals not properly oriented to bond with the hydrogens? If so, they would be non-bonding and would not go up or down in energy upon formation of the molecule.

e) Show the resulting molecular orbital energy level diagram for beryllium hydride.

f) Tetrahedral atoms are referred to as sp^3. What hybrid label would you give your beryllium with this geometry?

Answer

12.2

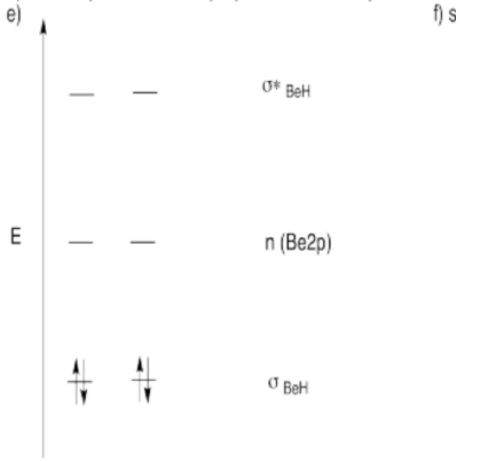
a) linear H−Be−H

b) yes

c) no

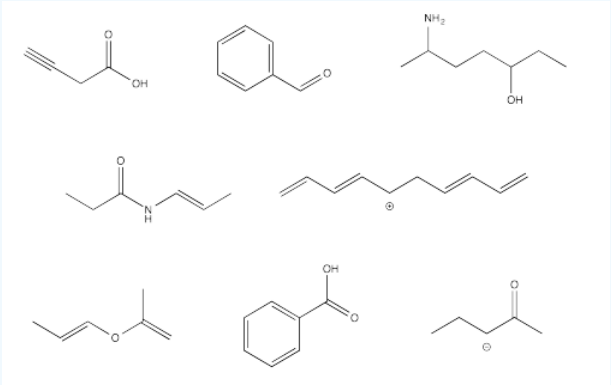
d) two Be2p orbital will be perpendicular to the plane of Hs

e) f) s



Exercise 13.12.3

Indicate hybridization of each carbon atom in the following molecules.

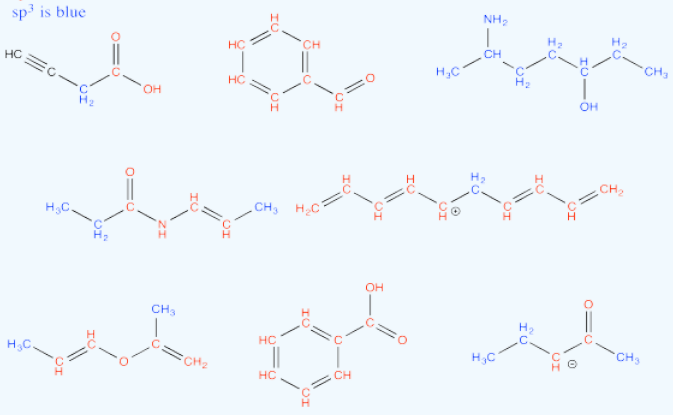


Answer

sp is black

sp^2 is red

sp^3 is blue



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13.13: Building a Molecule from Pieces

Sometimes, compounds are complicated enough that it can be easier to think about the bonding in one portion of the molecule at a time. Ethane, for example, does not contain one central atom like methane does. It contains two atoms that we would think of as being tetrahedral. That makes the potential orbital interactions slightly harder to think about.

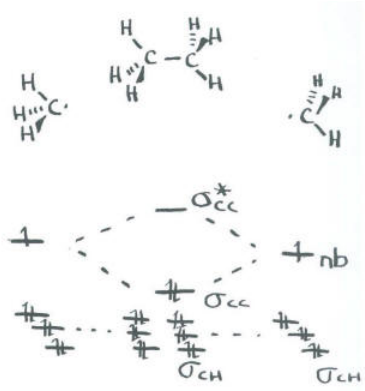
That does not mean this calculation poses any problem for a computational chemist. A quantitative molecular orbital approach on a computer would begin with a spreadsheet of data to submit for calculations. This data would include a list of all the atoms in the structure and the approximate position of each atom in three-dimensional space. These positions could be thought of in Cartesian coordinates (x,y,z), polar coordinates (r,q,f) or internal coordinates (a slightly complicated system relating the relative positions of the atoms with respect to each other: atom B is x distance from atom A; atom C is y distance from atom B and A-B-C forms an angle of z degrees, and so on). The computer does not need to know where the bonds are or where the electrons are; it will figure that out from its calculations. Ethane would prove to be very simple to calculate with a computer.

On paper, we might need to break ethane down into easier pieces. The obvious thing to do is break ethane into two smaller parts and then bring those parts together. Ethane could easily be thought of as two CH_3 units interacting together.

The geometry of a CH_3 unit may be debatable. Since we expect the carbon to be tetrahedral in ethane, it is probably easiest to think of CH_3 as pyramidal, in terms of the relationship of the four atoms. The three hydrogens form a triangle at the base of the pyramid, with the carbon at the apex of the pyramid.

Now we have two methyl groups. We can bring them both together and allow the previously non-bonding orbitals to interact with each other.

- If we take a hybrid approach to the methyl group, we can use the 2s orbital and all three 2p orbitals to bond with the hydrogens.
- There are only three hydrogens, so we only need three of the sp3 orbital set to bond with the hydrogens.
- There will be three bonding combinations using these orbitals and three antibonding combinations.
- These interactions describe the C-H bonds.
- The last of the sp^3 set will be left non-bonding. We don't care which orbital this is because we are taking a shortcut.



- The remaining orbital from the sp^3 set on one methyl interacts with the remaining orbital from the sp^3 set on the other methyl.
- There is a bonding and an antibonding combination.
- This interaction describes the C-C bond.
- The C-C bond is probably not at the same energy level as the C-H bonds.
- We know from experiment that C-C bonds are weaker than C-H bonds, so we will place it higher in energy than the C-H bonds.

This approach does not agree well with the exact energy levels of the C-H bonds as determined by both quantitative molecular orbital theory and photoelectron spectroscopy. However, it is a method that will allow us to tackle bigger problems without worrying about some of the details.

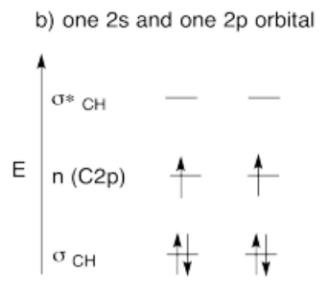
Exercise 13.13.1

Use the partial structure approach, with a hybridization model, to construct an approximate molecular orbital interaction diagram of ethene, connected CH_2-CH_2 (two H on the first carbon, two H on the second, the two carbons connected together).

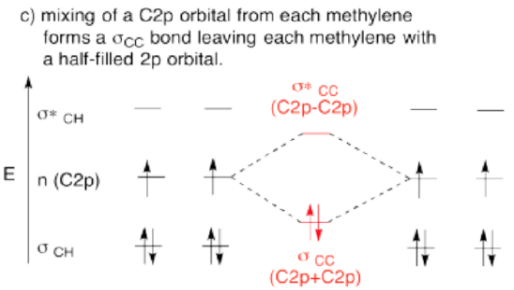
a. Build this model up from two methylene groups, CH_2 and CH_2. What will be the geometry of each carbon in ethylene?
b. Given that geometry, choose the appropriate set of carbon s & p orbitals to bond to the neighbors. Build the methylene molecular orbital energy level diagram.
c. Bring the two methylenes together. Let an unused orbital from your hybrid set interact with the same kind of orbital from the other methylene.
d. When finished, are there other unused atomic orbitals on each methylene? If so, could they form an additional bond?

Answer a

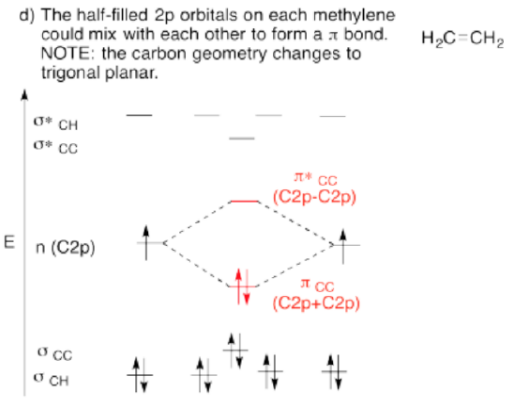
Answer b



Answer c



Answer d



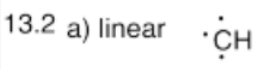
Exercise 13.13.2

Use the partial structure approach, with a hybridization model, to construct an approximate molecular orbital interaction diagram of ethyne, connected CH-CH (one H on the first carbon, one H on the second, the two carbons connected together).

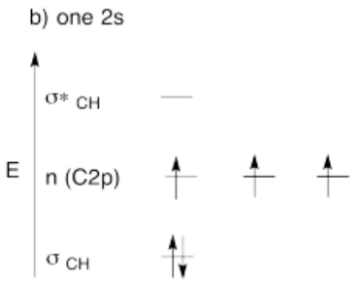
a. Build this model up from two methyne groups, CH and CH. What will be the geometry of each carbon in ethyne?
b. Given that geometry, choose the appropriate set of carbon s & p orbitals to bond to the neighbors. Build the methyne molecular orbital energy level diagram.

c. Bring the two methynes together. Let an unused orbital from your hybrid set interact with the same kind of orbital from the other methyne.
d. When finished, are there other unused atomic orbitals from each methyne? If so, could they form an additional bond?

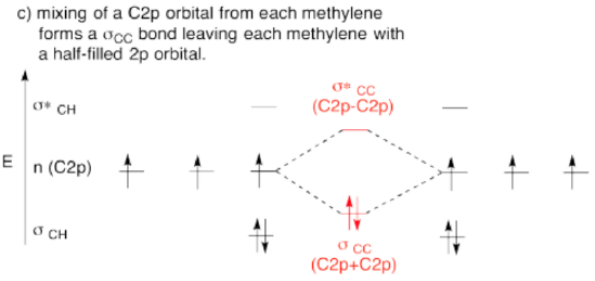
Answer a



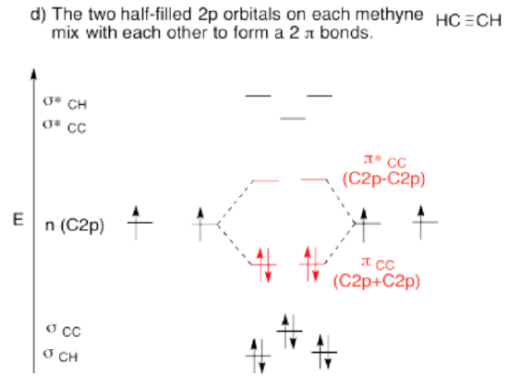
Answer b



Answer c



Answer d



Exercise 13.13.3

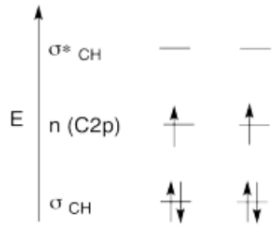
Use the partial structure approach, with a hybridization model, to construct an approximate molecular orbital interaction diagram of formaldehyde, connected CH_2-O (two H on the carbon, carbon connected to oxygen).

a. Build this model up from a methylene group, CH_2. What will be the geometry of each carbon in ethylene? What set of carbon s & p orbitals will bond to the neighbors? Build the methylene molecular orbital energy level diagram.
b. Bring the methylene with an oxygen. Let an unused orbital from your hybrid set on methylene interact with any orbital you think will overlap with it on the oxygen
c. When finished, are there other unused atomic orbitals on the methylene? If so, could they form an additional bond with any atomic orbital on oxygen?

Answer a

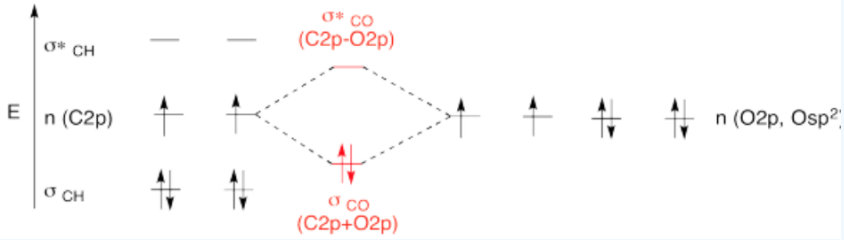
13.3 a) linear $\cdot\dot{C}H_2$

b) one 2s and one 2p orbital



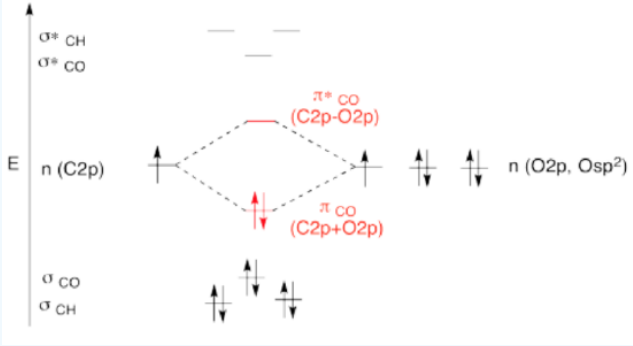
Answer b

c) mixing of a C2p orbital from each methylene forms a σ_{CC} bond leaving each methylene with a half-filled 2p orbital.



Answer c

d) The half-filled 2p orbitals on each methylene could mix with each other to form a π bond. NOTE: the carbon geometry changes to trigonal planar. $H_2C{=}O$



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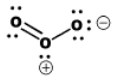
13.14: Delocalization

Ozone is a fairly simple molecule, with only three atoms. However, in order to focus on one aspect of ozone's structure, we will use a hybrid approximation in order to simplify the picture.



The Lewis structure of ozone is somewhat unsatisfactory. That's because the true structure of ozone can't be drawn easily using Lewis conventions. Ozone is an angular structure in which both oxygen-oxygen bonds are about 1.278 Angstroms long.

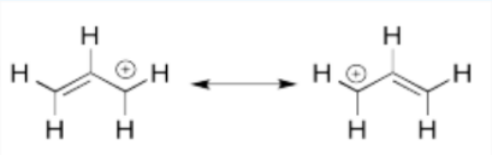
However, the Lewis structure of ozone does not reflect that reality. In the Lewis structure, one pair of oxygens is double-bonded and the other is single-bonded. If this were true, there would be two different bond lengths in ozone. One bond would be about 1.49 Angstroms long, like the O-O bond in peroxide. The other bond would be about 1.208 Angstroms long, like the O=O bond in dioxygen. The bond in ozone looks pretty close to a double bond, does not it? It is just a little longer, however.

In Lewis structures, we fix this discrepancy by drawing two resonance structures for ozone. In one structure, the double bond is between one pair of oxygens. In the other structure, the double bond is between the other pair. The resonance structures imply that the real structure is somewhere in between the two that are shown. Roughly speaking, there should be one-and-a-half bonds between the neighbouring oxygens. Nevertheless, Lewis structures have trouble illustrating the nature of the double bond in ozone, which seems to be both there and not there at the same time.

Exercise 13.14.1

Allyl cation, $CH_2=CHCH_2^+$, is another conjugated system. Use resonance structures to show how its double bond is delocalized.

Answer

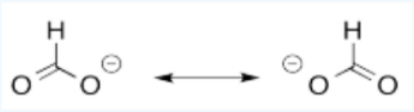


These two resonance structures follow the Lewis rules, but both are necessary to illustrate the delocalize electrons

Exercise 13.14.2

Use resonance structures to show that the negative charge in a formate ion (HCO_2^-, C is in the middle and attached to the three other atoms) is spread out (delocalized) over more than one oxygen atom.

Answer



These two resonance structures follow the Lewis rules, but both are necessary to illustrate the delocalize electrons

We could get another look at bonding in ozone using a molecular orbital approach. We are basically concerned with one question: what is the nature of the double bond?

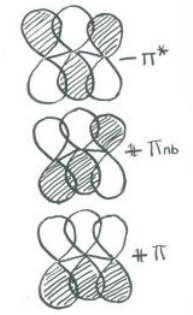
We already know about double bonds. We have seen them in compounds like nitrogen. A second bond is generally made through a pi bonding interaction. Therefore, we are only going to worry about the orbitals that will form pi bonds.

We have three orbitals to combine. Therefore, there will be three combinations.

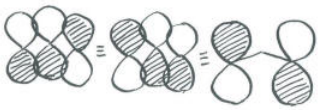
- Ozone is made of three atoms at an angle to each other. They are, by definition, a plane.
- A planar system can be described in a simple hybridization model using the s orbital and two of the p orbitals on each oxygen.
- We will assume some combination of these orbitals interact within the plane to form the first bonds between the oxygens. We won't worry about the details.
- Each oxygen on ozone has a p orbital that was left out of this sp^2 set.
- These leftover p orbitals could interact with each other to form a pi bond.

We have three orbitals to combine. Therefore, there will be three combinations.

- In one combination, all three orbitals are in phase. This combination will have a node through the plane of the molecule (because they are p orbitals) but none cutting through the molecule crosswise. This is a low energy, highly bonding combination.
- In another combination, all three orbitals are out of phase. This phase will have a node through the plane of the molecule (because they are p orbitals) and two more nodes cutting through the molecule crosswise. This is a high energy, highly antibonding combination.
- In a third combination, the middle p orbital can be thought of as out of phase with one neighbour but in phase with the other. This phase will have a node through the plane of the molecule (because they are p orbitals) and one more nodes cutting through the molecule crosswise. Because the bonding and antibonding interactions within this orbital cancel out, this is nonbonding combination.



- More correctly, this combination is usually drawn as a p orbital on each end of the molecule, out of phase with each other. The middle p orbital might as well sit out because overall it isn't doing anything. This depiction stil has one node cutting through the molecule crosswise, and is energetically equivalent to the other way we drew it. However, the first way we drew it is disqualified by symmetry rules (it is too lopsided).



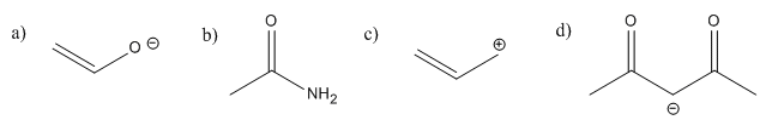
Populating these orbitals, and getting an exact energy, is not possible given the huge approximations we have made. However, in focusing on the pi bonding, we see something that we can't see in Lewis terms. There really is a pi bond that stretches the entire length of the ozone molecule. This is the lowest energy combination, with a wavelength steretching over twice the length of the molecule.

- Pi bonding in ozone is delocalized over all three oxygens.
- Delocalization is highly stabilizing.
- Delocalization allows electrons to achieve longer wavelength and lower energy

Because it is low in energy, the extended pi bond is pretty certain to be populated by electrons, and it will make some contribution to the structure of ozone. How much impact it has would depend on the population of the other combinations, which we can't predict without a more careful approach.

Exercise 13.14.3

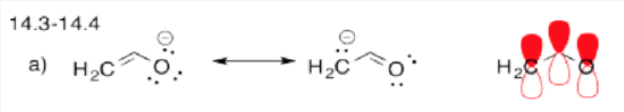
There is delocalization in the following species.



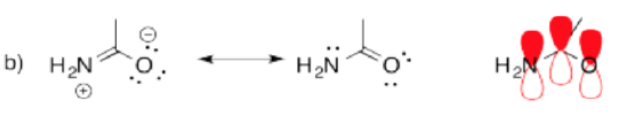
In each case:

i. add any missing lone pairs.
ii. show delocalization using resonance structures.
iii. show delocalization using drawings of the orbitals used in pi bonding.

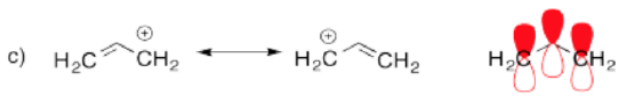
Answer a



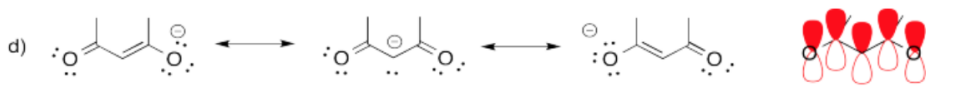
Answer b



Answer c



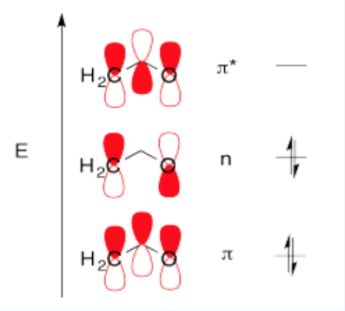
Answer d



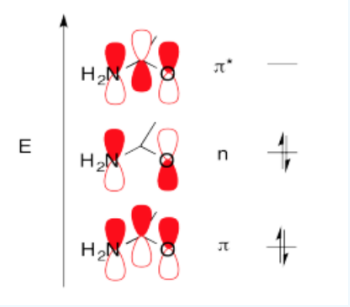
Exercise 13.14.4

Construct a Huckel MO diagram for each of the cases in Problem MO14.3.

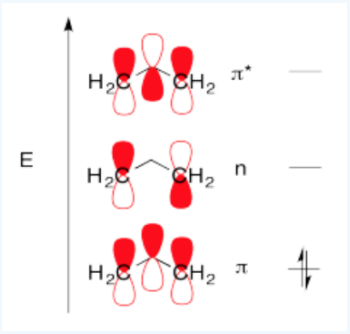
Answer a



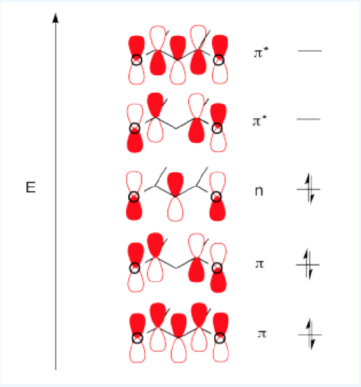
Answer b



Answer c

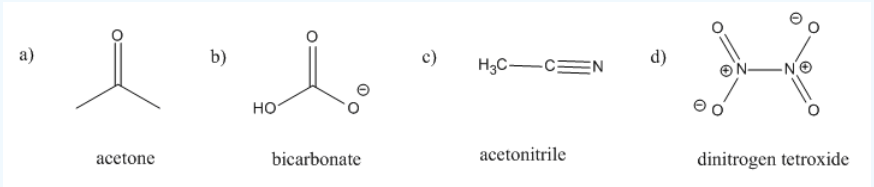


Answer d



Exercise 13.14.5

In each of the following cases, there may or may not be conjugation involving lone pairs and pi bonds. Show why or why not, using drawings of the orbitals involved.



Answer a

14.5

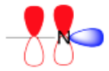
a) acetone, no conjugation as the oxygen lone pair elelctrons are perpendicular to the π orbital

Answer b

https://chem.libretexts.org/@go/page/192886

b) bicarbonate, this is a conjugated system as the oxygen lone pair elelctrons align with the π orbital

Answer c

c) acetonitrile, this is not a conjugated system as the oxygen lone pair elelctrons are perpendiculat to the π orbital 

(NOTE: second perpendicular π orbital is not shown)

Answer d

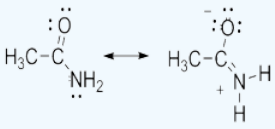
d) dinitrogen tetroxide, this is a conjugated system as the oxygen lone pair elelctrons align with to the π orbital

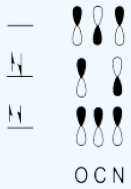
Exercise 13.14.6

The molecule acetamide is shown in problem MO14.1. Explain the following structural features.
a. In acetamide, the C-N and C-O bond lengths are 1.334 and 1.260 angstroms, respectively. For comparison, some typical bond lengths are C-N (1.47 A); C=N (1.38 A); C-O (1.43 A), C=O (1.20 A).
b. The two C atoms, plus the O, the N and the two hydrogens on the N lie in a plane.
c. The barrier to rotation about the C-N bond is approximately 11 kcal/mol, while the barrier to rotation about the C-N bond in CH3NH2 is about 2.4 kcal/mol.
d. The two hydrogens on the N are not in identical chemical environments.

Answer

All of the answers depend on an understanding of the contributions of two resonance structures to the overall picture of acetaminde, or alternatively, that actetamide forms a conjugated pi system with four electrons delocalized over the O, C and N.





Answer a

Contribution of the second resonance structure introduces some double bond character to the C-N bond and some single bond character to the C-O bond. Thus, both of these bonds are intermediate in length between single and double bonds.

Answer b

Since the C, N and O atoms are sp2 hybridized, the C-N pi bond can only form if the remaining p orbitals on these atoms align. This places the atoms participating in the sp2 sigma bonds in the same plane.

Answer c

Because of the partial double bond character there is a larger barrier to rotation than is typically found in molecules with only single bonds.

Answer d

Because of the partial double bond character and the restricted rotation, the two H's are not identical. (One is nearer the O and one is nearer the CH_3 and the restricted rotation prevents their interconversion.

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13.15: Polyenes

Bonding in ozone can be explained with conjugation. In conjugation, several p orbitals can interact with each other to create a delocalized pi bond.

Conjugation can also occur in polyunsaturated alkenes or olefins. Alkenes are compounds that contain carbon-carbon double bonds. A carbon-carbon double bond is sometimes described as unsaturated. This term distinguishes alkenes from alkanes or paraffins, which have only carbon-carbon single bonds. Alkanes can be made from alkenes through the addition of hydrogen gas in the presence of a transition metal catalyst. Whereas unsaturated alkenes can take up additional hydrogens to add to double-bonded carbons, alkanes are already full: they are saturated with hydrogen and can accept no more.

The conversion of unsaturated carbon chains into saturated ones is very common. A familiar example concerns cooking fats and oils. Many vegetable oils contain unsaturated fatty acids, which contain long chains of carbon atoms having at least one carbon-carbon double bond. These double bonds produce a kink in the carbon chain, making these compounds oils at room temperature. When dairy products were rationed during World War II, vegetable oils were converted into saturated fats through catalytic hydrogenation. Saturated fats have a regularly repeating, zig-zag shape in their carbon chains and they are solids at room temperature. The product of this conversion was called oleo, or later, margarine. Margarine remains a common substitute for butter today.

Exercise 13.15.1

Why does a kink in the carbon chain make a compound an (liquid) oil, when otherwise it would be a (solid) fat or wax?

Answer

15.1 Cis-alkenes in the carbon chains cause the packing to be less orderly than in saturated carbon chains

- Polyunsaturated alkenes, or polyenes, are compounds that have several carbon-carbon double bonds.
- The double bonds can be spaced out along the carbon chain, with several carbon-carbon single bonds separating them. In this case they are called isolated polyenes.
- Two double bonds could be attached to the same carbon, so that there are two double bonds in a row, but this situation is rare. This compound would be called a cumulene.
- Two double bonds could be separated by one single bond. Alternatively, a number of double bonds could be separated by single bonds, so that a carbon chain had alternating double and single bonds. This compound is a conjugated polyene.

Conjugated polyenes have a few unusual properties.

- First of all, they are slightly more difficult to hydrogenate than are other polyenes. Their double bonds somehow resist taking up hydrogen.
- Second, these compounds have "high rotational barriers" around their carbon-carbon single bonds.

Normally, single bonds between atoms are not difficult to rotate, and the atoms on one end of a bond can spin with respect to the other end. Double bonds, on the other hand, do not rotate easily, because the p orbitals forming the pi bond need to remain parallel to each other in order to bond. The single bonds in conjugated polyenes do not rotate freely; they behave a little more like double bonds.

- Finally, conjugated polyenes show a pronounced "red shift" in their ultraviolet-visible spectra.

When alkenes absorb ultraviolet light, an electron is promoted to a higher energy level. In alkenes, one of the electronic transitions that can occur involves the promotion of an electron from a p to a p * level. The frequency necessary to induce this electronic transition is usually in the ultraviolet range. However, increasing the number of conjugated double bonds moves this transition to lower and lower frequency, as shown in the table below. Some molecules, such as carotene, have many conjugated double bonds, and absrob visible light. Carotene absorbs blue and green light, reflecting red and orange. It is one of the pigments responsible for the orange and red color of leaves in the fall.

Compound	Absorption wavelength (nm)

$CH_2=CH_2$	180
$CH_2=CH-CH=CH_2$	210
$CH_2=CH-CH=CH-CH=CH_2$	240

All of these properties of polyenes can be explained using quantitative molecular orbital calculations. We can also get an idea of where some of the results come from by taking a very approximate qualitative MO approach.

Start with the first entry in the table above.

- Ethene, $CH_2=CH_2$, contains two trigonal carbons.
- As an approximation, we will say that these two planar carbons each use a set of sp^2 orbitals to bond to the hydrogens and each other.
- That leaves a leftover p orbital on each carbon to form a pi bond.

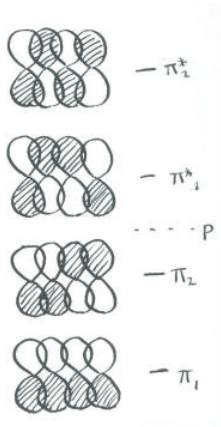
We aren't going to bother drawing a complete molecular orbital energy level diagram for ethene. We will only draw a Huckel diagram, which shows only the portion of the molecule involved in pi bonding.

- In the Huckel diagram, there is a bonding combination and an antibonding combination.
- In the absence of a complete calculation, we will guess from the Lewis structure and say that there is one pair of electrons to populate this set of orbital.
- They will go into the lower, bonding orbital.
- These electrons are delocalized over two carbons, with a half wavelength stretching over both carbons. A full wavelength would stretch to four carbons long.

For comparison, we can look at the next entry in the table. It is butadiene, $CH_2=CH-CH=CH_2$.

- As an approximation, we will say that these four planar carbons each use a set of sp^2 orbitals to bond to the hydrogens and each other.
- That leaves a leftover p orbital on each carbon to form a pi bond.
- In the Huckel diagram, there is a fully bonding combination (all in phase with their neighbors) and a fully antibonding combination (all out of phase with their neighbors, with three nodes).

There must be two other combinations, because we started with four p orbitals.

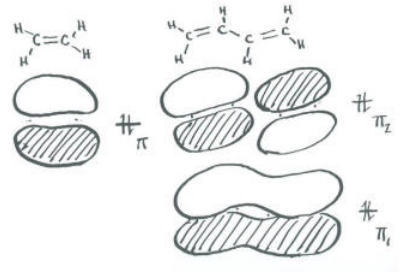


- The two pairs of orbitals on each end could be in phase, but out of phase in the middle. This combination contains one node.
- The opposite could be true: The two in the middle could be in phase, but out of phase with both ends. This final combination contains two nodes.

Notice that the number of nodes increases one by one, from the all-bonding combination to the all-antibonding.

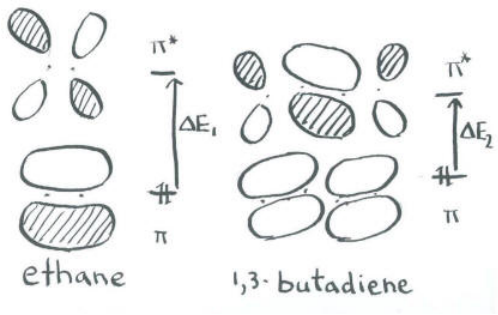
- We will guess from the Lewis structure and say that there are two pairs of electrons to populate this set of orbitals.
- They will go into the lower two orbitals.
- The lowest energy electrons are delocalized over four carbons. A full wavelength would stretch to eight carbons long.

This pair of low-energy electrons must be at least partly responsible for the stability of polyenes. These electrons are much lower in energy than they would be in two separate double bonds, which would be similar in energy to the double bonds in ethene.



In addition, this orbital explains the difficulty of rotating around the single bonds in butadiene. In a sense, there are no single bonds in butadiene. There are only double bonds.

The spectroscopy results require more attention to subtleties. Note that the next pair of electrons goes into an orbital that contains a node. In a quantitative MO calculation, the presence of this antibonding interaction in an otherwise bonding orbital raises its energy slightly above the energy of the pi bond in ethene. Also, the lowest lying empty orbital has a bonding interaction, lowering its energy slightly below that of the purely antibonding orbital in ethene. The energy gap between the p to a p * levels is slightly smaller in butadiene, requiring a lower-energy photon to promote an electron.

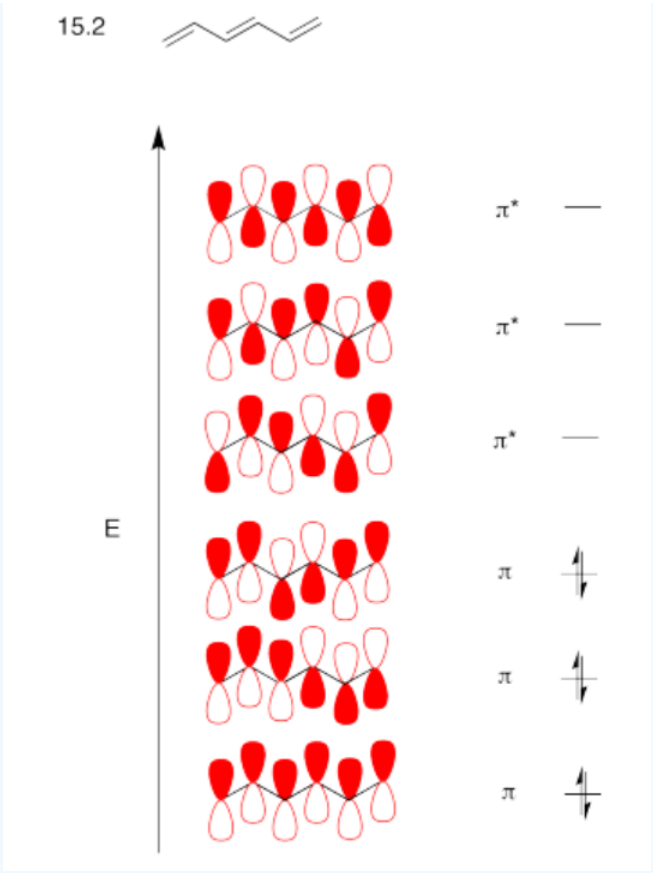


Exercise 13.15.2

Problem MO15.2.

Construct a Huckel MO diagram for 1,3,5-hexatriene, CH_2=CH-CH=CH-CH=CH_2.

Answer

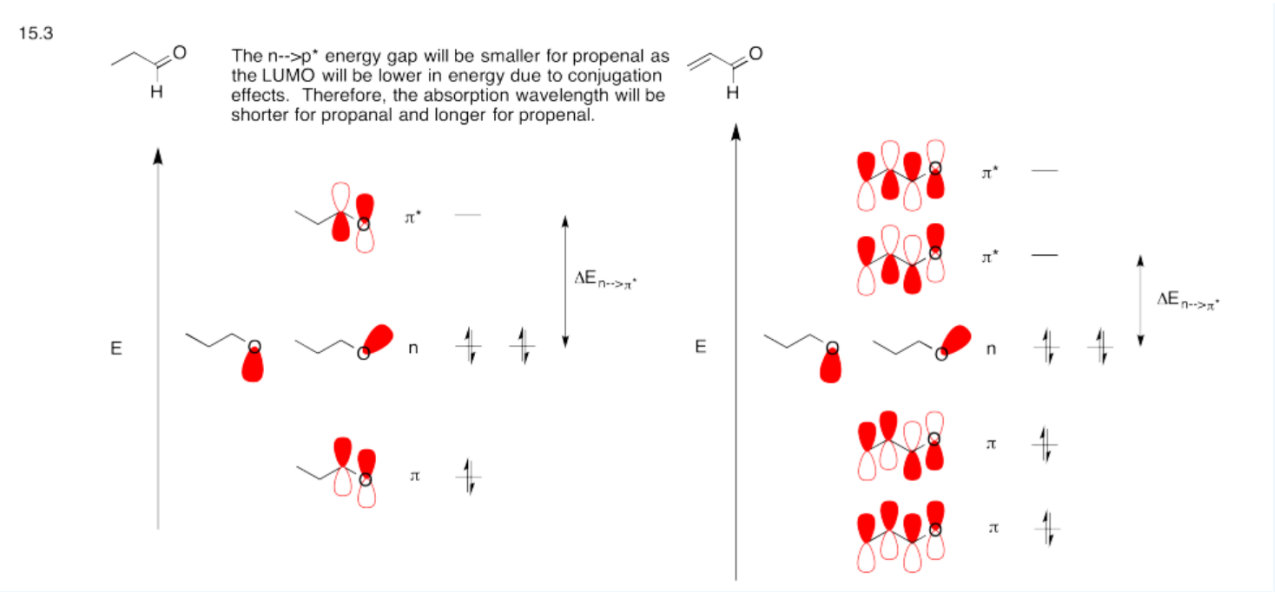


Exercise 13.15.3

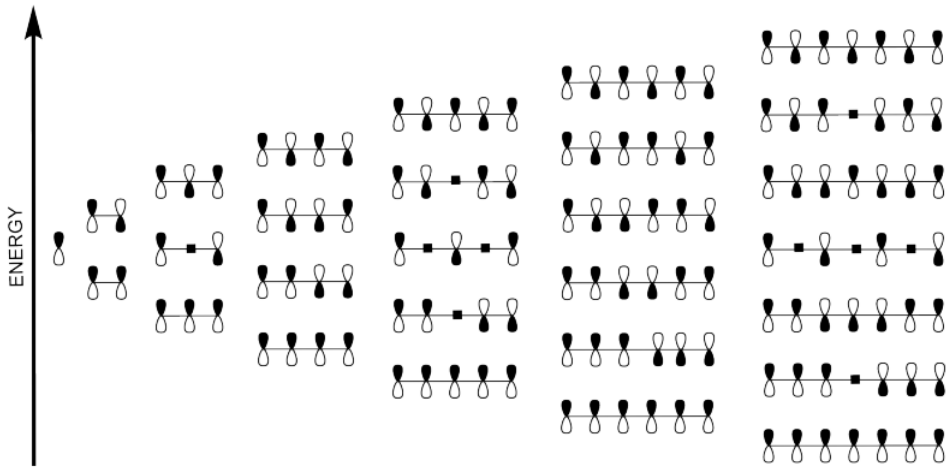
Problem MO15.3.

Another possible UV-visible absorption leads to n to p * transition in oxygen-containing compounds; the n refers to a nonbonding electron in a lone pair on oxygen. Construct Huckel MO diagrams for CH_3-CH_2-CHO (the last C is bonded to an H and also to an oxygen, as well as the next carbon) and CH_2=CH-CHO. Include the oxygen nonbonding energy levels in your diagrams. Compare the n to p * energy gaps in these two compounds. How do you expect their absorption wavelengths will compare?

Answer



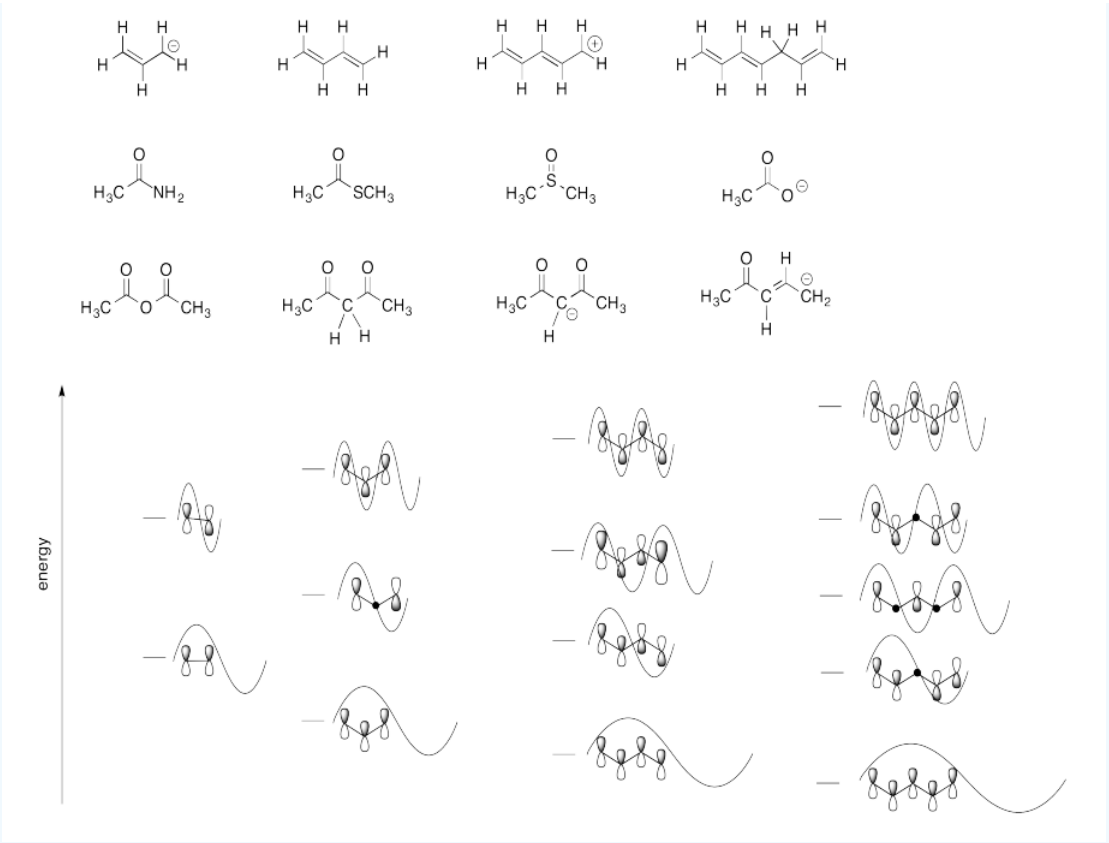
Polyenes, and other compounds in which orbitals are conjugated, form very predictable Huckel MO patterns. If there is no conjugation, then we just have one orbital, all by itself. If two orbitals are conjugated, then there are two combinations.



Exercise 13.15.4

Problem MO15.4.

Match each of the structures below to the correct Huckel MO diagram.



Answer

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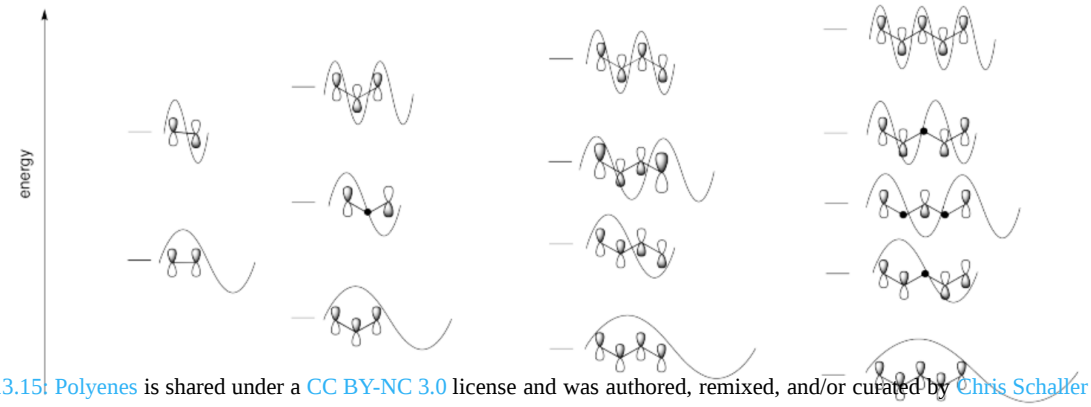
Problem MO15.4.



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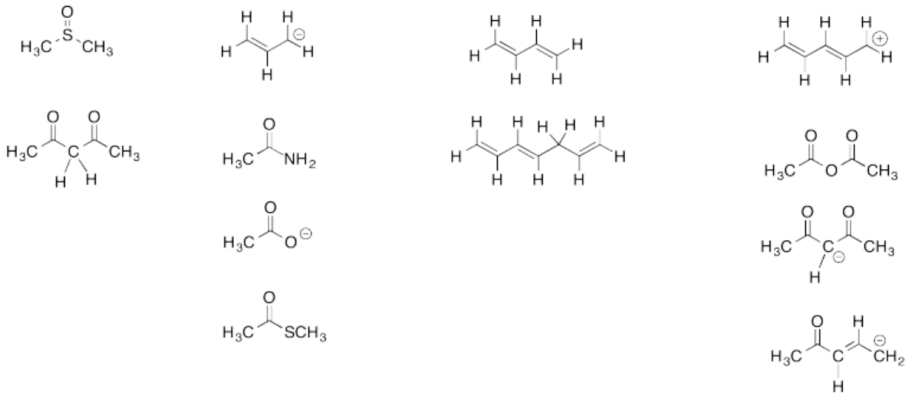


13.16: Delocalization in Aromatics

Aromatics are a special class of delocalized compounds. Benzene is the common example of an aromatic compound.

benzene

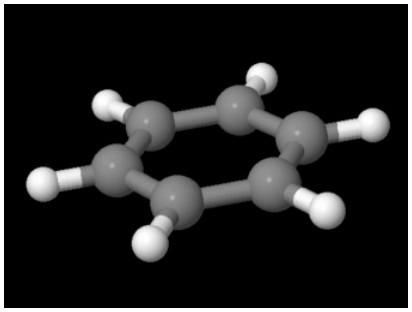
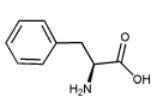


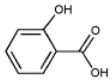
Figure 13.16.1: Ball-and-stick model of benzene.

Go to **Animation CA12.6.** A three-dimensional model of benzene.

Lots of compounds in nature contain "benzene units" within larger structures. It is so common that it has gotten a great deal of attention over the years.



phenylalanine
an amino acid



salicylic acid
a willow tree natural product
used for pain & fever relief

These benzene units are sometimes called "phenyls" or, more generally, "arenes".

Benzene is a good example of a delocalized structure. It is something that could be studied using a Huckel MO approach. One of the pieces of experimental evidence that benzene has delocalized bonding comes from crystal structures. The first X-ray crystal structure of benzene was performed in 1929 by Kathleen Lonsdale. This experiment allowed Lonsdale to measure the distances between the carbons in benzene. A C-C bond in benzene is 1.40 Angstroms long. By comparison, a typical C-C bond is 1.47 Angstroms long, and a typical C=C bond is 1.35 Angstroms long. The C-C bonds in benzene appear to be somewhere between a double and a single bond, and they are all the same. They are not alternating, double-single-double as the Lewis structure suggests.

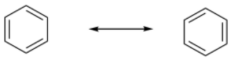
- Benzene has delocalized pi bonding.
- Despite what the Lewis structure says, all of benzene's C-C bonds are the same length.

We can try to show that benzene's bonds are all the same by using two resonance structures. When we do that, we are saying that the real molecule behaves a little like one Lewis structure and a little like the other.

Exercise 13.16.1

Draw two Lewis structures that together illustrate the delocalization in benzene.

Answer



Because the two resonance structures shows double bonds in two different places, the implication is that all of the bonds in benzene have some double bond and some single bond character. You can think of them all as being about 1.5 bonds.

In some ways, aromatics behave differently than other compounds with C=C bonds. For example, there are reactions that alkenes undergo pretty easily, but benzene does not. Bromine, Br_2 adds easily across alkene double bonds. Ethene, or CH_2=CH_2, would add

bromine to form dibromoethane, $BrCH_2$-CH_2Br. As a result, the red-brown color of bromine disappears instantly if it is added to an alkene, because the bromine is rapidly consumed.

Alkenes also react with hydrogen, H_2. Hydrogen can add across double bonds to form "saturated hydrocarbons" (hydrocarbons that don't have any double bonds). Hexene, CH_2=$CHCH_2CH_2CH_2CH_3$, could react with hydrogen to form hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$. This reaction is a lot more sluggish than bromination, though. Bromination often happens instantly. Hydrogenating something takes a lot of work. In general, some kind of catalyst, like powdered palladium metal, must be added before anything happens, and the alkene must be placed under an atmosphere of hydrogen for a long time.

Benzene can be hydrogenated (to form cyclohexane, C_6H_{12}), but it is even more difficult than usual. For a catalyst, palladium really won't do. This requires platinum or platinum oxide, which are a little more reactive. Also, high temperatures may be needed as well as high pressures of hydrogen (often several times greater than atmospheric pressure).

Maybe benzene can be brominated if the right catalyst is added. Ferric chloride works, but it turns out a completely different reaction takes place. C_6H_6 turns into C_6H_5Br. All the double bonds are still there. The bromine atom just replaces a hydrogen atom.

- Benzene does not undergo the same reactions as other compounds with C=C bonds.
- In some ways, aromatics are more stable than expected.

Historically, much has been made about benzene being a ring. When first isolated by Michael Faraday in the 1820's, people didn't have much idea about its structure, and what it might look like was debated for decades. There is a story that August Kekule reported about nodding off in an armchair and dreaming of a snake biting its tail; he says he woke up and had the idea that benzene was composed of a circle of carbon atoms (confirmed by Lonsdale about 65 years later). Maybe the special ring structure of benzene lends it extra stability.

- Benzene is delocalized and cyclic.

So maybe benzene's stability comes with having conjugation and being cyclic. But maybe that isn't enough, either. There are other compounds that are both delocalized and cyclic, but that do not display benzene's properties. For example, cyclopentadiene has long C-C bonds and short C=C bonds, and it behaves like an alkene. It is not aromatic. Why not? Maybe the difference is that cyclopentadiene does not have alternating pi bonds all around the ring. It does not have a conjugated p orbital on each carbon. There is a tetrahedral CH_2 unit in between two of the double bonds. That tetrahedral carbon, or sp^3 carbon, does not have a free p orbital it can use to make double bonds.

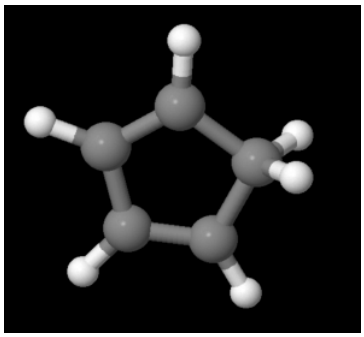


Figure 13.16.2: Ball-and-stick model of cyclopentadiene.

Go to **Animation MO16.2.** A three-dimensional model of cyclopentadiene.

- Benzene is fully conjugated, all the way around the ring.

Not only is benzene cyclic, and not only does it display conjugation, but the conjugation goes around and around and around the ring in an endless pi bond. That must make it different from other compounds with C=C bonds. However, cyclooctatetraene is cyclic and fully conjugated, with four double bonds and four single bonds in an eight membered ring. Cyclooctatetraene behaves exactly like other alkenes. It gets hydrogenated and it gets brominated and it loses its double bonds.

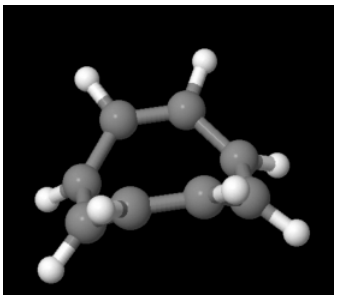


Figure 13.16.3: Ball-and-stick model of cyclooctatetraene.

Go to **Animation MO16.3.** A three-dimensional model of cyclooctatetraene.

Cyclooctatetraene is a basket. You could hold fruit in it.

- Benzene is flat.

Not only is benzene cyclic and fully conjugated all the way around the ring, but it's flat. Maybe that's important. After all, if it's flat, the p orbitals on adjacent carbons could line up right beside each other. They would be perfectly parallel, and they would have really good overlap. To be aromatic, a molecule needs all three of these characteristics.

A very similar molecule should fit these criteria. Cyclobutadiene, C_4H_4 , would be cyclic, conjugated and flat. It should be aromatic and extra-stable, just like benzene

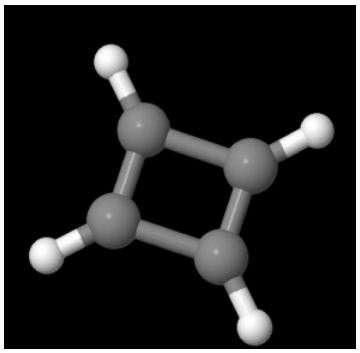


Figure 13.16.4: Ball-and-stick model of cyclobutadiene.

Go to **Animation MO16.4.** A three-dimensional model of cyclobutadiene.

The trouble is, cyclobutadiene is incredibly hard to make. People spent years trying. When they finally succeeded in making it (or compounds that contained a cyclobutadiene unit), they could just catch a fleeting glimpse of it using spectroscopic methods. Then it was gone. It reacted as soon as it came into being.

- Cyclobutadiene is even more reactive than most alkenes (other compounds with C=C bonds).

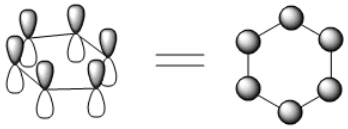
The spectroscopic techniques people used to detect cyclobutadiene seemed to give some additional information about it. Cyclobutadiene is not square; it's rectangular.

- Cyclobutadiene does not behave as if it has delocalized pi bonding. It does not seem to be conjugated.

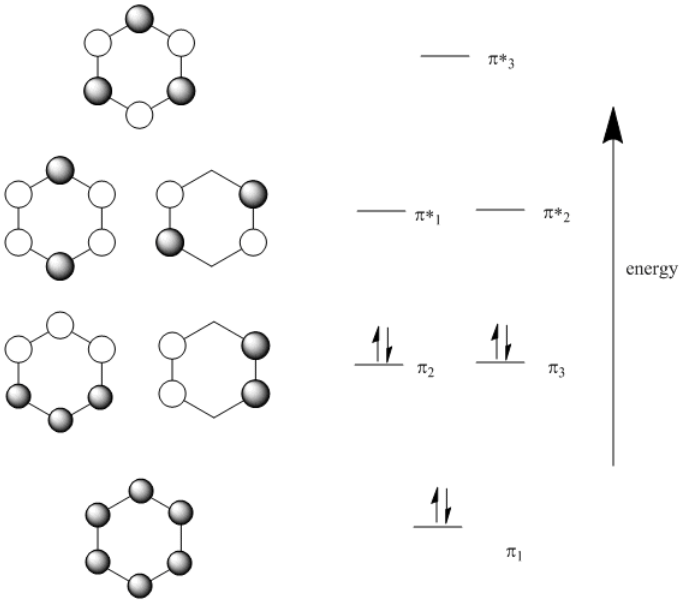
What's the difference? It's a simple question of numbers.

- Cyclobutadiene has an even number of pi bonds. It is not aromatic. It is called "anti-aromatic".
- Benzene has an odd number of pi bonds. It is aromatic.

A Huckel MO treatment of benzene and cyclobutadiene does reveal some differences. Before looking at that, we should see the way people often draw the p orbitals combinations on rings. Because people often have trouble drawing rings edge-on, they look at the ring from the top. If you look at the ring from the top, the p orbitals look like circles, because you can only see the lobe that is closest to you. That's much easier to draw.



Looking at benzene from above, we get the following molecular orbitals (below).



Note that:

- There are six p orbitals involved in pi bonding, so six MO combinations result.
- There is only one way to get all orbitals in-phase (either they are in phase or they are not).
- This combination has the most bonding interactions between neighbouring p orbitals. It produces a new MO that is all bonding.

There is one, lowest-energy molecular orbital that has no nodes through the edges of the ring. The electrons in this orbital have a much more extended wavelength than they would in either a p orbital or a regular pi bond.

- There is only one way to get all orbitals out-of-phase (either they are out-of-phase or they are not).
- This combination has six nodes. It is entirely antibonding.

Because there can only be even nodes in a ring (try drawing one in which p orbitals are out of phase in one spot but nowhere else), there can also be combinations with two nodes or four nodes. There are always alternate ways to arrive at these pictures, and there are always two of each of these combinations.

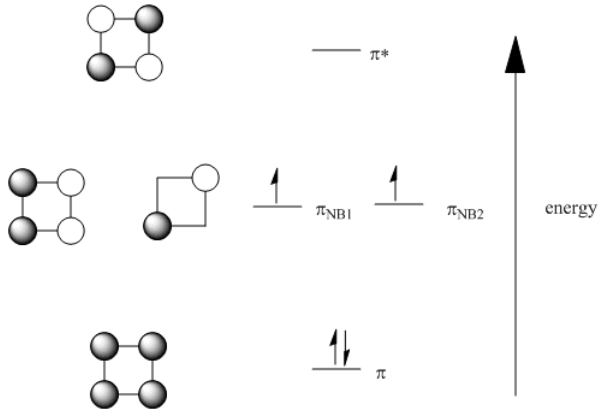
- The combination with two nodes is still mostly bonding. It has more in-phase interactions between neighbors than out-of-phase interactions.
- The combination with four nodes is mostly antibonding. It has more out-of-phase interactions between neighbors than in-phase interactions.

Because there are only six pi electrpons in benzene (count them in the Lewis structure), all of the pi electrons are in bonding orbitals. They are delocalized.

In cyclobutadiene, the orbital combinations work in a similar way. There is an all in phase combination and an all out of phase combinations. In addition, there are two ways of getting a combination that is equally in phase and out of phase.

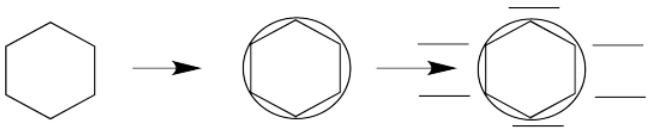
Note that, like in benzene, when there are multiple ways to represent a combination, one molecular orbital is usually represented to show both bonding and antibonding interactions. The other usually shows the net result, either just bonding or antibonding or, in the case of cyclobutadiene, no direct interaction between adjacent atoms because it is a non-bonding orbital. These two different representations are part of how two orbitals at the same energy level are ensured to be orthogonal to each other, just like two p

orbitals on the same atom could be along the x axis or along the y axis, but not both along the same axis. They need to get out of each other's way.



If delocalized, all the pi electrons in benzene are low in energy; they are bonding. However, in cyclobutadiene, only two of the pi electrons are actually bonding; the other two are non-bonding. What's more, the orbital diagram suggests two of the electrons are unpaired, a situation that usually makes organic molecules very reactive. It has been suggested that cyclobutadiene distorts into a rectangle to avoid this sitiuation.

The energy level diagrams for cyclic, fully conjugated systems can be drawn very quickly using the Frost circle method. To use the method, draw a circle. Draw the shape of the cyclic compound inside this circle. One corner of the shape must be at the very bottom of the circle. You are going to add levels around the edge of the circle, one for each place where a corner touches the circle.



If you look at enough such systems, a pattern emerges. Huckel's rule is used to determine whether a system is aromatic or "anti-aromatic." To apply the rule, the molecule must fit the following criteria:

- it is cyclic
- it is fully conjugated all the way around the ring
- it is flat

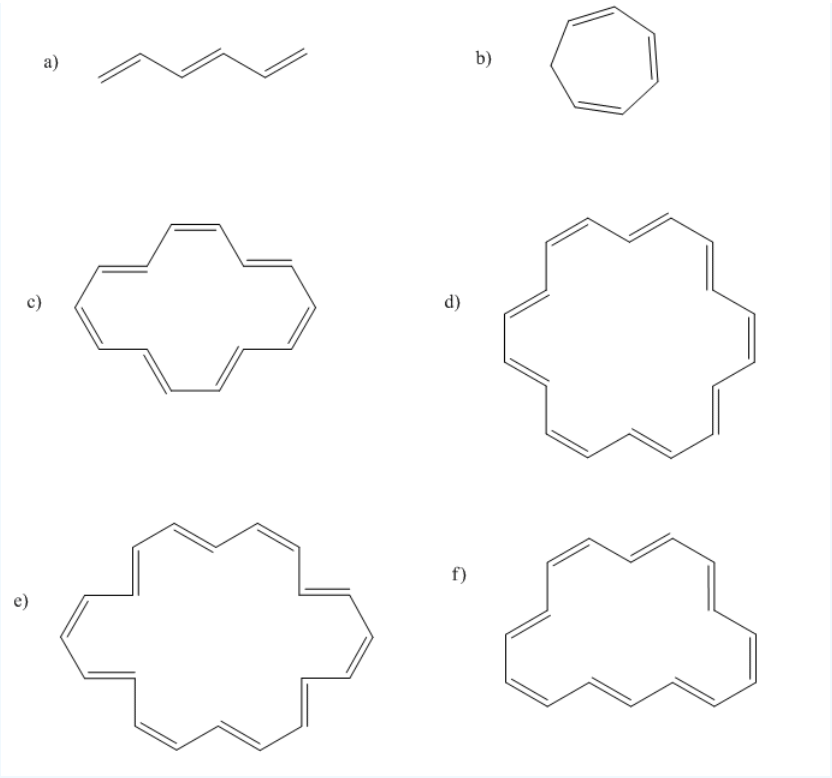
After that, whether it is aromatic or anti-aromatic depends on the following situations:

- Aromatic systems have an **odd** number of **electron pairs** participating in the pi system
- Anti-aromatic systems have an **even** number of **electron pairs** participating in the pi system

The pi system refers to delocalized bonds formed from p orbitals that are perpendicular to the plane of the ring. In a Lewis structure, these may be obvious pi bonds, or they may be lone pairs or even "empty" p orbitals.

Exercise 13.16.2

Indicate which of the following compounds would be aromatic, anti-aromatic, or neither. Just assume they are all flat.



Answer a

a) non-aromatic

Answer b

b) non-aromatic

Answer c

c) aromatic

Answer d

d) aromatic

Answer e

e) anti-aromatic

Answer f

f) anti-aromatic

The rules of aromaticity do not apply only to regular hydrocarbons. Sometimes, anionic or cationic hydrocarbons may have aromatic properties. As with benzene, the aromatic species have regular geometries all around, even though the Lewis structure suggests some of the carbon-carbon bonds are double and some are single. The cyclopentadienyl anion, $C_5H_5^-$, is a common example. It is frequently observed as a ligand in transition metal complexes.

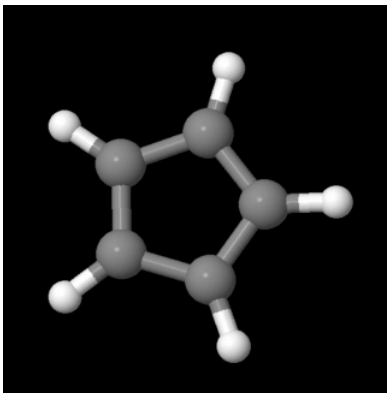


Figure 13.16.5 Ball-and-stick model of cyclopentadienyl anion.

Go to **Animation MO16.5.** A three-dimensional model of cyclopentadienyl anion.

Exercise 13.16.3

Indicate which of the following cations would be aromatic, anti-aromatic, or neither. Just assume they are all flat.

Answer a

a) aromatic

Answer b

b) non-aromatic

Answer c

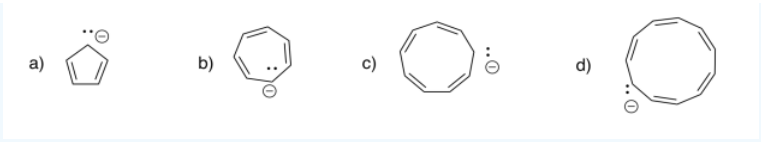
c) anti-aromatic

Answer d

d) aromatic

Exercise 13.16.4

Indicate whether the following anions would be aromatic, anti-aromatic, or neither. Just assume they are all flat.



Answer a

a) aromatic

Answer b

b) anti-aromatic

Answer c

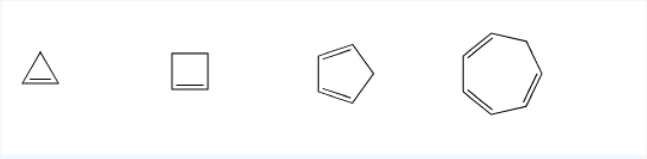
c) aromatic

Answer d

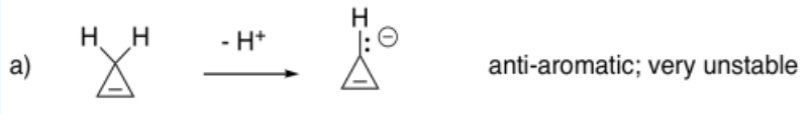
d) anti-aromatic

Exercise 13.16.5

Sometimes, hydrocarbons can be deprotonated (H+ removed by a very, very strong base) if the resulting anion is particularly stable. In the following cases, draw the anion that would result by removing a proton from a tetrahedral carbon, leaving behind a lone pair. Predict whether the anion would be especially stable.

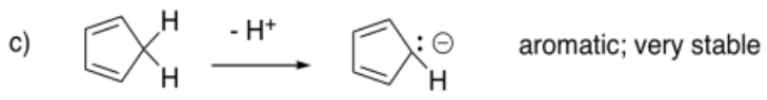


Answer a

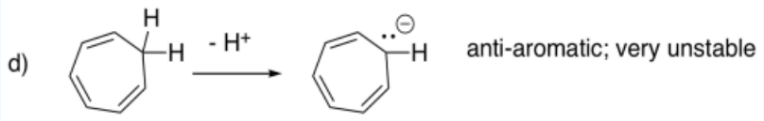


Answer b

Answer c

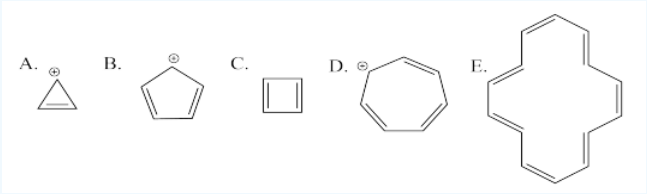


Answer d

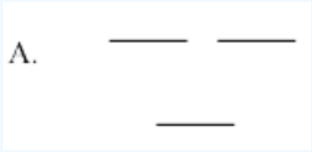


Exercise 13.16.6

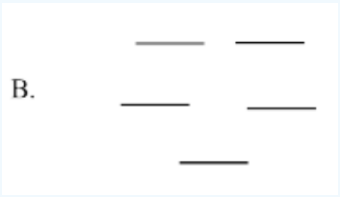
Use the Frost circle method to generate the pi orbital MO diagram for the following species. For E, you'll need to be creative in how to apply the Frost circle idea. (How many energy levels should be in the diagram?)



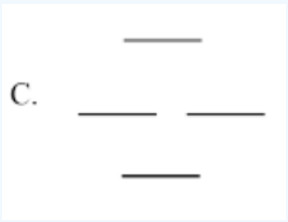
Answer a



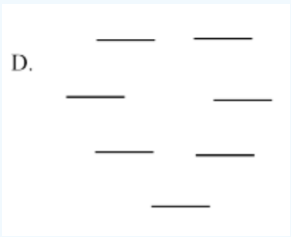
Answer b



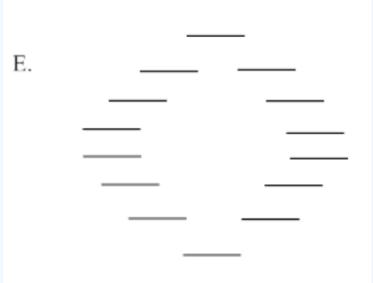
Answer c



Answer d



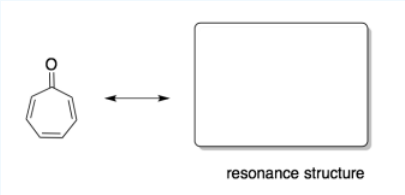
Answer e



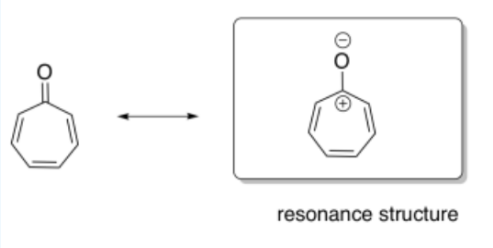
Exercise 13.16.7

A recent research report examined the influence of hydrogen bonding on aromaticity. (Adapted from Judy I. Wu, James E. Jackson, P. v. R. Schleyer, *J. Am. Chem. Soc.* **2014**, *136*, 13526-13529. Copyright 2014, American Chemical Society. Used with permission.)

a) Draw a resonance structure of tropone in which there is charge separation (a cation and an anion).



Answer a

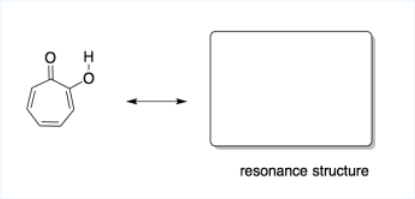


b) Which of the two structures shows aromatic character: the original one, or the one you drew?

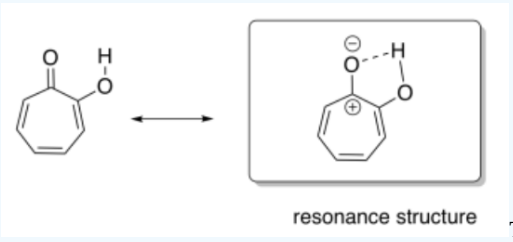
Answer b

In tropone, the resonance structure on the right shows more aromatic character, because it clearly shows a fully-conjugated ring with an odd number of electron pairs in the pi system. The carbonyl in the picture on the left makes that conjugation less obvious: does its carbonyl pi bond contribute to the conjugated system of the ring? If it does, that would mean four pairs of electrons in the pi system, and that would be an even number, so it would be anti-aromatic.

c) Hydroxytropolone was found to have more aromatic character than tropone. Draw a resonance structure to help explain why.



Answer c



The hydroxy group in hydroxytropolone would stabilize the compound in the structure shown on the right, via an ion-dipole interaction with the anionic oxygen. That makes the right-hand, explicitly aromatic structure the dominant one.

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13.17: Heteroaromatics

Many important biomolecules behave as aromatics, even though they don't contain benzene. Histidine is a very common amino acid with a cyclic side chain. The bases in nucleic acids, DNA and RNA, are also aromatic. Closer examination shows that these compounds follow some variation of Huckel's rules for aromaticity. The variations involve the inclusion of lone pairs in the pi bonding system.

Pyrrole is a five-membered ring with a nitrogen in it. It contains two C=C bonds. Pyrrole is aromatic. It usually reacts in a way similar to benzene, rather than like alkenes. But how does it fit the rules for aromaticity?

Pyrrole is cyclic. It is flat. Is it conjugated? It does have alternating double bond-single bond-double-single-*lone pair*. We have seen before that lone pairs can be conjugated with pi bonds. So, pyrrole is conjugated all the way around the ring. Counting the lone pair as a pair of pi electrons gives it an odd number.

- a lone pair can act like a pair of pi electrons if the molecule will become aromatic as a result.

Does a lone pair always have to act as a pi pair? Pyridine is a six membered ring, exactly like benzene, except that one CH unit is replaced by a nitrogen. The nitrogen has a lone pair. Pyridine already has three pi bonds. It is flat and fully conjugated. Does the lone pair add in to the system and make it anti-aromatic?

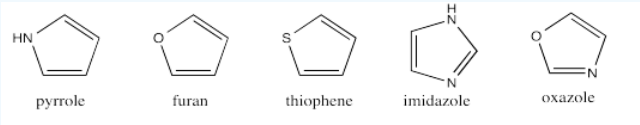
It turns out it can't. There is already a pi bond on that nitrogen, so it would be difficult for the lone pair to occupy the same space, above and below the ring. Instead, the lone pair remains orthogonal to the pi system. It is in the plane of the ring, rather than above and below it. It completely avoids interacting with the pi system.

- a lone pair can't act like a pair of pi electrons if there is already another pair of pi electrons on the same atom.

Exercise 13.17.1

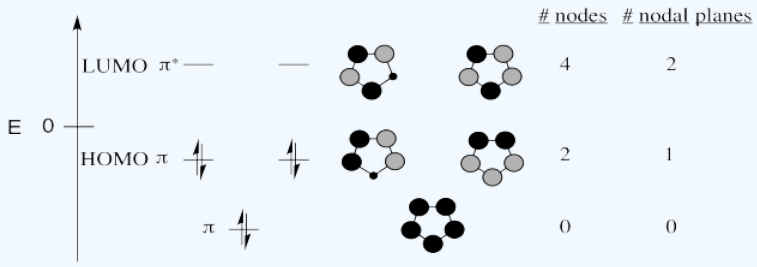
Create a Hückel MO diagram for each of the following 5-membered rings.

- Add electrons.
- Label the HOMO and the LUMO.
- Draw pictures of the molecular orbitals.
  Indicate the number of nodes for each orbital energy level.
- Label the energy levels (π, σ, n, π*, σ*)
-



Answer

All of the compounds are aromatic and have the same Hückel MO diagram.

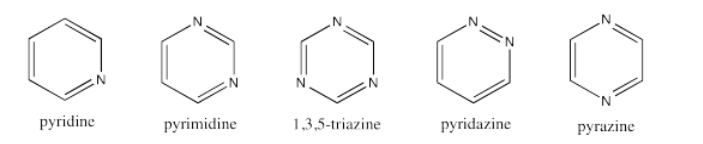


Exercise 13.17.2

Create a Hückel MO diagram for each of the following 6-membered rings.

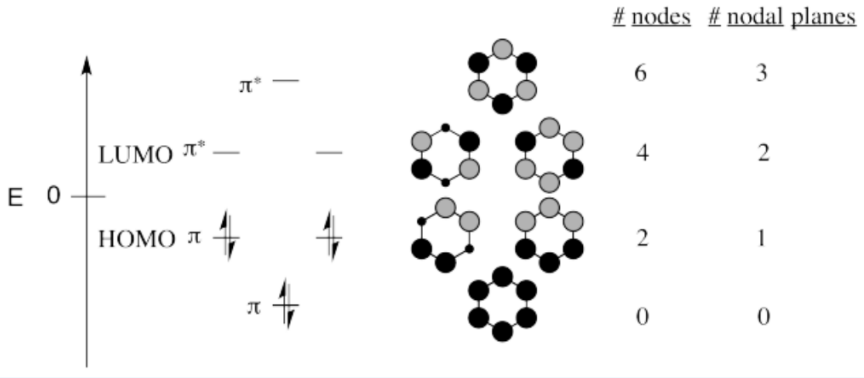
- Add electrons.
- Label the HOMO and the LUMO.

- Draw pictures of the molecular orbitals.
- Indicate the number of nodes for each orbital energy level.
- Label the energy levels (π, σ, n, π*, σ*)



Answer

All of the compounds are aromatic and have the same Hückel MO diagram.



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13.18: Frontier Orbitals

We said before that the energy of the electrons determine the behavior of the molecule. The populated energy levels contribute to the energy and behavior of the molecule. The other energy levels are only possibilities. The only case in which these orbitals are considered is when we think about adding additional electrons to the structure. That can happen during a reduction reaction, for instance. In that case, the next energy level may be a reasonable place to put another electron.

This description may be an approximation. Once another electron is added to the molecule, repulsive and attractive forces have been changed within the molecule, so the energies of all the electrons would have to adjust. Nevertheless, the LUMO is a good first guess at where an additional electron would go and what its energy would be.

Conversely, if a molecule is going to donate an electron (or an electron pair) in a reaction, frequently the electrons come from the highest occupied molecular orbital (HOMO). These electrons are often the most reactive, both because of their high energy and their accessible location, usually farther from the nucleus or on the edge of the molecule.

HOMO and LUMO orbitals are together called frontier orbitals, because they are at the edge of the real, occupied orbitals and the imaginary, unoccupied ones. Frontier orbitals are often considered when trying to understand reactions.

- The lowest unoccupied molecular orbital (LUMO) may describe an additional electron added to a molecule.
- An additional electron added to the molecule could have this energy and could be located in the area of space described by this orbital.

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13.19: Solutions to Selected Problems

Exercise 13.2.1:

When two s orbitals combine out-of-phase, destructive intereference occurs.

There is a node between the atoms.

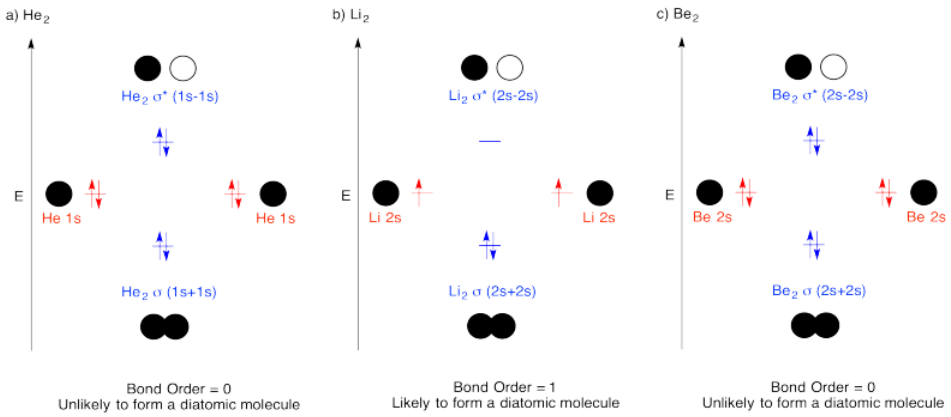
The energy of the electrons increases.

When two s orbitals combine in-phase, constructive interference occurs.

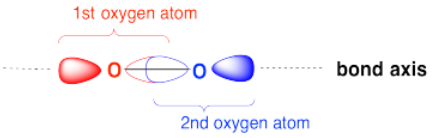
There is no node between the atoms; the electrons are found between the atoms.

The energy of the electrons decreases.

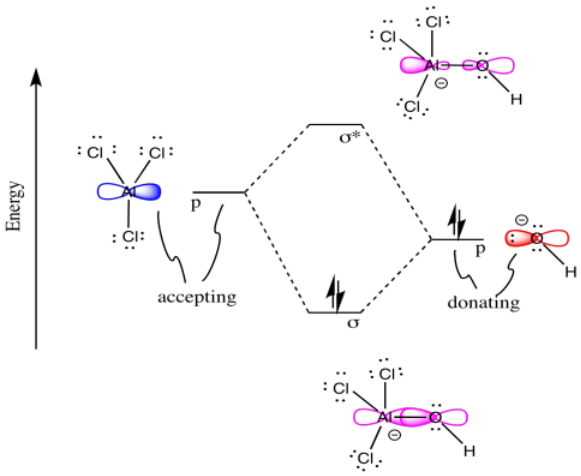
Exercise 13.3.1:



Exercise 13.4.1:

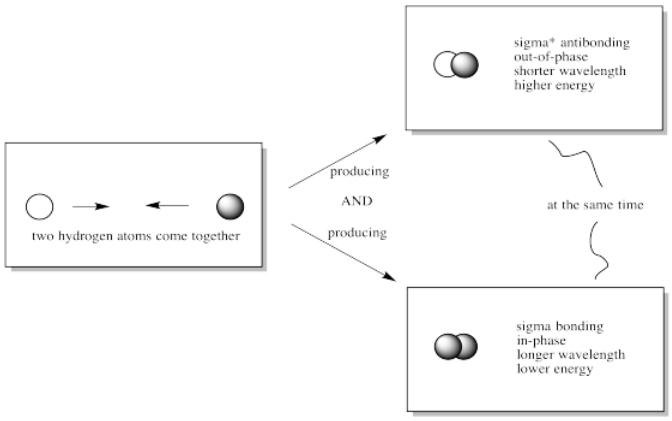


Exercise 13.4.2:



Exercise 13.5.1:

When 2 atomic orbitals are combined, 2 molecular orbitals are formed: one in-phase bonding orbital and one out-of-phase antibonding orbital.



Exercise 13.5.2:

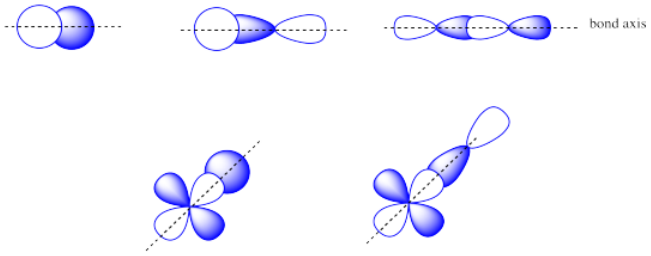
In-phase combinations of atomic orbitals give ***bonding*** orbitals.

Exercise 13.5.3:

Out-of-phase combinations of atomic orbitals give ***antibonding*** orbitals.

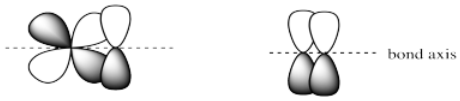
Exercise 13.5.4:

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



Exercise 3.5.5:

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



e) σ*

Exercise 13.5.7:

Li^+ and O^{2-} are more similar in size than K^+ and O^{2-}, so the bond between Li^+ and O^{2-} is stronger.

The energy difference between the 1s orbitals and 2s orbitals is too large, so they cannot interact. In order for orbitals to interact, the orbitals need to have the same symmetry, be in the same plane, and be similar in energy.

Exercise 13.5.8:

When two parallel p orbitals combine out-of-phase, destructive intereference occurs.

There is a node between the atoms.

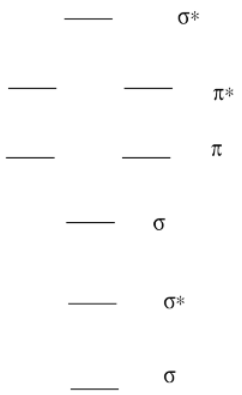
The energy of the electrons increases.

When two parallel p orbitals combine in-phase, constructive interference occurs.

There is no node between the atoms; the electrons are found above and below the axis connecting the atoms.

The energy of the electrons decreases.

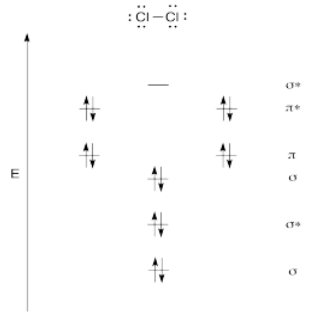
Exercise 13.6.1:



Exercise 13.6.2:

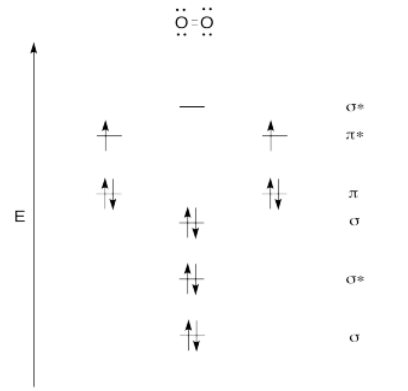
• Count the valence electrons on the molecule. That's the number of valence electrons on each atom, adjusted for any charge on the molecule. (eg C_2^{2-} has 10 valence electrons: 4 from each carbon -- that's 8 -- and two more for the 2- charge).
• Fill electrons into the lowest energy orbitals first.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

Exercise 13.6.3:



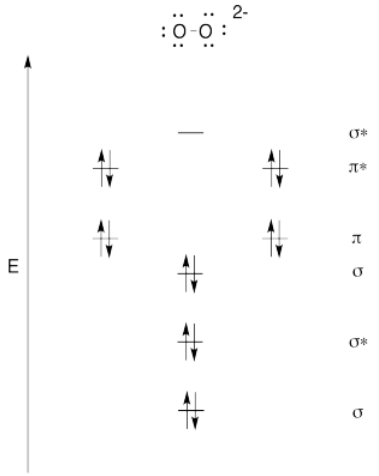
Bond Order = 1
MO diagram matches the Lewis structure

Exercise 13.6.4:



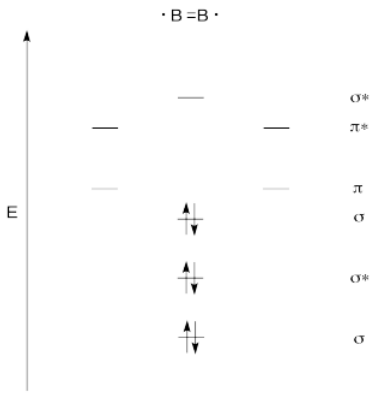
Bond Order = 2
MO diagram indicates two unpaired electrons and therefore does not match the Lewis structure. Based on the MO diagram oxygen would be paramagnetic and would be attracted to a magnetic field

Exercise 13.6.5:



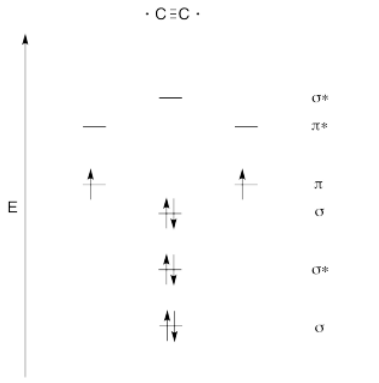
Bond Order = 1
MO diagram matches the Lewis structure. Both predict a Bond Order of 1 and 6 lone pairs of electrons. The addition of two electrons to O_2 to O_2^{2-} would be possible.

Exercise 13.6.6:



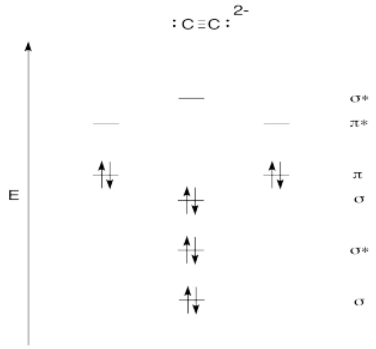
Bond Order = 1
Boron-Boron bonding should be possible

Exercise 13.6.7:



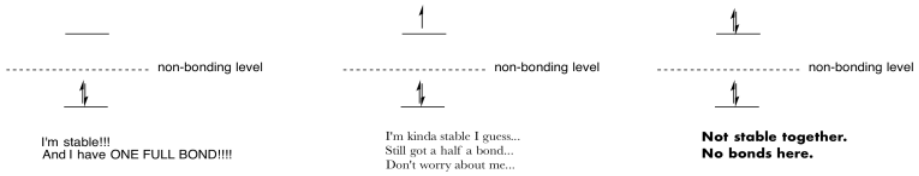
Bond Order = 2
MO diagram does not match the Lewis structure. However, the MO diagram does concur about the 2 unpaired electrons.

Exercise 13.6.8:



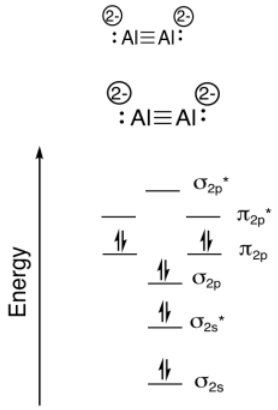
Bond Order = 3
MO diagram matches the Lewis structure. Both predict a Bond Order of 3 and 2 lone pairs of electrons. The addition of two electrons to C_2 to C_2^{2-} would be possible.

Exercise 13.6.9:



Exercise 13.6.10

a. Na, because Na has a lower ionization potential (and a lower electronegativity) than Al.
b. Al
c. 4-, because there are four Na^+
d. total e^- = 2 x 3 e^- (per Al) + 4 e^- (for the negative charge) = 10 e-



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

Exercise 13.7.1:

From MO6: 3. Diamagnetic (no unpaired electrons); 4. Paramagnetic; 5. Diamagnetic; 6. Diamagnetic; 7. Paramagnetic; 8. Diamagnetic

Exercise 13.7.2:

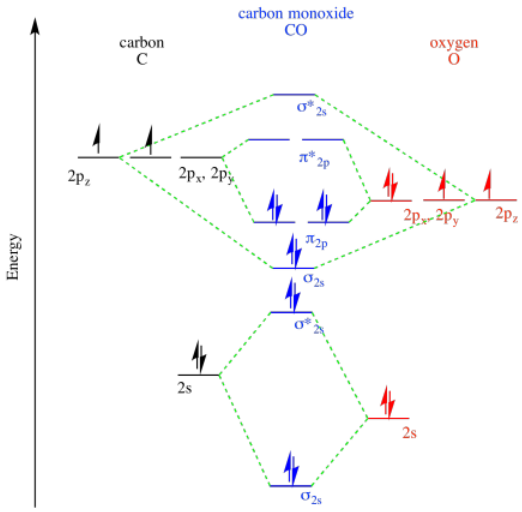
a. N_2^+. From the MO diagrams, N_2^+ has one less bonding electron. Thus, the bond order will be lower and the bond will be longer than in N_2.
b. N_2^-. From the MO diagrams, N_2^- has one more antibonding electron. Thus the bond order will be lower and the bond will be longer than N_2.

Exercise 13.7.3:

a. O_2^+ . From the MO diagram, O_2^+ has one less antibonding electron. Thus the bond order will be higher and the bond will be stronger than in O_2.
b. O_2. From the MO diagram, O_2 has one less antibonding electron. Thus the bond order will be higher and the bond will be stronger than in O_2^-.

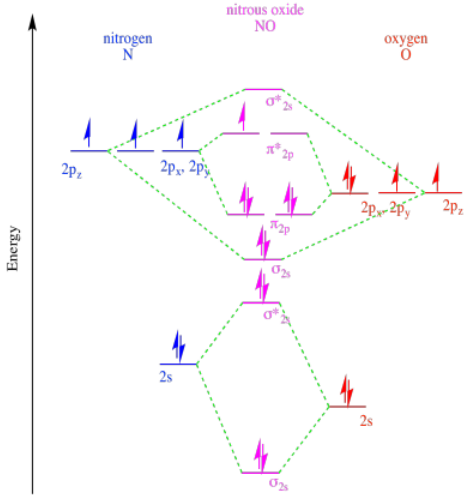
Exercise 13.9.1:

a)



diamagnetic; bond order = 3 (3 net pairs bonding)

b)



paramagnetic (one electron unpaired);
bond order = 2.5 (2 net pairs bonding; third bonding pair offset by one electron antibonding)

c)

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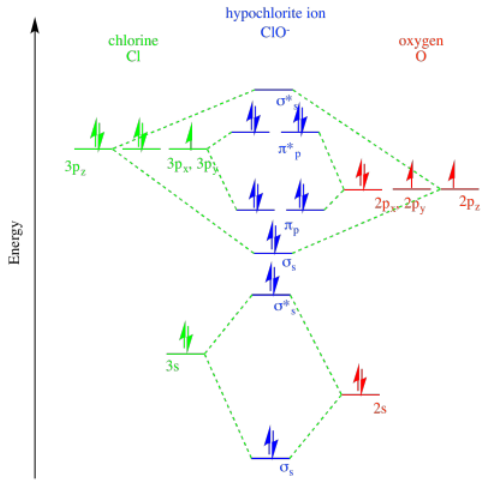
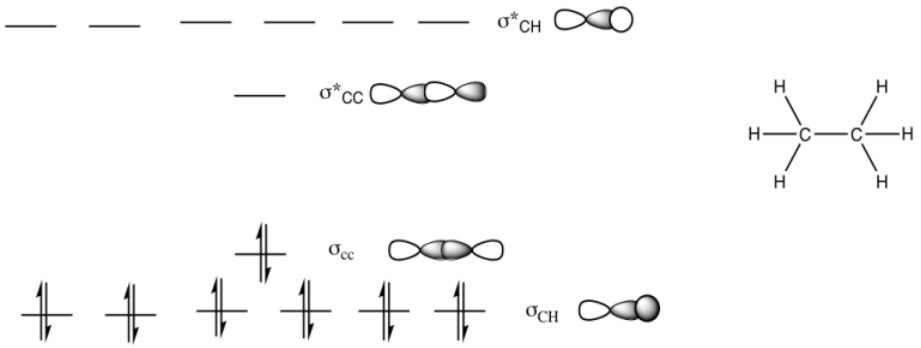


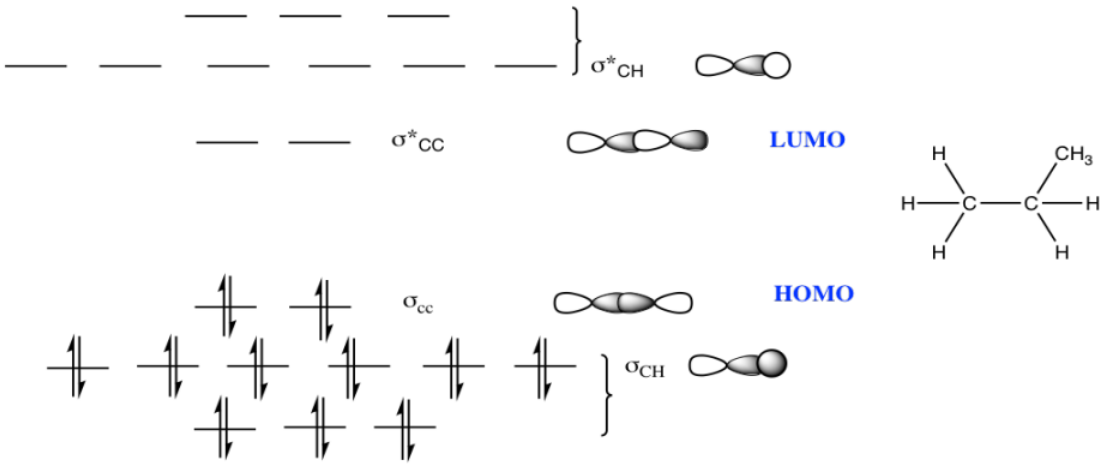
Note that the hypochlorite anion has one additional electron to make it negative.
diamagnetic; bond order = 1 (1 net pair bonding)

Exercise 13.11.1:

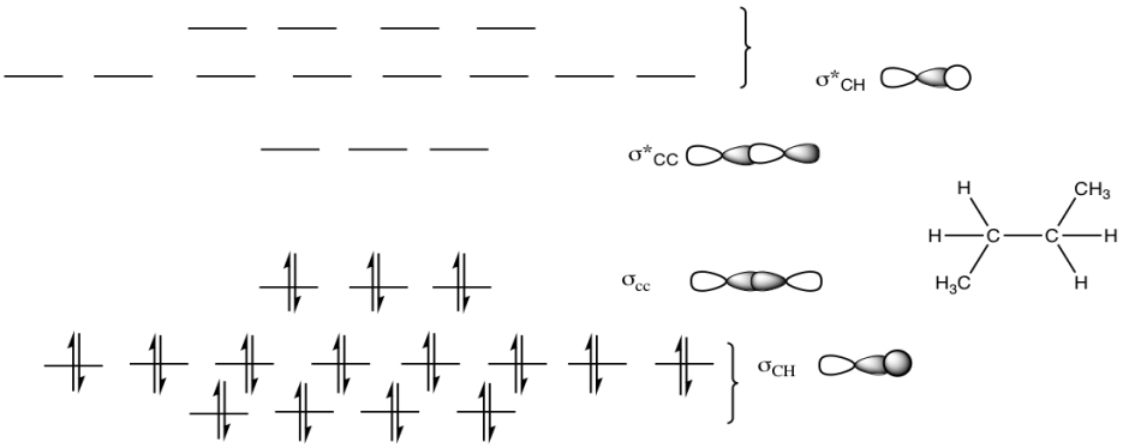
a)



b)



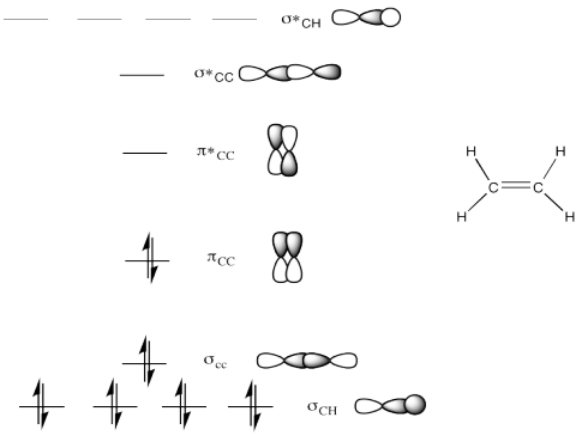
c)



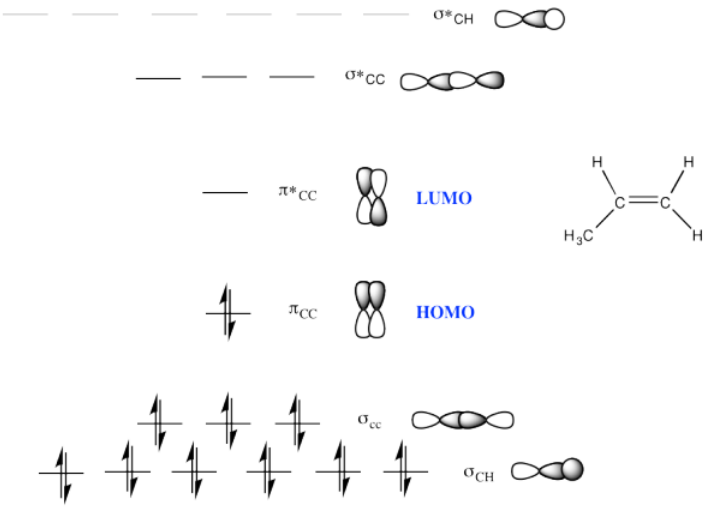
The number of orbitals = the number of bonds and the number of antibonds (thus twice as many orbitals as you would draw in a lewis structure.

Exercise 13.11.2:

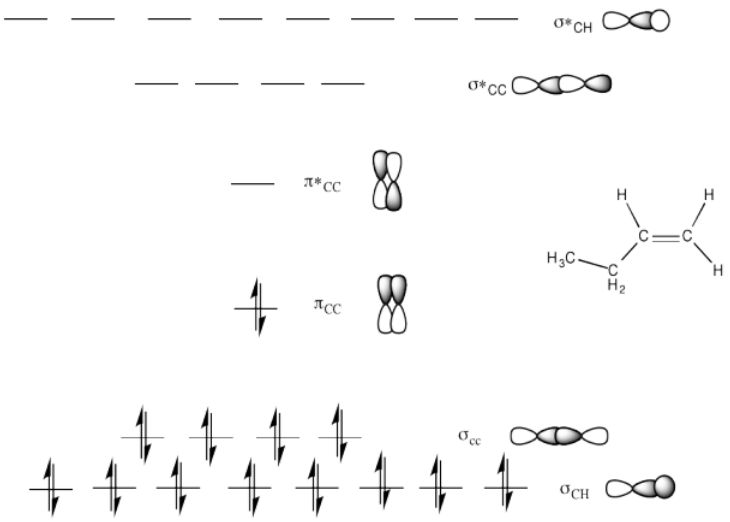
a)



b)

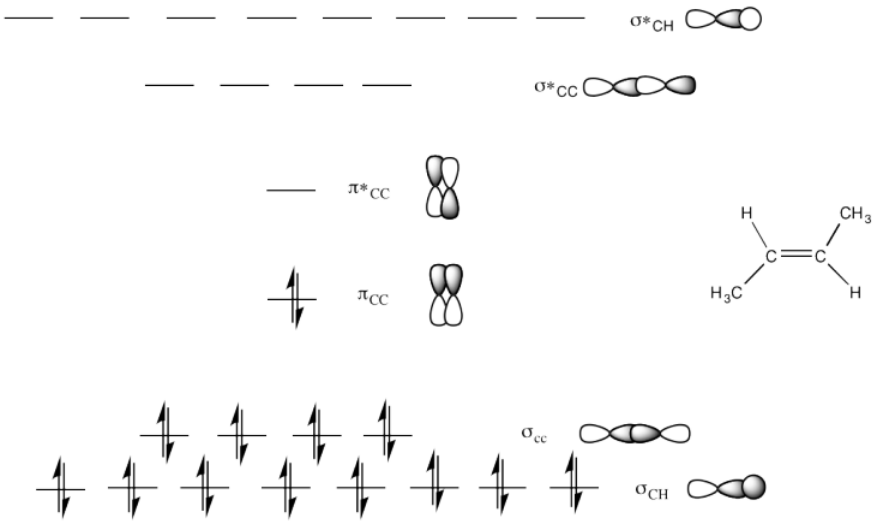


c)



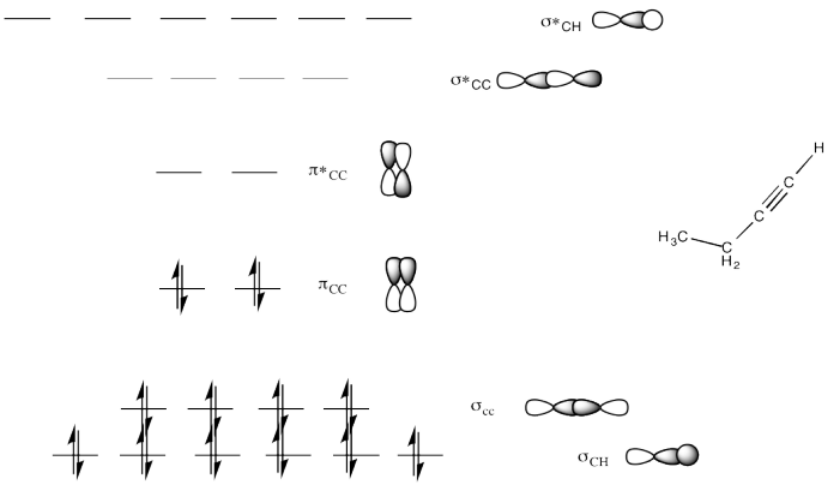
The number of orbitals = the number of bonds and the number of antibonds (thus twice as many orbitals as you would draw in a lewis structure.

d)



Location of pi bond makes little to no difference to the MO pattern.

e)



It results in the addition of another pi bond with approximately the same energy level.

Exercise 13.11.3:

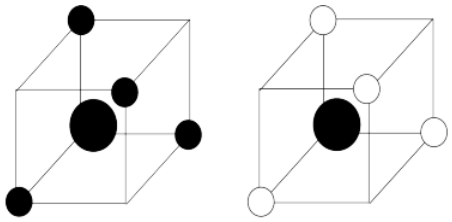
a)

tetrahedral

b)

p_x, p_y, p_z

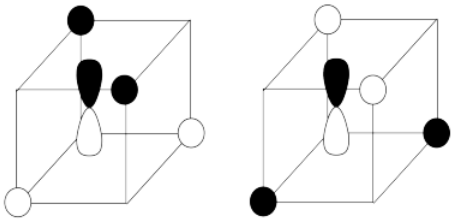
c)



all H1s orbitals in-phase with the B2s orbital

all H1s orbitals out-of-phase with the B2s orbital

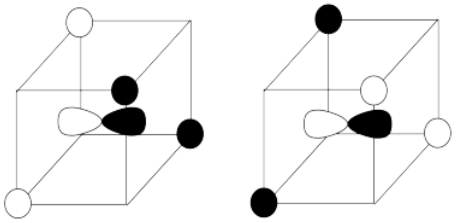
d)



all H1s orbitals in-phase with the B2p_z orbital

all H1s orbitals out-of-phase with the B2p_z orbital

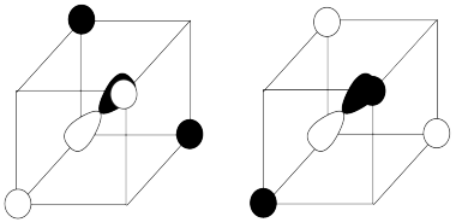
e)



all H1s orbitals in-phase with the B2p_y orbital

all H1s orbitals out-of-phase with the B2p_y orbital

f)



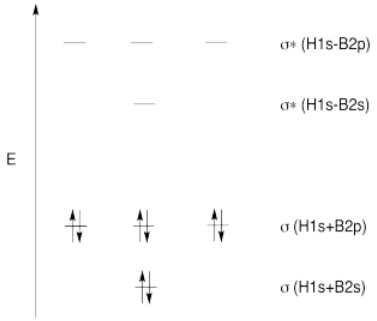
all H1s orbitals in-phase with the B2p_x orbital

all H1s orbitals out-of-phase with the B2p_x orbital

g) In each case all four H1s orbitals interact with each boron orbital.

h) The constructive overlap of the four H1s orbitals and the B2s orbital results in the lowest energy combination as it contains no nodes. (LOWEST ENERGY)
The constructive overlap of the four H1s orbitals with the three B2p orbitals results in bonding orbitals containing a single node. (MEDIUM-LOW ENERGY)

The destructive overlap of the four H1s orbitals with the B2s orbital results in an anti-bonding orbital. (HIGH ENERGY)
The destructive overlap of the four H1s orbitals with the three B2p orbitals results in anti-bonding orbitals. (HIGHEST ENERGY)



Exercise 13.11.4:

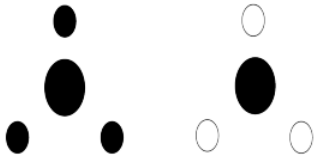
a)

trigonal planar

b)

p_x, p_y, p_z

c)



all H1s orbitals in-phase with the B2s orbital

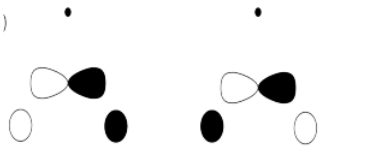
all H1s orbitals out-of-phase with the B2s orbital

d)

all H1s orbitals in-phase with the $B2p_z$ orbital, with one head-on σ overlap

all H1s orbitals out-of-phase with the $B2p_z$ orbital, with one head-on σ^* overlap

e)



two H1s orbitals in-phase with the $B2p_y$ orbital

two H1s orbitals out-of-phase with the $B2p_y$ orbital

f)

all the Hs are in the nodal plane

g) In some of the cases the one or more Hs may be in a nodal plane

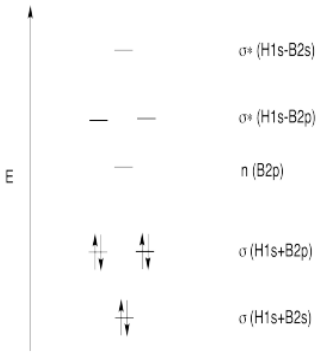
h) The constructive overlap of the H1s orbitals and the B2s orbital results in the lowest energy combination. (LOWEST ENERGY)

The constructive overlap of the three H1s orbitals with the B2p orbital results in a bonding orbital (MEDIUM-LOW ENERGY)

The constructive overlap of the two H1s orbitals with the B2p orbital results in a bonding orbital. (MEDIUM-LOW ENERGY)

The B2p orbital that is perpendicular to the plane of hydrogen atoms results in a non-bonding orbital. (MEDIUM ENERGY)
The destructive overlap of the two H1s orbitals with the B2p orbital results in an anti-bonding orbital (HIGH ENERGY)

The destructive overlap of the three H1s orbitals with the B2p orbital results in an anti-bonding orbital (HIGH ENERGY)
The destructive overlap of the three H1s orbitals with the B2p orbital results in an anti-bonding orbital (HIGHEST ENERGY)

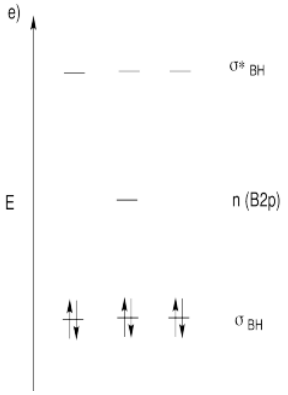


Exercises 13.12.1 & 13.12.2:

12.1

a) trigonal planar

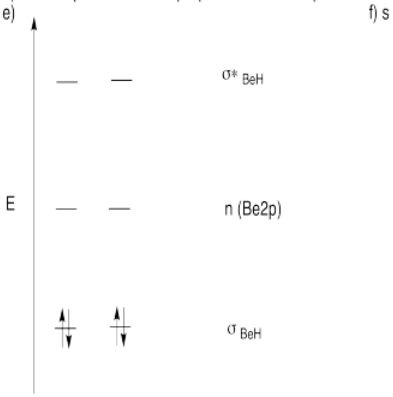
b) yes
c) no
d) one B2p orbital will be perpendicular to the plane of Hs
e)



f) sp^2

12.2

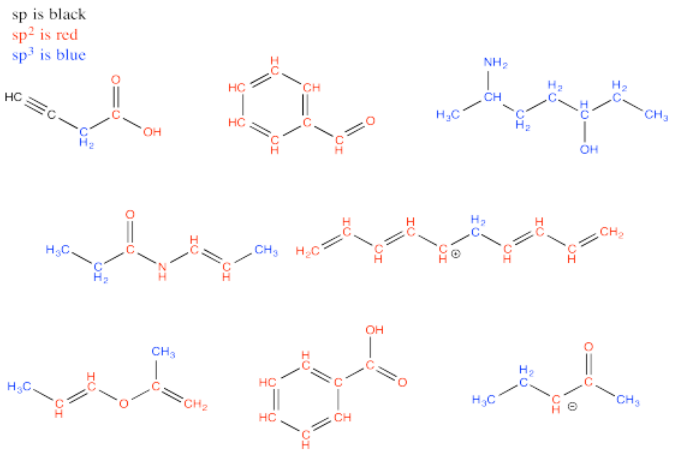
a) linear H–Be–H
b) yes
c) no
d) two Be2p orbital will be perpendicular to the plane of Hs
e)



f) s

Exercise 13.12.3:

sp is black
sp^2 is red
sp^3 is blue



Exercises 13.13.1-13.13.3:

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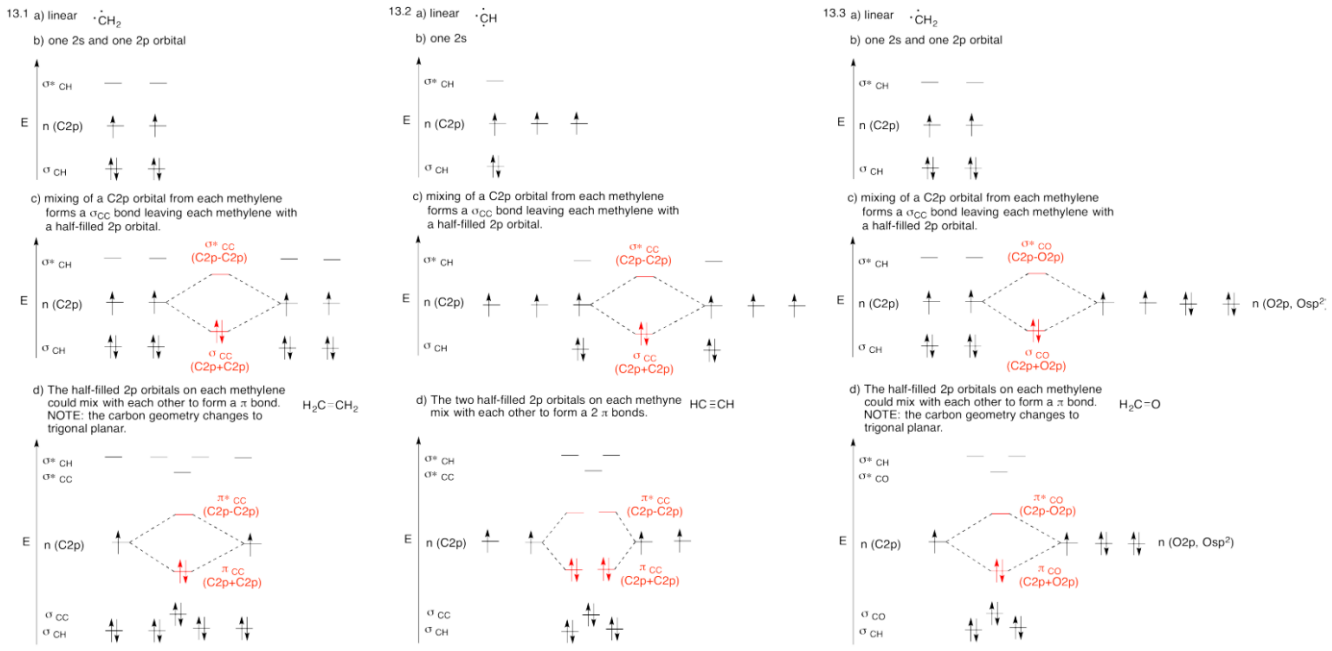
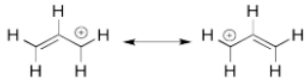


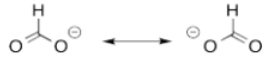
Exercises 13.14.1-13.14.5:

14.1



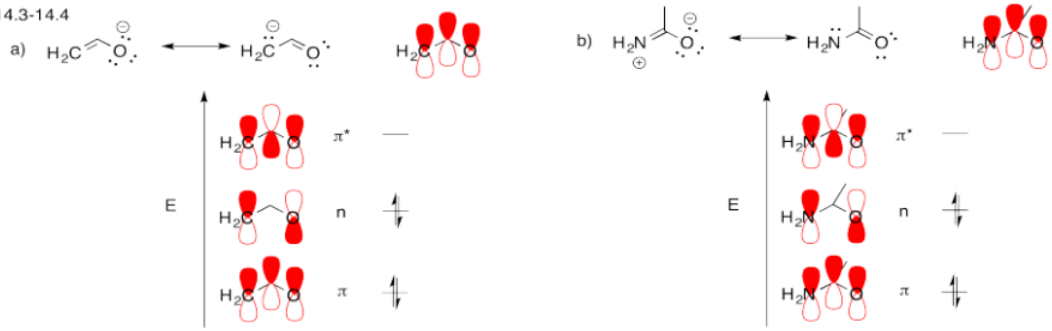
These two resonance structures follow the Lewis rules, but both are necessary to illustrate the delocalize electrons

14.2



These two resonance structures follow the Lewis rules, but both are necessary to illustrate the delocalize electrons

14.3-14.4



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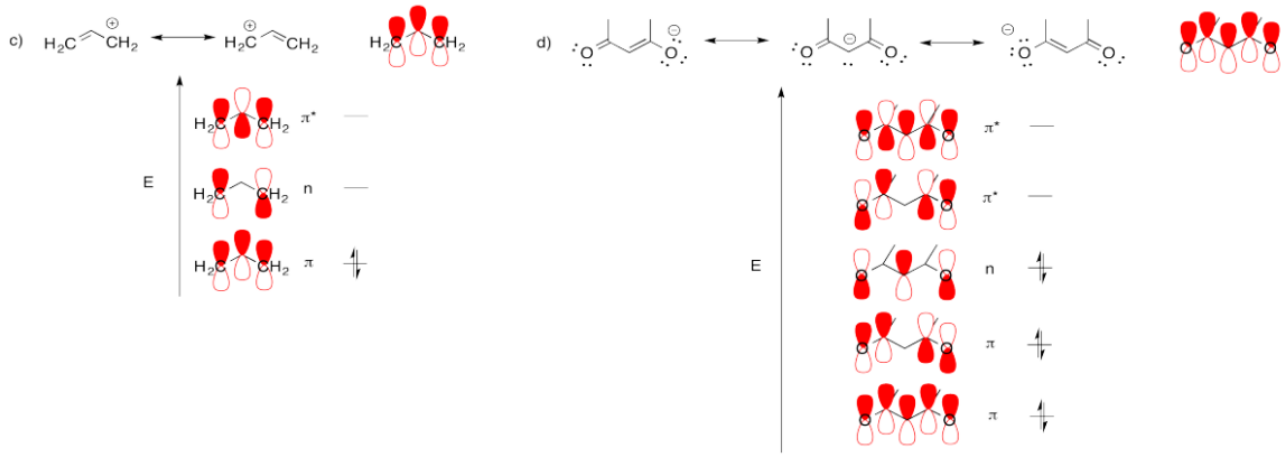


14.5

a) acetone, no conjugation as the oxygen lone pair elelctrons are perpendicular to the π orbital

b) bicarbonate, this is a conjugated system as the oxygen lone pair elelctrons align with the π orbital

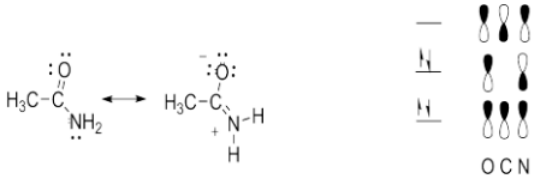
c) acetonitrile, this is not a conjugated system as the oxygen lone pair elelctrons are perpendiculat to the π orbital

(NOTE: second perpendicular π orbital is not shown)

d) dinitrogen tetroxide, this is a conjugated system as the oxygen lone pair elelctrons align with to the π orbital

Exercise 13.14.6:

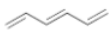
All of the answers depend on an understanding of the contributions of two resonance structures to the overall picture of acetaminde, or alternatively, that actetamide forms a conjugated pi system with four electrons delocalized over the O, C and N.

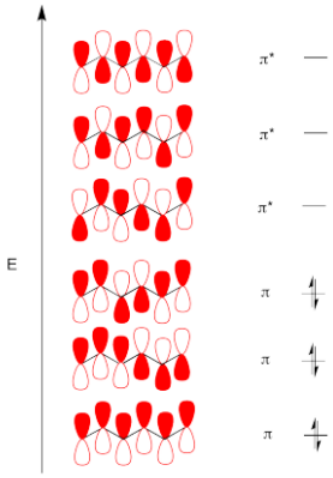


a. Contribution of the second resonance structure introduces some double bond character to the C-N bond and some single bond character to the C-O bond. Thus, both of these bonds are intermediate in length between single and double bonds.
b. Since the C, N and O atoms are sp2 hybridized, the C-N pi bond can only form if the remaining p orbitals on these atoms align. This places the atoms participating in the sp2 sigma bonds in the same plane.
c. Because of the partial double bond character there is a larger barrier to rotation than is typically found in molecules with only single bonds.
d. Because of the partial double bond character and the restricted rotation, the two H's are not identical. (One is nearer the O and one is nearer the CH3 and the restricted rotation prevents their interconversion.

Exercises 13.15.1-13.15.3:

15.1 Cis-alkenes in the carbon chains cause the packing to be less orderly than in saturated carbon chains

15.2 



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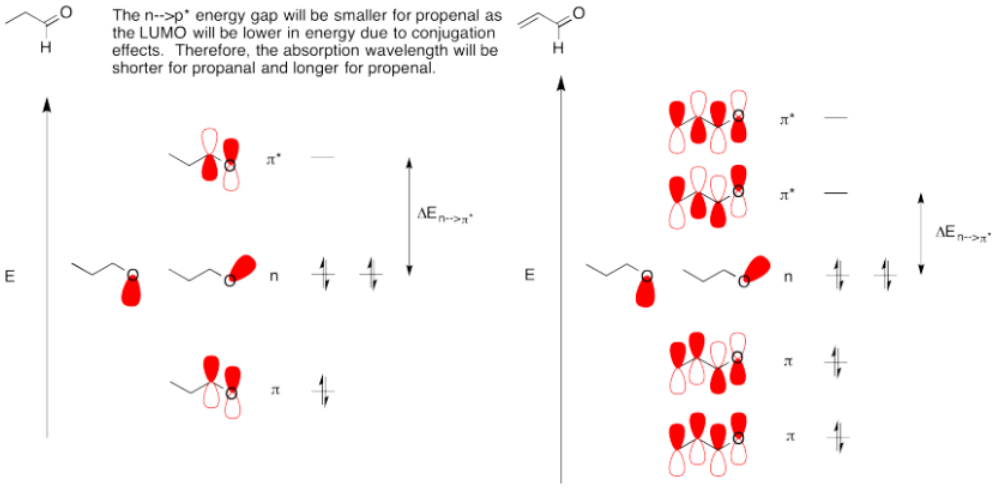

Exercise 13.15.4:

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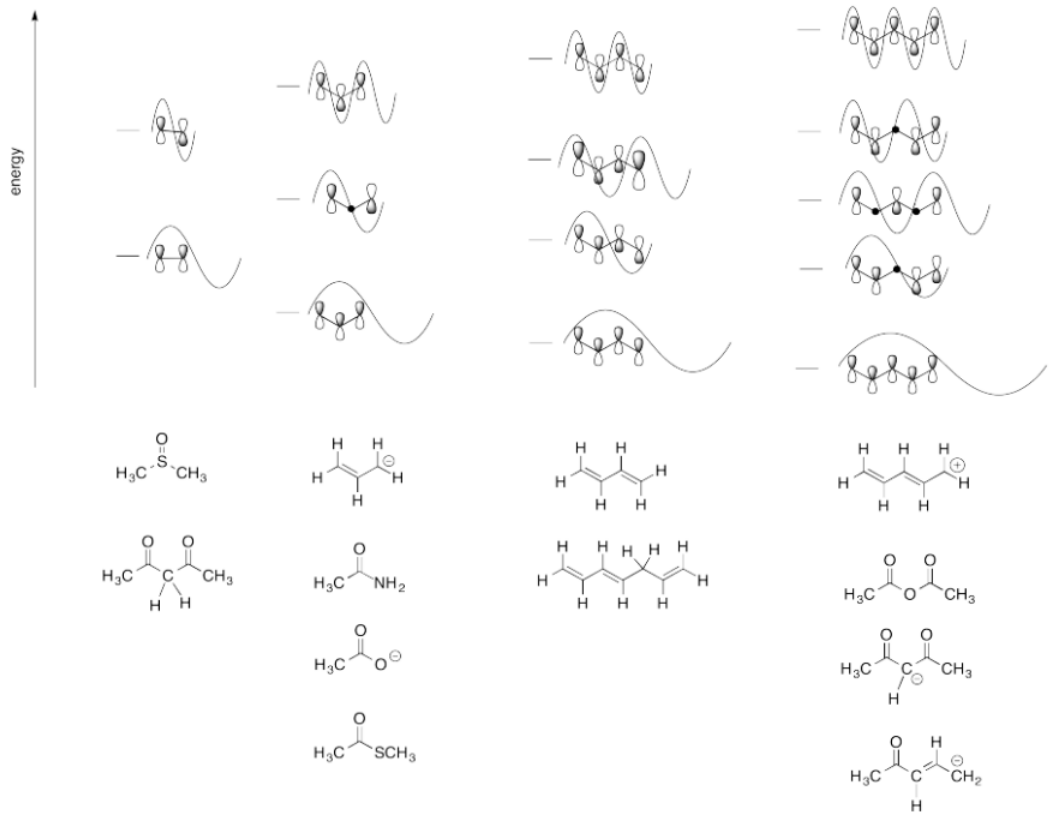


Exercise 13.16.1:

Because the two resonance structures shows double bonds in two different places, the implication is that all of the bonds in benzene have some double bond and some single bond character. You can think of them all as being about 1.5 bonds.

Exercise 13.16.2:

a) non-aromatic b) non-aromatic c) aromatic d) aromatic e) anti-aromatic f) anti-aromatic

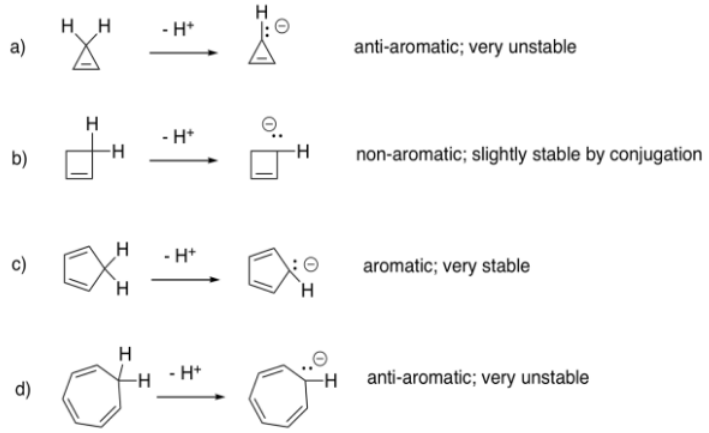
Exercise 13.16.3:

a) aromatic b) non-aromatic c) anti-aromatic d) aromatic

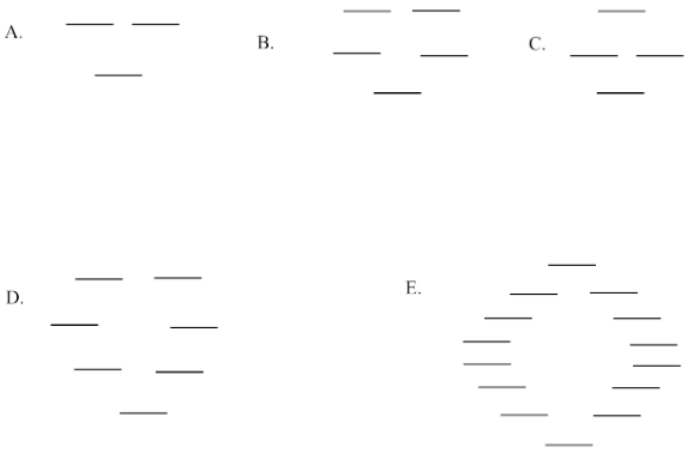
Exercise 13.16.4:

a) aromatic b) anti-aromatic c) aromatic d) anti-aromatic

Exercise 13.16.5:

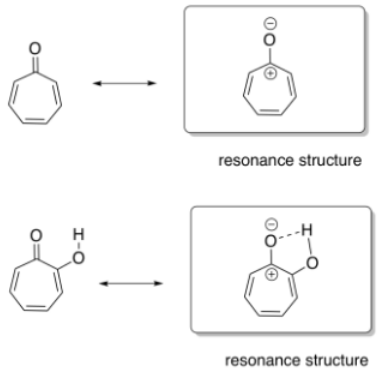


Exercise 13.16.6:



Exercise 13.16.7:

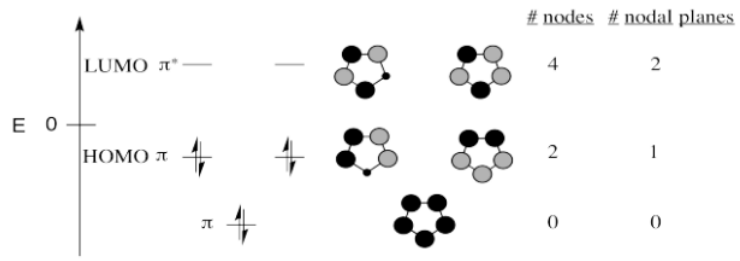
In tropone, the resonance structure on the right shows more aromatic character, because it clearly shows a fully-conjugated ring with an odd number of electron pairs in the pi system. The carbonyl in the picture on the left makes that conjugation less obvious: does its carbonyl pi bond contribute to the conjugated system of the ring? If it does, that would mean four pairs of electrons in the pi system, and that would be an even number, so it would be anti-aromatic.



The hydroxy group in hydroxytropolone would stabilize the compound in the structure shown on the right, via an ion-dipole interaction with the anionic oxygen. That makes the right-hand, explicitly aromatic structure the dominant one.

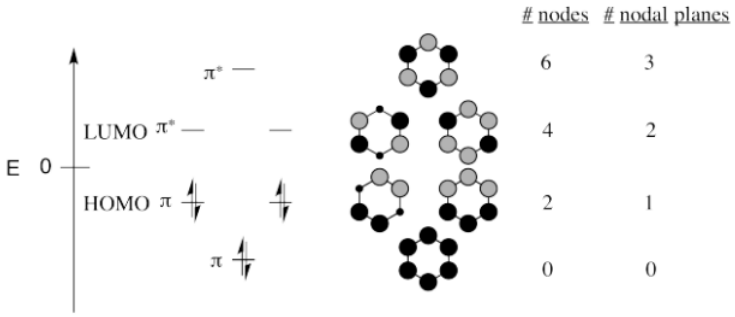
Exercise 13.17.1:

All of the compounds are aromatic and have the same Hückel MO diagram.



Exercise 13.17.2:

All of the compounds are aromatic and have the same Hückel MO diagram.



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CHAPTER OVERVIEW

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14.1: General Acidity and Basicity

Physical changes result in the transition of a molecular material from one form into another without any change in the composition of the material. A liquid compound can be cooled until it freezes or heated until it evaporates, but the atoms that make up the material are still connected together in the same way.

Chemical reactions result in a change in the composition of a material. Atoms become associated in different ways. Changes in bonding occur. Because bonding involves some kind of shared distribution of electrons between atoms, a chemical reaction involves some change in how electrons are arranged in the material.

- The standard way to think about a chemical reaction is to consider the movement of electrons in the reaction.

Reactions often involve many changes, so that one material is transformed into others via numerous redistributions of electrons. These individual steps within an overall reaction are sometimes called elementary reactions. One of the most common ways to analyze an elementary reaction is to understand in a very basic way where the electrons are moving from and where they are moving towards.

Figure 14.1.1: Electron movement and bond formation in a generalized reaction. Here, atom B is donating a pair of electrons to atom A.

- An atom or molecule that supplies a pair of electrons to form a new bond is an electron donor. An electron donor is often called a Lewis base.
- An atom or molecule that accepts a pair of electrons to form a new bond is an electron acceptor. An electron acceptor is often called a Lewis acid.

One of the most common Lewis acids, or electron acceptors, is a proton. It is so common that people often use the term "acid" just to describe compounds or solutions that supply protons.

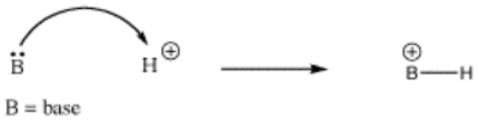

Figure 14.1.2: Proton as Lewis acid.

A Lewis base is anything with a lone pair. For example, water is a Lewis base because the oxygen atom has lone pairs. If we take a source of protons, such as hydrogen chloride (HCl, a colorless gas) and bubbler it into a flask of water, a reaction will result. The water will donate electrons to the proton in the HCl, producing hydrochloric acid, or aqueous hydrogen chloride: $HCl_{(aq)}$.

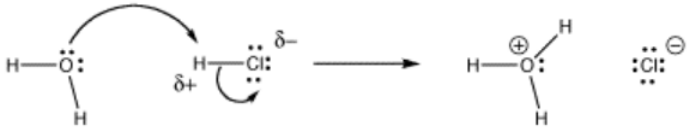

Figure 14.1.3: Donation of electrons from a water molecule to a proton.

Note that a hydrogen atom can only have one bond, so when the water donates its electrons to the hydrogen, the bond between the hydrogen and the chlorine has to be broken. The electrons in the bond move to the chlorine, which is more electronegative than the hydrogen.

Also, notice that the hydrogen atom did not even need a full positive charge to attract the water. A partial positive charge will still attract electrons.

Acids don't have to be protons or protons donors. Very often, metal ions are able to attract electrons, because metal ions are positively charged. Ca^{2+}, Sc^{2+}, Ti^{4+} are just a few common examples.

Figure 14.1.4: A calcium ion can attract electrons from a donor atom.

These ideas will be explored more fully in this chapter. They are some of the most important ideas in chemistry, forming the basis for most of what we know about the relationships between structure, properties, and reactivity.

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14.2: Lewis Bases

What makes a molecule (or an atom or ion) a Lewis base? It must have a pair of electrons available to share with another atom to form a bond. The most readily available electrons are those that are not already in bonds. Bonding electrons are low in energy. Non-bonding electrons are higher in energy and may be stabilized when they are delocalized in a new bond.

- Lewis bases usually have non-bonding electrons or lone pairs.

Ammonia, NH_3, has a lone pair and is a Lewis base. It can donate to compounds that will accept electrons.

Figure 14.2.1: Ammonia donating to an electron acceptor or Lewis acid.

Lewis bases may be anionic or neutral. The basic requirement is that they have a pair of electrons to donate. Examples of Lewis bases include halide ions such as bromide or chloride. To the right of the halides in the periodic table are Noble gases such as neon. Noble gases do have lone pairs, but are stable enough that they do not usually react. They are not very good Lewis bases. To the left of the halides, however, are other examples in oxygen and nitrogen compounds. Water also has lone pairs and is a common Lewis base, and so is hydroxide ion, HO^-.

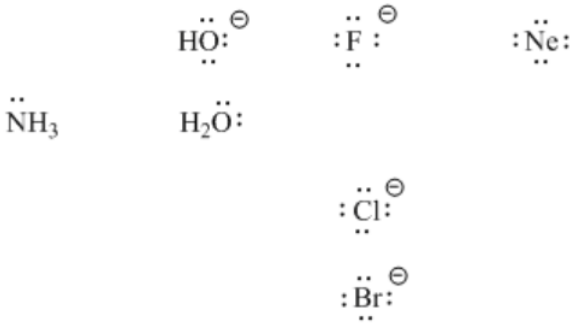

Figure 14.2.2: Some examples of Lewis basic ions and molecules. Note that neon, although it has nonbonding electron pairs or lone pairs, does not usually act as a Lewis base.

- Halides, water, ammonia and hydroxide ion are examples of Lewis bases.

One column further to the left in the periodic table from nitrogen is carbon. Carbon does not normally have a lone pair. For example, methane, CH_4, has all of its valence electrons in bonding pairs. These bonding pairs are too stable to donate under normal conditions. Methane is not a Lewis base.

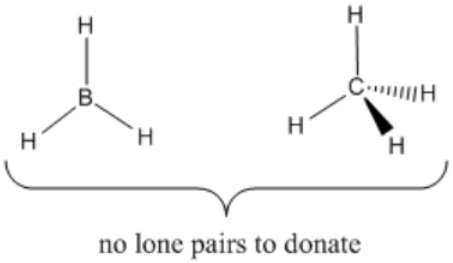

Figure 14.2.3: Carbon and boron "hydrides". Neither of these compounds has a lone pair, and neither is a good Lewis base.

Even further to the left is boron. A simple boron compound is borane, BH_3. Borane has no lone pairs; all its valence electrons are in bonds. Boron is not a good Lewis base.

Exercise 14.2.1

What structural feature is required in order to be a Lewis base?

Answer

A Lewis base must have lone pairs or non-bonding electron pairs so that it can donate them to a Lewis acid.

Alternatively, in some cases the electrons in a π-bond can be donated instead, so sometimes compounds with π-bonds can be Lewis basic.

Exercise 14.2.2

Which of the following compounds appear to be Lewis bases?

a) SiH_4 b) AlH_3 c) PH_3 d) SH_2 e) ^-SH

Answer

a. not a Lewis base

b. not a Lewis base

c. Lewis base

d. Lewis base

e. Lewis base

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14.3: Lewis Acids

Borane is unusual because it is a compound without an octet. The central boron atom has only six valence electrons. It needs one more pair of electrons to obtain an octet. The boron is a Lewis acid.

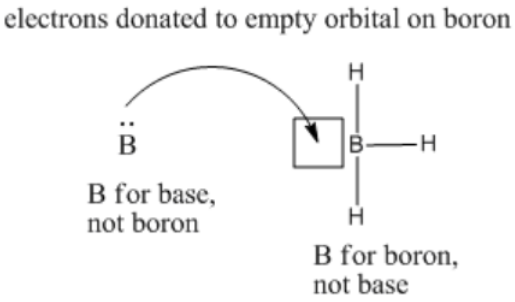


Figure 14.3.1: Borane is a Lewis acid. It can accept electrons from a donor atom. The square drawn beside the boron is used to reinforce the idea that there is a vacant site for electrons there.

- Lewis acids are often short of a complete octet.

In the main group of the periodic table, atoms in the Group IIIA column (including boron and aluminum) have three valence electrons to share in order to make bonds. Sharing these electrons with three electrons from neighbors would make three bonds, and provide six electrons, not eight, in the valence shell. Another pair of electrons must be accepted from a donor to achieve an octet.

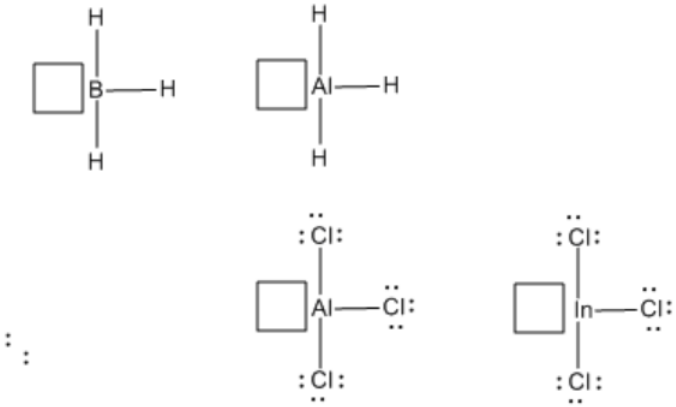


Figure 14.3.2: Boron, aluminum and indium are from the same column of the periodic table. All three are often Lewis acidic; they can accept electrons from donors.

- Boron, aluminum and indium compounds are often Lewis acids.

The eight-electron rule does not hold throughout the periodic table. In order to obtain noble gas configurations, some atoms may need eighteen electrons in their valence shell. For example, transition metals such as titanium often follow an eighteen-electron rule. Titanium has four valence electrons and can form four bonds in compounds such as titanium tetrakis(isopropoxide), below, or titanium tetrachloride, $TiCl_4$. However, the titanium atom in that compound has only eight valence electrons, not eighteen. It can easily accept electrons from donors.

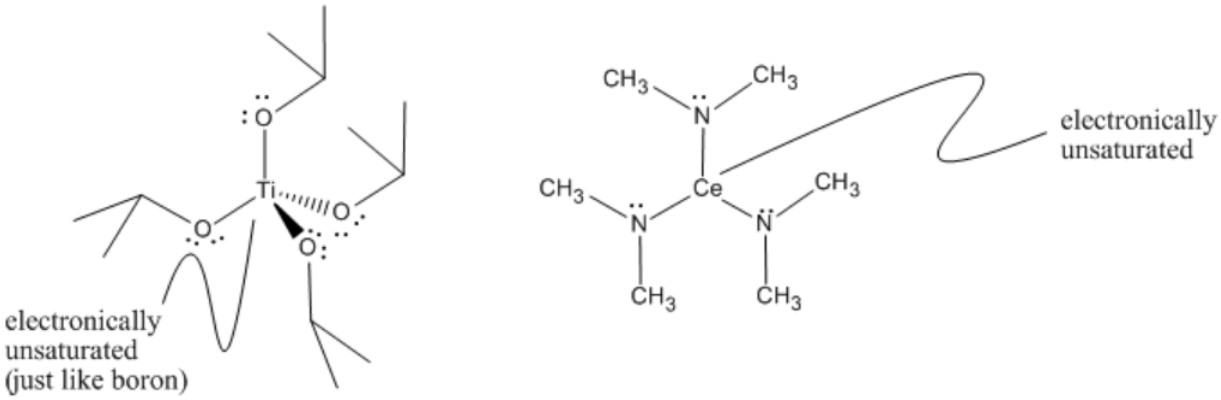


Figure 14.3.3: Although titanium has eight electrons in this molecule, titanium tetrakis(isopropoxide), it can accommodate up to eighteen. It is Lewis acidic. The cerium atom in cerium tris(dimethylamide) comes from a similar part of the periodic table and is also Lewis acidic.

- Transition metals such as titanium, iron and nickel may have up to eighteen electrons and can frequently accept electron pairs from Lewis bases. Transition metals are often Lewis acids.
- Lanthanides such as cerium and samarium could conceivably have up to thirty-two electrons in their valence shells! They never do. However, they are usually strong Lewis acids.

Positive ions are often Lewis acids because they have an electrostatic attraction for electron donors. Examples include alkali and alkaline earth metals in the group IA and IIA columns. K^+, Mg^{2+} and Ca^{2+} are sometimes seen as Lewis acidic sites in biology, for example. These ions are very stable forms of these elements because of their low electron ionization potentials. However, their positive charges do attract electron donors.

Figure 14.3.4: calcium ion essentially has a noble gas configuration. Nevertheless, its positive charge can attract electrons from a donor atom.

In a similar way, "early" transition metals -- those that are close to the left hand side of the periodic table, especially in groups IIIB, IVB and VB -- have low ionization potentials and have high positive charges or oxidation states. For example, Sc^{3+}, Zr^{4+} and V^{5+} are common forms of some early transition metals, and they are strong Lewis acids.

Figure 14.3.5: A few alkali, alkaline earth and transition metals that are commonly found as cations.

- Many cations such as Ca^{2+} or Sc^{3+} are good Lewis acids. Their positive charges attract electrons.

Sodium, potassium, calcium and magnesium are common ions in biology. Sodium, potassium and calcium have well-known roles in cell signaling. The build-up of these ions on one side or another of a cell membrane results in a charge separation across the membrane, called a membrane potential. However, the Lewis acidity of these ions are also important in biology. Because they attract electron donors, these ions are generally found in biological situations with water molecules stuck to them; remember that the oxygen atom in water is Lewis basic. That means that the proteins that form ion channels in cell membranes must somehow cope with the water molecules that are all around when they are transporting potassium ions or sodium ions across the membranes. A potassium ion covered in water molecules is a much larger object than a potassium ion by itself. The pore that opens up between the proteins must be big enough to allow the entire water-potassium complex through, or else there must be a way to separate the water molecules from the potassium ion. At the same time, the ion channel may exploit the Lewis acidity of the potassium ion; for

example, the channel proteins may contain oxygen atoms situated in such a way that they draw the ion into the channel. Exactly how ion channels work is a very active topic of current research at the interface of chemistry and biology.

There are other biological situations in which the Lewis acidity of these ions plays a role. For example, potassium ions bind to nucleic acids in DNA to form the telomeres at the ends of chromosomes. This binding involves the donation of lone pairs on the nucleic acids (guanidines in this case) to a potassium ion. Another common biological structure in which donor atoms bind to a Lewis acid is chlorophyll, in which a porphyrin ring binds to a central magnesium ion. Chlorophyll is involved in the absorption of sunlight and the initiation of electron transport to photosystem I and II, which are the engines of photosynthesis. One of the roles of the magnesium ion in this structure is to affect the color of the chlorophyll and hence the wavelengths of light absorbed; when other metal ions are bound by the porphyrin, different colors are absorbed.

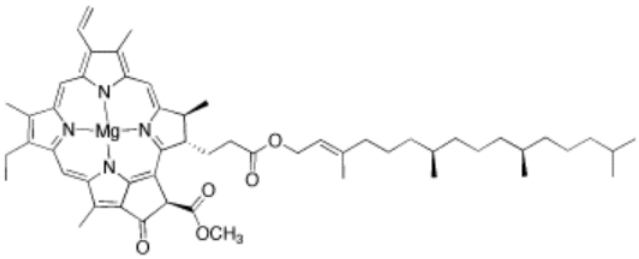


Figure 14.3.6: Chlorophyll A.

A number of biological molecules that contain metal ions perform tasks that require Lewis acidity. Many enzymes that contain metal ions, sometimes called metalloproteins, bind a substrate and carry out a transformation on it. The substrate is usually able to donate a pair of electrons to the metal ion and stick to it while a reaction occurs. For example, vanadium bromoperoxidase is a protein found in some kinds of marine algae. It can bind dissolved oxygen molecules as well as bromide ions from the surrounding saltwater. A subsequent series of reactions allows the bromine atom to be incorporated into large organic molecules. Halogens in organic molecules are extremely rare in nature, but it is perhaps not surprising that organisms surrounded by salt water have managed to make them. The resulting brominated compounds seem to be used as chemical defenses, making the algae less likely to get eaten.

A number of other metal ions are common in biology. Manganese is prominent in photosystem I and II, iron is found in hemoglobin, and cobalt is in vitamin B12. Hemoglobin may be familiar because of its role in transporting oxygen in the blood.

Figure 14.3.7: Some transition metal ions that are common in biology.

Atoms in the lower part of the periodic table often have variable oxidation states. They can form different numbers of bonds. Although carbon generally forms four bonds, forming compounds like carbon tetrachloride, CCl_4, tin can sometimes form two bonds as well as four. Tin forms stannous chloride, $SnCl_2$, as well as stannic chloride, $SnCl_4$. It is possible that stannous chloride, with sixteen valence electrons, could accept another pair of electrons.

It may be surprising that stannic chloride is also a Lewis acid. The tin atom in stannic chloride has a full octet (eighteen valence electrons), but it still attracts electron donors. Given the difference in electronegativity between tin and chlorine, however, it seems reasonable to think of these compounds in terms of very polar bonds.

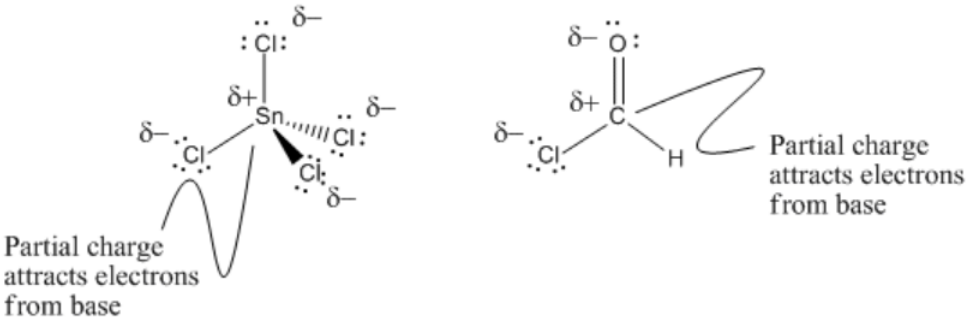


Figure 14.3.8: Tin and carbon atoms in environments that make them attract electrons.

- Atoms with an octet can still be Lewis acidic if they bear a large, partial positive charge.

Carbon atoms can be Lewis acidic even though carbon does not generally form ionic bonds. For example, formyl chloride, H-(C=O)-Cl, contains a carbon atom that is bonded to a chlorine and also double bonded to an oxygen atom. Although these bonds are certainly covalent, bond polarity places a large, partial positive charge on the carbon. Formyl chloride easily attracts a pair of electrons from a Lewis base.

Exercise 14.3.1

What structural feature is required to be a Lewis acid?

Answer

A Lewis acidis atom attracts electrons from a Lewis base.

The most common feature of a Lewis acid is an atom that is not "electronically saturated" or has not filled its octet. For example, an aluminum with only six electrons rather than eight is Lewis acidic.

Other atoms, like transition metals, have "octets" of eighteen electrons, so having fewer than eighteen electrons in their valence shell can make these atoms Lewis acidic.

Exercise 14.3.2

Which of the following compounds appear to be Lewis acids? Explain your reasoning in each case.

a) $CeCl_3$ b) BF_3 c) CH_4 d) CH_2O e) N_2

Answer

a. Lewis acid

b. Lewis acid

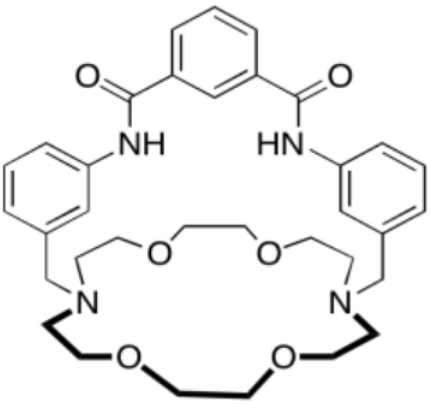
c. not a Lewis acid

d. Lewis acid

e. not a Lewis acid

Exercise 14.3.3

The Smith research group at University of Notre Dame has been working with molecules that can be used for imaging, sensing and related health care applications.



a. Circle the ring that contains several oxygens.
b. The part of the molecule you have circled would bind (choose one):

anions cations

c) Explain how these ions would be bound.

d) Put a box around the portion of the molecule capable of acting as a hydrogen bond donor.

e) The part of the molecule you have circled would bind (choose one):

anions cations

f) The Smith lab has shown that these molecules bind chloride ions. Draw a chloride ion in the correct position in the molecule.

g) In the presence of potassium ions, the molecule can bind both potassium and chloride. Add both ions in the correct positions in the molecule.

Measurement of the equilibrium of bound vs. unbound chloride ions showed that chloride binding was stronger when potassium ions were also bound.

h) Explain why chloride binding is stronger when a potassium ion is also bound to the sensor molecule.

Answer

a)

b) cations

c) possibly ion-dipole forces; alternatively, the oxygen atoms could act as Lewis bases, donating lone pairs to a cation.

d)

e) anions

f)

g)

h) When the chloride ion binds to the sensor molecule it gives the overall complex a negative charge and addition of the potassium ion cancels out this charge

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14.4: Lewis Acid-Base Complexes and Molecular Orbitals

What happens when a Lewis base donates a pair of electrons to a Lewis acid? The arrow formulism we have been using to illustrate the behavior of Lewis acids and Lewis bases is meant to show the direction of electron movement from the donor to the acceptor. However, given that a bond can be thought of as a pair of electrons that are shared between two atoms (in this case, between the donor and the acceptor), these arrows also show where bonds are forming.

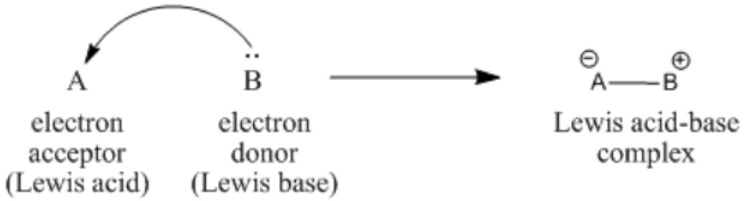


Figure 14.4.1: Donation of electrons from a Lewis base to a Lewis acid.

The electrons donated from a Lewis base to a Lewis acid form a new bond. A new, larger compound is formed from the smaller Lewis acid and Lewis base. This compound is called a Lewis acid-base complex.

A simple example of Lewis acid-base complexation involves ammonia and boron trifluoride. The nitrogen atom has a lone pair and is an electron donor. The boron has no octet and is an electron acceptor. The two compounds can form a Lewis acid-base complex or a coordination complex together.

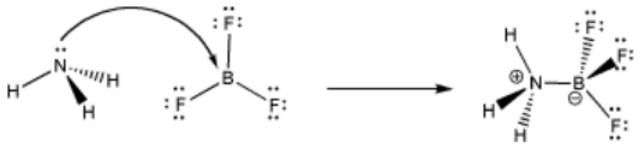


Figure 14.4.2: Formation of a Lewis acid-base complex from ammonia and boron trifluoride.

When the nitrogen donates a pair of electrons to share with the boron, the bond that forms is sometimes called a coordinate bond. Another term for this kind of bond is a dative bond. A coordinate or dative bond is any covalent bond that arose because one atom brought a pair of its electrons and donated them with another.

There is another piece of terminology you should get used to here. Sometimes, the electron donor is called a nucleophile and the electron acceptor is called an electrophile. Ammonia is a nucleophile and boron trifluoride is an electrophile.

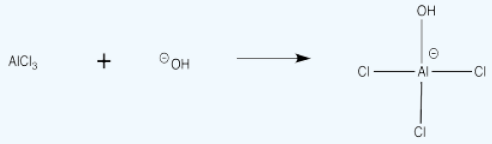
- Because Lewis bases are attracted to electron-deficient atoms, and because positive charge is generally associated with the nucleus of an atom, Lewis bases are sometimes refered to as "nucleophiles". Nucleophile means nucleus-loving.
- Because Lewis acids attract electron pairs, Lewis acids are sometimes called "electrophiles". Electrophile meanse electron-loving.

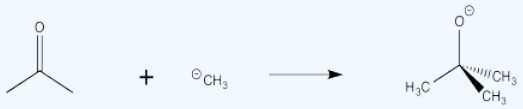
Lewis acid-base complexes frequently have very different properties from the separate compounds from which they were formed. For example, titanium tetrachloride is a yellow liquid at room temperature. It is so Lewis acidic that it reacts with moisture in the air, undergoing a reaction that generates HCl gas in the form of white smoke. Tetrahydrofuran (or THF), a mild Lewis base, is a colorless liquid. When THF and $TiCl_4$ are combined, a Lewis acid-base complex is formed, $TiCl_4(THF)_2$. $TiCl_4(THF)_2$ is a yellow solid at room temperature. Although it still reacts with the air, it does so very slowly, and shows no visible change when exposed to the air for several minutes.

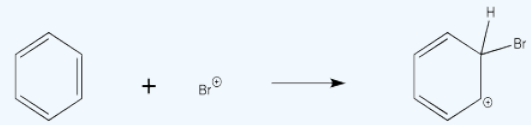
Figure 14.4.3: A Lewis acid-base complex between tetrahydrofuran (THF) and titanium tetrachloride.

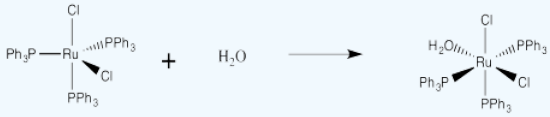
Exercise 14.4.1

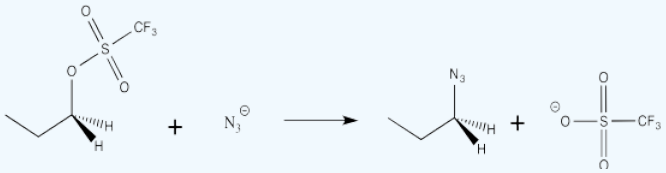
Use curved arrow notation to show the electron movement for the following reactions.











Answer

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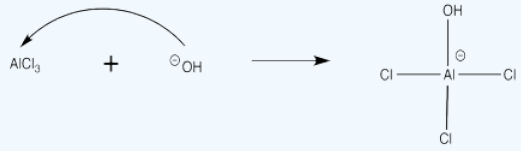
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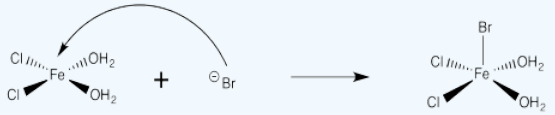
Al
Cl
Cl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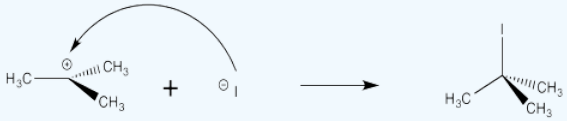
Cl
OH2
Br
Cl
Fe
Br
OH2
Cl
OH2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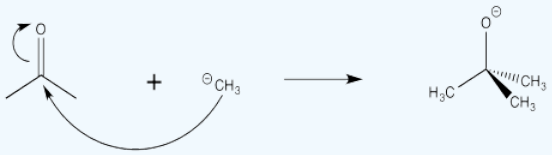
CH3
I
I
H3C
CH3
CH3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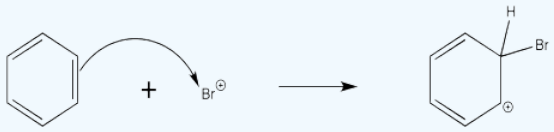
CH3
CH3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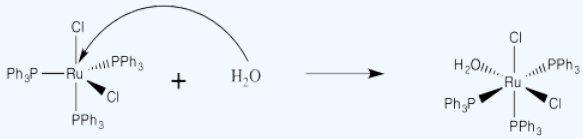
H
Br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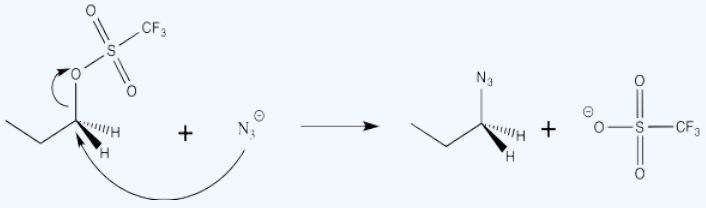
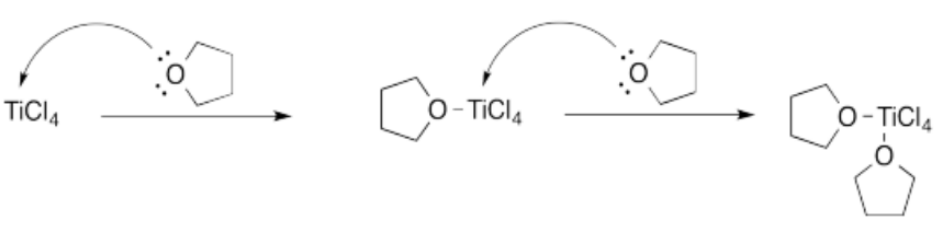
Ru
PPh3
Cl
PPh3
H2O
Cl
H2O
Ru
PPh3
Ph3P
Cl
PPh3


O
CF3
S
O
O
H
H
N3
N3
H
H
O
O
S
CF3
O

Exercise 14.4.2

Show, using arrow notation, the two-step reaction between THF and titanium tetrachloride to form the Lewis acid-base complex, $TiCl_4(THF)_2$. Also show the structures of the intermediate and final complexes.

Answer



Exercise 14.4.3

A similar Lewis acid-base complex is formed between THF and borane, BH_3.

a) Which compound is the Lewis acid? Which one is the Lewis base?

b) Which atom in the Lewis acid is the acidic site? Why?

c) Which atom in the Lewis base is the basic site? Why?

d) How many donors would be needed to satisfy the acidic site?

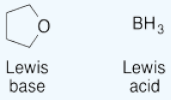
e) Show, using arrow notation, the reaction to form a Lewis acid-base complex.

f) Borane is highly pyrophoric; it reacts violently with air, bursting into flames. Show, using arrow notation, what might be happening when borane contacts the air.

g) Borane-THF complex is much less pyrophoric than borane. Why do you suppose that is so?

Answer

a.

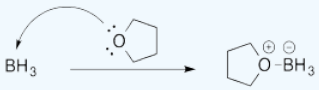


b. boron's empty p-orbital

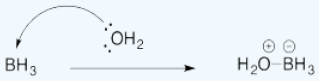
c. non-bonding electrons on oxygen

d. one pair of electrons

e.



f.



g. borane is already complexed with THF and will be slower to react with water in the atmosphere

Exercise 14.4.4

When a neutral Lewis acid combines with an anionic Lewis base, the product is called a complex ion. The same is true if a cationic Lewis acid combines with a neutral Lewis base.

Show the formation of the following polyatomic anions from the Lewis acid-base pairs that were combined in each case.

a) BF_4^- b) PF_6^- c) $AlCl_4^-$ d) AlH_4^- e) $Ag(NH_3)_2$

Exercise 14.4.5

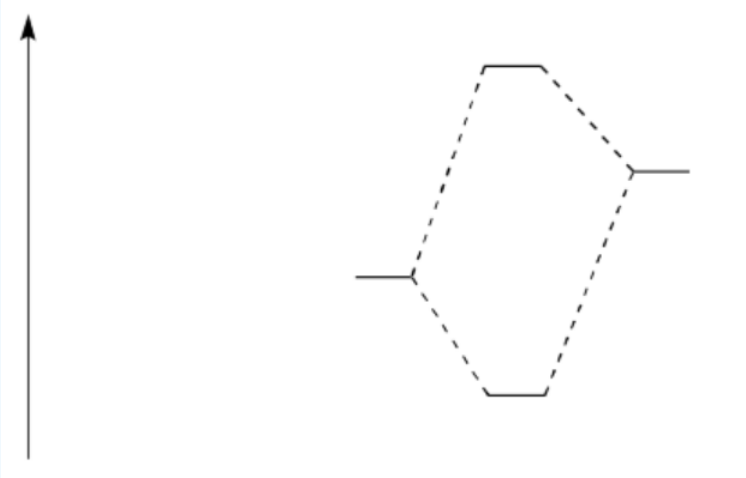
Consider the reaction below.

• Draw an MO mixing diagram for the reaction above, using the following steps:

o Draw the orbital from the base that is likely to donate its electrons.

o Draw the orbital from the acid that is likely to accept electrons.

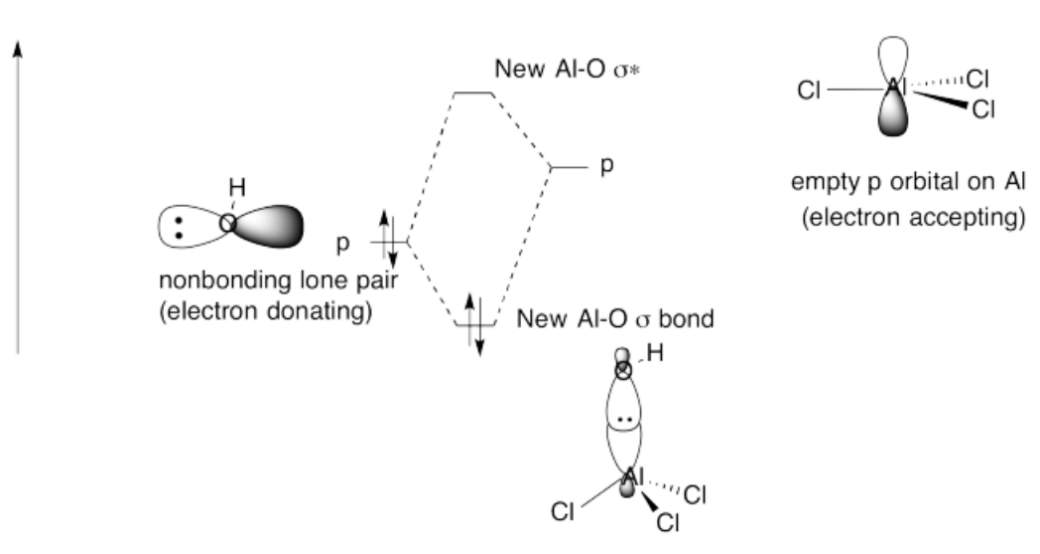
o Complete the MO mixing diagram of these two orbitals:



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

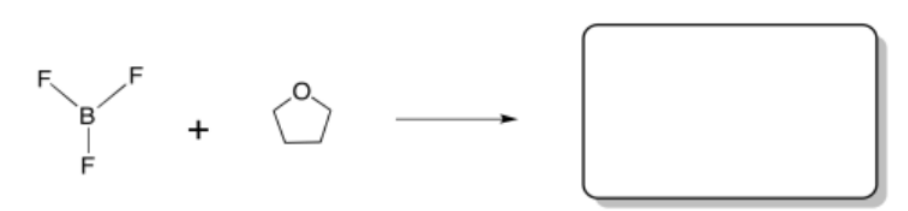
o Draw a cartoon showing the mixing of these orbitals.

Answer

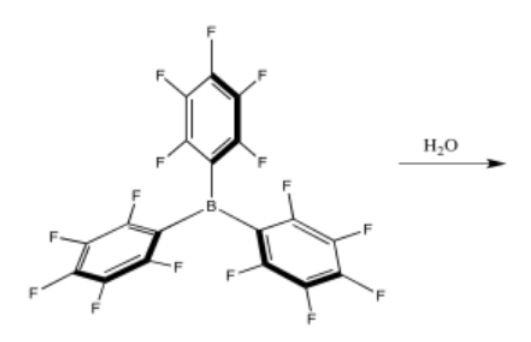


Exercise 14.4.6

a) A typical Lewis acid/base pair is shown below.

- Label the two compounds below as either Lewis acid or Lewis base.
- Draw curved arrows to show movement of electrons to form a bond.
- Draw the product of the reaction.
- 

b) The Lewis pair below reacts to form an adduct, but much more slowly than the one above.



- Suggest two reasons why the Lewis acid/base adduct forms so slowly.

Answer

a)

b)

- The benzene rings take up more space than a fluorine atom; they may get in the way, making it harder for the water molecule to approach.

Also, the aromatic rings may be able to form a conjugated system with the empty p orbital; if that p orbital is partially filled, the boron atom becomes less Lewis acidic.

- A larger group than fluorine may cause more steric hindrance. Replacing the two fluorines closest to the boron on each arene (aromatic ring) with a CH_3 or CF_3 group would slow down the formation of an adduct. Alternatively, a less electronegative group than fluorine would also make the boron seem less positive; a CH_3 or OCH_3 are two possibilities.
- An even more electron-withdrawing group than fluorine would make the Lewis acid more reactive. Examples include nitro (NO2) and carbonyl groups (such as CH3C=0); these groups are resonance-withdrawing. Alternatively, a smaller group such a hydrogen would lower steric resistance, but would also lead to lower electrophilicity at boron, owing to the lower electronegativity of hydrogen compared to fluorine.

Chemical reactions involve bond-making and bond-breaking events, as well as the movement of electrons. When we think about chemical reactions, we often think about where the electrons are coming from, and where they are going. In a Lewis structure picture, we most often think of the electrons as coming from a lone pair -- a non-bonding pair of electrons on one particular atom. We picture the electrons becoming attracted toward an atom that lacks electrons, maybe because it does not have a filled valence shell, or maybe because it has some amount of positive charge.

In addition to a Lewis picture, it's often useful to think about reactions in terms of molecular orbital interactions. That kind of consideration is especially useful in computational chemistry where, through the use of the right software, we can calculate energy changes that occur over the course of a reaction. It's also helpful to develop some conceptual understanding of these approaches qualitatively. This qualitative approach to molecular orbital interactions is routinely used by chemists because of the insight it can give into reactions.

One common way of thinking about reactions in this way is through the concept of frontier orbitals. This idea says that if one species is going to donate electrons to another in order to form a new bond, then the donated electrons are most likely going to come from the highest occupied energy level. In this level, called the highest occupied molecular orbital (HOMO), the electrons are further from the nucleus and therefore less tightly held by the protons in the nucleus. The electrons would be donated, in turn, to the lowest empty energy level on the other species, called the lowest unoccupied molecular orbital (LUMO).

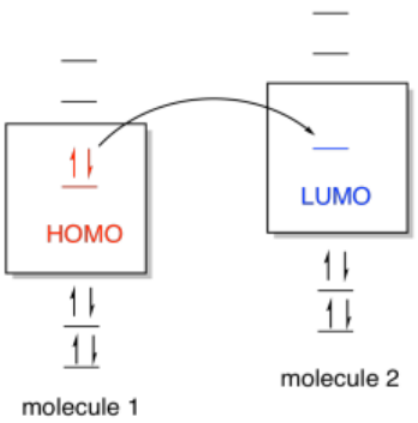


Figure 14.4.4: Molecular orbital interaction between frontier orbitals.

Consider an example of such an interaction, between a hydroxide ion and a proton. A hydroxide ion, HO^-, is a Lewis base. The oxygen atom has three lone pairs, any of which might be donated to a Lewis acid. A proton, H^+, is a Lewis acid. For a hydrogen atom, in the very first little row of the periodic table, the "octet rule" is two electrons, so a proton would be able to accept a pair of electrons from another atom and form a covalent bond.

Figure 14.4.5:

The atomic orbital diagram for a proton is very simple. Hydrogen has only a 1s orbital, and in H^+ that energy level is empty. This orbital corresponds to the LUMO for a proton.

The molecular orbital diagram for hydroxide ion is not much more complicated. This molecule is diatomic; it comes from the combination of an oxygen atom with a hydrogem atom, with the addition of an extra electron to provide the negative charge of the ion. In the diagram below, the hydrogen atom interacts with one of the p orbitals on the oxygen, but it does not matter exactly which oxygen orbital we use.

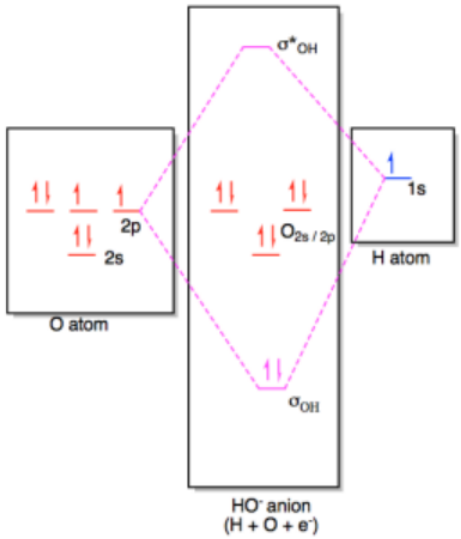


Figure 14.4.6: Molecular orbital interaction diagram for formation of hydroxide ion.

In most cases, we could come up with the MO diagram in another way. If we take the shortcut of working out an approximate MO diagram of a molecule based on its Lewis structure, and we know that hydroxide ion has one O-H bond and three lone pairs on oxygen, then we know there should be a bonding orbital at low energy, an antibonding orbital at high energy, and three non-bonding orbitals in the middle.

In a Lewis acid-base interaction, a pair of electrons would be donated from the non-bonding level on hydroxide (the HOMO) to the empty 1s orbital on the proton (the LUMO).

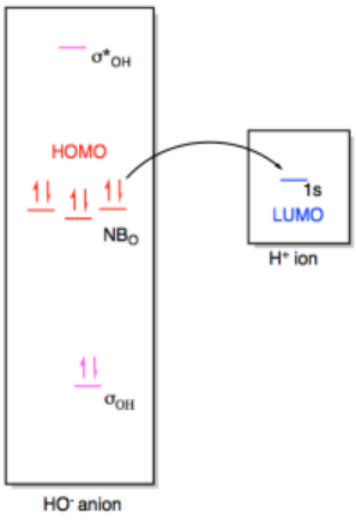


Figure 14.4.7: Frontier orbital interactions between a hydroxide ion and a proton.

What we have here is an interaction between two orbitals. A pair of electrons in one orbital is being shared with another orbital. We already know that an interaction between two orbitals results in two new orbitals. One of the new orbitals, resulting from

constructive interference, is lower in energy than either of the original orbitals. The other new orbital results from destructive interference and is higher in energy than either of the original orbitals.

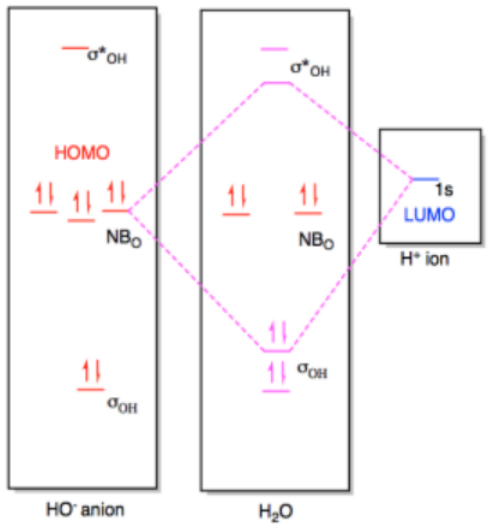


Figure 14.4.8: Frontier orbital interaction between a hydroxide ion and a proton, leading to the formation of a new bond.

In the end, the two electrons being donated slide down in energy to become an O-H bond. The combination that rises in energy does not really matter because there are no electrons at that level, anyway. Overall, the net energy of the proton and the hydroxide ion has decreased as the pair came together to form a water molecule.

Note that the MO diagram for the resulting water molecule resembles what we would expect from its Lewis structure. There are two low-energy O-H bonding pairs and two correspondingly high-energy antibonding orbitals. There are also two intermediate-level nonbonding pairs corresponding to the two lone pairs we see in the Lewis structure.

We can use the same approach to look at Lewis acid-base interaction in bigger molecules. The MO diagrams are a little busier, but the ideas are the same. For example, we could imagine a fluoride ion donating electrons to a molecule of borane, BH_3. The fluoride is a Lewis base because it has lone pairs. The borane is a Lewis acid because the boron atom lacks an octet; it has only six valence electrons in its structure.

Figure 14.4.9:

In this case, the borane contains three B-H bonds, so there will be three B-H bonding pairs and three empty B-H antibonding levels. There would be an empty orbital as well, corresponding to an empty p orbital on the boron. That empty p orbital is the lowest unoccupied molecular orbital (LUMO). A fluoride ion would have four lone pairs, and we would probably imagine a pair of electrons from one of its p orbitals as the highest occupied molecular orbital (HOMO). The interaction therefore involves donation from one of these orbitals on fluoride to the empty p orbital on borane.

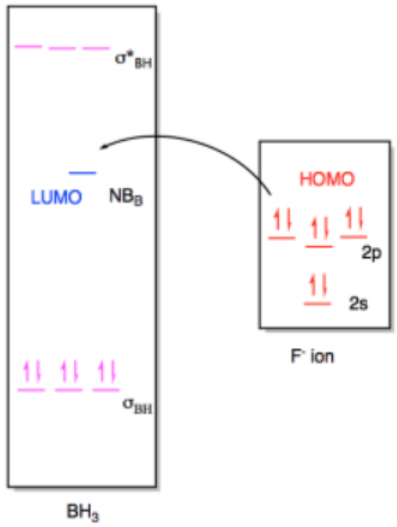


Figure 14.4.10: Frontier orbital interactions between a fluoride ion and borane.

Once again, this interaction would result in a new molecule with a new molecular orbital diagram. The only appreciable changes would involve the two orbitals that interact with each other, the HOMO and LUMO. The diagram for BH3F- ion is really a superposition of the two diagrams before, except that the HOMO and LUMO have formed a new bonding and antibonding orbital for the new B-F bond.

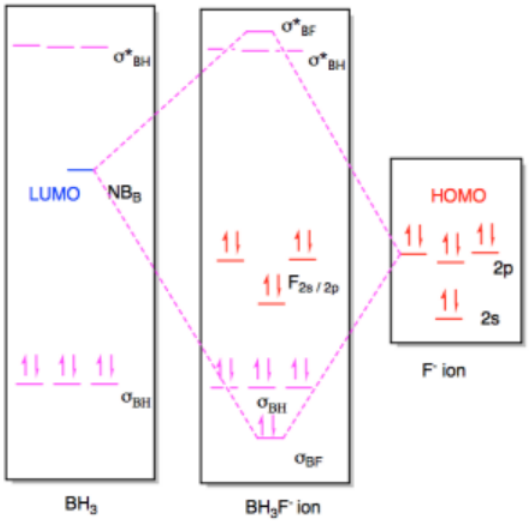


Figure 14.4.11: Molecular orbital interaction diagram for formation of an adduct between a fluoride ion and borane.

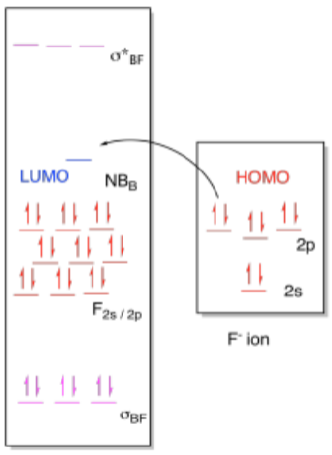
Exercise 14.4.7

For the following reactions, show (i) the HOMO-LUMO interaction and (ii) the molecular orbital interaction diagram for formation of the new molecule.

a. A fluoride ion donates to a boron trifluoride molecule (BF_3), forming a tetrafluoroborate ion (BF_4^-).
b. An ammonia molecule (NH_3) donates to a borane molecule (BH_3), forming the adduct BH_3NH_3.

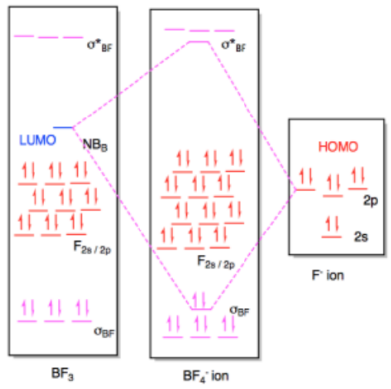
Answer
Answer a.(i

a) (i)



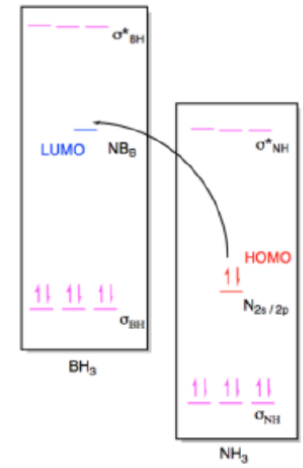
Answer a.(ii

(ii)



Answer b.(i

b) (i)



Answer b.(ii

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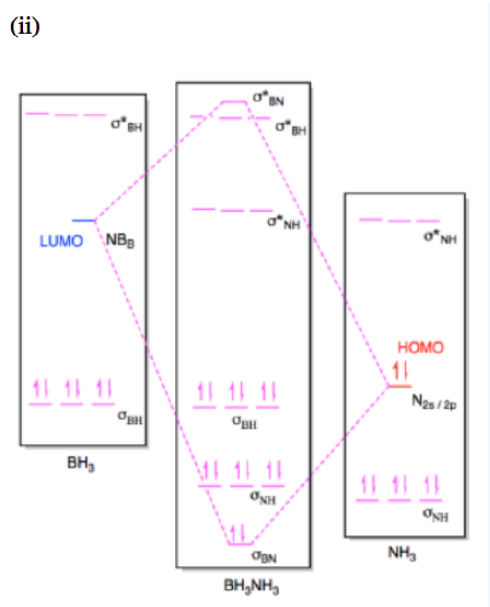

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14.5: Reversibility of the Dative Bond

A coordinate or dative bond is any covalent bond that arose because one atom brought a pair of its electrons and donated them to another.

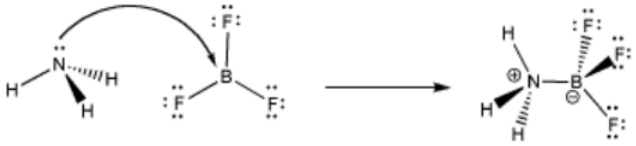


Figure 14.5.1: Formation of a dative bond or coordinate bond between ammonia and boron trifluoride.

When the nitrogen donates a pair of electrons to share with the boron, the boron gains an octet. Both atoms are electronically saturated. In addition, a pair of non-bonding electrons becomes bonding; they are delocalized over two atoms and become lower in energy. This development acts as a driving force for formation of the dative bond.

- Formation of dative bonds can be driven by electronic saturation; that means octets become filled.
- Dative bond formation is also driven by the fact that bond formation allows nitrogen's lone pair to become delocalized.

However, sometimes bonds can be broken again. In the case of dative bonds, that means a pair of electrons that were donated from one atom to another can be taken back again. This event is called dissociation. In dissociation, two atoms that were connected to each other become disconnected.

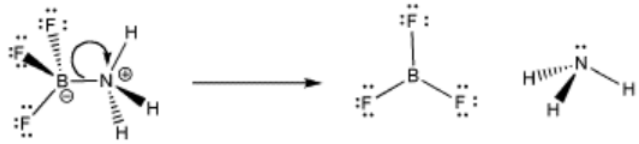


Figure 14.5.2: Dissociation of a Lewis acid-base complex.

Why might a dative bond be broken? From one point of view, maybe the nitrogen atom's positive charge in the Lewis acid-base complex is unfavorable. Nitrogen is a relatively electronegative element, and so it is easy to imagine the nitrogen pulling this pair of electrons back to itself, leaving the boron behind without an octet.

There is another reason Lewis-acid complexes can dissociate. That reason is entropy, or the distribution of energy. One of the fundamental laws of thermodynamics is that increased entropy is favorable. Looked at very loosely, that means it is favorable to have energy distributed in more states or packages. One of the ways of accomplishing this goal is to divide the available energy up between multiple molecules.

Even though it costs energy to break the B-N bond in the Lewis acid-base complex, doing so can still be energetically favorable if that increased amount of energy can be distributed better between two molecules than it was in one molecule. Exactly how that energy distribution is accomplished is the subject of statistical mechanics, and is beyond the scope of this course. However, energy distribution is generally related to the ability of atoms to move. In molecules, that means it is related to the ability of bonds to stretch and compress, of bond angles to squeeze down and widen out, and for molecules to tumble and zip around. There are more ways to tumble and zip around if two molecules are doing it, rather than one. That means energy may be better distributed by two molecules than by one.

- Entropy factors favor the dissociation, or break-up, of Lewis acid-base complexes.

The fact that there is a good reason for Lewis acid-base complexes to form, and also a good reason for them not to form, may be very unsatisfying. However, it simply means that there is a balance between a nucleophile and electrophile coming together (association) and going apart (dissociation). Which direction the system will go depends on the relative importance of these two factors. The relative importance of each factor will vary from one case to another. In many cases, there is a dynamic equilibrium between the two possible cases. That means that after complexes form, they will come apart again. After complexes come apart, they will form again. This process does not stop, but continues as long as there is enough energy around to keep things moving.

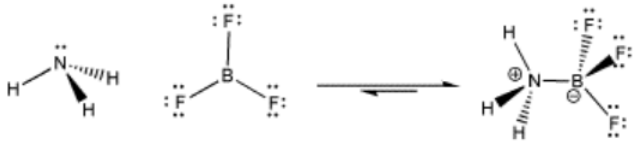


Figure 14.5.3: The balance between the dissociated and associated compounds.

If it were possible to take a picture of a collection of molecules, the picture might show some of the molecules coordinated together and some of them wandering on their own. The ratio between the associated pairs and the dissociated molecules is related to the point of equilibrium. At the point of equilibrium, different factors driving the reaction to one side or the other balance each other out.

- Equilibrium is the balance between two possible states. For example, it is the balance between dissociated and associated ammonia and boron trifluoride.

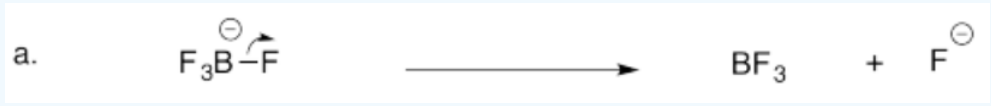
In this case, the equilibrium heavily favors the Lewis acid-base complex. A picture of millions of ammonia and boron trifluoride molecules would show most of them coordinated together. A few molecules would be found on their own, however.

Exercise 14.5.1

Use arrows and structures to show the dissociation of one nucleophile or Lewis base from each of the following polyatomic anions.

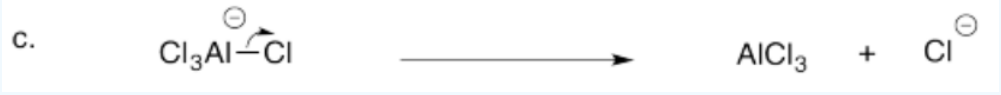
a) BF_4^- b) PF_6^- c) $AlCl_4^-$ d) AlH_4^- e) $Ag(NH_3)_2^+$

Answer a



Answer b

Answer c



Answer d

Answer e

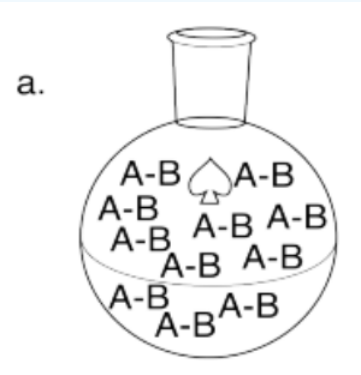
Exercise 14.5.2

Draw pictures to represent the following cases of equilibria. Use squares to represent Lewis acids and circle to represent Lewis bases.

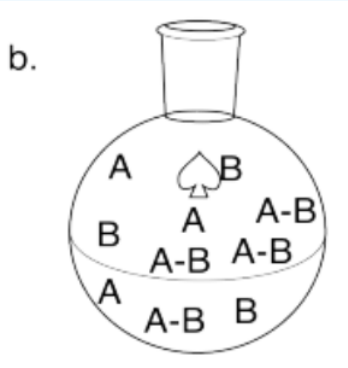
a. The Lewis acid-base complex is heavily favored.
b. The Lewis acid-base complex is slightly favored.

c. The Lewis acid-base complex is heavily disfavored.
d. The Lewis acid-base complex does not form at all.

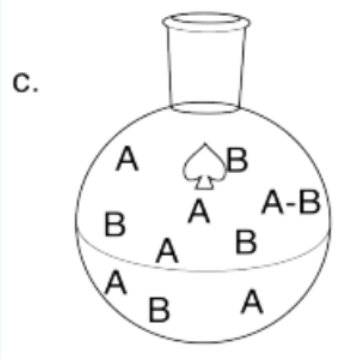
Answer a



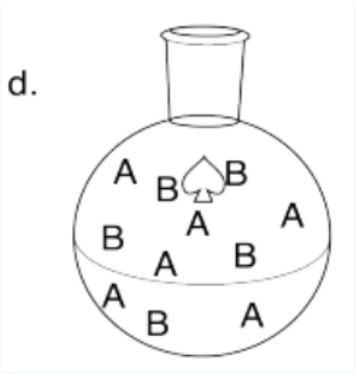
Answer b



Answer c



Answer d



Sometimes, Lewis acid-base complexes are stabilized by chelation. Chelation (from the Greek word, chelos, meaning "crab") refers to the situation in which a Lewis base has more than one electron-donating site. That means it can bind to a Lewis acid through more than atom (just as a crab could grab something with both its claws).

Figure 14.5.4: A general example of chelation.

The chelate effect refers to the fact that Lewis acid-base complexes are often more stable with respect to dissociation when they contain chelating electron donors. The equilibrium lies much farther towards the associated complex when chelation is a factor.

Chelation is seen in some very common biological molecules that incorporate Lewis acid-base complexes. For example, the heme subunit found in the oxygen-carrying proteins, hemoglobin and myoglobin, contains four electron-donating atoms that bind to iron. A very similar unit is found in a number of other molecules, including the important photosynthetic chromophore, chlorophyll. Related molecules are also found in the important biological cofactor, vitamin B12, and in cytochrome P450, which is involved in detoxification in the liver, among other tasks.

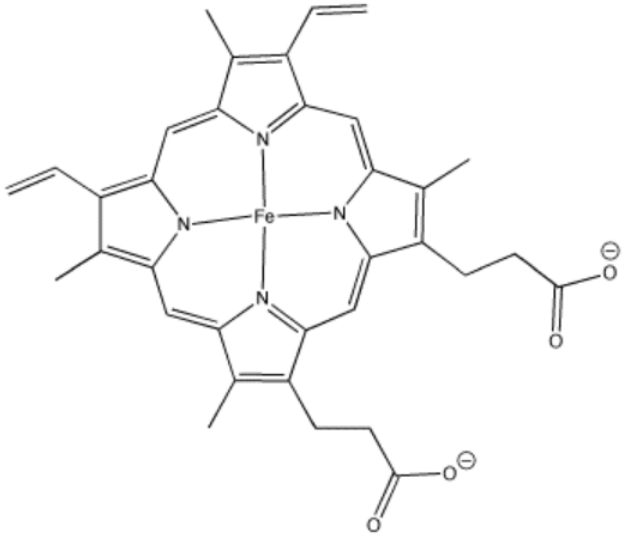
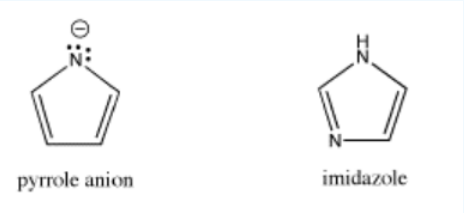


Figure 14.5.5: The heme subunit of hemoglobin and myoglobin.

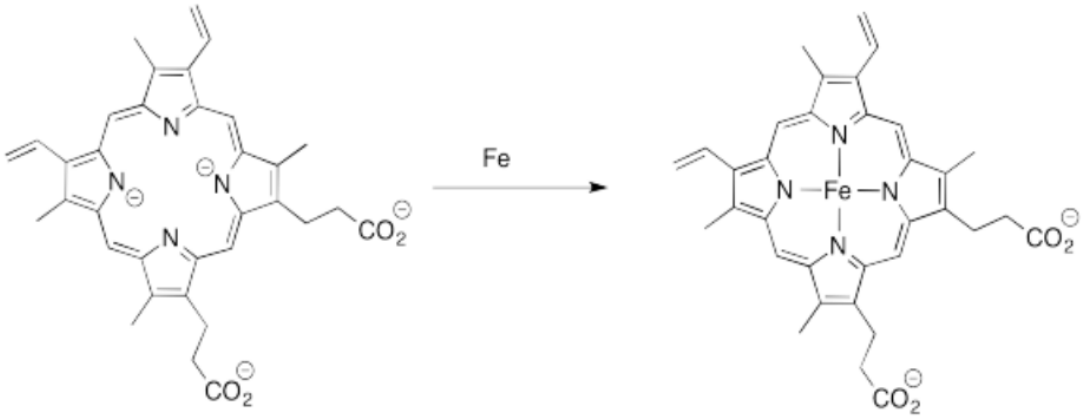
Exercise 14.5.3

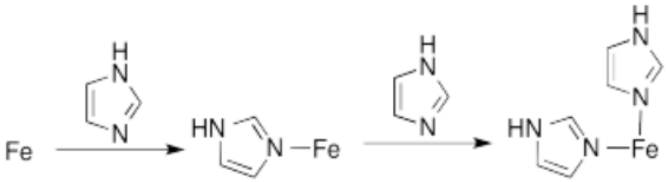
Using the concept of entropy, explain why an iron-heme complex is more stable than an iron ion complexed to four separate nitrogen donors, such as histidine or pyrrole anion.

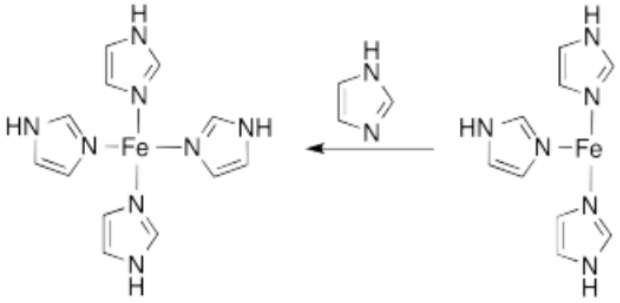


Answer

The heme subunit is tetradentate and forms 4 iron-ligand bonds. Four independent monodentate nitrogen ligands would be required to form a similar complex. Thus Iron binding to a heme does not produce the same of a loss o degrees of freedom as iron binding four independant nitrogen ligands.







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14.6: Coordination Complexes

The bond that forms between a Lewis base and a Lewis acid is sometimes called a dative bond or a coordinate bond. The term used for the donation of a Lewis base to a Lewis acid, without any other bonding changes, is coordination. Another term for Lewis acid-base complexes, especially used in the context of transition metal chemistry, is coordination complexes. Sometimes the Lewis base is referred to as a ligand; more generally, a ligand is just one molecule that binds to another.

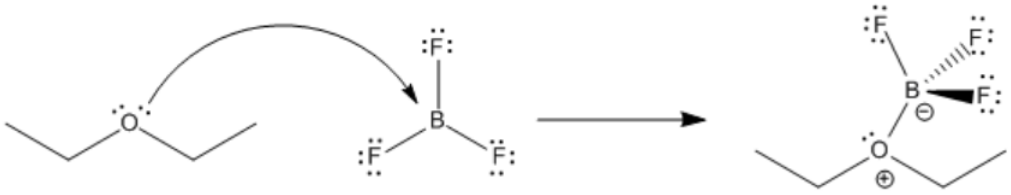


Figure 14.6.1: Formation of a Lewis acid-base complex.

An example of a coordination complex is hexaaquo cobalt dichloride, $Co(H_2O)_6Cl_2$. This compound contains a Co^{2+} ion. This electrophilic metal ion is coordinated by six nucleophilic water ligands. Because the water molecules are neutral, the complex still has a 2+ charge overall. There are two chloride counterions to balance the charge, but the chlorides are not attached to the complex ion.

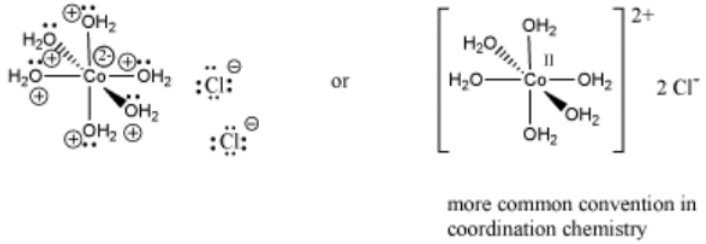


Figure 14.6.2: Representations of a transition metal coordination complex.

Notice that the usual Lewis conventions are usually abandoned in drawing coordination complexes of transition metals. With so many different nucleophiles sticking to the Lewis acid, the number of formal charges that must be drawn becomes very cumbersome. Usually the oxidation state of the metal cation is denoted. The oxidation state essentially means the charge on the metal cation and it is written in Roman numerals beside the metal atom. In addition, the overall charge on the Lewis acid-base complex is given, with square brackets indicating that the charge belongs to the entire complex within the brackets. Exactly where that charge resides is up to the reader to consider.

Coordination complexes are frequently useful in mining and metallurgy. For example, nickel can be extracted from nickel ore by converting the nickel into $Ni(CO)_4$ via addition of carbon monoxide. $Ni(CO)_4$, or tetracarbonyl nickel, is a gas that can be easily separated from the solid ore. When removed from the presence of carbon monoxide, the coordination complex decomposes back into Ni and CO.

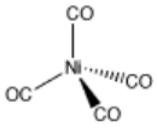


Figure 14.6.3: Tetracarbonyl nickel.

Exercise 14.6.1

These questions concern the formation of tetracarbonyl nickel.

a) Based on what you know about transition metals, is the nickel most likely a Lewis acid or a Lewis base?

b) Draw the Lewis structure for carbon monoxide, CO. Make sure each atom has an octet. Make sure you add formal charges.

c) Based on formal charge considerations, which atom in carbon monoxide will bind to the nickel?

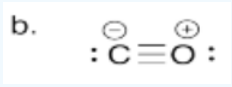
d) Using arrow notation, show the coordination of CO to Ni. Do this one step at a time, showng each CO molecule binding to the nickel and the new complex that results after each step.

e) Why does nickel bind four carbon monoxide ligands, and not three or five?

Answer a

Lewis acid

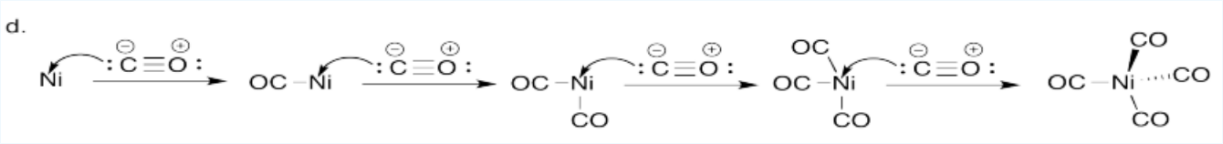
Answer b



Answer c

Carbon will be nucleophilic due to the lone pair electrons and the negative charge.

Answer d



Answer e

Ni^0 is d^{10} and with 4 CO ligands the nickel tetracarbonyl complex has 18 electrons.

Another example is seen in the liquid extraction of metals from ores. Often, a metal is coordinated by some kind of ligand that changes the solubility of the metal atom, so that it can be extracted from the ore with a solvent. The solvent is usually water, but other liquids could be used. One of the easiest cases to picture on paper is the leaching of gold from gold ores with cyanide.

Often, coordination of a ligand to a metal changes many properties of the metal, in addition to changing its solubility. Transition metals have different oxidation states, meaning they can give up different numbers of electrons and become cations with different charges. Sometimes, this event happens more easily upon coordination. In the case of gold, the gold atom can react with air and become a gold cation in the presence of cyanide.

Cyanide is an anion, so it would be added as a salt, such as sodium cyanide, NaCN, or potassium cyanide, KCN. The resulting complex, $Au(CN)_2$, is actually a complex anion, and it would be associated with one of the counterions added, such as $KAu(CN)_2$. It is not completely clear why the gold binds two cyanides, but binding two ligands is common in the chemistry of gold and silver, and is based on molecular orbital considerations that are beyond the level of this course.

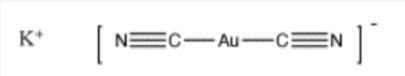


Figure 14.6.4: Gold dicyanide complex ion, shown here with a potassium counterion.

This complex salt is water-soluble, so it can be removed from the ore with water. Later, it must be converted back into pure gold via electrochemical reactions. These reactions are not related to acid-base chemistry and will not be covered in this course.

Exercise 14.6.2

These questions concern the formation of the potassium dicyano gold complex.

a) Based on what you know about transition metals, is the gold most likely a Lewis acid or a Lewis base?

b) Draw the Lewis structure for cyanide, CN^-. Make sure each atom has an octet. Make sure you add formal charges.

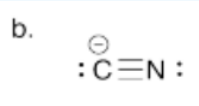
c) Based on formal charge considerations, which atom in cyanide will bind to the gold?

d) Using arrow notation, show the coordination of cyanide to Au^{+}. (We will simplify and assume the gold has already been oxidized). Do this one step at a time, showing each cyanide molecule binding to the gold ion and the new complex that results after each step.

Answer a

Lewis acid

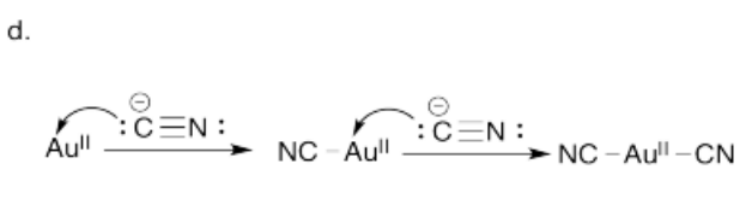
Answer b



Answer c

Carbon will be nucleophilic due to the lone pair electrons and the negative charge.

Answer d



Perhaps some of the most interesting coordination complexes involve transition metals in biology. The most familiar of these compounds is haemoglobin. Haemoglobin is a complex protein that contains a crucial iron atom. The iron is present as a 2+ cation, but the haeme ring that binds to the iron has a 2- charge, so overall there is no charge on the complex. The iron is still electrophilic, however, and it can bind an oxygen molecule. Much more oxygen can be carried in the bloodstream this way than if the oxygen simply dissolved in the blood.

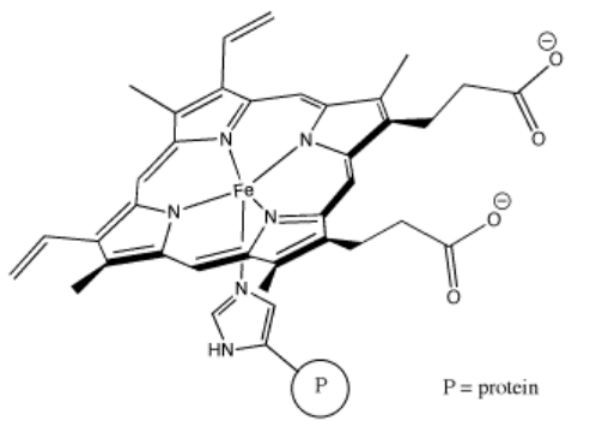


Figure 14.6.5: Hemoglobin. Most of the molecule is not shown. The iron-containing heme subunit is attached to a large protein via an imidazole ring in a histidine amino acid residue.

Exercise 14.6.3

These questions concern the formation of the oxyhaemoglobin.

a) Based on what you know about transition metals, is the iron most likely a Lewis acid or a Lewis base?

b) Draw the Lewis structure for oxygen molecule, O_2. Make sure each atom has an octet. Make sure you se if there are any formal charges.

N.B. This Lewis structure may not agree completely with the molecular orbital view of the molecule, but it is all we have to work with for our current method of understanding coordination.

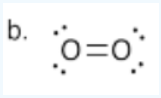
c) Using arrow notation, show the coordination of oxygen to Fe^{2+}.

d) There has been a great deal of research into the exact geometry of the dioxygen complex. Based on your Lewis structure of oxygen, show how you think the oxygen is attached to the iron. How would you describe the geometry?

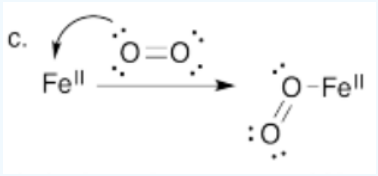
Answer a

Lewis acid

Answer b



Answer c



Answer d

The bound oxygen would be predicted to have a trigonal planar electronic (bend molecular) geometry based on the Lewis structure.

There is another interesting event that happens when oxygen binds to the iron in haemoglobin. After binding O_2, the iron actually transfers a single electron to the oxygen, becoming a Fe^{3+} cation. Although deoxyhaemoglobin, the Fe^{2+} or Fe(II) species, is purple, many Fe^{3+} or Fe(III) compounds are red. Thus, oxyhaemoglobin is red.

It is also interesting to note that we are used to seeing iron-containing materials turn a sort of red-brown color when they have been exposed to oxygen for a long time, especially in the presence of water and salts. Our cars, trains and bridges eventually rust as the iron in their steel turns to reddish iron oxide. William Tolman, a researcher in bioinorganic chemistry at the University of Minnesota, likes to raise the following question: we rely on iron complexes to carry oxygen through our salt-water bloodstream, so why don't we get rusty?

The answer is that, in a sense, we do. It has been estimated that after several passes through our bloodstream, a haemoglobin molecule meets its end when the oxygen fails to detach and the iron complex decomposes to an iron oxide. That's one reason why you need to eat a diet that contains iron, to replenish your iron stores in order to make new haemoglobin on a regular basis.

To see some additional problems that will help you get to know coordination compounds, go to the main coordination compound chapter. In particular, it is really useful to be able to count electrons in coordination chemistry. Counting electrons is just like learning Lewis structures, except that instead of going to a maximum count of eight electrons, we can go to a maximum of eighteen electrons. That's because the noble gas configuration for a transition metal would have eighteen electrons, not eight. To learn how to count electrons in coordination complexes, go here.

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14.7: Proton as a Common Lewis Acid

Perhaps the most common example of a Lewis acid or electrophile is also the simplest. It is the hydrogen cation or proton. It is called a proton because, in most hydrogen atoms, the only particle in the nucleus is a proton. If an electron is removed to make a cation, a proton is all that is left.

- H^+ is a very common Lewis acid or electrophile.

A proton is electrophilic for a couple of reasons. It has a positive charge, and so it will attract electrons, which are negative. Also, it lacks the electron configuration of its noble gas neighbour, helium. Helium has two electrons. If a Lewis base or nucleophile donates a pair of electrons to a proton, the proton will obtain a Noble gas configuration. That's part of the reason why, in some periodic tables, hydrogen is shown in two places: at the very left, illustrating its potential to lose an electron, like sodium and lithium; and at the right, illustrating its potential to take on helium's configuration.

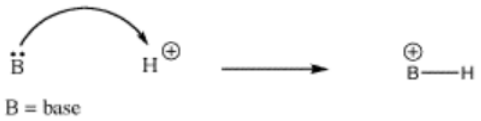


Figure 14.7.1: Proton as Lewis acid.

There is something about hydrogen cations that is not so simple, however. They are actually not so common. Instead, protons are generally always bound to a Lewis base. Hydrogen is almost always covalently (or datively / coordinately) bonded to another atom.

Many of the other elements commonly found in compounds with hydrogen are more electronegative than hydrogen. As a result, hydrogen often has a partial positive charge. Remember, that is one of the reasons that atoms can act as Lewis acids: with a partial positive charge, an atom becomes electrophilic.

Our statement about protons might better be expressed as:

- H^{d+} is a very common Lewis acid or electrophile.

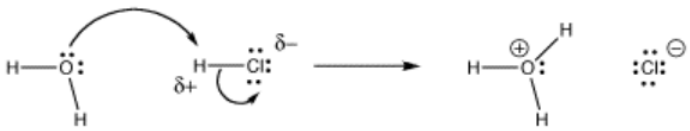


Figure 14.7.2: Proton transfer from one site to another.

If hydrogens are almost always bonded to other atoms, then the Lewis acid-base interactions we have looked at so far are slightly different here. Instead of two compounds coming together and forming a bond, we have one Lewis base replacing another at a proton.

- Protons are transferred from one basic site to another.
- Transfer occurs by donation of a lone pair to the proton.

Exercise 14.7.1

Use arrows to show water acting as a Lewis base and donating electrons to the proton in the following compounds.

a) HBr b) $HONO_2$ c) $CH_3(CO)OH$

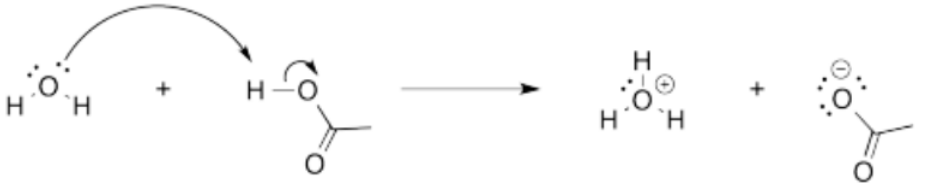
Answer a

Answer b

b.

Answer c

c.



Exercise 14.7.2

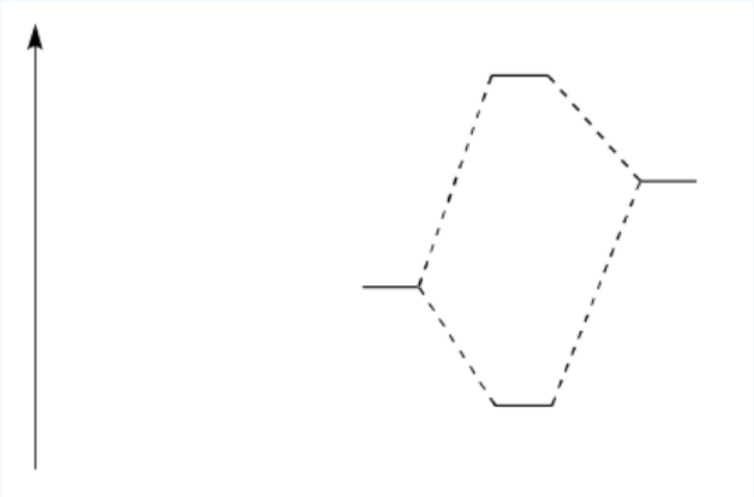
Consider the following reaction:

• Draw an MO mixing diagram for the reaction above, using the following steps:

o Draw the orbital from the base that is likely to donate its electrons.

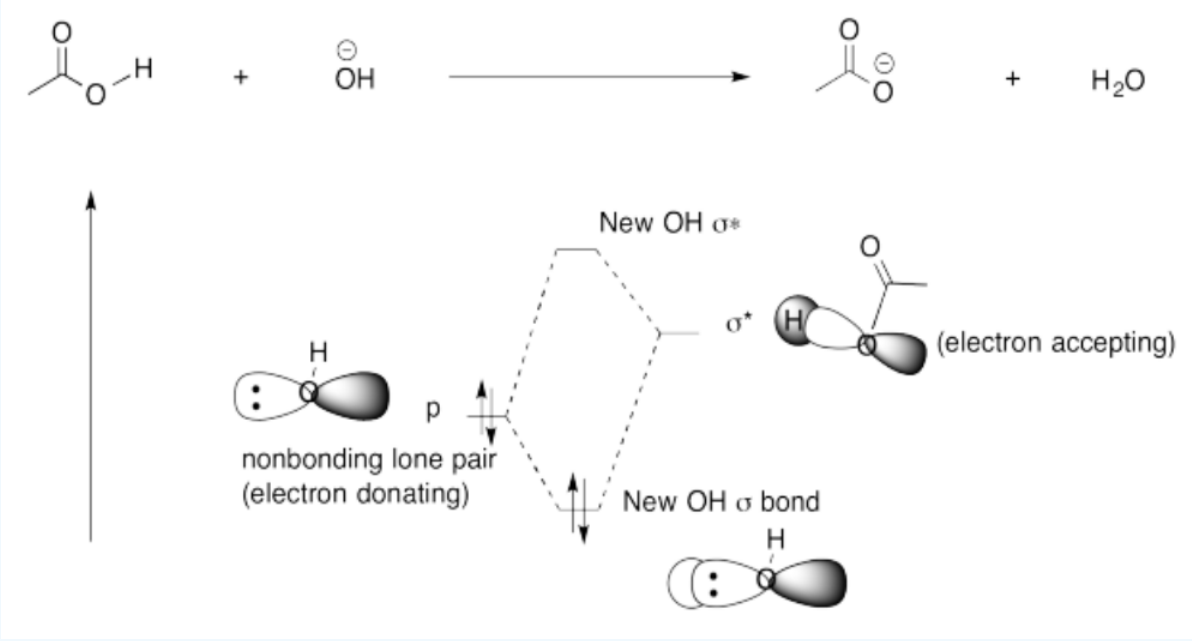
o Draw the orbital from the acid that is likely to accept electrons.

o Complete the MO mixing diagram of these two orbitals:



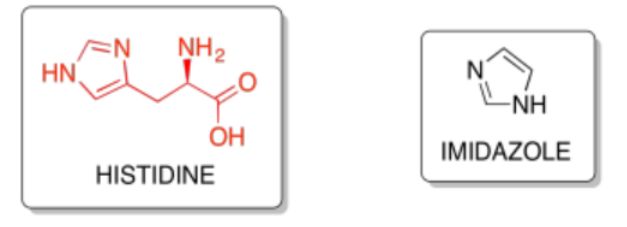
• Label the electron donating orbital
• Label the electron accepting orbital
• Populate the MO mixing diagram with electrons
• Draw a cartoon showing the mixing of these orbitals.

Answer



Exercise 14.7.3

Histidine side-chains contain an imidazole ring, which are unique as they can behave as either a proton-donor or a proton-acceptor depending on surrounding conditions.



a) Draw in the hydrogen at the chiral center of histidine.

b) Draw the *(R)*- enantiomer of histidine.

c) Circle the side chain of histidine.

d) Using the energy axis below do the following:

Draw the Hückel MO diagram for imidazole.

Populate the Hückel MO diagram with electrons.

Draw the MO pictures for 3 of the 5 MOs and label each as π, π* or n.

e) Based on your MO diagram, the imidazole is (choose one):

aromatic anti-aromatic non-aromatic

f) Show what imidazole would look like if it gave away a proton.

g) Circle the atom in imidazole that could donate electrons to a proton.

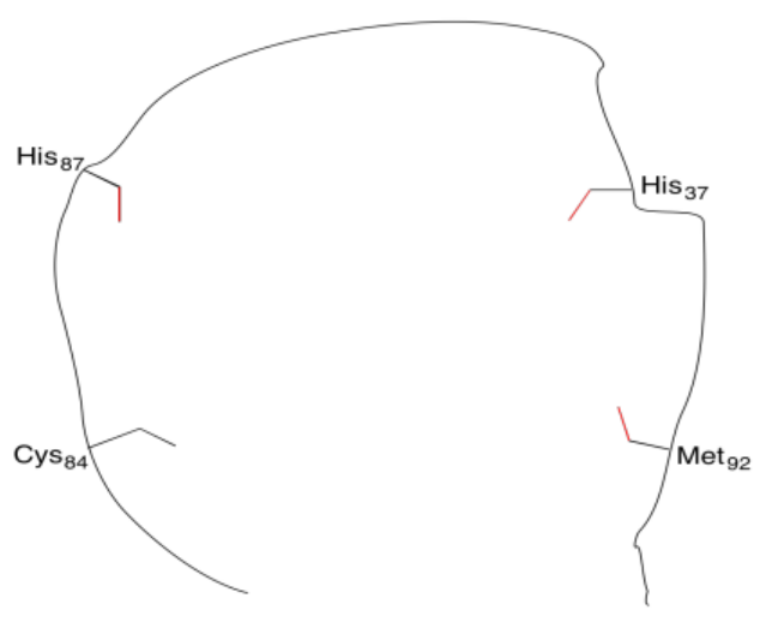
h) Why can't the other nitrogen donate electrons to a proton?

i) Show what imidazole would look like if it did pick up a proton.

Histidine residues frequently hold metal ions in place within enzymes. Enzymes are proteins that catalyze chemical reactions in biological settings. For example, plastocyanins contain a copper(II) ion (Cu^{2+}) which functions to store an electron as it is

transported from photosystem II to photosystem I during photosynthesis.

j) The drawing below is a cartoon of an enzyme active site, the place in an enzyme that carries out a specific task. Complete the blank active site by adding thestructures of the missing amino acid side-chains, as indicated by their three-letter codes.



k) Explain why each of these chains is able to bind a Cu^{2+} ion.

l) Draw a Cu^{2+} ion in the active site.

m) What is the coordination number for the copper ion in the complex you drew?

n) What is the geometry name for the copper ion in the complex?

o) Let's think about how many valence electrons surround that copper in the complex.

What is the number of valence electrons for copper metal?

What is the number of valence electrons for copper (II) ion?

How many electrons will the donor atoms contribute?

What is total valence electron count for the copper (II) complex?

p) At low pH (when there are lots of protons around), one of the histidines binds a proton. What happens to its ability to bind copper ion?

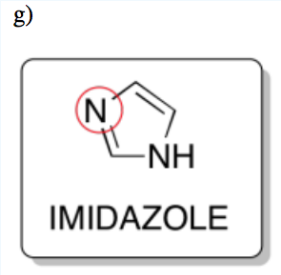
q) What is the coordination geometry of the copper ion in the complex at low pH?

Answer e

aromatic

Answer g

g)



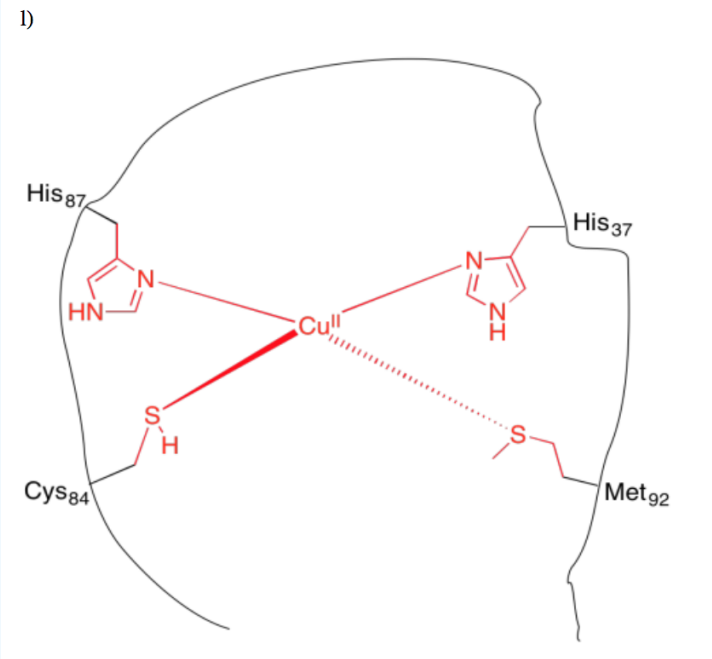
Answer h

This nitrogen atom can donate a lone pair of electrons without disturbing the aromatic character of the molecule.

Answer k

Each side chain has a Lewis base with a lone pair of electrons to donate the copper ion.

Answer l



Answer m

CN = 4

Answer n

tetrahedral

Answer o

Cu: 11 e^-

Cu(II): 9 e^-

4 x 2e^- = 8 e^-

8 e^- + 9 e^- = 17 e^-

Answer p

If the imidazole becomes occupied by a proton, then the imidazole no longer has the lone pair to donate to the copper ion.

Answer q

trigonal

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14.8: Proton Transfer from One Basic Site to Another and Molecular Orbital Interactions in Proton Transfers

Acidity involving protons is complicated because of the exchange of one base for another. The proton has attracted the electron pair from the base via its partial positive charge. Once the base arrives, however, the proton cannot bind to the new base and still retain its tie to the base to which it was already bound. A hydrogen can only have 2 electrons in its valence shell, not four.

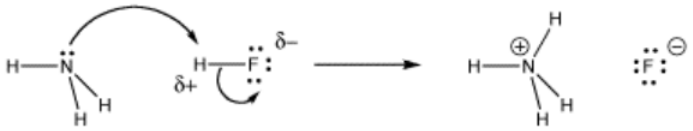


Figure 14.8.1: Proton transfer from hydrofluoric acid to ammonia.

What begins very much like the formation of an intermolecular hydrogen bond goes one step further. The proton forms a full bond to the incoming donor, and releases its bond to its former partner.

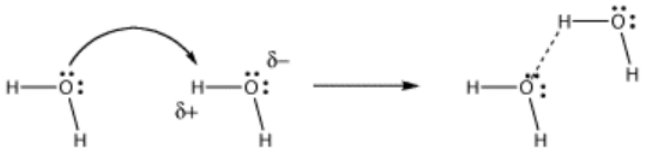


Figure 14.8.2: Electron donation to proton in hydrogen bonding.

In hydrogen bonding, the lone pair is partially shared with a proton, without actually displacing the other partner from the proton. A true bond is not quite formed between the donor and the proton. However, the distinction between hydrogen bonding and proton transfer can be blurred. Often, both cases happen at the same time in a given system.

- Hydrogen atoms can normally have only one bond.

A conjugate base is any Lewis base that forms as a result of a proton transfer. This label is only relative. Any Lewis base could be called a conjugate base if, in the present circumstances, it has lost a proton. Also, a conjugate acid is any compound that has just gained a proton.

However, the terms conjugate base and conjugate acid imply that these compounds can potentially act as bases and acids, respectively. because the conjugate base has a lone pair and is a Lewis base, it could in fact take a proton again. Because a conjugate acid has a proton, it could conceivably give the proton up again. Whether or not this event will actually occur is another matter. Later, we will develop more of an understanding of when proton transfers will actually occur.

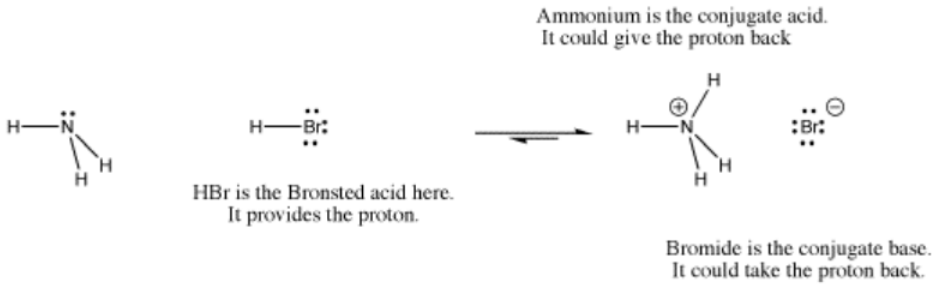


Figure 14.8.3: Some new terms to describe the players in proton transfer.

- The pair of electrons connecting the proton to the old Lewis base leave with the base. This base is called the "conjugate base".
- The proton is now bound only to the new Lewis base. This new compound is called the "conjugate acid".

We also need a new term to call the compound that provides the proton in these proton transfer reactions. The proton is the Lewis acid in these cases, but what do we call the entire compound that contains the acidic proton? This compound is commonly called a Brønsted acid. This term comes from studies of acids by Brønsted and Lowry, who independently observed that many reactions in chemistry involve proton transfers.

- A Brønsted acid is a compound that provides a proton for a base to take.

Again, the conjugate acid that forms after proton transfer is often a Brønsted acid; it could transfer the proton to another base. It could transfer the proton back to the conjugate base, reforming the starting materials. Alternatively, it could transfer the proton to a new base. In that case, the Lewis base in the first step has picked up a proton, turned into a Brønsted acid, delivered the proton to another base, and become a Lewis base again. It is like a taxicab that has picked up a passenger and dropped it off again. Sometimes in this situation, the Lewis base is called a proton shuttle.

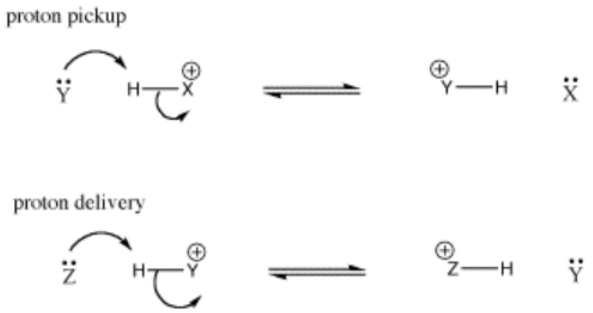


Figure 14.8.4: A schematic proton shuttle. Y acts as a base and picks up a proton; it becomes a conjugate acid; it delivers the proton to Z.

Delivery of protons is an essential task in a wide array of chemical processes. In biological systems, histidine residues in proteins commonly function as proton shuttles (although they play many other roles as well). For example, the interconversion of aldose and ketose sugars is a basic step in a variety of biosynthetic pathways. In an aldose, a C=O group is found at the end of a carbon chain. In a ketose, this C=O group is not at the end of the chain.

An aldose can be converted into a ketose essentially by moving some protons.

Figure 14.8.5: An aldose (left) and a ketose (right). R = a carbon chain, in this case probably having some additional OH groups on it.

When this transformation is carried out by the enzyme, glyoxalase, studies have shown that the proton marked with an asterisk in the aldose and ketose above are exactly the same proton, having moved from one position to another. The proton has simply been moved by a proton shuttle.

The evidence for the specific proton from the aldose ending up in the ketose comes from labeling studies. In a labeling study, a different kind of proton is placed in that specific position in the aldose. This task would involve a less-common isotope such as tritium or deuterium instead of the usual protium. Deuterium and tritium can both be distinguished from protium; for example, deuterium and protium both absorb radio waves in a technique similar to medical MRI, and by using this technique it is easy to distinguish one from the other. As a result, we can tell where a deuterium is found in a particular molecule. When the aldose is then exposed to glyoxalase, we can see that deuterium show up in a specific spot in the ketose.

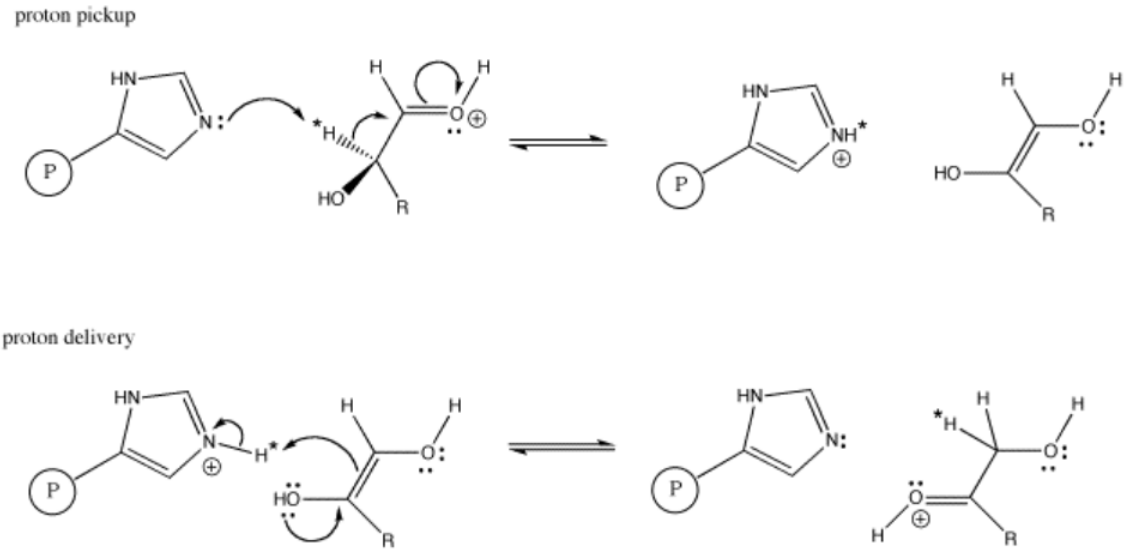


Figure 14.8.6: Histidine as a proton shuttle in glyoxalase. P represents an attached protein.

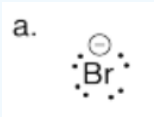
The scheme above shows only the transfer of the marked proton from one carbon to another. In addition, a proton must be placed on the oxygen of the C=O group in the aldose, and another proton must be removed from the OH group on the next carbon in the chain. Additional proton transfer steps would accomplish these tasks.

Exercise 14.8.1

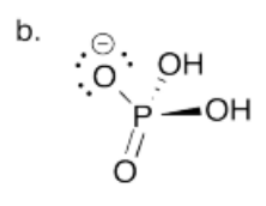
Provide the conjugate bases of the following mineral acids. In each case, assume only one proton is lost.

a) HBr b) H_3PO_4, connected $(HO)_3PO$ c) $HClO_4$, connected $HOClO_3$.

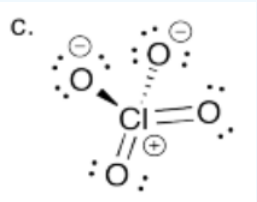
Answer a



Answer b



Answer c



Exercise 14.8.2

Provide the conjugate acids of the following bases.

a) H_2O b) NH_3 c) CH_3NH_2 d) CH_3O^- e) H^-

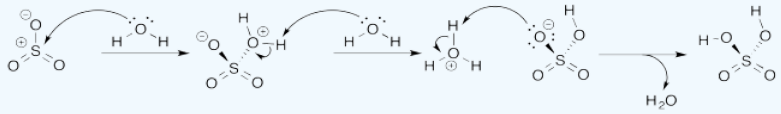
Exercise 14.8.3

Some of the more common mineral acids that you may be familiar with from high school chemistry are formed as a result of Lewis acid-base complexation, followed by proton transfer. Use arrow formalisms to show the elementary steps that occur when the following compounds are dissolved in water.

a) sulfur trioxide, SO_3, to give sulfuric acid, H_2SO_4 (connected $(HO)_2SO_2$).

b) nitric oxide ion, NO_2^+, to give nitric acid, HNO_3 (connected $HONO_2$).

Answer a



Exercise 14.8.4

Note that a number of common acids contain OH groups.

a) What is it about this group makes these compounds acidic?

b) Some compounds, such as NaOH or KOH, are not very acidic. In fact, they are termed Arhennius bases, meaning they are ionic compounds that dissociate in water to give hydroxide ions (OH-), rather than protons. Explain why these compounds behave differently from the acids containing the same group, and why the hydroxide ion is basic.

Answer a

The O-H bond is polar covalent. The oxygen is much more electronegative than the hydrogen, so the bond is easily ionized to give H^+.

Answer b

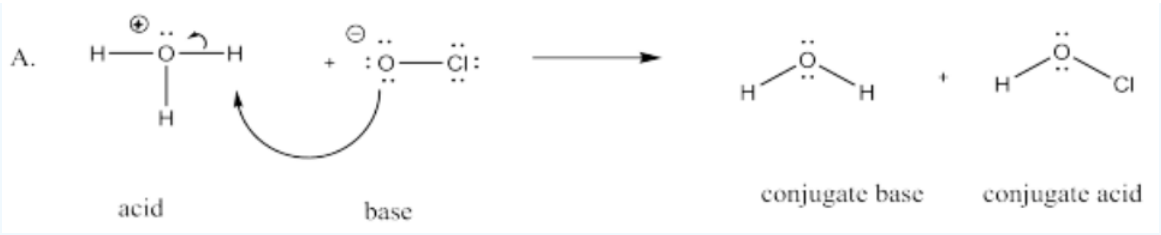
In a case like NaOH, the electronegativity difference between the sodium and oxygen is much greater than the electronegativity between the oxygen and the hydrogen. The Na-O bond is ionic. The removal of a proton from hydroxide ion is harder than the removal from a proton from hydroxide. It would make an oxide anion, O^{2-}; that buildup of negative charge is more difficult than the formation of ^-OH.

Exercise 14.8.5

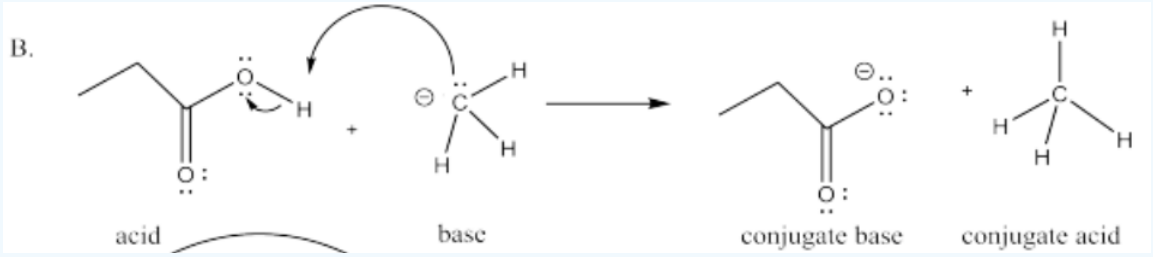
The following pairs of species will react with each other via an acid-base reaction. For each pair, complete the reaction by adding the products of the reaction, drawing a Lewis dot structure for all four reactants and products, labeling each species in the reaction as an acid, conjugate acid, base or conjugate base; and drawing arrows to show the electron flow.

A. $H_3O+ + OCl^-$
B. $CH_3CH_2COOH + CH_3^-$
C. $HClO_3 + OH^-$
D. $CH_3CH_2CH_2^- + H_2O$
E. $CH_3CHO + (CH_3)_3CO^-$
F. $NH_4^+ + NH_2^-$

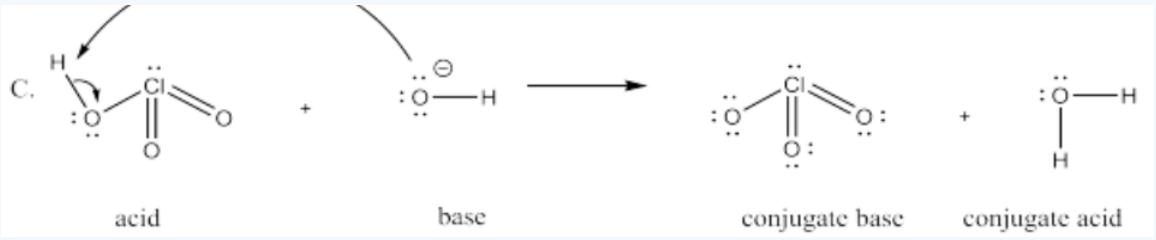
Answer A.



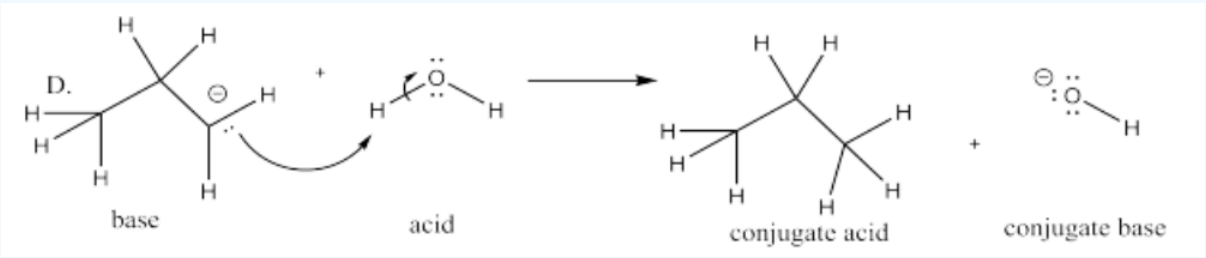
Answer B.



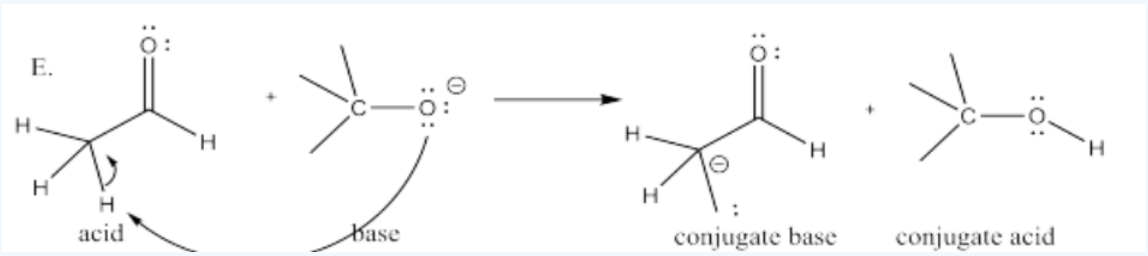
Answer C.



Answer D.



Answer E.



Answer F.

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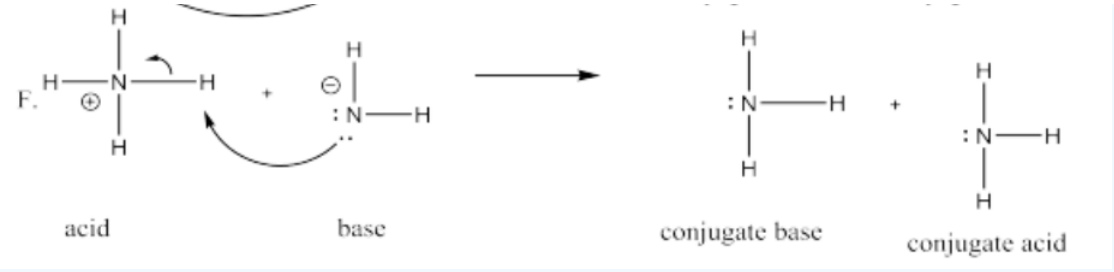


In Brønsted acidity, the Lewis acid is always a proton. However, protons aren't generally found by themselves. That's because they are such good Lewis acids; they are usually found sticking to a Lewis base already.

Earlier, we looked at how frontier orbitals are sometimes used to think about reactions. We think about the highest occupied molecular orbital on one reactant as the source of electrons. We imagine the lowest unoccupied orbital on the other reactant as the destination for the electrons.

Suppose a proton is transferred from a hydrogen chloride molecule, HCl, to a water molecule, H_2O. That's what will happen if hydrogen chloride, a gas, is bubbled into some water, forming aqueous hydrochloric acid.

The electrons are donated from a non-bonding pair of electrons on the oxygen atom in the water molecule. That part seems pretty straightforward from the Lewis structure, and we see the same idea conveyed in the MO diagram. But where do these electrons go? There is no obvious acceptor in the Lewis structure, because the hydrogen atom has two electrons and the chlorine has eight, so both octets are satisfied. We need to bring in the idea of electronegativity to see that the two electrons in the H-Cl bond are not shared evenly; there is a parital negative charge on chlorine and a partial positive charge on hydrogen. That fact make hydrogen seem like the electron acceptor. Sure enough, an O-H bond has formed in the product, suggesting the oxygen atom has donated a pair of its electrons to the hydrogen.

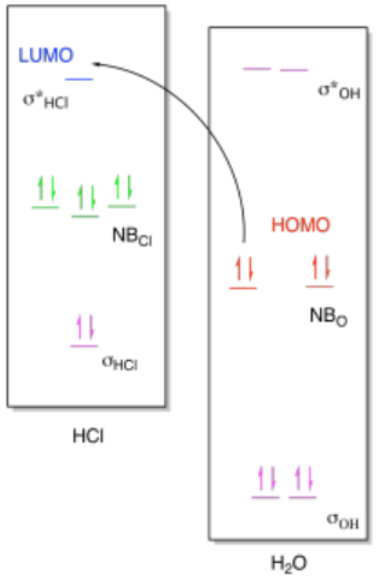


Figure 14.8.7: Frontier orbital interactions between a hydroxide ion and a proton.

If we look at the molecular orbital picture, we see that the LUMO on HCl is an antibonding orbital, the σ^*_{HCl}. The non-bonding electrons from oxygen will be donated into the empty antibonding orbital on HCl. Remember, putting electrons in an antibonding orbital always weakens or breaks the bond. That's because the energetic advantage of dropping electrons into a low-energy bonding orbital is negated by the energetic disadvantage of raising electrons into a high-energy antibonding orbital.

As a result, there is more going on in the molecular orbital interaction diagram than just bond formation. As in previous cases, the MO diagram for the product looks a little like the MO diagrams of the two reactants added together, but there are some changes. Once again, the HOMO from the base and the LUMO from the acid mix together to form a new low-energy bonding level and a new high-energy antibonding level in the product. Because the LUMO is an antibonding orbital, however, there is an additional consequence: the corresponding bondng orbital in the acid becomes a non-bonding orbital, because that bond must be broken.

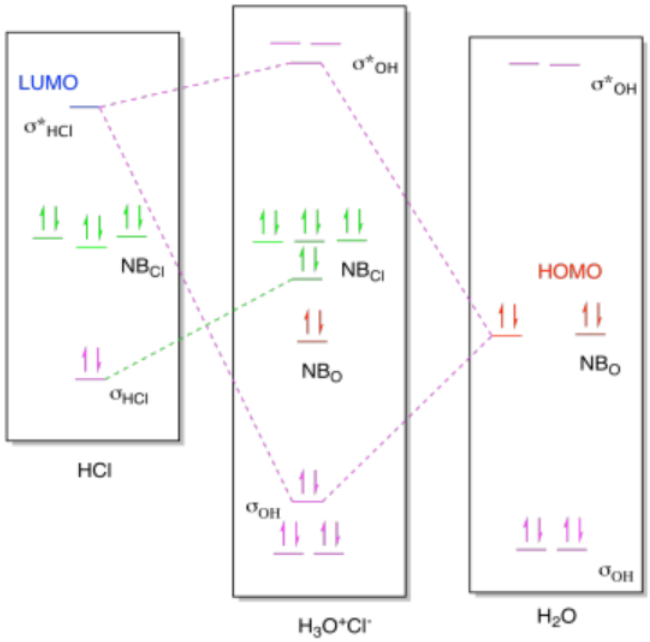


Figure 14.8.8: Molecular orbital interaction diagram for formation of hydronium chloride.

In this case, the MO picture reminds us of something in addition to the bond formation, and that i the bond-breaking that accompanies proton transfers.

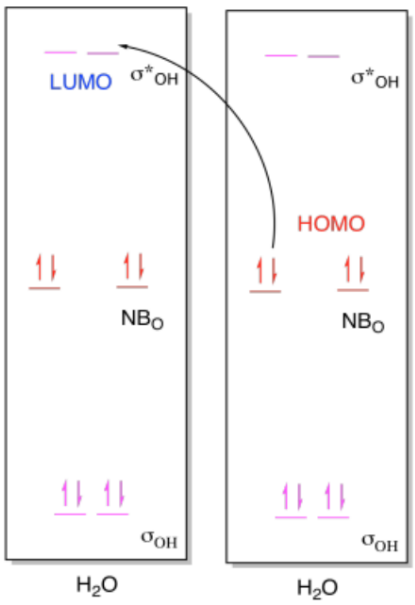
Exercise 14.8.6

For the following reactions, draw (i) MO diagrams showing the HOMO-LUMO interaction and (ii) the molceular orbital interaction diagram showing the formation of the product.

a. Two molecules of water react to form $H_3O^{+}{}^{-}OH$.
b. A molecule of methanal, H_2CO, reacting with hydrogen chloride, HCl, to form $H_2COH^{+}Cl^{-}$.

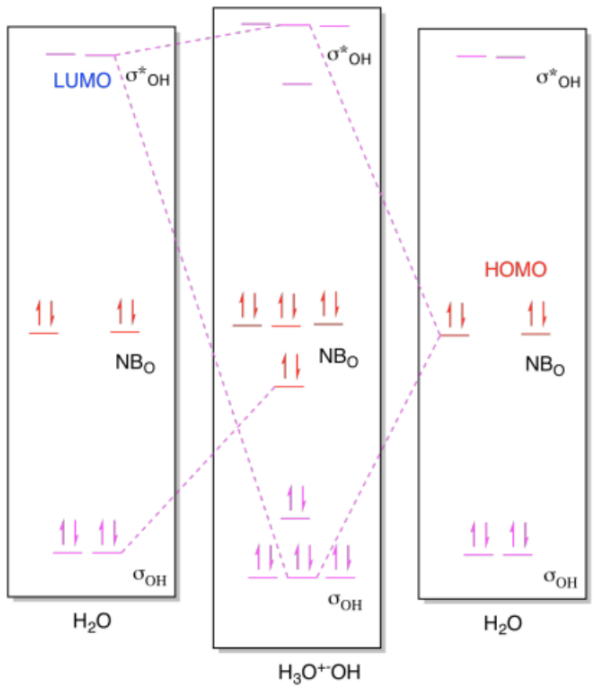
Answer a i

a) i)



Answer a ii

ii)



Answer b i

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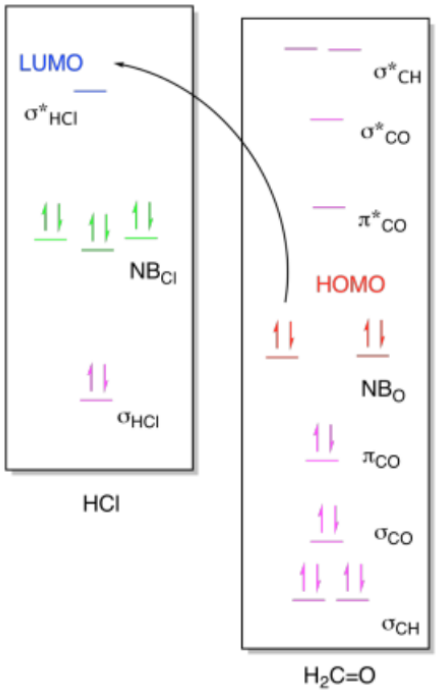
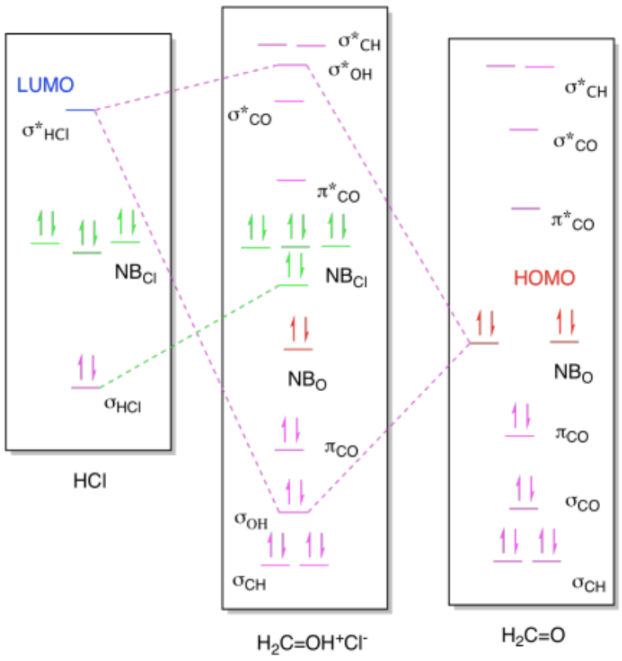
b) i)



Answer b ii

ii)



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14.9: Proton Donor Strength- pKa

It is helpful to have a way of comparing Brønsted-Lowry acidities of different compounds. If the chemistry of protons involves being passed from a more acidic site to a less acidic site, then the site that binds the proton more tightly will retain the proton, and the site that binds protons less tightly will lose the proton. If we know which sites bind protons more tightly, we can predict in which direction a proton will be transferred.

Figure 14.9.1: In which direction will the equilibrium lie? Which base gets the proton?

There is an experimentally-determined parameter that tells us how tightly protons are bound to different compounds. "Experimental" often implies to students "untested" or "unreliable", but here it means that someone has done the work to measure how tightly the proton is bound. Experimental in this sense means "based on physical evidence".

This experimental parameter is called "the pKa". The pKa measures how tightly a proton is held by a Brønsted acid. A pKa may be a small, negative number, such as -3 or -5. It may be a larger, positive number, such as 30 or 50. The lower the pKa of a Brønsted acid, the more easily it gives up its proton. The higher the pKa of a Brønsted acid, the more tightly the proton is held, and the less easily the proton is given up.

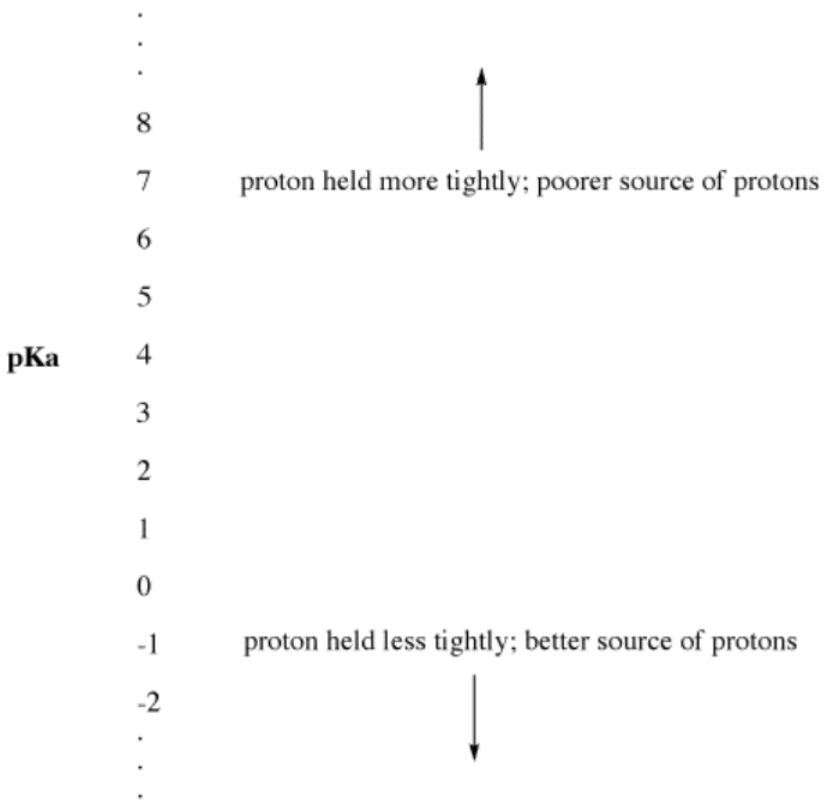


Figure 14.9.2: The pKa scale as an index of proton availability.

- Low pKa means a proton is not held tightly.
- pKa can sometimes be so low that it is a negative number!
- High pKa means a proton is held tightly.

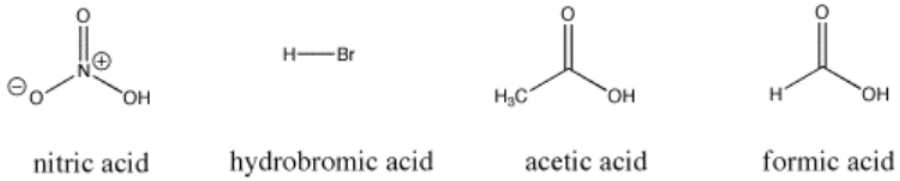


Figure 14.9.3: Some Brønsted acidic compounds; these compounds all supply protons relatively easily.

For example, nitric acid and hydrochloric acid both give up their protons very easily. Nitric acid in water has a pKa of -1.3 and hydrobromic acid has a pKa of -9.0. On the other hand, acetic acid (found in vinegar) and formic acid (the irritant in ant and bee stings) will also give up protons, but hold them a little more tightly. Their pKas are reported as 4.76 and 3.77, respectively. Water can certainly give up a proton, but not very easily; it has a pKa of around 14. Methane is not really an acid at all, and it has an estimated pKa of about 50.

Figure 14.9.4: Some not-so-acidic compounds. Water is very, very weakly acidic; methane is not really acidic at all.

The pKa measures the "strength" of a Brønsted acid. A proton, H^+, is a strong Lewis acid; it attracts electron pairs very effectively, so much so that it is almost always attached to an electron donor. A strong Brønsted acid is a compound that gives up its proton very easily.

A weak Brønsted acid is one that gives up its proton with more difficulty. Going to a farther extreme, a compound from which it is very, very difficult to remove a proton is not considered to be an acid at all.

When a compound gives up a proton, it retains the electron pair that it formerly shared with the proton. It becomes a conjugate base. Looked at another way, a strong Brønsted acid gives up a proton easily, becoming a weak Brønsted base. The Brønsted base does not easily form a bond to the proton. It is not good at donating its electron pair to a proton. It does so only weakly.

In a similar way, if a compound gives up a proton and becomes a strong base, the base will readily take the proton back again. Effectively, the strong base competes so well for the proton that the compound remains protonated. The compound remains a Brønsted acid rather than ionizing and becoming the strong conjugate base. It is a weak Brønsted acid.

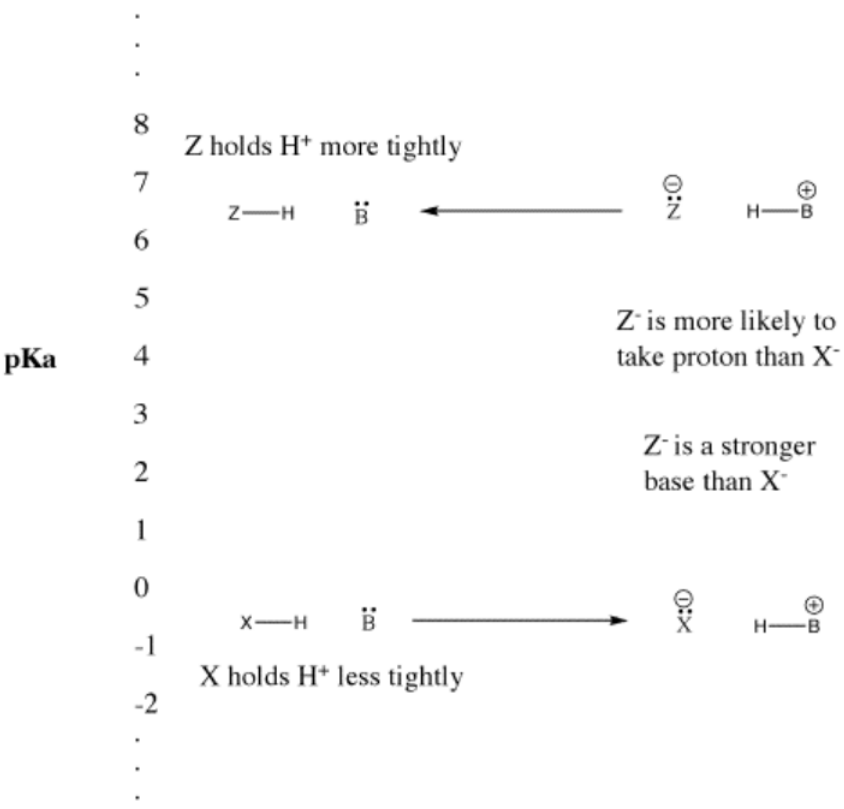


Figure 14.9.5: The pKa scale and its effect on conjugate bases.

- "Strong" Brønsted acids ionize easily to provide H^+.
- This term is usually used to describe common acids such as sulfuric acid and hydrobromic acid.
- "Weak" Brønsted acids do not ionize as easily.
- This term is often used to describe common acids such as acetic acid and hydrofluoric acid.

However, the terms "strong" and "weak" are really relative. pKa values that we have seen range from -5 to 50. If something with a pKa of 4 is described as a weak acid, what is something with a pKa of 25? A very, very weak acid? It is certainly a better source of protons than something with a pKa of 35. Is that a very, very, very, very weak acid? How many "verys" are there in a pKa unit?

This idea is also true when considering the opposite: a base picking up a proton to form a conjugate acid. How tightly that conjugate acid holds a proton is related to how strongly the base can remove protons from other acids. The weaker something is as a source of protons, the stronger its conjugate is as a proton sponge.

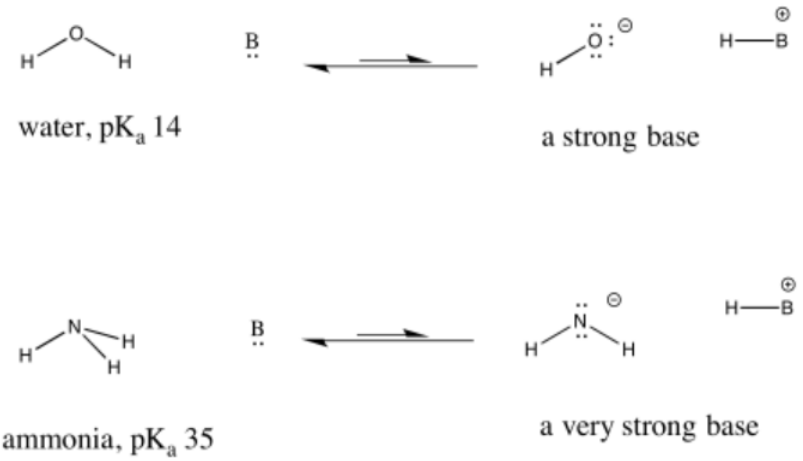
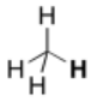
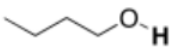
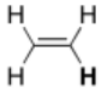
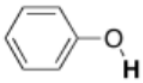
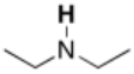
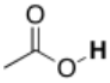
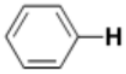
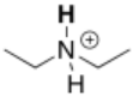
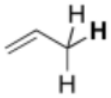
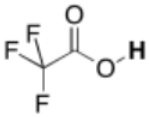
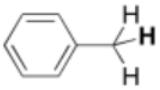
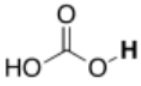


Figure 14.9.6: Examples of a strong base and an even stronger one.

- Be careful. The terms "strong acid" and "weak acid" can be used relatively, rather than absolutely.

- The same is true for "strong base" and "weak base".
- Sometimes, whether something is called "strong" or "weak" depends on what else it is being compared to.

Table 14.9.1 . Approximate pKa values for selected compounds.

C-H Bond	pK_a	O-H Bond	pK_a	Other Bond	pK_a
	56		18	H–H	34
	50		10		
	24				36
			5		
	43				10
	43		0		
	41		4		7

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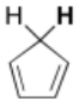
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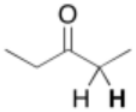
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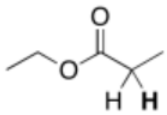
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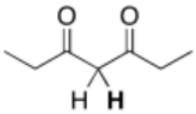
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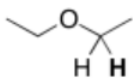
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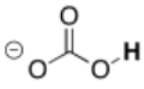
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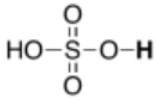
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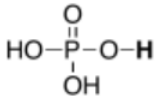
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H–F	3
H–Cl	-8
H–Br	-9
H–I	-10

A more extensive pKa table can be found at Prof. David Evans' site at Harvard.

Exercise 14.9.1

Find a pKa table. Use it to help you decide which of the following pairs is the most Brønsted acidic in water.

a) HNO_3 or HNO_2 b) H_2Se or H_2O c) HCl or H_2SO_4 d) $Be(OH)_2$ or $HSeO_3$

Answer a

a) HNO_3 ($pK_a = -1.3$); HNO_2 ($pK_a = 3.3$)

HNO_3 is a stronger Bronsted acid compared to HNO_2

Answer b

b) H_2Se ($pK_a = 3.9$); H_2O ($pK_a = 14$)

H_2Se is a stronger Bronsted acid compared to H_2O

Answer c

c) HCl ($pK_a = -8$); H_2SO_4 ($pK_a = -3$)

HCl is a stronger acid compared to H_2SO_4

Answer d

d) $Ba(OH)_2$ (pKa > 50); $HSeO_3$ (pKa = 6.6)

$HSeO_3^-$ is a stronger Bronsted acid compared to $Ba(OH)_2$

* A note on the pKa of water: physics and physical chemistry texts list 14 as the value of the pKa of water. Biochemistry and organic chemistry texts often list the value as 15.7. The latter texts have simply factored into the constant a molar value for the concentration of water; the former agree that this factor should be replaced by the activity of water, which has a value of 1.

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14.10: The Relationship Between Structure and Bronsted-Lowry Acidity

Structure plays a key role in determining how easily a compound can provide protons. For example, note that a number of common acids contain OH groups, such as sulfuric acid and acetic acid. What is it about this group that makes these compounds acidic?

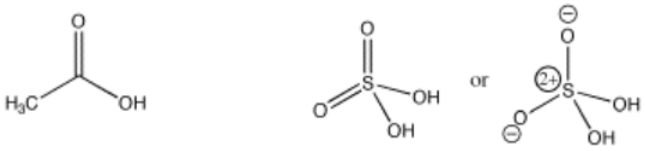

Figure 14.10.1: Acetic and sulfuric acid.

Probably it has something to do with the O-H bond being polar. However, water has an O-H bond, but it is not terribly acidic.

- A polar O-H bond may be one factor contributing to Brønsted acidity (the formation of H^+).
- However, it cannot be the only factor.

In contrast, some compounds, such as NaOH or KOH, are not very acidic. In fact, they are termed Arhennius bases, which means they are ionic compounds that dissociate in water to give hydroxide ions (HO^-). Remember, HO^- is a good Lewis base, because it has lone pairs to donate, and it also has a negative charge that makes it especially nucleophilic. Why do these compounds ionize to form HO^-, whereas other compounds containing the OH group ionize to form H^+?

The difference has to do with which bond to the electronegative element, oxygen, is most polar. The most polar bond is the one most likely to ionize.

In alkali metal hydroxides, such as NaOH, the Na-O bond is most polar. The electronegativity difference between sodium and oxygen is larger than that between oxygen and hydrogen. In fact, sodium is on the very left hand side of the periodic table, whereas oxygen is in the upper right hand corner. A combination like that results in an ionic bond, not a covalent one, so sodium hydroxide should be thought of as Na^+ and HO^-.

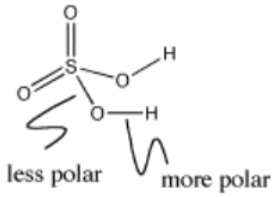

Figure 14.10.2: Bond polarity in sulfuric acid.

In main group hydroxyls such as nitric acid or sulfuric acid, the most polar bond is the O-H bond. N-O bonds or S-O bonds are not nearly as polar as O-H bonds. The O-H bond ionizes more easily.

However, relative bond polarity is not the only factor here. Acidity is strongly influenced by the structure of the ions produced in each case. More stable ions are produced more easily.

If HO^- dissociates to form a proton, a O^{2-} or oxide anion will result. That oxygen has a high nuclear charge and a high electron affinity, but a 2- charge is a lot of negative charge on one small atom. This ion will not be very stable.

On the other hand, nitric acid dissociates to form a proton and nitrate ion, NO^{3-}. This ion has a single negative charge on an element that has a high electron affinity, oxygen. In addition, there is an electronegative atom, nitrogen, attached to that oxygen, and another electronegative element, oxygen, attached to that one. Electronegativity is the ability to draw electronic charge through bonds. That means these other electronegative atoms will draw some negative charge away from the anionic atom. In this way, the negative charge is dispersed and stabilized.

- Dispersing or spreading charge out helps to stabilize charge.
- Concentrating more charge in one location is destabilizing.
- Nearby electronegative atoms can help stabilize negative charge.

There is another, related factor that stabilizes the nitrate anion by spreading out the negative charge. Notice that the negative charge could be drawn on two of the three oxygen atoms at once. The negative charge does not have to be on any particular oxygen. It can

really be shared by all three. In Lewis terms, we show that fact by drawing all three resonance structures for the nitrate ion.

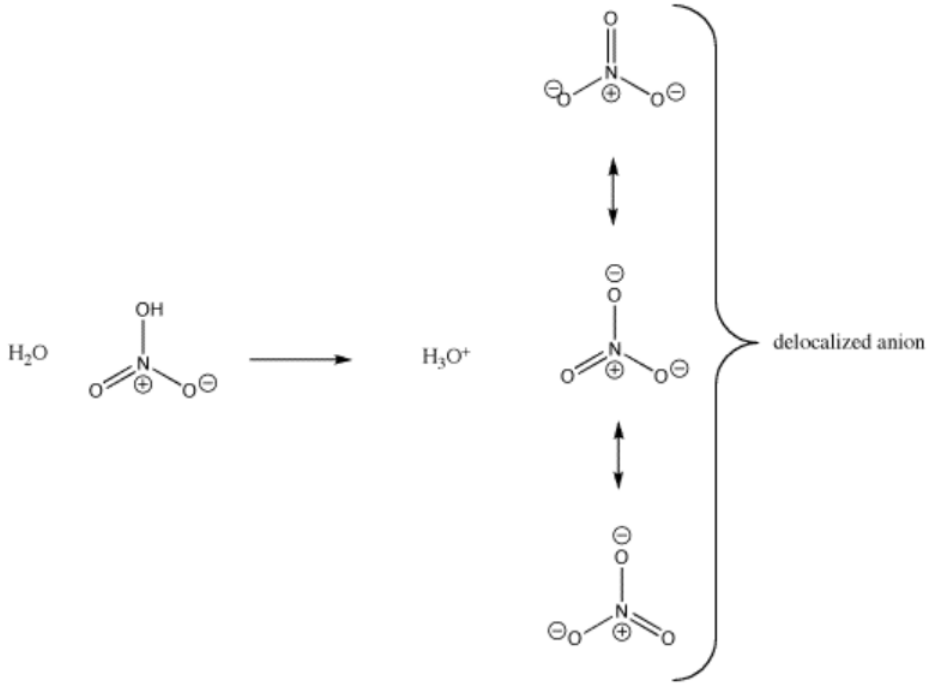

Figure 14.10.3: Charge stability in nitrate anion.

- Resonance or delocalization spreads out charge, stabilizing it.

In the subsequent sections, we can look at these and other factors in more detail.

Exercise 14.10.1

Which of the following acids do you think has the lowest pKa?

a) $HClO_2$ or $HClO_4$ b) H_3PO_3 or H_3PO_4

Answer a

$HClO_4$

Answer b

H_3PO_4

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Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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14.11: Factors Affecting Bronsted-Lowry Acidity- Local Factors

A Brønsted Acid provides a proton to an electron donor. In doing so, the former Brønsted acid becomes a conjugate base. We can understand a great deal about proton transfer by looking at that conjugate base. If the conjugate base is not very stable, then probably the proton will not be donated. If the conjugate base is very stable, then the proton may be given up more easily.

Electronegativity & Nuclear Charge

The first factor to consider is that atom attached to the proton in the Brønsted acid. That is the atom that will accept a pair of electrons from the covalent bond it shares with the proton. How easily can this atom accept a pair of electrons?

An obvious factor to consider is electronegativity. As the atom attached to the proton becomes more electronegative, the bonding pair of electrons becomes more strongly attracted to that atom, and less attracted to the proton. If the bond becomes more polarized away from the proton, it seems likely that the proton will more easily ionize. The molecule containing this bond will be a stronger Brønsted acid. It will not hold onto the proton as tightly. It will have a lower pKa.

Atoms with higher electronegativities are to the upper right in the periodic table. Moving to the right across a row, **the nuclear core charge is increasing**, so there is more attraction for electrons.

In addition, we should think about what happens after the proton has ionized. In most cases, a neutral (uncharged) Brønsted acid will give rise to an anionic conjugate base. Proton transfer is generally reversible, so it could always go back where it came from, unless something stabilizes the anion that forms. However, if an atom has a higher nuclear core charge, it will be more stable as an anion than would other atoms. That means a compound with a hydrogen attached to that atom will give up a proton more easily. When we consider anion stabilities, the trend across a row of the periodic table is exactly the same as the trend in bond polarity.

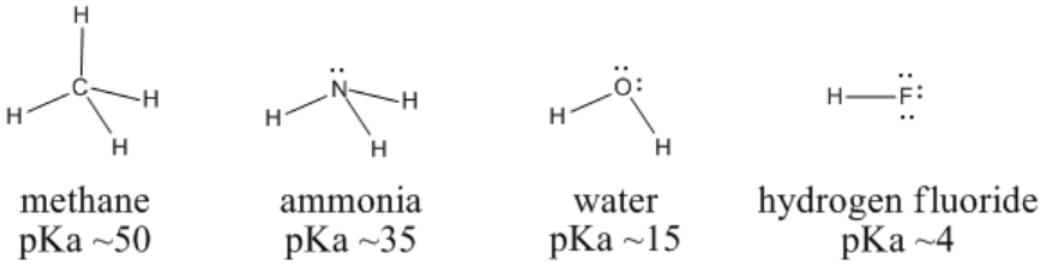


Figure 14.11.1: Variation in Brønsted acidity across a row in the periodic table.

We can compare the pKa's of methane (CH_4), ammonia (NH_3), water (H_2O) and hydrogen fluoride (HF) to examine these ideas. Carbon, nitrogen, oxygen and fluorine are all in a row in the periodic table. Fluorine, to the right, has the highest core charge and highest electronegativity. Carbon, to the left, has the lowest. Water should be a stronger acid than ammonia, which should be more acidic than methane.

In fact, the pKa of hydrogen fluoride is 4; that of water is 15; that of ammonia is 35; and methane's is about 50. Water is much more acidic than ammonia, which is much more acidic than methane. Hydroxide is a more stable ion than amide ion, NH_2^-, which is a more stable ion than methyl ion, CH_3^-.

- Electronegativity can reliably be used to compare acidities of two different X-H bonds in the same row.
- The higher the electronegativity of an atom, the more easily its X-H bond ionizes.
- Also, the higher the core charge of an atom, the more stable it will be as an anion, X^-, after the proton is lost.

Clearly, none of the compounds illustrated above is highly acidic. If you have learned any chemistry before, you may be familiar with the idea that hydroxide ion is a strong base. Hydroxide has a very strong attraction for protons. It binds a proton to form water, and is much more stable in that form.

However, these comparisons are relative. Amide ion is an even stronger base than hydroxide ion; it binds protons very tightly. Methyl anion is an extremely strong base that binds protons extremely tightly.

Exercise 14.11.1

In each case, choose the compound more likely to act as a proton donor.

a) H_2S or SiH_4 b) GaH_3 or AsH_3

c) PH_3 or AlH_3 d) H_2Se or HBr

Answer a

H_2S

Answer b

AsH_3

Answer c

PH_3

Answer d

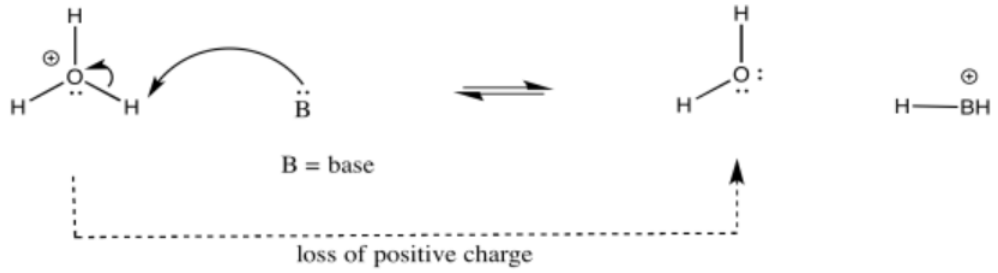
HBr

Charge on the proton donor

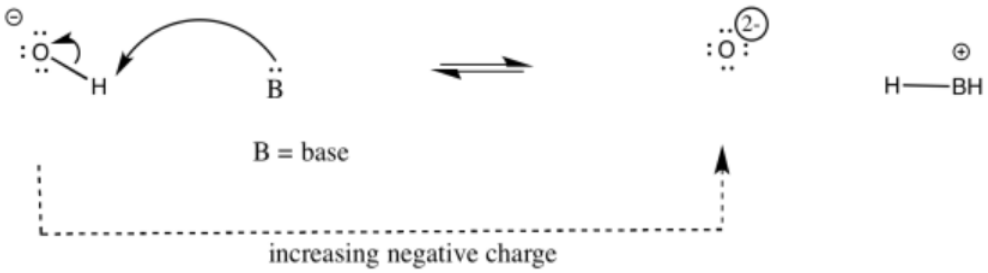
The atom attached to the proton influences the acidity in other ways. Whether or not that atom has a formal charge becomes very important. The reason is simple: when a proton is given up, the proton will have a positive charge, and the atom releasing the proton will become more negative. Consequently, if the atom attached to the proton already has a negative charge, it is less likely to give up the proton. If it did, it would take on a charge of 2-. That charge build-up would not be very favorable.

On the other hand, if the same kind of atom had a positive charge, it would be much more likely to give up a proton. Once it did, it would have no charge at all. That would be pretty favorable; no energy would have to be expended in stabilizing a charge that is no longer there.

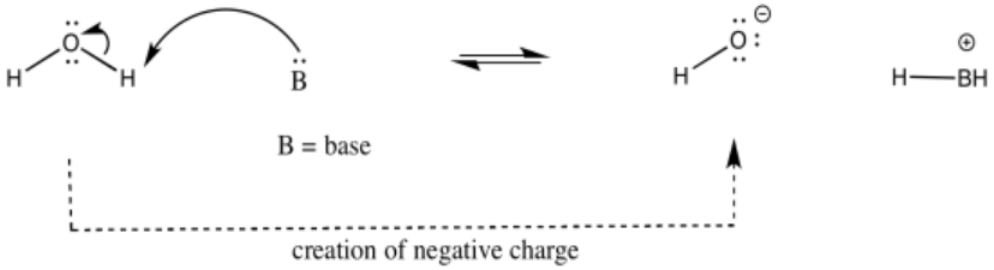
As an example, consider three related species: water (H_2O), hydroxide ion (HO^-), and hydronium ion (H_3O^+). Of the three, the hydronium ion would be the most likely to donate a proton, in order to relieve the oxygen atom of positive charge. Charge stabilisation costs energy, so having no charge at all is often better than having a charge.



The hydroxide ion would be least likely to give up a proton, because that would leave an oxide ion with a charge of 2-. That increase in negative charge on one atom costs energy.



The water ion would be intermediate. There would be an increase in charge on the atom, but it wouldn't be the same as a build up of a 2- charge on the atom.



In other words, hydronium ion is more acidic than water, and water is more acidic than hydroxide ion.

Of course, these general rules about acidity do not always apply in different situations. We know that halogens tend to be pretty stable as anions, for the most part, so their anionic form may be more stable than their neutral form. Conversely, positive metal ions may be more stable than the corresponding neutral atom. In the specific case of how likely an atom is to give up a proton, however, the development of charge or loss of charge does become an important factor. This factor is especially important when we are comparing two atoms of the same type, such as two oxygen atoms or two nitrogen atoms.

Exercise 14.11.2

In each case, assess whether a formal charge is present. Choose the compound more likely to act as a proton donor.

a) $^{+}NH_4$ or NH_3 b) PH_2 or PH_3 c) H_2O or $^{+}NH_4$ d) H_3O^{+} or CH_4

Answer a

$^{+}NH_4$

Answer b

PH_3

Answer c

$^{+}NH_4$

Answer d

H_3O^{+}

Polarizability

Let's look at another example, comparing the pKa's of hydrogen halides. These compounds are all much stronger acids than water. Hydrogen fluoride, HF, has a pKa of 4. Hydrogen chloride, HCl, has a pKa of -1. Hydrogen bromide, HBr, has a pKa of -5, and hydrogen iodide, HI, has a pKa of -7.

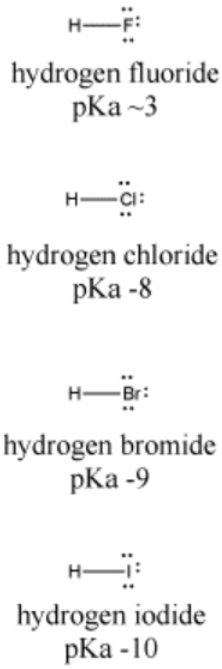


Figure 14.11.2: Variation in Brønsted acidity down a column in the periodic table.

Fluoride has the highest electronegativity of the four conjugate bases here, and iodide has the lowest. However, fluoride binds its proton most strongly, and HF has the highest pKa. Something other than electronegativity is at work here.

- Electronegativity differences cannot explain the differences in acidity of H-X bonds in a column of the periodic table.

One way of discussing this trend is in terms of polarizability. A polarizable atom is generally a large atom that can distribute charge easily over a greater volume; charge is less concentrated than it would be in a smaller atom. The distribution of charge is stabilizing.

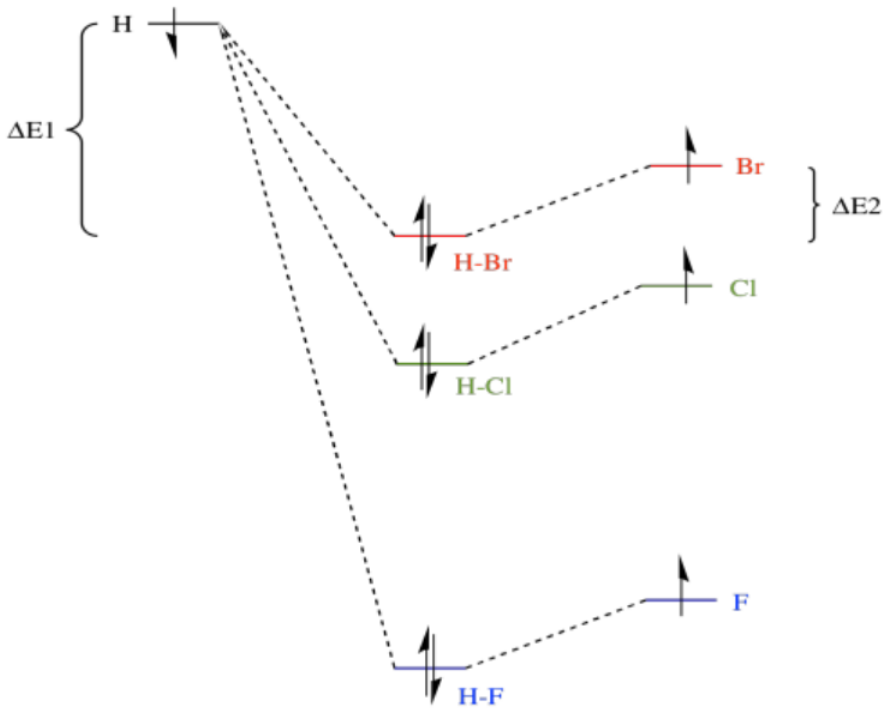
- When comparing anionic atoms from the same column of the periodic table, the polarizability of the atom (related to its size) can be used to explain different anion stabilities.

The reason polarizability dominates comparisons within a column, but not within a row, has to due with the relatively large change in size of atoms from one row to the next. As electrons occupy an additional energy level, the size of the atom increases greatly. Atoms also change size as we move across a row of the periodic table, getting a little smaller as the nuclear charge increases. However, this change is not as dramatic as the change in size from one row to the next.

Earlier, we looked at both sides of the equation, before and after ionization, in terms of core charge and electronegativity. Both considerations led to similar conclusions about which bonds would be most acidic. So far, we have looked at the anions formed when hydrogen halides ionize. Is there a factor (other than electronegativity) we can use in comparing the hydrogen halides directly?

Among these compounds, the bond strength increases from the bottom of the column to the top (from about 70 kcal/mol in HI to about 135 kcal/mol in HF). That means it is much easier to break a hydrogen atom away from an iodine atom in HI than to break a hydrogen atom away from a fluorine atom in HF. That isn't what we are doing when we ionize these bonds; we are breaking a proton away from an anion in each case, rather than a neutral hydrogen atom away from another neutral atom. Nevertheless, whatever factors influence bond strength may be affecting acidity as well.

Bond strengths actually vary in this way indirectly because of the relative electronegativities of the halogens. The valence electrons on fluorine, a more electronegative atom, are at a lower energy than those on either bromine or chlorine. When the valence electrons on a hydrogen atom and a halogen atom combine to form a bond, the bonding combination is at a lower energy than either of the originals.



Of course, the antibonding combination is at a higher energy than either of the originals, but since there are no electrons at that level we don't have to worry about that.

What is a bond strength? It's just the amount of stabilisation upon formation of the bond. Put in an allegorical way, it's how deep the gully is that the electrons have rolled into when the bond forms. To break the bond, the electrons would have to climb the hills back out of the gully again. For example, the bond strength of HBr involves the amount of energy by which the electron on hydrogen has fallen, ΔE1, plus the amount by which the hydrogen on bromine has fallen, ΔE2. To break the bond again, we would have to add in the sum of ΔE1 + ΔE2.

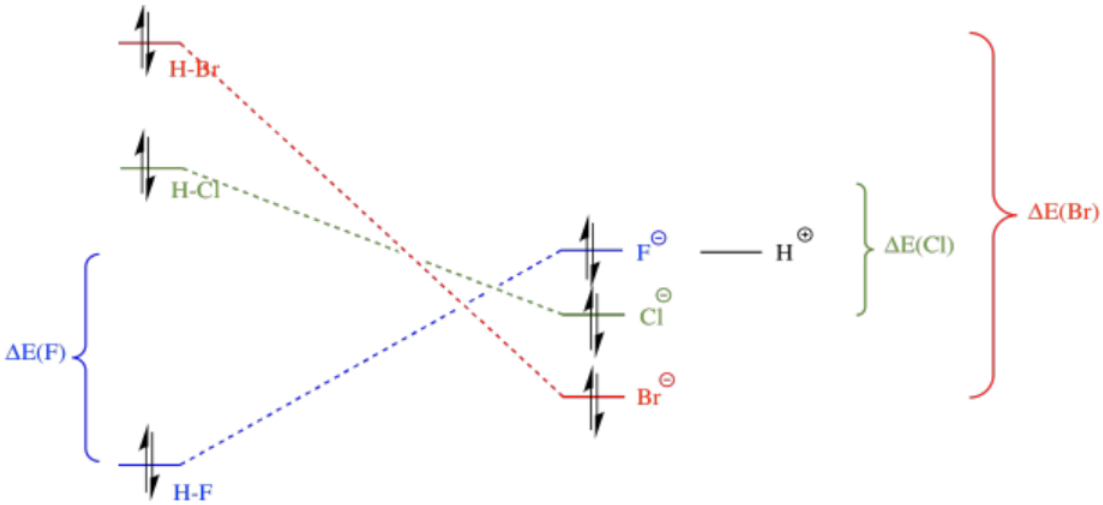
The analogous amount for HCl is greater, mostly because ΔE1 in that case is much larger, and it is even greater for HF. Thus, bond strengths vary in the order HF > HCl > HBr.

While we are looking at that picture, it's worth considering another common aspect of bond strengths. As a simple approximation, there are two important components that describe a bond. One component is overlap (how well the eletrons are shared; that is, how covalent is the bond). The other component is exchange (how much electrostatic attraction there is between the atoms; that is, how polar is the bond). In fact, bromine is better at sharing its electrons with hydrogen than is fluorine, but the H-F bond is more polar than the H-Br bond. The latter fact is another consequence of fluorine's electronegativity. Once again, the greater electronegativity of fluorine actually leads to a stronger bond in this case.

- In comparing two atoms in a column of the periodic table, bond strength with hydrogen is a good index of how acidic the bond will be.

Note that bond strength does not work as a comparison of H-X bonds in a row of the periodic table. An HF bond is stronger than an OH bond (about 110 kcal/mol) or CH bond (about 100 kcal/mol on average), yet it is much more acidic.

Now, in summary, we need to think about both sides of the equation. The H-F bond is the strongest; that is, it is lowest in energy. However, upon ionisation, bromide is the most stable anion, because it is the largest and most polarizable. Overall, the reaction from HBr to bromide is the most downhill in energy; that one will happen most easily. In contrast, the reaction from HF to fluoride is actually uphill in energy; that one will be most difficult to ionise.



Exercise 14.11.3

In each case, choose the compound more likely to act as a proton donor.

a) H_2S or H_2Te b) GeH_4 or SnH_4 c) HCl or HBr d) NH_3 or AsH_3

Answer a

H_2Te

Answer b

SnH_4

Answer c

HBr

Answer d

AsH_3

Exercise 14.11.4

Rank the following groups of compounds from most acidic to least acidic.

a) PH_3, NH_3, AsH_3 b) PH_3, H_2S, SiH_4, HCl c) BH_3, SiH_4, SeH_2, HI

Answer a

$AsH_3 > PH_3 > NH_3$

Answer b

$HCl > H_2S > PH_3 > SiH_4$

Answer c

$HI > SeH_2 > SiH_4 > BH_3$

Exercise 14.11.5

The relative acidities of compounds in some of the following pairs can be explained by polarizabilty. In others, they cannot. Explain why polarizability is or is not a useful comparison to make in each case.

a) CH_3OH, $(CH_3)_2CHOH$ b) SH_2, SeH_2 c) GeH_4, SiH_4 d) GeH_4, GaH_3

Answer a

Polarizability would not be useful as the atom that will be anionic in the conjugate base is the same (oxygen).

Answer b

Se is larger and therefore more polarizable leading to H_2Se being more acidic compared to H_2S.

Answer c

Ge is larger and therefore more polarizable leading to GeH_4 being more acidic compared to SiH_4.

Answer d

Polarizability would not be useful as the atoms are next to one another in the same row and therefore likely to have the same polarizability

Hybridization

There is a special case related to the electron affinity factor described above. It generally shows up in discussions of carbon or nitrogen compounds, and specifically deals with comparisons of two atoms of the same element having different geometry. For example, the C-H bond involving a tetrahedral carbon is extraordinarily non-acidic (pKa near 50), but a C-H bond involving a linear carbon is much more acidic (pKa of about 25).

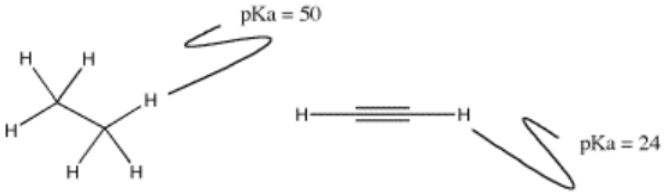


Figure 14.11.3: "Hybrid" energies in bonds involving linear and tetrahedral carbons.

In ethane, which has tetrahedral carbons, a similar argument is made. The difference is that a tetrahedron is a three-dimensional shape. The s orbital can still bond to neighbors in any direction because of its spherical symmetry. However, in order to bond with neighbors in all three dimensions, the entire set of p orbitals would be needed, because each p orbital lies along one dimension only.

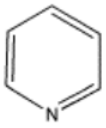
The energy of the electrons in this bonding situation will be an average of the energy of an s electron and *three* p electrons. In terms of carbon's energetic contribution, the energy of the electrons in the C-H bond will be *three-quarters of the way* between what would be expected if the bond formed between an H atom and a carbon 2s electron and if the bond formed between an H atom and a carbon p orbital. That is because the energy should be an average of the energies of all four orbitals that could contribute to that bond.

Because s electrons are lower in energy than p electrons, the energy of the (s + p) combination will be lower than the energy of the (s + p + p + p) combination. An electron in an "sp orbital" at linear carbon is lower in energy than an electron in the "sp3 orbital" at tetrahedral carbon. If the electron is at lower energy on a linear carbon than a tetrahedral carbon, then a linear carbon has a higher electron affinity than a tetrahedral one.

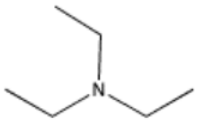
This comparison is much like the comparison of electron affinity on an oxygen vs a carbon. Oxygen, with a higher electron affinity, generally forms more stable anion than does carbon. An O-H bond is thus more acidic than a C-H bond. A liner C-H bond is more acidic than a tetrahedral C-H bond.

Exercise 14.11.6

Predict which of these two nitrogen compounds will be more basic.



pyridine

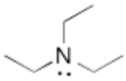


triethylamine

Answer

Triethylamine will be more basic than pyridine due to the hybridization effect. The nitrogen in triethylamine is sp^3 whil the pyridine nitrogen is sp^2.

pyridine



triethylamine

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14.12: Factors affecting Bronsted-Lowry Acidity- Distal Factors

Sometimes there are factors farther away from the proton that affect Brønsted acidity. In addition to considering the atom to which the proton is directly attached, we may need to consider other parts of the molecule to understand anion stability.

A first factor to consider is delocalization due to conjugation. In Lewis structure terms, that means resonance. Delocalization of charge is stabilizing, so if a negative charge can be distributed across multiple atoms via resonance, a conjugate base will be more stable.

- resonance can delocalize negative charge and stabilize an anion.
- a more stable conjugate base forms more easily. A Brønsted acid will give up a proton more easily if it gives rise to a stable conjugate base.

Many organic compounds contain hydroxyl or OH groups, some of which are acidic and some of which are not. Three kinds of compounds containing this group are alcohols, phenols and carboxylic acids. Examples of these functional groups include cyclohexanol, phenol and benzoic acid.

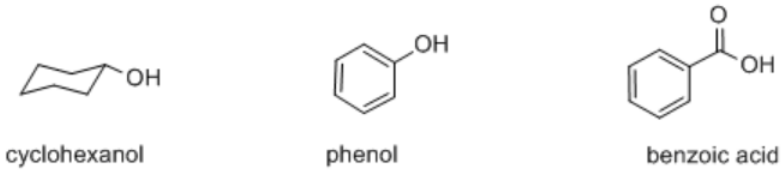


Figure 14.12.1: Cyclohexanol, phenol and benzoic acid.

Cyclohexanol is an alcohol. An alcohol contains an OH group connected to a tetrahedral carbon.

Phenol is slightly different; it contains an OH group connected to a trigonal planar carbon that is part of an aromatic ring. Aromatic rings are cyclic groups of atoms, usually carbons, with delocalized pi bonding all around the ring. Benzene is the most common example of an aromatic ring. It is a ring of six carbons and all of the carbons are trigonal planar. In the Lewis structure, it is drawn with alternating single and double bonds between the carbons.

Benzoic acid contains a very different functional group in which the OH is connected to a carbonyl. A carbonyl is a carbon-oxygen unit with a double bond, C=O. The carbon in a carbonyl is trigonal planar, as in a phenol, but the presence of the double bond to oxygen makes a big difference.

Cyclohexanol has a pKa of about 18. It is less acidic than water. It can give up a proton, but the proton is much more likely to be bound to the oxygen than disscociated. Phenol has a pKa of about 9 and is considered mildly acidic. Benzoic acid has a pKa of about 5; its acidity is similar to hydrofluoric acid, although not nearly as acidic as other hydrogen halides.

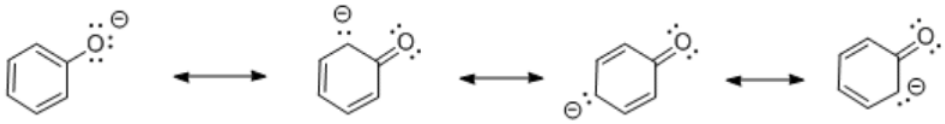


Figure 14.12.2: The anion resulting from deprotonation of phenol.

Figure 14.12.3: The anion resulting from deprotonation of benzoic acid.

Comparing the conjugate bases of cyclohexanol, phenol and benzoic acid reveals some differences.

- In cyclohexanol, the anion formed by loss of a proton is localized on the oxygen. There is no resonance stabilization.
- In phenol, the anion formed by loss of a proton is delocalized. Resonance structures show the negative charge can be shared between the oxygen atom and three of the carbons in the benzene ring.

- In benzoic acid, the anion is also delocalized. This time the negative charge is shared between two different oxygen atoms.

Resonance delocalization plays a clear role in stabilizing the conjugate base formed after loss of a proton. Despite the similar bond polarity in cyclohexanol and phenol, the proton is much more tightly bound in cyclohexanol. The greater stability of the phenolate anion compared to the cyclohexanoxide anion makes it easier to remove a proton from phenol than cyclohexanol.

- The atoms onto which the charge is delocalized still plays a major role in determining stability. Delocalization onto an additional oxygen atom may be more stabilizing than delocalization onto several carbons.

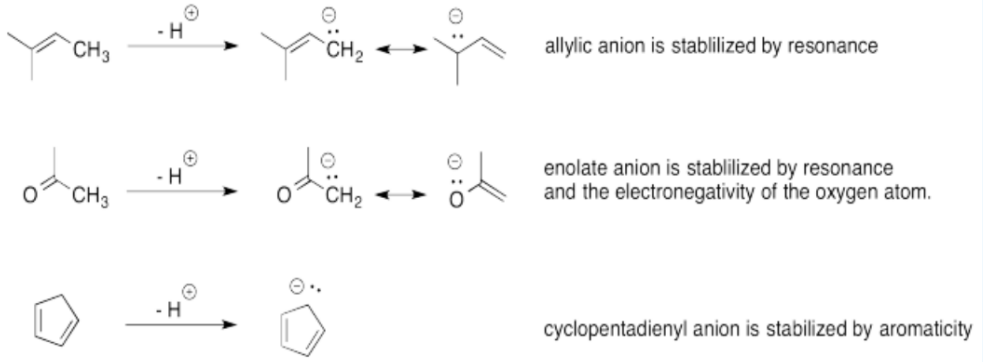
Exercise 14.12.1

Some compounds have acidic C-H bonds, despite the fact that many hydrocarbons have extremely high pKa's (such as methane, CH_4, pKa = 50). Explain the reason for the trend in pKa's among the following compounds.

cyclopentadiene, pKa 25 cyclopentanone, pKa 18 2,4-hexanedione, pKa 12

Answer

Alkanes typically have a $pK_a > 50$, however CH's adjacent to π systems lead to anions that are stablilized by conjugation or aromaticity. Examples of these are shown below:



Exercise 14.12.2

Compare the acidity of the following pairs of compounds.

a. ethanol, CH_3CH_2OH, and vinyl alcohol, CH_2=CHOH.
b. trimethylamine, $(CH_3)_3N$, and nitromethane, CH_3-NO_2.
c. acetonitrile, CH_3-CN, and trimethylamine, $(CH_3)_3N$

Answer a

Vinyl alcohol would be more acidic as its anion is stabilized by resonance while the anionic charge on ethoxide would be localized on the oxygen atom.

Answer b

Nitromethane would be more acidic as its anion is stabilized by resonance while the anionic charge of the trimethylamine anion would be localized on the carbon atom.

Answer c

Acetonitrile would be more acidic as its anion is stabilized by resonance while the anionic charge of the trimethylamine would be localized on the carbon atom.

There is another way that distant atoms can influence anion stability. It has to do with electronegativity.

Consider the pKa of these three, similar, halogenated carboxylic acids: bromoacetic acid, chloroacetic acid and fluoroacetic acid. The pKa of fluoroacetic acid is lower than that of chloroacetic acid, which is lower than that of bromoacetic acid. Fluoroacetic acid

is more acidic than chloroacetic acid, which is more acidic than bromoacetic acid.

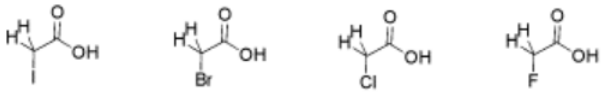


Figure 14.12.4: Acidity in some haloacetic acids.

When the proton is directly attached to these three halogens, the pKa runs in the opposite direction. HBr is more acidic than HCl, which is more acidic than HF. That was because of the greater polarizability of the bromide versus the chloride and fluoride.

In these haloacetic acids, the halogen can stabilize the conjugate anion via inductive delocalization. In an inductive effect, electronegative atoms can draw electron density toward themselves. That means the halogen shares the partial negative charge of the oxygen atoms in the carboxylate anion.

- electronegative atoms can draw negative charge toward themselves through bonds.
- this phenomenon is called an inductive effect.
- inductive effects spread out negative charge and stabilize anions.

The effect is additive. If more than one halogen is nearby, there is more electron-withdrawing effect. There is more positive charge on the proton, and when the proton is released, the resulting anion has more charge delocalization.

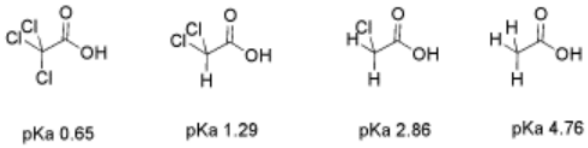


Figure 14.12.5: Additive inductive effects

Exercise 14.12.3

Predict the order of acidity in the following compounds.

a) CF_3CO_2H, CFH_2CO_2H, CF_2HCO_2H b) CF_3CHCl_2, CF_3CHClF, CF_3CHF_2

Answer a

$CF_3CO_2H > CF_2HCO_2H > CFH_2CO_2H$

Answer b

$CF_3CHF_2 > CF_3CHClF > CF_3CHCl_2$

An important limitation on inductive effects is seen in comparing a series of chlorobutanoic acid derivatives. In 2-chlorobutanoic acid, the presence of a chlorine next to the carbonyl, four bonds from the acidic proton, renders this compound much more acidic than butanoic acid; the pKa's are about 2.9 and 4.8, respectively.

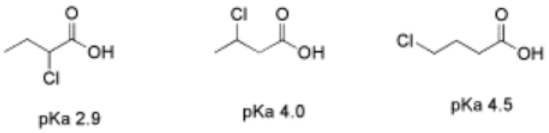


Figure 14.12.6: The effect of distance on inductive electron withdrawal.

In 3-chlorobutanoic acid, the pKa is 4.0, whereas in 4-chlorobutanoic acid, with the fluorine all the way at the end of the chain, six bonds away from the acidic position, the pKa is 4.5. The fluorine in these last two cases has relatively little effect.

- Inductive effects fall off quickly with increasing distance from the acidic site.

However, in aromatic systems the effect of distance is slightly weaker. In 2-chlorobenzoic acid, the effect of the chlorine is substantial, despite its distance from the acidic proton. The pKa of 2-chlorobenzoic acid is 2.94, as compared to 4.2 for benzoic acid, despite the fact that the chlorine is 5 bonds away from the acidic proton. This increased influence of inductive effects is common in aromatic systems such as benzene.

- Inductive effects are readily transmitted across conjugated systems like benzene.

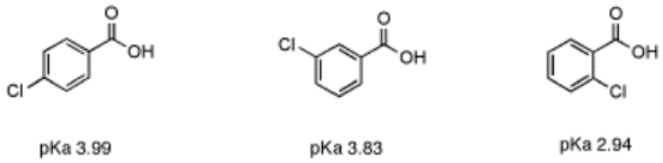
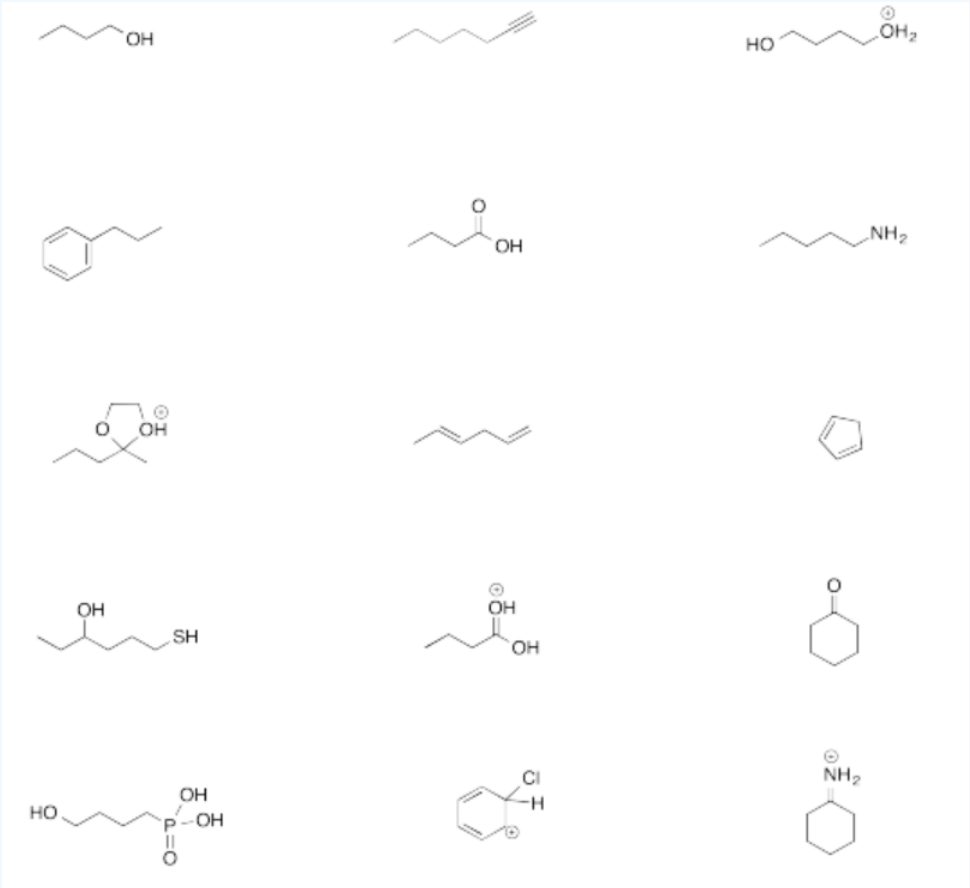


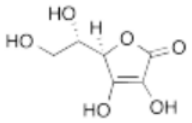
Figure 14.12.7: The effect of distance on inductive electron withdrawal in an aromatic system.

Aromatic systems contain delocalized, polarizable sets of electrons. In contrast to sigma bonds, in which electrons are delocalized between two atoms yet still located pretty reliably in between those two atoms, pi bonds hold electron density further from the nuclei, and are more easily distorted or polarized.

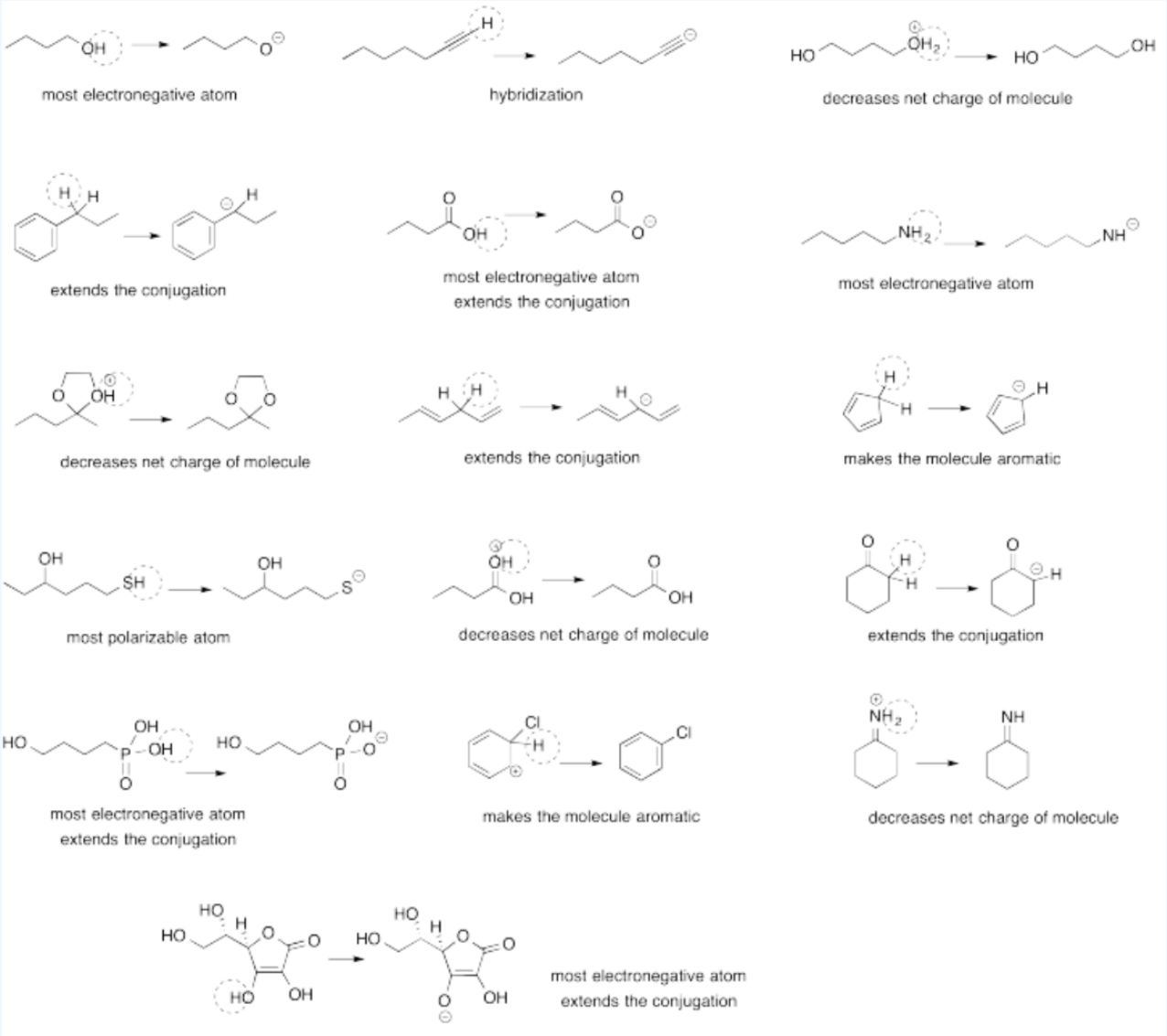
Exercise 14.12.4

For each of the following compounds:
a. Determine the most acidic proton and provide a reason for your choice.
b. Draw the conjugate base.





Answer



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14.13: Effects on Basicity (Attraction for Proton)

All of the factors that we have discussed for Brønsted acidity, or the ability of a compound to provide a proton to its surroundings, have an effect on basicity as well. In other words, factors like nuclear charge / electron affinity influence how strongly a compound will attract or bind a proton.

In summary:

- the higher the electron affinity or core charge of an atom, the less likely it is to donate its electrons to a proton.
- the greater the delocalization of electrons that could potentially donate to a proton, the less able they are to donate.
- the greater the electron-withdrawing effects in another part of a molecule, the less likely the electrons on a particular atom are to donate.

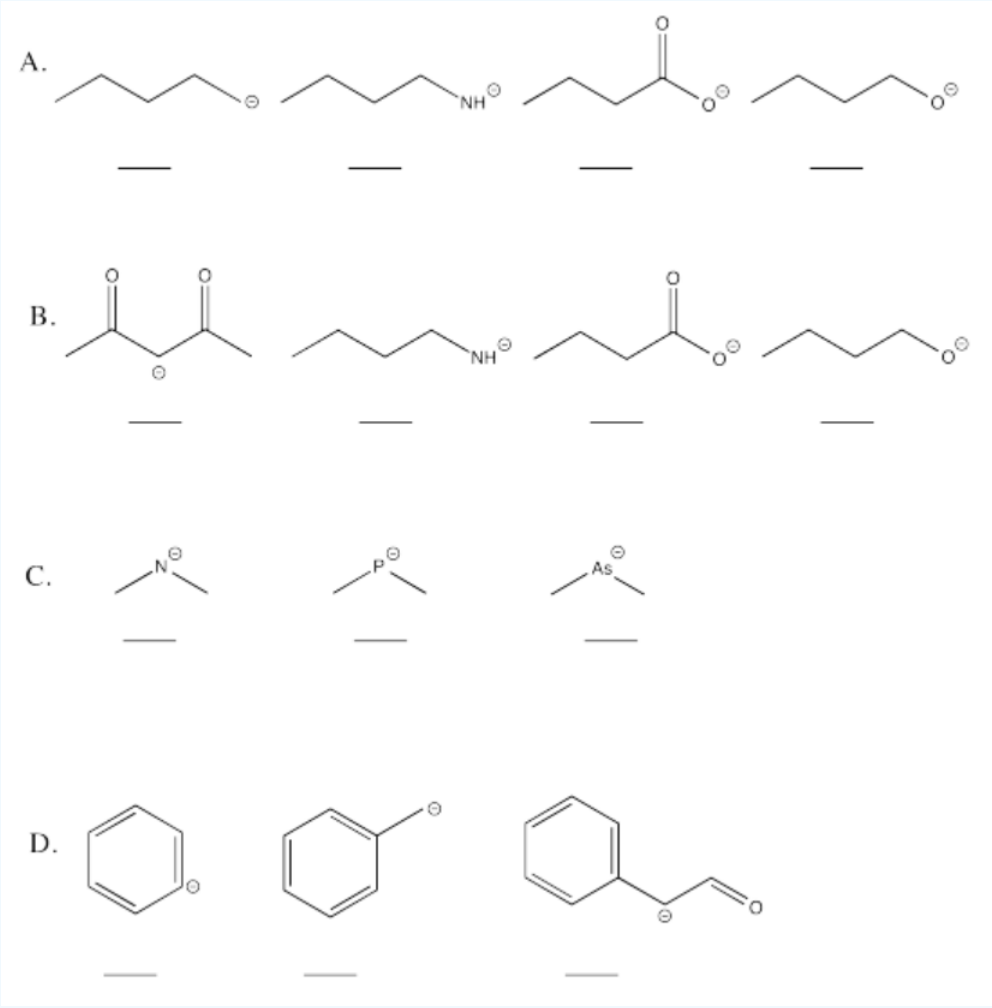
These factors are generally complementary to the effects on acidity. A factor that makes a Brønsted acid **more acidic** usually makes the corresponding conjugate base **less basic**.

However, sometimes things can be more subtle.

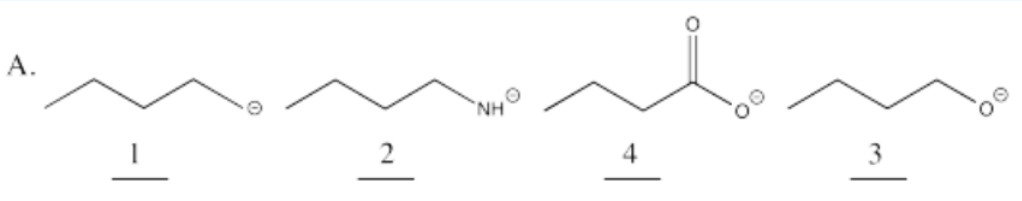
- the higher the polarizability of an atom (i.e. the larger an atom), the more easily it can donate to a Lewis acid (its electrons are not held very tightly because they are far from the nucleus, and so they can be donated easily).
- except: a larger atom cannot donate easily to a proton. In this specific case, the Lewis acid (the proton) is too small to get good covalent overlap with the Lewis base, so it can't form a very strong bond

Exercise 14.13.1

Rank the following in terms of base strength (1 = strongest base).



Answer a



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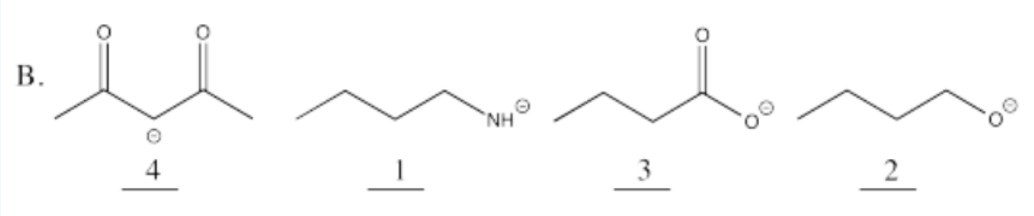
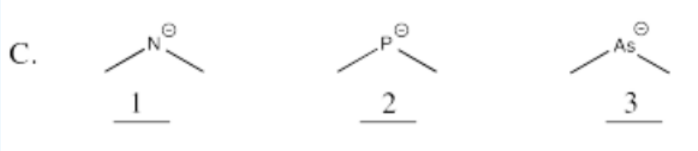
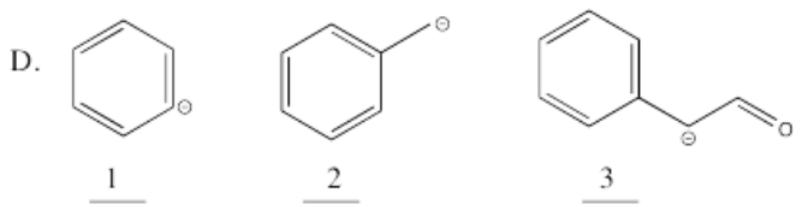


Answer c



Answer d



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14.14: The Direction of Proton Transfer

Brønsted-Lowry acidity is a special case of Lewis acidity. In Lewis acidity, an electron donor shares electrons with an electron acceptor, forming a bond. In some cases, the electron acceptor is a proton.

If the proton accepts electrons from the donor, but does not relinquish its bond to its previous partner, the interaction is called a hydrogen bond.

If the proton exchanges a new bond with the donor for an old bond with its previous partner -- if it releases a pair of electrons to its partned as it accepts a pair of electrons from the new donor -- the event is called proton transfer.

The compound that provided the proton is called a Brønsted-Lowry acid. The compound that donated the new bond to the proton is called the Brønsted-Lowry base.

Because the proton allowed its former partner to take the pair of electrons from their former bond, that partner becomes a Lewis base. In a proton transfer, the proton moves from one Lewis base to another. The proton could conceivably move back to its original partner, however. The original partner could simply donate its pair of electrons to the proton again. It would displace the new partner and win the proton back.

This situation is called reversibility. Reactions can often move back and forth. In order to convey this idea, when illustrating or writing about these reactions, a pair of opposing arrows are used to show that the reaction can go from left to right as written, as well as from right to left.

- In a reversible reaction, the change that occurs in the reaction can be undone. The reaction can move forwards and backwards.

In most cases, the reaction settles out on one side or the other. Either the reaction goes mostly forward or it goes mostly backward. The point where the reaction settles is termed the equilibrium. At equilibrium, the reactants that come together may mostly be converted into new products. Looking at an equation or diagram of the reaction, , the equilibrium is said to "lie to the right", because the products of the reaction are usually written on the right hand side of the reaction arrow or equilibrium arrow. Some reactions "lie to the left", meaning very little of the original reactants are ultimately converted to the products show.

- The equilibrium is the balance established between the products formed and the original reactants in a reversible reaction.

In a proton transfer, the equilibrium is determined by how tightly the proton is held by each Brønsted acid. The proton will simply remain bonded to whichever compound binds it more tightly. If the difference in binding is great, the equilibrium will lie far to the left or far to the right. If the difference in proton binding is small, there will be a mixture, in which the proton could be in either position.

Remember, most reactions involve zillions of molecules. There is plenty of room for mixtures.

We can predict where the proton will end up by looking at pKas.

- A higher pKa means the proton is more tightly held.
- By comparing the pKa's of the Brønsted acids on both sides of the equation, we can determine which compound will retain the proton.
- The equilibrium will lie towards the compound with the higher pKa.

This idea is illustrated in the equilibrium between hydronium ion and ammonium ion.

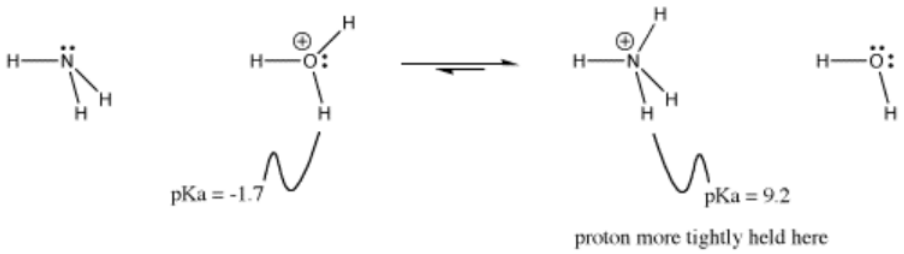


Figure 14.14.1: Direction of proton transfer between hydronium and ammonium ion.

As another example, if hydrogen chloride is dissolved in water, the HCl may give up its proton to the water. Water has a lone pair and can act as a base. However, in doing so, the water will form hydronium ion, H_3O^+. Hydronium ion is Brønsted acidic and can provide a proton to something else that has a lone pair, such as a chloride ion. This reaction could go back and forth. Where will it settle out?

HCl has a pKa of -8. Hydronium ion has a pKa of about -1.7. The equilibrium in the reaction described above lies to the right, towards the hydronium ion produced when the hydrogen chloride dissociates. The proton will remain on the oxygen.

Exercise 14.14.1

Write an equation for the proton transfer reactions that could happen in each of the following mixtures. Use structures in your equations. Predict the position of the equilibrium in each case.

a) HF plus water b) CH_3CO_2H plus ammonia

c) phenol (C_6H_5OH) plus sodium carbonate d) HCN plus acetonitrile

Answer a

a. $HF + H_2O \rightleftharpoons F^{\ominus} + H_3O^{\oplus}$

$HF\ pK_a = 3$ $\quad$ $H_3O^{\oplus}\ pK_a = -2$

At equilibrium the reactants will be favored

Answer b

b. $CH_3CO_2H + NH_3 \rightleftharpoons CH_3CO_2^{\ominus} + NH_4^{\oplus}$

$CH_3CO_2H\ pK_a = 5$ $\quad$ $NH_4^{\oplus}\ pK_a = 9$

At equilibrium the products will be favored

Answer c

c. $PhOH + CO_3^{-2} \rightleftharpoons PhO^{\ominus} + HCO_3^{\ominus}$

$PhOH\ pK_a = 10$ $\quad$ $HCO_3^{\ominus}\ pK_a = 10$

At equilibrium reactants and products will be present in equal amounts

Answer d

d. $HCN + CH_3CN \rightleftharpoons CN^{\ominus} + CH_3CNH^{\oplus}$

$HCN\ pK_a = 9$ $\quad$ $CH_3CNH^{\oplus}\ pK_a = -10$

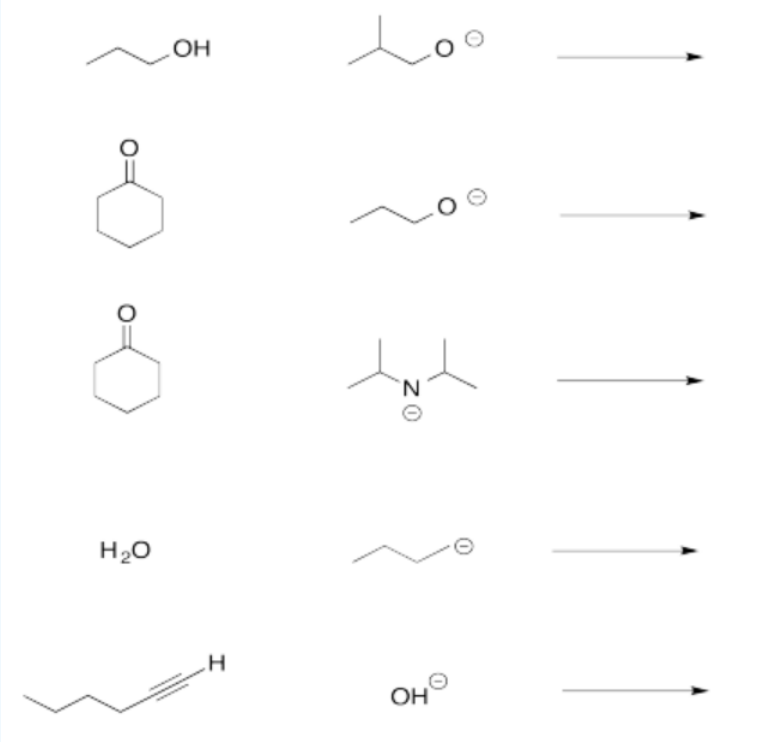
At equilibrium the reactants will be favored

Exercise 14.14.2

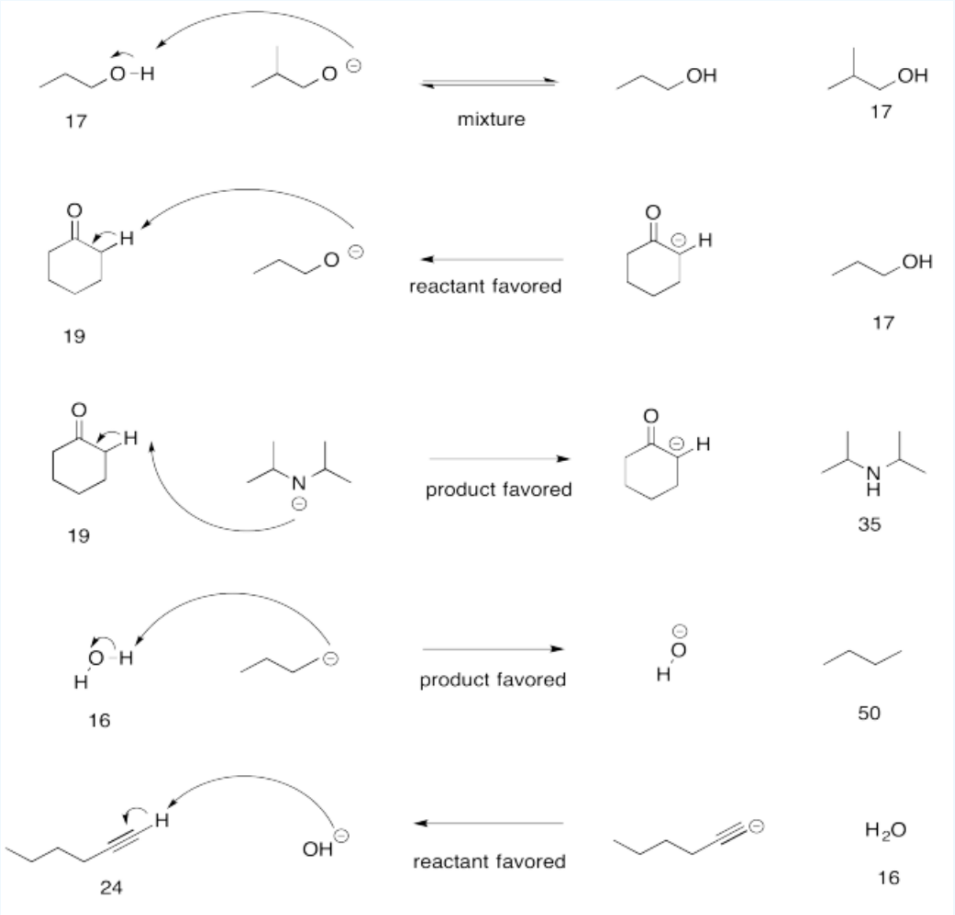
Use curved arrows to show the proton transfer reaction between the following compounds.

Predict the products for these proton transfer reactions.

Use pKa to determine whether each reaction is reactant favored OR mixture OR product favored.



Answer



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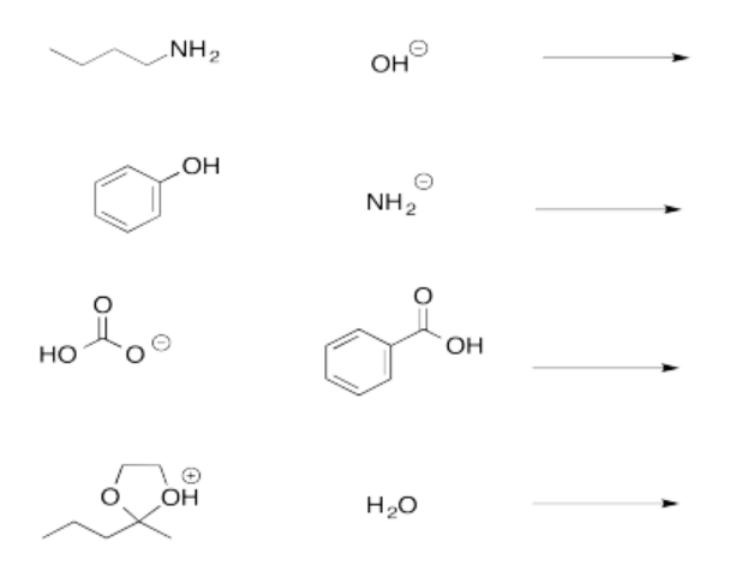

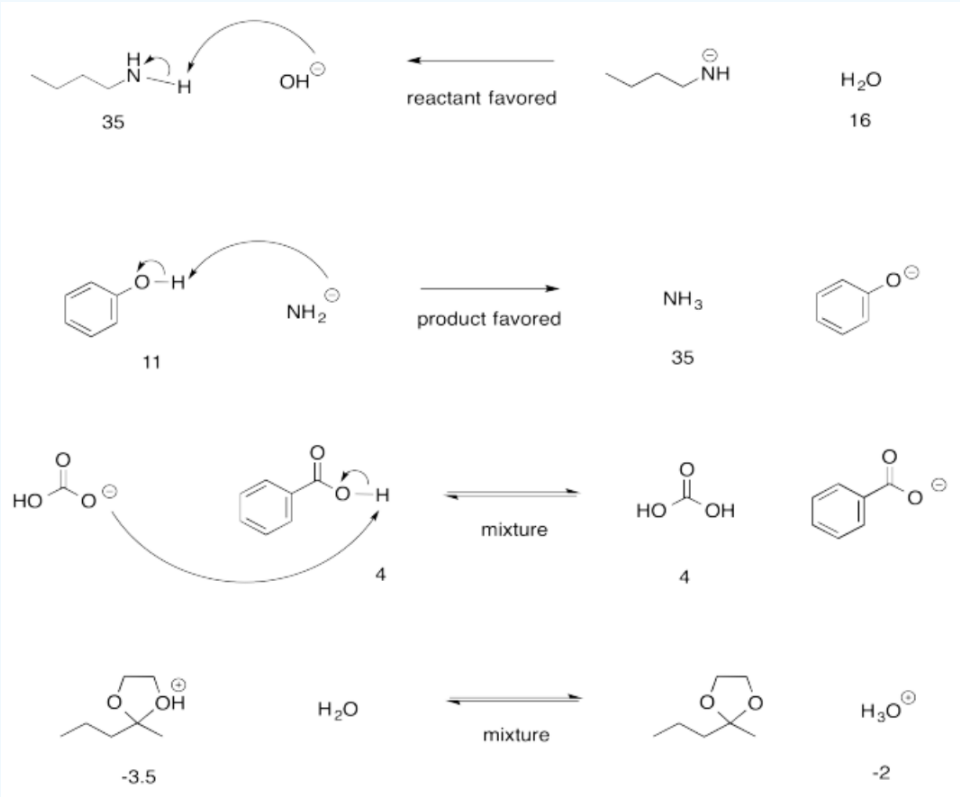

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14.15: Amino Acids and Peptides

Knowing something about proton transfer changes how we look at some important biomolecules. Amino acids are the fundamental building blocks of peptides and proteins. Peptides, which are chains of amino acids, are frequently used as signaling molecules within the body (some hormones are peptides). Proteins, which are very large peptides, have a variety of uses. They form the key components of muscles, for instance, and they also form enzymes that carry out a multitude of chemical reactions necessary for life.

Amino acids are so called because they all contain two common components. One is an amine, or a tetrahedral nitrogen attached to a carbon. The other is a carboxylic acid, which is a carbon that is double bonded to an oxygen and also attached to an OH or hydroxyl group.

We have seen that carboxylic acids are moderately acidic. Most of them have pKa's of 3 to 5. That means a small fraction of the OH groups are ionized in a large group of carboxylic acids.

Figure 14.15.1: A carboxylic acid in water.

We have also seen that tetrahedral nitrogens are somewhat Lewis basic. The nitrogen can donate its lone pair to Lewis acidic atoms. Protons are good Lewis acids. Amines are easily protonated if protons are available.

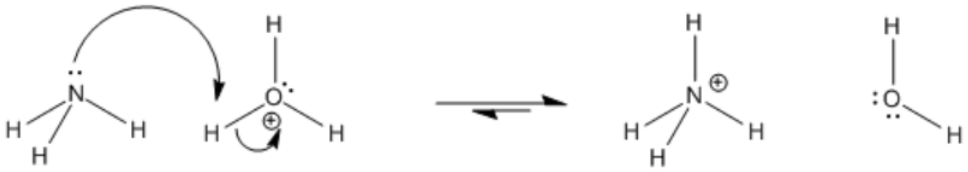


Figure 14.15.2: An amine in a proton-rich environment.

Because the carboxylic acid is a pretty good source of protons and because protons bind to amines pretty well, it seems reasonable that a proton transfer may occur from one site to the other.

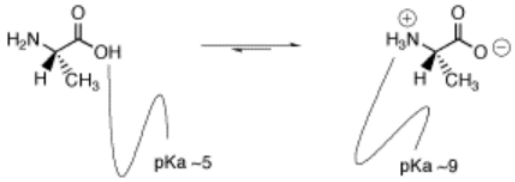


Figure 14.15.3: Two forms of an amino acid, related by proton transfer.

Does one of these forms dominate the equilibrium? Compare the pKa's. The pKa of the acid is near 5, and the pKa of the ammonium is near 9. The ammonium holds the proton more tightly than does the acid. The proton stays on the nitrogen.

Amino acids are zwitterionic. A zwitterion is a compound that has no overall charge but that has charge separation within it. The zwitterionic nature of amino acids has an effect on their properties. For example, they are usually pretty soluble in water and other polar solvents.

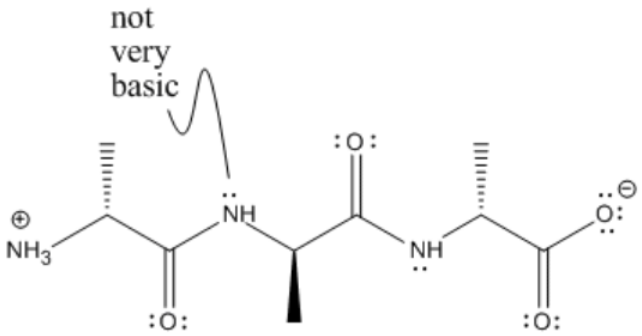


Figure 14.15.4: A peptide.

Amino acids are joined together via "amide linkages" to form peptides and proteins. In these structures, the individual amino acids no longer have the same acidic carboxylic acid group; the carbonyl (or C=O) no longer has a hydroxyl group attached. The amino acids no longer contain amines, either; a nitrogen attached to a C=O has very different properties than a regular nitrogen attached to carbon. Only the "N-terminus" and "C-terminus" are ionic. The nitrogens along the chain are not very basic and are not protonated.

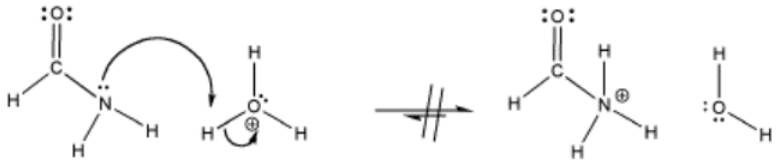


Figure 14.15.5: An amide, and the unfavorable protonation of an amide

Exercise 14.15.1

Explain why an amide nitrogen is not very basic.

Answer

the nitrogen lone pair electrons in an amide are delocalized making them less basic

Exercise 14.15.2

The favored site of protonation in an amide is the carbonyl oxygen. Show why.

Answer

protonation of the oxygen leads to a conjugate acid that is conjugated

The acidic and basic groups found in individual amino acids are masked in peptides and proteins. However, peptides and proteins do have basic and acidic sites. These sites are found on the side chains of the amino acids, the part that varies from one amino acid

to another. In some cases, the side chain contains an acidic group. Examples are aspartic acid and glutamic acid.

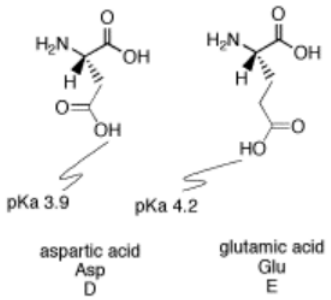


Figure 14.15.6: Acidic amino acids.

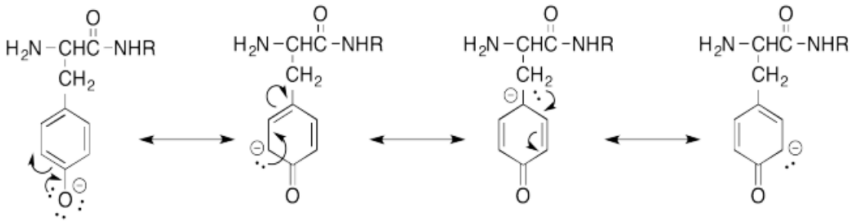
There are other side chains that are weakly acidic. For example, tyrosine is sometimes able to supply protons, and so is cysteine. The proton comes from the OH and SH groups, respectively, on these two compounds. However, neither of these compounds can supply protons as easily as aspartic acid or glutamic acid. Furthermore, serine, which also has an OH group, is not really able to supply protons that easily.

Exercise 14.15.3

Explain the difference in acidity between serine and tyrosine, which both contain OH groups.

Answer

The alcohol proton on tryosine is more acidic due the resonance stabilization of the conjugate base. The conjugate base of serine possesses a localized anionic charge and is relatively less stable.



resonance structures for the tyrosine anion

Exercise 14.15.4

Explain the difference in acidity between serine and cysteine, which have very similar structures but with a sulfur atom in place of an oxygen.

Answer

The thiol proton on cystine is more acidic due to the polarizability of the sulfur anion stabilizing the conjugate base's anionic charge. The oxygen anion is less polarizable and therefore less stable rendering the alcohol proton less acidic.

Sometimes the amino acid side chain contains a basic group. Examples are histidine, lysine and arginine. There is a big difference in basicity between these three compounds. The difference can be seen by looking at the pKa's of the conjugate acids in each case. The higher the pKa of the conjugate acid, the more tightly the proton is held, and so the more basic the nitrogen atom. Arginine is by far the most basic and histidine is the least basic.

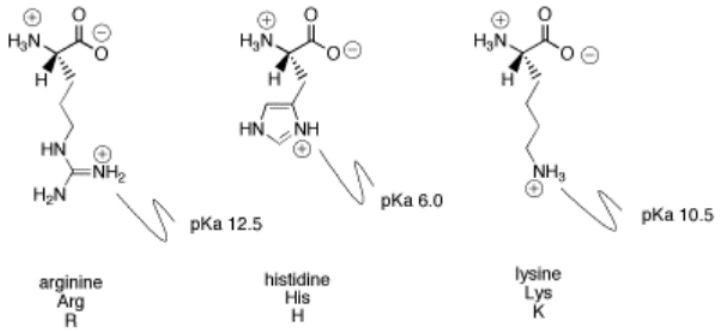


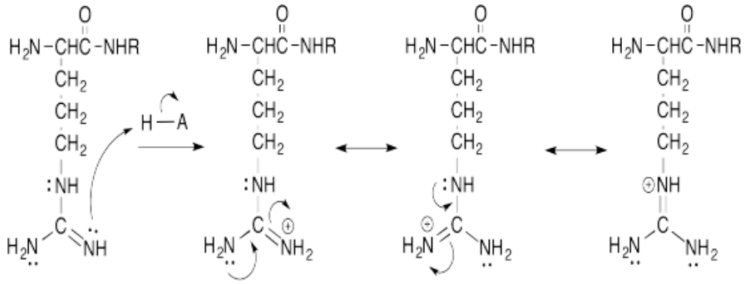
Figure 14.15.7: Basic amino acids

Exercise 14.15.5

Show why the indicated nitrogen in arginine's side chain is protonated, and not the others. Also, explain the difference in basicity between arginine and lysine.

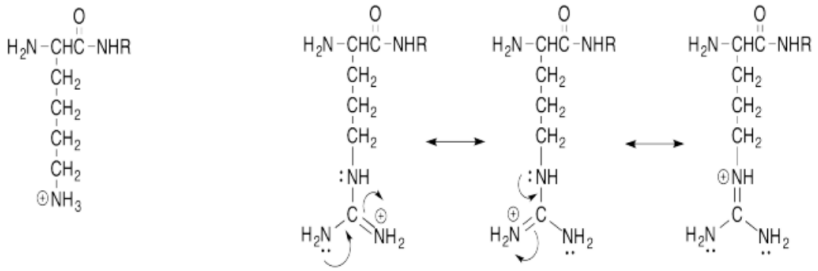
Answer

Protonation of the indicated nitrogen leads to a conjugate acid that still benefits from resonance stabilization, while protonation of the other two nitrogen atoms would decrease conjugation.



resonance structures of the conjugate acid of arginine

The pK_a of protonated arginine is higher than protonated lysine due to the resonance stabilization of the cationic charge



conjugate acid of lysine (no resonance stabilization)

resonance structures of the conjugate acid of arginine

Exercise 14.15.6

Explain the difference in basicity between histidine and lysine.

Answer

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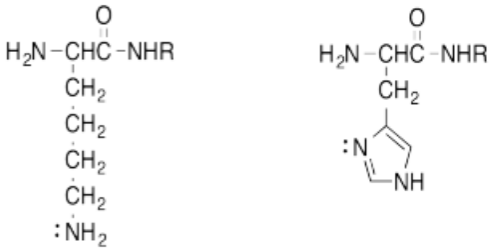
Lysine is a stronger amine base than histidine due to the difference in hybridization (sp^3 vs. sp^2)



In contrast to the basic amino acids shown above, other amino acids with nitrogen in their side chains are not considered basic. These compounds are not protonated easily on their side chains.

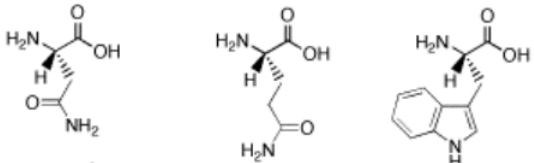


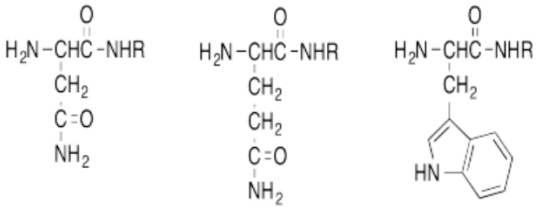
Figure 14.15.8: Some un-basic, nitrogen-containing amino acids.

Exercise 14.15.7

Explain why the three un-basic amino acids are not easily protonated on their side chain nitrogen atoms.

Answer

The lone pair electrons on the un-basic are resonance delocalized and not avaliable for protonation. The side chain nitrogens on asparagine and glutamine are found in amide groups and the nitrogen on tryptophan is part of an aromatic ring. Protonation of any of these nitrogens would break up a conjugated system.



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14.16: Relative Conditions and pKa

Reactivity is strongly affected by the environment around the molecules that are reacting. Usually the environment is a solvent; a solvent is a liquid in which the molecules are dissolved. Solvent effects (how different solvents behave) and solvation (how solvents organize around a solute molecule) are very important to consider in thinking about acidity.

Solvation is very important. When molecules are dissolved in a liquid, they can move around easily and mix with other molecules. That ease of motion facilitates reactions. In contrast, molecules in the solid state hardly move at all. Solid state reactions are very, very slow because molecules can't easily come into contact with each other. If two solids are mixed, molecules on the surface of the solid grains may react, but the molecules buried inside will be left untouched.

In order for one compound to dissolve in another, some intermolecular attractions must be present. In order to maximize these interactions, the solvent molecules probably need to arrange themselves somehow.

This organization of solvent molecules becomes even more important when ions are involved than when neutral molecules are dissolved. When ions are dissolved, anions are separated from cations. Solvent molecules must be able to interact with the ions so as to mitigate against the energetic costs of charge separation.

In organizing around a solute molecule, the usual interactions between the solvent molecules are disrupted. The solute molecule occupies a gap in the solvent molecules. For example, if the solvent is water, there must be a break in hydrogen bonding between water molecules to allow for the solute to swim among the waters.

Earlier we saw that larger atoms can more easily accommodate charge. This rule does not extend to the size of molecules. A larger molecular ion is generally not as easy to solvate as a small one. Larger ions require much more organization of solvent molecules. In addition, interactions between the solvent molecules (generally very favorable in solvents such as water) must be given up so that solvent molecules can move away from each other to open up space for the guest ions.

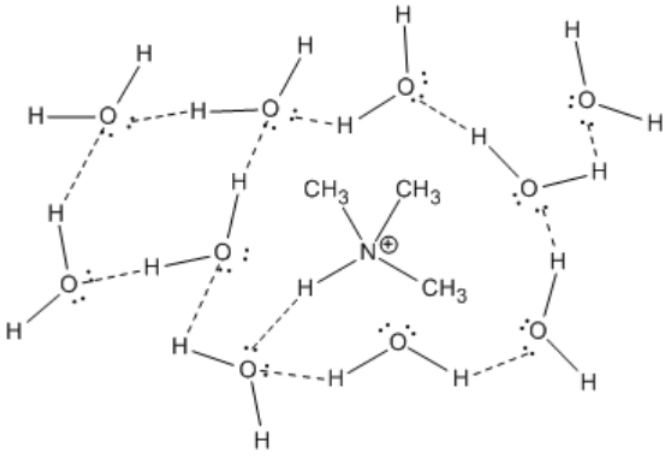

Figure 14.16.1: Solvation of the relatively small trimethylammonium ion.

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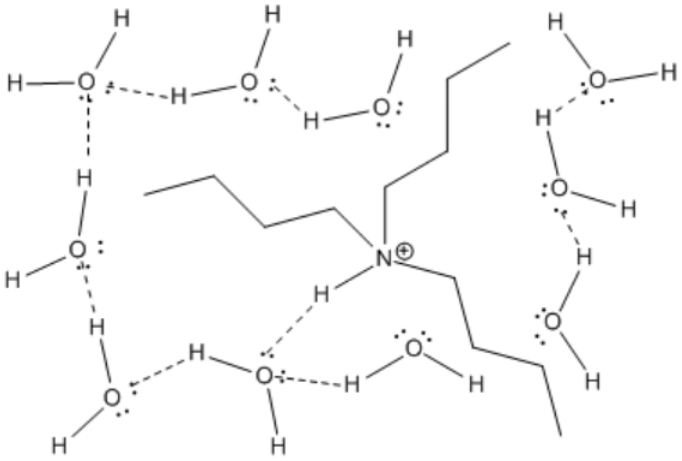

Figure 14.16.2: Solvation of the relatively larger tributylammonium ion.

- The size of a molecular ion being accommodated in a solvent matrix has an effect on the ion stability.

Different solvent effects arise partly because of different intermolecular attractions available to solvent molecules. Some solvents are hydrogen bonding. Water is a very common example, as are alcohols such as methanol. Others are only hydrogen bond-accepting, but not hydrogen bond-donating. Acetone and acetonitrile are examples.

Some solvents may more efficiently stabilize anions that form when Brønsted acids are deprotonated. As a result, pKa values may be different when measured in different solvents. For example, the pKa of water is reported as 15.7 in pure water, but when dissolved in DMSO it is reported as 32. Water is much less acidic in DMSO than when it is pure.

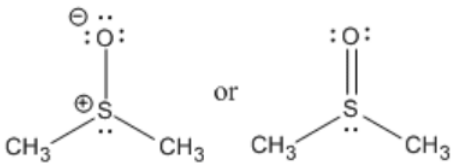

Figure 14.16.3: DMSO is a very polar, aprotic solvent.

DMSO has something in common with water. Water is very polar, with a polar O-H bond. DMSO is very polar, having a strongly polarized S-O bond. Water can hydrogen bond. DMSO is capable of accepting hydrogen bonds. That means DMSO can use its lone pairs to donate to protons on other molecules. However, DMSO is aprotic. It does not have very positive hydrogens that can participate in hydrogen bonding. That means one DMSO molecule cannot hydrogen bond to another DMSO molecule like water can. As a result, it is not able to donate hydrogen bonds to anions, as water can. Water is therefore more able to stabilize anions, so molecules can ionize more easily in water than in DMSO.

- Hydrogen bonding can be important in anion stabilization.

There is another reason to be aware of solvent effects in proton transfer reactions. Sometimes, solvents can themselves become involved in acid-base reactions.

For example, water is a very weak acid, but it can give up a proton. When it does so, it forms a hydroxide ion. Water could give its proton up to another anion if that anion could bind a proton more tightly than could hydroxide.

An example of this situation would occur if sodium amide were dissolved in water. Ammonia binds its proton more tightly than water. Thus, if sodium amide were dissolved in water, it would immediately become ammonia, removing a proton from water and forming sodium hydroxide.

As a result, the pKa of ammonia could not easily be measured in water because its conjugate base does not really exist in water. Assessing a pKa requires comparing how much of a compound remains protonated and comparing it to how much of the compound ionizes. As it turns out, the pKa of ammonia is around 41. That is high enough that this value was not determined directly. Instead, it had to be extrapolated by comparison with other data.

- Sometimes, solvent participate in reactions. They are not always innocent bystanders.

Exercise 14.16.1

Explain why ammonium bromide, NH_4Br, is more soluble in water than is sodium bromide, NaBr.

Answer

Ammonium bromide is more soluble because in water it can participate in both ion-dipole and hydrogen-bonding, while sodium bromide only benefits from ion-dipole interactions.

Exercise 14.16.2

The pKa of hydrogen cyanide, HCN, is about 13 in DMSO. Predict qualitatively how the pH would change if measured in a) water or b) pentane, $CH_3CH_2CH_2CH_2CH_3$.

Answer a

Hydrogen cyanide will be have a lower pKa in water as the resulting cyanide anion will be stabilized by both ion-dipole and hydrogen-bonding interactions.

Answer b

Hydrogen cyanide would have a higher pK_a in pentanes as the resulting cyanide anion would only experience ion-induced dipole interactions which are relatively weak.

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14.17: The Meaning of pKa- Product-to-Reactant Ratio and Equilibrium Constant

The index we have used to assess Brønsted acidity, pKa, is a measurable quantity. It is determined by measuring the ratio of products to reactants in a proton transfer reaction.

Figure 14.17.1: HCl dissolves and ionizes in water.

For example, if HCl is dissolved in water, much of it ionizes, transferring a proton to water to form hydronium ion and chloride anions. The concentrations of all four of these species could be measured and compared. The ratio of products to reactants is called the equilibrium constant, or K_{eq}:

$$K_{eq} = \frac{[H_3O^+][Cl^-]}{[H_2O][HCl]}$$

The concentrations of these species are generally reported in moles per liter. A mole, you may know, is a unit used to count very large numbers of molecules. Since molecules are very small, we usually deal with very large numbers of them at a time.

By convention, the concentration of water in itself is defined as 1. That leads to a slightly different expression.

$$K'_{eq} = \frac{[H_3O^+][Cl^-]}{[HCl]}$$

This ratio, dealing with proton transfer, is also called the acidity constant, Ka.

$$K_a = \frac{[H_3O^+][Cl^-]}{[HCl]}$$

Exercise 14.17.1

Write the expression for the Ka in each of the following mixtures.

a) HCN in water b) H_2S in water c) NH_3 in DMSO (DMSO = $(CH_3)_2SO$)

Answer a

$$\text{a.} \quad K_a = \frac{[NC^-][H_3O^+]}{[HCN]}$$

Answer b

$$\text{b.} \quad K_a = \frac{[HS^-][H_3O^+]}{[H2S]}$$

Answer c

$$\text{c.} \quad K_a = \frac{[H_2N^-][(CH_3)_2SOH^+]}{[HCN]}$$

The Ka is often a very, very small number or a very, very large one. In the case of HCl in water, the Ka is about 1 x 10^{-8}. Dealing with exponents can be cumbersome. In order to simplify comparisons, the equilibrium constant is expressed logarithmically.

$$pKa = -\log K_a$$

The Ka is often a very, very small number or a very, very large one. In the case of HCl in water, the Ka is about 1 x 10^{-8}. Dealing with exponents can be cumbersome. In order to simplify comparisons, the equilibrium constant is expressed logarithmically.

Exercise 14.17.2

Convert the following Ka's to pKa's.

a) 1 x 10^{6} b) 1 x 10^{-9} c) 3.5 x 10^{-25} d) 8.5 x 10^{-17}

Answer a

pKa = -6

Answer b

pKa = 9

Answer c

pKa = 24

Answer d

pKa = 16

Exercise 14.17.3

Convert the following pKa's to Ka's.

a) -3.5 b) 4.3 c) 9 d) 25

Answer a

Ka = $10^{3.5}$

Answer b

Ka = $10^{-4.3}$

Answer c

Ka = 10^{-25}

Answer d

Ka = 10^{-9}

Equilibrium constants are not restricted to proton transfer. They can be used to describe the extent to which any reaction occurs. For example, they can be written for other, reversible processes involving acid-base chemistry.

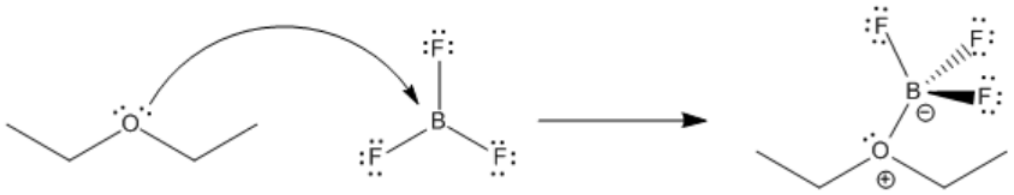

Figure 14.17.2: Equilibrium in the formation of a Lewis acid-base complex between diethyl ether and boron trifluoride.

Lewis acid-base interactions are very often reversible. For example, a Lewis base like ether can donate a pair of electrons to a Lewis acid such as BF_3. The ether can take its electrons back again and leave the BF_3 behind, too. How tightly the ether is held by the BF_3 is termed the binding constant. In this case,

$$K_{eq} = \frac{[BF_3][Et_2O]}{[BF_3OEt_2]}$$

In this case, the equilibrium constant has been reported to be about 0.25.

Exercise 14.17.4

What does the equilibrium constant for formation of a complex between BF_3 and diethyl ether (above) tell you about the position of the equilibrium?

Answer

At equilibrium formation of the Lewis acid-base complex is slightly favored.

Exercise 14.17.5

The equilibrium constant for complex formation between dimethyl ether (CH_3OCH_3) and BF_3 is 4.2. Compare this value with the one for diethyl ether and explain the difference.

Answer

At equilibrium formation of the Lewis acid-base complex of dimethylether and BF_3 is more favored than the corresponding diethylether BF_3 complex. This is likely due to the decreased steric bulk of the methy groups compared to the ethyl groups.

Exercise 14.17.6

Write expressions for the binding constant in the following cases.

a. $(NH_3)_2PtCl_2$ loses an ammonia
b. $Mo(CO)_6$ loses a carbon monoxide
c. $FeCl_4^-$ loses a chloride anion

Answer a

$$\text{a.} \quad K_{eq} = \frac{[(NH_3)_2PtCl_2]}{[(NH_3)PtCl_2][NH_3]}$$

Answer b

$$\text{b.} \quad K_{eq} = \frac{[Mo(CO)_6]}{[Mo(CO)_5][CO]}$$

Answer c

$$\text{c.} \quad K_{eq} = \frac{[FeCl_4^-]}{[FeCl_3][Cl^-]}$$

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14.18: pH and Buffers

The term pH refers to the amount of readily available protons present in the environment. If the environment is water, pH is an index of the concentration of hydronium ion (H_3O^+) in the water.

pH is related to pKa. Both indices work on a logarithmic scale to avoid carrying large amounts of decimal places in very small numbers. A pH of 6, typical in many biological environments, means that the hydronium ion concentration is about 10^{-6} moles/L (in which a mole is a unit used for convenient counting of nanoscopic things like molecules or ions, just like a dozen is used for counting eggs or doughnuts).

A low pH actually means there are lots of protons or hydronium ions around. At low pH, the environment is very acidic. Low pH is usually associated with the presence of strong Brønsted acids. The typical pH of about 3 in the stomach is produced by dilute hydrochloric acid, HCl.

A second factor that affects pH is the concentration of species in solution. For example, if a solution of HCl is more concentrated, then clearly more protons will be made available, so the pH will be lower. A solution in which the HCl concentration is 0.1 moles/liter (or 10^{-1} mol/ L) will have a pH of about 1, but a solution in which HCl concentration is 0.001 moles/liter (or 10^{-3} mol/L) will have pH of about 3. Note that pH is mathematically related to the exponent in the concentration of an acid when written in scientific notation.

Control of pH is very important in biological systems. Many biological processes operate at an optimum pH, and many biomoecules are stable only across a certain pH range. Proteins are particularly sensitive to conditions including pH. Changes in conditions can easily lead to proteins becoming denatured, which means the protein undergoes a shape change that severely affects its ability to function. This shape change is a conformational change, and it is brought about by changing interactions along the protein chain, including changing electrostatic interactions when different sites become protonated or deprotonated.

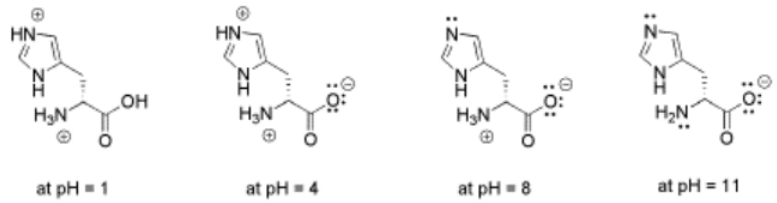


Figure 14.18.1: Structure of an amino acid, histidine, at a range of pH values. Note that the overall charge on the amino acid changes with availability of protons.

Different organisms can have different pH ranges over which they function best. Even different tissues within the same organism may work best at different pH values. In order to maintain pH balance at an optimum level, biological systems employ buffers. Buffers are compounds that can either absorb or provide protons in order to keep the pH of their environment from changing. Because they need to absorb or provide protons, buffers are weak Brønsted acids or weak bases, together with their conjugates.

Bicarbonate is an example of a buffer. When pH gets too high, bicarbonate can provide a proton, becoming carbonate.

Figure 14.18.2: The carbonate / bicarbonate buffer system provides protons.

When pH gets too low, the conjugate base, carbonate, can absorb a proton and become bicarbonate again.

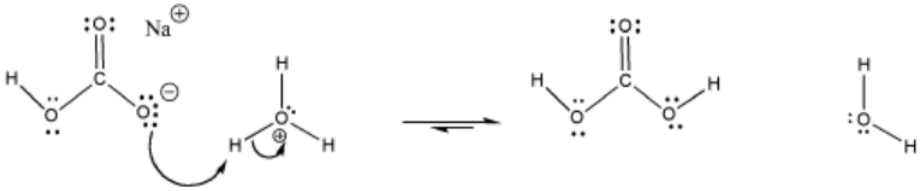


Figure 14.18.3: The carbonate / bicarbonate buffer system absorbs protons

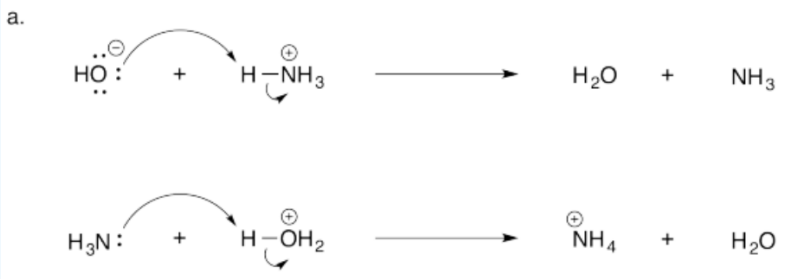
- Buffers maintain pH balance by intercepting acids & bases.
- Adding a strong base such as hydroxide would deplete protons from the system, raising pH; the buffer provides protons.
- Adding a strong acid such as hydronium chloride would drop pH; the buffer picks up the protons.

Exercise 14.18.1

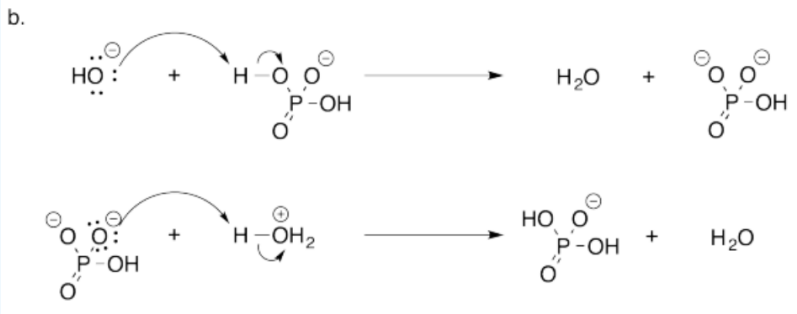
For the buffer systems described below, use arrows to show how the buffer system would neutralize (i) a hydroxide ion and (ii) a hydronium ion.

a. Ammonia (NH_3) / ammonium chloride (NH_4Cl)
b. Sodium dihydrogen phosphate ($NaO_2P(OH)_2$) / sodium hydrogen phosphate (Na_2O_3POH)
c. Sodium hydrogen phosphate (Na_2O_3POH) / sodium phosphate (Na_3PO_4)
d. Histidine (see above) / histidine hydrochloride (histidine.HCl)

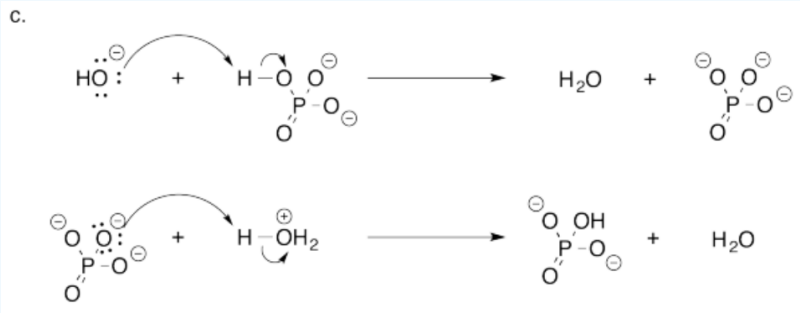
Answer a



Answer b



Answer c



Answer d

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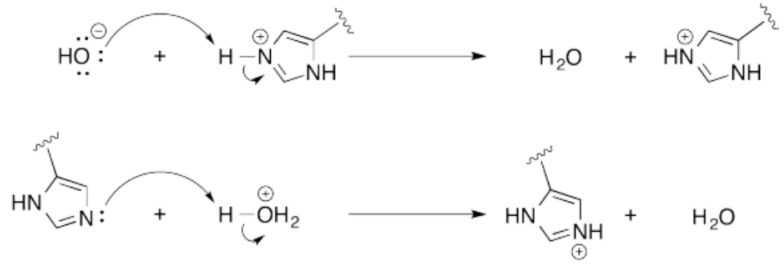
d.



Because the different Brønsted acids involved with these buffers have different pKa's, and so they hold protons more or less tightly, different buffers are able to operate at different pH ranges. This factor, together with control over the concentrations of the components of the buffer system, allows pH to be held fairly constant at almost any value necessary.

Attribution

- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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14.19: Application Problems

Exercise 14.19.1

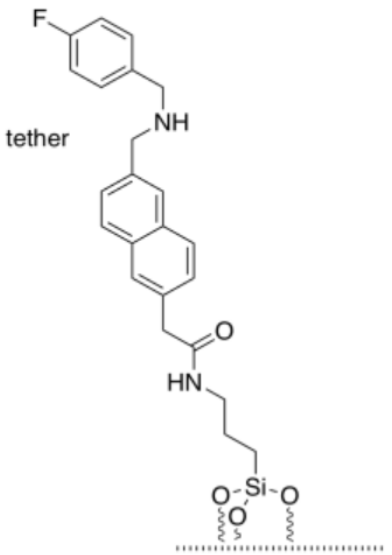
Fraser Stoddart (Northwestern University) shared the 2016 Nobel Prize in chemistry for the development of "molecular machines". The components of a simple molecular valve are shown here. (Adapted with permission from Nguyen, T. D.; Leung, K. C.-F.; Liong, M.; Pentecost, C. D.; Stoddart, J. F.; Zink, J. I. *Org. Lett.* **2006**, *8*, 3363-3366. Copyright 2006 American Chemical Society).

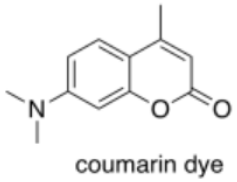
a) What structural feature do all bases have in common?

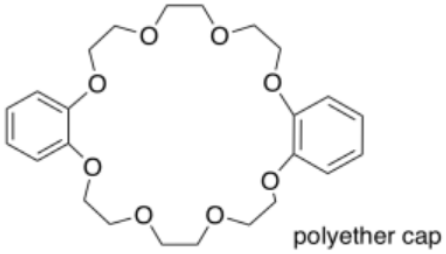
b) Which atoms in the molecules shown below could potentially be basic: F C N O Si H

Order these basic atoms from most basic to least basic.

State the reason for this order.







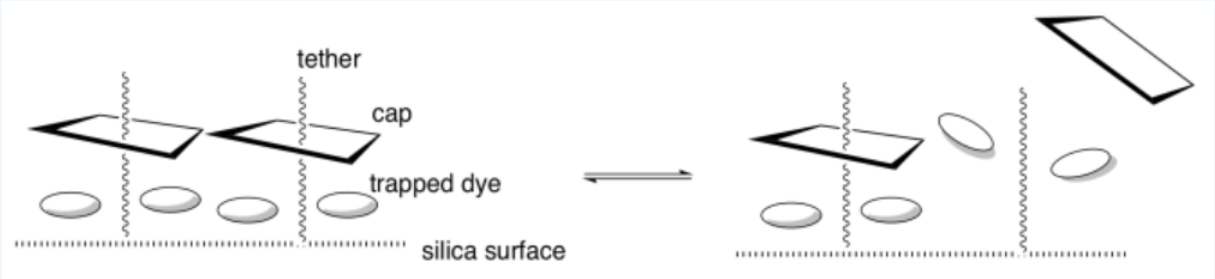
c) Circle the most basic site in each of the three molecules (one in the tether, one in the dye, one in the cap).

Box the most basic site of all.

State the reason for its superior basicity.

d) Modify the drawing above to show that site in its protonated state.

The tether is bonded to a silica surface. When the system is protonated, the cap remains bound to the tether (below, left).



e) What intermolecular force binds the cap and tether together?

f) Why does the dye get trapped?

When placed in water, the nanoparticles remain bright yellow and the water remains colorless. If triethylamine is added, the nanoparticles turn white and the water turns yellow.

g) After adding triethylamine, where is the dye?

h) Draw triethylamine.

Show, with curved arrows, what triethylamine does to the molecular valve. You don't need the entire structures; you can abbreviate to just the part you are using.

i) Indicate any changes in the intermolecular forces after addition of triethylamine.

N,N-Diisopropylethylamine can also release the dye, but more slowly. Triethylamine causes the dye to be released with a half-life of 100 seconds; the half-life for release with N,N-diisopropylethylamine is 300 seconds.

j) Draw N,N-diisopropylethylamine.

k) Why is release so much slower with N,N-diisopropylethylamine?

This system has the potential to be used in a number of applications, such as drug delivery: the slow release of pharmaceuticals into the bloodstream from silica nanoparticles.

If possible, a nitrogen is circled in each molecule. The cap has only basic oxygen atoms. If there is a choice between two nitrogens (in the tether) or two oxygens (in the cap), the non-conjugated lone pair would be most basic. Conjugated lone pairs are held in place by their stable interaction with their neighbors.

The most basic of all is the amine (non-conjugated) nitrogen in the tether.

Answer a

all bases have lone pairs.

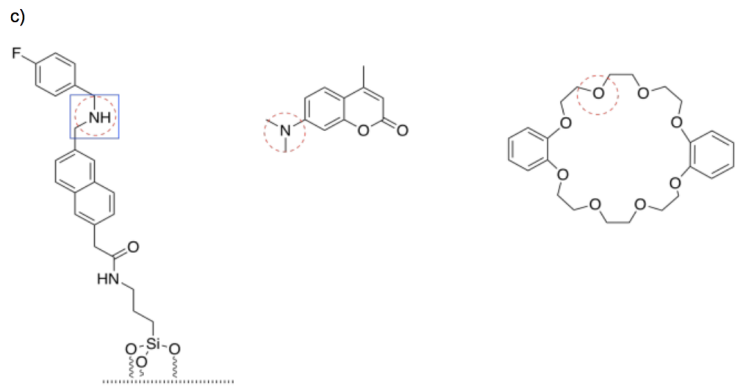
Answer b

F, N, and O have lone pairs. They can be bases.

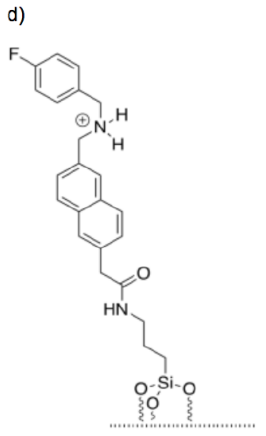
Their order of basicity would be N > O > F.

These three elements come from the same row of the periodic table and so they are of similar sizes. However, N is the least electronegative and F is the most electronegative. N is most able to donate electrons and most able to support a positive charge, compared to the other two.

Answer c



Answer d



Answer e

The cap and tether would be bound by hydrogen bonding. However, hydrogen bonding becomes much stronger if there is an ionic component. It is not a full ionic bond because the cap does not contain an anion, but its strength is between that of a normal hydrogen bond and an ionic bond.

Answer f

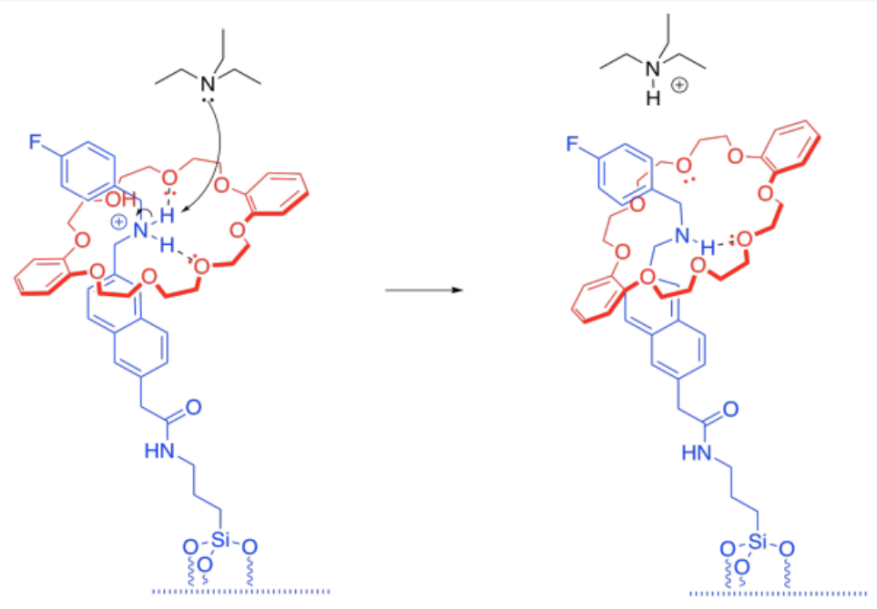
Steric crowding traps the dye between the cap above and the silica surface below. The dye is too big to squeeze past the cap.

Answer g

The dye has been released, and is now in the water.

Answer h

There is an equilibrium between the protonated tether and the protonated triethylamine.

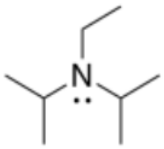


Answer i

Once the tether has been deprotonated, the tether-cap interaction is just a normal hydrogen bond. It's still strong, but not as strong as the ion-boosted hydrogen bonding that we had before.

Answer j

N,N-Diisopropylethylamine or Hunig's base:



Answer k):

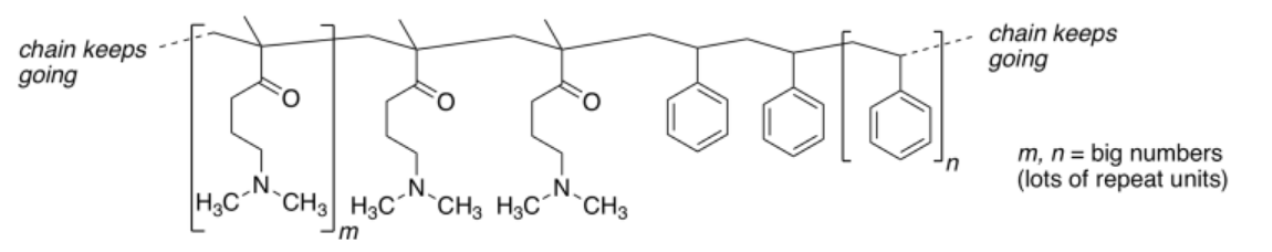
The lone pair in Hunig's base is much more crowded than the one in triethylamine, so it cannot remove the proton as quickly.

Exercise 14.19.2

The laboratories of Teresa Reineke and Tim Lodge at U MN collaborated to study the use of a polymer as a possible drug delivery device for gene therapy (Adapted with permission from Laaser, J. E.; Jiang, Y.; Sprouse, D.; Reineke, T. M.; Lodge, T. P. *Macromolecules* **2015**, *48*, 2677-2685. Copyright 2015 American Chemical Society).

Here is a section of their polymer:

Answer



These polymer chains coil up, forming spherical nanoparticles.

a) Add any lone pairs to the structure above.

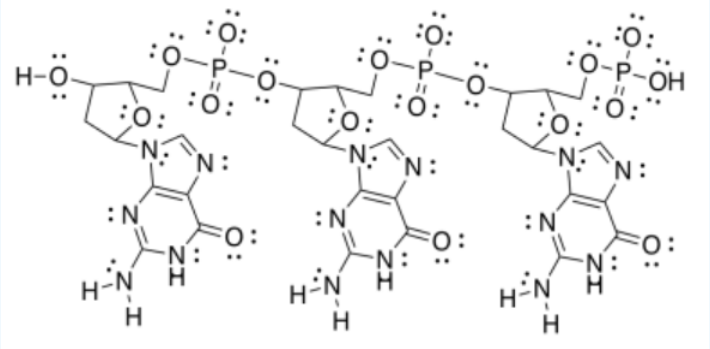
b) Show what happens to the polymer structure when aqueous HCl is added.

After treatment with HCl, the polymer nanoparticles expand, from spheres with radii of about 20 nm to spheres with radii of about 40 nm.

c) Show cartoons of a long polymer chain coiled up to form (i) a sphere of radius 20 nm; (ii) a sphere of radius 40 nm.

d) Why do the nanoparticles expand when HCl is added?

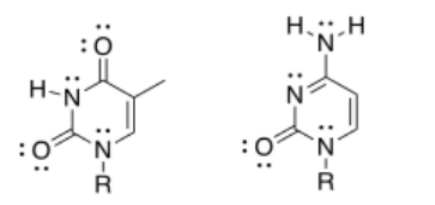
After treatment with HCl, the polymer binds DNA molecules. Here is a short section of DNA. It has three repeating units.



e) Add any formal charges.

f) Circle one sugar. Put a square around one phosphate. Put a triangle around one base (as in “DNA base pair”). Put a dashed circle around an aromatic ring.

g) Show how one of these other base pairs binds to the DNA strand



h) One of the base pairs binds more tightly than the other one to the DNA strand. Which one? Why?

i) Why do the acid-treated polymer nanoparticles bind DNA?

Salt solutions (such as aqueous NaCl) were subsequently shown to trigger DNA release from the DNA-nanoparticle complexes.

j) Why would these conditions lead to DNA release?

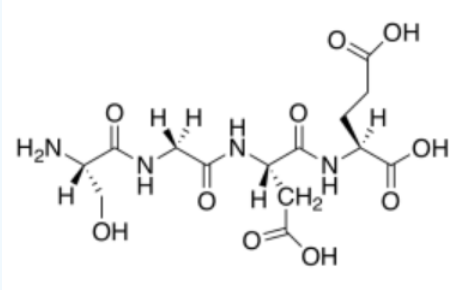
Triethylamine solutions ($[CH_3CH_2]_3N$) cause the nanoparticles to shrink and they also trigger DNA release.

k) Why would triethylamine inhibit DNA binding?

l) Why would triethylamine cause the nanoparticles to shrink?

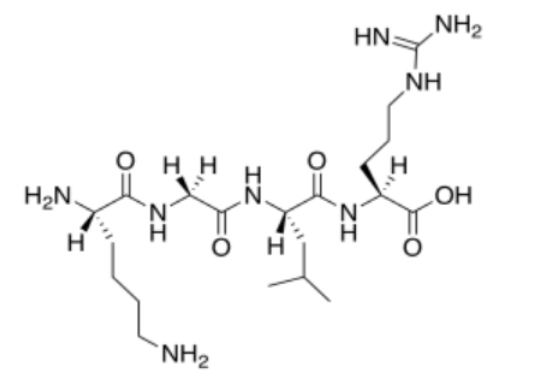
Certain peptide solutions also trigger DNA release.

m) This is not the structure of a peptide at neutral pH. Modify the structure to reflect neutral pH.



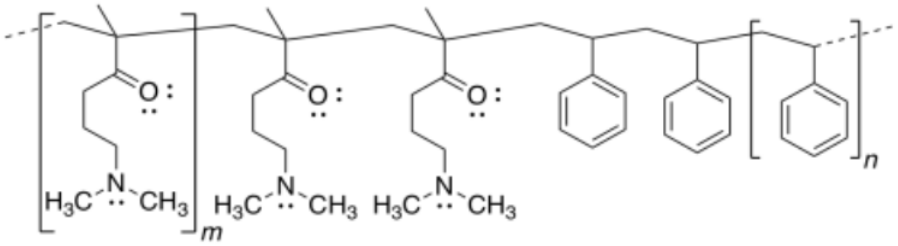
n) Why would this peptide trigger DNA release?

o) This peptide would probably not trigger DNA release. Modify the structure to show why.



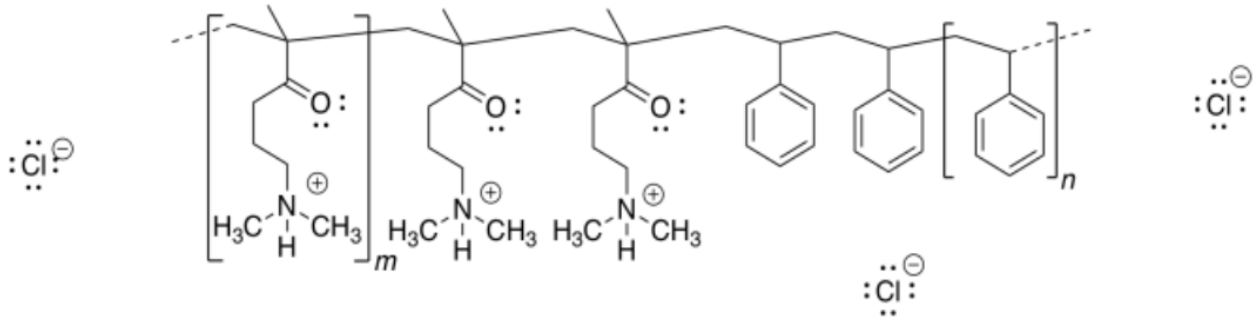
Answer a

a)



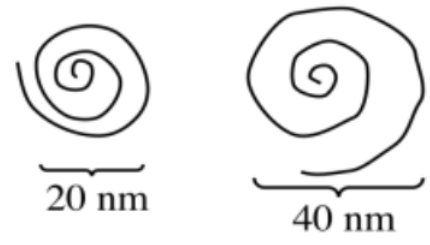
Answer b

b)



Answer c

c)

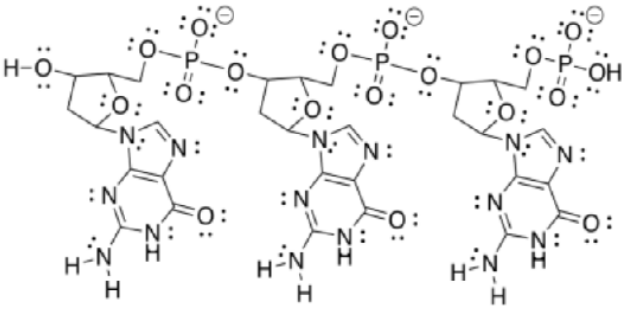


Answer d

Repulsion between the positively-charged quaternary ammonium groups (poly-CH_2-N(H)$(CH_3)_2^+$) would cause the nanoparticle to uncoil.

Answer e

e)



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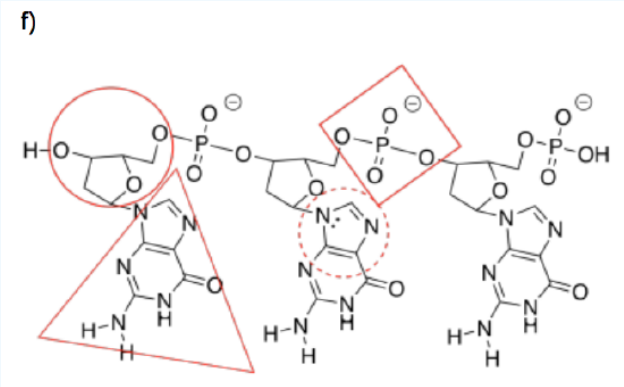
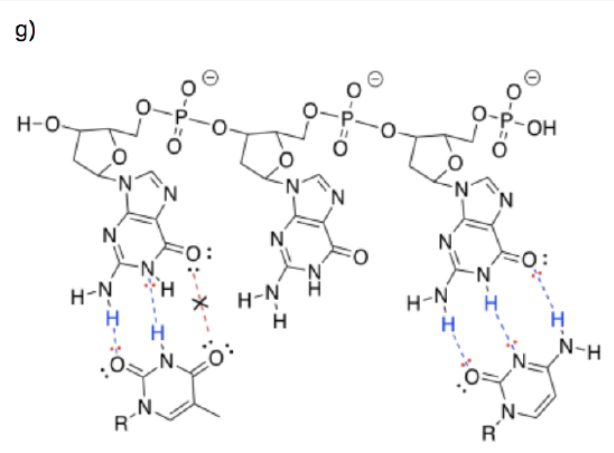
Answer f



Answer g



Answer h

The one on the right forms three hydrogen bonds with the DNA and binds more tightly than the one on the left, which forms only two hydrogen bonds with the DNA.

Answer i

The polymer is positively charged after acid treatment. It binds the negatively charged DNA via ion-ion interactions.

Answer j

If there are enough of them, the chloride anions could "wash out" the anionic DNA. These individual anions would replace the DNA anion previously bound to the nanoparticle.

Answer k

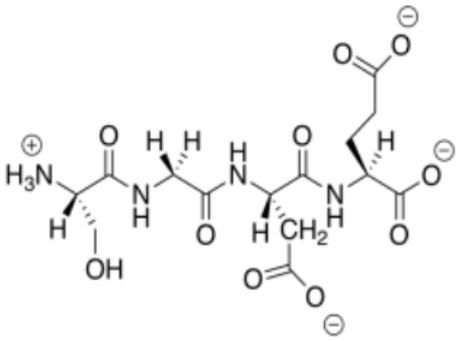
The triethylamine could remove the proton from the polymer chain. If the polymer chain were no longer charged, it would no longer bind the anionic DNA.

Answer l

Also, because the nanoparticles would no longer be charged, there would no longer be repulsive forces causing the polymer to uncoil.

Answer m

m)

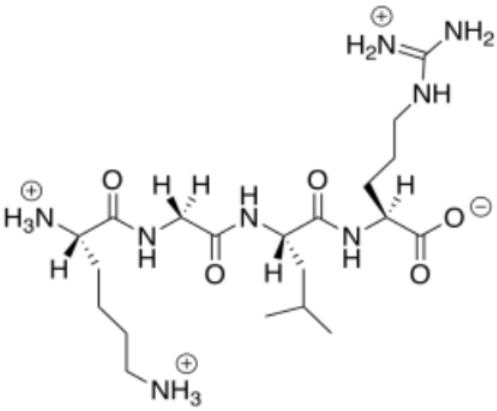


Answer n

This anionic (overall) peptide would bind to the cationic nanoparticles, replacing the DNA.

Answer o

o)



This cationic (overall) peptide would not bind to the cationic nanoparticles, so it would not displace the DNA.

Exercise 14.19.3

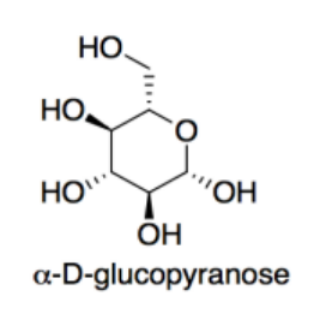
Frustrated Lewis pairs should react together but do not. An example of a frustrated Lewis pair is tri-t-butylphosphine, [(CH3)3C]3P, and tris(pentafluorophenyl)borane, B(C6F5)3.

a. Draw both structures.
b. Identify the Lewis acid and the Lewis base.
c. Draw a mechanism using curved arrow(s) to show how the acid and base would interact.
d. State why this interaction does not occur.
e. Stephan & Erker showed that the frustrated Lewis pair can work together to capture a molecule of carbon dioxide (Angewandte Chemie, 2015). Show a mechanism that explains how the Lewis acid would interact with the CO_2, including curved arrows.

Exercise 14.19.4

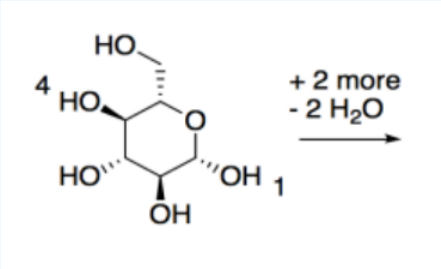
Researchers in the Rowan lab at University of Chicago have been experimenting with composite materials made from cellulose and plastic. (Adapted from Amanda E. Way, Lorraine Hsu, Kadhiravan Shanmuganathan, Christoph Weder, and Stuart J. Rowan, *ACS Macro. Lett.* **2012**, *1*, 1001-1006. Copyright 2012, American Chemical Society. Used with Permission.)

Cellulose is made of glucose building blocks or monomers.



a) Show the alpha-D-glucopyranose form of glucose in its most stable chair conformation.

When this form of glucose links with other molecules through its 1- and 4-positions, with loss of a water molecule, it forms cellulose, a polymer made of glucose building blocks.



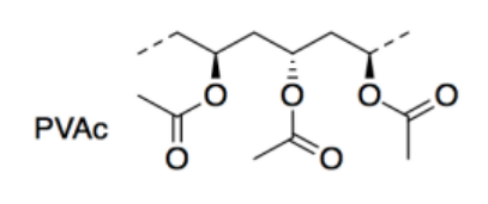
b) Show a small cellulose molecule 3 glucose units long.

c) Cellulose is an example of what class of biomolecules: carbohydrates / lipids / nucleic acids / proteins?

d) Name one common household material that is made of cellulose.

e) Draw a cartoon of the cellulose polymer, using just a wiggly line for the long polymer chain. Add the parts of the structure that you would need in order to show why two cellulose chains would stick to each other. Name this intermolecular attraction.

The researchers used poly(vinyl acetate) (PVAc; a short section is shown below) as the plastic in their study. PVAc is also a polymer; the dashed lines here indicate the units keep repeating in a long chain. PVAc is mostly used in latex paint.



f) Name the type of functional group in PVAc.

g) Draw a cartoon of the PVAc polymer, using just a wiggly line for the long polymer chain. Add the parts of the structure that you would need in order to show why two PVAc chains would stick to each other. Name this intermolecular attraction.

Below 35°C, PVAc is “glassy”, or strong and stiff, like the plastic in an automobile bumper. Above 35°C, PVAc becomes much softer or “rubbery”, like an eraser.

h) Explain why this property prevents the use of PVAc for medical implants such as an artificial hip.

Blending cellulose nanocrystals (CNCs) in with the PVAc keeps the material stronger up until about 45°C.

i) Show why the CNCs make the PVAc stronger.

Clearly, composite materials, in which other materials are mixed in with plastics to provide extra strength, can sometimes be better than the plastics by themselves.

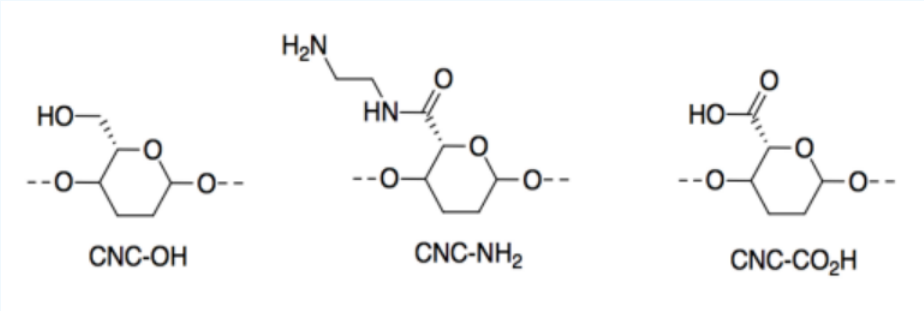
The Rowan lab is interested in something much more sophsticated than that, though. They want to make a material that can switch from rubbery to glassy, or vice versa, in an instant. They were inspired by tunicates, marine organisms that can change instantly from soft-shelled to hard-shelled if disturbed. Tunicate shells, it turns out, contains high levels of CNCs.

One possible stimulus is pH or acidity; this factor could be changed by adding HCl or NaOH.

j) HCl is (acidic / basic) because the H-Cl bond is polarized with electrons closer to (H / Cl).

k) NaOH is (acidic / basic) because the (Na-O / O-H) bond is more polarized, with electrons closer to (Na / O / H).

They modified the CNCs by adding different side groups. Only a portion of the cellulose chain is shown here.



The resulting materials respond to changes in pH or acidity levels; they display Brønsted acidity/basicity.

l) Which of these three materials would be most acidic? Explain why with a structure of the conjugate base.

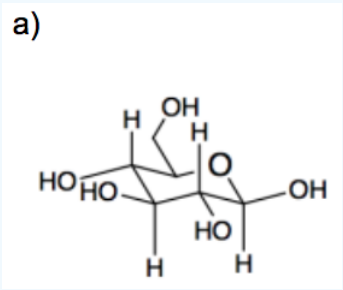
m) Which of these three materials would be most basic? Explain why with a structure of the conjugate acid.

n) CNC-CO_2H is more than twice as strong at pH 3 (i.e. when HCl is added) than at pH 11 (i.e. when NaOH is added). Why? Explain in terms of IMFs.

o) CNC-NH_2 is more than twice as strong at pH 11 (i.e. when NaOH is added) than at pH 3 (i.e. when HCl is added). Why? Explain in terms of IMFs.

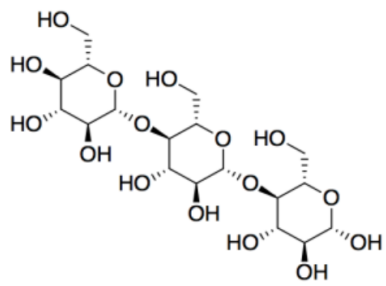
p) At neutral pH, a mixture of CNC-NH_2 and CNC-CO_2H also produced a very strong material. Show the structures of the two materials when mixed, and identify why the material is so strong.

Answer a



Answer b

b)



Answer c

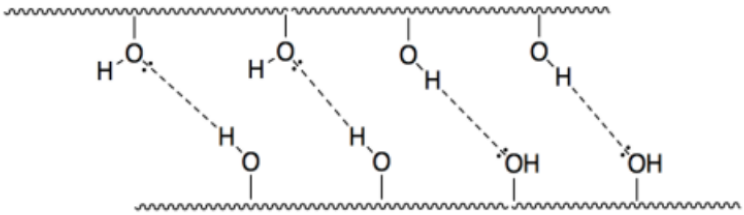
carbohydrates

Answer d

Cellulose is the major component of cotton (textiles and money) and paper.

Answer e

e)

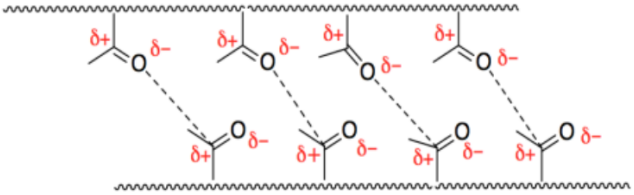


Answer f

ester

Answer g

g)

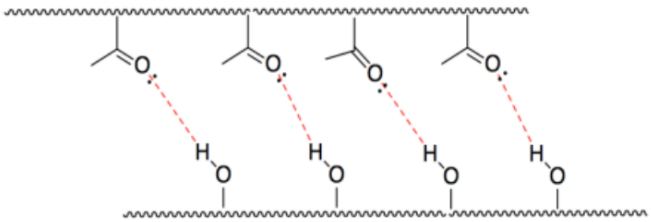


Answer h

Body temperature is closer to 40 degrees Celsius, so the hip would be soft and rubbery. That would making walking a little unpredictable.

Answer i

i)



Answer j

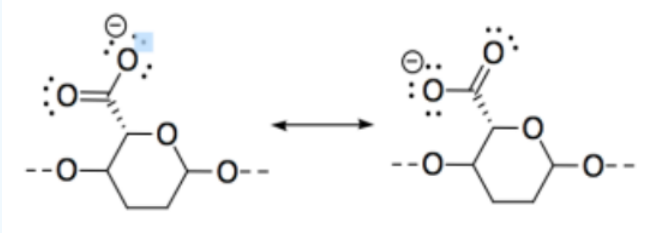
HCl is acidic because the H-Cl bond is polarized with electrons closer to Cl.

Answer k

NaOH is basic because the Na-O bond is more polarized, with electrons closer to O.

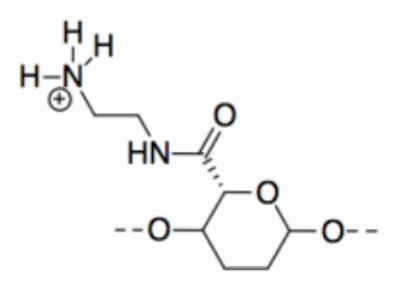
Answer l

CNC-CO_2H is most acidic because of the resonance stabilized anion in the conjugate base.



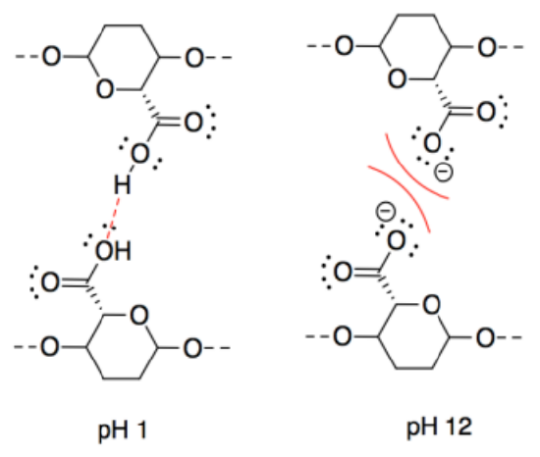
Answer m

CNC-NH_2 is most basic because, although all three compounds possess lone pairs, the lone pair on the nitrogen is on a less electronegative atom than the lone pairs on oxygens, so it is more readily donated to a proton.



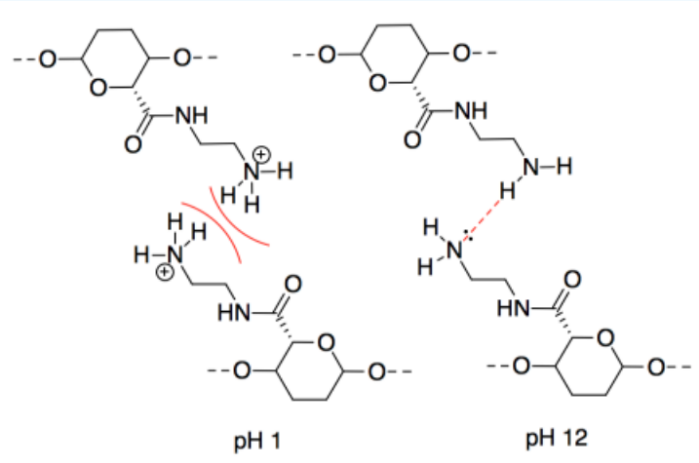
Answer n

This one may seem counterintuitive. The intermolecular forces at pH 11 are ionic, which should be stronger than hydrogen bonding. However, interactions between two anionic chains are repulsive, which would decrease the attraction between neighbouring CNC chains.



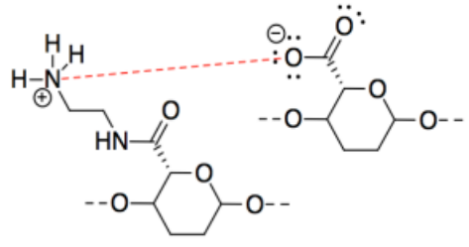
Answer o

The intermolecular forces at pH 3 are ionic, which should be stronger than hydrogen bonding. However, interactions between two cationic chains are repulsive, which would decrease the attraction between neighboring CNC chains.



Answer p

A proton would be transferred from the acidic site to the basic site. The oppositely charged CNC chains would attract each other strongly.



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14.20: Solutions to Selected Problems

With contributions from Nicholas Jones and Kate Graham, College of Saint Benedict / Saint John's University

Exercise 14.2.1:

A Lewis base must have lone pairs or non-bonding electron pairs so that it can donate them to a Lewis acid.

Alternatively, in some cases the electrons in a π-bond can be donated instead, so sometimes compounds with π-bonds can be Lewis basic.

Exercise 14.2.2:

a. not a Lewis base
b. not a Lewis base
c. Lewis base
d. Lewis base
e. Lewis base

Exercise 14.3.1:

A Lewis acid atom attracts electrons from a Lewis base.

The most common feature of a Lewis acid is an atom that is not "electronically saturated" or has not filled its octet. For example, an aluminum with only six electrons rather than eight is Lewis acidic.

Other atoms, like transition metals, have "octets" of eighteen electrons, so having fewer than eighteen electrons in their valence shell can make these atoms Lewis acidic.

Exercise 14.3.2:

a. Lewis acid
b. Lewis acid
c. not a Lewis acid
d. Lewis acid
e. not a Lewis acid

Exercise 14.3.3:

a)

b) cations

c) possibly ion-dipole forces; alternatively, the oxygen atoms could act as Lewis bases, donating lone pairs to a cation.

d)

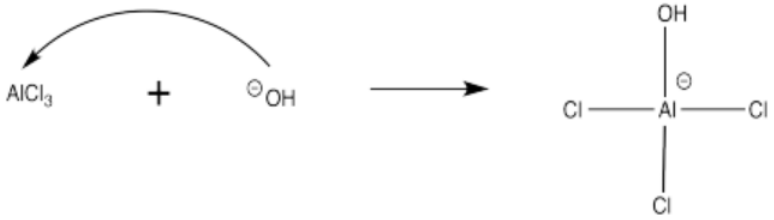
e) anions

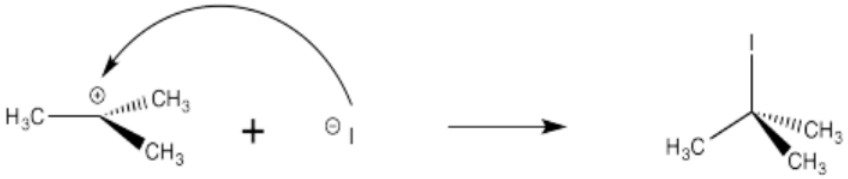
f)

g)

h) When the chloride ion binds to the sensor molecule it gives the overall complex a negative charge and addition of the potassium ion cancels out this charge.

Exercise 14.4.1:





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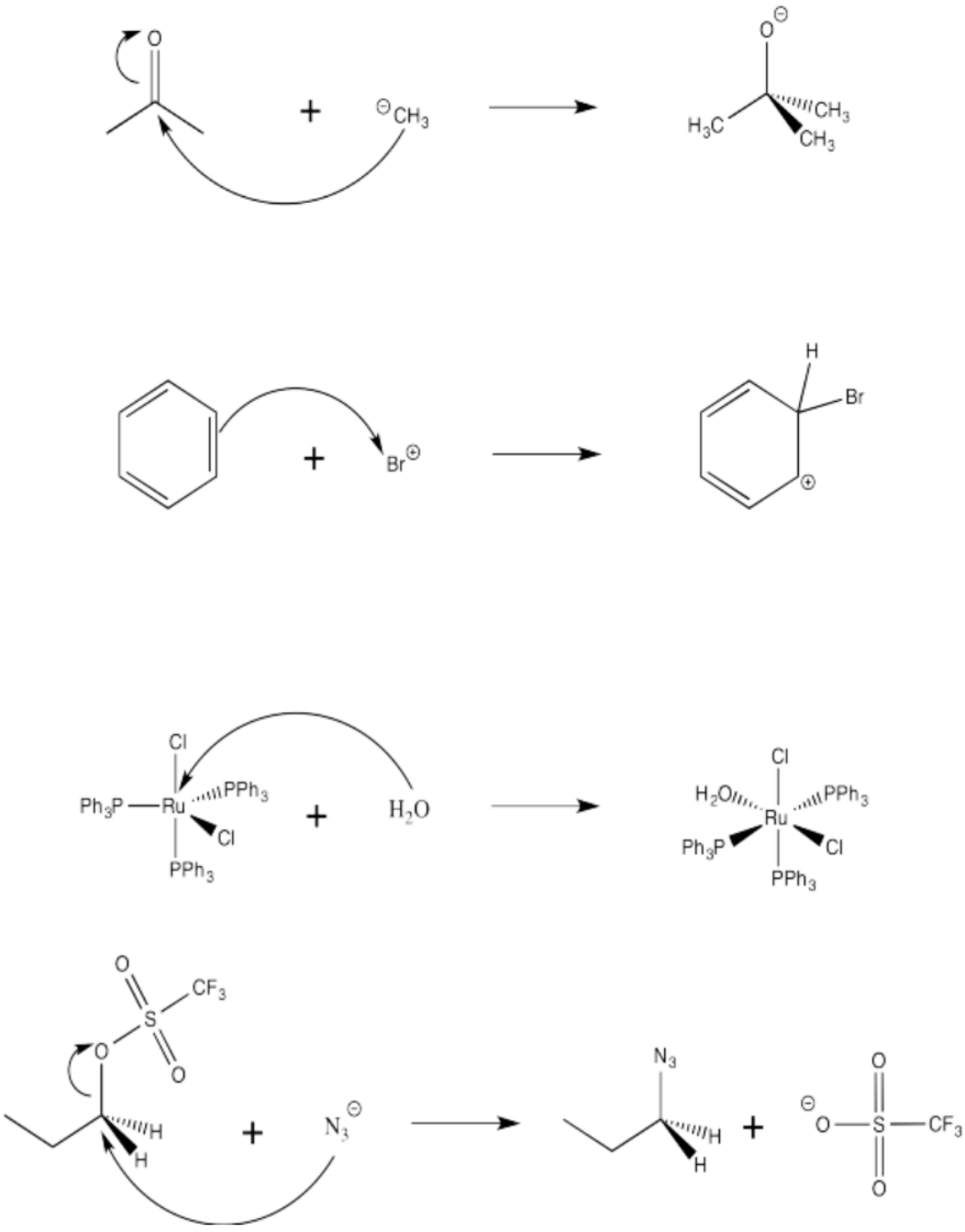

Exercise 14.4.2:

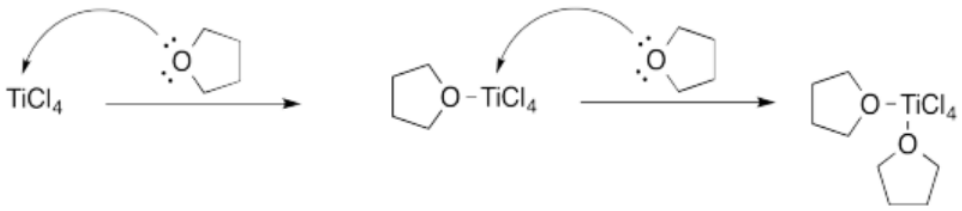

Figure 14.20.1:

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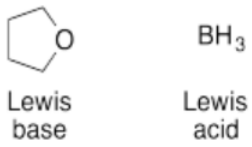
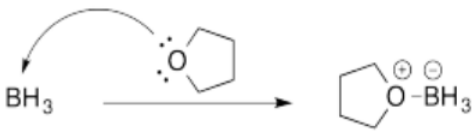
Exercise 14.4.3:

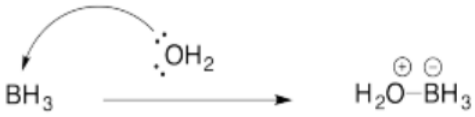
a. 

b. boron's empty p-orbital

c. non-bonding electrons on oxygen

d. one pair of electrons

e. 

f. 

g. borane is already complexed with THF and will be slower to react with water in the atmosphere

Figure 14.20.1:

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Exercise 14.4.5:

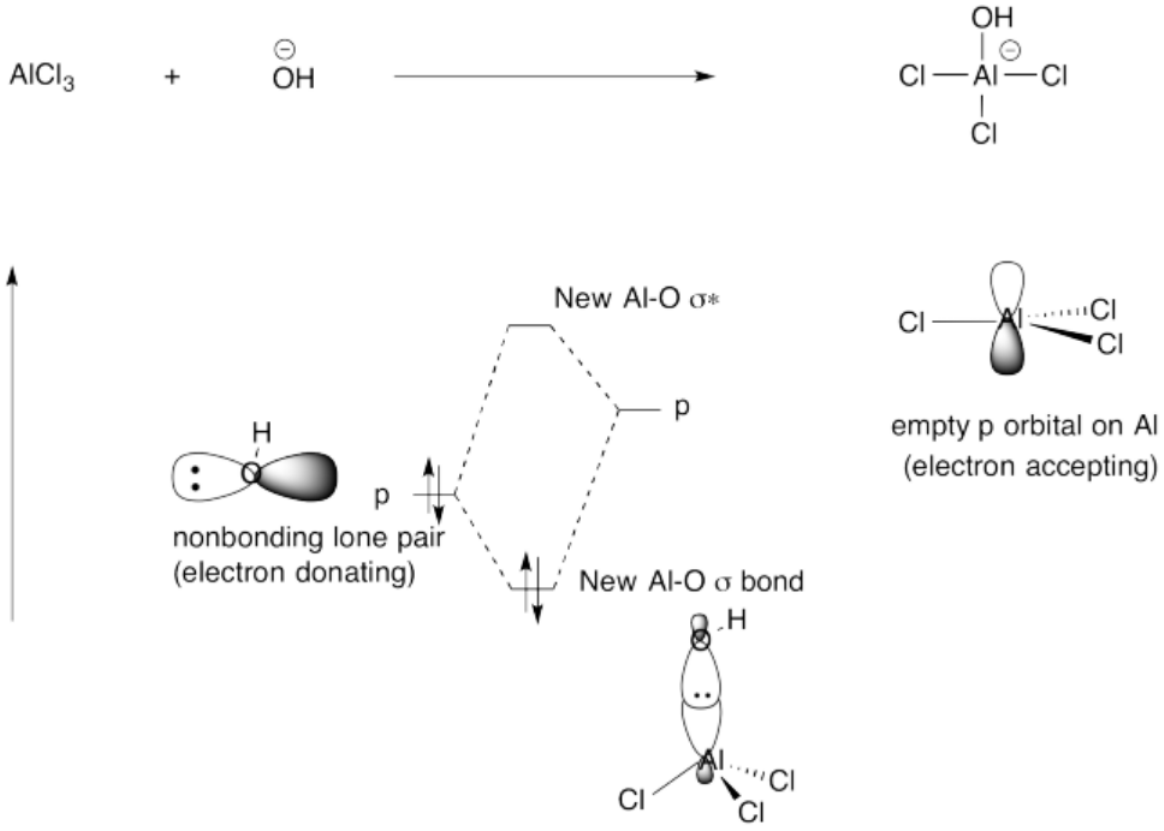


Figure 14.20.1:

Exercise 14.4.6:

a)

b)

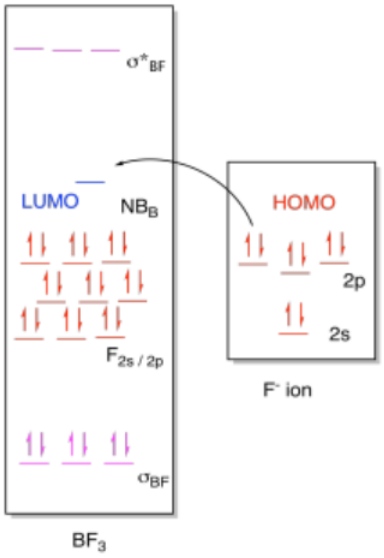
- The benzene rings take up more space than a fluorine atom; they may get in the way, making it harder for the water molecule to approach.

Also, the aromatic rings may be able to form a conjugated system with the empty p orbital; if that p orbital is partially filled, the boron atom becomes less Lewis acidic.

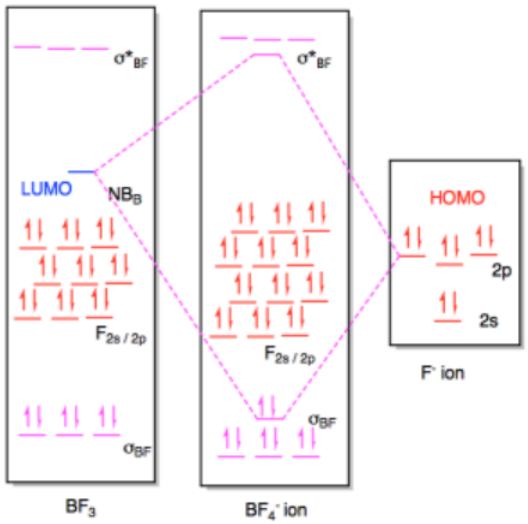
- A larger group than fluorine may cause more steric hindrance. Replacing the two fluorines closest to the boron on each arene (aromatic ring) with a CH_3 or CF_3 group would slow down the formation of an adduct. Alternatively, a less electronegative group than fluorine would also make the boron seem less positive; a CH_3 or OCH_3 are two possibilities.
- An even more electron-withdrawing group than fluorine would make the Lewis acid more reactive. Examples include nitro (NO2) and carbonyl groups (such as CH3C=0); these groups are resonance-withdrawing. Alternatively, a smaller group such a hydrogen would lower steric resistance, but would also lead to lower electrophilicity at boron, owing to the lower electronegativity of hydrogen compared to fluorine.

Exercise 14.4.7:

a) (i)



(ii)



b) (i)

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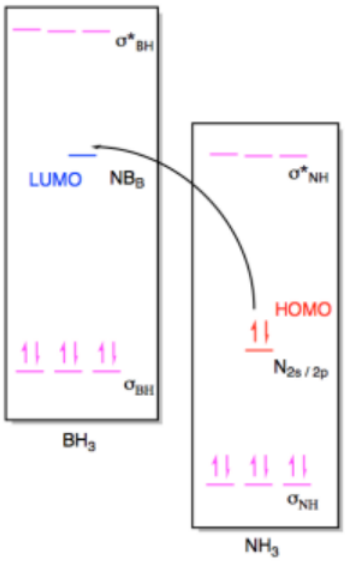
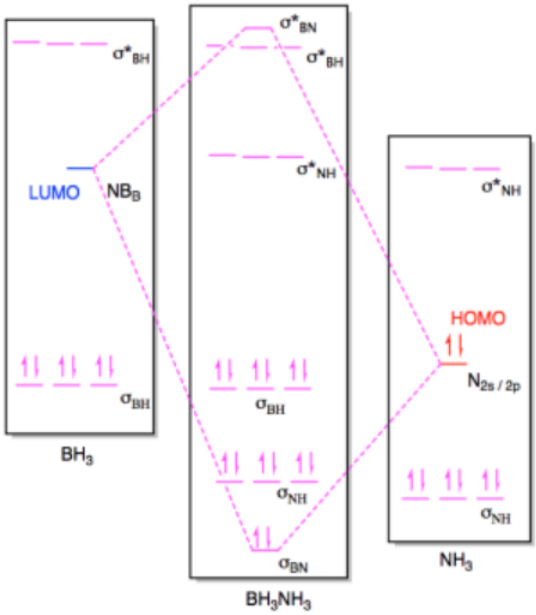


(ii)



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Exercise 14.5.1:

a.

b.

c.

d.

e.

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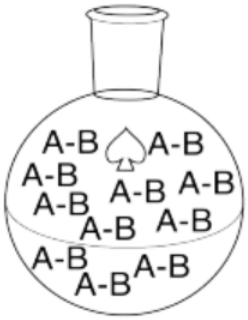
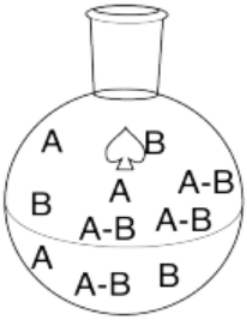
Exercise 14.5.2:

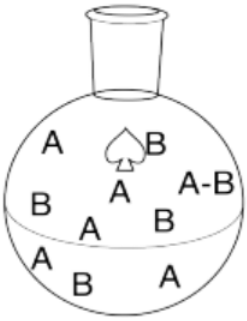
a.



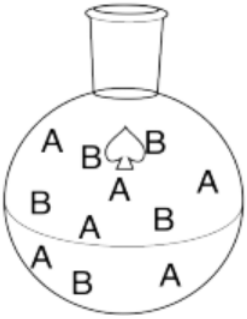
b.



c.



d.



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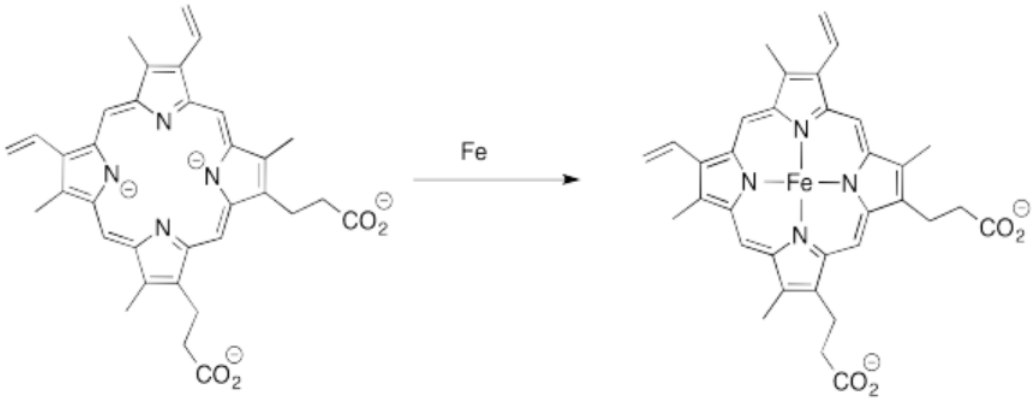
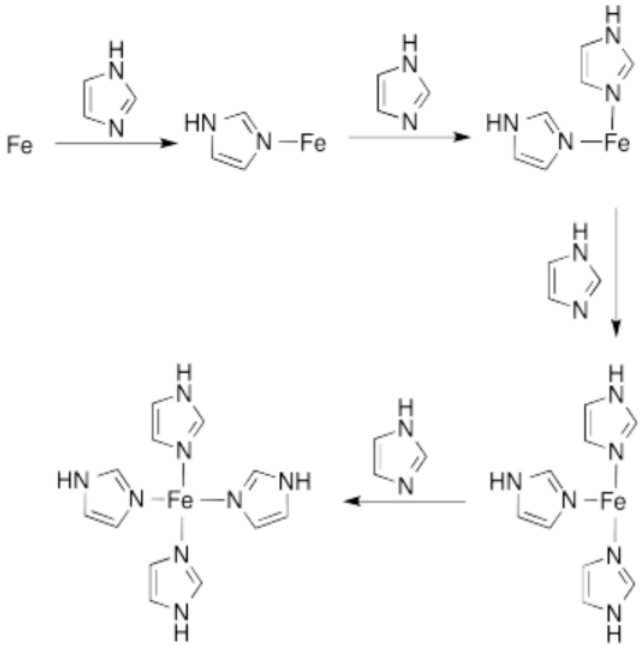
Exercise 14.5.3:

The heme subunit is tetradentate and forms 4 iron-ligand bonds. Four independent monodentate nitrogen ligands would be required to form a similar complex. Thus Iron binding to a heme does not produce the same of a loss o degrees of freedom as iron binding four independant nitrogen ligands.





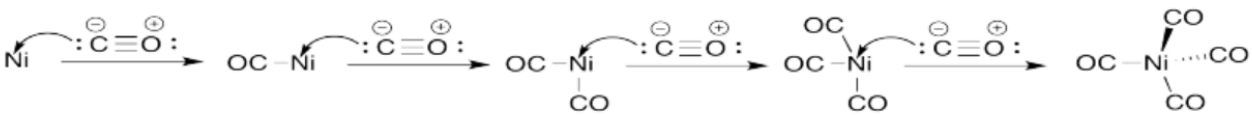
Exercise 14.6.1:

a. Lewis acid

b. $:C\equiv O:$

c. carbon will be nucleophilic due to the lone pair electrons and the negative charge

d.



e. Ni^0 is d^{10} and with 4 CO ligands the nickel tetracarbonyl complex has 18 electrons

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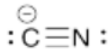
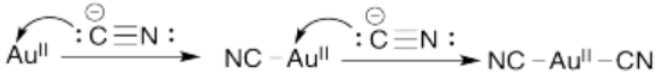
Exercise 14.6.2

a. Lewis acid

b. 

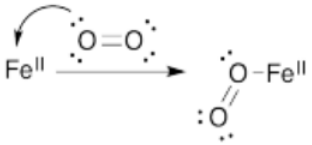
c. carbon will be nucleophilic due to the lone pair electrons and the negative charge

d. 

Exercise 14.6.3:

a. Lewis acid

b.

c. 

d. the bound oxygen would be predicted to have a trigonal planar electronic (bend molecular) geometry based on the Lewis structure.

Exercise 14.7.1:

a.

b.

c.

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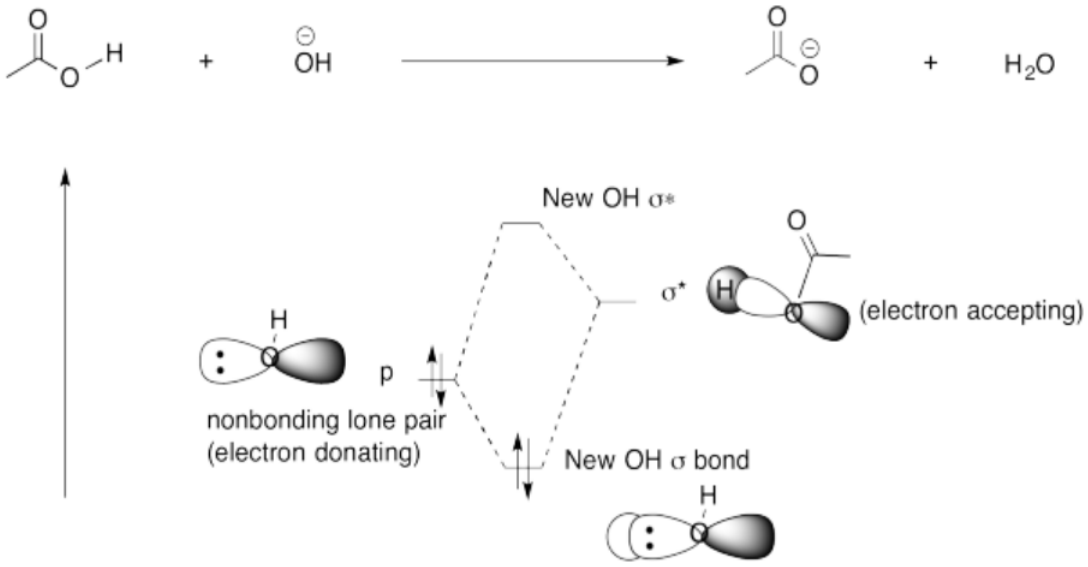
Exercise 14.7.2:



Exercise 14.7.3:

a)

b)

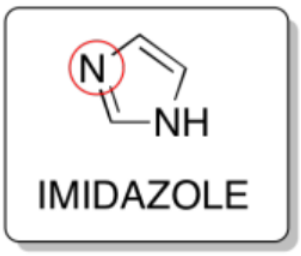
c)

d)

e) aromatic

f)

g)



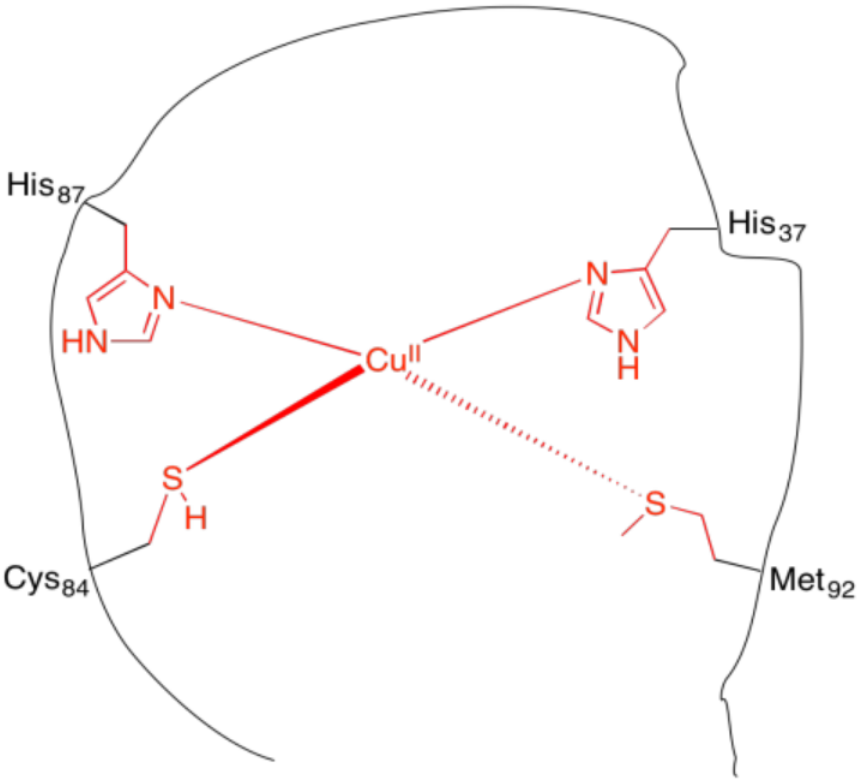
h) This nitrogen atom can donate a lone pair of electrons without disturbing the aromatic character of the molecule.

i)

j)

k) Each side chain has a Lewis base with a lone pair of electrons to donate the copper ion.

l)



m) CN = 4

n) tetrahedral

o) Cu: 11 e^-

Cu(II): 9 e^-

$$4 \times 2e^- = 8e^-$$

$$8e^- + 9e^- = 17e^-$$

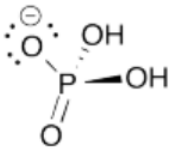
p) If the imidazole becomes occupied by a proton, then the imidazole no longer has the lone pair to donate to the copper ion.

q) trigonal

Exercise 14.8.1:

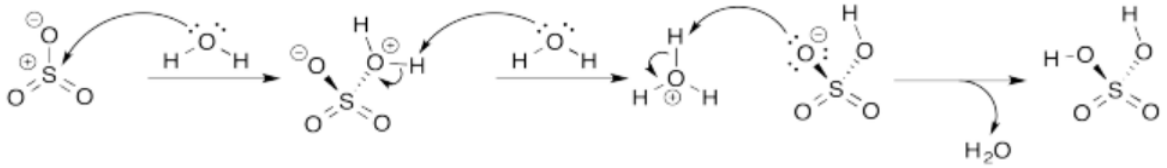
a.

b.

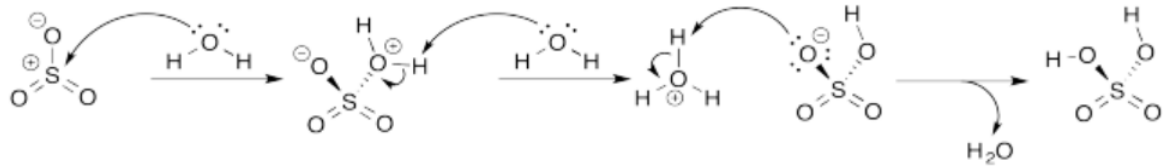


c.

Exercise 14.8.2:



Exercise 14.8.3:



Exercise 14.8.4:

a. The O-H bond is polar covalent. The oxygen is much more electronegative than the hydrogen, so the bond is easily ionized to give H^+.
b. In a case like NaOH, the electronegativity difference between the sodium and oxygen is much greater than the electronegativity between the oxygen and the hydrogen. The Na-O bond is ionic. The removal of a proton from hydroxide ion is harder than the removal from a proton from hydroxide. It would make an oxide anion, O^{2-}; that buildup of negative charge is more difficult than the formation of ^-OH.

Exercise 14.8.5:

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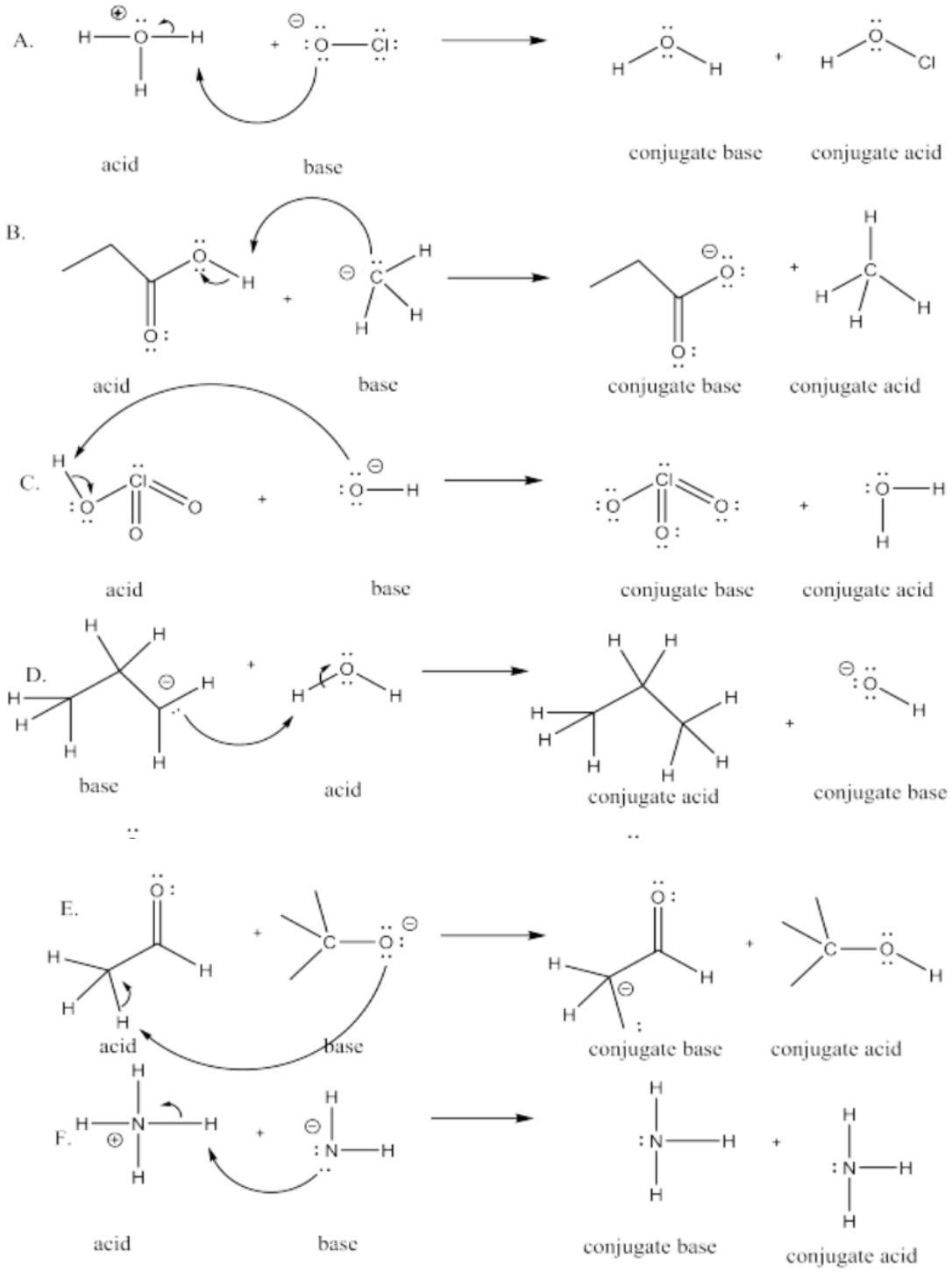

Exercise 14.8.6:

a) i)

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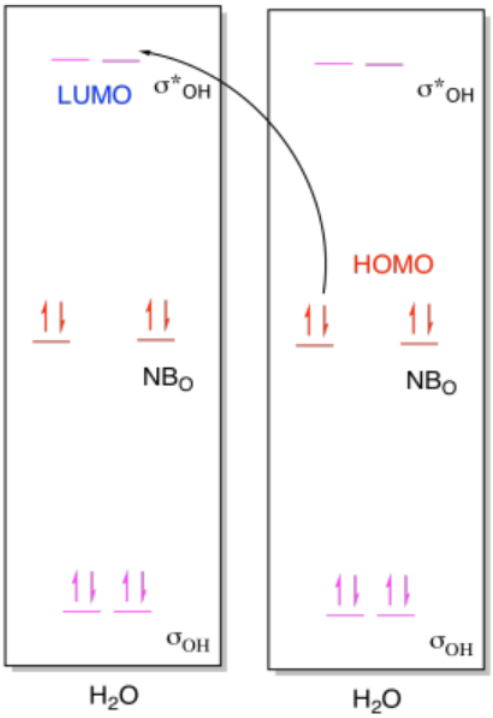
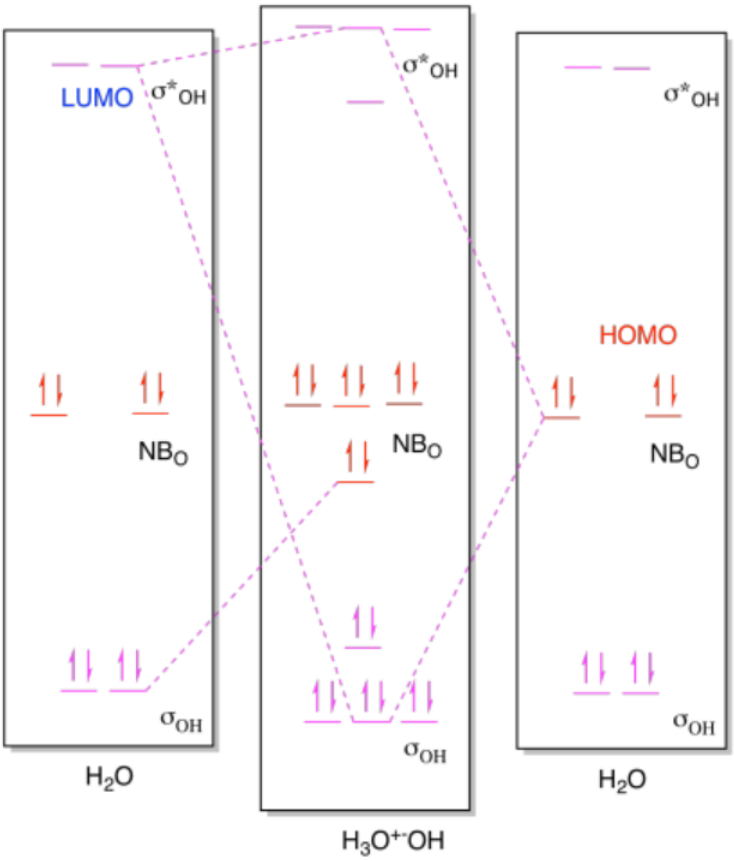

LUMO
σ*OH
σ*OH
HOMO
NBO
NBO
σOH
σOH
H2O
H2O

ii)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σOH
σOH
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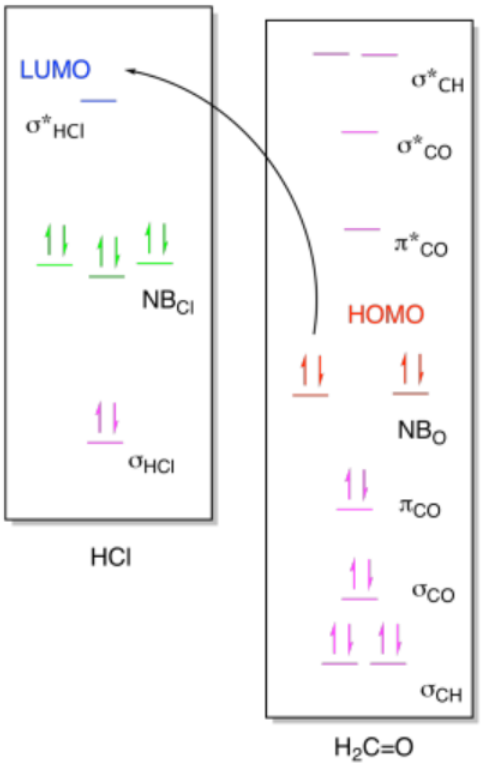
H3O+-OH
H2O

b) i)



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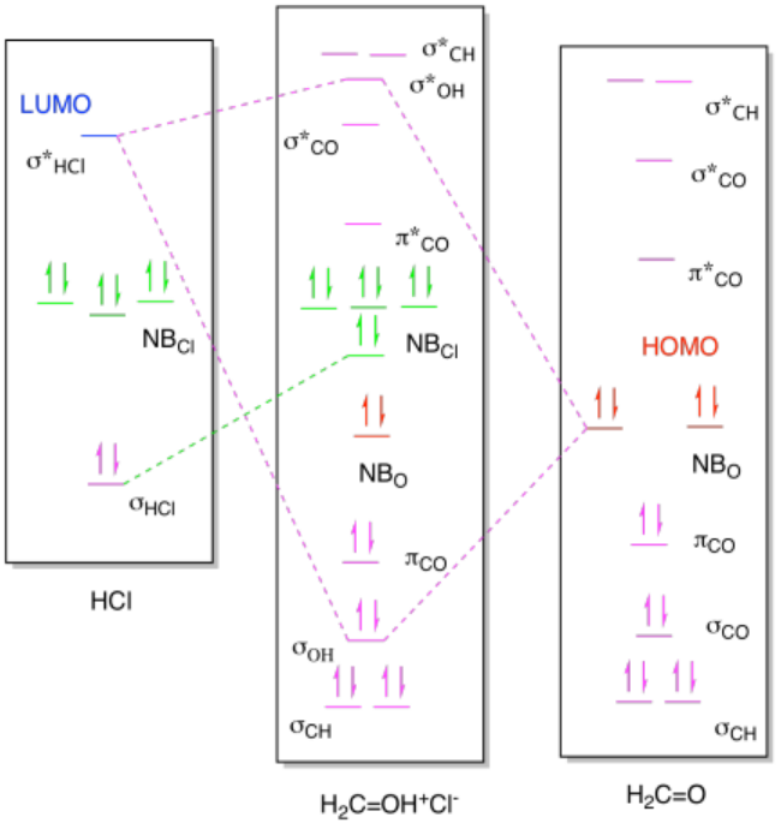


Exercise 14.9.1

https://chem.libretexts.org/@go/page/194555

a) HNO_3 (pK_a = -1.3); HNO_2 (pK_a = 3.3)

HNO_3 is a stronger Brønsted acid compared to HNO_2

b) H_2Se (pK_a = 3.9); H_2O (pK_a = 14)

H_2Se is a stronger Brønsted acid compared to H_2O

c) HCl (pK_a = -8); H_2SO_4 (pK_a = -3)

HCl is a stronger acid compared to H_2SO_4

d) $Ba(OH)_2$ (pKa > 50); $HSeO_3$ (pKa = 6.6)

$HSeO_3^-$ is a stronger Brønsted acid compared to $Ba(OH)_2$

Exercise 14.9.2:

a) NH_4^+ (pK_a = 9.2); HN_3 (pK_a = 4.7)

NH_3 is a stronger Brønsted base compared to N_3^-

b) HCN (pK_a = 9.4); HSCN (pK_a = 4)

^-CN is a stronger Brønsted base compared to ^-SCN

c) NH_3 (pK_a = 35); H_2O (pK_a = 14)

$^-NH_2$ is a stronger Brønsted base compared to HO^-

Exercise 14.10.1

a. $HClO_4$
b. H_3PO_4

Exercise 14.11.1:

a) H_2S or SiH_4 b) GaH_3 or AsH_3

c) PH_3 or AlH_3 d) H_2Se or HBr

Exercise 14.11.2:

a) $^+NH_4$ or NH_3 b) $^-PH_2$ or PH_3

c) H_2O or $^+NH_4$ d) ^+H_3O or CH_4

Exercise 14.11.3:

a) H_2S or H_2Te b) GeH_4 or SnH_4

c) HCl or HBr d) NH_3 or AsH_3

Exercise 14.11.4:

a. $AsH_3 > PH_3 > NH_3$

b. $HCl > H_2S > PH_3 > SiH_4$

c. $HI > SeH_2 > SiH_4 > BH_3$

Exercise 14.11.5:

a. Polarizability would not be useful as the atom that will be anionic in the conjugate base is the same (oxygen).

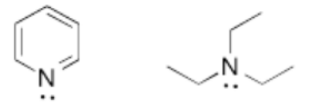
b. Se is larger and therefore more polarizable leading to H_2Se being more acidic compared to H_2S.

c. Ge is larger and therefore more polarizable leading to GeH_4 being more acidic compared to SiH_4.

d. Polarizability would not be useful as the atoms are next to one another in the same row and therefore likely to have the same polarizability.

Exercise 14.11.3:

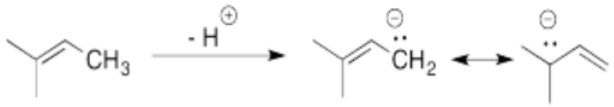
Triethylamine will be more basic than pyridine due to the hybridization effect. The nitrogen in triethylamine is sp^3 while the pyridine nitrogen is sp^2.



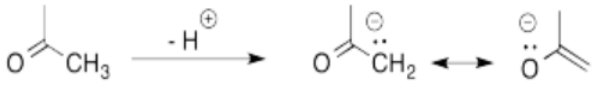
pyridine triethylamine

Exercise 14.12.1:

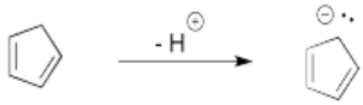
Alkanes typically have a $pK_a > 50$, however CH's adjacent to π systems lead to anions that are stablilized by conjugation or aromaticity. Examples of these are shown below:



allylic anion is stablilized by resonance



enolate anion is stablilized by resonance and the electronegativity of the oxygen atom.



cyclopentadienyl anion is stabilized by aromaticity

Exercise 14.12.2:

a. Vinyl alcohol would be more acidic as its anion is stabilized by resonance while the anionic charge on ethoxide would be localized on the oxygen atom.

b. Nitromethane would be more acidic as its anion is stabilized by resonance while the anionic charge of the trimethylamine anion would be localized on the carbon atom.

c. Acetonitrile would be more acidic as its anion is stabilized by resonance while the anionic charge of the trimethylamine would be localized on the carbon atom.

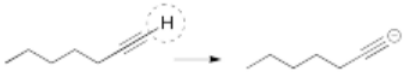
Exercise 14.12.3:

a. $CF_3CO_2H > HCF_2CO_2H > H_2CFCO_2H$

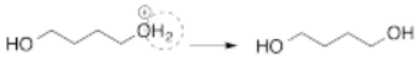
b. $CF_3CHF_2 > CF_3CHClF > CF_3CHCl_2$

Exercise 14.12.4:

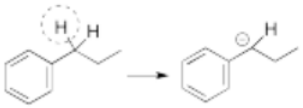
most electronegative atom



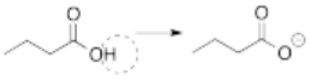
hybridization



decreases net charge of molecule



extends the conjugation

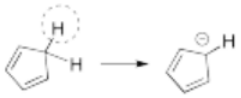


most electronegative atom
extends the conjugation

most electronegative atom

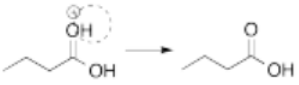
decreases net charge of molecule

extends the conjugation

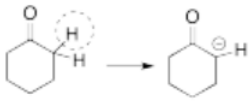


makes the molecule aromatic

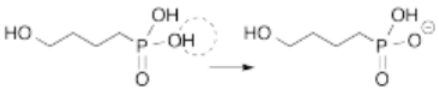
most polarizable atom



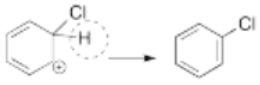
decreases net charge of molecule



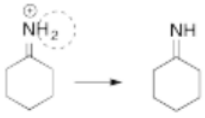
extends the conjugation



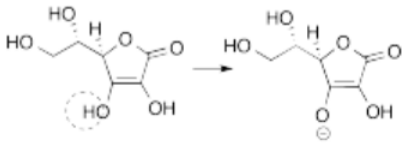
most electronegative atom
extends the conjugation



makes the molecule aromatic



decreases net charge of molecule



most electronegative atom
extends the conjugation

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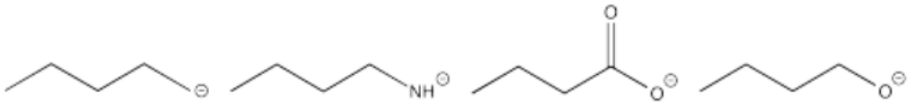
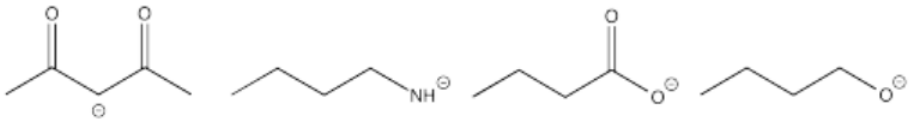
Exercise 14.13.1:

A.



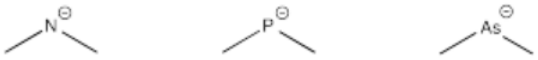
1 2 4 3

B.



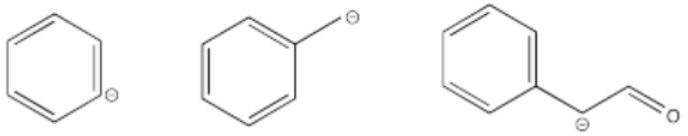
4 1 3 2

C.



1 2 3

D.



1 2 3

Exercise 14.14.1:

a. $HF + H_2O \rightleftharpoons F^{\ominus} + H_3O^{\oplus}$

$HF\ pK_a = 3$ $\quad$ $H_3O^{\oplus}\ pK_a = -2$

At equilibrium the reactants will be favored

b. $CH_3CO_2H + NH_3 \rightleftharpoons CH_3CO_2^{\ominus} + NH_4^{\oplus}$

$CH_3CO_2H\ pK_a = 5$ $\quad$ $NH_4^{\oplus}\ pK_a = 9$

At equilibrium the products will be favored

c. $PhOH + CO_3^{-2} \rightleftharpoons PhO^{\ominus} + HCO_3^{\ominus}$

$PhOH\ pK_a = 10$ $\quad$ $HCO_3^{\ominus}\ pK_a = 10$

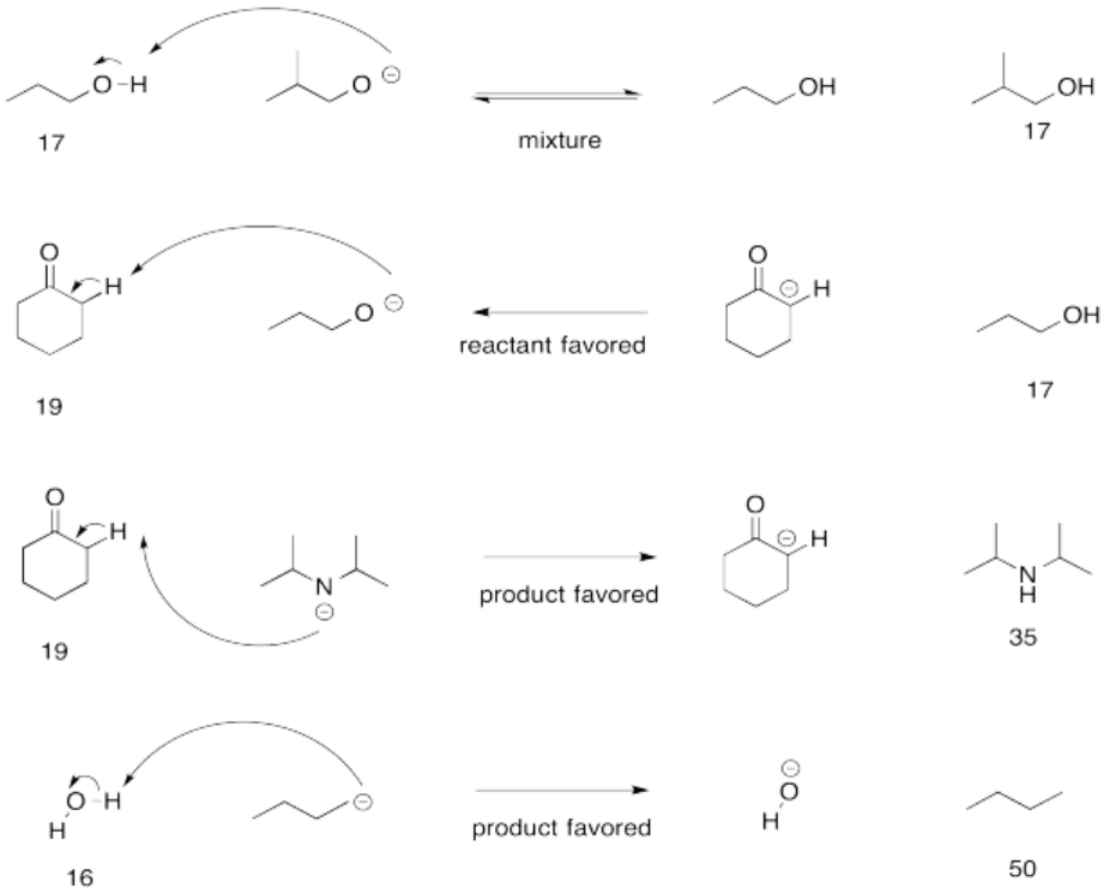
At equilibrium reactants and products will be present in equal amounts

d. $HCN + CH_3CN \rightleftharpoons CN^{\ominus} + CH_3CNH^{\oplus}$

$HCN\ pK_a = 9$ $\quad$ $CH_3CNH^{\oplus}\ pK_a = -10$

At equilibrium the reactants will be favored

Exercise 14.14.2:



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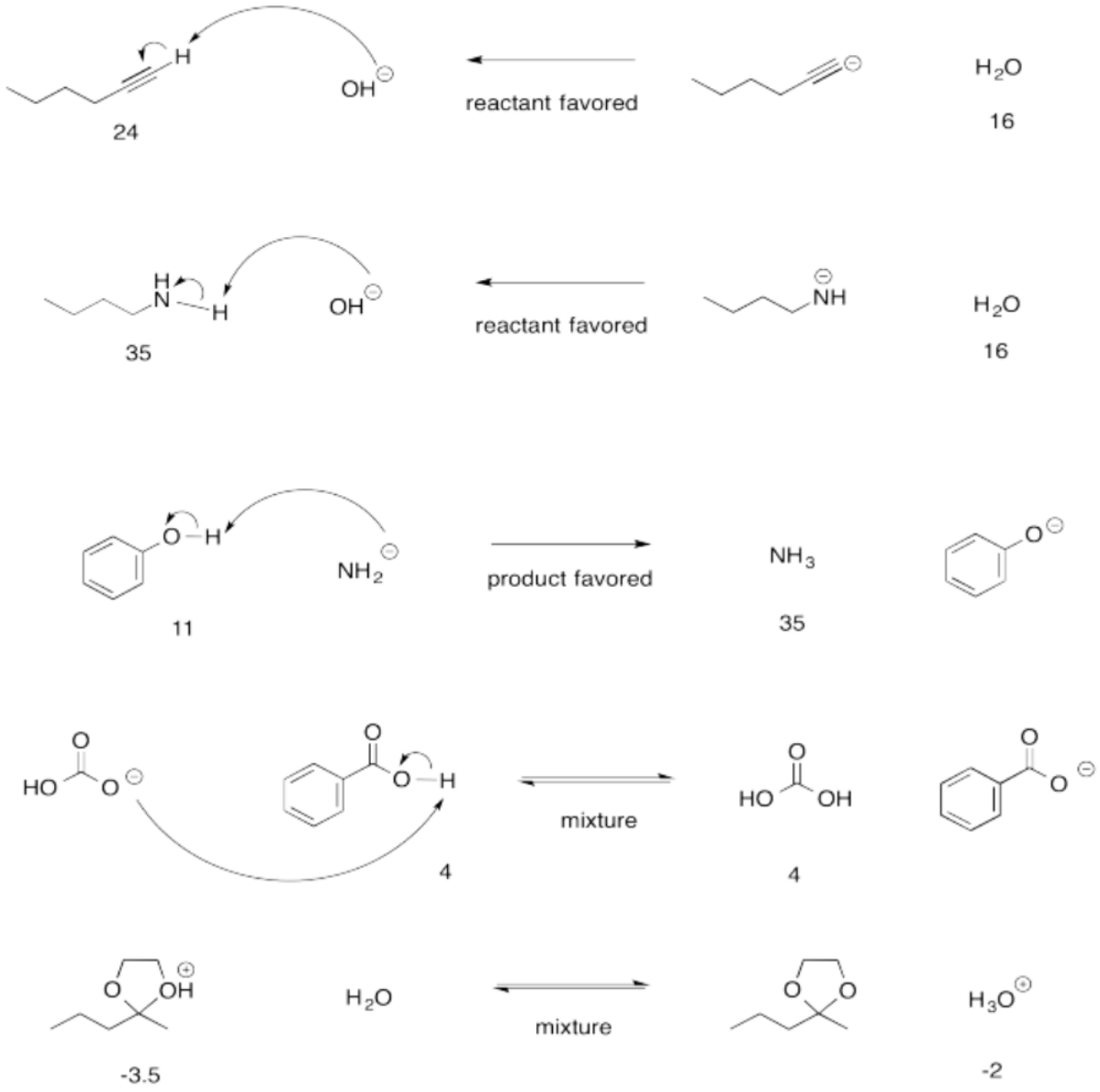

Exercise 14.15.1:

the nitrogen lone pair electrons in an amide are delocalized making them less basic

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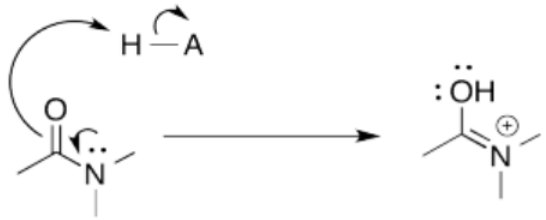
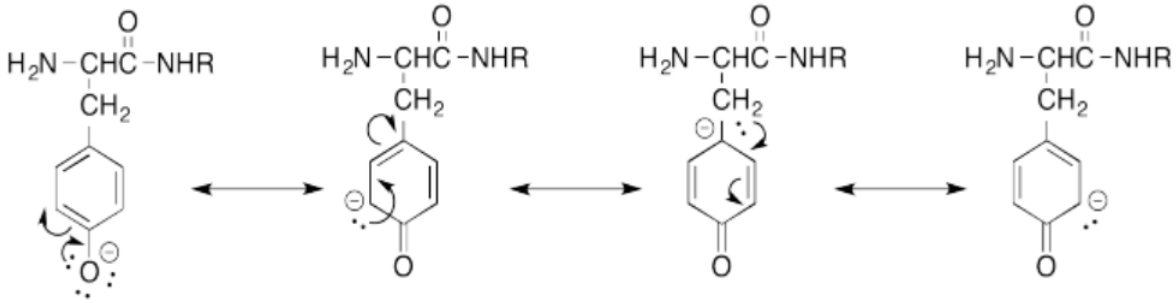
Exercise 14.15.2:

protonation of the oxygen leads to a conjugate acid that is conjugated



Exercise 14.15.3:

The alcohol proton on tryosine is more acidic due the resonance stabilization of the conjugate base. The conjugate base of serine possesses a localized anionic charge and is relatively less stable.



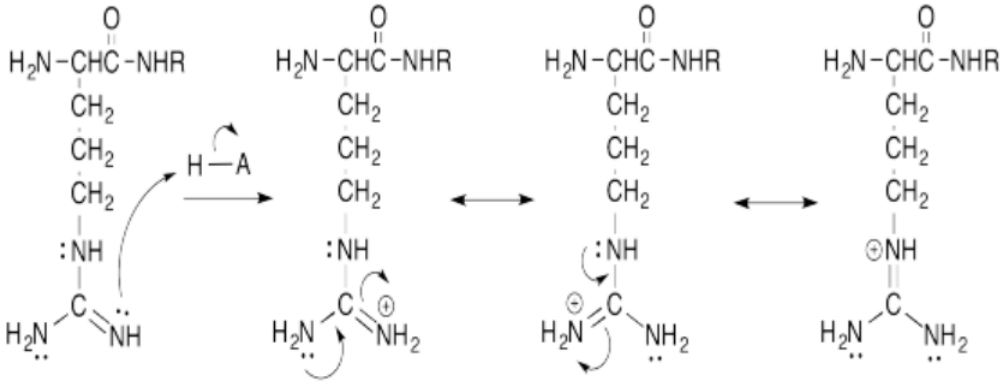
resonance structures for the tyrosine anion

Exercise 14.15.4:

The thiol proton on cystine is more acidic due to the polarizability of the sulfur anion stabilizing the conjugate base's anionic charge. The oxygen anion is less polarizable and therefore less stable rendering the alcohol proton less acidic.

Exercise 14.15.5:

Protonation of the indicated nitrogen leads to a conjugate acid that still benefits from resonance stabilization, while protonation of the other two nitrogen atoms would decrease conjugation.



resonance structures of the conjugate acid of arginine

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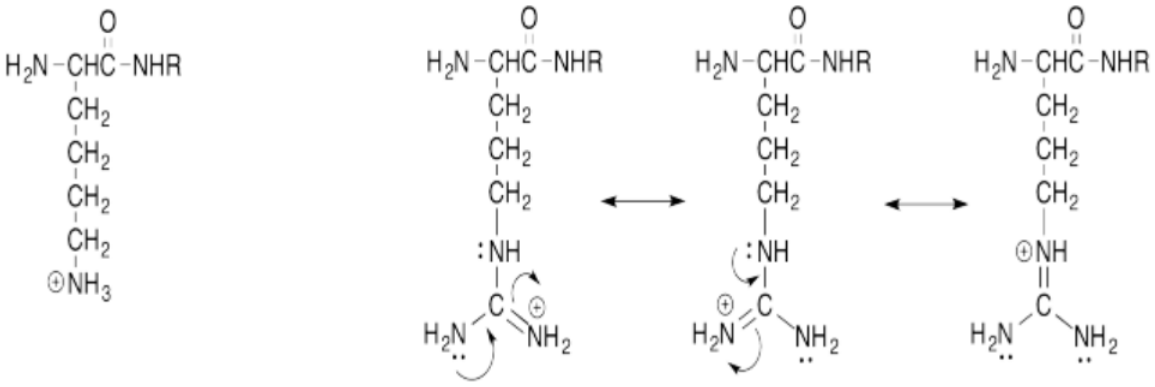
The pK_a of protonated arginine is higher than protonated lysine due to the resonance stabilization of the cationic charge

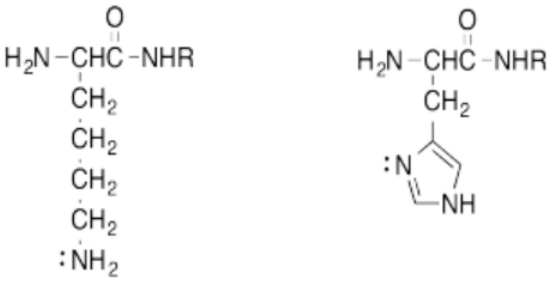


conjugate acid of lysine (no resonance stabilization)

resonance structures of the conjugate acid of arginine

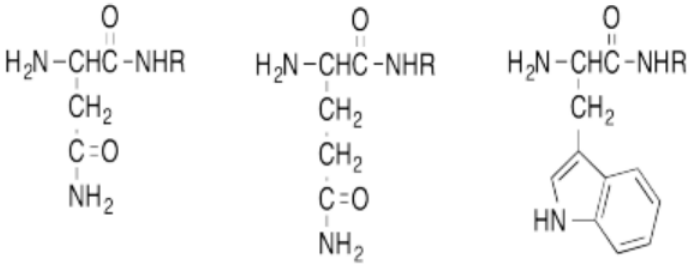
Exercise 14.15.6:

Lysine is a stronger amine base than histidine due to the difference in hybridization (sp^3 vs. sp^2)



Exercise 14.15.7

The lone pair electrons on the un-basic are resonance delocalized and not avaliable for protonation. The side chain nitrogens on asparagine and glutamine are found in amide groups and the nitrogen on tryptophan is part of an aromatic ring. Protonation of any of these nitrogens would break up a conjugated system.



Exercise 14.16.1:

Ammonium bromide is more soluble because in water it can participate in both ion-dipole and hydrogen-bonding, while sodium bromide only benefits from ion-dipole interactions.

Exercise 14.16.2:

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Hydrogen cyanide will be have a lower pKa in water as the resulting cyanide anion will be stabilized by both ion-dipole and hydrogen-bonding interactions. Hydrogen cyanide would have a higher pK_a in pentanes as the resulting cyanide anion would only experience ion-induced dipole interactions which are relatively weak.

Exercise 14.17.1:

a. $K_a = \frac{[NC^-][H_3O^+]}{[HCN]}$

b. $K_a = \frac{[HS^-][H_3O^+]}{[H_2S]}$

c. $K_a = \frac{[H_2N^-][(CH_3)_2SOH^+]}{[HCN]}$

Exercise 14.17.2:

a. pKa = -6

b. pKa = 9

c. pKa = 24

d. pKa = 16

Exercise 14.17.3:

a. Ka = $10^{3.5}$

b. Ka = $10^{-4.3}$

c. Ka = 10^{-25}

d. Ka = 10^{-9}

Exercise 14.17.4:

At equilibrium formation of the Lewis acid-base complex is slightly favored.

Exercise 14.17.5:

At equilibrium formation of the Lewis acid-base complex of dimethylether and BF_3 is more favored than the corresponding diethylether BF_3 complex. This is likely due to the decreased steric bulk of the methy groups compared to the ethyl groups.

Exercise 14.17.6:

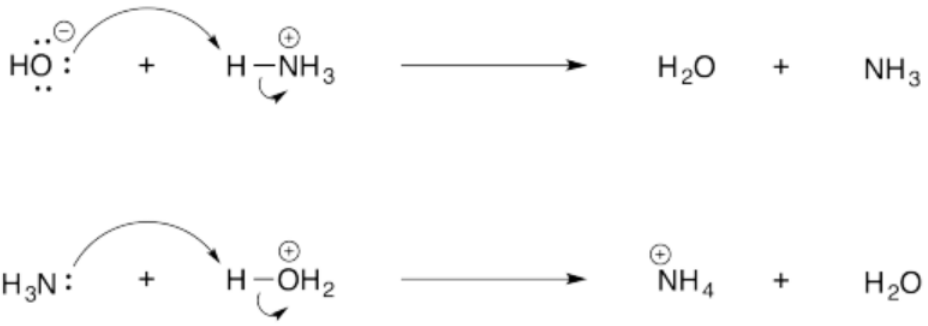
a. $K_{eq} = \frac{[(NH_3)_2PtCl_2]}{[(NH_3)PtCl_2][NH_3]}$

b. $K_{eq} = \frac{[Mo(CO)_6]}{[Mo(CO)_5][CO]}$

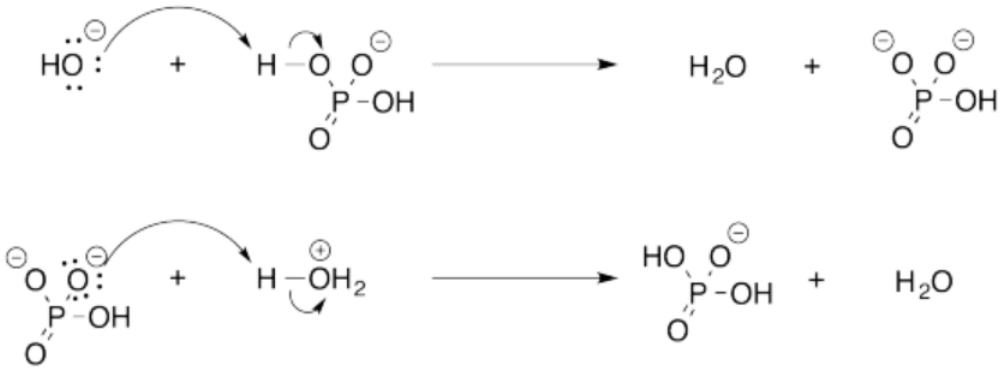
c. K_{eq}= \frac{[FeCl_{4}^{-}]}{[FeCl_{3}][Cl^{-}]

Exeercise 14.18.1:

a.



b.



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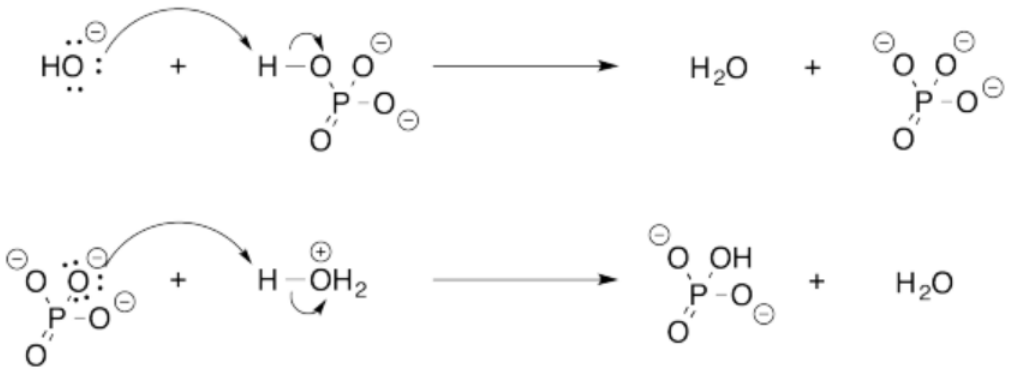
c.



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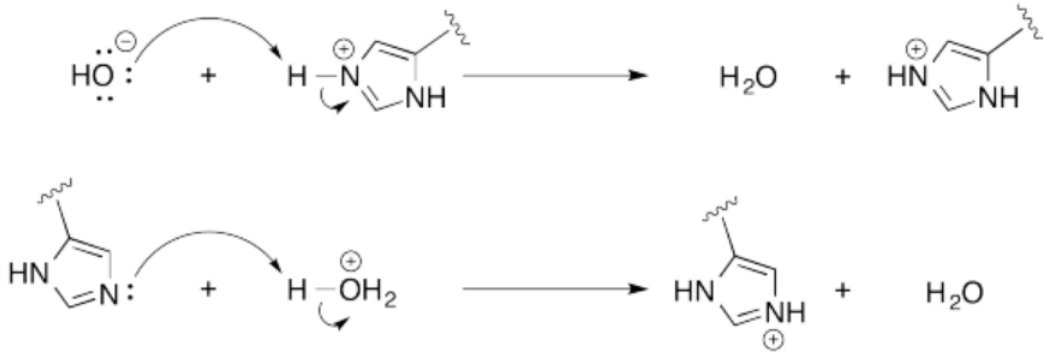


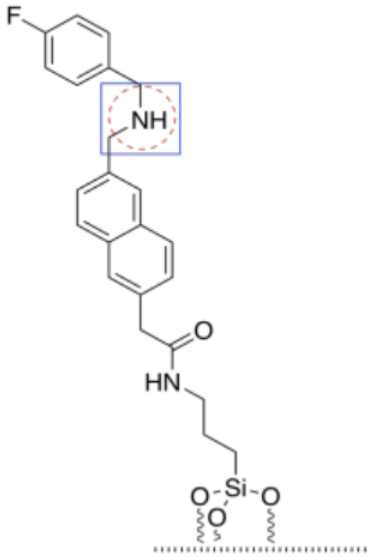
Exercise 14.19.1:

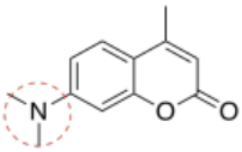
a. all bases have lone pairs.
b. F, N, and O have lone pairs. They can be bases.

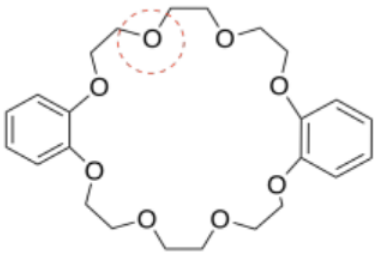
Their order of basicity would be N > O > F.

These three elements come from the same row of the periodic table and so they are of similar sizes. However, N is the least electronegative and F is the most electronegative. N is most able to donate electrons and most able to support a positive charge, compared to the other two.

c)



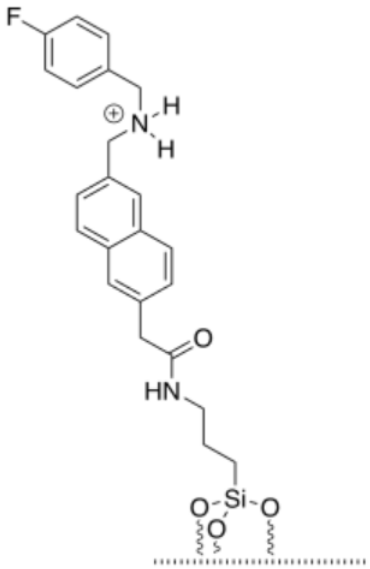




If possible, a nitrogen is circled in each molecule. The cap has only basic oxygen atoms. If there is a choice between two nitrogens (in the tether) or two oxygens (in the cap), the non-conjugated lone pair would be most basic. Conjugated lone pairs are held in place by their stable interaction with their neighbors.

The most basic of all is the amine (non-conjugated) nitrogen in the tether.

d)

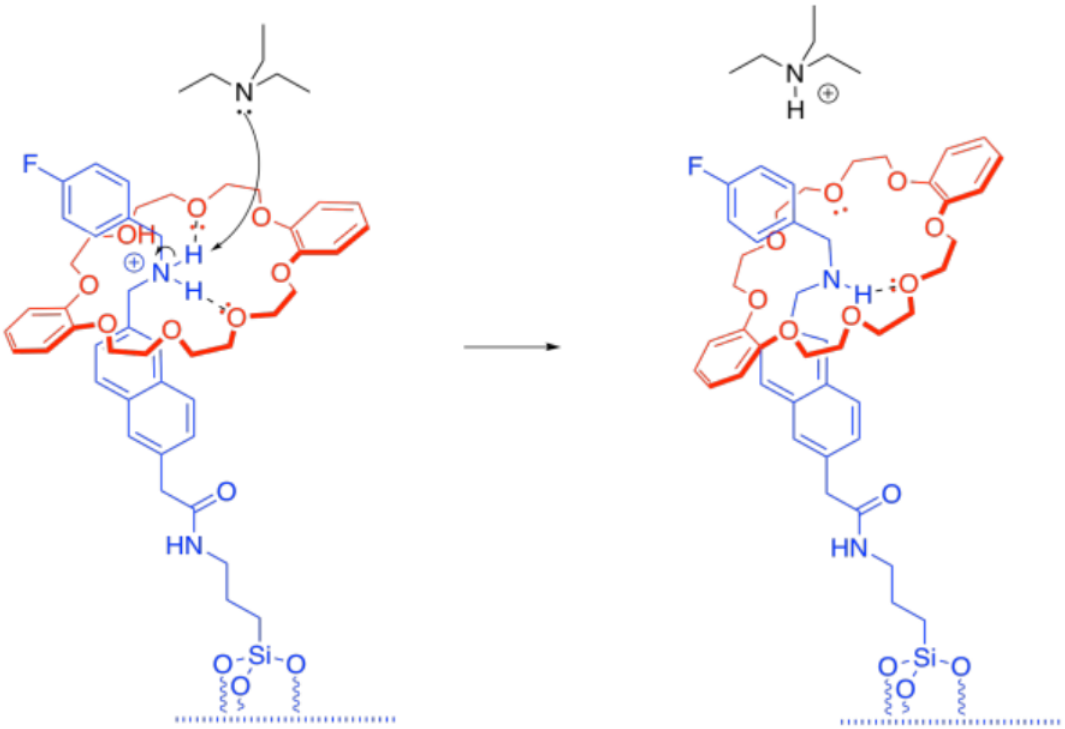


e) The cap and tether would be bound by hydrogen bonding. However, hydrogen bonding becomes much stronger if there is an ionic component. It is not a full ionic bond because the cap does not contain an anion, but its strength is between that of a normal hydrogen bond and an ionic bond.

f) Steric crowding traps the dye between the cap above and the silica surface below. The dye is too big to squeeze past the cap.

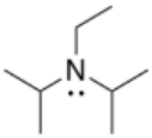
g) The dye has been released, and is now in the water.

h) There is an equilibrium between the protonated tether and the protonated triethylamine.



i) Once the tether has been deprotonated, the tether-cap interaction is just a normal hydrogen bond. It's still strong, but not as strong as the ion-boosted hydrogen bonding that we had before.

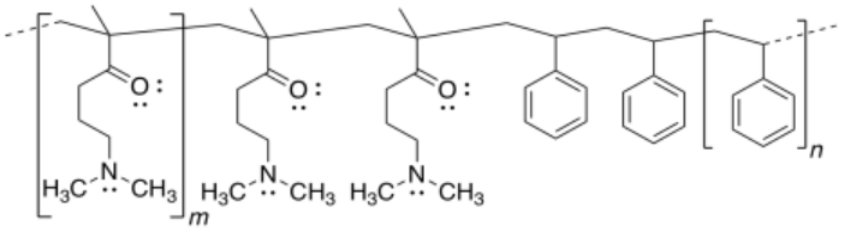
j) N,N-Diisopropylethylamine or Hunig's base:



k) The lone pair in Hunig's base is much more crowded than the one in triethylamine, so it cannot remove the proton as quickly.

Exercise 14.19.2:

a)



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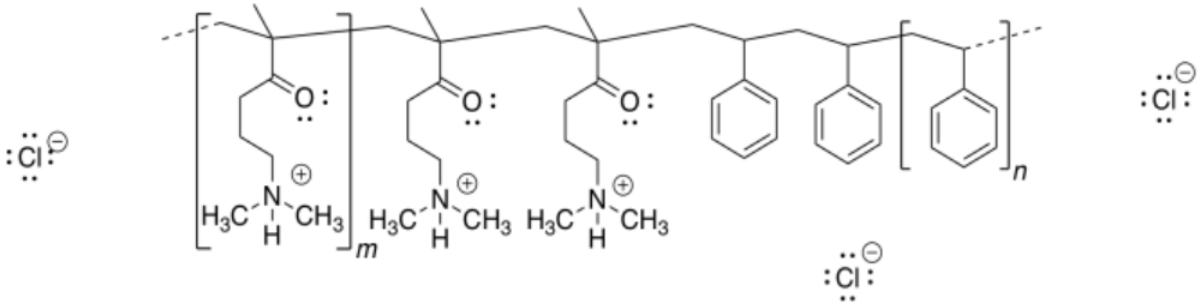
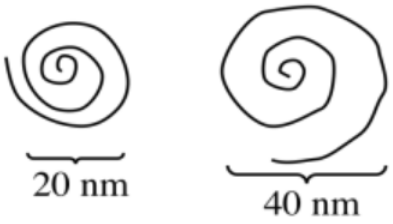
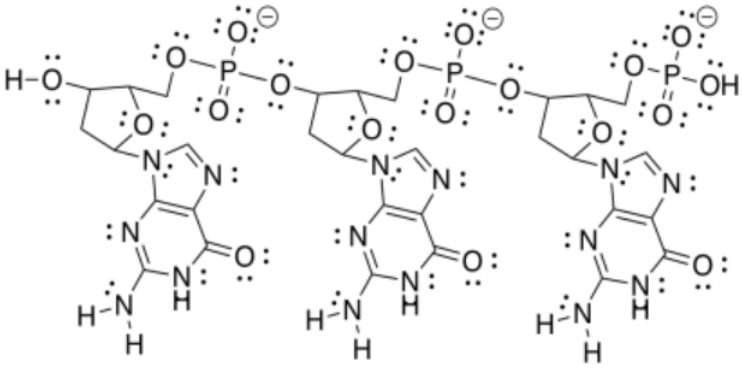


c)

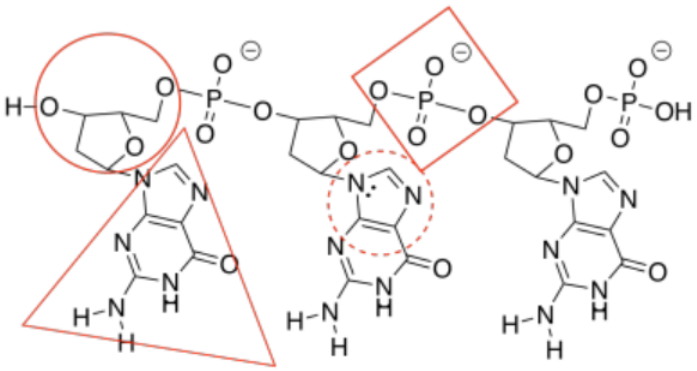


d) Repulsion between the positively-charged quaternary ammonium groups (poly-CH_2-N(H)$(CH_3)_2^+$) would cause the nanoparticle to uncoil.

e)



f)



g)

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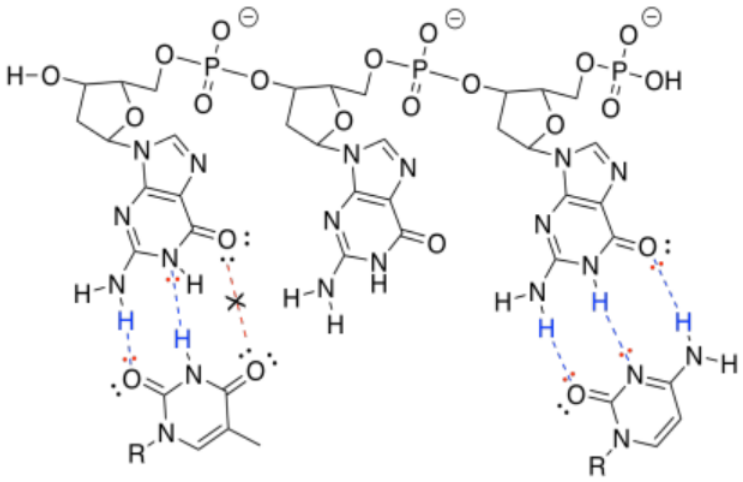


h) The one on the right forms three hydrogen bonds with the DNA and binds more tightly than the one on the left, which forms only two hydrogen bonds with the DNA.

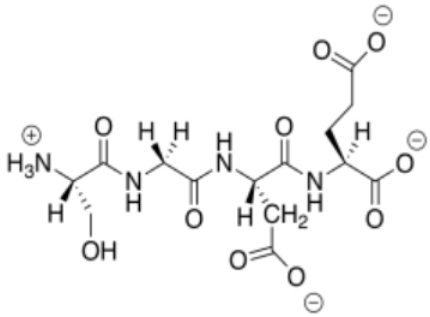
i) The polymer is positively charged after acid treatment. It binds the negatively charged DNA via ion-ion interactions.

j) If there are enough of them, the chloride anions could "wash out" the anionic DNA. These individual anions would replace the DNA anion previously bound to the nanoparticle.

k) The triethylamine could remove the proton from the polymer chain. If the polymer chain were no longer charged, it would no longer bind the anionic DNA.

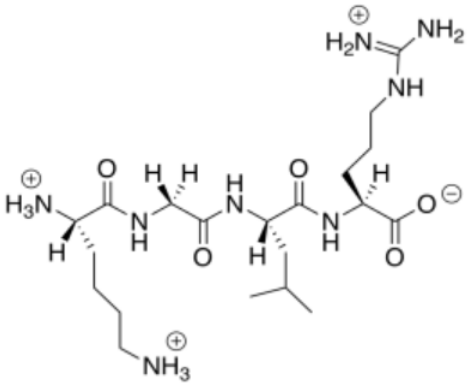
l) Also, because the nanoparticles would no longer be charged, there would no longer be repulsive forces causing the polymer to uncoil.

m)



n) This anionic (overall) peptide would bind to the cationic nanoparticles, replacing the DNA.

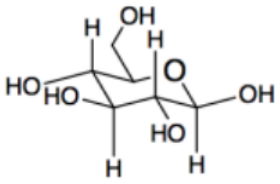
o)



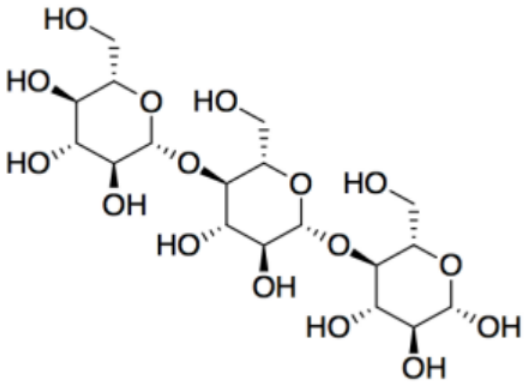
This cationic (overall) peptide would not bind to the cationic nanoparticles, so it would not displace the DNA.

Exercise 14.19.4:

a)



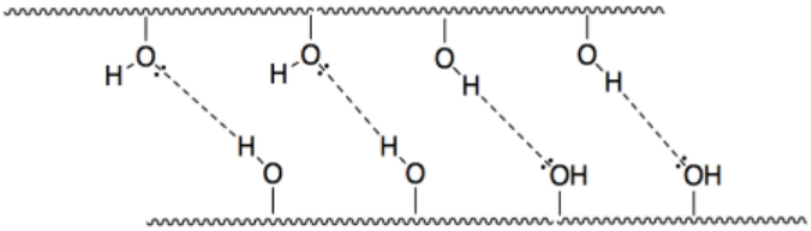
b)



c) carbohydrates

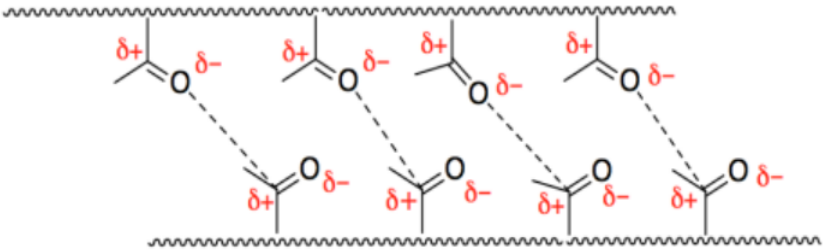
d) Cellulose is the major component of cotton (textiles and money) and paper.

e)



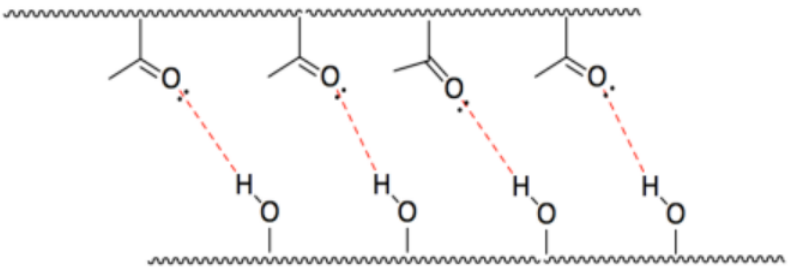
f) ester

g)



h) Body temperature is closer to 40%deg;C, so the hip would be soft and rubbery. That would making walking a little unpredictable.

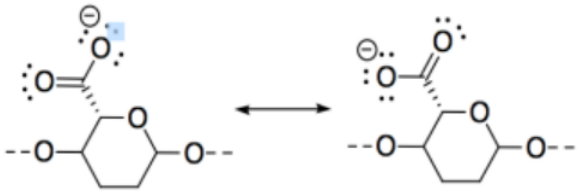
i)



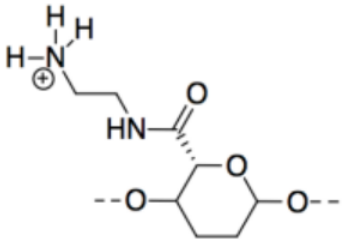
j) HCl is acidic because the H-Cl bond is polarized with electrons closer to Cl.

k) NaOH is basic because the Na-O bond is more polarized, with electrons closer to O.

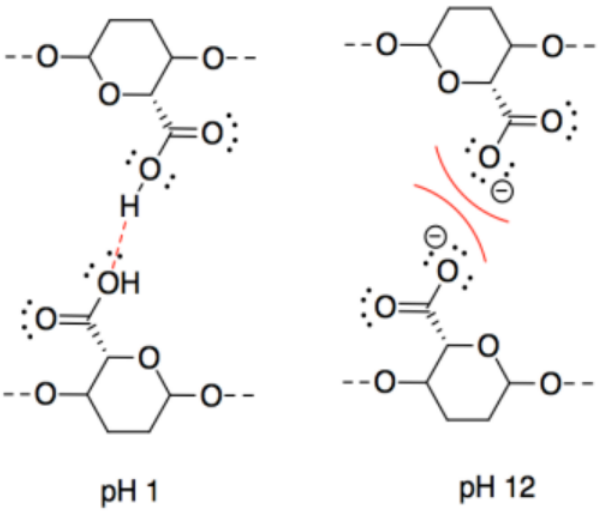
l) CNC-CO_2H is most acidic because of the resonance stabilized anion in the conjugate base.



m) CNC-NH_2 is most basic because, although all three compounds possess lone pairs, the lone pair on the nitrogen is on a less electronegative atom than the lone pairs on oxygens, so it is more readily donated to a proton.



n) This one may seem counterintuitive. The intermolecular forces at pH 11 are ionic, which should be stronger than hydrogen bonding. However, interactions between two anionic chains are repulsive, which would decrease the attraction between neighbouring CNC chains.



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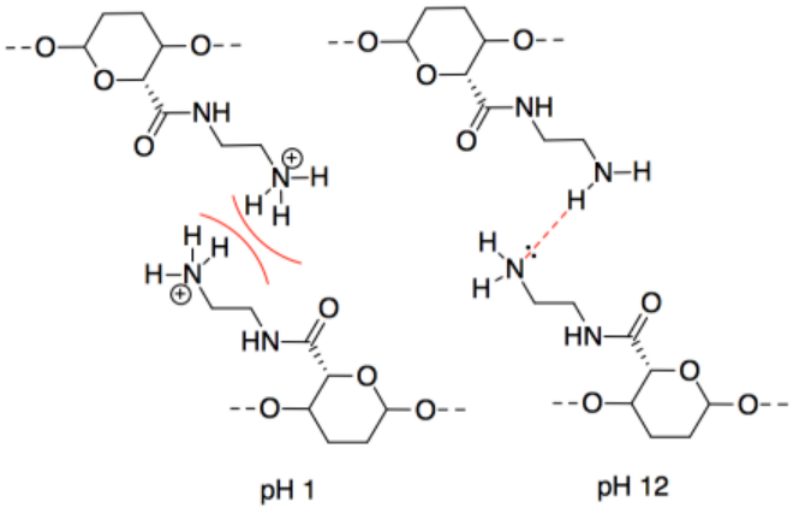
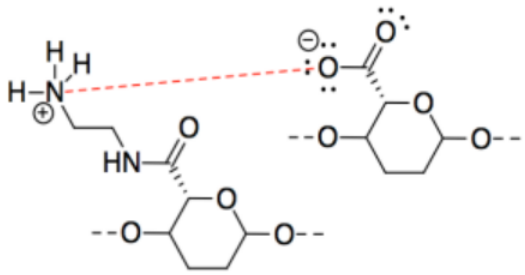
o) The intermolecular forces at pH 3 are ionic, which should be stronger than hydrogen bonding. However, interactions between two cationic chains are repulsive, which would decrease the attraction between neighbouring CNC chains.



p) A proton would be transferred from the acidic site to the basic site. The oppositely charged CNC chains would attract each other strongly.



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