GENERAL CHEMISTRY SUPPLEMENT

Emily V Eames

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Book: General Chemistry Supplement (Eames)

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CHAPTER OVERVIEW

Chemical Reactions and Interactions

Topic hierarchy

Contributors and Attributions

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Acid-Base Reactions

Skills to Develop

- Describe neutralization using chemical equations

Acids are familiar to you from everyday life, because acids are sour things, like vinegar and lemons. **Bases** might be less familiar to you. Common bases in regular life are baking soda and antacids that people take if they are having stomach trouble. Also, many soaps are basic, although this is just because of how they are made, not necessary to make them soapy. Bases make things feel slippery, and they taste bitter. They can be used to clean greasy things. Common acids and bases will react with each other and when they react completely, the products are usually a salt solution that isn't sour or bitter. This is called **neutralization**. Acid-base neutralization reactions are what make most cakes fluffy, because sometimes these reactions generate a gas that makes holes in the cake.

Some examples of common acids and bases sorted by their strength on a pH scale.

It is important to know that there are many different definitions of acid and base. This page describes the simplest and most specific definition. Practicing chemists use broader definitions that stretch the general concept to a variety of situations that are important in more advanced chemistry.

How does Neutralization work?

This description describes acid-base reactions in water. (It works a little bit differently in other solvents, but you don't need to think about that too much until you study more advanced chemistry). An acid is an electrolyte (strong or weak) that produces H^+ ions when it dissolves in water. Hydrogen ions are also called protons, because a hydrogen nucleus is just a proton (unless it is a heavier isotope, but this is rare). Acids are sometimes called "proton donors" meaning they give away protons, but this is not a very good word, because the protons are pulled away by the solvent, not dropped by the solute. Examples of strong acids include HCl and H_2SO_4, which are called hydrochloric acid and sulfuric acid. But sulfuric acid has 2 protons bound to sulfate ion, and only one comes off completely (just like the weak electrolytes discussed here), so a solution of sulfuric acid will have hydrogen ions, bisulfate ions, and sulfate ions in solution. Just like in the case of precipitation reactions, if a base is added, both protons might come off completely and react with the base. Acids are called **monoprotic**, **diprotic**, etc. depending on how many acidic protons they have. HCl, acetic acid (vinegar, CH_3COOH) and nitric acid (HNO_3) are monoprotic acids. (Acetic acid has other protons, but only the last one is acidic.) Sulfuric acid and many others are diprotic acids.

Examples of different types of acids (monoprotic, diprotic, triprotic)

A base is an electrolyte (strong or weak) that produces hydroxide ions when dissolved in water solution. This could be because it is a hydroxide salt, like NaOH, or because it takes hydrogen ions from water, leaving hydroxide behind. A good example of this is ammonia, NH_3, which is sometimes used in house cleaning products. Ammonia reacts with water to make ammonium hydroxide (but only a little bit, ~1% of the ammonia reacts):

$$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq) \tag{1}$$

In general, bases react with hydrogen ions. This is how neutralization happens. The acid produces hydrogen ions, and the base produces hydroxide ions. These react together to make water. The anion that came from the acid and the cation are left, so if you evaporate the water, you would get a salt. The general reaction looks like this:

$$X^-(aq) + H^+(aq) + M^+(aq) + OH^-(aq) \rightarrow H_2O(l) + X^-(aq) + M^+(aq) \tag{2}$$

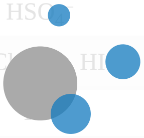
Overall, the reaction is:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{3}$$

Thus, the hydrogen ions, which makes acids acidic, are consumed, and the hydroxide which makes bases basic is also consumed, and if the moles of acid and base are equal, only neutral water and a salt is left. (Actually, it is a little bit more complicated than this if the acid or base is weak. The solution will only really become neutral when the moles are equal if both are strong.)

Need to Know Acids and Bases

Name	Formula	Comment
Ammonia	NH_3	weak base
Alkali Metal Hydroxides	LiOH, NaOH, KOH, RbOH, CsOH	soluble strong bases
Alkaline Earth Metal Hydroxides	$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$	soluble strong bases
Acetic Acid	$HC_2H_3O_2$	vinegar, weak acid
Perchloric Acid	$HClO_4$	strong acid
Chloric Acid	$HClO_3$	strong acid
Nitric Acid	HNO_3	strong acid
Carbonic Acid	H_2CO_3	a weak acid, in sodas
Bicarbonate	HCO_3^-	a weak base (baking soda)
Sulfuric acid	H_2SO_4	diprotic strong acid
Bisulfate	HSO_4^-	weak acid
Hydrohalic Acids	HCl, [illegible] HI	strong acids
Hydrofluoric Acid	[illegible]	weak acid, but very dangerous



Example

Q: How do acid-base reactions make cake fluffy?

A: Usually cakes include an acidic ingredient (this varies) and sodium bicarbonate, a base. When they react, the proton from the acid is transferred to the bicarbonate, making the weak acid carbonic acid. Carbonic acid is the product of an acid anhydride reaction between carbon dioxide and water. This reaction can be reversed, or carbonic acid can decompose into water and carbon dioxide. Especially at the high temperatures inside a baking cake, this decomposition will happen, and produce carbon dioxide gas. The pressure of the hot gas will form bubbles inside the cake, making it fluffy.

In the previous section (Precipitation), instead of having hydroxide react with hydrogen ions to form water, the acid base reaction made carbonic acid from protons and bicarbonate. In general, a base is something that will bind tightly to a proton. Bicarbonate and carbonate ions are bases, and so are sulfide ions. Both of these reactions can produce a gas, either carbon dioxide or hydrogen sulfide. In the lab, sodium bicarbonate is usually used to neutralize acid spills. When it reacts with acid it produces bubbles, so it's easy to see when the reaction finishes.

Most chemists agree that acid-base reactions are combination reactions without redox. This is a much more general definition than described here, but after you read about redox, go over these examples and convince yourself that they all fit that definition. What other examples can you think of that also fit this definition?

Summary

Acids are strong/weak electrolytes that produce H^+ ions when dissolved in water. A notable property of acids is that they have a sour taste. **Bases** are strong/weak electrolytes that produce hydroxide ions (OH^-) when dissolved in water. They are also known to have a bitter taste as well as a slippery or soapy texture. **Neutralization** is a type of reaction in which acids react with bases to form a salt solution (water and a salt), usually.

Outside Links

- CrashCourse Chemistry: Acid-Base Reactions in Solution (11 min)
- Khan Academy: Acid Base Introduction

(18 min, skip the last 3 min, optional: skip the first 4 min)

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Combination Reactions

Skills to Develop

- Describe the various types of combination reactions using chemical equations

Combination reactions describe a reaction like this:

$$A + B \rightarrow C \tag{1}$$

in which two or more reactants become one product (are combined). The problem with this term is that it doesn't give you much chemical insight because there are many different types of reactions that follow this pattern. So we'll break it into groups that reflect what's actually happening a little better.

Combination of Elements to Make Ionic Substances

In this category, an elemental metal and an elemental non-metal react to make an ionic substance that is neutral and has each ion in its correct charge state or valence. For instance,

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s) \tag{2}$$

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \tag{3}$$

$$2Al(s) + 3O_2(g) \rightarrow Al_2O_3(s) \tag{4}$$

If the metal is a transition metal, it will be much harder to predict the correct charge on the metal ion in the ionic compound. You can check the element info in the nomenclature section or the links from the periodic table section. As you practice, you'll start to get a sense for what common charges are, but even then it is often good to check, because it might not be what you expect! For example, what's the charge on iron in Fe_3O_4 (magnetite)?

Under what circumstances do these reactions happen? Often, an elemental metal and non-metal "want" to make an ionic compound, because this is a more stable state (think about a heavy ball on a table: it can easily roll to the ground, where it has less potential energy, so the table isn't a stable state; if the heavy ball is in a small hole in the ground, it can't easily move, and if it did, it would have more potential energy, so the hole is a stable, low energy state). However, that doesn't necessarily mean the reaction will just happen on its own. That depends on how easily the reaction can happen (think about a place you want to go, but don't go because traveling there is very inconvenient).

A ball being held above a ledge has more potential energy so it is in a less stable state than if it were at the bottom of the ledge.

For instance, the alkali metals and the halogens react pretty easily, so they will often react even without a "push." Oxygen is very reactive, which is why things burn, but you have to light them on fire to get them started. This is good, because otherwise we would burn in air at room temperature! Many of these elemental combination reactions might need a high temperature to get started, even if they want to happen. It won't be hard to remember that alkalis, alkaline earth metals and halogens react easily, because this is why they are very hard to find in elemental form! Oxygen and nitrogen are very abundant in elemental form because it is hard for them to react even if they want to. Nitrogen in particular reacts only with lithium metal and a few complicated compounds at room temperature, although it will react with many other elements at high temperatures. Most metals aren't found in elemental form in nature (except for ones that don't want to react, like gold), but if you find them in elemental form in your house, then probably they don't react easily.

Combination of Elemental Non-metals into Covalent Compounds

These reactions involve elemental forms of elements like H, C, N, O, Cl, S, P, etc. It will often be hard to predict the product because these elements can often combine in different ratios (this is where the law of multiple proportions comes from!). You can always expect that H will have a valence of 1, and O will usually have a valence of 2. Many of these reactions will happen quickly if you get them started with a little heat, especially if oxygen or a halogen is involved. Otherwise, they might happen very slowly or not at all except under special circumstances that we will talk more about later. Some examples:

$$C(s) + O_2(g) \rightarrow CO_2(g) \ (fast,\ once\ lit) \tag{5}$$

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \ (usually\ very\ slow) \tag{6}$$

Basic Anhydrides

Basic anhydrides are compounds that turn into a base (a hydroxide salt) when you add water. They are metal oxides. Here's an example:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \tag{7}$$

If the metal is an alkali or alkaline earth, the reaction probably happens quickly and produces a lot of heat. If the metal is a transition metal, the reaction might not happen so easily or at all.

Acid Anhydrides

Acid anhydrides are compounds that turn into an acid when you add water. They are non-metal oxides. These are a little more complicated than basic anhydrides, so don't worry too much about them right now. Here's an example:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq) \tag{8}$$

Other Combination Reactions

There are many other circumstances in which a combination reaction could happen. The types listed here are the simple ones that are good to know in the beginning.

Outside Link

- Reacting alkali metals with chlorine (3 min)

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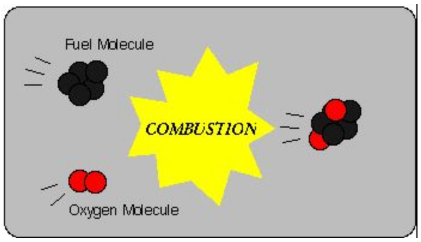
Combustion Reactions

Skills to Develop

- Identify a general chemical equation for combustion reactions
- Describe some of the characteristics of combustion reactions

Combustion reactions are common and very important. Combustion means burning, usually in oxygen but sometimes with other **oxidants** such as fluorine. A combustion reaction happens quickly, producing heat, and usually light and fire. Combustion describes how the reaction happens, not the reactants and products. Chemists as early as Lavoisier suggested that people get their energy from combustion-like reactions, but even though the products and reactants are the same when you burn food in a fire and in your body, the way it happens is different. In a combustion reaction, the thing that burns (the reactant that isn't O_2 or F_2) is called the **fuel**. Combustion reactions are a type of redox reaction.



A simplified diagram of a combustion reaction where oxygen is the oxidant.

The classic chemistry class combustion reaction involves a compound of C and H reacting with O_2 to form CO_2 and H_2O. Sometimes the reactant has some other elements, like O, S or N in it. The O will form water, the S will form usually $SO_2$and the N will often produce N_2, but sometimes a little bit of a nitrogen oxide. For class purposes, you can usually write equations in which carbon dioxide is produced. In real life, often some or a lot of CO is produced, depending on how much oxygen is present and other factors. In general, most elements in a compound that is combusted will form oxides, but you won't be able to say for sure how much of each oxide will be produced (CO or CO_2, SO_2 or SO_3, etc). Here are some example equations. When you balance combustion reactions, usually start with the C, and the fuel, and do the oxygen last.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g) \tag{1}$$

$$C_6H_{12}O_6(s) + 12O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g) \tag{2}$$

Reaction 4.2 is sugar burning, which may also represent an animal or plant using stored energy.

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Decomposition Reactions

Skills to Develop

- Describe decomposition reactions with chemical equations

Decomposition reactions are very common, and this word is used so much that many chemists just say "decomp". When people use this word in the lab, they might just mean that something didn't work, or that a chemical reacted in an unwanted way, especially while it was sitting in a bottle for a long time. The official meaning of decomposition is a little bit more specific, and means a reaction in which one chemical splits into two or more chemicals, like this:

$$A \rightarrow B + C \tag{1}$$

Decomposition reactions are often undesirable, but not always. For instance, many explosions are decompositions, and explosives are very important for many purposes other than weapons. Decomposition reactions might be hard to predict at first.

Some Simple Decomposition Patterns

The decomposition reactions in intro chemistry classes often result from heating a substance. For instance, when heated or struck, a salt of a complex anion (chlorate, carbonate, azide) may lose a gas (oxygen, carbon dioxide or nitrogen) leaving behind a simpler salt or metal. This could happen explosively, depending on the compound. Or, when heated, a metal hydroxide loses water to form the metal oxide (the reverse of the basic anhydride combination reaction). Here are some examples:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{2}$$

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2g) \tag{3}$$

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g) \tag{4}$$

$$Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(g \text{ or } l) \tag{5}$$

Note

Students often get confused into thinking that combination reactions, the opposite of decomposition reactions, are called composition reactions. Actually, composition is not a type of reaction, rather, it has a different meaning. **Composition** means the ratio of elements in a compound, such as 75% C and 25% H.

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Electrolyte Strength

Skills to Develop

- Define the 3 types of electrolytes
- Describe the relationship between solubility and electrolyte strength

Electrolyte means a solute that allows a water solution to conduct electricity. Electrolytes produce ions when they dissolve in solution. Salts are usually electrolytes, while molecular substances usually aren't, unless they are acids or bases.

Strong and Weak Electrolytes

The situation gets a little bit more complicated, though, because of the distinction between strong electrolytes and weak electrolytes. A strong electrolyte, like NaCl, splits up completely into sodium and chloride ions in solution. Likewise, a strong acid like HCl splits up completely into hydrogen and chloride ions in solution. Salts are often strong electrolytes, and strong acids are always strong electrolytes. Weak acids are weak electrolytes, and most other molecular compounds are non-electrolytes.

Many textbooks incorrectly state that all salts or ionic compounds are strong electrolytes. However, many ionic compounds or salts of transition metals or alkaline earth metals are not strong electrolytes. When they dissolve, some of the ions separate, but some stay together. Here are some examples:

$$K_2SO_4(s) + water \rightarrow K^+(aq)\ (70\%) + KSO_4^-(aq)\ (30\%) + SO_4^{2-}(aq)\ (for\ a\ 0.36\ M\ solution) \tag{1}$$

$$CdI_2(s) + water \rightarrow Cd^{2+}(aq)\ (2\%) + CdI^+(aq)\ (22\%) + CdI_2(aq)\ (76\%) + I^-(aq)\ (for\ a\ 0.5\ M\ solution) \tag{2}$$

As you can see, these salts are electrolytes (they do produce ions) but if you do calculations assuming that they separate completely into sulfate, potassium, cadmium(II) and iodide ions, you might get very wrong answers! They are not strong electrolytes. In general, the lower the concentration and the lower the charges on the ions, the "stronger" the electrolytes will be. Alkali metals other than lithium are usually strong electrolytes especially when the anion also has a small charge, and in dilute solutions (<0.1M). Alkaline earth metal compounds are weaker electrolytes, and other metals are even weaker still. We'll talk more about why this is later.

Solubility and Electrolyte Strength

Solubility can cause some confusion here. For instance, it's possible that a compound is a strong electrolyte, but just not very soluble. For this reason, it would not be able to produce a solution with lots of ions, because it isn't soluble, not because the ions are still attached to each other in the solution. In general, it makes sense to guess that if the ions in a compound are very strongly attracted to each other, the compound will be less soluble, and also it might be a weaker electrolyte because even in solution the ions will be bonded to each other. However, electrolytes also look stronger at lower concentrations, because if the ions split up, they are less likely to find each other again.

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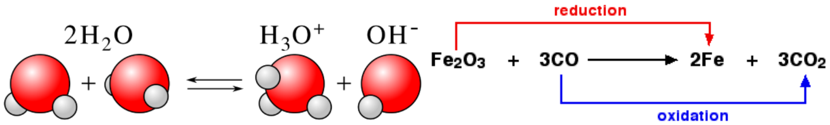
Overview

Skills to Develop

- Categorize the various types of reactions analyzed as acid-base or redox

So far we've seen a variety of types of reaction. This section is intended to help you fit all the pieces together. You've seen combination reactions and decomposition reactions. Sometimes these are the same reactions, just going in opposite directions. Likewise, dissolution and precipitation are opposite processes.

Many chemists think of reactions as falling into 2 main categories: acid-base type reactions and redox reactions. In an **acid-base type reaction**, an under-populated nucleus makes a bond with an over-populated nucleus, but the electrons don't change their primary loyalty. (The electrons from the over-populated nucleus do appreciate the better benefits they get from the under-populated nucleus, which has more pension money than it can spend on its own population.) In the classic acid-base reaction, the electrons on water really like oxygen as a home, but they are feeling a little crowded and poor; alliance with a hydrogen ion provides lots of money to make them happier, and a nice convenient vacation destination. In contrast, a **redox reaction** is any reaction in which electrons change their primary loyalties. Bonds between nuclei may change or not, but oxidation numbers do change. Try going through all the examples and deciding which category they fit and why.



Example of the classic acid-base reaction on the left and a redox reaction on the right.

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Redox Reactions

Skills to Develop

- Describe what occurs in a redox reaction
- Identify redox patterns in the periodic table

Redox reactions are reactions in which electrons shift allegiance. Allegiance means loyalty or commitment to a group, like your allegiance to your family or your country. If you decide to leave your home and become a citizen of a new country, you have shifted allegiance. Of course, you might be able to share your allegiance between your old country and your new country by being a citizen of both countries at the same time. This is similar to what electrons do. They have allegiance to a nucleus, and sometimes during a reaction they will shift allegiance to a different nucleus. They might shift allegiance completely, if the new nucleus is much better for them than the old one, or they might shift partially, and share their loyalty between the two. (Also, electrons, like people, can spend some time near nuclei they don't belong to, just like you can visit countries where you don't live, and then go back near their main nucleus, although electrons' trips are much shorter than ours!)

Redox Patterns in the Periodic Table

All neutral atoms have a population of electrons equal to their number of protons. Atoms, just like countries, always have elite citizens that they treat really well (power, money...) and these elite citizens are way too comfortable to shift allegiance unless they get kidnapped or something. Unlike countries, atoms always have only a small number of non-elite citizens, between 0 and 8, roughly, but usually no more than 3 or 4. These non-elite electrons will easily shift allegiance if they get a better offer.

What are the good parts of the periodic table? Fluorine is like heaven for electrons, they will basically never leave. If fluorine is accepting immigrants, electrons will leave anywhere else to move to F. Oxygen is second best. (Fluorine seems nasty to us because we don't want our citizen electrons to leave us for fluorine. We have jobs for them to do!) The noble gases are aloof nations, their populations of electrons hardly ever change. Their citizens don't want to leave, and they don't want any troublesome immigrants either. In general, the upper right corner of the periodic table are good comfortable nations to live in. The bottom left is such a bad place to live that electrons will destroy property in their rush to leave. (Watch this video for an example) This shows "standard of living" across the periodic table. Red elements will tend to keep their own electrons and attract electrons from other nuclei; yellow elements will tend to lose their non-elite electrons.

Ionic substances are like alliances between nations with really different standards of living. The non-elite electrons of the metal will try to shift allegiance to the non-metal. In molecular substances, also called covalent, the electrons will have dual citizenship, although they might have slightly greater loyalty to one nuclei than another, because these are alliances between similarly comfortable non-metal nuclei.

Another illustration of the redox patterns on the periodic table. The elements existing in nature with a negative charge are those that usually accept immigrants (electrons). Meanwhile the elements existing in nature with a positive charge are those that usually lose electrons.

Oxidation States: Redox from the Nuclei's Perspective

With all these dual citizen electrons, with partial loyalty to several nuclei, it can get hard to count the population of electrons at each nucleus. **Oxidation number** is one procedure for counting. In this procedure, electrons are counted as belonging completely to the nuclei they feel the greatest loyalty to. The number of electrons that feel primary loyalty to each nucleus is counted, and subtracted the number of protons in that nucleus. But there are shortcuts to make this faster using valence rules. For example, in CO_2, oxygen has a normal valence of 2. This means that it can accept 2 extra citizen electrons per nucleus, so it has an oxidation number of -2. Therefore, because there are 2 O nuclei, carbon loses 4 citizen electrons, who transfer their primary loyalty to O. Thus, carbon has an oxidation number of +4, because it has 4 fewer truly loyal electrons than protons.

How to count oxidation states:

- In elemental form, all nuclei have oxidations number 0
- In single-nucleus ions, the oxidation number is the charge
- Alkali nuclei always have an oxidation number of +1, unless in metallic form
- Alkaline earth nuclei always have an oxidation number of +2, unless in metallic form
- Oxygen nearly always has an oxidation number of -2, unless it is in an O-O unit like peroxide

- Non-metals have negative oxidation numbers when bound to metals and positive oxidation numbers when bound to O or F.
- Halogens have oxidation number of -1 unless bound to O or F. F is always -1 unless in elemental form.
- The sum of all the oxidation numbers of a molecule or ion is its overall charge (0 if neutral, +2 if a dipositive cation, etc)

Types of Redox Reactions

Oxidation refers to a process in which something loses electrons, and has its oxidation number increase. This usually happens to compounds that react with oxygen gas, which is why it is called oxidation. **Reduction** refers to a process in which something gains electrons, and its oxidation number is reduced. Actually this is not quite where the word came from. When a metal oxide is reduced to the elemental metal and an elemental non-metal or non-metal compound, the mass of solid decreases because the non-metal usually leaves as a gas. This reduction in quantity is where the word comes from. When you think about it, for one thing to be oxidized, another thing must be reduced (because electrons can't appear out of nowhere), which is why we often use the combination word redox.

An example of a redox reaction with the oxidation numbers above their respective elements (i.e. Mn in MnO_2 has an oxidation number of +4).

Many of the reaction types we've already seen involve redox. For instance, combination of elements is a redox reaction. Decomposition reactions are often redox reactions. Combustion reactions are redox reactions. (Dissolution/precipitation and acid-base are not redox reactions.) The examples of redox you've already seen involve electrons shifting loyalty at the same time that new bonds are made between nuclei. It's also possible for electrons to abandon one nucleus for another separate nucleus that isn't bonded to the first one. For example, if an elemental metal is placed in a solution of salt or acid, the metal can lose some electrons to the cation in the solution. The metal forms cations, and the former cation usually leaves the solution, forming hydrogen gas or elemental metal. Here are some examples:

$$Zn(s) + 2HBr(aq) \rightarrow ZnBr_2(aq) + H_2(g) \tag{1}$$

$$Fe(s) + Pb(NO_3)_2(aq) \rightarrow Fe(NO_3)_2(aq) + Pb(s) \tag{2}$$

All that happened in these reactions is that the disloyal electrons left a less-comfortable home country for a more comfortable one. These are called **displacement reactions** because one cation is displaced (replaced) by another. To predict what reactions will occur on this pattern, you can use the **activity series**, which is [illegible] ranking of "worst places to live". It's pretty good for making predictions, because in general electrons will move to places [illegible]er on the list, but it doesn't take into account all the specific circumstances, like current population pressures. You'll learn more reliable ways to make predictions later. The activity series is:

1. Worst place to live/easiest to oxidize: the alkali and alkaline earth metals
2. Bad: the active metals, aluminum, zinc, iron, and others from the middle of the transition metals
3. Better: tin, lead, hydrogen from acid, copper
4. Best place to live, hardest to oxidize: the noble metals, silver, mercury, platinum, gold

Copper metal doesn't react with acid, because copper comes after hydrogen in the list. However, some acids have other oxidants in them that are stronger than hydrogen ions. For instance, nitrate ions are oxidizing, and Cu will react with nitric acid. Even gold reacts with a concentrated acid mixture, aqua regia, made of nitric and hydrochloric acids.

Contributors and Attributions

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Solubility and Precipitation

Skills to Develop

- Describe what occurs in a precipitation reaction

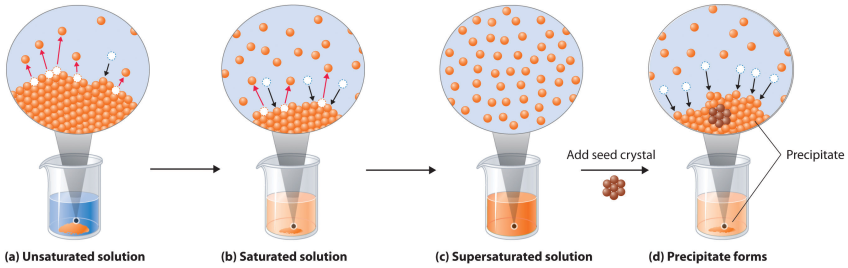
Precipitation is the process of a compound coming out of solution. It is the opposite of dissolution or solvation. In dissolution, the solute particles separate from each other and are surrounded by solvent molecules. In precipitation, the solute particles find each other and form a solid together. This solid is called the precipitate or sometimes abbreviated "ppt".

Solubility Equilibria

Precipitation and dissolution are a great example of a dynamic equilibrium (also described here). Any time there is a solution with a little bit of solid solute in it, both processes will be happening at once. Some molecules or ions will leave the solid and become solvated, and some solvated solute particles will bump into the solid and get stuck there. The rates of the 2 processes determine the overall effect: if precipitation happens faster, then a lot of solid can come out of the solution very quickly. If dissolution happens faster, than the solid will dissolve. As the solution becomes more concentrated, the rate of precipitation will increase and the rate of dissolution will decrease, so that eventually the concentration will stop changing, and this is equilibrium. When equilibrium is reached, the solution is **saturated**, and that concentration defines the **solubility** of the solute. Solubility is the maximum possible concentration, and it is given in M, g/L, or other units. Solubility changes with temperature, so if you look up solubility data it will specify the temperature.

Precipitation Reactions

Precipitation can happen for various reasons, such as that you cooled a solution, or removed some solvent by evaporation, or both. (This is often used as a way to purify a compound.) You can also have a precipitation reaction, when you mix two solutions together and a new combination of ions is **super-saturated** in the combined solution. For example, maybe you mixed a solution of silver(I) nitrate and sodium chloride. Silver(I) chloride is very insoluble, so it will precipitate, leaving soluble sodium nitrate in solution. Precipitation reactions can be a good way to prepare a salt you want from some other salts with the right anion and cation. Precipitation reactions can also be used to detect the presence of particular ions in solution. For instance, you might test for chloride, iodide and bromide in an unknown solution by adding silver(I) ions and looking for precipitation.



(a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

Predicting Precipitation Reactions

Beginning chemistry students usually memorize a list of solubility rules. Here it is (these rules will be a little bit different in different textbooks, because people might not have exactly the same definition of soluble or insoluble):

- Most nitrate and acetate salts are soluble

- Most alkali cation and ammonium salts are soluble
- Most chloride, bromide and iodide salts are soluble, except those of Ag(I), Pb(II) and Hg(I)
- Most sulfate salts are soluble, except those of barium, calcium and Pb(II)
- Most hydroxide salts are only slightly soluble, except those of sodium and potassium
- Most sulfide, carbonate and phosphate salts are only slightly soluble

You can use this list to predict when precipitation reactions will occur. For this purpose, you don't usually have to worry about whether the compounds are strong or weak electrolytes, you can think of the ions as being separate. The reason is that usually some of the ions will be separate, and once those precipitate with a new partner, more of the original compound ions will separate from each other, and the process will continue.

Writing Equations for Precipitation Reactions

Chemists may write equations in different ways to emphasize the important parts. For instance, we might write an equation like this, which describes mixing 2 solutions of different soluble salts and getting a precipitate:

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq) \tag{1}$$

Alternately, we might write the same reaction just focusing on the part that forms the precipitate, and leaving out the **spectator ions** that don't really do anything, just stay in solution:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \tag{2}$$

Chemistry students are sometimes asked to prove their understanding of dissociation by writing out all the ions separately, like this:

$$Ag^+(aq) + NO_3^-(aq) + Cl^-(aq) + Na^+ \rightarrow AgCl(s) + Na^+ + NO_3^-(aq) \tag{3}$$

No real chemist would be likely to do this because it is a nuisance. (It's also a little funny because many salts aren't strong electrolytes, so teachers might be telling their students to write an equation that doesn't show what's really happening.) However, it does help show what it means to be a spectator ion, since they are the same on both sides when you write it like this.

What Determines Solubility?

Solubility depends on the relative stability of the solid and solvated states for a particular compound. For instance, if it has very strong interactions between molecules or ions in the solid state, then it won't be very soluble unless the solvation interations are also very strong. (Ionic salts are a good example: usually they have strong interactions in the solid and solvated states.) If the interactions in the solid are weak, the compound can still be insoluble in polar solvents if the interactions with the solvent are weaker than the Coulomb interactions of the solvent molecules with other solvent molecules. (This is why wax is insoluble in water: it is non-polar, so the wax-wax interactions are weak, but the wax-water interactions are weaker than the water-water interactions.) We can't explain what makes these interactions strong or weak well until after we study chemical bonding, but in general ionic compounds with larger charges on the ions and smaller ions are less soluble, because they can have stronger Coulomb interactions in the solid.

Outside Links

- Solubility Explained (13 min)
- CrashCourse Chemistry: Precipitation (12 min)

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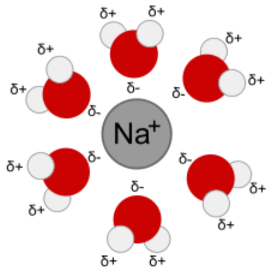
Solutions, Solvation, and Dissociation

Skills to Develop

- Describe factors affecting dissolution

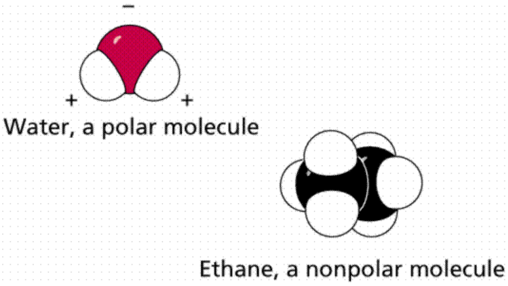
Dissolution means the process of dissolving or forming a **solution**. When dissolution happens, the **solute** separates into ions or molecules, and each ion or molecule is surrounded by molecules of **solvent**. The interactions between the solute particles and the solvent molecules is called **solvation**. A solvated ion or molecule is surrounded by solvent.



A sodium ion solvated by water, from Wikimedia Commons.

Technically a solvent can mean anything that is the more abundant component of a homogeneous mixture, but usually it means a volatile liquid that things can easily dissolve in. (Volatile means that it can easily evaporate, like water or alcohol.) The most common solvent is water. When you scuba dive in the ocean, you will need to rinse your gear with water afterwards to remove the salt. The salt dissolves in the water, gets washed away, and then the water evaporates, leaving the gear clean. This is the typical action of a solvent.

Solvents are either polar or non-polar. A **polar solvent** has partial negative and positive charges. For instance, water has a partial negative charge on O and a partial positive charge on H. The symbol δ means a partial charge, less than the charge on one proton or electron, such as δ+ or δ–. This helps the solvent interact with (solvate) ions and polar molecules through Coulomb interactions. A **non-polar solvent** is one that is electrically neutral all over, or almost so. Oil, or the gas in your car, are examples of non-polar liquids that could be used as solvents. Non-polar solvents are only good for dissolving non-polar solutes, which is why water, salt and sugar don't mix into oil.



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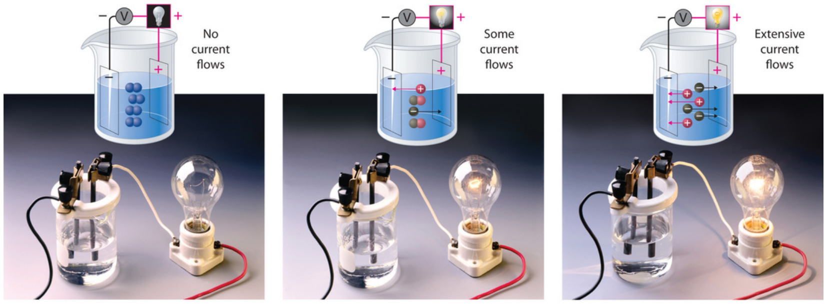
The Wild Ionists

Skills to Develop

- Discuss the significance of electrolytes and osmosis

Faraday proved that pure water doesn't conduct electricity, but conductivity increases when some types of solutes are added. These solutes are called **electrolytes**. For a long time, people thought that the ions that let water conduct electricity (to conduct, charged particles must move, such as electrons through a metal wire or ions through solution) were formed by the electricity.

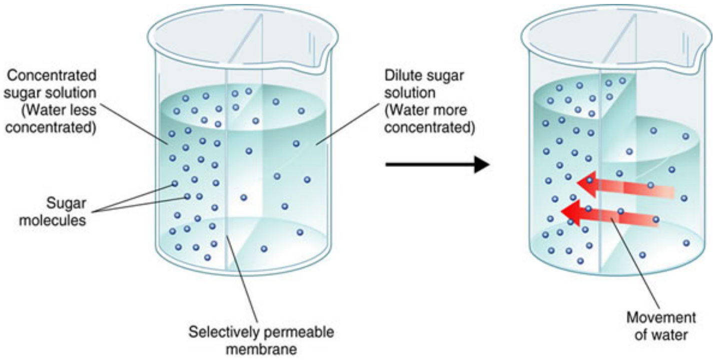
Svante Arrhenius was the son of a minor university employee in Sweden. For his doctoral research, he wanted to study whether molecular weights of compounds could be measured using the conductivity of their solutions (a subject his adviser told him not to work on—he often ignored his advisers' advice). To do this, he needed to understand how the conductivity of electrolyte solutions depends on concentration, but he found that his data were unexpectedly confusing. Wisely, he realized that explaining the conductivities would actually be more interesting and useful than his original plan to measure molecular weights. He found that the electrolytes fell into 2 types: strong and weak. **Strong electrolytes** (like salt and HCl) easily conduct electricity, and their conductivity is proportional to the concentration. **Weak electrolytes** (like vinegar and ammonia) conduct electricity much less, but their conductivity is not directly proportional to concentration. As concentration decreases, conductivity does too, but conductivity/mass of solute increases. He proposed that electrolytes had an active state (that conducts) and an inactive state (that doesn't conduct electricity); strong electrolytes were entirely in the active state, while weak electrolytes would have some molecules in the active state and some in the inactive state. As a weak electrolyte solution was diluted, the % of molecules in the active state would increase toward 100%. But this was vague, and his advisers didn't like it and gave him a very low grade. Because the grade was so low, he had to travel and do research without pay in other labs for many years to establish himself, instead of becoming a professor himself.



(a) Nonelectrolyte (b) Weak electrolyte (c) Strong electrolyte

A demonstration of the electrolytes' electrical conductivity based on their strength.

Arrhenius travelled and met other scientists. A professor named Ostwald helped introduce him. He became friends with Nernst (who would later do some important work on thermodynamics and electrochemistry). Nernst was a wild young man who thought about becoming an actor, had scars from fighting, and often got very drunk. He also began to correspond (write letters) with van't Hoff, whom we mentioned earlier. Van't Hoff had moved on from carbon chemistry and was studying osmosis. **Osmosis** occurs when water moves across a membrane (like the membrane of a biological cell) to go from a dilute solution on one side to a concentrated solution on the other. This can create a pressure difference. This is how some antibiotics kill bacteria: the bacteria explode from the pressure because the solution outside the cell is more dilute than the solution inside the cell. Van't Hoff found that the osmotic pressure depends on the concentration of the solutions, but for electrolytes, there's an extra "fudge factor"; the concentration seems higher than expected. It appeared that the electrolytes were breaking into pieces, and these pieces increases the apparent concentration of the solution when determining osmotic pressure. Arrhenius noticed that the "fudge factor" in Van't Hoff's data was related to the fractions in Arrhenius' active states.



An illustration of osmosis.

At this time, electrons hadn't been discovered yet. People thought that ions form in solution only when electricity is passed through. However, Arrhenius realized that electrolytes must be splitting into charged pieces (ions) when they dissolved, even without electricity, because these charged pieces affected van't Hoff's osmotic pressure measurements. The idea that salt, which forms so eagerly from the elements, would split up completely in water, seemed crazy to most scientists. (Now, we know that splitting into ions vs splitting into atoms is very different!) But Ostwald, Nernst and van't Hoff agreed with Arrhenius, and they were called "the wild army of the Ionists". They convinced other chemists pretty quickly that this new theory of ionization was correct.

Acknowledgement

This discussion was inspired by first chapter of the book *Cathedrals of Science* by Patrick Coffey.

Outside Link

- CrashCourse Chemistry: Water and Solutions (13 min)

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CHAPTER OVERVIEW

Chemistry Basics

Topic hierarchy

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Alchemy

Skills to Develop

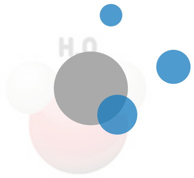
- Distinguish physical properties from chemical properties
- Understand the difference between homogeneous and heterogeneous mixtures

If everything is made of the same 4 elements in different ratios, perhaps you can adjust the ratios of elements through various processes and change one material into another. This was called **transmutation**. In particular, people wanted to change inexpensive metals into gold.

There were known examples of one material turning into another. For instance, there's a reddish mineral called cinnabar, and if you heat it, you get silvery liquid mercury. Oddly, if you heat it again, you get another red solid. We'll explain that in chemical terms soon (it's a chemical change!) but it looked like a proof of principle for transmutation, with one substance becoming another.

Also, some people claimed to be able to make gold. The problem here was that they weren't distinguishing between a **pure substance** and a **mixture**. A pure substance is composed of a single type of molecule. Gold (theoretically) is a pure substance: not just a pure substance, but a pure element. However, you can make compounds that look a little like gold, that are yellow and shiny, by mixing different metals, such as copper and tin. We call that a mixture (or more specifically an alloy, which is a mixture of metals).

A **compound** is a substance that contains multiple elements. Water is a compound of hydrogen and oxygen. However, water is a pure substance, because each molecule of water is the same. Air is a mixture, not a pure substance, because it contains different types of molecules, some of which are compounds, like carbon dioxide, which is a compound of carbon and oxygen. The difference between a compound and a mixture is that in a compound you always have the same ratio of the elements: in carbon dioxide, the ratio is there in the name: one carbon atom, two (di) oxygen atoms. Carbon dioxide is CO_2. In a mixture, the ratio can vary. Air contains nitrogen (N_2) and oxygen (O_2) molecules and many other components, and a sample from a lecture hall and a sample from a forest would probably have slightly different ratios.



Alchemists did not always distinguish between mixtures and pure compounds or elements, for instance gold vs bronze (an alloy of copper and tin). We can distinguish different materials by using the **properties** of the materials. Properties are things like what temperature it melts at, whether it dissolves in acid, and so on. We can distinguish **physical properties** and **chemical properties**. Melting point is a physical property, and solubility in acid is a chemical property.

Alchemists developed many of the techniques of chemistry that we still use. For instance, a **heterogeneous** mixture of a solid and a liquid, such as sugar in oil, could be separated by filtration. If you have a solution, like sugar in water, that is **homogeneous**, because all the sugar has dissolved, you can't filter it. Instead, you could let the water evaporate slowly until big crystals grow. (We call that rock candy in English.) This process is called **recrystallization**, and is used to purify solids. To purify liquids, you can use **distillation**, which is based on different boiling points: heat at a temperature where one component boils and the other doesn't, and collect the vapor. **Sublimation** is similar: some solids will vaporize with heat, and can then be recollected from the vapor on a cold surface, where they solidify.

Overall, alchemists were sometimes excellent experimentalists, and they definitely spent time "in the lab." However, their explanations and reasons for beliefs may seem strange from a modern perspective. For instance, if a theory had parallels to Christian religious events, that might be considered evidence that it was correct. The other "unscientific" thing about their practice was that they often reported results in a way that was intended to confuse the reader, if they reported the results at all, and they often looked to ancient texts as an authority, even when there was no evidence that the authors had accomplished anything. Finally, the goals they chose were very ambitious, so instead of trying to look at the simplest questions first, to get clear answers, they used many complicated procedures and got results that are hard to explain even now.

Summary

Transmutation involves changing one material into another by adjusting the ratios of elements through various processes. A **pure substance** has a chemical composition of only one type of molecule .A **compound** is a substance that contains 2 or more types of atoms chemically bonded together. **Mixtures** have two or more substances physically combined, meaning that each component retains its chemical composition and properties. The components of a **heterogeneous** mixture are not uniformly combined while the components of a **homogeneous** mixture are. A substance's **physical properties** can be observed without changing its chemical composition (i.e. color, volume, melting point) while its **chemical properties** are observed through chemical changes (i.e. burning, rusting).

Outside Link

- MissBettsChem: Homogeneous and Heterogeneous Mixtures (8 min)

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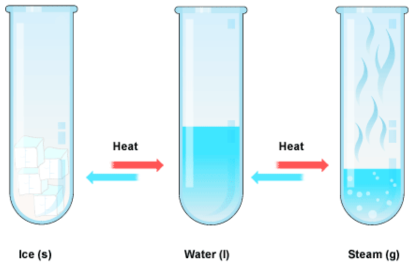
Ancient History

Skills to Develop

- Distinguish physical changes from chemical changes
- Identify the three states of matter and their respective properties
- Understand some of the history behind identifying the three states of matter
- Define matter and its components (i.e. mass, weight, volume)

Humanity's first chemical knowledge was mostly **technology**, like metal working, ceramics, cooking, etc. Early civilizations learned to control fire, to cast metals and make alloys, to make glass and ceramics, and so forth. The first chemical thinking, as opposed to chemical applications, asked: What is **matter**? Matter is stuff. It's what we are made of, what the earth and the air are made of. Matter is anything that has mass... what is **mass**? It's the amount of stuff. Not how much space it occupies (that's **volume**) but how much stuff is there. We measure mass using **weight**, which is how strongly the stuff in question is attracted to the earth by gravity.

What is matter made of? Well, one philosopher of ancient Greece proposed that all matter is made of *water*. He observed that water can "become air" by **evaporation**, or become solid by freezing into ice. He reasoned therefore that water can convert into everything, and matter is made of water. Now, we call those changes **physical changes**. The water is still water when it boils and turns into steam. The water is still water when it freezes into ice. We changed its *temperature*, not its nature.



Physical Changes of Water

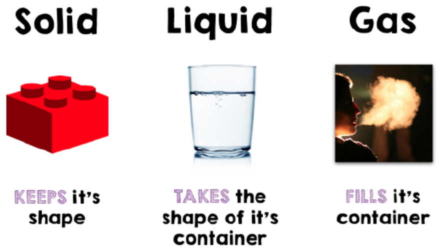
Another Greek philosopher said that everything was made of *air*: when air becomes less compressed, it becomes fire, and when more compressed, it turns into water, stones, and so forth. He offered the proof that when you breathe through open lips, the air is warm, and when you compress it by breathing through puckered lips, it's cold, and condenses into liquid or solid. Air turning into stone would be a **chemical change**, in modern terms. In terms of Dalton's Atomic Theory, a chemical change means that the atoms form new combinations, like one atom of A combining with an atom of B. Before A and B were separate, but now they are attached. That's a chemical change.

Others proposed 5 elements, with distinct shapes: **octahedra**, **tetrahedra**, **cubes**, etc. For a long while, the four element model (earth, air, fire, water) was popular. (In Greece it was proposed by a man who was asked to become king of his city, but created a democracy instead. Then he declared himself a god and jumped into a volcano. It's said that the volcano tossed back his sandals to prove he wasn't a god.) This model, which Plato and Aristotle also used, suggested that all matter was composed of these four elements in different ratios. For instance, when wood is burned, you get smoke (air), ash (earth), pitch (a viscous liquid, here identified with water), and fire, so wood is made of all these things. Wood burning is a great example of a chemical change.

From a modern perspective, in all these theories an important element was lacking: experimentation. The Greeks preferred thinking to trying things, and you might say that it shows in their theories. For them, the fundamental difference was what we now call the **state of matter** or the **phase of matter**. **Solid**, **liquid** and **gas** are the three main states of matter.

- Ice, wood and stone are all solids
- Water is a liquid, like oil
- Air is a gas, like steam, and like the gas that you use in a stove

The three states are fundamentally different in nature. Gases take up as much space as they can, in whatever shape they can: the molecules are far apart, and try to spread out. Liquids change shape but have a constant volume. Solids have a constant shape and volume. Now we know that you can change the state of matter just by changing the temperature and pressure, and the molecules stay the same. So the wrong theories of the Greeks were based on not recognizing the difference between physical changes, which are changes in the state of matter, and chemical changes, changes in the combination of atoms.



Summary

Matter is anything that has volume and mass. **Mass** is the amount of matter in a substance. **Physical changes** involve processes that change the form of a substance but not its chemical composition. **Chemical changes** involves processes in which a new substances are formed with new chemical compositions. **Weight** is the force resulting from a mass being pulled towards a particular location as a result of gravity. The three **states of matter** are: solid, liquid, and gas. A **solid** is an object with a fixed shape and volume. **Liquids** are fluids have a constant volume but are capable of changing their shape. **Gases** are fluids that do not have constant shape or volume so they take up as much space as they can within a given container.

Contributors and Attributions

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Atomic Structure

Skills to Develop

- Define the sub-atomic particles making up an atom
- Distinguish isotopes from typical atoms of an element
- Identify the atomic mass and mass number of an element
- Understand how to utilize units such as coulombs, atomic mass units, and angstroms

Atoms of an element are not all identical and indivisible as Dalton said. They are made of three mains types of particles.

Particle	Mass (amu)	Charge
Electrons	5.5×10^{-4}	Negative (1–)
Protons	1.0073	Positive (1+)
Neutrons	1.0087	Neutral

The protons and neutrons together form a very small dense center of the atom, called a **nucleus**. The nucleus contains all the mass of the atom except the small mass of electrons. The electrons move around the nucleus, and occupy a much bigger space than the nucleus, so that most of the atom is empty space.

An element is defined by the number of protons, or atomic number, which is equal to the number of electrons in the neutral element. Atoms of an element can have different numbers of neutrons, resulting in different masses. **Isotopes** are atoms that have the same number of protons, but different numbers of neutrons. Chemical properties depend mostly on the atomic number, so isotopes are nearly the same chemically. The **atomic mass** is the average mass of the atom, including all the different isotopes that are likely to be present. If you want to show what isotope of an element you can use special notation, like this: ^{12}C. This is read as carbon-12. The 12 is the **mass number**, or the number of protons + neutrons. Since carbon always has 6 protons, ^{12}C must have 6 neutrons also.

We use some very small units to describe atoms. For instance, the charge of a proton or electron (which we will use as the unit of charge) is 1.602×10^{-19} coulombs (C). The atomic mass unit, or amu, is 1.661×10^{-24} g. Sizes of atoms are usually measured in angstroms or Å, which is 1×10^{-10} m. The diameter of most atoms is 1-5 Å. The diameter of nuclei is roughly 10^{-4} Å. Electrons are smaller than nuclei, so most of the atom is empty.

Outside Links

- Khan Academy "Elements and Atoms" (13 min)
- CrashCourse Chemistry 1: The Nucleus (10 min)

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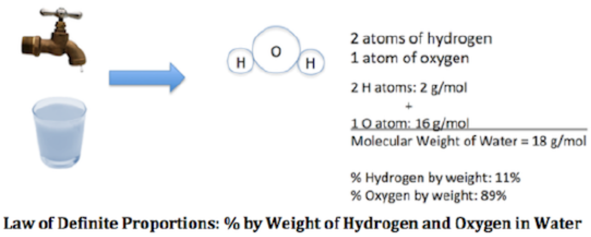
Atomic Theory

Skills to Develop

- Describe the law of conservation of mass, the law of definite proportions, and the law of multiple proportions
- Describe Dalton's atomic theory

The **law of conservation of mass** was established by Lavoisier, although others had used it before. It said that in any chemical reaction, the total mass of products is the same as the total mass of reactants. No matter is created or destroyed during the reaction.

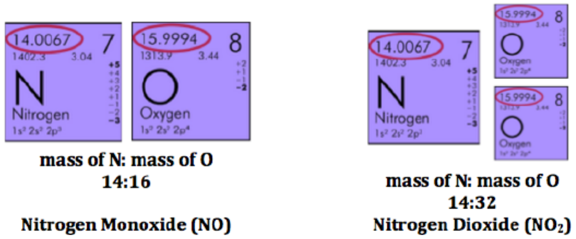
There was a debate over whether elements always combine in exactly the same ratio, which is called **composition**. It was well known that the elemental ratios in many materials are approximately constant. Water is made by burning hydrogen in oxygen. The composition is about 11.1% hydrogen and 88.9% oxygen, by mass. The oxides of metals also generally have consistent compositions. For instance, mercuric oxide is 92.6% mercury, and mercurous oxide is 96.2% mercury; no bigger or smaller ratios were known. Berthollet, a respected scientist, argued that the consistent ratios observed arise from the conditions of the experiment; for instance, the most insoluble or volatile composition will be preferentially produced because it removes itself from the reaction. In the absence of such influences, he believed the ratios could vary continuously.



The law of definite proportions illustrates how a specific compound has a constant mass ratio of elements, or a fixed composition.

Another scientist, Proust, said that the proportions were always the same, and eventually persuaded Berthollet of the **law of definite proportions**. Proust was more careful to study only pure compounds, and knew how precise his measurements were, so that even though the exact numbers didn't always come out the same, once he rounded to the correct number of significant figures, the ratios were the same, no matter how the material was prepared. Review the difference between accuracy and precision on the previous page (Lavoisier), and how to use the correct number of significant figures. (Some types of materials, like minerals or alloys, can have variable proportions; Berthollet was also right that in solution compositions might be possible that were not observed in the isolated substances. Berthollet's arguments on composition were inspired by his correct understanding of chemical equilibrium, but because he was wrong about definite proportions for pure compounds, this contribution to scientific knowledge was not recognized for a long time.)

Studying the data of people like Proust and Lavoisier, Dalton noticed a remarkable pattern. Carbon and nitrogen both combine with oxygen in several different definite ratios to form several different products. Likewise sulfur and phosphorus, which is why there are sulfates and sulfites. For example, carbon combines with oxygen in the ratios of 3:4 and 3:8 (3g carbon for each 4g of oxygen). Of course, 2 x 4 = 8. One compound had exactly twice as much oxygen as the other. Nitrogen combines with oxygen in ratios of 7:4, 7:8, and 7:16. In each case, the amount of oxygen doubles. This is called the **law of multiple proportions**.



The law of multiple proportions utilizes two or more compounds with the same elements in different proportions to show how the elements are combined in small whole-number ratios.

These laws all made good sense if each element has atoms that combine as whole atoms. An **atom** is a very small, distinct thing, like a ball. Now we know that atoms can be divided into smaller parts, but an atom is the smallest amount of an element you can have, because if you divide it into smaller parts, the properties will change.

The Atomic Theory

John Dalton's atomic theory:

- Matter is composed of atoms
- Atoms come in different types, called elements
- Atoms of each element have a distinct mass
- Each atom of a given element is identical to every other atom of that element
- Atoms are not created, destroyed or changed when chemical changes occur

In more modern terminology, we say that atoms of different elements are combined to make molecules. Chemical reactions change how the atoms are combined, but the number of each type of atom doesn't change.

Outside Link

- CrashCourse Chemistry: The Fundamental Law (11 min)

Contributors and Attributions

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Discovering Sub-atomic Particles

Skills to Develop

- Describe the three types of radioactivity
- Understand the difference between atoms. ions, and isotopes
- Define the subatomic particles that make up atoms

At the end of the last section (Valence), we mentioned the problem of the masses of iodine and tellurium, which were "out of order" in the periodic table. This was only one of several problems facing chemists at this point. Another was the **rare earth elements** (the lanthanoides and actinoides, at the bottom of the periodic table). The rare earth elements were extremely similar to each other, so it was very hard to separate them, determine the masses, and fit them into the periodic table.

Another problem was **ions**. Ions were charged chemical entities that moved through solutions carrying electric current when electricity was applied. Chemists knew they existed, but could not explain how they formed. Cations were positively charged, while anions were negatively charged. Hydrogen was known to form positive ions with a particular charge. But where did the charges come from? Berzelius had thought that the atoms themselves were charged, but this didn't make sense after Avogadro's hypothesis was accepted, since in that case the two O atoms in O_2 would repel each other, not form a molecule. Of course, this was mostly a problem to physical chemists, because physicists mostly still didn't believe in atoms.

Experiments by Davy, Faraday and others showed that solids usually conduct electricity without changing themselves; liquids are decomposed by electrical current, and gases conduct badly and only at high voltage, but become better conductors at low pressure. Glass tubes of low pressure gas glow; examples include neon lights in store windows, fluorescent light bulbs, and yellow sodium lamps sometimes used at street lights. When glass tubes full of very low pressure gas were made by expert glassblower Geissler after 1850, a glowing spot would appear somewhere on the glass when the tube was connected to a high voltage. This spot could be moved by a magnet, suggesting that it was negatively charged. A beam or ray was coming out of the cathode (the electrode to which cations move), and this beam caused the glass to glow. (This is exactly how old TVs work, from before there were flat screens.)

A cathode-ray TV and its components

But what was the beam that came out of the cathode? Some thought it was negatively-charged particles, while others (especially physicists) thought it was a wave. Thomson convinced himself that the beam is a negatively charged particle, which can be moved using electric or magnetic fields. He estimated that the particle has a charge/mass ratio 1000x greater than the hydrogen ion, but with the opposite charge. The ray that comes out of the cathode is the same whatever the material, and he found that you can generate the same particle by heating metal filaments very hot or exposing a metal surface to UV light (the light that gives you sunburns).

What are cathode rays? **Electrons**! When Thomson suggested in 1897 that either they had a much higher charge or a much smaller mass than hydrogen ions, many people were skeptical. However, careful measurements by Millikan (starting 1908, continuing for almost 10 years!) of falling droplets of mist in an electric or magnetic field revealed that electrons have the same charge as hydrogen ions, but are almost ~1/2000 less massive, so in fact Thomson guessed electrons were twice as big as they really are.

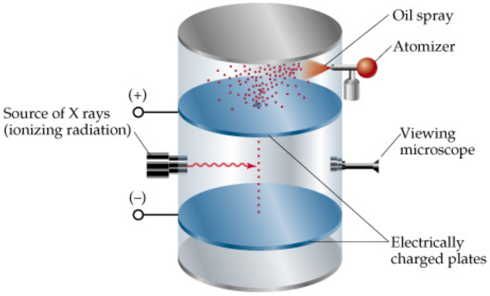


Diagram of the apparatus in the Millikan oil-drop experiment

In summary, electrons have an equal but opposite charge to hydrogen ions, but hydrogen ions weigh 2000x more than electrons. Electrons are part of every kind of atom.

Other than electrons, what are atoms made of? X-rays were discovered in 1895 when Roentgen noticed a ray that passed through the glass of his cathode ray tube and developed photographic film placed in its path, even if it was wrapped in dark paper. Inspired by this discovery, Becquerel studied the fluorescence (this means glowing after being exposed to light) of minerals and whether this could develop film through dark paper. He used sunlight to make the minerals fluoresce, but discovered that some minerals fluoresce even without sunlight. Minerals that contain the elements uranium and thorium have this property, which is called **radioactivity**. Three types of radioactivity were discovered, α (positive charge), β (electrons, same as cathode rays) and γ (light, similar to x-rays). This radiation is a property of the element, and is not changed by chemical combinations. It was also discovered that radioactive elements decay into products that closely resemble known elements, except that the masses are different. These decay products have exactly the same chemical properties as the known elements, and once mixed together, they can't be separated by chemical means. But the masses were different. The evidence against Dalton's "identical and indivisible atoms of each element" was getting strong.

Rutherford studied the α-radiation, and found that it had a positive charge, and an e/m (charge/mass) ratio 1/2 that of a hydrogen ion. Later he proved that it is a charged form of the element helium (He).

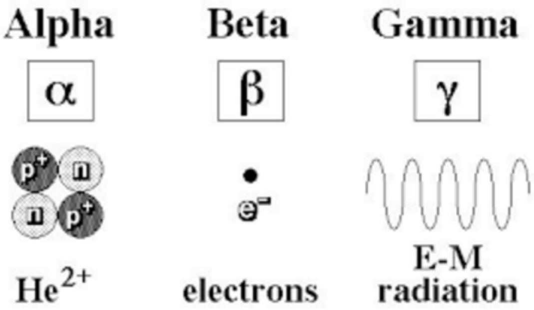


Illustration of the particles involved in alpha, beta, and gamma radiation.

Finally, using an early version of the mass spectrometer, which measures e/m by accelerating charged particles in an electric or magnetic field, Aston determined that neon (Ne) atoms have masses of 20 or 22, not 20.2, then the accepted value. Here's another case where knowing the precision of your experiment is important: if he couldn't tell the difference between 20.0 and 20.2, this wouldn't have been useful! The two versions of Ne are called **isotopes**. Isotopes are atoms of the same element with have the same chemical properties, but have different masses.

What is the structure of an atom? At this point, it was clear that Dalton had not been entirely correct, because atoms of one element could exist in different forms, or isotopes. It was also becoming clear that atoms could be divided into smaller parts, like electrons. But how were the electrons and the positive parts (like the part of He that is α-radiation) arranged, and what was the positive particle? It seemed like there was a lot of empty space in atoms, because cathode rays could pass through aluminum windows. Many theories were considered, but ultimately two of Rutherford's students, Geiger and Marsden, found an answer. They observed that α-rays directed at a thin gold (Au) foil usually passed through the foil (though not usually quite straight), but sometimes the foil knocked them back in the direction they came from. These α-particles must have bumped into (or been repelled by a large positive charge in) something very heavy, to have so large a change in direction. In 1911, Rutherford proposed that atoms consist of a small dense particle, the **nucleus**, which contains most of the atom's mass and all of its positive charge, with electrons moving through a large empty space around the nucleus. But they were a little confused about the mass and charge of the nucleus.

Diagram of the apparatus in the Rutherford gold-foil experiment

In 1913, a very young chemist named Henry Moseley measured the fluorescence wavelength produced when x-rays shine on pure elemental samples. He discovered that if you graph the square root of the fluorescence frequency vs the element's location in the periodic table (such as H, 1; C, 6; Hg, 80) you get a straight line. The location in the periodic table is called **atomic number**. This confirmed the ordering of Te/I in the periodic table and a few other similar problems. He was also able to determine where undiscovered elements were missing in the table, and clarify identification of rare earth elements, which was very difficult because they were so similar. He was 26 years old, and he died a year later in WWI. Moseley's work showed that the ordering of the periodic table is based on the atomic number, which is the number of positive charges in the nucleus and also the number of electrons. The unit of positive charge is a hydrogen nucleus, or **proton**.

The mass of the nucleus continued to be confusing even after the amount of positive charge had been determined by Moseley's atomic numbers. The atomic weights were about double what they should be if the nucleus held only protons. A proposal to explain this was that there were some electrons in the nucleus, canceling out the charge of half the protons. Later radiochemistry experiments showed the existence of the **neutron**, which has about the mass of a proton and no charge. This was understood to be the extra mass in nuclei. Now, though, we know that neutrons can decay into protons and electrons (and some other less familiar particles), so the earlier idea wasn't far off.

Summary

Atoms are composed of protons, neutrons, and electrons. Protons and neutrons make most of the atom's mass and all of its positive charge in the **nucleus**. **Protons** are subatomic particles that contain a positive charge. Essentially, they are hydrogen nuclei. **Neutrons** are subatomic particles that have the same mass as a proton but not charge. **Electrons** are subatomic particles with a negative charge that are found outside of the atom's nucleus. An element's **atomic number** provides its location on the periodic table as well as describe how many protons are in an atoms of that particular element. **Ions** are atoms that are either positively or negatively charged due to the number of protons or electrons in an atom not being equal to each other. **Isotopes** are atoms that have a different number of neutrons in the nucleus than normal. There are three main types of **radioactivity**: α , β, and γ. α (Alpha) radiation involves the emission of a helium nucleus, which is two protons and two neutrons. β (Beta) radiation involves the emission of an electron from the atom's nucleus. γ (Gamma) radiation involves the emission of high-energy electromagnetic radiation.

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Electricity and Electrochemistry

Skills to Develop

- Distinguish between static and current electricity
- Describe the electrostatic force and Coulomb's Law
- Define ionic compounds, an electrolyte, and the components of an electrolyte
- Describe electrolysis and Berzelius' dualistic theory

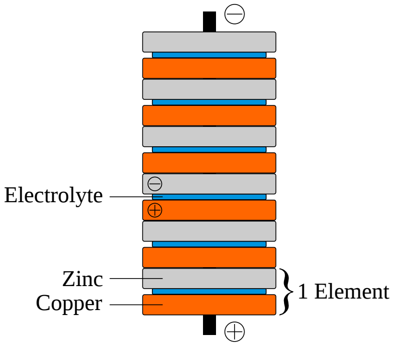
The earliest studies of electricity focused on electrostatics. **Static electricity** can be produced when certain materials are rubbed together, like silk or hair on some metals or plastics (this is called the **triboelectric effect**). This leads to a separation of **charge**, with positive charge on the silk or hair and negative charge on the metal or plastic. You've probably noticed how this can lead to things sticking to each other if they have opposite charges, and you can also observe that the same charges will repel each other. Benjamin Franklin (one of the few early American scientists) proposed that the positive and negative charges resulted from having either too much or too little of the same "electrical fluid".

The **electrostatic force** had been studied by many scientists, some of whom suggested that it followed a law similar to Newton's law for gravity, but Coulomb gets credit for this, because he did many experiments that improved understanding. In 1785, he published the law in its current form. The equation is:

$$F = \frac{kQq}{r^2} \tag{1}$$

where F is the force, k is a constant, Q and q are two charges, and r is the distance between Q and Q. Like charges (+/+ or -/-) repel and opposite charges (+/-) attract.

Current electricity, like the electricity used in any electrical device today, was discovered a little later. Galvani was studying physiology, and noticed that the legs of dead frogs twitched when in contact with two different metals. He attributed this to "animal electricity." Volta did many more experiments and discovered that animals were unnecessary for the effect. He put a piece of paper soaked in saltwater (the **electrolyte**, because it conducts electricity) between disks of two different metals, then connected the metals with wire and noticed that electrical current flowed. When he stacked these on top of each other, alternating the metals, the effect increased. This device for generating current came to be called a "voltaic pile."



A voltaic pile with the "electrolyte" being paper soaked in saltwater.

Volta published his pile reports in 1800. That same year, two English scientists published their results of splitting water into hydrogen and oxygen using a Voltaic pile. This is an example of **electrolysis**, which means using electricity to break chemical compounds.

Humphry Davy was a scientist and popular lecturer who had discovered "laughing gas" or nitrous oxide, which is still used by doctors and dentists. He did many electrochemical studies after 1800. He noticed that during electrolysis of various compounds, hydrogen, metals, or bases appear around the negative pole, and oxygen or acid appears around the positive pole. Based on this, he guessed he could use electricity to break chemical bonds. The strong bases KOH and NaOH (potassium hydroxide and sodium hydroxide) had been known for a long time. (A **base** neutralizes an **acid**.) Sodium and potassium were believed to be elements but had not been isolated. Davy was able to isolate them by melting and electrolyzing the solid sodium hydroxide and potassium hydroxide. The solid bases didn't conduct electricity, but once melted they did conduct, and then they separated into shiny metal and a gas.

K and Na are **alkali metals**. When Davy isolated them, he found that they were light, soft metals that react vigorously and spontaneously with water and air. So they have to be stored under oil. Davy also isolated magnesium, calcium, strontium, and barium (Mg, Ca, Sr, and Ba) using a slightly modified procedure involving mercury. These are the **alkaline earth metals**. They are also soft, light metals, but they are not quite as reactive as the alkali metals.

Berzelius was a very influential chemist who worked very hard and very carefully to determine atomic weights, without using Gay-Lussac's law or Avogadro's hypothesis, and whom we mentioned earlier because he introduced the idea of isomerism. He also did many electrochemical studies and took Davy's hypothesis, that chemical and electrical attraction are the same force, much farther. His **dualistic theory** said: elements have positive or negative polarity, and chemical reactions partially neutralize that polarity. For example:

$$Cu \text{ (positive)} + O \text{ (negative)} \rightarrow CuO \text{ (approximately neutral)}$$

He used the terms **electropositive** and **electronegative**, which are still used today with a somewhat different meaning. He thought oxygen was the most electronegative element, while metals were generally electropositive. He also considered the element polarity to be on a spectrum, so that sulfur, for instance, was positive with respect to oxygen and negative with respect to metals. Thus it could combine with both; this is very different from the modern understanding of Coulomb attraction because he did not have a clear sense of neutrality.

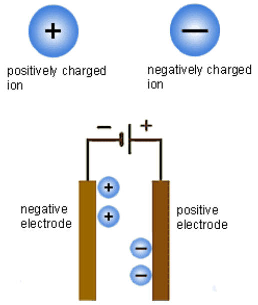
Ionic compounds are usually composed of a metal and a non-metal. For instance, salt, and many rocks, are ionic compounds. They are different from molecular compounds because they do not have distinct molecules that vaporize as a unit. They are held together by charges, not quite as Berzelius thought, but close enough that his theory worked all right for them.

Table salt (NaCl)

However, Berzelius' theory did not work well for molecular compounds! He said Avogadro must be wrong because two oxygen (O) atoms would have the same polarity and thus repel each other. Now we know that chemical bonding is more complicated than Berzelius realized. O atoms don't repel each other, and do form a diatomic molecule.

Berzelius' theory delayed the progress of science for about 50 years because he didn't believe Avogadro's hypothesis, which was needed for the next big breakthrough in chemistry.

Faraday was born to a poor family, and discovered chemistry when working in a book-making shop, where we worked on Jane Marcet's Conversations on Chemistry (one of the most popular textbooks at the time, it is surprising that it was written by a woman). He became Davy's assistant, and became a great experimentalist. He helped invent the words used for electrochemistry, such as ion, anion, cation, electrolyte and electrolysis. At that time, **anion** and **cation** meant the parts of the electrolyte (the salt used to make water conductive) that appeared at each electrode. Faraday studied the amount of current necessary to produce an amount of an electrolysis product. For instance, the current that produced 1g of hydrogen produced 8g of oxygen, 36g of chlorine, 125g of iodine, 104g of lead or 58g of tin. Faraday called the O, Cl and I anions, meaning that they were produced at the positive pole, and Sn and Pb cations, meaning that they were produced at the negative pole. These numbers could have solved the atomic weights problem, just like Avogadro's hypothesis, but Faraday wasn't interested in atomic weights or theories, and Berzelius, who was, didn't believe Faraday's electrical laws, just like he didn't believe Avogadro's hypothesis.



Outside Link

- Khan Academy: Electrostatics (Part 1) (14 min)

Contributors and Attributions

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Gay-Lussac's Law

Skills to Develop

- Describe Gay-Lussac's Law and Avogadro's hypothesis

Dalton's atomic theory led to a new question: if each element has atoms with a characteristic mass, what are those masses? If water is 88.9% O, 11.1% H, what is the atomic mass of O in terms of H (if you assume H is 1.00)? To answer, you need the formula: H_2O (2 H atoms for 1 O atom) (11.1)/2 = 5.55 → (88.9)/5.55 = 16.0 (this is the atomic weight of O, assuming H is ~1)

But early chemists didn't know the formulas, because they didn't know the atomic weights! Dalton assumed that the simplest formula (example: HO) was right, but this was usually wrong! How could they figure out the formulas?

In 1808, Gay-Lussac published results that showed what volumes of gases combined with each other in chemical reactions. For instance (O is oxygen, H is hydrogen, N is nitrogen, L is liters):

- 2 L H + 1 L O → 2 L water (steam)
- 3 L H + 1 L N → 2 L ammonia (NH_3)
- 2 L "carbonic oxide" + 1 L O → 2 L "carbonic acid" (using the old names for the compounds)
- 1 L N + 1 L O → 2 L nitric oxide (NO)

Based on Gay-Lussac's Law, we can guess the following: equal volumes of gas at the same temperature (T) and pressure (P) have the same number of "particles".

Gay-Lussac's law describes how increasing the temperature of a gas with a fixed volume and a constant number of "particles" will result in a similar increase in the pressure of the gas, and vice versa. Likewise, decreasing the temperature will decrease the pressure of the gas and vice versa.

What are these "particles?" Many of them are **molecules**, strongly-bonded collection of atoms. Molecules usually remain intact when vaporized into the gas phase. Molecular compounds (compounds containing molecules, as compared to ionic compounds discussed later) are usually made of non-metal elements such as C, O, S, P, H, Cl, etc.

How was Gay-Lussac's law received? Dalton didn't believe in it because the densities of the gases seem wrong. Oxygen gas is denser than steam (water gas), even though water is oxygen plus hydrogen. Also, Gay-Lussac didn't push the conclusions of his law as far as he could have because Berthollet (who believed that combining ratios of elements could vary) was his mentor.

In 1811, Avogadro explained the problems with Gay-Lussac's law by saying that equal volumes of gases (at the same T and P) have the same number of molecules. The elemental gases were present not as single atoms but as diatomic molecules (such as H_2, O_2, N_2). Now the equations from Gay-Lussac's law are:

- 2 L H_2 + 1 L O_2 → 2 L H_2O
- 3 L H_2 + 1 L N_2 → 2 L NH_3
- 2 L CO + 1 L O_2 → 2 L CO_2
- 1 L N_2 + 1 L O_2 → 2 L NO

This resolves the issue of gas density (O_2 is denser than H_2O because H_2 weighs less than O). Avogadro's hypothesis could have cleared up all the confusion about formulas, and allowed good atomic weight calculations. But people either ignored him or said it was impossible.

Outside Link

- CrashCourse Chemistry: The Fundamental Law (11 min)

Contributors and Attributions

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Introduction

Skills to Develop

- Understand some of the historically fundamental aspects of chemistry

Chemistry is different from physics. The chemical theories that we use to understand and predict aren't written in math. They also aren't based on anything we can see directly, like a ball falling. Instead, they are based in images, patterns, symmetry and imagination. How do we know what metaphors we can use to imagine, and predict accurately, things that we can't see? When you think about it, it's amazing how much chemists were able to figure out.

John Dalton proposed his **atomic theory** around 1805. He said:

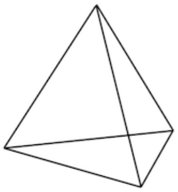
1. All **matter** is composed of **atoms**
2. Atoms come in different types, called **elements**
3. Atoms of each element have a distinct **mass**
4. Each atom of a given element is identical to every other atom of that element
5. Atoms are not created, destroyed or changed when chemical changes occur

Scientists scoffed, laughed at him, or at least remained skeptical, for at least 50 years after that, because how could he know? But he was almost completely right.

A little later, in 1830, Jons Jacob Berzelius proposed that even if you have the same **composition** (the same number of atoms of each element) you can have two different **molecules** (a combination of atoms), because the atoms are arranged differently. The first example discovered was silver fulminate (AgCNO, very explosive) and silver cyanate (AgOCN, a non-explosive grayish powder).

And then in 1874 Jacobus H proposed that when carbon atoms form bonds to four other atoms, those other atoms around them have a particular arrangement **dron**. A critic said:

"A Dr. J. H. van't Hoff who is eterinary School in Utrecht appears to find exact chemical research unsuited to his tastes. He finds it more suitable to mount Pegas ed from the Veterinary School) and to proclaim ... how, during his flight to the top of the chemical Parnassus, the atoms appeare n the universe." (In ancient Greek mythology, Pegasus is a horse with wings, and Parnassus is a mountain associated with art and knowledge because the Muses were said to live there.)



A tetrahedron.

You can tell from that how weird it seemed, at the time, to claim a particular spatial arrangement of tiny particles that nobody had ever seen. But van't Hoff, like Dalton and Berzelius, was right. How did they manage this? That will be one of the questions we answer in this class.

In fact, before the physicists had admitted that atoms exist, before they had been proven directly, chemists had already published many **chemical structures** showing how atoms were arranged in molecules.

Summary

Chemistry is the study of the composition and structure of chemical substances and the changes that they undergo. An **element** is one type of atom. An **atom** is the smallest particle of an element that retains all of the element's properties. A **molecule** is a combination of atoms of the same element. A substance's chemical **composition** involves having a piece of the substance being made of the same number of atoms as well as the the same type(s) of atoms.

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Lavoisier

Skills to Develop

- Understand why Lavoisier is sometimes called "the Father of Modern Chemistry"
- Distinguish accuracy from precision

So what happened to turn alchemy, which was like magical potion-brewing in Harry Potter, into the science of chemistry? It was **measurement**. Careful, careful measurement of quantities, such as masses, volumes, densities, temperatures, pressures.

An early hero of measurement was Antoine Lavoisier. He was one of the first true chemical scientists. He conducted careful experiments, and tried to draw no conclusions except those required by his data. He said fact, idea, and word should be as closely connected as possible: that you can't improve your language without improving your thinking, and you can't improve your thinking without improving your language. So he pioneered a systematic chemical **nomenclature** that is essentially what we use today. Remarkably, if you read his text, written in 1789, intended to introduce chemistry to beginners, much of it is still perfectly understandable and even correct by modern standards.

Antoine Lavoisier

Lavoisier first describes the **states of matter**: gases, liquids and solids. He points out when a solid material is heated, it tends to expand, becoming first a liquid, which takes up a constant volume, but can be poured, unlike a solid. More heating, and it becomes a gas, which he describes as elastic because it will expand or compress to different volumes depending on the pressure. Unlike the Greek philosophers, he understood that this is a **physical change**, not a **chemical change**, and he has a good submicroscopic-scale intuition of what's happening: the particles of the material don't change, they just get further apart.

He recognized the following as elements: oxygen, nitrogen, hydrogen, sulfur, phosphorus, chlorine and fluorine (although he did not know their elemental forms), carbon, iron, copper, silver, gold, mercury, lead, tin, antimony, arsenic, bismuth, cobalt, manganese, molybdenum, nickel, platinum, tungsten, and zinc.

He burned sulfur and phosphorus and charcoal (carbon) and made careful observations, often using the bell jar over a bucket of mercury as shown in the drawing from his book, Figure 1. This is an example of a chemical change or chemical **reaction**, in which **reactant** chemicals turn into different **product** chemicals. If you light the sulfur in the dish labeled D under the bell jar of air, it burns until it goes out leaving some extra sulfur. The air remaining in the jar is no longer good for breathing. If you put a mouse in the jar, it will die, just as the flame did. This demonstrates the concept of **limiting reactant**. The reaction or burning stopped when it ran out of oxygen, leaving primarily nitrogen (and a few trace other gases) in the jar. Priestley, another scientist, showed him how to prepare pure oxygen gas, and he used this to do many burning experiments as well.

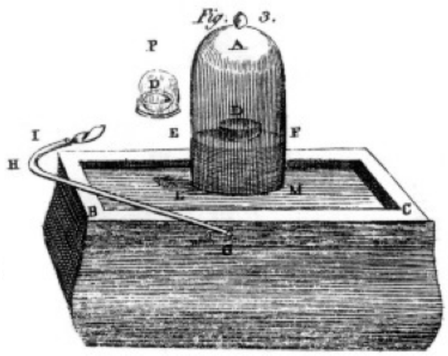
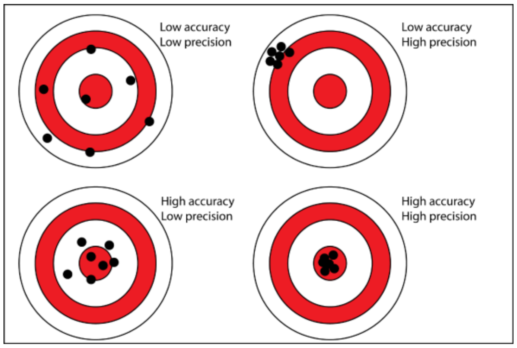


Figure 1: An apparatus for burning sulfur, phosphorous, and charcoal (carbon).

Lavoisier was obsessed with measurement. He developed elaborate apparatus for measuring everything. He would burn phosphorus, as shown in Figure 1, and observe the formation of a white flaky *product*. The phosphorus (the *reactant* in this case) wasn't water soluble, but the product was, so he collected the product very carefully, separating it from the unreacted phosphorus by washing with water. After drying, he could measure how much phosphorus had burned, how much oxygen had been consumed (because he knew the density of oxygen gas), and how much product had formed. He found that the mass of product was the sum of the masses of reactant consumed, in every experiment. This is the **law of conservation of mass** (which, actually, some earlier alchemists and chemists had also used). He also observed that the phosphorus has no taste, but the product, which he called phosphoric acid, is sour. He knew from these experiments that in many cases elements combine in only certain proportions, and also that oxygen can combine with sulfur, phosphorus, etc in two different ratios. He gave us the terminology we still use today: sulfuric acid is composed of sulfur and more oxygen, sulfurous acid is composed of sulfur and less oxygen. -ous means less oxygen; -ic means more oxygen. See the nomenclature page for details.

Lavoisier paid close attention to **accuracy** and **precision**. For instance, in the experiment we just described, he measured the volume of gas in the bell jar, before and after the reaction, but noted that after the reaction, you must wait until the temperature returns to what it was when you measured originally. If the gas is hot when you measure its volume after the reaction, it will have expanded, and your standard density will not apply. This would introduce a systematic error into the measurements: each time you perform the experiment, you will think that there is more gas leftover than there actually is, and your measurement won't be accurate. If the average result of your experiment is near the correct value, it is accurate. However, if your experiment gives very different numbers each time, even if the average is correct and the experiment is accurate, it is not precise. Precision is the difference between meeting "around 2 o'clock" and meeting "at 3 minutes and 27 seconds before 2 pm." Precision is how specific you are, how much detail you use. Lavoisier also helped develop the system of units (kg, L, m) that are currently in use in Korea and many other countries.



An illustration of the different effects of accuracy and precision.

Overall, while he didn't do very many original experiments that nobody else had done before, he did his experiments very carefully, so they were as accurate and precise as possible, and then he thought about them clearly and created words to describe the chemicals and ideas that helped make everything clearer. If you read a chemistry textbook written before Lavoiser, you will be very confused because the names for chemicals would be based on history (and would sound like they came from Harry Potter), rather than being based on what the chemicals are. If you read a chemistry text written after Lavoiser, you will recognize the language as similar to what we use today.

Summary

Accuracy describes how close a measured value is to the actual value. **Precision** describes how well a group of measured values agree with each other. The **law of conservation of mass** states that matter can neither be created nor destroyed by a chemical or physical process. This results in the sum of the masses of reactant consumed in any experiment is equal to the mass of product. Chemical changes involve changing a substance's chemical identity such that new substances are formed. Physical changes involve altering a substance without changing its chemical identity. Combustion and rusting are two examples of chemical processes while boiling and melting are examples of physical processes. Chemical **reactions** involve turning **reactants**, chemicals that get consumed in the process of chemical change, into **products**, chemicals produced through the process of chemical change that have a different composition from the reactants. A **limiting reactant** determines, or limits, the amount of product that can be produced from a chemical reaction.

Outside Link

- CrashCourse Chemistry: The Fundamental Law (11 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Meet the Periodic Table

Skills to Develop

- Associate family name to description (especially for groups 1 - 2 and 16 - 18)

The Periodic Table is an essential tool for chemists. I have provided a simple version here. It shows the symbols, atomic numbers, and average atomic masses for each element. If you point at a symbol, it will show the element name. You can search for an element by name or symbol and it will be highlighted so it's easy to find.

How do you use the periodic table? It can help you predict many important properties of elements. To make these predictions, you will need to know a little about the different families or **groups**, which are the columns of the table. The term for the rows is **period**. Here is some info about the important groups.

Group Number	Family Name	Description
1	Alkali Metals	soft, extremely reactive metals, valence 1, almost always M^+ ions
2	Alkaline Earth Metals	soft, less reactive metals, valence 2, almost always M^{2+} ions
13	Boron Group	non-metals and metals, valence 3
14	Carbon Group	non-metals and metals, valence 4
15	Pnictogens	non-metals, valence 3
16	Chalcogens	non-metals, valence 2, often X^{2-} ions
17	Halogens	non-metals, very reactive, volatile elements, valence 1, usually X^- ions
18	Noble Gases	very unreactive monatomic gases, valence 0
3-12	Transition Metals	metals with multiple valences and ionic forms, initially hard to fit into periodic table, many exist as M^{2+}
*, **	Rare Earth Metals	(lanthanoides, actinoides) similar to each other, most have M^{3+} ionic form

To learn your way around the table, try going to this much fancier periodic table. Notice how metals are on the left and bottom of the periodic table, while non-metals are on the right and top. **Metals** are shiny, and they conduct heat and electricity. Non-metals don't conduct, and are often softer or easier to break than metals. Some elements are called **metalloids** because they are in between metals and non-metals, and you can see that the metalloids are also in between the metals and non-metals in the periodic table. The most reactive elements are on the edges of the table (groups 1 and 17), and the most reactive non-metals are O and F, in the top right corner.

Outside Links

- CrashCourse Chemistry: The Periodic Table (11 min)
- Khan Academy: Classification of the Elements (9 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Nomenclature

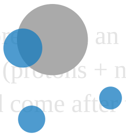
Chemical **nomenclature** is the names we use for chemicals. For instance, H_2O is called "water", and CH_4 (the gas you burn in a stove) is called "methane." You should learn the chemical nomenclature here on this page now, so that you will be able to understand when it is used.

The Basics

Here is some important info about how we write chemicals.

1. Elements have symbols of one or two letters. The first is a capital letter (ABC). If there is a second letter, it is a lower-case letter (abc). For instance, "m" is one unit, and "M" is a different unit. "K" is the symbol for one type of constant, and "k" is the symbol for a different type. You need to remember that capital letter symbols are usually different from lower-case symbols. For instance, Co is cobalt, a metal element next to iron, and CO is carbon monoxide, a poisonous gas made of one carbon atom and one oxygen atom.
2. We write the charge of a chemical using a superscript, which looks like this: H^+or $H^–$. If we write just H, that means an H atom, which is one proton and one electron. H^+ means 1 H atom – 1 electron, so it means just one proton, also called hydrogen ion. If we write $H^–$ this means one hydrogen atom + one electron, so a proton and 2 electrons, also called hydride ion. If there's an number in the superscript, that says how many electrons are added or removed. For instance, Ca^{2+} is a calcium atom – 2 electrons, or calcium ion. $S^{2–}$ is sulfide, or sulfur + 2 electrons.
3. We indicate the number of atoms of a particular type using a subscript, like this: CO_2. This means one carbon atom and 2 oxygen atoms. If we write O_2 that means the oxygen molecule, which is two atoms of oxygen connected together. Sometimes people might write O2 to mean the same thing. If the number comes first, though, it has a different meaning. 2 O means 2 atoms of oxygen that aren't connected to anything.

1 ball is used to show atomic oxygen. 2 conjoined ball is used to show diatomic oxygen and 3 conjoined ball represents ozone.



4. If we want to show how many protons and neutrons are present in an atom, we can use the mass number, as a superscript *before* the element symbol, such as^{13}C. This means carbon with (protons + neutrons) = 13. You can tell that this is different from the charge, because the charge will always include + or – and come after the symbol.
5. Most molecules or ions that are stable have an even number of electrons. If they have an odd number of electrons, this is called a radical. For instance, H is a radical, because it has one electron. Because this is unusual, it might be indicated with a dot, like this: $H^•$. For instance, water is H_2O, and if you remove hydrogen ion, you are left with hydroxide ion, $OH^–$. If you remove $H^•$ from water, you are left with OH molecule, which is neutral. This is also called hydroxyl radical, written $OH^•$.
6. The phase of a substance is often indicated by a letter in () after the symbol. For instance, He is almost always a gas, written He(g). If it's a liquid (4.2K or below, less than -269° C) that is written He(l). You'll probably never hear about He(s), since it would be very hard to make it a solid. You might also see something written with (aq), which means "dissolved in water." For instance, NaCl(aq) means salt dissolved in water so there is no solid left. Or you might just see K^+(aq), meaning potassium ions dissolved in water.

Elements

There are lots of elements and you don't need to memorize them all. Here are a few that you should learn right now, though, because they are common or important, so that you won't be confused when they are mentioned later. They are organized by their type.

1. Non-metals

- Light elements: the elements with smallest mass
    - Hydrogen (H): exists as H_2 or in combination with other elements, such as in water
    - Helium (He): named after the sun, because it was discovered in the sun before being discovered on Earth (we'll explain how later); it doesn't react with anything
- Major gases in air
    - Oxygen (O): we get most of our energy from reactions with oxygen, when we breathe or when we burn fuel; O_2 is 21% of air
    - Nitrogen (N): often the limiting factor for agriculture or population growth, even though N_2 is 78% of air, because it only reacts under special circumstances.
- Halogens: reactive elements that make salts; common negative ions
    - Fluorine (F): the lightest halogen and most reactive element in the periodic table, people say that it killed the first two chemists who tried to isolate F_2
    - Chlorine (Cl): part of normal salt, NaCl, it is common in the ocean and in your body
    - Bromine (Br): one of only two elements that are liquid at room temperature, bromine is also found in salts and minerals
    - Iodine (I): a soft, shiny silver solid that easily evaporates to a purple gas, iodine can be used to disinfect cuts and is essential for human brains, suggesting that humans may have evolved to live near the ocean, which provides sources of iodine in fish and seaweed
- Main group solid non-metals: non-conductive and usually soft materials
    - Carbon (C): the element on which biology is based, also found in diamond, graphite, coal, and charcoal
    - Silicon (Si): the basis of the electronics industry; also a main component of sand, glass, and most rocks
    - Sulfur (S): a smelly yellow solid, used to make strong a[illegible] industry, also common in minerals and essential to life
    - Phosphorus (P): first isolated from urine, although comm[illegible] minerals; essential for life, often glows

2. Metals: soft or hard, light or heavy, usually solid electric conductors

- Alkali metals: soft, light, common soluble positive ions
    - Lithium (Li): the lightest alkali, used in batteries and anti-depressants
    - Sodium (Na, you may know it as natrium): common in the ocean and salt
    - Potassium (K, you may know it as kalium): also common, high concentration inside cells
- Alkaline Earth metals: like alkalis, but less so, less reactive, less soluble, positive ions more common in rocks, but also abundant in ocean
    - Magnesium (Mg): common in rocks, essential for life, especially photosynthesis
    - Calcium (Ca): common in biomaterials such as bone, tooth, and shells, also essential for muscles
- Main group metals
    - Aluminum (Al, also called aluminium): requires lots of energy to produce the metal from the mineral sources, but very common and useful metal
    - Tin (Sn, from Latin stannum): used since ancient times, especially in alloys such as bronze; still used in solder and many other applications
    - Lead (Pb, from Latin plumbum): very heavy, soft, sweet-tasting toxic metal, commonly used since ancient times, now used to shield radiation and in bullets, among many other uses
- Transition Metals: a widely varied group, often characterized by complex chemical properties
    - Iron (Fe, from Latin ferrum): most abundant element on earth, essential in steel, with complex reaction properties essential to life
    - Copper (Cu, from Latin cuprum): less reactive metal, with characteristic colors, commonly used in coins and electronics

- Silver (Ag, from Latin argentum): used in jewelry, coins and other ornaments and utensils since ancient times, it didn't tarnish until after the industrial revolution, and now also used in electronics
- Gold (Au, from Latin aurum): used since ancient times in coins and jewelry, to color stained glass, also in dentistry and other applications
- Mercury (Hg, from Latin hydrargyrum): also called quicksilver, because it is a silver liquid, it is toxic but very important in the history of science; it may be familiar from thermometers

Common Positive Ions (Cations)

"[element name](charge in Roman numerals if needed) ion"

Cation is another word for positive ion. The common positive ions are the ions of the alkali and alkaline earth metals and ammonium, NH_4^+. The alkali metals form +1 cations, such as Na^+ and K^+. The alkaline earth metals form +2 cations, such as Ca^{2+} and Mg^{2+}. The hydrogen ion, H^+ is a very common cation. For these cations, you can call them "[element name] ion", such as sodium ion or calcium ion.

You'll also see transition metal cations or main group metal cations, but it is harder to predict what charge they will have, especially because some of them can have different charges, like iron, which is commonly Fe^{2+} or Fe^{3+}. The charge on a transition metal cation can also be indicated using Roman numerals in parentheses, which looks like Fe(II) or Fe(III). The Roman numerals you will need to know for chemistry are:

1	2	3	3	5	6	7	8	9	10
I	II	III	IV	V	VI	VII	VIII	IX	X

For cations that have uncertain charge, you should call them "[element name](charge in Roman numerals) ion." For instance, iron(II) ion or sometimes just Fe(II).

Sometimes people use special names for these ions, in which the higher charge ion is called "[name]-ic ion" and the lower charge ion is called "[name]-ous ion," such as ferrous for Fe(II) and ferric for Fe(III), or cuprous ion for Cu(I) and cupric ion for Cu(II). I think this is most common for Fe, and I've never heard anyone call nickel(II) nickelous ion because that sounds ridiculous.

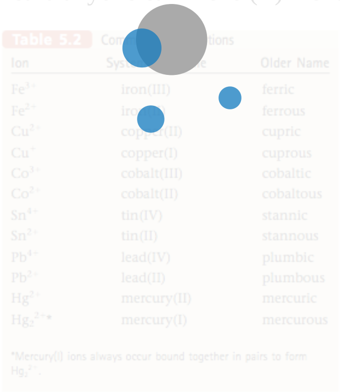


Table 5.2 Com[illegible]tions

Ion	Syst[illegible]e	Older Name
Fe^{3+}	iron(III)	ferric
Fe^{2+}	iron(II)	ferrous
Cu^{2+}	copper(II)	cupric
Cu^{+}	copper(I)	cuprous
Co^{3+}	cobalt(III)	cobaltic
Co^{2+}	cobalt(II)	cobaltous
Sn^{4+}	tin(IV)	stannic
Sn^{2+}	tin(II)	stannous
Pb^{4+}	lead(IV)	plumbic
Pb^{2+}	lead(II)	plumbous
Hg^{2+}	mercury(II)	mercuric
Hg_2^{2+}*	mercury(I)	mercurous

*Mercury(I) ions always occur bound together in pairs to form Hg_2^{2+}.

Here's a list of common cations with less predictable charges:

- Ag^+
- Cu^+
- Cu^{2+}
- Fe^{2+}
- Fe^{3+}
- Hg_2^{2+}
- Hg^{2+}
- Pb^{2+}
- Sn^{2+}
- Al^{3+}

Elements not on the list above, that you may see soon anyway: zinc(II): Zn^{2+}, cadmium(II): Cd^{2+}, cobalt(II): Co^{2+}, manganese(II): Mn^{2+}, nickel(II): Ni^{2+}, chromium(III): Cr^{3+}.

Common Negative Ions (Anions)

"[base name] + (-ide,-ate, or -ite)"

Anion is another word for negative ion. Common negative ions are the halide ions, formed from the halogen elements: fluoride, F^-; chloride, Cl^-; bromide, Br^-; and iodide, I^-. As you may have noticed, the names of anions have "-ide" at the end when they are formed from elements. Other examples include oxide, O^{2-}, sulfide, S^{2-}, and nitride, N^{3-}.

Common Anions

Charge	Formula	Name
1−	H^-	Hydride ion
	F^-	Fluoride ion
	Cl^-	Chloride ion
	Br^-	Bromide ion
	I^-	Iodide ion
	CN^-	Cyanide ion
	OH^-	Hydroxide ion
2−	O^{2-}	Oxide ion
	O_2^{2-}	Peroxide ion
	S^{2-}	Sulfide ion
3−	N^{3-}	Nitride ion

There are also many important polyatomic anions, which means anions that include more than one atom. These include toxic cyanide ion, CN^-, common hydroxide ion, OH^-, and peroxide ion, O_2^{2-}. Other important anions include acetate ion ($C_2H_3O_2^-$), which is in vinegar, the chlorate ion (ClO_3^-), the perchlorate ion (ClO_4^-) which is often explosive, the nitrate ion (NO_3^-), the carbonate ion (CO_3^{2-}) found in shells, the sulfate ion (SO_4^{2-}), and the phosphate ion (PO_4^{3-}). All of these end in "-ate", which means that they have more oxygen. Also, notice that "per-___-ate" means more oxygen than just "-ate", as in perchlorate.

Less common but still important are some "-ite" anions, which have less oxygen, such as nitrite (NO_2^-), sulfite (SO_3^{2-}), chlorite (ClO_2^-) and hypochlorite (ClO^-). Notice that "hypo-___-ite" means less oxygen than just "-ite" as in hypochlorite. Sulfite and nitrite are used to preserve foods. Sulfite salts are used in wine, dried fruit and preserved radish (mu). Nitrite salts are used in preserved meats.

One more rule says that if you take an anion like carbonate or sulfate and add one hydrogen ion, then you call that "bicarbonate" (HCO_3^-) or "bisulfate" (HSO_4^-). Or you might see it called "hydrogen carbonate" or "hydrogen sulfate." Note that because we added a hydrogen ion, the charge on the bicarbonate ion is one less than the charge on the carbonate ion. Also, note that "disulfate" is $S_2O_7^{2-}$, quite different from bisulfate.

Chemical Nomenclature for Ionic Compounds

"[cation name] + [anion name]"

Ionic compounds are compounds that include at least two components, a positive ion and a negative ion. Often the positive ion is a metal element ion and the negative ion is a non-metal ion. To name an ionic compound, you usually just give the cation followed by the anion, such as "sodium chloride" or "ammonium nitrate." If the cation is the type that could have different charges, than you should say what the charge is, such as "mercury(I) iodide" or "cupric sulfate."

Chemical Nomenclature for Acids

"(hydro if -ide)[anion base name] + (-ic if -ide, -ate; -ous if -ite) + acid"

Acid usually means an anion combined with the hydrogen ion as the cation. For instance, HCl is a common acid, which is the hydrogen ion and the chloride anion. If the anion ends in "-ide" then usually the acid is called "hydro-___-ic acid" such as "hydrochloric acid" for HCl. You'll see this for all the "hydrohalic acids" which are H + a halogen, such as "hydrofluoric acid" or "hydroiodic acid." You might also see "hydrocyanic acid" for HCN. If the anion ends in "-ate" than you call the acid "___-ic acid," such as "sulfuric acid," which is H_2SO_4, or "nitric acid." HNO_3. If the anion ends in "-ite" than the acid name is "___-ous acid." such as "hypochlorous acid" for HClO. Notice that earlier "-ic" and "-ous" meant more and less charge for cations, such as ferric and ferrous ions of iron. Now it also means more and less oxygen in acids.

Chemical Nomenclature for Non-metal Compounds

"(prefix, not mono)[less anion-like atom name] + (prefix)[more anion-like atom name]-ide"

Non-metal compounds are often called covalent compounds. They are named following a different rule from ionic compounds. You will need these "prefixes" which indicate how many of each type of atom are present:

1	2	3	3	5	6	7	8	9	10

mono	di	tri	tetra	penta	hexa	hepta	octa	nona	deca

The prefixes come from Greek. You will put the element that is more left on the periodic table first, unless it is oxygen, which is always last unless it is in a compound with fluorine. This follows the same pattern as ionic compounds. In ionic compounds, the cation is written first, and you will notice that it is usually more to the left in the periodic table than the anion, which is written last. When you name covalent compounds, the atom that's more like an anion is written last. Fluorine is always most "anionic," and oxygen is next most "anionic," so they will always be last. (Fluorine is actually most electronegative, but we will study this concept much later, which is why right now I'm calling it "anion-like.") If both atoms are in the same group (same column of the periodic table) then the lower one is named first. Notice that the two most "anion-like," F and O, are in the upper right of the periodic table. The atom written second, that's more "anion-like" is named like an anion, with the "-ide" ending. For example, CO: carbon is on the left, so we can write "monocarbon monoxide." Actually people usually just call it "carbon monoxide." You can skip "mono" for the first element. For instance, SO_3 is called "sulfur trioxide" and N_2O_4 is called "dinitrogen tetroxide." XeO_2 is xenon dioxide, even though xenon is more to the right than oxygen, because oxygen is more like an anion than anything except fluorine. If the compound involves hydrogen, then you can leave out the prefixes, such as "hydrogen chloride" for HCl or "hydrogen sulfide" for H_2S, because the numbers of each atom can be predicted as if it were an ionic substance. But actually many compounds of hydrogen have special names, such as "ammonia" for NH_3, "methane" for CH_4, "borane" for BH_3, "silane" for SiH_4 and "phosphine" for PH_3. You should learn the first two of these now.

Summary

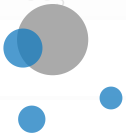
Key Info for Common Elements

Element name	Symbol	Atomic number	Commonly found as...
Hydrogen	H	1	H_2(g), water (H_2O), acid (H^+(aq))
Helium	He	2	He(g), He(l) if you want to make things very cold
Lithium	Li	3	Li^+ always, (aq) or in solids with anions, lithium metal Li(s) only in chem class
Carbon	C	6	Covalent compounds, making 4 bonds
Nitrogen	N	7	N_2(g) in air, in ammonia (NH_3(g or l)), in basic covalent compounds, in proteins
Oxygen	O	8	O_2(g) in air, in water, in rock and glass, usually combined with Si
Fluorine	F	9	F^-(aq) or with cations in rock, in covalent compounds with carbon (non-stick pans)
Sodium (Natrium)	Na	11	Na^+(aq) or with anions in salts, sodium metal (Na(s)) only in chem class
Magnesium	Mg	12	Mg^{2+}(aq) or with anions in salts and rocks

Element name	Symbol	Atomic number	Commonly found as...
Aluminum (Aluminium)	Al	13	Al^{3+} with anions in rocks and salts, industrially made Al(s) metal
Silicon	Si	14	Industrially made Si(s) in computer chips, Si(IV) oxides in sand, glass, most rocks
Phosphorus	P	15	Phosphates: PO_4^{3-}, $P_2O_7^{4-}$, etc. in rock, DNA
Sulfur	S	16	$S_8(s)$, S^{2-} or sulfate (SO_4^{2-}) in salts or rocks
Chlorine	Cl	17	$Cl^{-}(aq)$ or with cations in salts, $Cl_2(g)$ or $ClO^{-}(aq)$ in disinfectants
Potassium (kalium)	K	19	$K^{+}(aq)$ or with anions in salts, potassium metal (K(s)) only in chem class
Calcium	Ca	20	$Ca^{2+}(aq)$ or with anions in salts and rocks
Iron	Fe	26	Fe(s) metal industrially made, Fe(II) or Fe(III) oxides or sulfides and other minerals
Copper	Cu	29	Natural Cu(s) metal, Cu(I) or Cu(II) salts or minerals, usually blue or green
Bromine	Br	35	$Br^{-}(aq)$ or with cations in salts
Silver	Ag	47	Natural Ag(s) metal, Ag(I) or Ag(II) in salts or sulfide minerals
Tin	Sn	50	Industrially made Sn(s) in alloys, Sn(II) or Sn(IV) salts and oxide or sulfide minerals
Iodine	I	53	$I^{-}(aq)$ or with cations in salts
Gold	Au	79	Natural Au(s) metal, rarely Au(I) or Au(III) salts
Mercury	Hg	80	Natural (but rare) metal Hg(l), Hg(II) sulfides and halides, Hg(I) exists as Hg_2^{2+}
Lead	Pb	82	Pb(s) in alloys, Pb(II) sulfide, carbonate and sulfate minerals, sometimes Pb(IV) salts or minerals

Common Polyatomic Ions

Name	Formula	Where you find it

Name	Formula	Where you find it
Ammonium	NH_4^+	Soluble salts, fertilizer
Cyanide	CN^-	Toxic, in some plant products and dyes
Hydroxide	OH^-	In bases and some minerals
Peroxide	O_2^{2-}	In bleaches and disinfectants
Acetate	$C_2H_3O_2^-$	In vinegar
Perchlorate	ClO_4^-	Soluble salts and explosives, a strong acid
Chlorate	ClO_3^-	Similar to perchlorates but less stable
Chlorite	ClO_2^-	Disinfectants and bleaches, some explosive salts
Hypochlorite	ClO^-	Disinfectants and bleaches, most salts unstable
Nitrate	NO_3^-	Soluble salts, fertilizer, explosives, a strong acid
Nitrite	NO_2^-	Preservatives for food
Carbonate	CO_3^{2-}	In rock, seashells, cement; a base
Bicarbonate	HCO_3^-	A base (baking soda), in soda, in blood
Sulfate	SO_4^{2-}	In salts, plaster, detergent, a strong acid
Bisulfate	HSO_4^-	Food additives
Sulfite	SO_3^{2-}	Salts, food preservatives
Phosphate		Salts, rock, fertilizers, a strong acid, in ATP and DNA

Outside Link

- CrashCourse Chemistry: How to Speak Chemistrian (11 min)

Contributors and Attributions

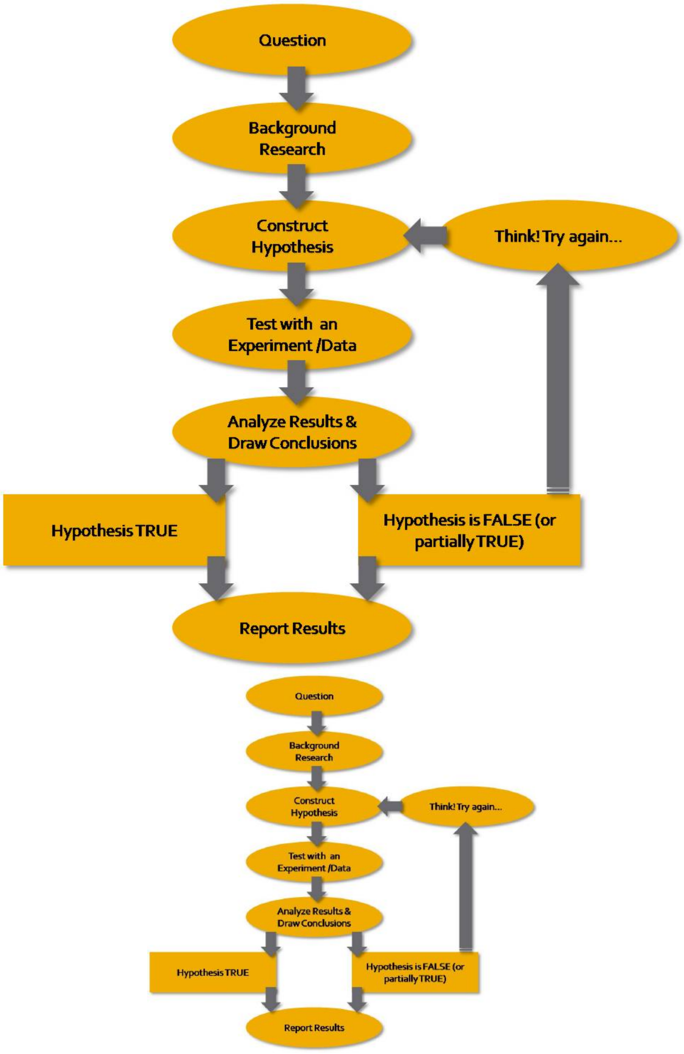
- Emily V Eames (City College of San Francisco)

Scientific Method

Skills to Develop

- Understand what is the scientific method and how to apply it

You know what science is. A **method** is a way to do something. The **scientific method** is how scientific knowledge is produced. You have probably learned science before as a set of knowledge that is just given to you, and you have to memorize facts and procedures to follow to get answers. This way of learning that you have probably experienced is completely different from how science professionals think of science and do science. Now it is time to learn science like a scientist. Because scientists create new knowledge, they have to be able to think independently. Even if this seems very hard or unfamiliar, you can learn to make new scientific conclusions yourself.



General flowchart describing the various stages of the scientific method.

The basic steps of the scientific method involve *collecting* observations about what actually happens, *thinking* about what the observations mean, making *guesses* about what will be observed in the future, and then making *observations* to see if the guesses are right. The **observations** are evidence or **data**, the results of experiments. The guesses are usually called **hypotheses**. If the hypotheses fit a lot of data and seem to work well, then they are called **theories**. In science, a **law** describes a pattern of consistent results. For instance, you know that when you drop things, they fall. That could be called the law of gravity. If we had a good explanation of why that happens, we would call that a theory of gravity. Gravity is easy to describe (in Newton's law, which describes how things move on Earth and how planets and moons and stars moves in space) but very hard to explain: how can objects that are very far apart feel a force towards each other?

The real test of whether something is science is whether it works reliably. An experiment is good and useful if you can *repeat it* (if someone different can repeat it) and *get the same result*. There will be some small differences in the data because measurements are always a little imprecise and there might be some small differences in the way the experiment was done, but the data should be the same within the "error range." Likewise, a law is good if observations always follow it within the context it describes. And a theory is good if it explains all the available evidence. For theories, it's also important that it be possible to prove the theory wrong, that it makes predictions that can be tested. Otherwise, it might be true but it isn't useful.

A useful skill for learning science is building "mental models" of how things work. A **model** is a bigger or smaller version of something, depending on the size of the original object, that shows all its parts and how they are related. For instance, an architect builds a small 3-D model of a new building before people start constructing the building. The architect also has complex computer models of the building showing how it stays up, how the doors don't bump into each other, etc. These models help the architect predict whether their design will be successful or not.

3-D model of a building

Summary

The **scientific method** is a structured approach to gathering and analyzing data, and drawing conclusions about various subjects or phenomena. **Observations** consist of evidence or data that may verify or falsify ideas about what actually happens in a given event. These ideas are usually **hypotheses**, educated guesses about how or why the particular event occurred which could lead to experiments to test the guesses. If a hypothesis seems reasonable and fits with a lot of data through rigorous testing, the hypothesis evolves into a **theory**. Good experiments have replicable results, meaning that other scientists should be able to come up with the same results or conclusions after repeating the experiment. A **scientific law** describes what will be observed in the future given a pattern of consistent results on the phenomenon. A **model** is a visualization of something to show how all of its parts are related.

Other Links

- SciShow: The Times and Troubles of the Scientific Method (11 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Valence and the Periodic Table

Skills to Develop

- Understand and describe how the periodic table was first organized

Many chemists were interested in knowing the "chemical equivalents" of different substances. For instance, what mass of acid A neutralizes base B? These numbers were easy to measure and practically useful. But what about elements? For instance, what mass of element A reacts with 1 g of element B? Knowing these numbers could be very useful, but it was hard to relate the equivalent masses to the actual masses of the atoms because they didn't know the formulas. There were two good ways available to figure this out. One was Avogadro's hypothesis based on Gay-Lussac's law, which allowed chemists to relate the equivalent masses to equivalent volumes. The other was Faraday's law, which measured masses of elements produced by a set amount of current. However, Berzelius, who was working hardest on this problem, didn't believe either Avogadro or Faraday.

Berzelius' beliefs held up the progress of science for about 50 years. Eventually, Cannizzaro revived Avogadro's hypothesis at a big meeting of chemists in 1860. His paper explaining how to calculate molecular weights was distributed to everyone, including Julius Lothar Meyer, who wrote that when he read it "doubts disappeared and a feeling of quiet certainty took their place". Avogadro's hypothesis let chemists figure out atomic weights and formulas together. Once Cannizzaro convinced most chemists to accept it, chemists were able to study the actual atomic weights and formulas.

Scientists soon observed patterns in the **valence** of the different elements. Valence is the number of connections an atom tends to form. H is defined to have a valence of 1. For instance:

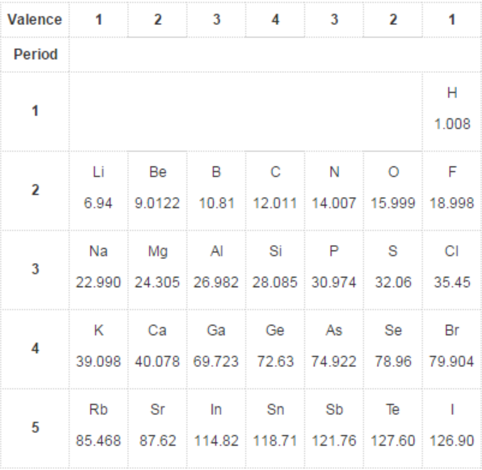
- methane, CH_4: carbon atoms have a valence of 4
- water, H_2O: oxygen has a valence of 2
- lithium oxide, Li_2O: lithium has a valence of 1
- hydrogen sulfide, H_2S: sulfur has a valence of 2
- aluminum oxide, Al_2O_3: aluminum has a valence of 3

By the 1860s, ~60 elements were known. Using Cannizzaro's atomic weights, Mendeleev and Lothar Meyer made a great discovery, the periodic law: If you arrange the elements by their atomic weights, there is a periodic repetition in properties such as valence. The modern version of this periodic arrangement is the Periodic Table.

Also, within a group (sharing a valence) properties like density, boiling point, heat capacity, etc follow a simple progression. Mendeleev used this to predict the properties of undiscovered elements.

Here's a smaller version of the periodic table that leaves out the elements Mendeleev and Meyer found most problematic (transition metals, rare earths) and the group that hadn't been discovered yet (noble gases). Notice how the the valences repeat every 7 elements when they are arranged according to atomic mass.

Partial Periodic Table



Valence	1	2	3	4	3	2	1
Period							
1							H 1.008
2	Li 6.94	Be 9.0122	B 10.81	C 12.011	N 14.007	O 15.999	F 18.998
3	Na 22.990	Mg 24.305	Al 26.982	Si 28.085	P 30.974	S 32.06	Cl 35.45
4	K 39.098	Ca 40.078	Ga 69.723	Ge 72.63	As 74.922	Se 78.96	Br 79.904
5	Rb 85.468	Sr 87.62	In 114.82	Sn 118.71	Sb 121.76	Te 127.60	I 126.90

But there were some problems with the table. For instance, tellurium (Te) was clearly a chalcogen, in the oxygen family, and iodine (I) was clearly a halogen, based on their properties, but the weights were wrong. (Check the table!) Mendeleev said that the atomic weights must not have been determined correctly, but they were correct.

Outside Links

- Khan Academy: Groups of the Periodic Table (12 min)
- CrashCourse Chemistry: The Periodic Table (11 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

CHAPTER OVERVIEW

Chemistry Calculations

Topic hierarchy

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Chemical Equations

Skills to Develop

- Write and interpret chemical equations

Chemical equations are a way to show what happens in a chemical reaction. A chemical equation looks something like this:

$$A \rightarrow B \tag{1}$$

In this case, A represents a reactant or reagent, and B represents a product. Usually one element doesn't turn into another element, so A and B might represent different molecules that are too complicated to just write the formulas. There might also be multiple reactants and products, like this:

$$A + B \rightarrow C + D \tag{2}$$

In this class, we will mostly study reactions of simple molecules, so we will use their formulas in equations, like this:

$$Cl_2 + Mg \rightarrow MgCl_2 \tag{3}$$

Often, we might want to show the state of the reactants and products, so we can use (g, l, s, or aq) to show if it is a gas, liquid, solid, or in a water solution (solutions in water are called **aqueous** solutions). For the example above, this becomes, assuming we do the reaction dry

$$Cl_2(g) + Mg(s) \rightarrow MgCl_2(s) \tag{4}$$

Notice that the numbers showing how many atoms of each element are in the formula go after the element, as a subscript $_{\text{like this}}$. When we write chemical equations, usually we want them to be **balanced equations**, which means that they have the same number of each kind of particle on each side of the equation. Here's an example of an unbalanced equation:

$$Br_2(l) + Na(s) \rightarrow NaBr(s) \tag{5}$$

In this example, there are 2 bromine atoms on the left, and only 1 on the right. We always have to balance the number of each type of nucleus on each side, like this:

$$Br_2(l) + 2Na(s) \rightarrow 2NaBr(s)\$\$ORlikethis:\$\$\frac{1}{2}Br_2(l) + Na(s) \rightarrow NaBr(s) \tag{6}$$

Notice that we have put the number of sodium atoms needed for the reaction in front of the symbol for sodium, and not in a $_{\text{subscript}}$ after the symbol. This is called a **coefficient**, and it is different because it tells us how many of a molecule we need, not how many atoms are in the molecule, like this:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \tag{7}$$

We also have to balance the number of electrons on each side. The easiest way to do this is usually to make sure the charges on both sides add up to the same number. For example, here's an equation that isn't balanced for electrons, even though it is balanced for nuclei:

$$Mg(s) + Ag^{+}(aq) \rightarrow Mg^{2+}(aq) + Ag(s) \tag{8}$$

To balance this equation we have to make both the charges and the nuclei balanced, like this:

$$Mg(s) + 2Ag^{+}(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s) \tag{9}$$

Equations Need to Represent What's Actually Happening in a Reaction

This means that the number of each type of particle must be the same on both sides of the equation, because particles (nuclei or electrons) can't appear or disappear (except under special circumstances, which we call nuclear chemistry, so don't worry about that right now). This is why equations need to be balanced.

The second important thing is that the formulas in the equation need to match the actual molecules that are used or produced in the reaction. So if you are given the formulas, and you change them instead of changing the coefficients when you balance the equations, the equation and the reaction it represents has changed! You can't do this. On the other hand, if you are trying to write a chemical equation but you aren't sure what the formulas are, you can definitely use balancing to help you decide, and in this case you could change the formulas and the coefficients, as long as the formulas you use match all the information you have.

Balancing Equations to Avoid Mistakes

Here's an example of how balancing equations can help you avoid mistakes, based on some wrong answers my students gave on an exam last year. The question was, what reaction happens between calcium ions and carbonic acid in the ocean (a water solution)? To answer this, we have to translate it into formulas. Calcium ions: this is an alkaline earth metal, so Ca^{2+}. Carbonic acid is H_2CO_3. Carbonic acid will dissociate a little bit, making some hydrogen ion (H^+), some bicarbonate ion (HCO_3^-), and some carbonate ion (CO_3^{2-}). Calcium carbonate is insoluble, so it will form a solid, ionic material. You could write the reaction like this:

$$Ca^{2+}(aq) + H_2CO_3(aq) \rightarrow CaCO_3(s) + 2H^+(aq) \tag{10}$$

This equation is balanced. What if you wrote it like this?

$$Ca^{2+}(aq) + H_2CO_3(aq) \rightarrow CaCO_3(s) + H_2(aq) \tag{11}$$

Now it isn't balanced, because the charge on the left side is 2+ and the charge on the right side is 0. This means that there are 2 more electrons on the right than on the left, which is a problem! They can't come from nowhere, so this isn't a complete equation: we are missing the source of the electrons. The mistake may have been confusing $2H^+$ with H_2 (the difference between 2 before H and 2 after H is important!), or it might have been confusing Ca^{2+} with Ca metal. For instance, this reaction is fine:

$$Ca(s) + H_2CO_3(aq) \rightarrow CaCO_3(s) + H_2(aq) \tag{12}$$

However, in the context of the question, it would be very surprising to have Ca(s) in the ocean, because alkaline earth metals, like alkali metals, react with water. So we have lots of Ca^{2+}, Mg^{2+}, and Na^+ ions in the ocean, but no atomic Ca, Mg, or Na in the ocean.

Outside Links

- Khan Academy: Balancing Chemical Equations (14 min)
- CrashCourse Chemistry: Stoichiometry (13 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Dimensional Analysis

Skills to Develop

- Use dimensional analysis to calculate solutions with the correct units

A **dimension** is any measurable extent, such as length, time, and mass. **Units** help describe the measurement according to certain standards. In the metric system for example, a one-dimensional (1-D) length is measured in meters (m) a two-dimensional (2-D) area is measured in meters squared (m^2), and a three-dimensional (3-D) volume is measured in meters cubed (m^3). Other types of quantities (time, mass, temperature) are measured using different units because they have different dimensions. **Analysis** means to think about something, often focusing on one part at a time. Putting it all together, **dimensional analysis** means thinking about units piece by piece. Dimensional analysis can by to correctly go between different types of units, to catch mistakes in one's calculations, and to make many useful calculations in real life.

Essentially, dimensional analysis means multiplying by one. You collect a set of "conversion factors" or ratios that equal one, and then multiply a quantity that you are interested in by those "ones." For example, if you want to know how many seconds it would take to get from New York to Philadelphia, you'd do it like this:

First, using the express train it takes 2.5 hours to get to Philadelphia from a station in New York. Then, we know that 1 hour = 60 minutes and 1 minute = 60 seconds, so (1h / 60 min) = 1, and (1 min / 60 s) = 1. Now, all we have to do it multiply our starting number (2.5 h) by "one" twice, making sure that the units cancel correctly so that we have only seconds at the end.

$$(2.5\ \cancel{h})\left(\dfrac{60\ \cancel{min}}{1\ \cancel{h}}\right)\left(\dfrac{60 s}{1\ \cancel{min}}\right) = 9.0\times 10^{3} s \tag{1}$$

If each part is not put in the right place, the units will come out wrong. For example:

$$\left(\dfrac{1}{2.5\ \cancel{h}}\right)\left(\dfrac{1\ \cancel{h}}{60\, m\ \cancel{min}}\right)\left(\dfrac{1\ \cancel{min}}{60\ s}\right) = 1.1\times 10^{-4} s^{-1} \tag{2}$$

In this case, we put the starting quantity on the bottom, so we got s^{-1} when the units are canceled out. Here is an example of not being able to cancel out the units correctly:

\[(2.5 h)\left(\dfrac{1 h}{60 min}\right)\left(\dfrac{60 s}{1 min}\right) = 2.5 s\cdot h^2\cdot min^{-2}$$

The important part is that if you check the units to make sure that they come out right, you can be pretty sure you set the calculation up right!

Here is an example of how dimensional analysis can help. A student was calculating initial velocity (v_0) from this equation:

$$d = (v_0)t + \frac{at^2}{2}$$

But the student had derived the equation incorrectly, and used this equation instead:

$$v_0 = \frac{d}{t} - \frac{at^2}{2}$$

So the student had the wrong answer, but didn't know that because he just put the numbers for d, t, and a into his calculator using the wrong equation. If he had checked the units, he would have seen that (d/t) has units of meters per second (m/s) while (at^2)/2 has units of meters (m).

Dimensional analysis is often useful when you want to estimate some quantity in the real world. For instance, maybe you want to know how much money you spend on coffee each month. If you spend $5 per cup and have 2 cups per day, and there are approximately 30 days in a month, than you can set up a calculation just like those above to calculate dollars per month spent on coffee. This works for many important, less obvious situations, for instance in business, to get an approximate idea of some quantity.

Contributors and Attributions

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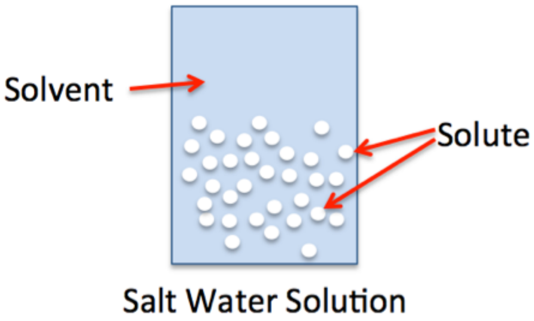
Molarity

Skills to Develop

- Distinguish the parts of a solution
- Define the units for concentration

Concentration means how much of something there is in a given volume, kind of like density, except that it describes **solutions**. A solution is some compound, called the **solute** that is dissolved in another, more abundant compound, called the **solvent**. To be a solution, the molecules or ions of the solute must be separated from each other and surrounded by solvent molecules or ions. If very small bits of one compound are mixed into another compound, but not actually dissolved into molecules or ions, that is called a **suspension** (a solid in a liquid) or **emulsion** (two liquids). In a solution, both the solute and solvent can be any phase, solid, liquid or gas. The concentration of a solution is the amount of solute divided by the total amount of solution, usually. However, there are many different units used for concentration, and some of them assume that there is so much more solvent than solute that you can use amount of solvent instead of amount of solution.



Parts of a Solution: Solute and Solvent

Units for Concentration

There are many, many units used for concentration. Some are mostly used to describe concentrated solutions (that have a lot of solute) and others are mostly used to describe dilute solutions (that have very little solute). The most common unit in chemistry is **molarity** (abbreviated M), which is moles of solute divided by liters of solution.

$$Molarity = \frac{(moles\ of\ solute)}{(liters\ of\ solution)} \tag{1}$$

For example, if you dissolve 1 mol of NaCl in 1L of water, that is a 1 M (read "1 molar") NaCl solution.

Another common unit is weight %, which means

$$Weight\ (Mass)\ \% = \frac{(mass\ of\ solute)}{(mass\ of\ solution)} \times 100\% \tag{2}$$

This is often used for very concentrated solutions. For very dilute solutions, you'll see ppm (parts per million) or ppb (parts per billion):

$$ppm = \frac{(mass\ of\ solute)}{(mass\ of\ solution)} \times 10^6 \tag{3}$$

$$ppb = \frac{(mass\ of\ solute)}{(mass\ of\ solution)} \times 10^9 \tag{4}$$

Many compounds are important even at these very low concentrations. Some chemicals used in agriculture or industry are called "endocrine disrupters" and studies suggest that they can be dangerous for living things at the ppb level. (Example abstract of a scientific paper: note that ppm is described as "high concentration.") In semiconductors, which are what computer chips and LEDs are made of, ppm-level solid solutions enable the essential properties.

Example

HCl (hydrogen chloride) is a really nasty, dangerous gas, but dissolved in water it makes a convenient acid (hydrochloric acid) for many applications in the lab or in industry. When working with an HCl solutions in the lab, we often want to measure the mass of volume of solution used and know how many moles of HCl we added. Unfortunately, when you buy HCl, it usually comes as concentrated HCl, and the bottle will say something like "32% by weight, density 1.1593." Convert this to molarity.

To solve this, we need to think of it like a unit conversion. A good trick for dealing with % quantities is just to translate that into g/g, like this: 32 weight % = (32 g HCl)/(100 g solution). Now we do our usual unit conversion:

$$\left(\frac{32\ \ g\ \cancel{HCl}}{100\ \ g\ \cancel{solution}}\right)\left(\frac{1\ mol\ HCl}{36.46\ \ g\ \cancel{HCl}}\right)\left(\frac{1.1593\ \ \cancel{g}}{1\ \ mL\ \cancel{solution}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right)=10\ M\ HCl \tag{5}$$

Here we started with units of g HCl/g solution, and converted the g HCl to moles, and the g solution to liters using the density, which is (g/ml). Notice that the number of significant figures is fairly low. This is because the gas HCl can evaporate out of the solution, just like the water, so the concentration might change a little over time. If you want to know the concentration more precisely, see the next section on titrations to find out how to measure it.

Now suppose you want to make 2.5 M HCl using the 10 M HCl. You will need to dilute it, which means adding solvent to decrease the concentration. If you want to make 1 L of 2.5 M HCl, how much 10 M HCl do you dilute?

To solve this, we can still think about it like a unit conversion. We want 1 L of 2.5 M HCl solution. In the first step, we will convert to the number of moles of HCl needed to make that solution. In the second step, we will find how many ml of 10 M solution have this number of moles HCl.

$$(1\ \ \cancel{L\ of\ 2.5\ M\ HCl})\left(\frac{2.5\ \ mol\ \cancel{HCl}}{1\ \ \cancel{L\ of\ 2.5\ M\ HCl}}\right)\left(\frac{1000\ mL\ of\ 10\ M\ HCl}{10\ \ mol\ \cancel{HCl}}\right)=250\ mL\ of\ 10\ M\ HCl \tag{6}$$

To make the solution, we will take 250 mL of 10 M HCl, and we will put it in a 1 L volumetric flask, and then add water slowly, with mixing, until the volume reaches the 1 L mark. The reason we do it this way, instead of just adding 750 mL of water, is that the density can change because of the solute. If we use the volumetric flask, we can be sure that we have exactly 2.5 mol HCl in exactly 1 L of solution.

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Moles

Skills to Develop

- Define a mole
- Distinguish theoretical yield from actual yield

Moles are a convenient unit used in chemistry to convert between amounts of a substance in grams and numbers of atoms or molecules. This is useful because we usually measure how much of a molecule is used or produced in a reaction by massing it, but as a chemical equation shows, the reaction will happen between atoms or molecules. For example, suppose we combine 1.0 g of calcium oxide (CaO) with 1.0 g of water (H_2O). The product we get is $Ca(OH)_2$. Here's the equation:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s \text{ or } aq) \tag{1}$$

This is balanced. Thus every molecule of water reacts with one CaO formula unit (it's not called a molecule because it's an ionic solid, and each Ca^{2+} ion is surrounded with oxide ions that it interacts with equally). How much calcium hydroxide is produced by this reaction? Once all of one reactant has been used, whatever is left of the other will stop reacting, because of the law of definite proportions: we won't change the ratio of O:H:Ca in the product. So will we get solid calcium hydroxide with calcium oxide left over, or will we have water left over, and thus get $Ca(OH)_2(aq)$? To answer this question, we can convert both masses (1 g of each) to the number of molecules or formula weights, but this would be inconvenient because the number would be very very big!

Instead, we use **moles**. A mole (abbreviation: mol) is like a pair, which means 2 of something. You can have a pair of people, a pair of apples, whatever. A mole is 6.022 x 10^{23} of something. This is a convenient quantity because it converts amu (atomic mass units) to grams. The atomic weight of carbon is (on average) 12.011 amu/atom. It is also 12.011g/mol. In other words, 1g = 6.02 x 10^{23} amu. Usually, a mol of a substance is a useful, practical amount, somewhere between a few grams and a few kg. The number of things in a mole, 6.022 x 10^{23}, is called Avogadro's number, and abbreviated as N_A. It is named after Avogadro, the scientist who proposed that a liter of any gas at the same temperature and pressure has the same number of molecules in it. To summarize:

1 mole of [thing] = N_A things = 6.022 x 10^{23} things

So the way to answer the question above is to convert both quantities to moles. The maximum amount of product that can be formed is the smaller number of moles. The formula weight is just the sum of the atomic weights.

$$(1.0 \;\; g\, \cancel{CaO}) \left(\frac{1 \;\; mol\, \cancel{CaO}}{56.08 \;\; g\, \cancel{CaO}} \right) \left(\frac{10^3 \; mmol\; CaO}{1 \;\; mol\, \cancel{CaO}} \right) = 17.8 \; mmol\; CaO \tag{2}$$

$$(1.0 \;\; g\, \cancel{H_2O}) \left(\frac{1 \;\; mol\, \cancel{H_2O}}{18.01 \;\; g\, \cancel{H_2O}} \right) \left(\frac{10^3 \; mmol\; H_2O}{1 \;\; mol\, \cancel{H_2O}} \right) = 55.5 \; mmol\; H_2O \tag{3}$$

After we make 17.8 mmol (milimoles) of $Ca(OH)_2$, we will use up all the CaO, so the reaction won't continue. The maximum amount of $Ca(OH)_2$ possible to make is 17.8 mmol. If we wanted to know the **theoretical yield** (maximum mass of product) of $Ca(OH)_2$, we could do it in a one-step calculation like this:

$$(1.0 \;\; g\, \cancel{CaO}) \left(\frac{1 \;\; mol\, \cancel{CaO}}{56.08 \;\; g\, \cancel{CaO}} \right) \left(\frac{1 \;\; mol\, \cancel{Ca(OH)_2}}{1 \;\; mol\, \cancel{CaO}} \right) \left(\frac{74.09\; g\; Ca(OH)_2}{1 \;\; mol\, \cancel{Ca(OH)_2}} \right) = 1.3\; g\; Ca(OH)_2 \tag{4}$$

Here, we knew that the **limiting reactant** (or limiting reagent), which is the reactant that will run out first, is CaO because the masses are the same, the coefficients in the equation are the same, and the formula weight of CaO is bigger than the molecular weight of water. So we start with the limiting reactant mass, convert it to moles (using 1 mol = 56.08 g), then "convert" between moles of CaO and moles of $Ca(OH)_2$ using the coefficients from the balanced equation (1 mol of CaO produces 1 mol of $Ca(OH)_2$), then we convert to g of $Ca(OH)_2$ (using 1 mol = 74.09 g). This is just an example of using dimensional analysis to convert units. We check to make sure we have always multiplied by 1 (because 1 mol CaO = 56g CaO, so (1 mol CaO/56 g CaO)=1), and that the units cancel out to leave the correct final units (g $Ca(OH)_2$), and we can be pretty sure that we got it right.

Here's a slightly more complicated example. This time, we add 2.0 g of water to 2.5 g of Li_2O. This will produce LiOH as the major product. What is the most LiOH (in g) that could be produced, also called the theoretical yield?

To answer, first we need to write and balance the chemical equation. It's going to look pretty similar to the previous one, because this is a similar reaction.

$$Li_2O(s) + H_2O(l) \rightarrow 2LiOH(s\ or\ aq) \tag{5}$$

Which is the limiting reactant? The formula weights are 18.01 g and 29.88 g. Water is still in **excess**, which means it will be left over. Here's the unit conversion:

$$(2.5\ \ g\ \cancel{Li_2O}) \left(\frac{1\ \ mol\ \cancel{Li_2O}}{29.88\ \ g\ \cancel{Li_2O}}\right) \left(\frac{2\ \ mol\ \cancel{LiOH}}{1\ \ mol\ \cancel{Li_2O}}\right) \left(\frac{23.95\ g\ LiOH}{1\ \ mol\ \cancel{LiOH}}\right) = 4.0\ g\ LiOH \tag{6}$$

Note

This time we used 1 mol Li_2O producing 2 mol LiOH, using the coefficients from the balanced equation.

Outside Links

- Khan Academy: The Mole and Avogadro's Number (10 min)
- Khan Academy: Molecular and Empirical Formulas (15 min)
- CrashCourse Chemistry: Stoichiometry (13 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Significant Figures

Skills to Develop

- Be able to understand how to interpret and report significant figures

Suppose you were measuring the diameter of the box below and you needed to report its circumference. You used a ruler and found the diameter to be 31 mm. Then you do the calculation on your calculator and get 97.389372261284 mm. So what do you say the circumference of the circle was? You certainly don't know the circumference more precisely than you knew the diameter, which was between 30 and 32 mm. Going through the calculations with these values would tell you that the circumference was between 94.25 mm and 100.53 mm. This is where significant figures come in handy.

A circular box

Significant figures, often called sig figs, are the number of digits in a given value, or number. For instance, 18 has 2 sig figs, and 3.456 has 4 sig figs. However, both 10 and 1000 have only 1 sig fig. The reason is because the zeros have to be there to show what the number is, so they don't count as significant digits. What about 1001? It has 4 sig figs. We could have "rounded" it to 1000, showing that the last digit wasn't significant, but we didn't. This shows that the 1 on the right is significant, and so if the smallest digit (representing 1s) is significant, then the bigger ones (representing 10s and 100s) must be also. However, if the zeros are significant, then a period or decimal point would be added to the end. For example, if given a problem in which 20. mL are used, then there are 2 sig figs in the number 20.

> You may forget to include the decimal point, particularly in your lab notebook when working in the lab. But you can assume that you used the standard measuring tools in the lab and use the significant figures based on the tools' accuracy. For example, a graduated cylinder could be accurate to 2 mL. So recording 20. mL would be like saying the measurement was between 18 - 22 mL. This means that recording the data with 2 sig figs would be correct. Generally, including an extra sig fig, especially in the middle of calculations is reasonable.

When measuring a quantity, the significant figures describe how precise the measurement was by listing the digits in a measured value which are known with certainty. For example, suppose you measure the length of a box with a normal ruler with increments, or markings, for millimeters (mm). You can be sure that your measurement is no more than 1 mm different from the real length of the box if you measured carefully. So, for instance, you could report the length as 31 mm or 3.1 cm. You wouldn't round to 3 cm or 30 mm since you were able to measure the box more precisely than that. But since you were only able to accurately measure to the nearest millimeter, the certainty of your measurement is within a millimeter of the reading. So you would read your measurement of 3.1 cm as 31 mm ± 1 mm.

Now suppose you wanted to know the length of the box much more precisely. To do that you will need a better tool. For instance, you could use a dial caliper to measure to the nearest 0.02 mm. Now you could report your length as, say, 31.14 mm, which means that your are certain your measurement was between 31.12 mm and 31.16 mm. If you measured with a ruler but wrote 31.1 mm, or 31.12 mm, people going through your numbers would probably think that you used a better tool than you actually did, so that would be almost dishonest

.

A dial caliper.

Going back to the original problem, one rule for using sig figs when doing multiplication with a measured number is to report the answer with the same number of sig figs and the number you started with: 2 sig figs, so 97 mm. The uncertainty is a little bigger than it was before, 97 ± 3 mm. But you shouldn't write 100 mm (1 sig fig) because you don't mean 0 - 200 mm, but you also don't mean 90 - 110 mm (sig fig change!).

> If you wanted to say 100 mm with 2 sig figs, you would have to write it as 10. cm or use scientific notation and write it as 1.0 x 10^2 mm.

Some numbers are counted or defined, meaning that they are not measured. These are exact numbers. For instance, there are exactly 1000 grams (g) in 1 kilogram (kg), because that's the definition. Or if you use a volumetric pipette to add 1.00 mL of liquid twice, then the total amount added was 2 x 1.00 mL = 2.00 mL. You used the pipette exactly twice, so the 2 is exact, and you don't have to round to 1 sig fig (2 mL) for the total volume.

Contributors and Attributions

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Stoichiometry

Skills to Develop

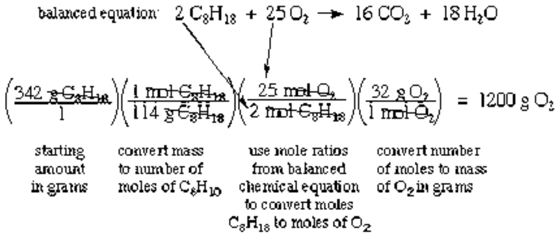
- Perform stoichiometry calculations
- Distinguish dynamic equilibrium from equilibrium
- Describe why actual yield may be less than theoretical yield

Stoichiometry is a general term for relationships between amounts of substances in chemical reactions. It also describes calculations done to determine how much of a substance will be used in a reaction, left over after a reaction, produced by a reaction, etc.

How do you use it?

The calculations of theoretical yield in the previous section are simple stoichiometry calculations. To do stoichiometry calculations, you'll need:

1. A balanced chemical equation: you may need to write the equation and balance it yourself, based on what you know
2. Formula weights or molecular weights (abbreviated FW or MW) for relevant compounds: you will often need to calculate these for yourself using the periodic table and the formulas; just add up the atomic weights according to the formula
3. Usually, you'll need to figure out how many moles react; to do this, you'll need to decide what is the limiting reactant, by comparing the number of moles of each compound that are present and the coefficients in the equation
4. Finally, once you have all the parts you can do a dimensional analysis-style unit conversion to find the answer. Make sure you understand what each step does and that each step is multiplying by 1. You might also need to do some other addition or subtraction, depending on what the question asks for, such as subtracting the amount of a compound that reacts from the initial amount to find the part left over



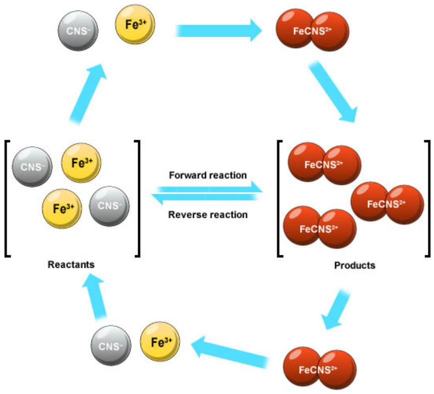
An example of a stoichiometry calculation.

Stoichiometry and Reaction Concepts

Doing stoichiometry calculations isn't just a procedure to solve a problem in a book. It is a way to describe things that actually happen, and it is related to concepts and understanding of chemistry.

Stoichiometry calculations are based on the conservation of mass (see the Lavoisier page) and the idea that particles like nuclei and electrons aren't created or destroyed during reactions, just rearranged. These understandings allow us to make these calculations.

Stoichiometry calculations are also related to the concept of chemical equilibrium. **Equilibrium** means a stable state in which opposing forces are balanced. For instance, when you stand on one foot, to maintain your balance and not fall over, if you move a little to one side, you will need to correct that and move back a little in the other direction so you don't lose your balance. In chemistry, equilibrium means a state in which 2 opposite processes are occuring, but at the same rate. For instance, the reaction may go in the forward direction (to the right), and at the same time some molecules of product are turning into reactants, going in the reverse direction (to the left). In many chemical reactions, both directions are possible; when they are happening at the same rate, that is called **dynamic equilibrium**, which means "moving equilibrium", because the individual molecules are moving back and forth between "reactant" and "product" (which are really just defined by how you write the equation), but the total amounts of reactant and product aren't changing.



A reaction in a state of dynamic equilibrium.

When we do stoichiometry calculations, we assume that the reaction will be complete, meaning that the limiting reactant will react completely, so none is left, forming as much product as possible. However, this is only sometimes what happens. There are several reason why this might not happen.

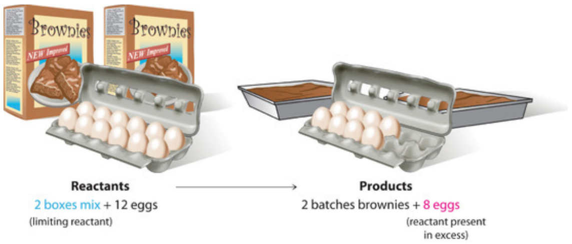
Possible Reasons why Actual Yield is Less than Theoretical Yield

- **Rate** describes how fast a chemical reaction happens. Some chemical reactions are very slow, like the ones that dissolve rock and change the shape of mountains; others are very fast, or in between. In general, the rate of a reaction will depend on the conditions, such as temperature. Right now, we will mostly talk about reactions that happen pretty quickly, but if a reaction doesn't finish before you measure it, it could be because it's too slow. This is discussed more when you study chemical kinetics.

Iron rusting - a CHEMICAL REACTION with a *slow* reaction rate.

Wood burning - a **CHEMICAL REACTION** with a ***fast*** **reaction rate**.

- The position of the equilibrium is another possible reason a reaction might not produce as much product as you calculate. For all reactions, equilibrium is reached before all the reactant is used; it might use almost all the reactant, so that you don't notice the tiny bit left over, or it might reach equilibrium with more than half the reactant left. If equilibrium is reached (if the reaction is fast enough), the predicted theoretical yield will only be reached if the equilibrium is almost all product. Later, you'll learn ways to predict where the equilibrium is. For now, just know that reactions can go both directions, and that the equilibrium isn't always all product.



Equilibrium may be like how many brownies you want to bake. If you want a lot, you use more ingredients (reactants). If you don't want as much, you use less ingredients, leaving more as excess.

The last possible complication is **side** or **competing reactions**. This means that some other reactions you haven't thought of or learned about might be happening, that use up some of the reactant or product. Because chemistry is really complicated and very few materials are actually truly pure, almost every real system or reaction will have some side reactions. Sometimes they are very important and prevent the thing you want to happen from happening; other times they don't matter at all.

Example of competing reactions during the formation of acyl azide from carboxylic acid.

For your calculations, you don't usually need to really worry about rate, equilibrium or side reactions, because we haven't learned strategies for dealing with them yet. However, to keep your mental models of chemical reactions matching real chemical systems, it's important to know that real reactions are more complicated than we make them seem in the first few weeks of chem class.

Contributors and Attributions

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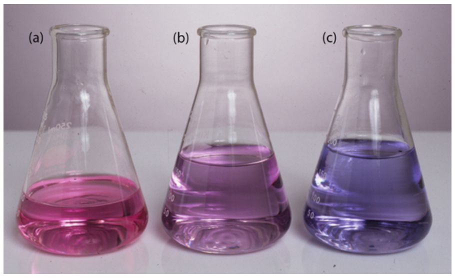
Titrations

Skills to Develop

- Perform and interpret titration calculations

A **titration** is a laboratory technique used to precisely measure molar concentration of an unknown solution using a known solution. The basic process involves adding a **standard solution** of one reagent to a known amount of the unknown solution of a different reagent. For instance, you might add a standard base solution to an mystery acid solution. As the addition takes place, the two reagents in the solutions, in this the acid and base, react. You also add an **indicator**, which is a molecule that changes color when the original reagent (the acid in the mystery solution, say) is completely consumed by reaction with the standard solution reagent. If you know exactly how much standard was added before the color change, you can calculate how many moles of the unknown were present at the beginning, and thus the concentration of the unknown.



Examples of solutions with an indicator added.

Many of the standard reagents you might use in the lab, especially HCl and NaOH, which are very common and important, are hard to prepare at precise concentration without titration. The reason is that HCl is purchased as a concentrated solution, which can vary a little in concentration because both the HCl and the water can evaporate. NaOH can be purchased as a solid, but it is **hygroscopic** which means that it absorbs water from the air. It can absorb so much water that it actually dissolves. For this reason, even if you buy it dry, once you open the bottle, it might start to absorb water, and it would be difficult to know when you measure it what % water it is. Thus, if you work in a biochemistry lab, for instance, you might want to control the pH of your solutions by adding a little bit of dilute HCl or NaOH, because chloride and sodium ions are very common and probably are already included in the solution, but you might want to know how concentrated your solutions are. To determine this, you would use a standard solution made of some easier-to-mass acid or base to titrate the solution you actually want to use. Once titrated, you could dilute it precisely to the concentration you want. Some other reagents you might want standard solutions of react with air; these you might also titrate if they have been waiting a long time so you know what the current concentration is.

Titrations might seem a little old-fashioned. Actually, the number of automated titration machines available (try a google search!) suggest that titrations are still very important in industry. One reason might be that titrations can be good for studying newly discovered molecules, for instance to measure the molecular weight and other properties that we will study more later.

Traditionally, you take a known mass or volume of the unknown solution and put it in a flask with the indicator. Then you add the standard solution in a buret, which is a special tube for adding solution slowly and measuring the volume added at the end. These days, it might be easier to use a plastic squeeze bottle instead of a buret. You put the standard solution in the squeeze bottle, get the mass of the bottle, do the titration, and then mass the bottle again. Now you know exactly how much standard was added!

Example 1

We have a solution of HCl whose concentration is known imprecisely (~2.5 M). (We made this solution in the previous section on molarity.) We want to determine the concentration more precisely. We have a solution of NaOH that is known to be 5.1079 M. We place 100.00 ml of the HCl solution in a flask with a drop of an indicator that will change color when the solution is no longer acidic. Then we add NaOH slowly until the indicator color changes. At this point, we have added 46.67 ml NaOH. Calculate the precise concentration of the HCl.

Solution

To answer, we need to know that the reaction is

$$HCl + NaOH \rightarrow NaCl + H_2O \tag{1}$$

So the ratio is 1 HCl:1 NaOH. We calculate the number of moles of NaOH added:

$$(5.1079\ mol/L)(46.67\ mL) = 238.4\ mmol \tag{2}$$

This is also the number of moles of HCl in the original 100.00 mL of solution, because the reaction ratio is 1:1. To calculate the concentration of the HCl solution, we just divide the number of moles of HCl by the volume.

$$(238.4\ mmol)/(100.00\ mL) = 2.384\ M \tag{3}$$

We could do this in one step using dimensional analysis:

$$(46.67\ \ mL\ \cancel{NaOH})\left(\frac{5.1079\ \ mol\ \cancel{NaOH}}{1000\ \ m\cancel{L}}\right)\left(\frac{1\ mol\ HCl}{1\ \ mol\ \cancel{NaOH}}\right)\left(\frac{1}{100.00\ mL}\right) = 2.384\ M \tag{4}$$

Now, we diluted 250 mL of the original stock solution to 1.00 L to make this solution. What is the concentration of the 10 M HCl, precisely? First we calculate the moles of HCl in the whole "2.5 M" solution, which is equal to the number of moles of HCl in quantity of stock solution ("10 M") that was used to make it (250ml).

$$(1.00\ \ L\ of\ \cancel{diluted\ solution})\left(\frac{2.384\ mol\ HCl}{1\ \ L\ of\ \cancel{diluted\ solution}}\right)\left(\frac{1}{0.250\ L\ of\ conc.\ \ solution}\right) = 9.536\ M \tag{5}$$

Why so low? HCl is a gas, and can evaporate out of solution. The stock solution must have been pretty old.

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CHAPTER OVERVIEW

Gases

Topic hierarchy

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Diffusion and Effusion

Skills to Develop

- Describe the interactions involved with effusion and diffusion

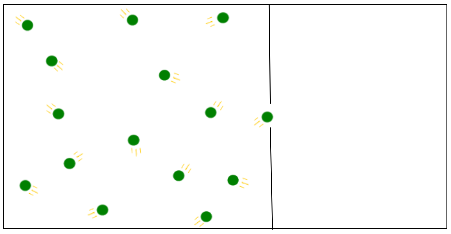
In this section we discuss movements of gases. This is actually a very complicated field (called fluid dynamics) and we will not go very deep.

Effusion

Effusion is the movement of a gas through a tiny hole into a vacuum. We want to know the rate of effusion, which is how much gas moves through the hole per unit time. We assume that the gas particles don't bump into each other while they move through the hole (this means it's a narrow hole in a thin wall). So the rate of effusion just depends on how often the particles bump the hole. This depends on their density and speed. Because at a given temperature, all gases have the same kinetic energy, their speed is inversely proportional to $m^{1/2}$, the square root of the mass. Thus, the relative effusion rates for different gases at the same temperature is

$$\frac{Effusion\ rate\ for\ gas\ 1}{Effusion\ rate\ for\ gas\ 2} = \frac{M_2^{\frac{1}{2}}}{M_1^{\frac{1}{2}}} \tag{1}$$

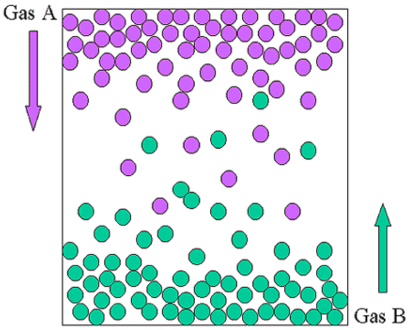
where M_1 and M_2 are the molecular weights of gas 1 and gas 2.



Effusion: a gas moving through a small hole into a vacuum

Diffusion

Diffusion is a more complicated process. It means the movement of gases through each other or the spreading of one gas through another. Because there are many collisions, the gases move much slower than we might expect from the average speeds near 400-700 m/s. (This is why it will take a moment to smell perfume when someone walks into a room.) Technically, many processes that sound like this are not exactly simple diffusion. We have to be careful about whether there are pressure differences or flows of gases (like wind). If there are then the process isn't simple diffusion and it won't follow the equations for simple diffusion perfectly. (The equation for simple diffusion is the same as for effusion, but for different reasons, see below.) For our purposes, when you want to predict relative rates of movement of gases, you can start with the effusion/diffusion equation. It will be exactly right in a few situations, and close enough in some others. The other situations you can study in a more advanced class if you are interested.



A diagram of gases slowly diffusing across an enclosed space.

Diffusion Equation Explanation

Why is the diffusion equation the same as the effusion equation, but for a different reason? In simple diffusion, 2 gases move in opposite directions through a medium with the same pressure everywhere. If the pressure in the medium is constant, then the collisions of one gas with the medium are balanced by the collisions of the other gas. The momentum given to the medium by one gas in an average collision is mV, where m is the mass and V is the diffusion velocity (which is different from the average speed of the particles: it's the overall rate of movement of the gas). The number of collisions is proportional to nv, where n is the number of particles and v is their average speed. Since there is no pressure difference,

$$(m_1V_1)\,(n_1v_1) = (m_2V_2)\,(n_2v_2) \tag{2}$$

When we rearrange, the relative diffusion flux (nV, amount of particles moving times speed of diffusion) of the gases 1 and 2 is

$$\frac{n_1V_1}{n_2V_2} = \frac{m_2v_2}{m_1v_1} \tag{3}$$

Because v is proportional to $m^{-1/2}$, this gives us the same result as the effusion equation. However, the reason is different.

Outside Links

- Khan Academy Medicine: Graham's Law of Diffusion (9 min)
- CrashCourse Chemistry: Passing Gases - Effusion, Diffusion, and Velocity of Gases (12 min)

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Gas Laws

Skills to Develop

- Explain the following laws within the Ideal Gas Law

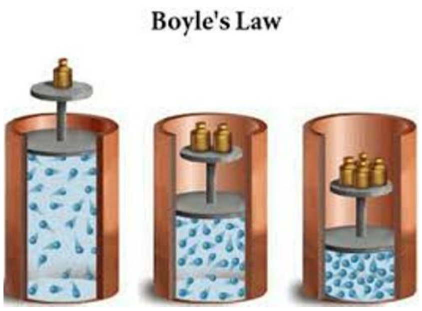
Boyle's Law

Boyle was an Irish nobleman who is often described as one of the first modern chemists, as opposed to the old alchemists. However, many of his ideas and experiments came from earlier chemist/alchemists.

Boyle observed that for a particular sample of gas at a constant temperature, if the pressure or volume is changed, the initial and final pressure and volume are related:

$$P_0V_0 = P_1V_1 \tag{1}$$

This is now called Boyle's Law. Later it was shown that Boyle's law is an approximate law, not an exact law. Most gases follow it pretty closely at normal pressures, but less closely at large pressures.



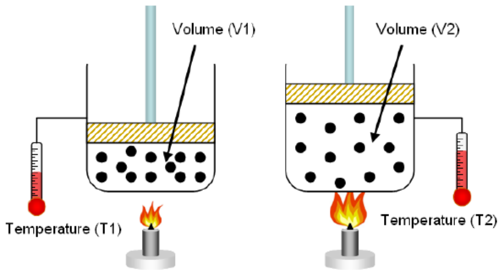
A model demonstrating how volume decreases as pressure increases.

Charles' Law and Absolute Temperature

Charles made the first solo flight in a hot-air balloon filled with hydrogen. He also observed that at constant pressure, the volume of a gas increases linearly with temperature. This can be written

$$V = kT \tag{2}$$

Notably, although he couldn't measure volumes at very low temperatures, all the lines for different gases pointed to the same temperature point. The temperature at which each gas was predicted to have V = 0 was the same, although the slopes were different. This temperature is now called 0 K = -273 °C, or absolute zero. Since gases can't have negative volume, this temperature seems to be special: the lowest possible temperature. Although in fact gases won't have zero volume at absolute zero (they'll be solids, and solids have volume), modern theory does still consider absolute zero special. In fact, we have to use temperature in Kelvin for any gas law problem.



A diagram showing how volume increases as temperature increases.

Avogadro's Hypothesis

We discussed this earlier. Although often called Avogadro's Law, it was actually a hypothesis. The hypothesis is that at the same temperature and pressure, all gases have the same number of particles (molecules). Avogadro guessed that this was true based on

Gay-Lussac's law, but he had no way to measure it directly, so it couldn't really be called a law. However, now we can be pretty sure that it is approximately true.

Ideal Gas Law

The Ideal Gas Law combines Boyle, Charles and Avogadro's laws. The Ideal Gas Law says that

$$PV = nRT \tag{3}$$

where P is pressure, V is volume, T is temperature, n is the number of moles, and R is the molar gas constant. We can express it another way too:

$$PV = nk_BT \tag{4}$$

where everything is the same except n is now the number of particles, and k_B is the Boltzmann constant. As you can see, the gas constant R is just the Boltzmann constant multiplied by Avogadro's number (the number of particles in a mole). The Boltzman constant essentially provides a conversion factor between temperature in K and energy in J. Because temperature and energy are closely connected, k_B appears in many important equations.

You can use the Ideal Gas Law to make predictions about how gases will react when you change pressure, volume or temperature. It gives you a good intuition for what gases do. The predictions it makes aren't always very accurate: they're pretty good at normal temperature and pressure, but actually for most engineering work they aren't good enough, so people use other equations or data tables instead. The Ideal Gas Law is a scientific law: it describes mathematically what happens under certain conditions, in this case low pressure. In the next section we'll describe the theory that explains the behavior of gases, which will also tell us when we should expect the Ideal Gas Law to be inaccurate.

You can use the ideal gas law to make various calculations, including with density and molar mass. We need to be careful with the units, because there are so many pressure units. Check that your value of R has the right unit for pressure, and isn't using an energy unit (because sometimes it's convenient to use energy units for R, but not in the ideal gas equation). Also make sure you use temperature in K. For example of a calculation, the ideal gas law says that the molar volume of any gas should be almost the same, and under standard conditions (1 atm and 0 °C) it should be close to 22.4 L.

Outside Links

- Khan Academy: Ideal Gas Equation (10 min)
- Khan Academy: Ideal Gas Equation Example 1 (10 min)
- CrashCourse Chemsitry: Ideal Gas Law (12 min)
- CrashCourse Chemistry: Ideal Gas Problems (12 min)

Contributors and Attributions

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Intro to Gases

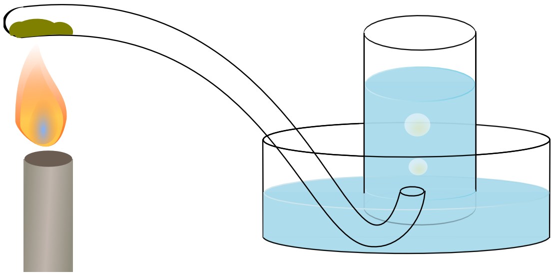
Skills to Develop

- Describe some of the history behind defining "gas"

We've described gases before, so you already know that gases are a phase of matter, like liquids and solids. Like liquids, gases can flow and change shape to fit their container; unlike liquids, gases can expand or be compressed quite a lot. They will always increase in volume to fill their container, and if you squeeze them, you can force them into a small space.

The most familiar gases are probably air and steam. People have been thinking about these gases for thousands of years. In the early study of chemistry, studying gases was very important. People didn't know at first that there are different gases made of different atoms and molecules (all gases seemed like "air"). Some very early work suggested different types of gases, while other work (like Boyle's Law) suggested that all gases were the same, since they seemed to follow the same law. It was also hard to study gases at first, because they often broke the containers scientists tried to collect them in. Lavoisier calls gases "airs"; Van Helmont created the word "gas" using the Greek word for "chaos" because when he tried to collect gases as products of reactions, the containers often shattered.

Hales, a biologist, found a good way to collect gases. He filled a bottle with water, then set it upside-down in a dish of water. He put a sample of wood, sugar, seashell, etc at the closed end of a bent metal tube, and the open end into the upside-down bottle. Then he heated the closed end, so whatever gases formed went into the bottle. But Hales thought all these gases were "air", so he just measured the amount, instead of studying their properties.



Hales' system for collecting gases produced when a material is heated

A little after Hales' work, soon Black, Priestley, Cavendish and others were discovering all the different gases: carbon dioxide, nitrogen, oxygen, hydrogen, ammonia, nitrous oxide... these studies, and especially Gay-Lussac's law, were important for discovering the basic facts of chemistry.

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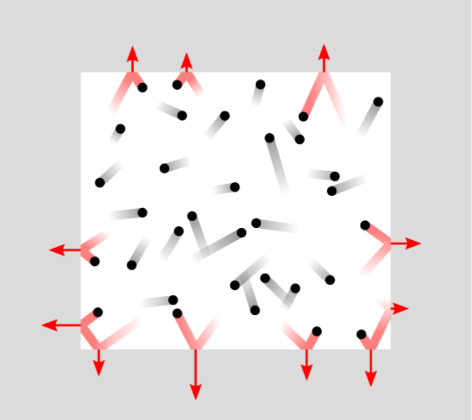
Kinetic-Molecular Theory

Skills to Develop

- Define the kinetic-molecular theory and its relationship to the ideal gas equation

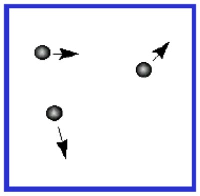
Boyle's Law was published around 1660. In 1718, a mathematician named Bernoulli proposed an explanation for Boyle's Law. Although this was almost a hundred years before Dalton's Atomic Theory, atomistic theories (also sometimes called "corpuscular theories") had been around a long time. Boyle himself had made some arguments similar to Dalton's that he borrowed from Sennert. Bernoulli assumed that the gas was made of many small particles moving quickly. They move straight until they bump into another particle or a wall, then they bounce off according to conservation of momentum. Pressure comes from the impact when these particles bump into the walls.



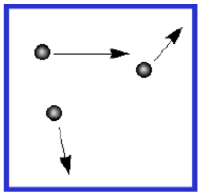
An illustration of Bernoulli's explanation of gas pressure.

How does the pressure depend on the volume? Bernoulli gives this explanation. If we compress a gas, the particles will bump the walls more often. This happens for 2 reasons: first, there are more particles in the layer next to the wall, where they can bump it. Second, particles moving away from the wall are more likely to bump into another particle, change direction, and bump the wall again. Imagine we have a cubic container, with each side length s. If volume is decreased from 1 to s^3, then the number of particles in the layer next to the wall increases by $s^2/1$. Also, the number of collisions between the wall-layer particles and the wall increases by s/1. Combining these, the number of collisions increases by s^3 when the volume decreases by $1/s^3$. The pressure is the number of impacts multiplied by the momentum of the particles, mv, where m is the mass of a particle and v is the average velocity. When you calculate the average momentum change from each collision and the average number of collisions per area of wall, the result is $P = nmv^2/3V$, where n is the number of particles and V is the volume. You can see that this matches Boyle's Law: $PV = nmv^2/3 =$ constant. Later, mv^2, the kinetic energy, was shown to be proportional to the temperature: $kT = mv^2$. This is the ideal gas equation.

How fast do gas particles move? Because the average kinetic energy is proportional to the temperature, heavier gases move slower than light gases at the same temperature. There will be a big range of speeds for different molecules, because they change speed as they bump off each other. For N_2 at 0 °C, the range might be 0-1300 m/s, with the average speed about 500 m/s. As the temperature gets bigger, the range gets bigger and so does the average speed. So the particles are usually moving very fast! How far do they go between collisions? This depends on the conditions, but the average distance between collisions might be 10^{-7} m, so not far!



Lower average kinetic energy
Lower absolute temperature



Higher average kinetic energy
Higher absolute temperature

Thus, we imagine a gas as many small particles that bump off each other perfectly elastically (with conservation of momentum). They behave like hard little balls, and don't attract each other at all. Their kinetic energy depends on the temperature. In the derivation of the ideal gas law, we assume that there are no attractive forces between the particles and that the particles don't take up any space. These two assumptions are obviously incorrect: if there are no attractions between particles, there would be no liquids or solids. Likewise, the particles do take up a little space. Since we know that attractive forces become important at low temperatures, and that the volume of the particles will be important we the volume is relatively low (meaning pressure is high) we can predict that the ideal gas equation works best a high temperatures and low pressures.

Outside Link

- CrashCourse Chemistry: Passing Gases - Effusion, Diffusion, and Velocity of Gases (12 min)

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Partial Pressures

Skills to Develop

- Define partial pressure using math equations

What if we have a mixture of different gases? We might want to know how much of each there is. We can define the mole fraction of a particular gas A as the number of moles of A divided by the total number of moles of gas:

$$x_A = \frac{n_A}{n_{total}} \tag{1}$$

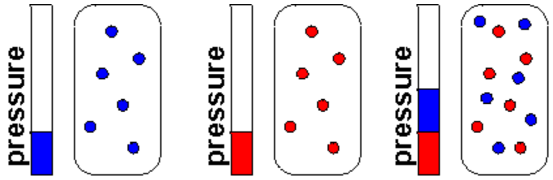
Then we can define the partial pressure of A as:

$$p_A = x_A P \tag{2}$$

This works for real or ideal gases. Partial pressures are often used to describe concentrations of gases. If the gas is ideal, then the partial pressure is the same pressure that the gas would make if all the other components of the mixture weren't there, because:

$$p_A = \frac{n_A RT}{V} \tag{3}$$

In a real gas, this might not be true because the different gases might interact a little bit differently.



An illustration of partial pressures.

Outside Links

- Khan Academy: Partial Pressure (15 min)
- CrashCourse Chemistry: Partial Pressure and Vapor Pressure (12 min)

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Pressure

Skills to Develop

- Describe the significance (and applications) of measuring pressure

What is Pressure?

Pressure is defined as force/area. For instance, the pressure from snow on a roof would be the weight of the snow divided by the area of the roof. In chemistry, usually pressure comes from gases. When you blow up a balloon, you put gas inside. The gas molecules bump into each other and into the walls of the balloon. Although the force from each molecule bumping the balloon is very small, when you put enough air in, all the collisions add up and make the balloon stretch and get bigger.

Figure 1: An illustration of pressure exerted by the air inside a balloon.

The absence of pressure is called **vacuum**. For hundreds of years, people thought that vacuums were impossible and unnatural: "nature abhors a vacuum." This isn't actually true. Miners had noticed that they could only pump water about 10 m up a pipe; the vacuum at the top from the pump wasn't strong enough to lift the water any higher. In 1641, Berti tried an experiment. He built a giant pipe about 13 m tall next to his house and filled it with water. The top of the tube was sealed. The bottom was in a big bucket. The he made a hole at the bottom so water could flow out of the tube into the bucket. Water flowed down until the water column was about 10.3 m high. Then it stopped.

Torricelli, later a companion of Galileo, experimented further. He noticed that a column of mercury (similar to the column of water in Berti's experiment) will be 760 mm high. Water has a density of 1 g/mL, while mercury has a density of 13.5 g/mL. 10.3 m/13.5 = 763 mm. From this he concluded that the column of liquid is held up not by pull from the vacuum above but by push from the weight of air (the atmosphere) on the open surface of the bucket. The weight of the mercury column, water column and air column were the same. Traditionally, pressure was measured using a **barometer**, which originally was just a tube with a column of liquid. The greater the height of the liquid, the higher the external pressure. Barometers can be used to measure pressure, which can be used to predict weather. Often low pressure means rain or storm is coming.

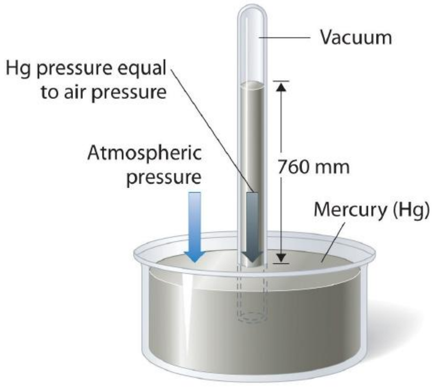
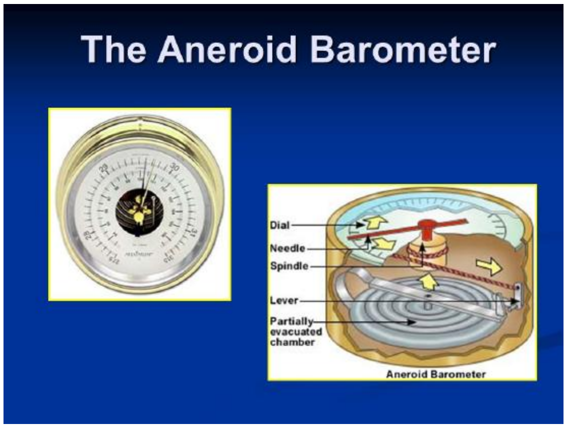


Figure 2: A diagram of a mercury barometer.

How do we Measure Pressure?

We can use a column of liquid, or other methods. One involves a small flexible container with a vacuum inside it, prevented from collapsing by springs. It expands or shrinks depending on the pressure, and this can be measured. Now there are also even smaller, simpler electrical barometers.



The Aneroid Barometer

What Units should we use?

There are a crazy number of units for pressure! A traditional unit is the torr or mmHg. This just means the height of a column of mercury. Atmospheric pressure is about 760 torr or mmHg, as discussed above. You might also see mmH_2O, which uses the same concept, but in this case because water is less dense than mercury, atmospheric pressure is about 10.3 mH_2O.

There are some more modern units also. In SI, we use Pascals: 1 Pa = N/m^2. Often it's more convenient to use bar: 1 bar = 10^5 Pa. Another unit you may have used before is the atmosphere: 1 atm = 1.01325 bar = 760 torr. The atm is close to the average atmospheric pressure.

When you use pressure units, because there are so many of them, you should be extra careful to check your units and make sure they cancel properly (see Dimensional Analysis for more). If you are using SI units in the rest of your calculation (like forces in N, mass in kg, etc) your pressure will probably come out in Pa.

How do we Control Pressure?

Often we want to control pressures, making them either higher or lower than atmospheric pressure. For instance, in chemical industry, many reactions are run at high pressures. In the lab, we might use low pressure to pull a liquid through a filter or evaporate a solvent. We also can use vacuum techniques to do "air-free" chemistry, if we want to study molecules that react with water or air, by removing all the air from our containers before adding the chemicals. Many important instruments used in physics and chemistry, like electron microscopes, only work under vacuum.

To make a vacuum, we usually use a pump to remove air. We can't make a perfect vacuum that doesn't have any gas molecules, but we can reduce the number of molecules to quite low levels. To get ultrahigh vacuum, or even just high vacuum, we might use 2 or more different types of pumps. Some pumps work by repeatedly expanding a volume, so that the gas expands into the bigger space, then gets separated from the area that is being evacuated. (See some images on Wikipedia.) Or we could absorb the gas molecules onto a surface to remove them the space being evacuated. Normal vacuum cleaners used in homes might be at 0.2 atm, while ultrahigh vacuum in a lab might be 100 nPa.

To make very high pressures, scientists sometimes use diamond anvils. For instance, geochemists who study how rocks form might put a bit of water and mineral powder between the tips of two small, pointy diamonds (just like you might see in an engagement ring). Then they push the diamonds together, and the force gets concentrated onto just the tiny tips of the diamonds, so the pressure is huge, like 3 million atm. And because the diamonds are clear, the scientists can watch what happens right through the diamond!

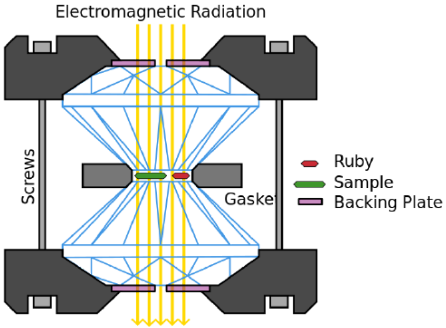


Figure 3: Cross section of a Diamond Anvil Cell. The following things are included: The two diamonds in between which the pressure is created. The sample. A Ruby which is usually used as a pressure indicator. The Gasket which seals the sample chamber The casing with the screws. Tightening of the screws moves the casings and the diamond closer together and builds pressure. The backing plate which holds the diamond in place. Electromagnetic rays which pass through the sample chamber to allow measurements. (CC-SA-BY-3.0; Tobias1984)

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Real Gases

Skills to Develop

- Describe how real gases differ from ideal gases
- Derive the Van der Waals equation from the ideal gas equation

By the kinetic-molecular theory of gases, we imagine a gas as many small particles that bump off each other perfectly elastically (with conservation of momentum). They behave like hard little balls, and don't attract each other at all. Their kinetic energy depends on the temperature. In the derivation of the ideal gas law, we assume that there are no attractive forces between the particles and that the particles don't take up any space. These two assumptions are obviously incorrect: if there are no attractions between particles, there would be no liquids or solids. Also, the particles do take up a little space. Since we know that attractive forces become important at low temperatures, and that the volume of the particles will be important when the volume is relatively low (meaning pressure is high) we can predict that the ideal gas equation works best at high temperatures and low pressures.

If we want to make another equation that is closer to the real behavior of gases, we can make a few changes in the Ideal Gas Equation. First, we will assume that the particles have some volume. Instead of V we will use (V - nb) where n is the number of molecules or moles, and b is a constant for each different gas that means roughly how big it is.

Second, we need to include the effect of attractions between particles. If the particles attract each other, they will stay closer together and pump the walls a little less, so the observed pressure will be lower than we would expect. The higher the concentration of the gas (bigger n/V), the more important the attractive forces are. Actually the attractive forces depend on $(n/V)^2$, because this tells us how many other particles each particle can interact with. So we replace P with $(P + a(n/V)^2)$, where a is a constant that depends on the gas, and tells approximately how big the attractive forces are. This makes sense because bigger attractive forces happen when the particles are very close together (V is small), and they cause the pressure to seem lower.

Putting this together, we have the Van der Waals equation:

$$\left(P+a\left(\frac{n}{V}\right)^2\right)(V-nb)=nRT \tag{1}$$

This equation describes real gases pretty well, although there are other equations used also. The constants a and b are found by fitting the real data for each gas to this equation. You can look up values of a and b in tables.

Outside Link

- CrashCourse Chemistry: Real Gases (12 min)

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CHAPTER OVERVIEW

Lewis Bonding Theory

Topic hierarchy

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Drawing Lewis Structures

Skills to Develop

- Establish a general procedure for drawing Lewis structures
- Describe the interactions between atoms using Lewis structures (what happens to the valence electrons)

Everyone who has studied chemistry should be able to draw Lewis structures. Although there are many complicated situations, and some people try to stretch Lewis structures to be an accurate description of molecules even when they don't work well, the basic idea is simple. Here's how I draw Lewis structures.

1. You count the valence electrons. Count the valence electrons for each atom, add them up, and add or remove electrons if there is an overall charge.
2. You figure out what the connections between atoms are. Sometimes you might look this up. Other times, you have to guess. If the molecule is linear (like HCN) usually it is written in the correct order. If it is a polyatomic ion, like sulfate or nitrate, usually you put the heavy atom, or the atom to the left in the periodic table, in the center. You should probably not put all the atoms in a line if there are more than 4 (single-bonded chains are usually very unstable, except for carbon). Elements like N, C, S, P, Cl and the heavier elements in these groups can easily connect to 4 other atoms, so often they go in the middle. O should not connect to more than 2 atoms, and often only connects to one. If O connects to 2 atoms, usually at least one is C or H. H and F will almost always make just one bond. (Hydrogen bonds, which you may have heard of, are much weaker than the covalent bonds shown by Lewis structures.)
3. Once you have chosen an arrangement of atoms, add the right number of electrons. Try to make sure every element gets the right number of electrons, using **lone pairs** of electrons which are not shared, or shared pairs (which are bonds). You can draw single, double, or triple bonds. Make sure that H has 2 electrons (never more) and C, N, O, F have 8 electrons (never more, and not less unless the molecule has an odd number of electrons). The heavy elements under C-F should have at least eight electrons, and they can also connect to 6 or even 7 other atoms. B often has 6 electrons, and Be often has 4. Move the electrons around until it works. Make sure your final structure has the right total number of electrons, and that none of the atoms have too many or too few.
4. Unpaired electrons are called **radicals**, and you should avoid them. When you draw the Lewis structure, make all the electrons paired unless there is an odd number of electrons. All electrons should be in lone pairs or bonding pairs. (There are molecules, like O_2, which have unpaired electrons even though they could all be paired, but you can't predict that with Lewis structures, so assume they are all paired.)

Table 1*: Acceptable Numbers of Electrons and Connected Atoms for Common Elements*

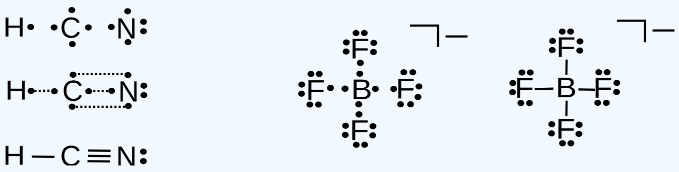
Element	Number of Electrons (including shared)	Number of Connected Atoms	Exceptions
H	2	1	Sometimes connects to 2 atoms, in H-bonding or with boron
Be	0, 4, 6, 8	2 - 4	Can be shown as ionic (0 electrons) or covalent (4, 6, 8)
B	6, 8	3, 4	Sometimes has less than 8 electrons
C	8	1 - 4	Less electrons if compound is a radical
N	8	1 - 4	Less electrons if compound is a radical
O	8	1 - 2	Sometimes connects to 3 atoms, such as in H-bonding
F	8	1	Sometimes connects to 2 atoms, such as in H-bonding

Element	Number of Electrons (including shared)	Number of Connected Atoms	Exceptions
P and below	8 or more	3 - 6	
S and below	8 or more	2 - 6	
Cl and below	8 or more	1 - 6	Can connect to 7 atoms
Xe	8 or more	0 - 6	Xe compounds with O and F are known

Example 1

First, let's do hydrogen cyanide, the poison that might have killed Lewis. The formula is HCN. As usual, this is the correct order of the atoms. The number of valence electrons in the molecule is (1 + 4 + 5) = 10. When I'm putting the electrons in, I usually start by putting each atom's valence electrons around it, then I connect the dots into lines. (These steps are shown in the picture).

For a second example, let's do the tetrafluoroborate ion, BF_4^-. In this case, we have to put B in the middle, because F shouldn't make more than 1 bond. We count electrons: (3 + 7 x 4 + 1) = 32. Remember to count +1 for the negative charge on the ion. Because B needs to make 4 bonds, we'll give it the extra electron. Then we'll connect the electrons into bonds. In this case, you know that F pulls on electrons much harder than B, so the "shared pairs" will probably be closer to F, even though the picture doesn't show that.



The construction of Lewis dot structures for HCN on the left and BF_4^- on the right.

Outside Links

- readysetorgo: dot structures I (7 min)
- readysetorgo: dot structures II (6 min)
- CrashCourse Chemistry: Bonding Models and Lewis Structures (12 min)

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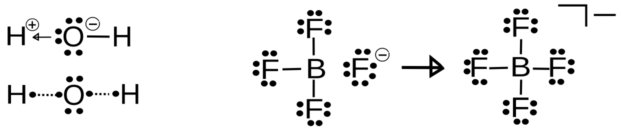
Lewis Acid-Base Theory

Skills to Develop

- Define Lewis acids and Lewis bases

Previously we said that an acid produces H^+ when dissolved in water, and a base produces OH^- when dissolved in water. Then the acid and base (meaning H^+ and OH^-) can react (without redox) to make water. This is a pretty good definition, but it is kind of small.

Lewis explained that in many reactions that form new bonds, both electrons in the new bond come from 1 atom (or 1 reactant) only, instead of 1 electron coming from each. He called all these reactions **acid-base reactions**. The picture shows water forming from the elements, in a redox process, and water forming from hydrogen ion and hydroxide ion, in an acid base process. It also shows how the tetrafluoroborate ion, BF_4^- can form from boron trifluoride and fluoride ion.



Left top, water forming by an acid-base reaction. Left bottom, water forming by a redox reaction. Right, a Lewis acid-base reaction.

In general, if we can draw a good Lewis structure by making two molecules or ions share an electron pair, it's likely that the reaction can happen. For instance, BH_3 can react with NH_3, because N has an extra lone pair, and B only has 6 electrons and 3 connected atoms. So a **Lewis acid** is something than can fit 2 more electrons from a different molecule. It can share another molecule's lone pair. A **Lewis base** is any molecule or ion with a lone pair to share. It's easy to see what can be a Lewis base just by drawing a Lewis structure. Lewis acids are usually cations, like H^+or Al^{3+}. Boron is a famous Lewis base because it often makes **electron-deficient** compounds, like BH_3, in which it only has 6 electrons. Try drawing Lewis structures for an acid-forming anhydride combination reaction. Is the anhydride a Lewis acid or base?

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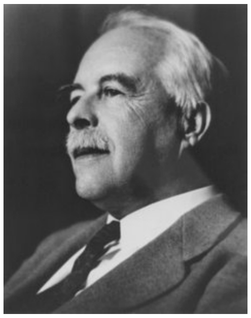
Lewis and Lagmuir

Skills to Develop

- List some of the achievements from Gilbert Newton Lewis and Irving Langmuir
- Describe the relationship between Lewis and Langmuir

You have probably already heard of Gilbert Newton Lewis' ideas. He was one of the great chemists of the 1900s, and developed the basic concepts of chemical bonding still taught to all chemistry students today. He also introduced an important acid-base theory, and did a lot of work in physical chemistry, making the energy concepts (like enthalpy and equilibrium relationships) truly useful to chemists. Although I think it is generally agreed now that he deserved at least one Nobel Prize, he did not get it at all because he did not advertise his work, and made himself a little unpopular.



Gilbert Newton Lewis

You probably haven't heard of Irving Langmuir, another great chemist from the same time. He worked on surface chemistry, and did most of his research in an industrial lab, where he invented a better light bulb and hydrogen arc welding, which is much hotter than previous welding techniques. When he and Lewis first met, they were friendly and impressed with each other. Lewis vigorously defended Langmuir when another chemist tried to steal credit for one of Langmuir's ideas. Later, though, Lewis wrote a few brilliant papers on chemical bonding, then served in World War I. The papers were not noticed, until Langmuir read them and was instantly converted. He published several more papers on the same topic, applying Lewis' ideas, and then traveled widely speaking about the theory. It became well-known and accepted because of Langmuir's efforts. Although Langmuir credited Lewis for the original idea, perhaps he didn't give Lewis as much credit as he should have. And other people associated the theory with Langmuir, because he was the one who popularized it. Lewis began to feel that Langmuir had stolen his ideas.

Irving Langmuir

The story has a sad end. When Lewis was 70, he still had not won the Nobel Prize, while Langmuir had won it for his work on surface chemistry. One day Langmuir visited University of California at Berkeley, where Lewis had built the chemistry department and run it for years. Langmuir gave a talk, and a few days later was given an award by the Berkeley chemistry department. That day, Lewis had planned an experiment using hydrogen cyanide, a deadly poison, as a solvent. About an hour after Lewis started work, he was found dead. It's not clear exactly how he died: perhaps it was a heart attack, or perhaps it was a suicide using the hydrogen cyanide. Whichever it was, it may not be coincidence that Lewis had lunch with Langmuir that day.

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Magnetism

Skills to Develop

- Describe 2 types of dipoles
- Distinguish paramagnetism from diamagnetism

In 1923, Lewis wrote that the study of spectra and magnetism are the 2 best ways to learn about chemical bonding. Some types of spectra are discussed here. In this section, we will describe the magnetic evidence Lewis used. You are familiar with normal magnets, like the ones used to stick restaurant menus to fridges. In this section, however, we are more interested in the magnetic properties of molecular materials, rather than metallic or semi-ionic solids. Most materials are non-magnetic. The molecular materials that are magnetic still wouldn't stick to your fridge, because they only really act magnetic in a magnetic field. Normally, each molecular magnetic has a random direction because the interactions between the molecules are weak. (Just like how molecular materials melt at lower temperature than metals or rocks). If you put them in a magnetic field, if they are cold enough, they will start to line up with the field. If they are too hot, they will continue to move randomly. This is called **paramagnetism**.

Dipoles

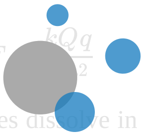
Let's start by reviewing electric dipoles. An **electric dipole** is something that had separated electrical charges. For instance, an HF molecule or a water molecule have an electric **dipole moment** defined as

$$\mu = q \times d \tag{1}$$

where q is the partial charge on each end of the molecule and d is the distance between the charges.

The electric dipole moment of water with δ representing the partial charges.

Generally, solvents with large dipoles have high **dielectric constants**. In Coulomb's law, the dielectric constant D reduces the force between charges.



$$F = \frac{kQq}{Dr^2} \tag{2}$$

Bigger D means less force. This explains how ionic substances dissolve in solvents with large dipole moments and large D. When the ions separate and have water between them, they no longer attract each other strongly.

Although you can have a point charge, magnets are always dipoles (have a North and South pole). Just like solvents and other materials have dielectric constants, they also have magnetic permeabilities.

Magnetic Measurements

How do you measure **magnetic moments** or magnetic dipoles in molecules? The old way is to put the molecular material between the poles of a big magnet and see what forces are present. For instance, if you put a paramagnetic material (that is cold enough) between the N and S magnetic poles, it will line up with the field and be attracted by the field. Thus if you weigh a paramagnetic material in a magnetic field, it will be heavier than without the field. Most materials are **diamagnetic**, and get lighter in magnetic fields, because they are repelled by the field. So the easiest way to see if a material is magnetic is to weigh it with and without a magnetic field. (Now there is a fancier method also, called SQUID, which is too complicated to explain here.)

An illustration of a magnetic moment generated from a charged, spinning nucleus.

How is Magnetism Related to Chemical Bonding?

Lewis correctly realized that molecules with an odd number of electrons (such as NO, with 7+8 =15, but not CO, with 6+8 =14) have some unusual properties. They are paramagnetic, usually strongly colored, and quite reactive. The huge majority of molecules have even numbers of electrons, and are diamagnetic. Thus, paramagnetism seems to be a result of unpaired electrons, while diamagnetism is a result of paired electrons. Transition metal compounds are often colored and magnetic; most compounds of C,H,O,N etc (such as in your body) have little color, are diamagnetic, and not so reactive. Basically, almost all molecules have all their electrons in pairs.

An illustration of the difference between paramagnetism and diamagnetism.

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Polarity of Chemical Bonds

Skills to Develop

- Distinguish polarity from polarizability
- Define polarizability

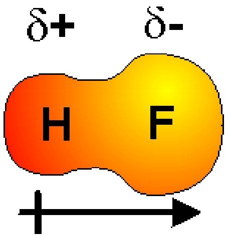
Polarity means separation, in this case of electrical charge. If a bonding pair of electrons are pulled more toward one atom and away from the other, this will cause the first atom to be partially negatively charged, and the second to be partially positively charged. This will create an electric dipole moment, such as the the dipole moment in water that makes water so good as a solvent.

Although covalent and ionic substances might seem really different, with Lewis theory we can think of them as being basically similar. At one extreme, we have a complete transfer of an electron, such as in CsF, making a positive and negative ion that are then attracted to each other. At the other extreme, we have a completely equally shared pair, such as in F_2. In between, we have bonds with unequal sharing. Either way, usually all atoms will have a **noble gas electron configuration**, either by sharing or by losing electrons.

Examples of noble gas electron configuration for various ions.

In addition to average polarity of a bond, we can have temporary polarity. The electrons move around, and sometimes it will happen that both of them move toward one atom. In general, the more electrons an atom has, the looser they are held. For example, iodine has 53 electrons, which is a lot! They can move around pretty easily. Even though I_2 has a non-polar bond on average, because the atoms are the same, it can easily become polar because the electrons are held loosely. In solution, I_2 can split a little bit into I^+ and I^-.

To keep these ideas separate, **polarity** means the permanent average separation of charge, and **polarizability** means the ability to become polarized temporarily. In a non-polar polarizable molecule like I_2, the average polarity is 0, but if we take many precise measurements of the instantaneous (very short time) polarity, many of them will be far from 0. In a polar, non-polarizable molecule like HF, all the instantaneous measurements will be very similar, but the average will not be 0. AgI is both polar and polarizable. Both of these have important effects on properties of materials, such as reactivity, solubility, and boiling point, that we will talk about later.



An illustration of the polarity of HF.

Outside Link

- CrashCourse Chemistry: Atomic Hook-ups (10 min)

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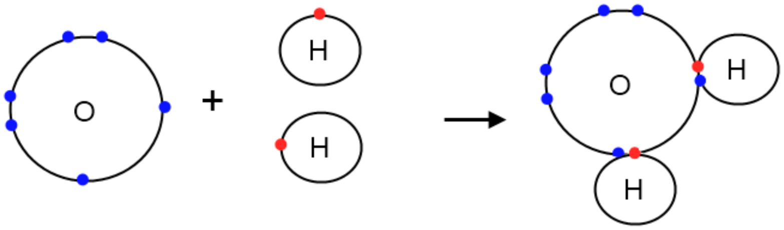
The Octet and Other Stable Groups

Skills to Develop

- Explain the stable groups described by Lewis

Lewis considered the "group of two" to be of greatest importance for understanding molecules and chemistry. However, he had also described the "group of eight", which just said that many atoms gain, lose or share electrons until they have 8 valence electrons. But he later said that the "group of eight" was less fundamental than the "group of two". This may be in part because Langmuir invented the term "octet" to replace "group of eight" and tried to force many compounds to fit it, even if they didn't seem to. Lewis recognized that not all stable compounds follow the **octet rule**. Although it usually works pretty well for elements in the p-block, the transition metals usually follow the "18-electron rule". You can see that the rule matches the periodic table: hydrogen and helium want 2 electrons, p-block elements want 8, d-block elements 18, etc.



An example of the octet rule with the formation of H_2O.

The essence of Lewis' theory is that stable compounds can be predicted and understood using what are now called "Lewis dot structures". These show the arrangement of valence electrons in a molecule. For stable molecules, it is usually possible to draw a structure in which electrons are shared so that every atom has its octet (8 electrons), either by adding, losing, or sharing electrons.

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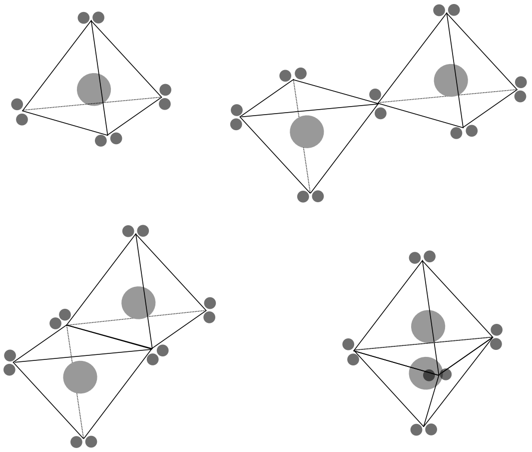
The Two-Electron Bond

Skills to Develop

- Describe Lewis' theory for bonds between atoms

The facts described in the previous section, that almost all molecules have all their electrons paired, lead Lewis to the conclusion that **electron pairs** are of central importance in chemistry. He proposed that in atoms, and especially in molecules, electrons are usually paired. He proposed this theory a little after Bohr's theory of quantum mechanics, which proposed orbits for electrons, and thought that 2 electrons could fit in each orbit. Lewis imagined that when 2 H atoms form a molecule, the 2 electrons would share an orbit "between" the 2 atoms. He didn't talk about what the orbits would really look like, but he did propose that the electrons could be imagined as sitting on the corners of tetrahedra. When atoms made bonds, they could share electrons on the points of the tetrahedra, as shown. Thus they could make single, double or triple bonds (such as in F_2, O_2 and N_2).



Lewis' idea of electron pairs on the vertices of tetrahedra, including a single atom, and single, double and triple covalent bonds. Electron pairs are shown as small grey dots and nuclei as large grey dots.

In Lewis' theory, there is no fundamental difference between covalent and ionic bonding. (Actually, he invented the idea of covalent bonding, while Langmuir invented the word "covalent," but it had been known for a while that molecules made of only non-metals had different properties from those made of metals and non-metals together). Electrons can be shared between atoms, and the sharing is more equal if the atoms are similar or the same, and more unequal if the atoms are different. Two shared electrons make one chemical bond.

Outside Link

- CrashCourse Chemistry: Atomic Hook-ups (10 min)

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CHAPTER OVERVIEW

Molecular Orbital Theory

Molecular Orbital Theory is another theory to explain chemical bonding using orbitals. It was developed about the same time Valence Bond Theory was developed, primarily by Mulliken and Hund. (Mulliken was mentioned earlier because he proposed a definition of electronegativity, and Hund because of Hund's Rule.) It is a little harder to learn than Valence Bond Theory, but very useful.

Contributors and Attributions

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Frontier MOs: An Acid-Base Theory

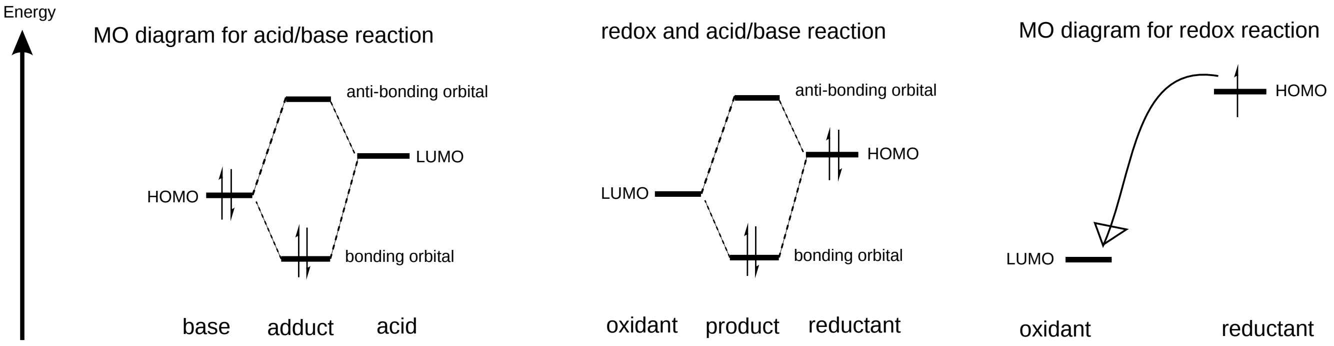
Skills to Develop

- Distinguish and describe the significance of frontier MOs

Frontier means a border area, between two things (often, between 2 countries). In this case, we are interested in the MOs at the border between occupied and empty. The **frontier MOs** are called the HOMO and the LUMO. HOMO is Highest Occupied MO, the highest-energy MO that has electrons in it. LUMO is Lowest Unoccupied MO, the lowest-energy MO that doesn't have any electrons in it.

Frontier MOs are very important for reactivity. Earlier, we said that most reactions can be called either Lewis acid/base or redox. In a Lewis acid/base reaction, an electron pair from the base is shared with the acid. What this really means is that the base has a HOMO that is pretty high-energy (a lone pair), and the acid has a LUMO that is pretty low energy. (A lone pair in MO theory is an electron pair in a non-bonding MO. A low LUMO usually means an empty valence orbital, like on B or on a cation.) We can make a bonding and anti-bonding combination of the base HOMO and acid LUMO, and that will stabilize the electrons from the base's HOMO, lowering the total energy. This creates a bond between the acid and base.

In a redox reaction, the oxidant has a low LUMO, and the reductant has a high HOMO, but this time the oxidant LUMO is lower than the reductant HOMO, so that the electrons in the reductant HOMO move completely to the oxidant LUMO. Often the energy match is bad, so that no covalent bond forms, just the electron moves. Sometimes a covalent bond forms also. This depends on the AO energies, which depends on the electronegativity, just like you would expect. You can still predict covalent/ionic bonding based on electronegativity.

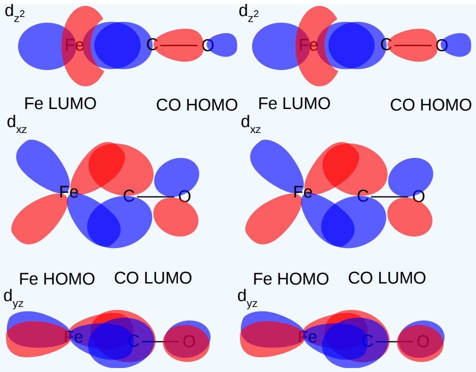


Diagrams of acid/base, redox, and both reactions.

Molecules with low HOMO and high LUMO, a big HOMO-LUMO gap, are not very reactive! Hydrocarbons are a good example (like oil, etc). They do burn easily, but you have to get them hot first. At room temperature, they don't react. This is why if you want to store something reactive like K metal, you probably keep it in a bottle of oil.

Example $FrontierMOs.1$: CO Toxicity

You probably know that CO is toxic (which is why you shouldn't stay in a garage with a car running, because the CO from incomplete combustion can kill you). The reason CO is toxic is because it binds metal ions really tightly. You use Fe(II) ions in your blood to bind O_2 and carry it to your cells. CO binds to the Fe(II) more tightly than O_2, so if you breathe too much CO, your cells won't get any oxygen, because all the Fe(II) in your blood bound CO instead. We can understand how and why CO binds Fe(II) using MO theory. Go back and look at the MO diagram for CO. The HOMO is a slightly-bonding orbital that is mostly on carbon. It is pretty high-energy. The LUMO is a π* orbital that is also mostly on carbon, and it is kind of low-energy because the splitting of π MOs is smaller than σ MOs (because of less overlap). CO has a small gap between the HOMO and LUMO. Fe(II) also has a small gap between HOMO and LUMO, because it has 6 electrons in 3d orbitals. The HOMO is high, because 3d is not so stable, and the LUMO is low, because it is also 3d and not much higher than the HOMO (there is a gap because the other atoms around the Fe(II) in hemoglobin make the d orbitals different energies). So what can happen is that the HOMO on CO makes a σ bond with the LUMO on Fe(II), and the HOMO on Fe(II) makes a π bond with the LUMO on CO. This "multiple bond" between CO and Fe(II) makes CO toxic. And because the HOMO and LUMO of CO are big on carbon, you won't be surprised that the bond is Fe-C=O, not Fe-O=C.



MO interactions between Fe and CO frontier MOs. Top: σ interaction. Bottom: π interactions (2 CO LUMOs, 2 Fe HOMOs, related by 90° rotation)

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Intro to MO Theory

Skills to Develop

- Compare and contrast MO Theory and Valence Bond Theory

Molecular Orbital (MO) Theory is another theory to explain chemical bonding using orbitals. It was developed about the same time Valence Bond Theory was developed, primarily by Mulliken and Hund. (Mulliken was mentioned earlier because he proposed a definition of electronegativity, and Hund because of Hund's Rule.) It is a little harder to learn than Valence Bond Theory, but very useful.

Robert S. Mulliken, left, and Friedrich Hund, right.

Why do we need another theory after learning Valence Bond Theory? Although Valence Bond Theory works well to explain some properties of certain types of molecules, like shape and bond strengths in organic molecules, there are many situations when it doesn't work very well. For example, it isn't very good for predicting the magnetic properties of molecules. From Valence Bond Theory, you would not expect O_2 to have 2 unpaired electrons, but it does. It also isn't good for predicting the spectroscopic properties of molecules, including what color they are. For example, you can do Photoelectron Spectroscopy on molecules, in which you knock electrons off molecules using high-energy photons. By knowing the energy of the photons and the kinetic energy of the photoelectrons, you can find the binding energies of the electrons in the molecule. For water, you would expect from the Lewis structure that there are 2 different binding energies for valence electrons (because they are either lone pairs or bonding pairs) and another higher energy for the O 1s electrons. However, the data shows 4 different energies, meaning that the 4 electron pairs in the Lewis structure all have different energies. MO Theory can explain this. MO theory is also good for predicting how strong bonds are, for predicting stability of weird molecules (like C_2), and for describing bonding in molecules that have resonance structures.

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MO Diagrams for First Row Diatomic Molecules

Skills to Develop

- Construct MO diagrams for simple diatomic molecules

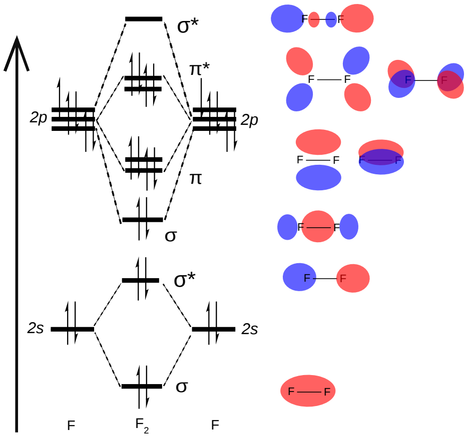
Overview

In this section, we will compare MO diagrams for diatomic molecules X-X, from Li_2 to Ne_2. We will predict their bond order and see how the energies of the different orbitals change. We will also compare our predictions to experimental evidence. First, though, we need to talk about a new effect, s-p mixing.

s-p Mixing

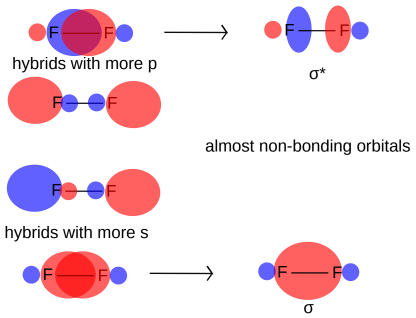
Let's think about the orbitals we use to make MO diagrams for the first row elements, Li-Ne. We don't have to worry about 1s orbitals, because their interactions don't have much effect on the properties of the molecule. The core orbitals are completely full, so there can't be any net bonding between them. They are also smaller, so they have worse overlap with core orbitals on other atoms, and lower energy, so they have bad energy match with valence orbitals on other atoms.

We will use 2s and 2p orbitals. The 2p orbitals that make π combinations don't do anything new. But we have to think more about the σ orbitals. Both 2s and $2p_z$ can make σ bonds. Do they do this separately? It turns out that sometimes they do and sometimes they don't. In molecules like F_2, they mostly interact separately, because the energy match between them is very bad. F 2s is much lower energy than F 2p. So you get an MO diagram as shown in the figure. You can see that including the 2s orbitals does not change the bond order, because both the bonding and anti-bonding combination are filled.



Full valence MO diagram for F_2, showing all valence orbitals and electrons.

However, in elements with less difference between the 2s and 2p energies, like carbon, the 2s and $2p_z$ orbitals can mix. This means that we can add some p-character to the bonding s combination, so the overlap is better. And we can add some p-character to the s anti-bonding combination so that the overlap is worse, and it is less anti-bonding. (Basically they form sp hybrids, like you have seen before. However, they are unequal hybrids, with more s in one and more p in the other.) We can picture sp hybrids making 4 combinations. We get a strongly bonding combination, a weakly bonding combination, a weakly anti-bonding combination, and a strongly anti-bonding combination. Or you can think of it as making a bonding, 2 non-bonding, and an anti-bonding combination. The combinations are shown in the figure.



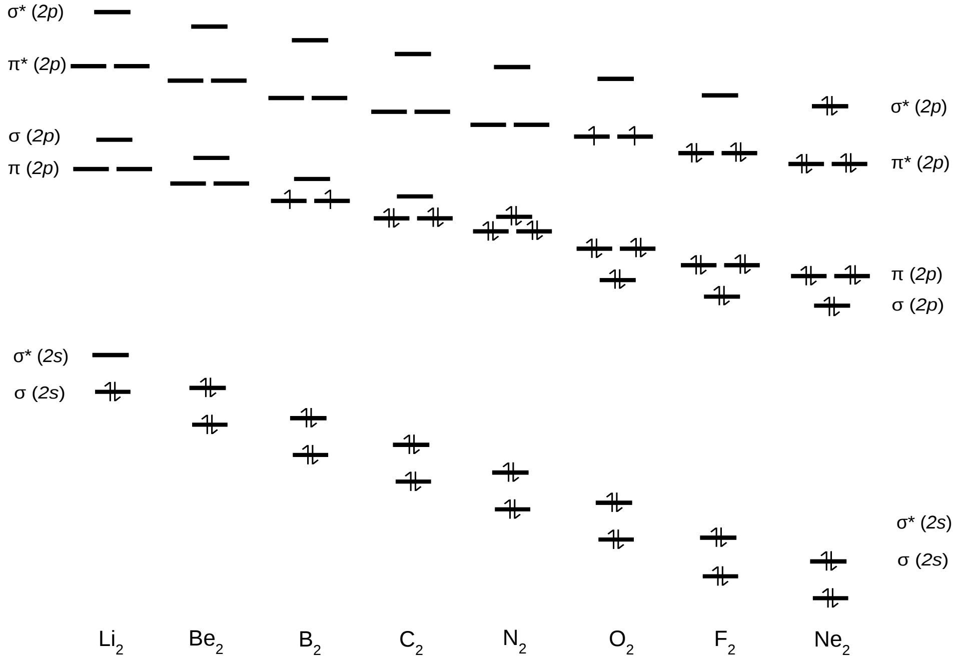
MOs made from sp hybrid orbitals. The slightly anti-bonding orbital is lower than the slightly bonding orbital, because it is still mostly made of s orbitals.

What effect does sp-mixing have on the MO diagram? The 2s bonding orbital becomes more bonding, and gets lower in energy. The 2p anti-bonding orbital becomes even more anti-bonding, and gets higher in energy. The two in the middle might be harder to predict (especially because the molecule will use whatever ratios of s and p in the hybrids is best for lowering the total energy) but probably the lower one gets lower and the higher one gets higher. We would have to use complicated computer calculations to know exactly, but we can make pretty useful predictions just by thinking about it.

MO Diagrams

Now we're ready to look at MO diagrams for the first row series. Note that the molecules that aren't common and stable might still be more stable in the gas phase than single atoms. For instance, in a gas of Li metal, diatomic molecules will form.

The figure shows a summary of the energy levels, so we can see how they change. The number of electrons increases as we move from right to left. You can also see that the gap between the s and p-based orbitals gets bigger from left to right. (Also see that here.) The result is that sp-mixing decreases from left to right, because orbitals only mix well if they have similar energies. Between N and O the σ(2p) crosses below the π MOs. We can match up the MO diagrams with the experimental data, such as bond length and bond strength, which suggests the bond order, and the magnetic properties, which tell us how many unpaired electrons the molecule has.



Energy levels for homonuclear diatomic molecules.

Let's go through the list. Also, you can check the table below for some data.

- Li_2: Using Lewis structures, we predict 1 bond. MO theory also predicts 1 bond. This is a longer and weaker bond than in H_2 because we are using 2s orbitals instead of 1s orbitals. The Coulomb attractions between the nuclei and bonding electrons are weaker because they are farther apart, and there is electron-electron repulsion. However, in the gas phase the molecule is stable.

- Be_2: Using Lewis structures, we predict 2 bonds. MO theory predicts <1 bond, however, because 2 electrons are in a bonding orbital and 2 are in a weakly anti-bonding orbital. The molecule is not normally stable, but has been detected at very low temperatures in the gas phase.
- B_2: Using Lewis structures, we predict 3 bonds and no unpaired electrons. Experimentally, B_2 is paramagnetic, with 2 unpaired electrons. MO theory can explain this once we include sp-mixing, which makes the 2p σ bonding orbital mostly non-bonding, moving it above the π bonding orbitals. Following Hund's Rule, we put electrons in the π orbitals unpaired. What is the bond order? It depends how much sp-mixing there is, which we can't know without computer calculations, but it should be between 1 and 2 bonds. This is a shorter and stronger bond than in Li_2 so probably it is close to a double bond.
- C_2: Using Lewis structures, we probably aren't sure how to draw it. MO theory suggests that it has 2 π bonds, and a partial σ bond (we don't know how anti-bonding the 2s σ* orbital is because we aren't sure about sp-mixing). The bond length and strength match a bond order of 2-3.
- N_2: Using Lewis structures, we predict a triple bond. MO theory also predicts 3 bonds, which match the experimental very short strong bond. Notice that in MO theory, the "lone pairs" (the 2 mostly non-bonding σ MOs) are shared over both atoms, and have different energies.
- O_2: Using Lewis structures, we predict 2 bonds and no unpaired electrons. MO theory also predicts 2 bonds, but correctly predicts 2 unpaired electrons. This is a longer and weaker bond than in F_2 as we would expect. If we reduce O_2 by adding electrons, they go into the π* orbitals, and make the bond weaker; this matches experimentsm showing that peroxide has a longer, weaker bond.
- F_2: Using Lewis structures, we predict 1 bond. MO theory also predicts 1 bond. This matches experiments showing a long, weak bond.
- Ne_2: Using Lewis structures, we predict no bond. MO theory also predicts no bond. Ne_2 has never been detected experimentally.

Bond Enthalpies (kcal/mol) and Bond Lengths (Å) for the Homonuclear Diatomic Molecules

Molecule	**D (kcal/mol)**	**r (Å)**
H_2	103	0.74
Li_2	26	2.67
B_2	66	1.59
C_2	144	1.24
N_2	225	1.10
O_2	118	1.21
F_2	37	1.42

Contributors and Attributions

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MO Diagrams for Heterodiatomic Molecules

Skills to Develop

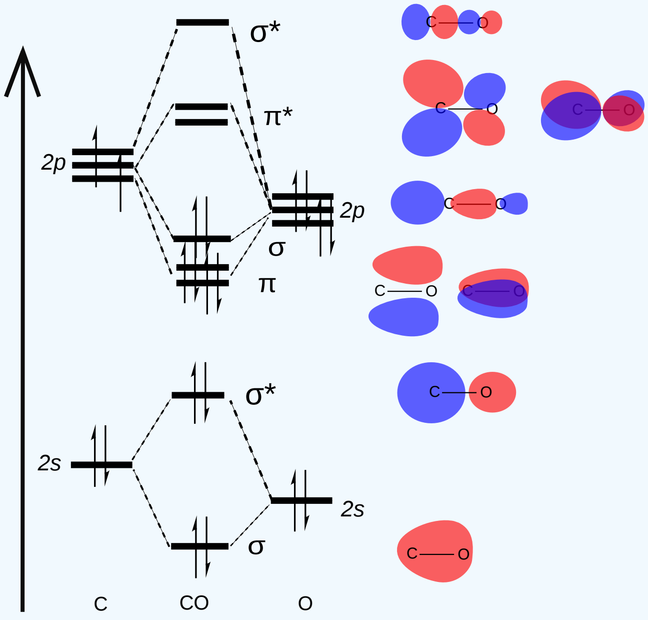
- Construct MO diagrams for simple diatomic compounds

What's Different if we have 2 Elements?

If the elements are different, the main thing is that the AOs won't have the same initial energy. If they don't have the same energy, then the splitting will be smaller. Also, the bonding MO will have a higher % of the lower energy AO and the anti-bonding MO will have a higher % of the higher energy MO. This is exactly the same as saying that it will make a polar covalent bond. The electrons will usually be in the bonding MO, not the anti-bonding MO. The bonding MO has more of the lower energy AO, so the electrons will spend more time next to the atom with lower AOs, which is the same as the more electronegative atom. The bigger the difference in electronegativity/AO energy, the smaller the splitting and the more the bonding MO looks like the AO of the electronegative atom. When the difference is really big, the bond becomes completely ionic, and the "bonding MO" basically is the lower energy AO.

Example 1: CO

This diagram is based on calculations and comparison to experiments. (But it is not drawn exactly, just approximately.) It would be hard to guess all the details, especially about the sp-mixing and the shapes and sizes of MOs. Notice that the bonding orbitals are bigger on the oxygen and the antibonding orbitals are bigger on the carbon. We will talk more about the consequences of this later.



MO diagram for CO.

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MO Diagrams for Linear Triatomic Molecules

Skills to Develop

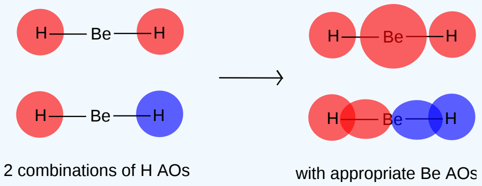
- Construct MO diagrams for simple linear triatomic molecules and/or compounds

What's Different if we have 3 Atoms?

We won't go into the details of MO theory for complex molecules, because that's a topic for more advanced classes, like Inorganic Chemistry. However, we'll show a couple examples of simple molecules so you can get the idea. We'll focus on molecules with 1 central atom and some others around it. In this case, first we combine the AOs of the outer atoms into sensible combinations, then we see how these combinations interact with the AOs on the central atom. Don't forget about **net overlap**, which is important for deciding how the orbitals interact. If they don't have net overlap, they can't interact.

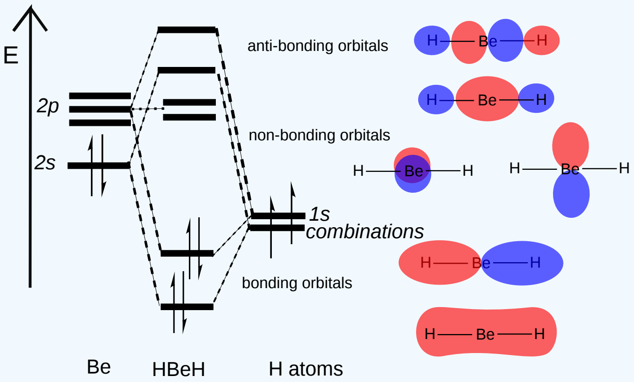
2

BeH_2 might be hard to make, but it's very nice and simple as an example! Using the electron domain model we predict that it will be linear. Be has 2s and 2p orbitals, and it is in the middle. H has 1s orbitals; there are 2 H atoms on the outside. We need to make combinations of the H AOs, and we'll use the same combinations we used to make H_2, except now they aren't touching. These combinations will match the 2s and $2p_z$ on Be, as shown in the figure.



Forming MOs for $BeH_{2.}$

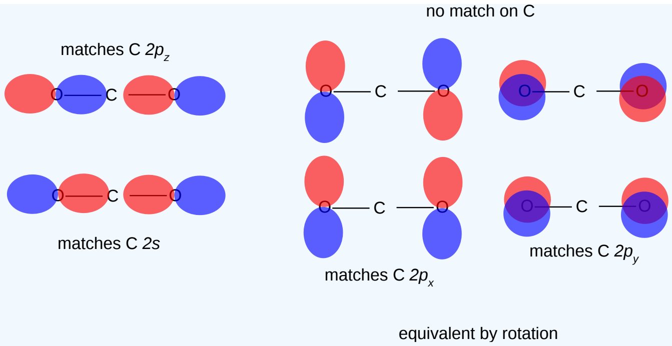
Then we can put the MO diagram together just the way we usually do, starting with the outside, drawing in bonding, non-bonding and anti-bonding MOs, and filling the electrons. The bond order is 2.



MO diagram for BeH_2.

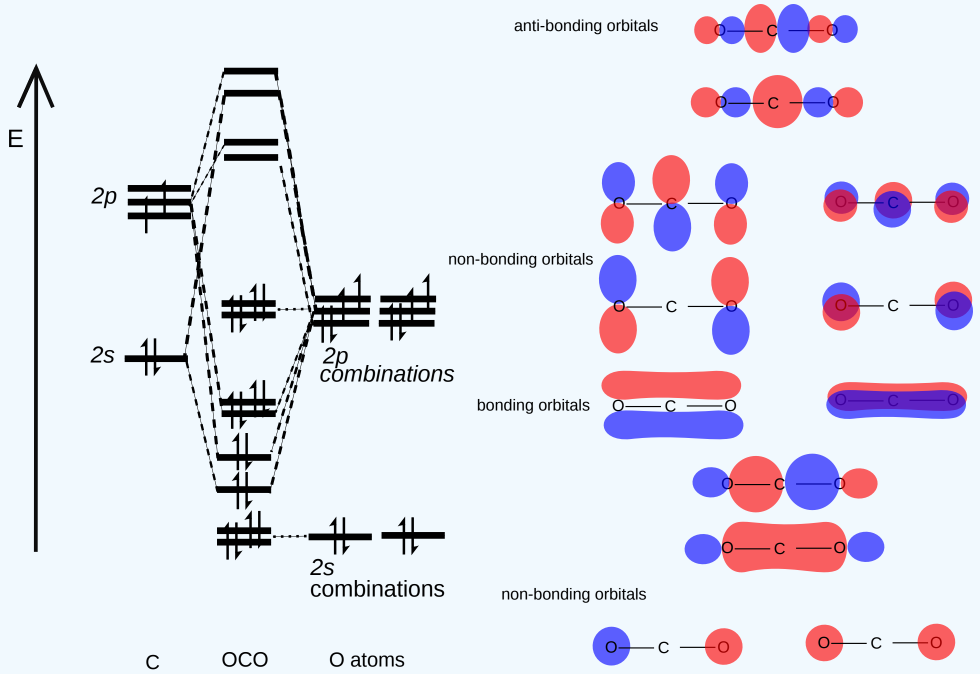
2

This is a little more complicated example. Now we have to make combinations of 4 different AOs from oxygen. We can combine 2s orbitals, $2p_x$ orbitals, $2p_y$ orbitals and $2p_z$ orbitals. Each pair will make the same add/subtract combinations we've seen before. However, for a basic diagram, we will include only the O 2p orbitals, because the O 2s orbitals are much lower in energy; they have a bad energy match so they won't interact very much. The O 2p combinations that we will use are shown in the figure, and labeled with which carbon AO they match.



Oxygen AO combinations for CO_2.

Then we combine these oxygen AO combinations with the AOs on C. We still make bonding and anti-bonding combinations just like before. And there are some non-bonding orbitals too. Just as we expect from Lewis structures, there are 2 σ bonds and 2 π bonds. However, each of these is **delocalized** over the whole molecule. The bonds aren't just between 2 atoms at a time, they connect all 3 atoms.



MO diagram for CO_2.

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MO Diagrams for Water and Nitrate Ion

Skills to Develop

- Construct MO diagrams for simple non-linear molecules and/or compounds

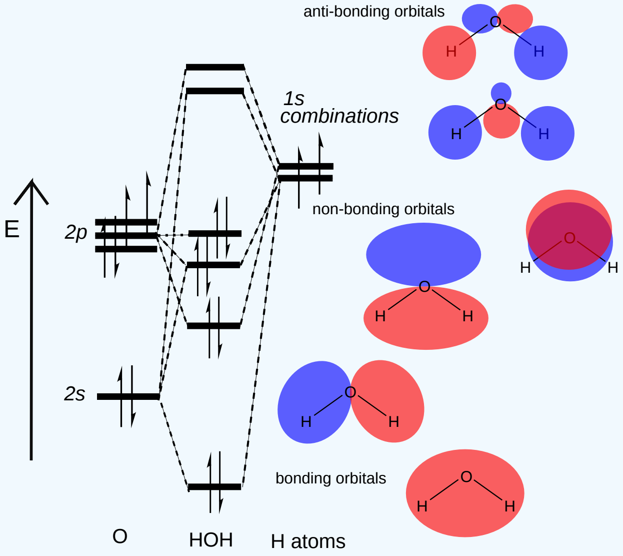
Non-linear Molecules

If you take an Inorganic Chemistry class, you'll learn ways to make MO diagrams for more complicated, non-linear molecules. Here we won't really explain these methods, just show some results. First we'll look at an MO diagram for water, because it's pretty simple and water is very important. Then we'll look at the π MOs for the nitrate ion, so we can see the difference between MO theory and valence bond theory.

Example 1: Water

This diagram is based on calculations and comparison to experiments. (But it is not drawn exactly, just approximately.) It would be hard to guess all the details, especially about the sp-mixing and the shapes and sizes of MOs. Notice that the bonding orbitals are bigger on the oxygen and the antibonding orbitals are bigger on the hydrogen. This produces the polarity that makes water a good solvent, because there is more electron density on the O and less electron density on the H.

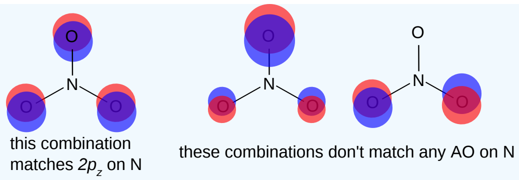
We start by making the same H AO combinations we used for H_2 and also for BeH_2. Then we do sp-mixing on O, making one orbital pointed toward the H atoms and one pointed away (which will be mostly non-bonding, like a lone pair). Then we make bonding and anti-bonding combinations of H and O orbitals that match.



MO diagram for water.

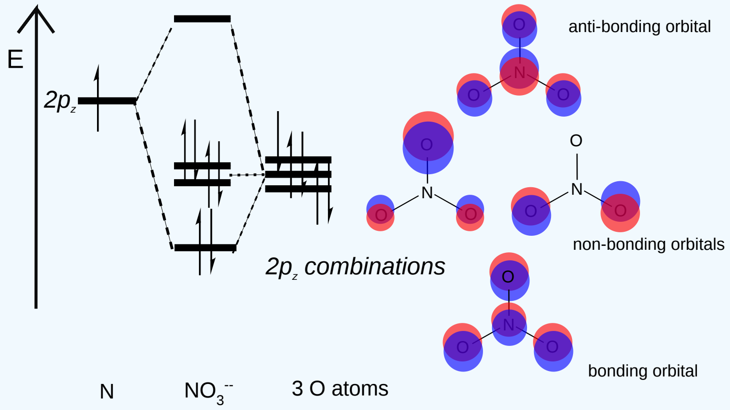
Example 2: Nitrate ion π MOs

In the section on multiple bonds using Valence Bond Theory, we talked about nitrate ion (NO_3^{-}), which has 1 π bond shared over 4 atoms (3 different resonance structures). That might have seemed kind of weird, so let's look at it again using MO theory, which treats resonance much more naturally. Let's just think about the 4 $2p_z$ orbitals, on 1 N and 3 O atoms. These orbitals point out of the plane of the molecule and will be used to make π bonds. First we will make combinations of the oxygen AOs. The combinations are shown in the figure. Don't worry about where these combinations came from too much, because that's a little too advanced for us (you'll see, if you take an Inorganic Chemistry class).



Oxygen π AO combinations for nitrate ion.

You can see that 2 of the combinations don't match the AOs on N, so they will be non-bonding MOs (like 2 lone pairs shared over 3 O atoms). One combination matches the N orbital, so it will make bonding and anti-bonding combinations. There are 6 π electrons in nitrate, so the bonding and non-bonding MOs will be filled. This means there is one π bond shared over the 4 atoms, which is just what valence bond theory says also.



π MO diagram for nitrate ion.

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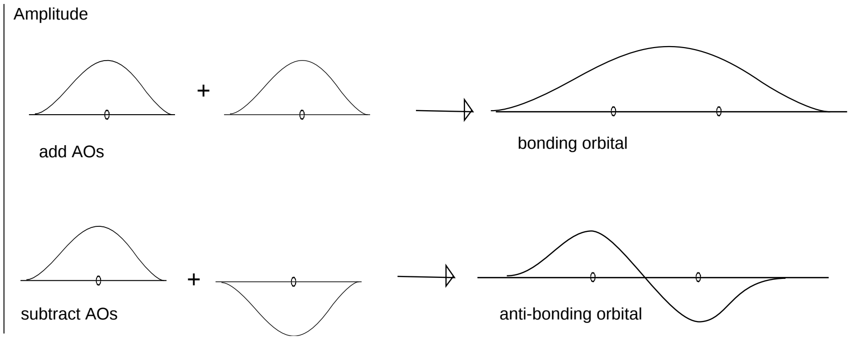
MO Theory: Simplest Examples

Skills to Develop

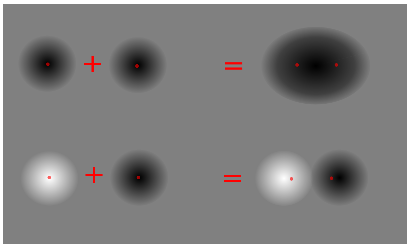
- Construct MO diagrams for H_2 and He_2
- Define bond order in theory and calculation

MO Theory for H_2

Let's find the MO description of H_2. We are going to use one electron on each H atom, each in a 1s orbital. When we bring the 2 atoms next to each other, we can make 2 MOs out of the 2 1s AOs. As always, we will do a + combination and a — combination. These combinations are illustrated in the figure below.



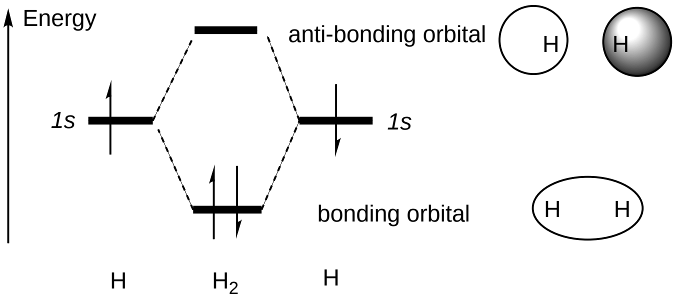
The formation of MOs from 1s orbitals, illustrated with approximate 1D waves, showing Ψ vs radius. The small circles show the positions of the nuclei. We add the 2 waves on the left to get the total wave on the right.



The formation of MOs from 1s orbitals, illustrated with approximate 2D drawings. The small pink dots show the position of the nuclei. Positive amplitude of Ψ is shown with black, negative amplitude of Ψ is shown with white, on a gray background. Where positive and negative amplitude waves overlap, the sum approaches zero (gray background).

Notice that the + combination produces an MO with more electron density between the nuclei, because the waves interfere constructively. The — combination produces an MO with a node between the nuclei, and not much electron density there, because the waves interfere destructively. If you think about the Coulomb's law forces, and imagine putting 2 electrons in the + MO, they will usually be between the nuclei, and the attractions between the electrons and nuclei will hold the nuclei together, making the molecule. For this reason, the + MO is called a **bonding MO**. On the other hand, if we imagine putting 2 electrons in the — MO, they will usually be on the outside of the nuclei, so the repulsion between the nuclei will push them apart, and no molecule will form. For this reason, the — MO is called an **anti-bonding MO**.

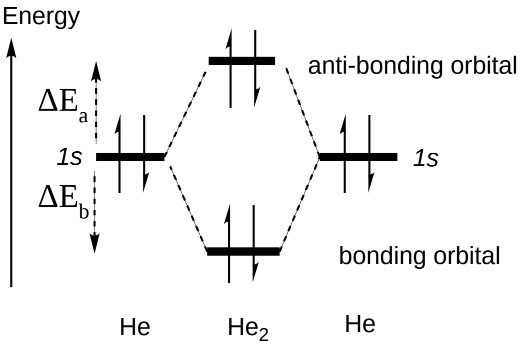
You've seen before that more nodes means higher energy. (For instance, if you try to swing a jump rope so it has a standing wave with 2 nodes, that is much harder than making a standing wave with no nodes.) So it makes sense that the bonding MO (no nodes) is lower in energy than the anti-bonding MO (1 node). Thus, in H_2, both electrons will go in the bonding MO, and the molecule is stable. In fact, the bonding orbital will be lower in energy than the AOs it was made from, because of the increased Coulomb attractions. The anti-bonding orbital will be higher in energy than the AOs because of the increased Coulomb repulsions. We can represent this with an MO diagram, shown in the figure.



MO energy level diagram for H_2. The vertical axis represents energy and the thick bars represent orbitals. The outside bars (labeled 1s) represent the H AOs. The middle bars represent the bonding and anti-bonding MOs. Because the bonding MO is lower in energy, both electrons (↿ and ⇂) go there.

MO Theory for He_2

Now let's think about He_2. We still have a combination of 2 AOs, both 1s. The bonding and anti-bonding orbitals will look very similar. But now we have 4 electrons, so we will have to put 2 electrons in each MO. Because the molecule He_2 does not exist, we can conclude that the anti-bonding orbital increases in energy more than the bonding orbital decreases in energy, so that He_2 is higher energy than 2 He.



MO energy level diagram for He_2. Because He_2 doesn't exist, we can conclude that $\Delta E_a + \Delta E_b > 0$.

Bond Order in MO Theory

One great thing about MO theory is that it makes it really simple to think about partial bonds and weird molecules, like radicals. The table shows some data for a few examples.

Molecule	Bond Length (Å)	Bond energy (kcal/mol)
He_2	*	*
H_2^+	1.06	61
He_2^+	1.08	55
H_2	0.74	103

Now try drawing the MO diagram for each molecule. What do you notice? If we calculate

net bonding electrons = (number of bonding electrons) — (number of anti-bonding electrons)

we get:

Molecule	Bonding Electrons	Anti-Bonding Electrons	Net Bonding Electrons	Bond Length (Å)	Bond energy (kcal/mol)
He_2	2	2	0	*	*
H_2^+	1	0	1	1.06	61

Molecule	Bonding Electrons	Anti-Bonding Electrons	Net Bonding Electrons	Bond Length (Å)	Bond energy (kcal/mol)
He_2^+	2	1	1	1.08	55
H_2	2	0	2	0.74	103

The number of net bonding electrons predicts the length and strength of the bond! Since we normally think of a chemical bond as a 2-electron bond, we can define the bond order like this:

$$Bond\ Order = \frac{(bonding\ e^-) - (anti\text{-}bonding\ e^-)}{2} \tag{MO Theory.1}$$

If bond order = 1, there is a single bond (H_2, for instance). If bond order = 0, we expect no bond. If bond order = 0.5, we have a 1-electron bond or a half bond. It's approximately half as strong as a 2-electron bond.

Outside Link

- ChemSurvival: A Brief Introduction to Molecular Orbital Theory (10 min)

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Mixing Orbitals to Make MOs

Skills to Develop

- Describe and illustrate MOs in a molecule

Molecular Orbitals or MOs are orbitals in a molecule. Remember that atomic orbitals (AOs) are "electron probability clouds." We can't know exactly where an electron is or what path it follows, because of the Uncertainty Principle, but we can find a mathematical function that tells us how likely we are to find the electron at each position around an atom. If we think of electrons behaving like waves, which they do, the wavefunction Ψ tells us the amplitude of the "electron wave" at each point around the atom. Ψ^2 tells us the probability of finding the electron there. When we combine atoms to make molecules, there's wave interference between the electron waves on different atoms. The electrons in a molecule occupy molecular orbitals, or MOs, that are combinations of the atomic orbitals made using the basic rules of wave interference.

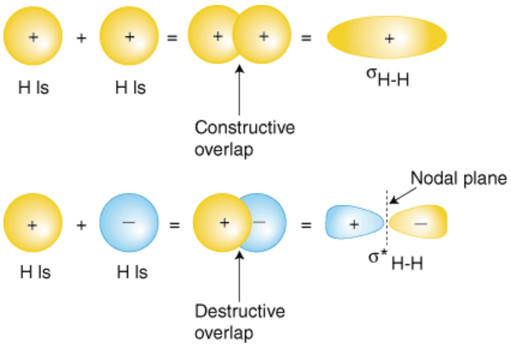
MOs have the same basic properties that atomic orbitals have. Each MO can hold 2 electrons with opposite spins. Ψ^2 still represents the probability of finding the electron. Each MO has a specific energy, and removing an electron from that MO requires that much energy. However, MOs can have very different shapes compared to MOs, and they can be spread out over many atoms in a molecule.

We make MOs in a way similar to how we made hybrid orbitals. If we combine 2 AOs (call them φ_A and φ_B) on different atoms, we will make 2 new MOs (call them ψ_1 and ψ_2).

$$\Psi_1 = C\left(\varphi_A + \varphi_B\right) \tag{1}$$

$$\Psi_2 = C\left(\varphi_A - \varphi_B\right) \tag{2}$$

We will make one MO by adding the AOs and the other by subtracting the AOs. C is a constant that "normalizes" the wavefunction so that the total probability of finding the electron over the whole atom is 1.



An example of making one MO by adding AOs, top, and another by subtracting AOs, bottom.

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Reading and Writing MO Diagrams

Skills to Develop

- Construct MO diagrams for simple diatomic molecules and/or compounds

We saw two simple MO diagrams in the section on H_2. Now let's think about how to make some slightly more complicated MO diagrams. First, we need to know a little about how big the energy **splitting** between the bonding and anti-bonding MOs is. Splitting is the energy difference between the bonding and anti-bonding orbitals. Usually the bonding orbital goes down almost as much as the anti-bonding orbital goes up, so the average energy stays almost the same. The size of the splitting depends on the **energy match** and the **overlap**.

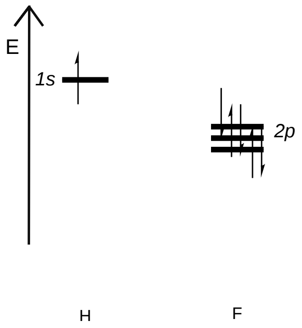
Energy match means how close the orbital energies are. The reason we can consider only valence orbitals is that the core orbitals have much lower energy, and the higher empty orbitals have much higher energy, than the valence electrons. Interactions between completely completely empty orbitals don't matter because there are no electrons. Interactions between completely filled orbitals are usually repulsive, which is why the noble gases don't usually make bonds. Interactions between partially-filled valence orbitals and either core orbitals or higher shell orbitals aren't important because the energy match is bad, so the splitting is almost zero.

We talked about overlap a little in the previous section. Overlap means how much the orbitals touch. For example, usually σ combinations have bigger overlap than π combinations, because the orbitals are pointed right toward each other. You can see this in the pictures on the previous page. For this reason, usually σ MOs have bigger splitting than π MOs.

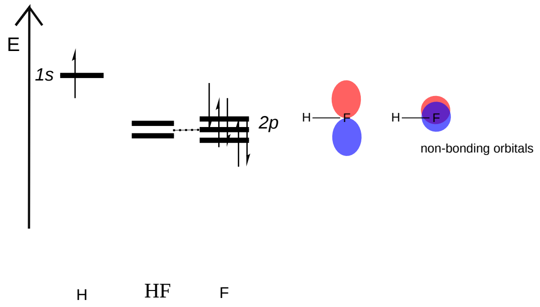
MO Diagram for HF

In the last section, we talked about the bonding, non-bonding, and anti-bonding MOs in HF. Now let's put these ideas together to make an MO diagram for HF.

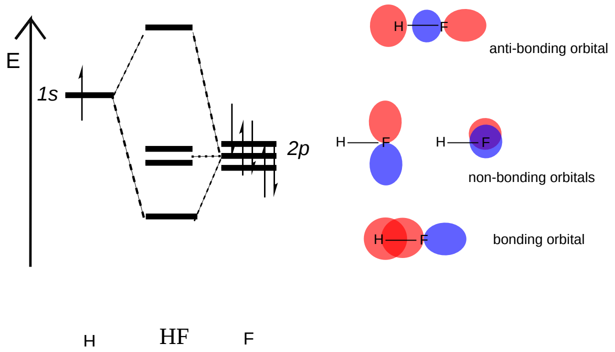
1. We need to know what orbitals we are using. We are only going to consider valence orbitals. H has a 1s orbital. F has a 2s orbital and 3 2p orbitals (x,y,z).
2. We want to know the energies of the orbitals. We can use photoelectron spectroscopy data, which tells us the energy of the different orbitals. Here is some data you can use. We see that H 1s orbital has energy -13.6 eV, F 2s has energy -40 eV and F 2p has energy -18.7 eV. Because there is a big energy difference, more than 12eV, between H 1s and F 2s (bad energy match), we can put just H 1s and F 2p in our diagram.
3. We draw the AOs on the outside of the diagram and include the right number of electrons. H has 1 valence electron, and F has 7 valence electrons. We are only including the F 2p orbitals, which have 5 electrons; the F 2s orbital holds 2 electrons and isn't in the diagram (it's like a lone pair).



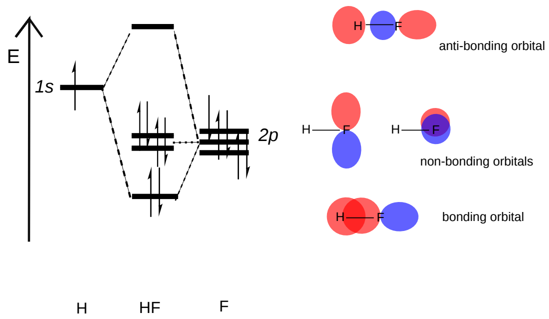
4. We remember which orbitals interact. Before, we saw that bonding and anti-bonding combinations only form between H 1s and the F 2p orbital that points straight toward it. The other 2p orbitals are non-bonding, so we can draw them in the middle at the same starting energy.



5. The H 1s and F $2p_z$ make a bonding and anti-bonding combination, so we draw these new MO energy levels. We don't know exactly how big the splitting is, but that's ok, don't worry about it.



6. We put the same number of valence electrons we had in the AOs on the outside into the MOs at the center, starting at the bottom. In this case, we have 6 electrons. They will go into the bonding MO and the 2 non-bonding MOs. The anti-bonding MO is empty because it is too high in energy. We're done!

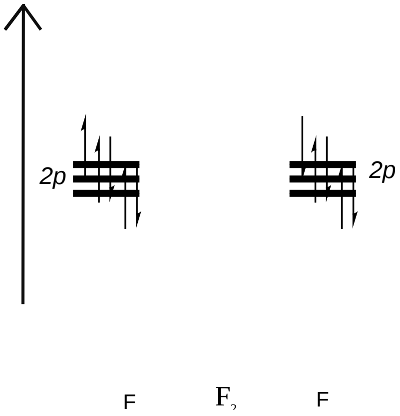


MO diagram for HF. Notice that the bond order is 1, as we expect from the Lewis structure (2 electron in bonding MO, 4 electrons in non-bonding MOs).

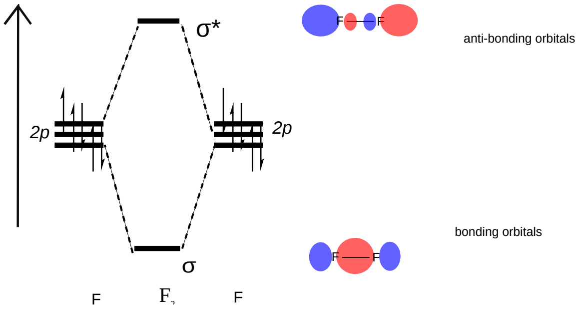
MO Diagram for F_2

Let's do another example. This time we'll do F_2, which is a little more complicated. This time we'll use σ and π bonds.

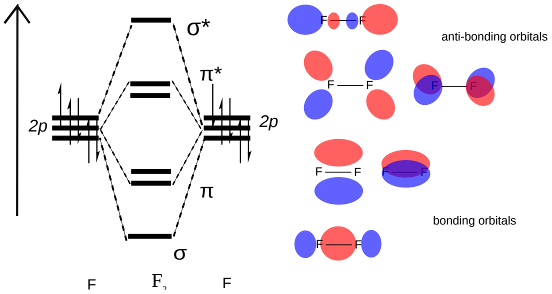
1. What orbitals we are using? F has a 2s orbital and 3 2p orbitals (x,y,z). For now, let's just consider the 2p orbitals. We'll see what happens with 2s orbital in the next section.
2. We don't need to worry about the energies this time, because they all start the same.
3. We draw the AOs on the outside of the diagram and include the right number of electrons. F has 7 valence electrons. We are only including the F 2p orbitals, which have 5 electrons; the F 2s orbital holds 2 electrons and isn't in the diagram yet.



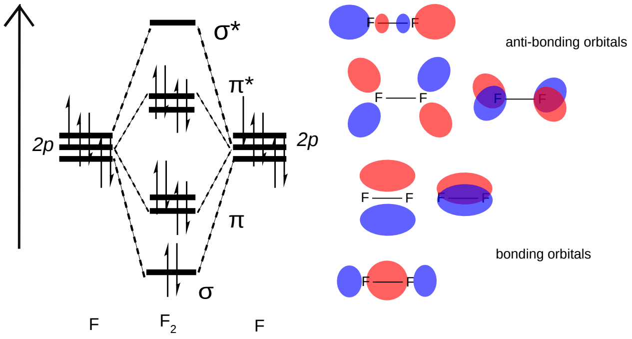
4. We remember which orbitals interact. Before, we saw that we make σ bond and anti-bonding combinations using the 2p orbitals that point toward each other. Let's draw those in.



5. We also make π bonding and anti-bonding combinations using the other 2p orbitals. Because these have less overlap than the σ combinations, the splitting will be smaller, so we'll draw these in between the σ bonding and anti-bonding orbitals. There are 2 of each (π bonding and anti-bonding), so we draw 2 lines for each. They are the same energy because the are the same except rotated 90°.



6. We put the same number of valence electrons we had in the AOs on the outside into the MOs at the center. In this case, we have 10 electrons. They will go into the σ bonding MO and all 4 π MOs. Only the σ* MO is left empty. We're done!



MO diagram for F_2. Notice that the bond order is 1, as we expect from the Lewis structure (6 electrons in bonding MOs, 4 electrons in anti-bonding MOs).

Reading MO Diagrams

When you look at an MO diagram, you can see what AOs are included by checking the outside of the diagram. The middle shows you how they combine and approximately what the energies of the combinations are. You can tell which orbitals are bonding because they have lower energy than the AOs. Non-bonding orbitals have about the same energy as the AOs, and anti-bonding orbitals have higher energy than the AOs. You can use the number of electrons in each type of MO to find the bond order. You can also tell how many unpaired electrons there are, which tells you about the magnetic properties. You can make some guesses about colors, because these usually come from having a small gap between full and empty orbitals. Finally, you can tell which parts of the molecule are most reactive: they will have a low energy empty MO or a high energy full MO. We'll see some more examples of this later.

Contributors and Attributions

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Types of MOs

Skills to Develop

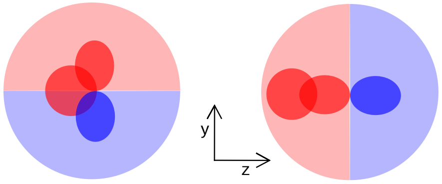
- Label the parts of an MO diagram

Bonding, Anti-bonding, and Non-bonding MOs

In the previous section, we introduced bonding and anti-bonding MOs. Bonding MOs have more electron density between the nuclei, and lower energy than the atomic orbitals they were made from. Putting electrons in bonding orbitals tends to make a bond between the nuclei, because when the electrons spend time between the nuclei, both nuclei are attracted to the negative charge between them.

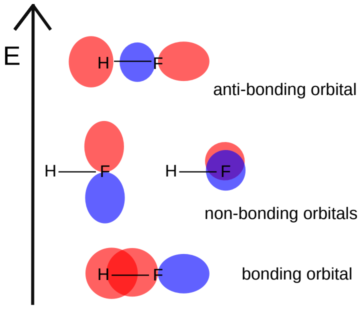
Anti-bonding orbitals have less electron density between the nuclei, because they have a node there. They have higher energy than the AOs they were made of. Putting electrons in anti-bonding orbitals tends to break bonds, because with the electrons on the outside, the nuclei repel each other and all the electrons repel each other.

There is a third type of MO: non-bonding MOs. In order to make a bond, orbitals have to have **net overlap**, which means that if you multiply them together and take the integral over the whole molecule, the integral isn't 0. Consider the HF molecule. The H 1s orbital can make a bond with the F 2s or F $2p_z$ orbital. However, there is no net overlap between the H 1s and the F $2p_x$ and $2p_y$. This is shown in the figure. When we multiply Ψ_{1s}times Ψ_{2p}, the top half is + * + = +. The bottom half is + * — = —. Except for the sign, the top half and bottom half are symmetrical, so when we add up the values of $\Psi_{1s}\Psi_{2p}$ everywhere, the top half and bottom half cancel out, and $\int \Psi_{1s}\Psi_{2p}\, dV = 0$. (Note that multiplying the wavefunctions is different from adding them, which would give us the wave interference patterns we saw in hybrids and MOs.) For this reason, the F $2p_x$ and $2p_y$ orbitals in HF are called **non-bonding orbitals**. In contrast, the $2p_z$ orbital does have net overlap with 1s, because $|\Psi_{1s}\Psi_{2p}|$ on the red side in the figure is bigger than $|\Psi_{1s}\Psi_{2p}|$ on the blue side.



Overlap between an s and p orbital, such as in HF. The s orbital is shown as a small red circle. The p orbital is shown in red and blue, representing the sign (+/—) of the wavefunction. The large circle in light red and light blue shows that the p orbital has a small amplitude over a large area. Left: the 1s and $2p_y$ orbitals have no net overlap. Right: the 1s and $2p_z$ orbitals do have net overlap.

The figure below shows a summary illustration of bonding, non-bonding, and anti-bonding orbitals in HF.

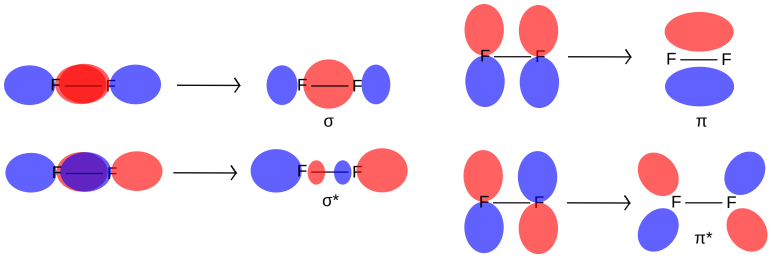


Types of MOs in HF. The sign (+/—) of the wavefunction is shown using red and blue. The MOs are ordered from bottom to top by increasing energy. Electrons in bonding MOs form bonds, electrons in anti-bonding orbitals break bonds, and electrons in non-bonding orbitals don't have any effect on bonding.

σ and π MOs

The bonding and anti-bonding MOs shown above are both σ-type MOs. Recall from the section on multiple bonds that we can classify bonds as σ or π bonds. σ-bonds are symmetrical around the bond (if you rotate them around the bond, they don't change). π-bonds change sign when you rotate them 180° around the bond.

If we think about making MOs for F_2, we can imagine making a bonding and anti-bonding combination of the $2p_z$ orbitals, which point toward each other. This will make a σ-bonding MO and an σ-anti-bonding MO. We can also make σ-type combinations of the 2s orbitals. When we combine the $2p_x$ and $2p_y$ orbitals, these are perpendicular to each other, so they will make π-type bonding and anti-bonding combinations. These are shown below. Note that for both σ combinations and π combinations electron density increases between the nuclei in bonding MOs and decreases between nuclei in anti-bonding MOs.



Formation of σ and π bonding and anti-bonding MOs in F_2. The sign (+/—) of the wavefunction is shown using red and blue. Left: σ MOs. Right: π MOs. Top: bonding MOs. Bottom: anti-bonding MOs.

Naming MOs

The easiest way to name and label MOs is using σ and π. Anti-bonding character is shown using a *, such as π* which means a π-type anti-bonding orbital. Each MO in the figure above is labeled in this way. There are other more complicated ways to name MOs, but you won't learn them unless you take Inorganic Chemistry.

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CHAPTER OVERVIEW

Periodic Trends

Periodic trends are specific patterns that are present in the periodic table that illustrate different aspects of a certain element, including its size and its electronic properties. Major periodic trends include: electronegativity, ionization energy, electron affinity, atomic radius, melting point, and metallic character. Periodic trends, arising from the arrangement of the periodic table, provide chemists with an invaluable tool to quickly predict an element's properties. These trends exist because of the similar atomic structure of the elements within their respective group families or periods, and because of the periodic nature of the elements.

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Characteristics of Metals

Skills to Develop

- List and explain the properties of metals

Remember that metals are on the left and bottom of the periodic table. Based on the periodic trends in the last 3 sections, this means that they are usually bigger, more likely to lose electrons, and less likely to gain electrons, than the non-metals.

Elemental Properties

In the elemental form, metals are usually shiny, can be bent or stretched, and conduct heat and electricity. This is because metals hold their valence electrons kind of loosely, because of the low IE. It's a general pattern that the closer an atom is to the noble gas electron configuration, the fewer bonds it makes. Metals are far from the noble gas configuration, so they usually make bonds to many neighbors. Thus, they have have structures in which each atom touches many neighbors (sometimes 6, usually 8 or 12). Because they don't have very many electrons, the valence electrons are shared by many atoms in a "delocalized ocean" of electrons that aren't really attached to particular atoms. These "free floating" electrons allow the metal to conduct heat and electricity. Also, because the bonds in a metal aren't pointed directly from atom to atom, they don't break easily. This means the metals can be bent and stretched. The technical words are malleable (can be pounded into foil) and ductile (can be stretched into wire). The sea of valence electrons allows the nuclei to be pushed around without separating. I don't think there's a simple explanation for why metals are shiny, though.

Reaction Patterns

Metals can mix with each other to form alloys that are similar to elemental metals. When they react with non-metals, they usually lose electrons to form cations. The cations are then attracted to the anions, so the result are ionic or sort of ionic compounds. The easier it is for a metal to lose electrons, the more reactive it is. If you haven't already, watch this video about the reactivity of the alkali metals. The metals on the right that have bigger ionization energies form more covalent compounds with non-metals, with more electron sharing and less pure electrostatic attraction. These metals are also more flexible about what ionic charge they have. See why by going to Ptable and watching the purple move right as you go from IE_1 to IE_4 or higher. The transition metals stay green: they don't take a sudden jump to much higher IE.

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Characteristics of Nonmetals

Skills to Develop

- List some characteristics of nonmetals
- Contrast metals and nonmetals

Remember that non-metals are on the right and top of the periodic table. Based on the periodic trends in the last 4 sections, this means that they are usually smaller, more likely to gain electrons, and less likely to lose electrons, than the metals.

Elemental Properties

In the elemental form, non-metals can be gas, liquid or solid. They aren't shiny (lustrous) and they don't conduct heat or electricity well. Usually their melting points are lower than for metals, although there are exceptions. The solids usually break easily, and can't bend like metals. It's a general pattern that the closer an atom is to the noble gas electron configuration, the fewer bonds it makes. Non-metals are close to the noble gas configuration, so they usually make a few bonds to a few neighbors. The noble gases make no bonds, and are monatomic (single atoms); halogens make 1 bond to 1 other atom, etc. This means that they don't usually form extended structures (except diamond and graphite). Instead, they form separate molecules. These molecules aren't held together tightly, so solids can easily melt or break. The electrons are held tightly by just 1 - 2 atoms, so they can't conduct electricity.

Reaction Patterns

Non-metals can react with each other to form compounds in which electrons are shared. These compounds have some of the same characteristics as the elementals forms: usually they melt or boil at relatively low temperature and don't conduct heat or electricity. When non-metals react with metals, they usually gain electrons to form anions. The cations are then attracted to the anions, so the result are ionic or sort of ionic compounds. The more a non-metal wants to gain electrons, the more reactive it is. Thus, the halogens are all reactive, but iodine is pretty safe, while bromine, chlorine and especially fluorine are really nasty and dangerous! Oxygen only seems safe and friendly to us because we are adapted to it. When oxygen first appeared in the atmosphere due to photosynthesis, most of the early life forms probably died from it; we descended from the survivors.

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Effective Nuclear Charge

Skills to Develop

- Explain the difference between nuclear charge and effective nuclear charge

The reason electrons are attached to atoms is the Coulomb's law attraction between the positively charged nucleus and the negatively charged electrons. Without the **nuclear charge** holding on to the electrons, they would have no reason to stay in orbitals near nuclei. So it makes sense that energy of the orbitals and their size depend on the nuclear charge. For instance, equivalent orbitals get lower in energy and smaller (more density closer to the nucleus) when nuclear charge increases. (If you want to see where nuclear charge is in the orbital equations, follow this link and click on an orbital; then scroll down to see the equation. Z_{eff} is the effective nuclear charge.)

There are 2 reasons an electron might not spend that much time actually right next to the nucleus, even though there is an attraction. One is **angular momentum**. Remember from physics that angular momentum is basically the momentum in the "around the center" direction multiplied by r, the distance from the center. Thus, if the electron is "in" the nucleus, r = 0, and angular momentum is 0. Remember also the second quantum number is the angular momentum quantum number ℓ, which corresponds to s, p, d and f orbitals. For s orbitals, ℓ = 0, and angular momentum is zero, so the electron can hang out at the nucleus. For the other shapes (p,d,f) angular momentum is not zero, and there is a node at the nucleus. So only s orbitals can hang out right at the nucleus.

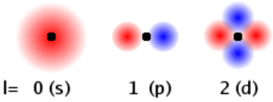

Figure 1: A basic illustration of orbital shapes with varying angular momentum and the nucleus being the black dot in the center.

The other reason an electron might not be able to get that close to the nucleus is because of the other electrons. Electrons repel each other, and because of the exclusion principle there can only be 2 electrons in each orbital. So think about lithium, element 3. Its first 2 electrons are in 1s. The third electron is in 2s. Because the principal quantum number is bigger, the 2s electron is usually farther from the nucleus than the 1s electrons. That means that often the 1s electrons are between the 2s electron and the nucleus. This means that the total Coulomb attraction felt by the 2s electron is smaller than you would calculate using just nuclear charge and distance, because there is also the electron-electron repulsion. This is the basis of the **effective nuclear charge**. Because of the electron-electron repulsions, the outer electrons in a many-electron atom feel less attraction toward the nucleus, so they feel like the nuclear charge is smaller than it actually is. So effective nuclear charge is always smaller than actual nuclear charge.

Effective nuclear charge depends on the type of electron. Electrons in s orbitals, even 4s or 5s, still spend some time right at the nucleus, and when they are there, they feel the full nuclear charge, so on average the s electrons feel a nuclear charge closer to the actual nuclear charge. Electrons in d or f orbitals really don't get very close to the nucleus, so they really get blocked, or **shielded** by inner electrons. They feel a smaller effective nuclear charge than s electrons. And electrons in p orbitals are in between.

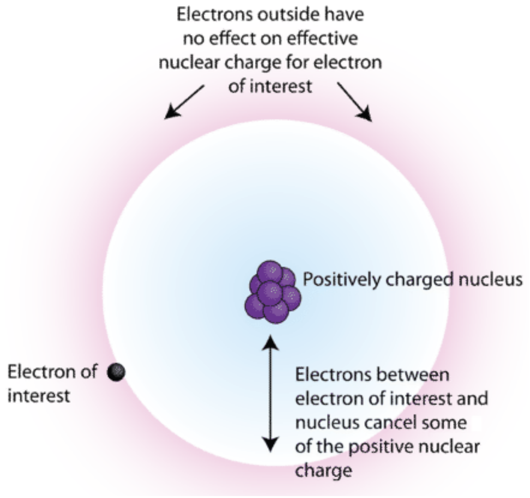

Figure 1: An illustration of the effects of electron shielding on outer electrons. (CC BY-NC; CK-12)

Usually if you do any calculation of orbitals for many-electron atoms, you will use effective nuclear charge instead of actual nuclear charge. The size and energy of the orbitals will depend on effective nuclear charge, not on actual nuclear charge. Size and energy of orbitals determines some very important chemical properties, including the size of the element (as an atom, ion, or in a molecule) and how easily it loses or gains electrons. Electrons take up most of the space in an atom, so orbital size tells you size. Losing electrons requires the energy by which they are bound, which is the roughly same as the orbital energy. Adding electrons only works if the orbital where they will go is lower energy than where they came from.

Outside Link

- Effective Nuclear Charge (10 min)

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Electron Affinity

Skills to Develop

- Define electron affinity
- Describe the periodic trend of electron affinity

Electron affinity is a measure of how much an atom wants to gain an electron, becoming an anion. Unfortunately 2 different definitions are used: intro textbooks use 1 definition and everyone else uses the other! I think you should use the standard advanced definition, according to which electron affinity EA = IE_0, the energy of this reaction:

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

The other definition just has the opposite sign, because it's the energy of this process:

$$A(g) + e^-(g) \rightarrow A^-(g) \tag{2}$$

Why does Electron Affinity matter?

Like ionization energy, electron affinity tells us how likely an atom is to steal electrons from other atoms, or just convince them to transfer their loyalty partially.

Predicting Relative Electron Affinities

It pretty much follows the same pattern you would expect based on ionization energy. If the new electron goes into an orbital that feels high effective nuclear charge, gaining an electron is good. If it goes into an orbital that is in a higher shell or subshell, or that feels low effective nuclear charge, gaining an electron is bad. The only other thing is that it's easier to add electrons to bigger atoms, because then they can spread out and not have so much electron-electron repulsion. For this reason, chlorine has more favorable EA than fluorine (in the gas phase, fluorine is still much more reactive).

Look at EA for yourself!

Go to Ptable's electron affinity page. See the general trend (bigger middle and right) with big effects at the end and middle of each block (noble gases, mercury family, alkaline earths, nitrogen, manganese).

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Ionization Energy

Skills to Develop

- Describe the significance and periodic trend of ionization energy

Ionization energy is the energy needed to remove an electron from an atom or ion. Unlike atomic radii, we can and do measure ionization energies in the gas phase, when the atom or ion is not interacting with anything else. The first ionization energy, IE_1, is the energy of this reaction

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

The **second ionization energy**, IE_2, is the energy of

$$A^+(g) \rightarrow A^{2+}(g) + e^-(g) \tag{2}$$

You can also measure third, fourth, etc. All of these assume that the highest energy electron is knocked off. If you are removing core electrons, you would write them like this: IE_{1s}, to show what orbital the electron comes from.

How do you Measure Ionization Energy?

Generally you do this by shining high energy photons on the material you want to study. UV will ionize valence electrons and X-ray can ionize core electrons. You can vary the wavelength of the photons, and also measure the kinetic energy of the electrons that come off, to see what the binding energy (orbital energy) for each electron is. You can also measure the ionization energy of molecules, which is very interesting because it can tell you how the orbital energies change because of bonding.

Why does it matter?

Ionization energy tells us how likely an atom is to form a cation, and if so, what charge. In general, it tells us how tightly the electron is bound, how stable it is. It can tell us the energies of real orbitals, the effects electrons have on each other, and help us predict reactivity and properties of molecules. (We'll talk more about this when we get to bonding!)

Predicting Relative Ionization Energies

Ionization energy depends on orbital energy, which depends on the type of orbital and the effective nuclear charge. Thus, it follows predictable patterns in the periodic table. As you go down, n increases, and the energy of the orbital increases. That means the orbital is less stable, so it's easier to pull off the electron, so ionization energy decreases. (Stable, bound electrons have negative energies; electrons that aren't in an atom have 0 energy.) As you go across the periodic table, usually the type of orbital is the same, and the effective nuclear charge increases, making the orbital more stable, so ionization energy increases. But when you change subshells, the ionization energy might increase less, because the new subshell is less stable. Also, remember Hund's rule: electrons are more stable when they don't share the same orbital. So if you have to put a new electron into an occupied orbital, that also makes the ionization energy increase less.

You can predict any relative IE just by thinking about how big the Coulomb forces are. Bigger n, means bigger distance, weaker force. Removing an electron from a neutral atom is easier than removing an electron from a cation, because of the charge. Also consider effective nuclear charge and electron-electron repulsions (especially in the same orbital). In summary, mostly IE increases up and to the right, because of low shells and high effective nuclear charge.

Look at IE for yourself!

Go to Ptable's ionization energy page. You can look at first, second, third, etc. See the general trend (bigger up and right), and also notice some exceptions as you change blocks (s-block or d-block to p-block).

Outside Links

- Khan Academy: Periodic Table Trends - Ionization Energy (12 min)
- CrashCourse Chemistry: The Electron (13 min)

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Sizes of Atoms and Ions

Skills to Develop

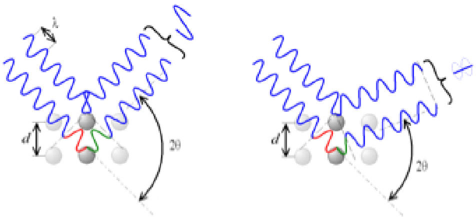
- Describe the significance of and periodic trend for atomic radii

What are Atomic Radii?

Atomic radii are the radii of atoms, a measure of how big the atoms are. That seems kind of simple. It's a useful idea because if we know the radii, we can predict how big molecules are, whether different parts will touch each other, etc. This is good for designing molecules for particular purposes, or interpreting data, and other things.

How do you Measure Atomic Radii?

This is where the trouble starts! Atoms are more like clouds than metal balls. It's easy to measure the diameter of a metal ball, because it doesn't change; the ball is hard. But how do you measure the size of a single cloud that is touching many other clouds? Remember from the nuclear model of the atom that the nucleus is very tiny. Almost all the space in an atom is taken by the electrons in their orbitals, and the orbitals, like clouds, don't have obvious edges; also, they can change size and shape when other atoms are nearby because of Coulomb forces from other nuclei and electrons. We usually measure the size of atoms using **X-ray crystallography**. Basically we shine X-rays on a **crystal** (like a salt crystal or a diamond, a crystal is an orderly arrangement of atoms with sharp, straight edges). The X-rays interact with the electrons in the crystal, and the picture we get from the X-rays can tell us the electron density at each point in the crystal. Most atoms have lots of electron density because they have 6 or more electrons. We can see how far apart these electron density peaks are, and that tells us where the atoms are. Then we guess their size based on how far away they are from each other. I say "guess" because the distance between atoms depends on whether they are bonding or not bonding, etc. So the size depends on the type of environment we look at. We can't look at all types of atoms in the same environment because they have different bonding properties, but by looking at lots of different situations we can see some general trends.



An illustration of x-ray crystallography with constructive, left, and destructive, right, wave interference.

Predicting Relative Sizes

Because electrons are what take up space in atoms, the result is that the size of the biggest filled orbital determines the size of the atom or ion. Sizes of orbitals depend on the quantum numbers (n = 1, n = 3, etc.) and also on the effective nuclear charge. An orbital of any type will get smaller as the effective nuclear charge gets bigger, because the attraction to the nucleus is greater. As you go down the periodic table, usually atoms get bigger because n gets bigger (there are electrons in higher shells). Effective nuclear charge does get bigger too going down the periodic table, but this effect is smaller than the change in shell. As you go left across the periodic table, the effective nuclear charge increases. The number of electrons also increases, but they are usually in the same shell or subshell, so the effective nuclear charge increase is more important, and the atoms or ions get smaller going left. There are many exceptions, but for now bigger to the right and down is what you should remember.

A simple illustration of the trend for atomic radii across the periodic table.

The sizes of ions follow a simple pattern. When you remove electrons, making cations, there are less electrons and less electron-electron repulsions, so the cation is smaller than the atom. The more electrons you take off, the smaller it gets. Anions are the opposite. When you add electrons, they repel each other, and there are more of them, so anions are bigger than atoms, and get bigger as you add electrons. You can combine these patterns with the general pattern for atoms to predict relative size of ions.

In general, to predict relative sizes, ask: How many electrons? What shell? What effective nuclear charge? Find the differences between the particles you are comparing, and see what effect the differences should have.

Check out the Atomic Radii for yourself!

Go to Ptable's radius page, and look at the radii. Try selecting different types of radii, like calculated, empirical, covalent, and Van der Waals. Notice that some types of radii only have data for some elements, and that the patterns change a little depending on how you measure.

Outside Link

- Ionization Energy and Atomic Radii (10 min)

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Slater's Rules for Effective Nuclear Charge

Skills to Develop

- Describe how to calculate the shielding constant using Slater's rules
- Identify a periodic trend for effective nuclear charge
- Calculate effective nuclear charge

Effective nuclear charge is really important, because it determines the size and energy of orbitals, which determine most properties of atoms. So it's useful to be able to predict effective nuclear charge! Slater's rules give a simple approximation of effective nuclear charge that works pretty well.

Based on the last section, we can expect that effective nuclear charge will depend on the number of electrons that might get between, so it depends on the electron we are looking at. For any electron, to find the effective nuclear charge it feels, we need to know how many other electrons might get in the way, and how much time it spends near the nucleus. Based on these, we will calculate a **shielding constant**, S. Then,

$$Z_{eff} = Z - S \tag{1}$$

where Z is the actual nuclear charge (which is the same as the atomic number) and Z_{eff} is the effective nuclear charge.

To calculate S, we will write out all the electrons in atom until we get to the group of the electron we want, like this:

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

1. Each other electron (not counting the one we have picked) in the same group () as the chosen electron, contributes 0.35 to S. (This means electrons in the same group shield each other 35%.
2. If the chosen electron is d or f, every electron in groups to the left contributes 1.00 to S. (This means that d and f electrons are shielded 100% by electrons with lower n or same n and lower ℓ.)
3. If the chosen electron is s or p, all the electrons in the next lower shell (n - 1) contribute 0.85 to S. (This means that s and p electrons are shielded 85% by the electrons one shell lower.) And all the electrons in even lower shells contribute 1.00 to S. (All electrons in shells n - 2 or lower shield 100%.)

The outcome of this is that Z_{eff} changes suddenly when going from one period to another. As you go from Li to Be, Z_{eff} (for the new electron) increases, because you add one proton (Z + 1) and it is only shielded 35% (S + 0.35). When you get to B, you added one proton, and it still shields 35%. So Z_{eff} increases until you go from Ne to Na. Now, suddenly, the (1s) electrons shield 100% instead of 85%, and the (2s,2p) shield 85% instead of 35%! So Z_{eff} goes down suddenly. From Na to Ar, Z_{eff} increases slowly again. From Ar to K, it drops again.

For an example, let's calculate Z_{eff} for a d electron in Zn, atomic number 30. Notice that although 4s is filled, we don't include it because it comes to the right of the d electrons we are looking at.

(1s)(2s,2p)(3s,3p)(3d)

$$S = 18(1) + 9(0.35) = 21.15 \tag{2}$$

$$Z_{eff} = 31 - 26 = 5 \tag{3}$$

You can see that just like changing periods (going to a new shell), going from the d-block to the p-block also gives a drop in Z_{eff} (partly because you actually are going to a new shell, as well as subshell).

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CHAPTER OVERVIEW

Phases and Intermolecular Forces

Topic hierarchy

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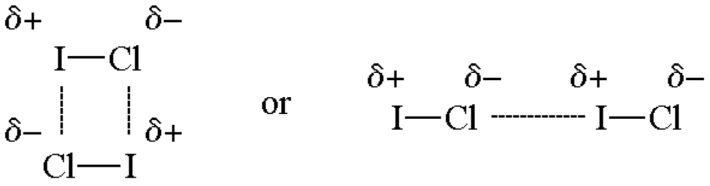
Dipole-dipole Forces

Skills to Develop

- Define and illustrate dipole-dipole forces

Dipole-dipole forces are probably the simplest to understand. You probably already know that in an ionic solid like NaCl, the solid is held together by Coulomb attractions between the oppositely-charges ions. The Na^+ and Cl^- ions alternate so the Coulomb forces are attractive. Dipole-dipole forces work the same way, except that the charges are smaller. A good example is HF (this is also an example of a special type of dipole-dipole force called a hydrogen bonding). In HF, the bond is a very polar covalent bond. That means there is a partial negative (δ-) charge on F and partial positive (δ+) charge on H, and the molecule has a permanent dipole (the electrons always spend more time on F). In the liquid or solid HF, the molecules arrange themselves so that the δ- and δ+ are close together. These partial charges attract each other, and this attraction is what we call dipole-dipole forces. Any molecule with a permanent dipole has dipole-dipole forces that hold the molecules next to each other as a solid or liquid.



An example of dipole-dipole interactions.

Outside Links

- Khan Academy: States of Matter (19 min)
- Khan Academy: Van der Waals Forces (12 min)
- CrashCourse Chemistry: Liquids (11 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Hydrogen Bonding

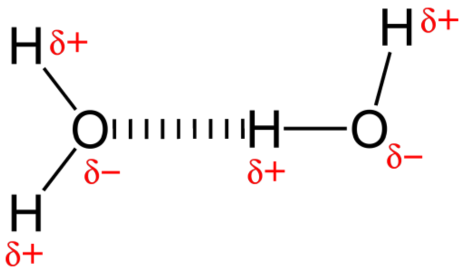
Skills to Develop

- Define and illustrate hydrogen bonds

It's a general rule that "hard" things like to bond with other hard things, and "soft" things like to bond with other soft things. (See the previous section for an explanation of hard and soft.) The reason for this is because hard-hard combinations are very favorable. Remember that hard means "hard to polarize", which usually means small and highly charged. Hard-hard combinations are based on strong Coulomb forces, between relatively big charges relatively close together.

Hydrogen bonds are a special case of hard-hard interaction that occurs in covalent molecules. Hydrogen that is bonded to very electronegative elements (N, O and F) will have a big δ+ (partial positive charge). N, O or F bonded to C or H will have a big δ- (partial negative charge). If the N, O or F has lone pairs, these can make interactions with a hydrogen on another molecule. The partial charges are pretty big, because of the big difference in electronegativity. Also, they can get very close together because these elements (especially H) are very small.

Hydrogen bonds are also an example of a dipole-dipole force, but they are extra big dipole-dipole forces because the charges are big (for partial charges) and the distances are short. They are also an example of Lewis acid-base interactions (because the electrons in the interaction come from a lone pair on N, O or F). And they are also an example of a HOMO/LUMO interaction. The H which is bound to a very electronegative atom has a low LUMO, because the energy match is bad between very different electronegativity atoms, leading to low splitting. The lone pair on the N, O or F is a high HOMO, because it is non-bonding, not bonding. These can then make a new bond.



Hydrogen bonding between two water molecules is represented by the dashed lines.

Hydrogen bonds are very important. Because they are very strong, water is a liquid over a much wider temperature range than we would expect otherwise. Hydrogen bonds are also extremely important in biochemistry. They help hold proteins in their correct shape, help DNA store genetic information, and help enzymes make reactions go quickly.

Outside Links

- Khan Academy: Van der Waals Forces (12 min)
- CrashCourse Chemistry: Liquids (11 min)

Contributors and Attributions

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Intro to Phases and Intermolecular Forces

Skills to Develop

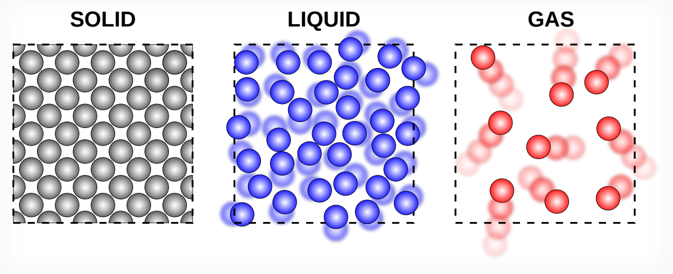
- Describe phases and phase changes on a molecular level

Phases of matter mean the state of a material, like solid, liquid or gas. How can we predict whether a material will be a solid, liquid or gas under certain conditions? We have to know about the forces that hold the material together.

In solids, the separate molecules or ions are held tightly in their positions by some type of force. They might vibrate a little bit in place, but they don't move around. For this reason, solids don't easily change shape. You might be able to bend or break them, but usually they don't change shape by themselves.

In liquids, the separate molecules or ions are held close together by some type of force, but they can move around while staying close together. For this reason, a liquid can change shape to fit whatever is holding it. But like solids, liquids have approximately constant volume. Even if the liquid flows into a new shape, the distance between the molecules doesn't change, so the total volume stays the same.

In a gas, usually the molecules bounce around as though there are no forces between them. (See Kinetic-Molecular Theory of Gases.) At very high pressure, when they are forced to be close together, we might start to notice that there are some forces between the molecules (because the pressure is less than we expect from the Ideal Gas Law) but usually they move around separately. Because they aren't really attracted to each other and have a lot of kinetic energy (at least at normal temperatures), they fill the whole space they have. So gases can take any shape, and also can change volume a lot.



An illustration of the 3 phases of matter.

The higher the temperature, the more kinetic energy the molecules or ions have. With more kinetic energy, it's harder for them to stay in their place in a solid, or not to bounce right out of a liquid and become a gas. So as we increase the temperature, we might see **phase transitions** from solid to liquid to gas. We can think about these transitions using equilibrium, like when we think about reaction and solubility equilibria. Think about a liquid in a closed container, like a bottle half full of water. Some of the molecules have bigger kinetic energy and some have smaller kinetic energy. If a molecule with big kinetic energy is on the surface of the liquid, it might fly off and enter the gas state. At the same time, other molecules in the gas state might bump the surface of the liquid, and if they don't have very much kinetic energy, they might stay there and join the liquid. This is a dynamic equilibrium: the molecules go back and forth between the 2 states. If we increase the temperature, the average kinetic energy increases, and that means the molecules are more likely to have enough kinetic energy to go into or stay in the gas phase. Liquid molecules will become gas molecules more often, and gas molecules will become liquid molecules less often. Then the equilibrium will move, so a bigger % of the total molecules are gas.

In many cases, there is a specific temperature above which all of a material goes from solid to liquid (a melting point) or from liquid to gas (a boiling point). What temperature that is depends on the strength and type of forces between the molecules and ions. If the forces are strong, then more kinetic energy is needed to make the molecules move around or separate and become gas, which means the melt point and boiling point are higher. If the forces between molecules are very weak, then the material may be a gas, and it may be hard to cool it enough to make a liquid.

A graph showing phase changes with respect to changes in temperature.

In the next sections, we will talk about the forces between molecules that determine boiling points and melting points and other important properties. (Thus, they are called **intermolecular forces**, to separate them from the forces inside molecules that hold the molecules together.) These forces are often called Van der Waals forces after Johannes van der Waals, who wrote the equation for real gases. Van der Waals figured out that the reason gas pressures are often lower than we expect (at high pressure) is because there are attractions between the molecules. Actually Van der Waals was the son of a carpenter who wasn't allowed to enter university because he didn't have the right expensive primary education. But he took classes anyway, became a teacher, and eventually they changed the rules for university admission, so he got a doctorate, became famous, became a professor, and won the Nobel Prize.

Outside Links

- Khan Academy: States of Matter (19 min)
- CrashCourse Chemistry: Liquids (11 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Liquids

Skills to Develop

- Explain some of the properties of liquids
- Distinguish cohesive and adhesive forces

In general, liquids are harder to describe than gases (in which interactions between particles are simple collisions) and solids, in which particles stay mostly still in an organized arrangement. So we will only describe some properties here. Certain properties of liquids also depend on the intermolecular forces, like the **viscosity** and **surface tension**. These roughly describe the shapes liquids take when poured, or as droplets, etc.

Viscosity

Viscosity means how thick or sticky a liquid is. For instance, water pours easily and quickly, so it is pretty low viscosity. Honey is a thick, sticky liquid that pours slowly, so it has higher viscosity. Viscosity depends on how easily the molecules can flow past each other. The smaller they are, and the weaker the forces between them, the easier they flow. If the molecules are big and flexible, they might be able to get a bit tangled together, and that could make them flow more slowly.

Surface Tension

Surface tension means how much the liquid wants to minimize its surface area. If the intermolecular forces are big, then molecules would rather be inside the liquid where they have favorable intermolecular interactions instead of being on the surface. This could make the liquid pull itself into rounded shapes to make the surface area smaller. You've probably seen water do this, like on a non-stick pan, because water has strong hydrogen-bonds. In this case, they are called **cohesive forces**, which means forces that pull the material together. (A cohesive team is very close and works well together.) On the other hand, water can have good interactions with glass surfaces, so it doesn't mind so much spreading out on glass. In fact, the forces that make water stick to glass, called **adhesive forces** are bigger than the cohesive forces in water, which is why the water in a glass tube is higher around the edges.

In contrast, mercury doesn't spread out over glass, and in a glass tube, it is higher in the middle. This means that mercury has bigger cohesive forces than adhesive forces toward glass.

Outside Link

- CrashCourse Chemistry: Liquids (11 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

London Dispersion Forces

Skills to Develop

- Define London dispersion forces

It's not too hard to see why dipole-dipole forces hold molecules like HF or H_2O together in the solid or liquid phase. However, let's think about the halogens. F_2 and Cl_2 are gases, Br_2 is a liquid, and I_2 is a solid at room temperature. But I_2 has no dipole moment to make attractions between the molecules. But actually, although I_2 has no permanent dipole moment, it can have a temporary dipole moment. We mentioned this before, when we talked about polarizability. Go back and read that section.

London dispersion forces can explain how liquids and solids form in molecules with no permanent dipole moment. "Dispersion" means the way things are distributed or spread out. Because the electrons move around a lot, sometimes they may move in a way that creates a temporary dipole moment. The more electrons an atom has, the more easily this can happen, because the electrons are held more loosely, far from the nucleus. (Basically, the energy gaps between orbitals become smaller as we move to higher shells, allowing the electrons to more easily move into excited states, occupying orbitals higher than they need to. This gives them more flexibility to move around and create temporary dipole moments.) The technical word for an element that is polarizable, or able to have temporary dipoles, is "soft". In other words, it can squish and change shape. Elements that can't polarize easily (which usually means low atomic number) are called "hard".

An example of London dispersion forces for one helium atom causing a dipole to be created on a nearby helium atom.

Fluorine is really really hard. In F_2, both F atoms are holding all the electrons really tightly, trying to grab them and not share. In contrast, iodine is really soft. It's electrons are far away from the nucleus, and they can move around easily. If they all happen to move one direction, creating a temporary dipole, the other molecules nearby can adjust, making more dipoles to attract the first one. These are called induced dipoles, because they appear in response to the original accidental dipole. Lots of induced dipoles can create attraction between molecules, called London dispersion forces.

London dispersion forces are always present, but they vary widely in strength. In light atoms, they are very small, because there aren't many electrons and they are held tightly. In large atoms, they can be very big, because the atoms are very soft and easy to polarize. Generally, London dispersion forces depend on the atomic or molecular weight of the material. Heavier atoms or molecules have more electrons, and stronger London forces. This means that they are harder to melt or boil. This explains the states of the halogen molecules at room temperature.

Outside Links

- Khan Academy: Van der Waals Forces (12 min)
- CrashCourse Chemistry: Liquids (11 min)

Contributors and Attributions

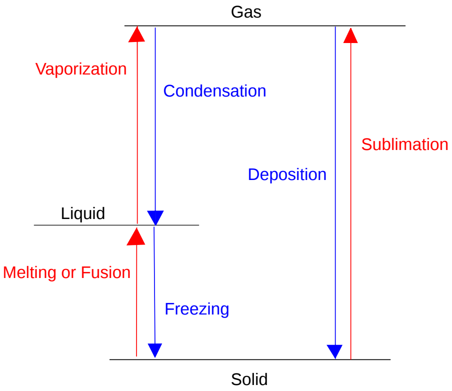
- Emily V Eames (City College of San Francisco)

Phase Changes

Skills to Develop

- Describe the relationship between heat (energy), bonding forces, and phase changes

Most phase changes occur at specific temperature-pressure combinations. For instance, at atmospheric pressure, water melts at 0 °C and boils at 100 °C. In this section, we will talk about when and how they happen. The names of the different phase changes are shown below:



Important terms describing phase changes

Predicting Phase-Change Temperatures

We can predict the relative temperature at which phase changes will happen using intermolecular forces. If the intermolecular forces are strong, then the melting point and boiling point will be high. If the intermolecular forces are weak, the melting and boiling point will be low.

London forces vary widely in strength based on the number of electrons present. The number of electrons is related to the molecular or atomic weight. Heavy elements or molecules, like iodine or wax, are solids at room temperature because they have relatively strong London forces, which correlate with big molecular weights. London forces are always present, but in small molecules or atoms, like helium, they are quite weak.

Dipole-dipole forces are present in molecules with a permanent dipole. We can predict this by drawing a Lewis structure, identifying polar bonds using electronegativity, predicting the shape of the molecule, and seeing if the bond dipoles on different molecules can touch. If they can, there will be dipole-dipole forces. The bigger the dipoles (bigger electronegativity difference, etc.) and the closer together they can get, the bigger the dipole-dipole forces are.

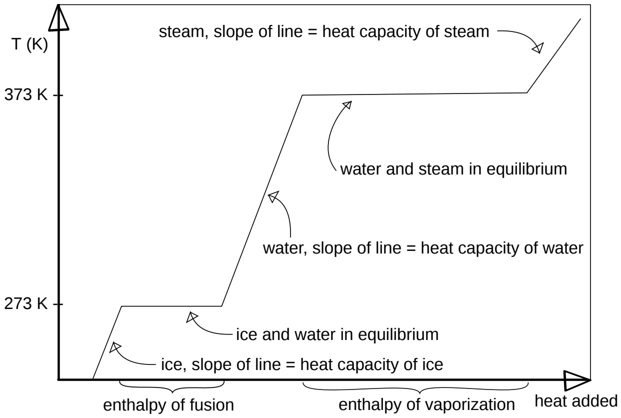
Hydrogen bonds occur only when there are H atoms bonded to N, O, or F and lone pairs on N, O, or F. Look for both of these in molecules to see if they can hydrogen bond.

If you can find which types of intermolecular forces are present in a molecule, you can make some guesses about which molecules have higher or lower melting or boiling points. For instance, let's compare methane (CH_4), silane (SiH_4), hydrogen sulfide (H_2S) and water (H_2O). Methane and silane are non-polar, because of the tetrahedral shape and also the small electronegativity differences. Because these don't have dipole-dipole forces, the boiling point will depend on how strong the London forces are. Silane is heavier, so it has bigger London forces and a higher boiling point. Between water and hydrogen sulfide, both are polar, and have dipole-dipole forces, so they have higher boiling points than methane or silane. But water has hydrogen bonds, which are extra-strong dipole-dipole forces. Water boils much hotter than hydrogen sulfide.

Energy and Phase Changes

We can't really explain phase changes in terms of energy without entropy, which we haven't talked about yet. For now, we can just say that as we add energy to a substance, it usually gets hotter and the particles have more kinetic energy. This will make it easier for them go from solid to liquid, or liquid to gas. Gases have more energy than liquids, which have more energy than solids. As we increase the temperature, the stable form of the substance goes from solid to liquid to gas. The transition temperatures (melting point, boiling point) are the temperatures at which both phases are stable and in equilibrium. Actually, there will be some gas in equilibrium with solid and liquid all the time, because a few molecules can always escape the solid/liquid, but the solid or liquid won't be present above certain temperatures.

For instance, imagine heating a solid. The molecules start moving more, and the temperature increases as predicted by the heat capacity. At some point, they have so much energy that it's hard for them to stay in the orderly solid, so the solid starts to melt. As we add more heat, the temperature doesn't change, because all the heat we add goes into melting the solid. The solid can't get any hotter than it is, and the liquid can't increase it's temperature because its kinetic energy is absorbed to melt the remaining solid. The amount of energy needed to melt the solid is the **enthalpy of fusion**. When all the solid is melted, if we keep adding heat, the temperature will rise again. As the temperature rises, the vapor pressure increases, because more molecules have enough kinetic energy to escape. Still, most of the molecules are in the liquid form, because the total pressure pushes on the liquid and keeps it from expanding into a gas. When the temperature increases to the boiling point, then the vapor pressure will be equal to the outside pressure. Now, because the vapor pressure is equal to the atmospheric pressure, bubbles form in the liquid. It can expand into a gas, because it's pressure is the same as the atmospheric pressure. The temperature will stay constant again as all the liquid become gas, while you add the **enthalpy of vaporization**. Then if you keep heating the temperature of the gas will increase. This is shown in the diagram below:



Heating diagram for water, showing change in temperature and heat is added.

Outside Links

- Khan Academy: States of Matter (19 min)
- Khan Academy: Specific Heat, Heat of Fusion and Vaporization (15 min)

Contributors and Attributions

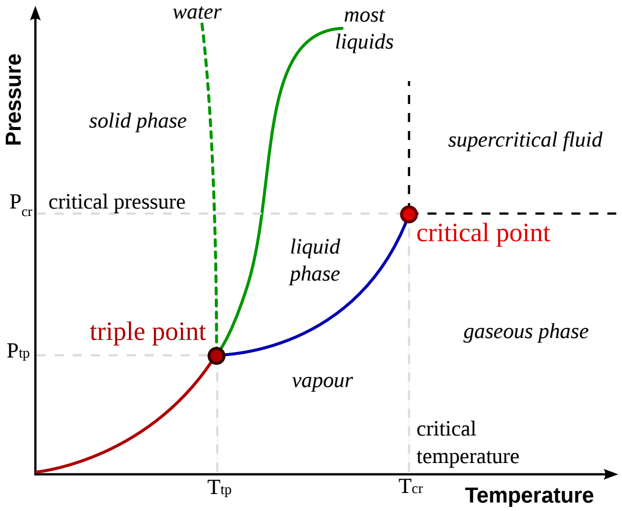
- Emily V Eames (City College of San Francisco)

Phase Diagrams

Skills to Develop

- Identify and describe the parts of a phase diagram

You know that phase changes usually depend on temperature, which determines the kinetic energy of atoms and molecules. We mentioned before that they also depend on pressure. In the section on phase changes we said that the boiling point is the place where vapor pressure is the same at the external pressure, so clearly boiling point depends on pressure! Melting temperature also depends on pressure (usually the density of solid and liquid are different, so it makes sense) but not nearly as much as boiling point, since the volume changes are smaller. We use **phase diagrams** to show how the transition temperatures depend on temperature and pressure both.



A generic phase diagram. The triple point and critical point are labeled. The solid green line represents the melting point of most liquids, and the dotted green line represents the unusual behavior of water. Figure adapted from Matthieumarechal via Wikimedia Commons.

Look at the diagram. Notice that the gas phase is on the bottom, where the pressure is low. Solid is on the left, where the temperature is low. Liquid is in between. The red line shows the sublimation point: along this line, a low pressure, solid turns directly into gas without going through liquid. The point where liquid become stable is called the triple point, where all three phases (solid, liquid and gas) are all in equilibrium. The blue line is the boiling point. Notice that the boiling temperature changes a lot with a change in pressure. The solid green line shows the melting point of most liquids. Notice that the melting point doesn't depend on pressure nearly as much as the boiling point (which makes sense, because the change in volume from solid to liquid is small). Most liquids are less dense than the solid phase, so higher pressure increase the melting point. The dotted green line shows the melting point for water. Water is denser as a liquid, so higher pressures decrease the melting temperature.

The second red point in the diagram is the **critical point**. The dotted black lines show the area where a **supercritical fluid** exists. This is the high-temperature, high-pressure part of the diagram. Because the temperature is high, the molecules have lots of kinetic energy, so a liquid form isn't really stable because the intermolecular forces aren't strong enough to hold such energetic molecules together. However, the pressure is so high that the molecules can't really get away from each other either, so they bump into each other a lot, and feel some attractions, and don't really act like a normal gas (certainly not an ideal gas!). Past the critical point, there's no distinct liquid or gas, just a supercritical fluid with some special properties.

Supercritical fluids can make good solvents. For instance, supercritical CO_2 is commonly used because it is a safe, inert, inexpensive non-polar solvent. Most non-polar solvents are not very safe (toxic and flammable), and disposing of them is expensive; supercritical CO_2 avoids these problems.

Outside Link

- Khan Academy: Phase Diagrams (13 min)

Contributors and Attributions

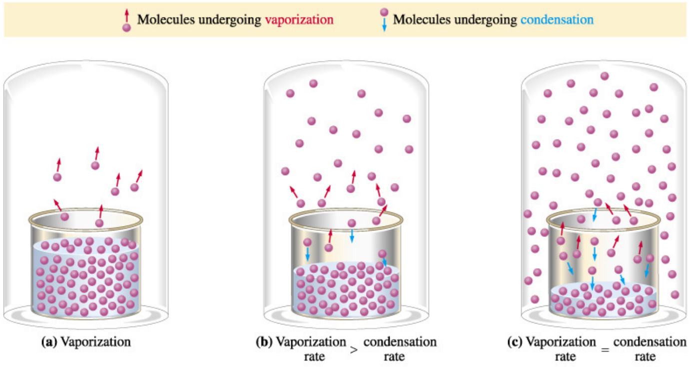
- Emily V Eames (City College of San Francisco)

Vapor Pressure

Skills to Develop

- Define vapor pressure

Whenever we have a liquid with some space above it, some of the molecules on the surface of the liquid might escape into the space and become gaseous if they have enough kinetic energy. If the liquid is in a closed bottle, then the molecules in the gas phase can't get away completely. There will be the liquid, and above it, a gas of the same molecule. The gas particles will sometimes bump the liquid, and if they have small enough kinetic energy, they might stay in it. Thus, molecules can go back and forth between the liquid and the gas. As the amount of gas increases, it is more likely to bump the surface and get stuck, so the rates of becoming gas and becoming liquid become the same. An equilibrium will be established. The partial pressure of that gas above the liquid at equilibrium will depend on the type of molecule and the temperature. If the temperature of the liquid increases, more molecules will have enough kinetic energy to escape the liquid and be gas. If the molecule has strong intermolecular forces, it will take more kinetic energy to escape the liquid.



An example of vapor pressure in a closed container.

In an open container, a liquid like water will completely evaporate eventually, even at low temperatures (even ice will disappear eventually, because solids also have vapor pressure). This happens because when the molecules become gas, they can diffuse away instead of staying near the surface, and maybe bumping it and getting stuck again.

The vapor pressure of a liquid doesn't depend on the pressure in general (at least not much). The presence of other gas molecules won't really affect the rates of the liquid molecules leaving the surface or returning to it, because their collisions with the liquid don't matter. When we collect gases over a liquid, like in Hales' method, we should include a correction for the vapor pressure of the liquid. We can find this in a table if we know the temperature.

Some liquids have a high vapor pressure and others have low vapor pressure. This depends on the intermolecular forces, like London dispersion forces, dipole-dipole forces, and hydrogen bonds. If the intermolecular forces are strong, the vapor pressure will be low. If they are weak, it will be high. **Volatile** liquids have high vapor pressure.

Outside Links

- Khan Academy: Partial Pressure (18 min)
- CrashCourse Chemistry: Partial Pressure and Vapor Pressure (12 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

CHAPTER OVERVIEW

Quantum Chemistry

Topic hierarchy

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Atomic Orbitals

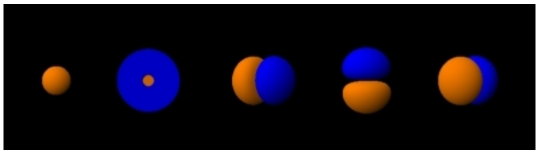
Skills to Develop

- Illustrate the general shape of atomic orbitals
- Identify the relationship between quantum numbers

The "old quantum mechanics" introduced the idea of quantization, and it was good for describing the position of spectroscopic lines of single electron atoms. But it couldn't predict how strong the lines were. The "new quantum mechanics" of Schrodinger and Heisenberg took the wave-particle duality to its logical conclusion. While Bohr's model was still "classical" in that there was a defined orbit or trajectory (a path that could be calculated) for the electron, Schrodinger and Heisenberg changed that. Basically, where is a wave? If a particle behaves as a wave, you can't point to the exact spot where it is. Also, if light energy is quantized, it turns out that you can't measure the path taken by an electron without changing the path. In microscopy, which is using microscopes to look at small things, you can't separate things that are closer together than the wavelength used. This is why we use X-ray diffraction and electron microscopes with very short wavelengths to look at atoms and molecules. So if you want to measure the electron's path with light, and measure it precisely on an atomic scale, you have to use a short wavelength of light. But if you use a short wavelength then it has a lot of energy (E = hν), enough to change the electron's direction. This is the basis of the Uncertainty Principle.

The result of this (and also of Schrodinger's 3-D, space-filling wavefunction) is that we no longer describe electrons using orbits, or defined paths. Instead we talk about **orbitals**, which are defined by wavefunctions $\Psi(x,y,z)$ like the one calculated in the previous section. It turns out (although I think Schrodinger didn't exactly intend this at first) that $\Psi(x,y,z)^2$ is the probability of finding the "particle" at position (x,y,z).

Schrodinger found the standing waves or $\Psi(x,y,z)$ for the electron in a hydrogen atom. These are much more complicated that the wavefunction we found because they are in 3-D and also have a potential energy to worry about. (But they aren't that complicated: you can look at them here.) There are an infinite number of functions that solve the equation, just like in the simple example. In the 1-D example, we used 1 **quantum number** n to determine the energies. As n increased, so did the energy, and so did the number of nodes (places where the amplitude is zero). In 3-D, the standing waves are specified by 3 quantum numbers. (Actually, Bohr and others were using 3 quantum numbers before Schrodinger published this, because it makes sense in 3-D.) The principal quantum number n corresponds roughly to the radius of the orbit in the Bohr model, or to the "most probable distance from the nucleus" in the orbital model. This also corresponds to the energy: the electron is lower energy when it is close to the nucleus, because of the Coulomb attraction. The second quantum number ℓ gives the shape. In the Bohr model this meant ellipse or circle. In Schrodinger's model the shapes are 3-D. You can look at them in detail on Wikipedia (scroll down to the table of images) or with an animated applet like this. This is also a good time to check out the "orbitals" tab on Ptable. Pick an element, then move over the arrows to see a picture of each orbital.



The first 5 hydrogen orbitals, from Wikimedia Commons

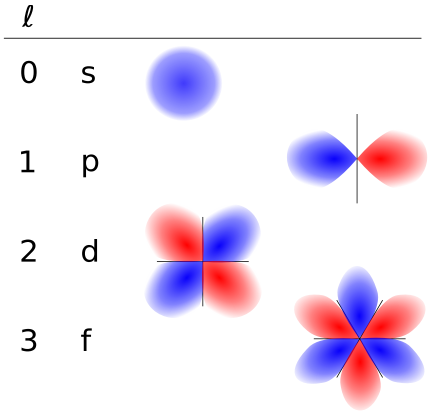
Finally, the third quantum number tells the orientation. In the Bohr model this meant what plane the orbit was in. In the figure, you can see that the last 3 orbitals have the same shape but point along different directions (x, y and z).

Notice that standard pictures of orbitals show most of them with 2 colors. This represents the phase of the orbital (whether Ψ is + or − at that point). This doesn't effect the energy or the probability of finding the particle there, but it is very important when atoms interact with each other, like forming bonds, which is what chemistry is all about! When waves interact with each other, it matters a lot whether the peak (high point) overlaps with the trough (low point) or not. This is true of water waves, sound waves, light waves and electron waves.

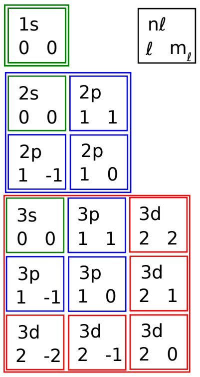
There are lots of ways of showing orbitals, but usually they just draw a surface so that you have 50% or 90% or whatever chance of finding the electron inside the surface. (Always, the probability of finding the electron becomes 0 as you get far enough from the nucleus.) The second orbital in the picture is shown as a slice, so you can see that the inside near the nucleus has the opposite phase as the outside. Wherever the color changes, there must be a node (Ψ passes through 0 as it goes from + or −). Thus the first orbital has no node, which makes sense because more nodes mean higher energy. The second has 1 spherical node. The next three have a planar (flat) node. If you look at more orbitals, you'll notice that the nodes keep increasing.

Here's the pattern of orbital shapes and quantum numbers.

- The principal quantum number n tells you how big the orbital is and what the energy is. It also tells you how many spherical nodes the orbital has. The values go from n = 1, 2, 3, 4, 5, 6, 7... they could keep going but we haven't found elements that need that many orbitals yet! The number of spherical nodes in the orbital is $n - \ell - 1$.
- The angular momentum quantum number ℓ tells you the shape. If $\ell = 0$, the orbital has spherical symmetry (it's round), and we say it is an "s orbital". If $\ell = 1$, the orbital has one planar node, and it's called a "p orbital". See the figure below for d and f orbitals, with 2 and 3 planar nodes each. The possible values of ℓ are 0, 1, ... $n - 1$.
- The magnetic quantum number m_ℓ tells the orientation of the orbital. The possible values are $-\ell$, $-\ell + 1$, ... 0, 1, $\ell - 1$, ℓ. For instance, for the p orbitals, it can be -1, 0, 1. You can remember the number of orientations using the table below.



Shapes of orbitals can be easily predicted by knowing the number of planar nodes, shown as black lines. The nucleus is at the center of each orbital. (Note that there are other possible positions of the nodes for d and f orbitals, but don't worry about this now. Also note that shapes shown here are approximate, not calculated.)



A geometric pattern for remembering the number of each type of orbitals and the possible values of the quantum numbers.

Outside Links

- Atomic Orbitals Explained, by DCauld (15 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Describing Waves

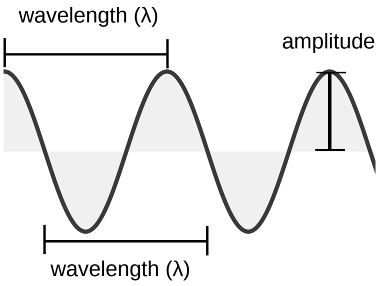
Skills to Develop

- Describe the basic wave properties and resonance
- Distinguish the 2 types of wave interference
- Explain the significance of standing waves

Understanding waves is essential to understand the rest of this section, because we will be talking about many different types of waves. Light has wave properties, and standing electron waves explain many chemical properties.

Basic Properties of Waves

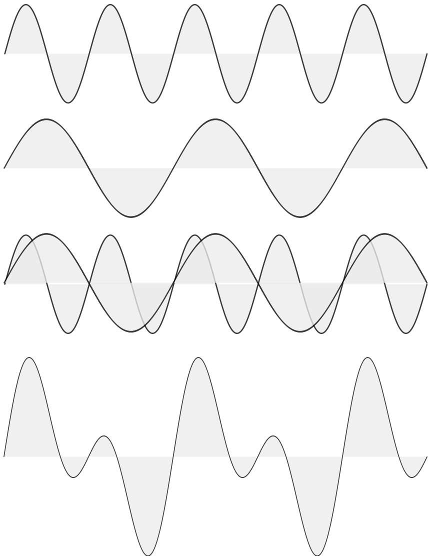
You have probably studied **waves** a little bit in a previous class. Waves include sound waves, ocean waves, and light waves. You have probably also studied sine and cosine waves in math class. Here will will review some of these topics. A wave is defined as "a periodic disturbance that moves through space." The disturbance could mean the high and low parts of an ocean wave, or the high and low pressure parts of a sound wave, etc. **Periodic** means that the disturbance repeats. As an example, consider a graph of y = sin(x). This is a wave. In this case, the **amplitude** is 1, because this is the distance between the average value of y and the maximum value. The **wavelength** is 2π. In non-mathematical waves, wavelength (abbreviated λ) is given in meters. A **cycle** is when the wave goes through one wavelength, so it ends at the same part of the wave where it started. The **frequency** of the wave is the number of cycles/second. So if you look at one position, you will see the wave go up and down at that point. The time it takes for the wave to go through one cycle at that point (from the top to the bottom to the top again) is the **period**. Frequency is 1/period, (we'll abbreviate it ν) and is usually reported in Hertz, which is just s^{-1}. You can think of it as cycles/second, but sometimes people use radians/second instead (you can convert between these using 1 cycle = 2π radians). Because wavelength is meters/cycle and frequency is cycles/second, wavelength x frequency is meters/second or velocity.



A wave, showing wavelength and amplitude.

Wave Interference

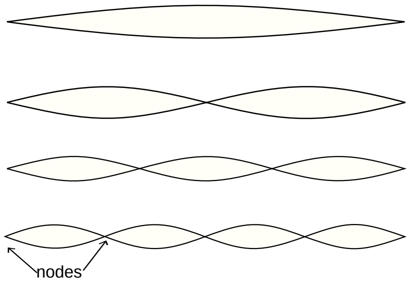
This describes what happens when waves interact with each other, or overlap. The best way to see what this means is to watch: try watching the video on the Double Slit experiment to see waves interacting. Basically, to find the total wave made of several different waves, you just add the amplitude at each point. For instance, if the high part (amplitude 1, say) of one wave overlaps the low part of another (-2, say, this wave is bigger), the result is a smaller wave (-1, here), called **destructive interference**. If the 2 peaks (high parts) overlap, then the wave get bigger, called **constructive interference**. In the graph below, the sum wave has big peaks in regions of constructive interference, and small peaks in regions of destructive interference.



Two sine waves, plotted separately (top), on the same axes (middle), and summed to show the total wave with regions of constructive and destructive interference (bottom).

Standing Waves

An important type of wave for us is a **standing wave**. Standing waves are present in musical instruments, and are how the instrument produces sound of the correct frequency (or pitch, the term used in music). Standing waves don't travel, because they are confined in the instrument. For instance, in a stringed instrument like a guitar or a violin, the whole string vibrates, but the wave doesn't travel because it is trapped in the string, and the string has end points (where it is attached to the instrument, or held down by the musician's finger). Because the ends are fixed in place, the amplitude at these points has to stay zero, but the amplitude in the middle of the string can change. This limits the wavelengths possible to the string. The properties of the string, like its mass/length and tension, will determine the velocity, and the frequency is determined from the combination of wavelength and velocity.



Harmonics, or standing wave frequencies, in a string.

What does velocity mean? The standing wave comes from the wave traveling down the string, reflecting off the fixed ends, reversing direction, reflecting again... when the frequency/wavelength/velocity all match up, the wave reflections reinforce each other, or interfere constructively, which is called **resonance**. Resonance generally describes a vibration that is reinforced by the particular properties of the surroundings because it matches their natural frequencies. When waves with the wrong wavelength bounce back they will cause destructive interference with themselves. The result is that the string can easily vibrate at its natural, resonant frequencies, but can't really vibrate at other frequencies because those waves cancel themselves out. For instance, a harp (an instrument with many strings) will laugh with you, because some of the strings will match some of the frequencies in your laugh and start to resonate, creating sound waves in the air. Here's a 1 min video of using resonance to break a glass. Here's an amazing video showing the location of 2-D standing waves using metal plates and the bow of a violin.

Outside Links

- Khan Academy: Introduction to Waves (13 min)
- Amplitude, Period, Frequency, and Wavelength of Periodic Waves (14 min)
- Brightstorm: Wave Interference (8 min)

- Veritasium: The Original Double Slit Experiment (8 min)
- Brightstorm: Standing Waves (10 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Discovery of Quantization

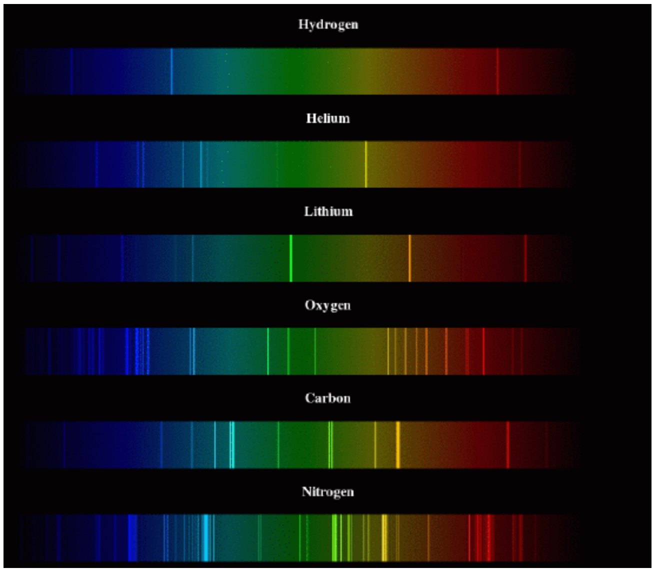
Skills to Develop

- Explain the significance of spectroscopy, wave-particle duality
- Describe the contributions of Bohr and Planck to "old quantum mechanics"

The history of quantum mechanics is often divided into 2 parts: the "Old Quantum Mechanics" and the "New Quantum Mechanics." Before either quantum mechanics, physicists described the world using "Classical Mechanics," which is like what you've probably studied before in physics class: Newtonian mechanics (forces, accelerations, etc), electricity and magnetism using Maxwell's equations. . . all these approaches work well for big things that aren't moving too fast. There are two qualities of classical mechanics that quantum mechanics altered. First, in classical mechanics energy and velocity and such quantities can have any value. If you drop a ball, it accelerates smoothly from 0 to a final velocity, rather than moving jerkily from step to step. The "Old Quantum Mechanics" got rid of the assumptions that energy and velocity should be "continuous." The other aspect of classical mechanics was the idea of a trajectory: the path taken by a moving object. If you launch a missile or a space shuttle, you can calculate almost exactly the path it will follow; if you have perfect knowledge of the forces acting on it, you can calculate its path perfectly. The "New Quantum Mechanics" which is described more in the later section on orbitals essentially said that there is no trajectory for small particles, so you can only describe them using statistics, not actually know where they are or what path they follow.

Spectroscopy

The discovery of **spectroscopy** in 1859 presented a problem for chemists. Spectroscopy essentially means looking at the wavelengths of light that are absorbed or emitted from a sample. Any time you look at colors, you are doing a sort of spectroscopy, because color comes from particular wavelengths of light. Paint absorbs certain wavelengths, so what we see is the color of the other wavelengths. Computer screens can emit certain wavelengths of light so we see the colors that correspond to those wavelengths. But you can look more carefully, by splitting light into its component wavelengths, using a prism or a diffraction grating. If you do this with sunlight, as Newton did, you see a rainbow. If you do this with the light emitted by a very hot sample of an element, you will see just a few separate lines: the sample emits only specific wavelengths, instead of a smooth rainbow with a little of each. But chemists had trouble explaining why only these particular wavelengths were emitted. The wavelengths are called **lines**, and the collection of lines is the **spectrum**.



Examples of an element's spectrum

In 1885 (25 years after the introduction of the spectrometer), Balmer, a teacher, studied the 4 lines emitted by very hot hydrogen atoms, and noticed a pattern. The wavelengths could be calculated from

$$\lambda = C\frac{n^2}{n^2 - 2^2} \tag{1}$$

where C is a constant and n is a whole number (3, 4, 5, or 6 for the 4 known lines). He suggested that there might be other lines corresponding to replacing the 2^2 in his formula with 3^2, 4^2, etc. Rydberg later rewrote Balmer's formula as follows, using the wavenumber (1/λ) which is still commonly used in labs today with the unit cm^{-1}

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{2}$$

where R is called the Rydberg constant, and n_f and n_i are integers, and n_i is larger than n_f. Until 1908, the only known lines had n_f = 2, but then finally lines given by n_f = 3 were found, and later lines with n_f = 4, 5 were found also, proving Balmer correct.

The "Old Quantum Mechanics"

This is a good time to review the previous section Discovery of Sub-Atomic Particles. Recall the use of gas discharge tubes in discovering X-rays. This started a long debate about whether X-rays were waves (like light) or particles, like electrons. They couldn't be charged particles, because they weren't affected by magnets, but they didn't seem to reflect or diffract either. (Diffract means waves changing direction after passing through a gap about the size of the wavelength.) Eventually Stokes realized that X-rays were light with a very short wavelength, so it wouldn't diffract without very tiny gaps. Von Laue proposed that salt crystals could be used to diffract X-rays, because the gaps between ions in crystals are very small. This is the basis of X-ray diffraction, which is now used commonly to find structures of molecules. Also, remember the young chemist Moseley who figured out the fundamental order of the periodic table? He was essentially doing X-ray spectroscopy, using an electron beam to make elemental samples emit X-rays. He measured the wavelengths of these X-rays using diffraction by salt crystals. Like Balmer, he found a fascinating pattern in his line spectra.

Review as well Rutherford's nuclear model of the atom in the same section, proposed in 1911 (around the time that Balmer's hypothesis was proved correct). After various proposals, his experiments showed clearly that there was a dense, central part of the atom with most of the weight and the positive charge, which is called the nucleus. Around the nucleus, electrons move, occupying a much larger volume than the nucleus. But the physicists had some problems with this model. If the electrons weren't moving, they should "fall" into the nucleus. If they were moving around the nucleus, when they changed direction (to stay near the nucleus) they should emit light. The oscillating charged particles would be like a miniature cell phone tower, emitting radiation at high frequency. Emitting light would cause them to lose kinetic energy, and very quickly they should fall into the nucleus. To solve this problem, Bohr employed **quantum theory**, which had been introduced by Planck in 1900.

Planck used quantum theory to explain blackbody or **thermal radiation**. Recall the problem with Rutherford's model, that acceleration (including direction change) of charged particles produces light (not necessarily visible light, but electromagnetic radiation of some wavelength). The atoms and ions in normal objects are always moving a little, and the hotter they are, the more they move. These movements mean that they bump into each other and change direction; these collisions result in emission of radiation if charged particles are involved. The light emitted by normal objects at normal temperatures is usually IR or lower energy (animals emit IR thermal radiation, which is how night-vision goggles work); incandescent (normal old-fashioned) light bulbs emit visible light and IR because the filament is much hotter than room temperature. In English, we talk about "red-hot" or "white-hot" to describe temperatures: glass or metal that is being shaped is often red-hot, hot enough to emit red light. White-hot is even hotter, hot enough to emit white light (all the colors). But it was very hard to explain the spectrum of thermal radiation produced by objects at different temperatures (what wavelengths of light were produced and how much of each). Planck had to introduce **quantization** to get a good model. He proposed that light isn't just a wave, but it comes small separate packages, called **quanta**. The energy of a quantum of light is

$$E = hu \tag{3}$$

where h is Planck's constant (6.626 x 10^{-34} Js) and ν (Greek letter read as "nu") is the frequency of the light in Hz. Most scientists didn't like this idea (it seemed very strange!) but it worked.

Wave-Particle Duality

The **Wave-Particle Duality** means that something can behave like a wave and also behave like a particle. This was first applied to light. Before quantization was proposed, physicists knew that light behaves as a wave (as described in the previous section. When Planck proposed quantization, he thought it was a property of atoms, not light. However, Einstein applied Planck's theory to explain the photoelectric effect, and clearly showed that light is a particle. The **photoelectric effect** means that when light (such as UV light) shines on a metal surface, sometimes it knocks electrons off the surface, creating a "photocurrent". It turns out that photocurrent is only produced when light has a sufficient frequency, and that increased intensity of light only produces more photocurrent, not photoelectrons with higher kinetic energy. And higher frequencies of light produce photoelectrons with more kinetic energy, but not more electrons. Einstein explained this by saying that light comes in particles with energy proportional to frequency (E = hν, which is the same formula Planck used in which ν is the frequency and h is a constant). To create a photoelectron, the light particle or **photon** must have more energy than the energy holding the electron on the surface. Any extra energy in the photon turns into kinetic energy for the electron.

Bohr's Model

Bohr used Planck's quantum concept to try to explain the Rutherford model of the atom. He focused on the hydrogen atom, with just one electron around the nucleus. Surprisingly, it was dimensional analysis that lead him to Planck's theory. He liked the "solar system" model, in which electrons orbit the nucleus like planets orbit the sun. He realized that an orbit would have a characteristic radius (distance between nucleus and electron) and also that $h^2/m \cdot e^2$ would have units of length (check this yourself, but note that you'll need to include another quantity, the permitivity of free space). So he used classical physics, including Coulomb's law and

$$a = \frac{v^2}{r} \tag{4}$$

to look for an equation for stable orbits (he just assumed that in a stable orbit, the acceleration wouldn't cause radiation). He got part of the way (calculating the total energy of the orbits including kinetic and potential energy), then got stuck. Luckily, a spectroscopist then introduced him to Balmer's formula. When he saw that, the answer suddenly became clear to him. He assumed that the lines in the spectrum come from electrons moving from one stable orbit to another, and the wavelength of the light emitted equals the energy difference of the orbits. He amazed everyone by deriving the Rydberg constant (which was experimentally known to be 109677 cm^{-1}) in terms of fundamental constants:

$$R = \frac{e^4 m}{8\epsilon_0^2 h^3 c} \tag{5}$$

and it worked out correct! (Check for yourself; ε_0 is again the permitivity of free space.) So Bohr's model worked well for explaining the hydrogen spectra: in stable orbits, which had only certain allowed energies, there was no radiation; light (a single photon) was absorbed or emitted when changing orbits, and its wavelength matched the energy difference of the orbits. This theory also worked to explain some lines in the sun's spectrum, which came from He^+; to calculate these you have to use the atomic number Z to account for the larger charge in the nucleus. It turned out that his formula works for all single-electron atoms.

Essentially, his model predicted stable orbits with energies determined by a **quantum number,** corresponding to the integers in Rydberg's formula. Orbits with one value of the quantum number are called a **shell**. He also figured out that orbits didn't have to be circles, and didn't have to all be in the same flat plane. He added 2 more quantum numbers to indicate the shape (circle or ellipse) and the orientation of the orbits.

However, his theory didn't work for multi-electron atoms very well. Bohr worked on extending it for more electrons, and he found that this was easiest for alkali atoms. Bohr found that he could do ok by treating the alkali atoms as having only one electron, and including all the other electrons as part of a bigger "nucleus" with a +1 charge. Bohr used spectroscopic data to arrange the elements in roughly the same pattern as a modern periodic table, with periods of 2, 8, 8, 18, 18, and 32 elements, and some divisions between the electrons in each period, that he did not get exactly right. Each row consisted of filling one shell. Recall that early periodic tables didn't have the modern shape; it was at this time that the modern shape started to emerge. Other chemists we'll study later (Lewis and Langmuir) were arranging the elements by chemical properties, with similar results. The mathematical basis of this pattern didn't become clear until the "new quantum mechanics" was introduced.

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Electron Configurations

Skills to Develop

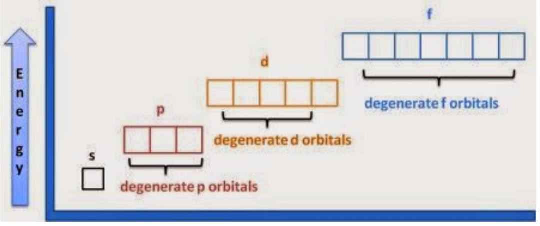
- Predict and illustrate electron configurations

The wavefunctions in the previous section were derived for single-electron atoms only. It's really hard if not totally impossible to solve the Schrodinger equation perfectly when there are 2 or more electrons, because of electron-electron repulsions which make the Hamiltonian incredibly complicated. However, it turns out that we can approximate the orbitals in other atoms with small modifications of the hydrogen wavefunctions, like decreasing the nuclear charge to account for electron repulsion.

Electron Configurations

Bohr figured out the number of electrons in each **shell**, where a shell is all the electrons with the same principal quantum number. The pattern he used, which you can verify with the periodic table, was 2, 8, 8, 18, 18, 32, 32. However, he was not as clear about the arrangement into **subshells**, which are groups of electrons with the same principle and angular momentum quantum numbers, such as 1s or 2p. This became much clearer after Schrodinger's wavefunctions for the hydrogen atom were introduced, because the solution wavefunctions clearly had only certain allowable ℓ values and m_ℓ values. Although all the orbitals in a shell have the same energy in a single electron atom, when there are more electrons the subshells have different energies. This is because the larger ℓ is within a shell, the farther the electron usually is from the nucleus. In s orbitals, the electrons are often close to the nucleus, so other electrons don't block the nuclear charge much. In d and f orbitals, the electrons are far from the nucleus and do get blocked. Thus, orbitals tend to fill in the order of lowest n and lowest ℓ first.

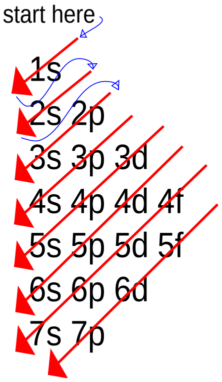
Orbitals with the same energy are called **degenerate**. (In other contexts, degenerate means immoral, or other bad things.) In general, the more complications you add, like more electrons, neighboring atoms, magnetic fields, etc, the fewer orbitals are degenerate. So for a hydrogen atom by itself, all the orbitals in each shell are degenerate. When you move to a lonely helium atom, the orbitals in the subshells are degenerate. When you make chemical bonds, the orbitals in subshells are no longer degenerate. When you apply a magnetic field, the electrons in the same orbital are not degenerate.



A simple diagram showing degenerate orbitals.

Simple Rules for Predicting Electron Configurations of Atoms

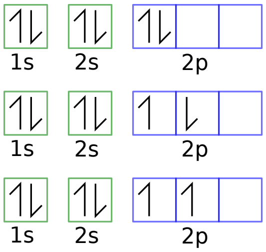
How to predict **electron configurations** for elements? Electron configuration just means how many electrons in each orbital. You will need to know the number of electrons you are using. You can get this from the periodic table (the atomic number − charge if it's an ion). Or you might just be given the atomic number. If you have a periodic table, it's easy, because of the shape of the table. If you go to the periodic table on this site, you'll see it has a blue block, a red block, a yellow block and a green block. The code is blue = s; yellow = p; red = d; and green = f. The alkali metals and alkaline earth metals have their highest energy electrons in an s orbital. The highest energy electrons, the ones in the highest shell, are called **valence electrons**. The main group (yellow) including halogens and noble gases, have their highest electrons in p orbitals. The transition metals have theirs in d orbitals, and the lanthanoides and actinoids in f orbitals. Notice that each section is 2, 6, 10 or 14 elements across, because there are 1,3,5,7 orbitals in the s, p, d, and f subshells, and each orbital holds 2 electrons. So you can write the electron configuration just by looking at the periodic table. Follow your way along, writing how many electrons are in each subshell, until you have the right number of electrons total. For instance, for Al, you would have $1s^22s^22p^63s^23p^1$. Notice that we indicate the number of electrons in each subshell using superscripts we we write electron configurations.



Another trick you can use to write electron configurations is to follow the arrows on this diagram. The filling pattern is named "aufbau" which means "building up" in German, or so I've heard. Notice that you don't actually fill all the subshells in one shell before moving on to the next. This can be a little confusing (espcially because the s orbitals are only slightly lower than the previous d orbitals, and in ions the energy order switches back!). Either use this diagram or a periodic table, and you'll get the right answers as long as you are careful to count from the top of the periodic table. Notice how the first row of d comes after the 4th row of s? But we can have 3d orbitals, so the first row of d is 3d, not 4d.

Often we don't want to write out all the electrons for a heavy atoms, because the inner ones are just the same as all the other elements. So we might show only the valence electrons, which means in this case the ones added on this row of the periodic table, or after the last noble gas. So we might write Ti as $[Ar]4s^2 3d^2$, which just means that it has the same configuration as argon, + $4s^2 3d^2$.

The next question comes when not all the orbitals in a subshell are filled. Do you pair electrons or put them in separate orbitals? For instance, consider carbon. You can represent its electron configuration like this, with the arrows up and down representing the electron spin.



But which of the 3 possibilities is it? Remember that electron spin showed up in spectroscopy with magnetic fields. The electrons are like tiny magnets, and when they are paired (one up, one down) they cancel each other out and don't seem magnetic unless you look really hard. But you know that there are lots of very magnetic materials out there (maybe you use them on your fridge; you also use them in headphones and other devices). The reason they are magnetic is because the bottom arrangment is the lowest energy. Electrons prefer to have the same spin in different orbitals, where they repel each other less (among other more complicated reasons). This is called Hund's Rule. The reason the best magnets are transition metals or lanthanoides is that d and f orbitals have space to spread out 5 or 7 electrons with the same spin.

The only other thing you need to know about electron configurations right now is that there are some exceptions to the rules about what order they fill in (mostly in the d and f blocks). These aren't very important. The other thing you might want to know is whether the electron configuration in isolated atoms is important to chemists. Mostly only the valence electrons are affected by bonding, so the elemental configuration will probably still apply to the core electrons. And the atomic electron configurations match the reactivity patterns that the periodic table was originally based on, so that's useful. The other reason is that these rules apply almost the same to real chemical situations. Even if the orbitals are more complicated molecular orbitals (we'll study these later) instead of atomic orbitals, you still fill them from lowest to highest and use Hund's rule.

Outside Links

- CrashCourse Chemistry: The Electron (13 min)
- Khan Academy: Electron Configurations 2 (10 min)

Contributors and Attributions

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Electron Configurations According to Bohr and Pauli

Skills to Develop

- Describe the Pauli Exclusion Principle

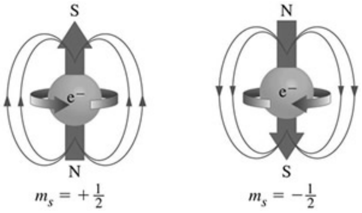
Many-electron Atoms

If there are multiple electrons, which orbits do they occupy? In atoms larger than hydrogen, the larger nuclear charge means that the orbits should be closer to the nucleus. If all the electrons are in the lowest energy orbit, even if repulsion expands the orbit a little, then the size of elements would get smaller as they get heavier. Also, it would get harder and harder to pull electrons off heavier elements, because they would be bound much more tightly to the more charged nuclei. Both of these are the opposite of the facts: sizes of elements increase a little as you go down the periodic table, and it is hardest to remove electrons from the lightest elements. Thus, it was clear that only some electrons could be in the lowest orbit.

Pauli was a theoretician "so good that experimental apparatus broke when he walked through the lab door." (It's a joke that theorists, who usually just think, can't handle lab equipment.) He suggested that theory and data would fit well if each orbit (defined by 3 quantum numbers) could hold exactly 2 electrons. Thus as soon as each orbit was full, with 2, the next electron would have to go in the next higher orbit. Using this rule, Bohr and others determined the electron configurations (which electrons were in which state or orbit) of most of the elements, and found that the order matched the periodic table nicely! The movement to the next principal quantum number started a new period, so the theory fit all the data on valence and other properties.

Electron Spin

Pauli didn't know at the time why each orbital holds 2 electrons, but later it was found that a fourth quantum number was needed, because strong magnetic fields split the energy of the 2 electrons in one orbit into 2 different levels. (This is the basis of many important experimental techniques, especially NMR, used by chemists, and MRI, used in medical imaging.) A proposed explanation for this is that the electrons can "spin" in either direction, just like the earth spinning to give us day and night. This isn't exactly what happens, but the word **spin** is still used to describe this effect. The **spin quantum number** has values of +1/2 or −1/2. Thus, Pauli's idea is now called the Pauli Exclusion Principle, and it says that no 2 electrons in one atom can have exactly the same quantum numbers. Two electrons can occupy one orbit, but they must have opposite spins.



An illustration of the different spin quantum numbers.

Electron Configurations

Bohr figured out the number of electrons in each **shell**, where a shell is all the electrons with the same principal quantum number. The pattern he used, which you can verify with the periodic table, was 2, 8, 8, 18, 18, 32, 32.

Based on Bohr's model, you can find the number of **valence electrons** or electrons in the highest shell by looking at the periodic table. (For now, let's not worry about transition metals, and lanthanoides.) Alkalis have 1 valence electron, because we have just started a new shell. Alkaline earths have 2, B has 3, C has 4, N has 5. Chalcogens have 6, halogens have 7, noble gases have 8. (You can see that this is kind of close to the valence we mentioned earlier.

Outside Link

- CrashCourse Chemistry: The Electron

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Light as a Wave

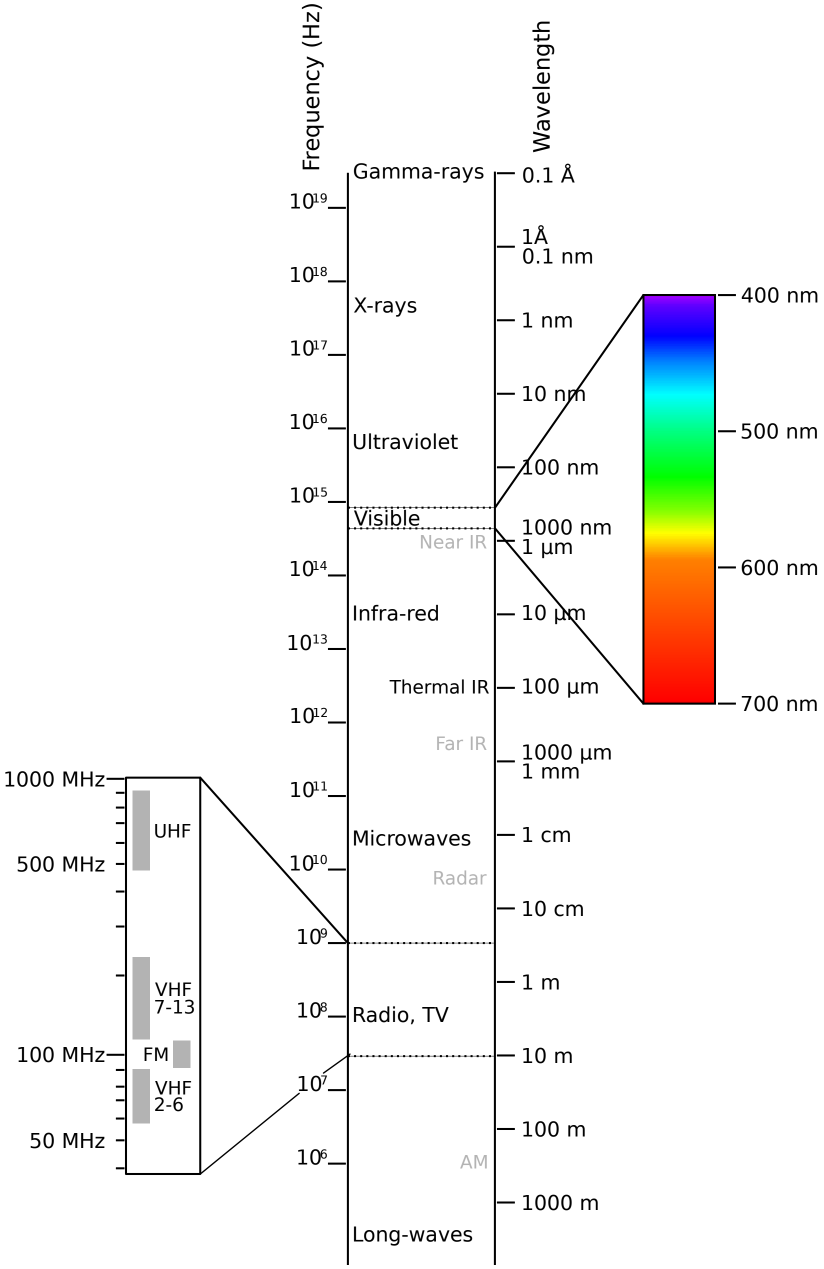
Skills to Develop

- Relate the wavelength and frequency of light using a mathematical equation
- Define electromagnetic radiation

Light is a little different from sound waves, water waves and string waves, because it can move through a vacuum. In general, the velocity of light is constant, $c = 3.00 \text{ x } 10^8$ m/s. So for light, wavelength λ and frequency ν are related by

$$c = \lambda\nu \tag{1}$$

Light is called **electromagnetic radiation**, which basically means that it radiates (travels) and the wave part is oscillating electric and magnetic fields. You don't need to worry about the details of this now. The properties of different types of light depend on their wavelength. X-rays used in medicine have very short wavelengths and high frequencies; UV (ultraviolet) light gives you sunburns and helps you make vitamin D, visible light is normal light, IR (infrared) is used for night-vision goggles, microwave is used in cooking, and radio is used in radios.



created by Victor Blacus, via Wikimedia Commons

Outside Link

- Veritasium: The Original Double Slit Experiment (8 min)

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Particle in a Box

Skills to Develop

- Derive Schrodinger's Equation (optional)
- Verbalize the solution of Schrodinger's Equation (optional)

Many introductory chemistry textbooks introduce the Schrodinger Equation, but students don't understand what it means. This section is optional; if you want to know where orbitals come from, it can help you understand. It will be easier to follow this section if you know a little calculus (basically, what a derivative is).

The Schrodinger Equation is the starting point for describing the motions of electrons as waves. De Broglie suggested that their stable "orbits" in the Bohr model were standing waves analogous to those in a guitar string. Schrodinger extended this theory using the wave equation and wavefunction. Instead of circular orbits, Schrodinger's waves were 3D and took up the whole space of the atom, more like vibration of air in a spherical flute than the vibration of a circular string. The wavefunction Ψ(x, y, z, t) describes the amplitude of the electron vibration at each point in space and time. Oddly, Schrodinger seems to have proposed the wavefunction without fully understanding what it means, but it worked! Here we will describe the time-independent Schrodinger equation for simplicity, which describes the standing waves. We will also consider only a 1-dimensional system, such as a particle that only moves linearly, also for simplicity. Thus, we will find Ψ(x) for a very simple situation.

Schrodinger proposed that a standing wave is described by the wavefunction Ψ when the it fits the following differential equation

$$H\Psi = E\Psi \tag{1}$$

where H is the Hamiltonian operator, which finds the total energy of the system E. (This approach uses the linear algebra concept of an eigenfunction and eigenstate, but don't worry if you don't know what these are.) Kinetic energy KE is given by

$$KE = \frac{p^2}{2m} \tag{2}$$

where p is the momentum (p = mv). For a particle moving in 1D (along x) Schrodinger assumed that a permissible general form of Ψ is

$$\Psi(x,\ t) = Ae^{\frac{i(px\ -\ Et)}{\hbar}} \tag{3}$$

where A is a constant and i is the imaginary number (i^2 = -1). (This comes from the equations E = hν and the de Broglie relationship λ = h/p. These equations connect energy to time and distance to momentum through Planck's constant. These are also the quantities that are mutually limited by the Uncertainty Principle.) If this is true, the derivative of the wavefunction with respect to x is

$$\frac{d\Psi}{dx} = \frac{ip}{\hbar}\Psi \tag{4}$$

Notice that this is kind of like the equation HΨ = EΨ in that we get the original wavefunction multiplied by some important quantity, like energy or momentum. So the momentum operator **p** (like the Hamiltonian operator, which gives the energy) gives the momentum p, and can be written like this:

$$\mathbf{p}\Psi(x,\ t) = -i\hbar\frac{d\Psi}{dx} \tag{5}$$

We can write the Schrodinger equation using this Hamiltonian (which gives total energy, KE + PE)

$$H\Psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = E\Psi(x) \tag{6}$$

The potential energy is given by V(x), which just depends on the position. The kinetic energy is calculated using the equation above, using the square of the momentum operator (thus, the first derivative in the momentum operator becomes a second derivative when the operator is squared). Now, if we choose a function V(x) we can find the wavefunctions that fit! We will use a simple example: a particle in a box (in 1-D). The potential is 0 inside the box and infinite outside the box. So we will just know that the particle has to be inside the box, but use V = 0. Then our Schrodinger Equation looks like this

$$H\Psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi(x) \tag{7}$$

or basically the second derivative of Ψ is a constant times Ψ. There are different forms of the solution, but we'll just choose a simple one.

$$\frac{d}{dx}\, sin(ax) = a\ cos(ax) \tag{8}$$

$$\frac{d}{dx}\, cos(ax) = -a\ sin(ax) \tag{9}$$

Thus,

$$\frac{d^2}{dx^2}\, sin(ax) = -a^2\ sin(ax) \tag{10}$$

So we can pick sin(ax) or cos(ax) or a sum of these for the wavefunction:

$$\Psi(x) = sin(ax) + cos(bx) \tag{11}$$

So far, there is no quantization! The coefficient a can have any value. But just like a string on a guitar, the amplitude of Ψ has to be 0 at the edges of the box. If we just use Ψ(x) = sin(ax), then if the box is from x = 0 to x = L, we need to have an integer number of half-wavelengths in the box. So

$$a = \frac{n\pi}{L} \tag{12}$$

so that

$$\Psi(0) = \Psi(L) = 0 \tag{13}$$

To summarize,

$$\Psi = sin\left(\frac{n\pi x}{L}\right) \tag{14}$$

is a solution of the Schrodinger Equation for the 1-D particle-in-a-box system. Try putting this in and see what the energy is! You should get:

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} \tag{15}$$

There are an infinite number of solutions, or wavefunctions that satisfy the Schrodinger Equation, corresponding to n = 1, 2, 3... and any sum of these wavefunctions is also a solution. What do they mean? The amplitude of the particle wave is given by Ψ. The next section explains the meaning of the wavefunction in more detail, now that you have been introduced to the math.

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

The New Quantum Mechanics

Skills to Develop

- Describe some of the contributions of de Broglie and Heisenberg to "new quantum mechanics"

The "New Quantum Mechanics" was introduced a little after the "Old Quantum Mechanics" which was developed by Planck and Bohr. This is when quantum mechanics became very confusing to people. In the old quantum theory, we could think about particles moving in normal ways. The electrons orbit the nucleus just like planets orbit the sun. But this was wrong. The new quantum theory says that tiny particles behave in ways that are totally different from normal objects that we can see, like basketballs or planets. In fact, it is impossible to know exactly where they are or what they do.

Einstein had convinced physicists that light was a particle (now called photon) in 1905. Later in 1925, de Broglie proposed that particles like electrons could also be waves. De Broglie was a French prince who was initially interested in history, but during World War I he joined the army as a radio operator and became interested in waves. He was also a lover of music. These qualities lead him to interpret Bohr's atoms as "musical instruments." Bohr assumed that his energy levels were quantized, but didn't explain why. De Broglie proposed that quantization arose from the same effects as the quantized frequencies (fundamental and overtone) present in a guitar string, that make it work as an instrument. (Review standing waves in this section if needed.) De Broglie thought that electrons in "orbits" like in the Bohr model were like strings on instruments. A string has to have nodes at each end; an electron in an orbit also has to be a standing wave, with a whole number of wavelengths around its path. In other words,

$$n\lambda = 2\pi r \tag{1}$$

where n is an integer. Thus, the wave interferes constructively with itself when it makes a full circle.

According to his theory,

$$\lambda = \frac{h}{mv} \tag{2}$$

He derived this equation using the radii Bohr calculated for his orbits. You can see that the wavelength effect is only important for very small particles, like electrons (check this out for yourself!). He thought that the "wave-ness" of electrons would be present outside of atomic orbits as well, and this proved true. A beam of electrons accelerated by high voltage is predicted to have similar wavelength to X-rays, and like X-rays, can be diffracted by a crystal. The diffraction pattern let researchers measure the wavelength of electrons (whose velocity was known, because they were accelerated by a known voltage) just as Moseley had measured the wavelength of emitted X-rays to determine atomic numbers. Later the wavelengths of atoms were measured as well. The experimental wavelengths matched de Broglie's prediction, and the wave-particle duality for electrons was accepted, just like the wave-particle duality for light.

Heisenberg developed a way to work with the allowed energies of atoms using matrices. He believed that we must work with the quantities we can observe experimentally, like energies (via spectroscopy). This led him to the Uncertainty Principle which says that certain pairs of quantities (position and momentum, energy and time) can't be measured precisely at the same time. For instance, if you want to know exactly where a particle is, you can't also know exactly what its velocity is. This was part of the new "statistical" quantum mechanics. In classical mechanics, you can know everything about particles (like balls): exactly where they are, exactly where they are going, and predict exactly the results of collisions or other events. In the new quantum mechanics, it was argued that this perfect knowledge of particles was simply impossible. For instance, exactly where is a wave?

Although Heisenberg's matrix quantum mechanics is probably used more often because it works well with computer calculations, an equivalent description developed by Schrodinger gives more intuition, so we will describe it in detail. The methods give the same answers but use very different math. Schrödinger extended de Broglie's theory by applying well-known physics of waves (for instance, in instruments) to describe electrons. There's a detailed example in the next section.

Outside Links

- The Wave Behavior of Matter, by DCauf (15 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

CHAPTER OVERVIEW

Solids

Topic hierarchy

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Covalent-Network Solids: Semiconductors and Insulators

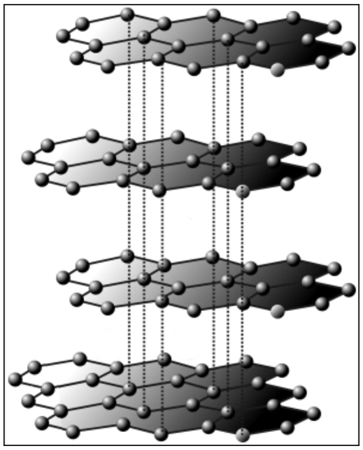
Skills to Develop

- Explain the properties of some covalent-network solids
- Describe semiconductors and some of their properties

You can read a quick introduction to covalent-network solids in the intro page. The basic idea is that to make a network of covalent bonds, each atom (or many of the atoms) have to make 3 or 4 bonds to other atoms. This means that covalent-network solids usually include carbon, silicon, and their neighbors in the periodic table. Here, we'll focus on simple, orderly structures like diamond, graphite, and pure silicon. There are also covalent-network solid oxides, like the silicates, in which oxygen atoms connect 2 silicon atoms, and each silicon atom connects to 4 oxygens. Partially covalent oxides are what most rocks and ceramics are made of.

Graphite

Carbon has 2 **allotropes**, or pure elemental forms. The more stable form is graphite, a dark, slippery material used in pencils and lubricants. Remember that carbon typically makes 4 bonds. The structure of graphite is flat hexagonal sheets; a single sheet is called **graphene**. Each carbon atom makes 3 σ bonds and the leftover p orbitals form a delocalized π-bond network over the whole sheet, very similar to the π-bonding in benzene. The π-bond system actually forms bands, like in a metal, allowing graphite to conduct electricity along the sheets. Weak interactions, like London dispersion forces, (called π-stacking in this case) hold the sheets loosely together. Because they can slide past each other (especially when impurity atoms are trapped in between) graphite is a good lubricant.

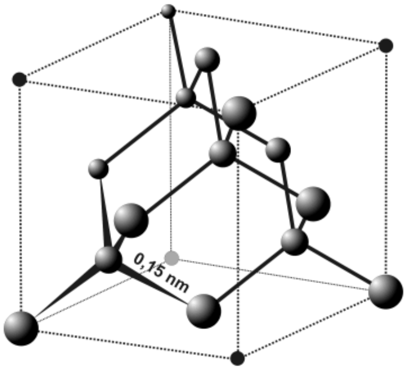


Graphite structure via Wikimedia Commons

Diamond Structure

The other bulk allotrope of carbon is diamond. In diamond, each carbon makes 4 bonds in tetrahedral directions to other carbon atoms. The structure is like the zinc blende ionic structure, except that all the atoms are the same. The properties of diamond (insulator, hard) come from the strong covalent bonds. Remember that C-C bonds are some of the strongest covalent bonds. It's easiest to think about diamond as forming with sp^3 hybrid orbitals on each atom. It's hard to imagine the MO interactions, but the main thing we can know is that because there is good energy match and good overlap between the atoms, the splitting (energy difference) between bonding and anti-bonding MOs will be big (and there won't be any non-bonding MOs, because each atom has 4 orbitals and makes 4 bonds). There will still be bands like in metals, but now there are 2 bands with a big energy gap in the middle. The low-energy, bonding band is called the **valence band**, and there are exactly enough electrons to fill it. The high-energy, anti-bonding band is called the **conduction band**, and it is empty.

If it was hard to understand the previous paragraph, let's just imagine making 1 bond between 2 atoms. We use one sp^3 hybrid on each atom. These point right at each other, have exactly the same energy, and have good overlap. We can imagine drawing an MO diagram just like for H_2, with a big energy gap between the bonding and anti-bonding orbitals. Each atom has 4 electrons total, and makes 4 bonds just like this, so each bond gets 1 electron from each atom: just enough to fill up the bonding MO. When we multiply this over all the bonds in the diamond, we get the full valence band and the empty conduction band. The energy gap between them is called the **band gap**. In diamond, the band gap is big, and so diamond is an insulator.



Diamond unit cell, by Anton via Wikimedia Commons

Semiconductors

Silicon has a structure just like diamond. (It doesn't make graphite, because mostly π-bonds are weak for the second-row elements.) However, silicon has a smaller band gap than diamond. Germanium, which is below silicon in the periodic table, has the same structure, and an even lower band gap. Generally, as we go down the periodic table, covalent bond strengths get smaller, which is the same as saying that the splitting between bonding and antibonding orbitals gets smaller. It's hard to say why, but if you assume that heavier atoms have worse orbital overlap, you will usually make good predictions.

Semiconductors are materials that conduct electricity just a little bit. They are the basis for all computing and electronics. Semiconductivity comes from having a not-quite-full valence band, a not-quite-empty conduction band, or both. If there are a few electrons in the conduction band, they can conduct electricity just like in a metal (except less, because there aren't very many of them!). If there are a few electrons missing from the valence band, the empty spots are called holes and they can move around, also conducting electricity. If the band gap of a material is not too big compared to the thermal energy, then a few electrons can be in the conduction band even though there is room for them in the valence band (because of thermal energy). For this reason, semiconductors conduct better at higher temperature, because more electrons will be in the conduction band.

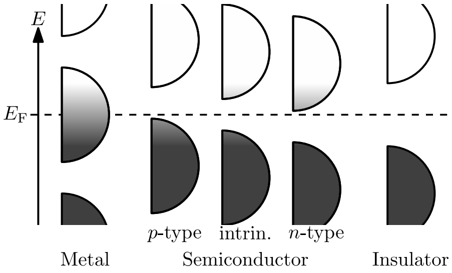


Diagram showing the difference between bands in metals, semiconductors and insulators. E_F, the Fermi energy, represents roughly the cutoff between full and empty MOs: the energy of a state that has a 50% chance of being full at equilibrium. The intrinsic semiconductor has electrons in the conduction band due to thermal energy.

Doping Semiconductors

The other way to make a semiconductor, with a material whose band gap is too big at room temperature, is by adding some impurity atoms with different numbers of electrons, which is called **doping**. Imagine that you have silicon with just a few nitrogen atoms replacing silicon atoms. Each N has an extra electron. Now there will be a few electrons in the conduction band, so it's a semiconductor! And we can control the conductivity by controlling how much N we add. We can do the same thing if we add a little bit of boron, which has 3 electrons. In this case, there would be a few holes in the valence band. These are called p-type (positive, less electrons, like with B) or n-type (negative, extra electrons, like with N) semiconductors. Lots of important devices, like LEDs, solar cells and transistors (the basis of computer chips) are made of layers of p-type and n-type semiconductors.

Compound Semiconductors

We can also make semiconductors that are compounds, like gallium arsenide (formula GaAs). These have an AB formula, and there are always 8 valence electrons in the formula. For example, Ga has 3 and As has 5, so GaAs has 8. Another example is ZnSe, (Zn has 2 valence electrons in 4s, Se has 6 valence electrons just like O). Thus, they have the same number of valence electrons as C or Si. They also have the same structure (zinc blende, just like diamond except that that atoms alternate types). By combining many different elements, we can change various properties, like band gap, to be exactly what we want. Generally, the band gap increases as the 2 elements are farther apart (the bonding becomes more ionic, and ionic solids aren't conductive). We can even mix 3 or more elements, like in CdZnTe (the actual formula would probably be written (Cd,Zn)Te, meaning that the number of Cd + Zn = Te). To make semiconductors with the right properties, we can use different combinations of elements and also dope with many different elements.

Outside Links

- Clayton Spencer: Metals, Bonds, and Band Theory Part 2 (10 min)
- Clayton Spencer: Metals, Bonds, and Band Theory Part 3.1 (9 min)
- CrashCourse Chemistry: Network Solids and Carbon (9 min)
- CrashCourse Chemistry: Silicon - The Internet's Favorite Element (9 min)

Contributors and Attributions

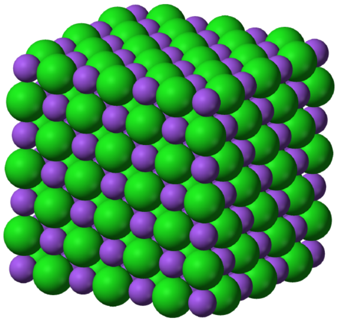
- Emily V Eames (City College of San Francisco)

Crystalline Solid Structures

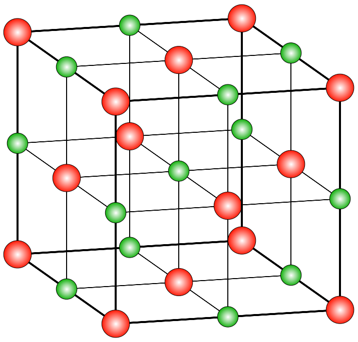
Skills to Develop

- Define a unit cell and its parts

Many solids are crystalline, which means that they have atoms or ions or molecules arranged in an ordered pattern. For instance, think about NaCl. This ionic solid has an alternating arrangement of Na^+ and Cl^- ions, as shown in the image below.

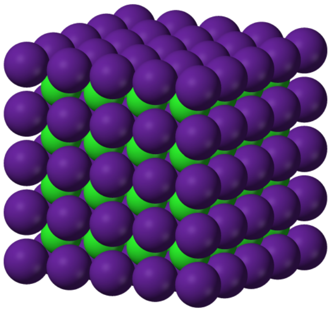


In a crystal structure, we can think about the **unit cells**, which are the smallest repeating unit of the structure. Basically, a unit cell is a box, and if we stack many unit cells, we get the total structure. Here's the unit cell for the NaCl lattice above.

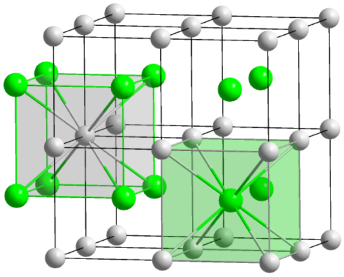


By Prolineserver via Wikimedia Commons

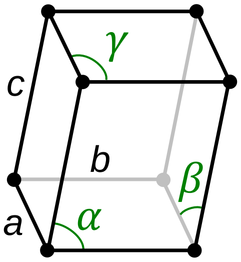
Not all salt structures are the same. For instance, here is the cesium chloride structure, which is a little different from the NaCl structure.



Here's another view of CsCl. You can see 2 different (equally valid) unit cells (the shaded cubes), each of which has an ion at each corner of the unit cell box, and the other ion in the center of the box. If we repeat either unit cell, we'll get the crystal structure.



We can describe the unit cell using **lattice vectors** which are usually called a, b and c. These show the lengths of each side of the unit cell box. The angles between the lattice vectors are called α, β and γ. Here's a general unit cell, showing the lattice vectors and angles. The lengths a, b and c can be the same or different, and the angles can be 90° or not. There are different names for unit cells with particular shapes, but you don't need to learn them now, except for cubic, which means that the sides are the same and all the angles are 90°.



In simple salts, the atoms might be on the lattice points (the corners of the unit cells) but they don't have to be. Inside each unit cell, there will be some arrangement of atoms or molecules, called a **motif**. We can make to whole crystal by repeating the unit cells that contain the motifs.

Contributors and Attributions

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Intro to Solids

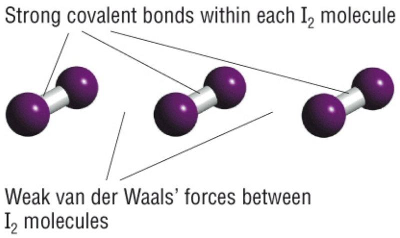
Skills to Develop

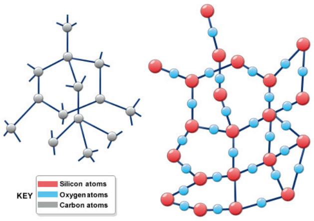
- Relate the different types of solids to the 3 main types of bonding
- Describe some of the properties of solids

Solids are one of the most interesting and important topics in general chemistry because they are important for so many things. We use solids as building materials, to make tools of all kinds, to make computer chips, energy storage devices, solar cells, catalysts... Nearly all technology depends on the properties of solids.

Types of Solids

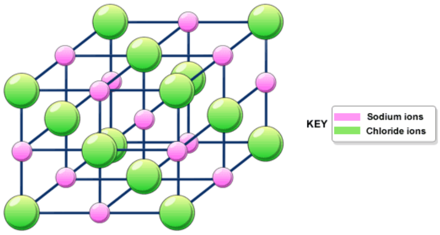
We can categorize solids in many ways. The most common way is by the type of bonding. There are three main types of bonding. So far we have focused on **covalent** bonding. There are two types of covalent solids: **molecular** and **covalent-network**. Molecular solids are made of covalent molecules, and the solids are held together by Van der Waals forces between the molecules. These molecular solids usually have low melting points and are easy to break, because the forces between molecules are weak. Covalent-network solids are different because there are no separate molecules: the whole solid is held together by covalent bonds between atoms. For example, in diamond, each C atom makes 4 covalent bonds to 4 other C atoms in a tetrahedral arrangement. Covalent-network solids usually have high melting points and are relatively hard because they are held together by very strong bonds. Diamond is the hardest material known, because C-C bonds are among the strongest single bonds known. (Could you make a covalent-network solid using the even-stronger bonds?)





An example of a covalent molecular structure, left, and a covalent-network structure, right.

We have also talked a little bit about **ionic** bonding. Basically, you probably know that most ionic materials are solids at room temperature, and they are made of ions, such as a metal cation and a non-metal anion. Ionic solids are held together by strong electrostatic (Coulomb's law) forces between the ions, so they are usually hard and have high boiling points.

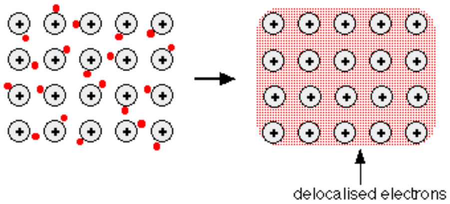


An example of a structure with ionic bonding.

There are also many solids that are on the border between covalent and ionic: they are made of metals and non-metals, but both covalent bonding and ionic bonding are important. This includes most rocks, minerals and ceramics. For instance, sapphire, another of the hardest materials, is aluminum oxide.

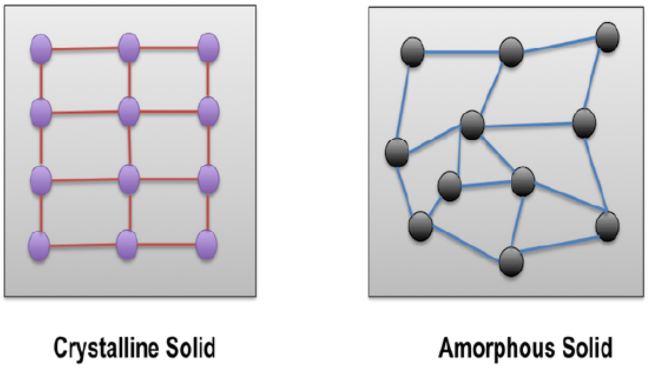
An illustration of bonds forming in aluminum oxide.

Finally, there is **metallic** bonding. Metallic bonding is sort of like covalent bonding, because it involves sharing electrons. The simplest model of metallic bonding is the "sea of electrons" model, which imagines that the atoms sit in a sea of valence electrons that are delocalized (spread out) over all the atoms. Because there aren't specific bonds between individual atoms, metals are more flexible than covalent-network solids. The atoms can move around and the electron sea will keep holding them together. Some metals are very hard and have very high melting points, while others are soft and have low melting points. This depends roughly on the number of valence electrons that form the sea.



A simple diagram of the "sea of electrons" model for metallic bonding.

There are actually some other types of solids also. One way we can separate solids into categories is **crystalline** or **amorphous**. Crystalline solids have ordered arrangements of atoms or ions. Amorphous (which means "no-shape") solids have disorganized arrangements. Metals, ionic solids, covalent-network and molecular solids are usually at least sort of crystalline and orderly, although they are never completely perfect. Crystalline solids often have faces or facets (flat surfaces at particular angles), like most of the gem-stones used to make jewelry. An important type of amorphous materials are polymers, which include most plastics. Polymers are usually made of really long, skinny covalent molecules that are tangled together. They are often flexible. There are also amorphous stones, like opal (which is usually polished to a rounded shape, because it doesn't make nice facets).



We can also classify solids by their size. **Nanomaterials** are solids that have very small sizes. Nanomaterials can be made from metallic or covalent-network materials, but because of their small size, they have different properties.

Properties of Solids

As you read about solids, think about how the structure relates to the important properties of the solids that determine how we can use it. Here we will describe some of these properties.

For structural materials (materials that we use to build, support, protect) the strength and hardness can be very important. **Hardness** means how easy it is to change the shape of the material, such as by stretching or denting it, or how elastic it is in a collision. **Strength** of materials means how well they resist applied forces, such as compression or stretching. This is important if you want to build a bridge or a building, for example. We will describe solids as **brittle** if they break into pieces, such as ionic or covalent solids. Metals don't usually break into pieces, but they can stretch into wires (ductility) and be pounded into sheets (malleability).

Conductivity is another important type of property. Do the materials conduct electricity? If so, how much? Do they conduct sound or heat, and how well? We might also want to know about the reactivity of solids. Are they inert (non-reactive) at high temperature in acid? Do they catalyze (speed up) certain reactions on their surfaces? Do they absorb or emit light, and if so, at what energy? Are they magnetic? Are they porous (full of tiny holes)? All these properties can be important for different applications.

Valence and Solids

As you read about solids, it can be helpful to remember the ideas about valence we have discussed earlier. Different atoms have different numbers of valence electrons, which determines how many electrons they usually lose or gain, and how many bonds they usually make. Another way to think about this is with coordination number, which is how many other atoms one atom interacts with. In molecules, coordination numbers are usually pretty low, like 1-4. In ionic solids, each ion might have 2-8 neighbors. In metals, each atom might have 12 neighbors. The stable coordination number of an atom or ion depends on the situation, and how many electrons it needs. To form a covalent-network solid, at least some of the atoms in the formula have to make many bonds (like carbon or silicon, which usually makes 4 bonds). You can't make a good network with only atoms that form 2 bonds, because you can't have branches. In molecular solids, all the bonds are inside the molecule. In metals, in order to gain the electrons they want, because they start with fewer valence electrons, they usually have high coordination numbers, which requires that they have certain structures.

Defects

A really important topic in solids is **defects** or places where the arrangement of atoms isn't perfect. All examples of a particular molecule are exactly the same, because if one of the atoms is different or the arrangement is different, it would be a different molecule. But solids can be mostly one formula and structure, with some impurities or places where the structure isn't exactly orderly. In fact, solids always have defects. Many of the most important properties of solids depend on the defects, like having a few atoms of different types, or an atom missing, etc. So remember that sometimes the bulk description (how most of the solid is) isn't actually the most important part. The most important part might be the rare spot where a few atoms aren't in their places. This can make solids very confusing to study!

Outside Links

- Khan Academy: Covalent Networks, Metallic and Ionic Crystals (9 min)
- CrashCourse Chemistry: Doing Solids (10 min)

Contributors and Attributions

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Ionic Solids

Skills to Develop

- Describe the coordination number and some characteristics of a unit cell
- Relate lattice energy and some of the properties of ionic solids

Ionic solids are made of lattices of alternating ions. They can't be close-packed structures, because then like ions would have to touch. We've already seen 2 common ionic unit cells: the CsCl structure and the NaCl structure, on the lattices page. We'll show a few more below, but first, let's talk about interpreting unit cells a little more.

Interpreting Unit Cells

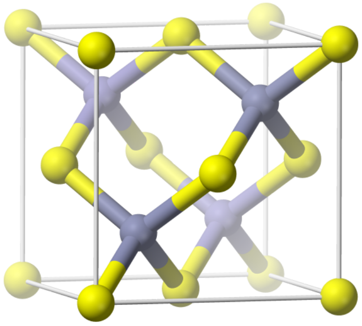
When you look at a unit cell, it's good to be able to figure out what the coordination number of each atom is, and what the overall formula is. When you do this, you need to remember that the unit cell repeats. So to count the number of atoms of each type in the unit cell, we have to count the atoms at the corners as 1/8, the atoms on edges as 1/4, and the atoms on faces as 1/2. The rest of these border atoms are in other cells. When you count coordination number, you also have to remember that atoms might have neighbors in other cells. Here's a formula that can help you:

$$\frac{number\ of\ cations\ per\ unit\ cell}{number\ of\ anions\ per\ unit\ cell}=\frac{anion\ coordination\ number}{cation\ coordination\ number} \tag{1}$$

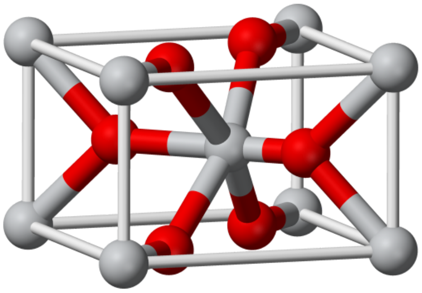
The key thing is that the number of cations and anions in the unit cell is the same as the overall formula, and, for example, if the formula is AB_2, then the coordination number of A is double the coordination number of B.

Unit Cells for Ionic Crystals

In addition to the ones we saw before, a common structure for the formula AB is called the zinc blende or ZnS structure. Let's analyze this unit cell as shown below. We can see that the grey ions have tetrahedral coordination, and there are 4 of them inside the unit cell. What is the coordination number of the yellow ions, and how many of them are there? It might be a little hard to answer the first question. Let's count them first: each corner has a yellow ion, but since they are on corners, 8 x 1/8 = 1. Then there is a yellow ion on each face of the unit cell, and there are 6 faces. 6 x 1/2 = 3. So there are 4 yellow ions inside each unit cell. This is the same as the number of gray ions, so the formula is AB, as we said. Since the formula is AB, the coordination number of the yellow ions must also be 4. Try to convince yourself that this is true. If you think about each of the corner positions as the same (each corner atom has the interactions of all the corners added together) you can see that they also have tetrahedral coordination.



Let's look at an example of an AB_2 structure. Below is the rutile structure, which is quite common, and occurs in many materials including the very common TiO_2, which is used in everything from sunscreen to paper to paint. Let's analyze this one also. In the rutile structure, we have a red ion on each corner and one in the middle, so that's 2 red per unit cell. Then we have 2 gray in the middle and 4 on faces (it's a little hard to be sure they're on the faces from the picture, but they are), so that's 4 gray ions total. The formula is AB_2. What are the coordination numbers? The gray in the middle is clearly octahedral (6-coordinate). The gray on the corners is also octahedral. If we consider all the interactions between the corners and the inside of the cell, we have 4 bonds to reds that are fully inside, and 4 bonds to reds on faces. We have to count the reds on faces as 1/2, so the coordination number is still 6 for the corners. We can count the red coordination number as 3 easily for the middle, and as 3 for the reds on faces also if we are careful. This fits the equation.

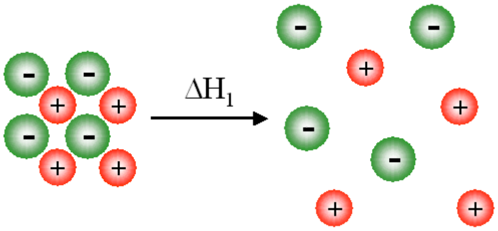


There are many, many other structures. Some are very regular and symmetric, and some are distorted. Some structures are more complex to fit more complex formulas. We don't need to worry about the others now. If you are curious why some materials have one structure and some have another, there are 2 main effects to consider. First, it depends on the relative sizes of the ions. If the ions are similar sizes, the CsCl structure is good, because it has the highest coordination number (more favorable interactions between opposite ions). If the ions aren't the same size, then in the CsCl structure the big ions might touch each other, so the NaCl structure (with coordination number 6) becomes more stable, so the big ions can be farther apart. For even less equal sizes, the zincblende structure might be necessary. The other effect is how covalent the bonds are. If the bonds are partly covalent, even if the sizes aren't so different, the zincblende structure might be better because it allows better orbital overlap (just like in diamond, which has the same structure but with all the atoms the same).

Properties of Ionic Solids

Ionic solids are usually insulators, because electrons are held tightly to the ions. They are hard and have high melting points, because ionic bonds are strong. However, they are brittle because if the crystal gets knocked so that the wrong ions are touching, it will shatter.

A key concept for ionic bonding is the lattice energy. If you compare the electron affinity for a non-metal and the ionization energy for a metal, you'll notice that forming ions is endothermic. However, remember that electron affinities and ionization energies are defined for gases. Making ionic solids from the elements is very exothermic, because bringing the ions together into the crystal lattice is releases a lot of heat. The **lattice energy** is the energy released when the solid forms from ions in the gas phase. The lattice energy includes all the ion-ion interactions in an infinite lattice, so it is a little complicated to calculate. The main thing to know is that the smaller the ions and the larger the charge, the bigger the lattice energy is, and the more stable the solid.



An illustration of lattice energy (ΔH_1).

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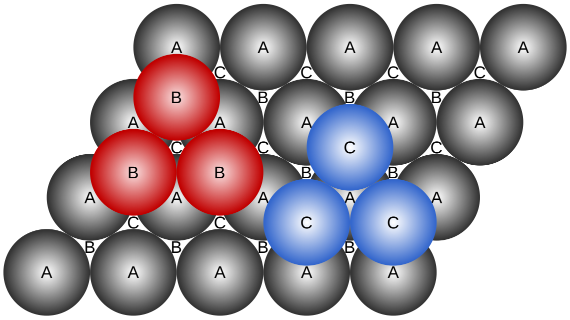
Metal Crystal Structures

Skills to Develop

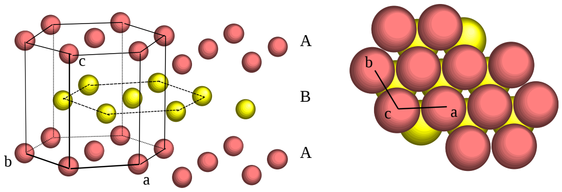
- Describe the different types of unit cells and alloys

Most metals want to have high coordination numbers (lots of neighbors for each atom). The highest coordination number possible with spheres is 12. There are 2 regular arrangements that give 12 neighbors, and they are called **close-packing**. These are the densest possible ways to arrange spheres. Both are based on hexagonal planes of atoms that are stacked. Each plane's atoms sit in the holes of the lower plane. Look at the figure.



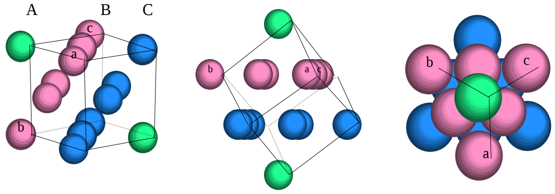
by Life of Riley via Wikimedia Commons

The gray A spheres represent the bottom plane. The holes in this plane are labelled B and C. The next layer will go over either the B holes or the C holes. It doesn't matter which. The 2 types of close-packing come from what happens to the third layer. If the layers are ABAB (which is equivalent to ACAC or BCBC), that forms one type of close packing, called **hexagonal close-packed**, or hcp. The other type of close packing has layers ABCABC and is called **cubic close-packed** or ccp. Cubic close-packed is also called **face-centered cubic** or fcc because it is a cubic structure with an atom on each face and corner of the cube. Each atom in a close-packed structure has 12 neighbors (6 in its plane, and 3 in the planes above and below).



hexagonal close-packed (hcp) ABAB

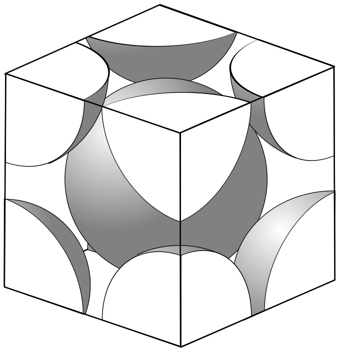
A layer atoms are in red and B layer atoms are in yellow. Notice that the overall arrangment makes a hexagonal structure (lattice vectors are labelled a,b,c). By Maghemite via Wikimedia Commons.



cubic close-packed (CCP) ABCABC

A layer atoms are in green, B layer atoms pink and C layer atoms blue. Notice that the overall arrangment makes a cubic structure with atoms on the corners and faces of the cube (lattice vectors are labeled a,b,c). By Maghemite via Wikimedia Commons.

Not all metals make close-packed structures. A few have a **simple cubic structure** (just one atom on each corner of the cubic unit cell), so in this case each atom has a coordination number of 6. Another more common structure is called **body-centered cubic** or bcc, in which there is an atom on each corner and in the center of the cubic unit cell, so that each atom has 8 neighbors. Here's a different view of the bcc unit cell, using a "space-filling" picture of the atoms. Notice that each corner of the unit cell actually has 1/8 of an atom. (If there were a whole atom on each corner, then we'd get the wrong structure when we stack the unit cells.)



Space-filling view of the bcc unit cell, by Cdang and Samuel Dupre, via Wikimedia Commons.

Alloys

Alloys are metal solutions or compounds. Some alloys have different metal atoms arranged in a regular structure. These alloys have a precise formula, such as Ni_3Al. Others have a random replacement of one type of metal atom with another, like gold/silver alloys. Both gold and silver have the fcc/ccp structure and the atoms are similar sizes, so they can make mixtures with almost any % Au and Ag. This is called a **substitutional alloy** because one type of atom substitutes for another. A third type have a smaller atom (like carbon in steel) that occupies some of the holes between the majority metal atom. This is called an **interstitial alloy**. Alloys are important for many applications because they have different properties compared to the pure metals.

Outside Link

- CrashCourse Chemistry: Doing Solids (11 min)

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Metallic Bonding

Skills to Develop

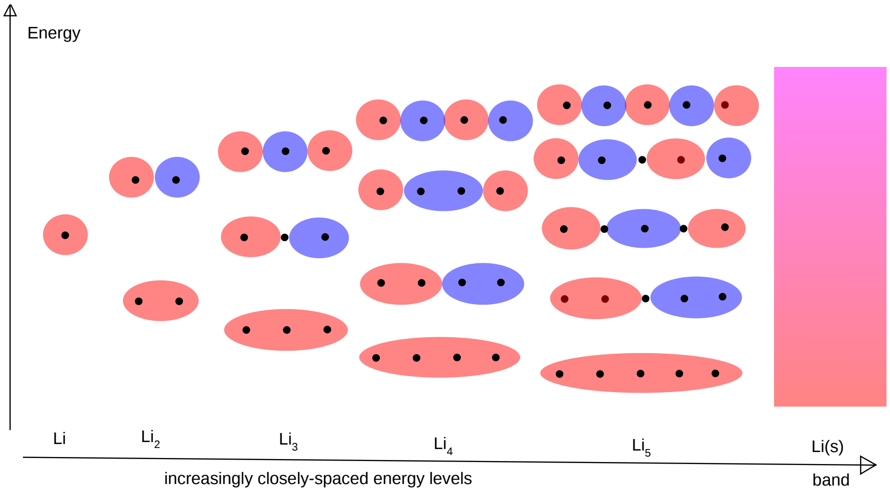
- Describe metallic bonding using MO theory

We previously discussed the "electron-sea model" of metallic bonding in the intro section and metal characteristics sections. This is a good time to review those sections, before we describe a better model. Why do we need a different model for metallic bonding than the electron-sea model? Although it explains some general properties of metals, like malleability and conductivity, it doesn't explain the relative properties of metals, like their hardness and melt points. These properties depend on how strong the bonding in the metals is. By the electron-sea model, we might think that more electrons makes the bonds stronger, so hardness and melt point would increase across the periodic table.

We can explain these properties using MO theory. In this case, we imagine combining many atomic orbitals (1 or more for each atom) to make and equal number of MOs that extend over the whole solid. Some MOs will have fewer nodes and be lower energy, while others will have more nodes and be higher energy. Each MO can hold no more than 2 electrons. Filling the lower energy MOs (bonding MOs) makes the bonds stronger, which is why alkali metals have low melt points and are soft (not many bonding MOs filled). Filling the higher energy MOs (antibonding MOs) makes the bonds weaker, which is why Cu, Ag, Au and Zn are soft and melt at low temperatures (Hg is a liquid at RT!).

When we have a really big number of MOs, some interesting things happen. One mole of Fe is about 7 mL or 7 cc (a pretty small amount). In each atom of Fe, we have 1 4s orbital, 5 3d orbitals, and 3 4p orbitals that can be involved in bonding. In a mole of Fe, we have 9 times Avogadro's number of AOs that can be involved in bonding. That's about 10^{24} AOs, which means the same number of MOs. There just isn't space to have much difference in energy between all those MOs. The MOs have to have energies not too different from the AOs (they are definitely higher and lower, but not by too much), so they are limited to a relatively narrow range of energies. This means that the energies form **bands** rather than separate energy levels.

We can start to see how this happens by imagining a line of Li atoms. As we increase the number of Li atoms, the orbitals get closer together. When the number of Li atoms reaches infinity, the MOs become infinitely close together.



Formation of a band in a chain of Li atoms: the MO energy levels become closer together as the number of MOs increases, until they are no longer separate.

Band theory explains the conductivity of metals: for electrons to move, electrons have to be able to change MOs without gaining much energy. If a band is partly-filled with electrons, they can easily change states because there are empty states almost the same energy as the full states. We can tell that the bands from s, p and d orbitals must overlap in metals, because the alkaline earth metals are conductors. If there were an energy gap between the s band and the p or d band, they would not conduct because the s band would be full.

Outside Links

- Clayton Spencer: Metals, Bonds, and Band Theory Part 1 (10 min)
- Clayton Spencer: Metals, Bonds, and Band Theory Part 2 (10 min)

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Other Solids: Polymers, Nanomaterials, Foams, etc.

Skills to Develop

- Describe some of the properties and/or characteristics of polymers and nanomaterials

There are many other types of solids, or other important qualities that distinguish solids, like catalysis, porosity, etc. We haven't described minerals or ceramics very well, or superconductors, magnetic materials, etc. For now, we'll just describe two more types: polymers and nanomaterials. Polymers are familiar and important from life, because we use them for almost everything. Nanomaterials are less familiar, but are starting to be used in commercial products although we don't always understand them too well.

Polymers

Polymers are also called **macromolecules**, which means big molecules. Polymers are usually long chains made of small molecules covalently bonded together. The important properties of the polymer come from the "intermolecular" or non-covalent forces that determine how the polymer chains fold up or tangle together. Most important biomolecules (like DNA, proteins and starch) are polymers. We also make a wide variety of polymers, usually starting with hydrocarbon molecules from oil, that are used in clothing, plastics, construction materials, etc. Many different molecules and reactions can be used to make polymers. The properties of the polymer will often depend on the structure, which is usually amorphous or disorganized. If the macromolecules are more orderly and rigid, the structure may be more crystalline and less flexible, with a higher melting point (because the molecules can pack together well with relatively strong intermolecular forces). If the macromolecules are very different sizes and have irregular shapes, then the polymer might be more flexible. Sometimes covalent bonds are added between the molecules, which can also make the material tougher. (For example, rubber is made by stronger by heating with sulfur, which can connect the chains together.)

Nanomaterials

Nanomaterials are very small solids, like extremely fine powders only smaller. They have dimensions measured in nanometers, or 10^{-9} meters. At this scale, they are too small to have all the normal properties of solids, because they have so much edge. For example, nanomaterials have bigger band gaps than the same material in bigger chunks. The smaller the particles, the bigger the band gap. (Molecules have bigger HOMO/LUMO gaps than solid materials; nanoparticles are in between molecules and normal solids.) People are pretty excited about nanoparticles (they're popular!) but it's good to remember that we don't really know much about their health effects yet, except to say that they are complicated and need more study. I don't recommend running out and buying the new nano-shampoo or nano-silver handwipes or whatever you might encounter unless it's noticeably superior to the non-nano alternative.

Nanostructures and nanoparticles can be natural or manufactured. For example, most birds that look blue don't have blue pigment, they have nanostructures on their feathers that scatter light. These days, most electronic devices are based on nanostructures also: each individual transistor in a computer chip is nanosized, and it may not be possible to make them much smaller than they are now without too many size-based complications.

Outside Link

- CrashCourse Chemistry: Polymers (10 min)

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CHAPTER OVERVIEW

Thermochemistry

Topic hierarchy

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Basic Definitions

Skills to Develop

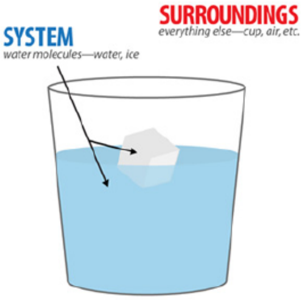
- Understand the fundamental concepts of thermodynamics

Thermodynamics

Thermodynamics is the study of heat, energy, and work and how they move. This is important because we have to move or generate heat to stay comfortable in winter and summer; we need to do work by moving things for many different purposes; we need to generate chemical energy to live and grow our bodies, etc.

System and Surroundings

In thermodynamics, we often separate the universe (that is, everything that exists) into 2 parts: the **system**, which is the small part we are interested in, and the **surroundings** which is everything outside the system. This will help us think about how heat, energy and work move between parts of the universe.



Open, Closed, and Isolated Systems

Open systems allow energy and matter (stuff) to enter and leave the system. A pan on the stove is an open system because water can evaporate or be poured in, and heat can enter the pan if the stove is turned on, and leave the pan also. A **closed system** does not allow matter to enter or leave, but does allow energy to enter or leave. A covered pot on the stove is approximately a closed system. An **isolated system** does not allow either matter or energy to enter or leave. A thermos or cooler is approximately an isolated system. There are no truly isolated systems.

State Functions

State functions are quantities that don't depend on path. Your bank balance is a good example. It doesn't matter how the money entered your bank account, the total amount there at any given time is what it is and you can measure it easily. It doesn't matter if you put it in all at once, or a little bit every month, or put a lot in then spent it slowly... any time you want to know how much is there, you just check. Most of the quantities you know are state functions, like pressure, volume, temperature, location, etc. But some quantities that are important in thermodynamics, like heat and work, are only defined by a process, so they aren't state functions.

Extensive vs. Intensive

Extensive refers to properties that depend on how much stuff there is. For instance, the volume or pressure created by a sample of gas depend on how much gas is in the sample, so they are extensive. **Intensive** quantities don't depend on how much there is. For instance, temperature, density, etc. If you divide a sample in 2, it does not change temperature. Density is a ratio of 2 extensive properties, so it is intensive.

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Calorimetry and Reaction Enthalpy

Skills to Develop

- Perform and describe calorimetry calculations

How do you measure ΔH?

If you want to measure ΔH, you usually use calorimetry, which just means measuring heat. The usual way this is done is by measuring how much the temperature of a system increases when the process occurs. For instance, perhaps we have 2 solutions (like an acid and a base solution) and we mix them in a thermos. We measure the temperature of the solutions before mixing and also after the reaction. Because we run the reaction in a thermos, we expect that almost all the heat from the reaction will stay in the thermos. Also, we don't close the thermos all the way, so the pressure is always atmospheric pressure. The reaction enthalpy is related to the temperature change, but how, exactly?

Heat Capacity

Heat capacity tells us how much heat is needed to increase the temperature of an object or substance by a certain amount. The unit **calorie** is the energy needed to increase the temperature of 1 g of water by 1 degree (either Celsius or Kelvin). 1 calorie = 4.18 J. Generally, the heat capacity is

$$C = \frac{q}{\Delta T} \tag{1}$$

Depending on what is convenient, heat capacity can be defined in different ways. Sometimes it is defined using heat transferred at constant pressure, and other times heat transferred at constant volume. Specific heat is the heat capacity per unit of mass:

$$C = \frac{q}{\Delta T \ \times m} \tag{2}$$

Molar heat capacity is the heat capacity per mole of substance. If you know the heat capacity of the system, you can calculate ΔH using the temperature change data from a calorimetry experiment. In the example of the acid-base reaction in the thermos, you would want the heat capacity of the thermos and you would add the heat capacity of the solution, which you could calculate using the specific or molar heat of water.

Doing Calorimetry Calculations

First, you need to be a little careful about whether the experiment was done at constant pressure or constant volume. This will determine whether you calculate enthalpy or internal energy of reaction. Second, make sure you figure out the heat capacity of the system correctly. You might have to add up heat capacities of different parts of the system using (mass x specific heat) or (moles x molar heat capacity) of each part. Once you've figured that out, you can usually think of it as a "unit conversion" and use dimensional analysis to combine all the quantities you know to find the quantity you want.

Outside Links

- Khan Academy: Specific Heat, Heat of Fusion, and Vaporization Example (15 min)
- CrashCourse Chemistry: Calorimetry (12 min)

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Fuels and Enthalpy

Skills to Develop

- Perform enthalpy calculations and describe the process and results

What is Fuel?

One of the most important applications of chemistry is the study of **fuels**. Fuel basically means a chemical that can provide energy. We use fuel to do nearly everything. Food provides fuel to our bodies. Gasoline provides fuel for our cars. Many different chemicals, from coal and gas to uranium, provide fuel for the power plants that make electric power. When we use a fuel, it becomes a reactant in some type of reaction. Most often, fuels are burned in air to provide heat, and the heat is converted to work. For this reason, we often want to know how much heat we can get out of a chemical reaction.

Enthalpy

When our systems includes chemicals that participate in a reaction, the system may gain or lose heat because of the reaction, and the system may also do work, or work may be done on the system. How would the system do work? Suppose you burn some propane (C_3H_8). Write a balanced equation for this reaction, and convince yourself that there are more moles of gas present in the products than the reactants. Also, you know that burning propane raises the temperature. If you burn some propane, the system will increase in volume, because there is more gas, and it is hotter. (If you burn the propane in a very strong container, then the volume will stay the same and the pressure will increase.) When the volume of the system increases in an open container, it will push on the surroundings, like the atmosphere, and do pV work. We might be able to use this work (in an internal combustion engine like in a car, for instance) but only if we control the volume. If we do the reaction open to the atmosphere, at constant pressure (atmospheric pressure), then we won't be able to use the work done by the reaction.

In chemistry, because reactions are often done at atmospheric pressure, we often want to know how much heat is available from a reaction that occurs at constant pressure. To make this convenient, we can define a new quantity, related to internal energy, which is called **enthalpy**, abbreviated H:

$$H = E + pV \tag{1}$$

Here's why this definition is useful. The work done by a reaction at constant pressure is

$$w = -p\Delta V \tag{2}$$

where p is the pressure, and ΔV is the change in volume of the reaction system, and the sign of w is negative because the system is doing work. The change in enthalpy for a reaction is

$$\Delta H = \Delta(E + pV) = \Delta E + p\Delta V (at\ constant\ p) \tag{3}$$

Since ΔE = q + w,

$$\Delta H = (q + w) + p\Delta V = (q + w) - w = q \tag{4}$$

Thus, the enthalpy change in a reaction tells us exactly how much heat the reaction can provide if it runs at constant pressure. We don't need to worry about calculating the work done by the reaction pushing back the atmosphere because it is already removed from the definition of enthalpy. Enthalpy is a state function because E, p and V are all state functions. Enthalpy doesn't have a molecular meaning like internal energy, but usually pV is small, so enthalpy is similar to internal energy.

When ΔH is positive, then heat has entered the system, and the process is called **endothermic**. Endothermic reactions feel cold to the touch because they pull heat from your hand into the reaction system. Evaporation is endothermic, which is why sweat helps us cool off. When ΔH is negative, heat leaves the system, and the process is called **exothermic**. Exothermic processes feel hot. This is why flames will burn you.

Outside Links

- Khan Academy: Enthalpy (15 min)
- CrashCourse Chemistry: Enthalpy (11 min)

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Hess' Law and Enthalpy of Formation

Skills to Develop

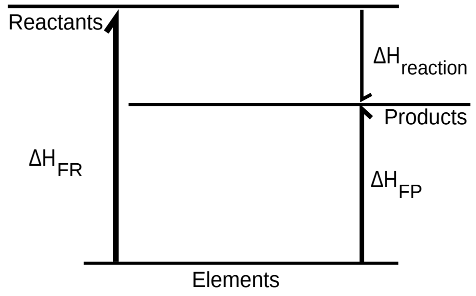
- Calculate enthalpies of reactions using Hess' Law
- Define "standard state"

What is Hess' Law?

Hess' Law is an early statement of the law of conservation of energy (1840). It says that the heat liberated by a process doesn't depend on how the process happens (only on the starting and ending states: in other words, it's a state function). Now we know we should really use enthalpy for this, not heat, because enthalpy is a state function, so this is true, while heat is a process. Hess' Law lets us break a reaction or process into a series of small, easily measured steps, and then we can add up the ΔH of the steps to find the change in enthalpy of the whole thing. Hess' law is a great way to think about chemical processes and make predictions. We'll see lots of applications of Hess' law, but right now let's start with finding reaction enthalpies using standard enthalpies of formation.

Standard Enthalpies of Formation

Standard enthalpies of formation help us predict reaction enthalpies for many reactions if the products and reactants are well-studied, even if the specific reaction is new. To do this, we imagine that we take the reactants and separate them into their pure elements in a **standard state**. The standard state is the element in its most stable form at room temperature and atmospheric pressure. Then we take the elements and recombine them to make the products. The reaction enthalpy is equal to the difference in the enthalpies of these processes.



A diagram showing the application of Hess' law to reaction enthalpy calculated from enthalpies of formation.

Example

Let's look at a specific example. Here are some enthalpies of formation (in kJ/mol of reaction):

$$C(s) + O_2(g) \rightarrow CO_2(g)\ \Delta H_f = -394\ kJ\$\$\$\$C(s) + 2H_2(g) \rightarrow CH_4(g)\ \Delta H_f = -75\ kJ\$\$\$\$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)\ \Delta H_f = -572\ kJ \tag{1}$$

Let's use these enthalpies of formation to calculate the enthalpy of combustion for 1 mol of methane. The reaction we want is

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \tag{2}$$

If we reverse a reaction, we change the sign on ΔH, and if we multiply the reaction by a constant coefficient, we multiply ΔH by the same coefficient. Let's combine the formation constant equations so they add up to the reaction we want:

CH_4 (g)	→	C(s) + $2H_2$(g)	ΔH_f = 75 kJ
C(s) + O_2(g)	→	CO_2(g)	ΔH_f = -394 kJ
$2H_2$(g) + O_2(g)	→	$2H_2O$(l)	ΔH_f = -572 kJ

That's almost right but we're missing the state of the water:

$$H_2O(l) \rightarrow H_2O(g) \;\Delta H = 44\; kJ \tag{3}$$

The full set is

$CH_4(g)$	→	$C(s) + 2H_2(g)$	$\Delta H_f = 75$ kJ
$C(s) + O_2(g)$	→	$CO_2(g)$	$\Delta H_f = -394$ kJ
$2H_2(g) + O_2(g)$	→	$2H_2O(l)$	$\Delta H_f = -572$ kJ
$2H_2O(l)$	→	$2H_2O(g)$	$\Delta H_f = 88$ kJ
$CH_4(g) + 2O_2(g)$	→	**$CO_2(g) + 2H_2O(g)$**	**ΔH = ?**

Note that everything but the desired reaction cancels. Now we just add up the enthalpies of each step, and we find that the enthalpy of combustion of 1 mole of methane is -803 kJ.

General Procedure for Hess' Law Calculations

Determine the equation for the desired process (the process for which you want to know the enthalpy change). Break it into steps for which you can look up the enthalpy changes. This probably means steps like formation from elements, and changes of state. (Later, we'll include other processes like ionization, etc) Arrange the steps so that everything cancels out leaving just the desired reaction. Make sure the coefficients on equations are correct (multiply the equation and ΔH by a constant if needed) and that all the components are in the correct state (like the example above, we had to convert from liquid water to gaseous water). Then just add it up!

Outside Links

- Khan Academy: Enthalpy of Formation (12 min)
- Khan Academy: Hess's Law and Reaction Enthalpy Change (16 min)
- Khan Academy: Hess's Law Example (12 min)
- CrashCourse Chemistry: Enthalpy (11 min)

Contributors and Attributions

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History of Thermodynamics

Skills to Develop

- Describe the 2 theories for heat
- Explain Mayer's argument

For a long time, physicists and chemists debated whether heat was a fluid (like a mysterious liquid) or came from the motion of particles. Many early scientists, like Newton, had thought that heat might be caused by small movement of particles, and greater heat meant greater velocities or kinetic energies. Lavoisier, however, thought that heat was a massless fluid that he called "caloric."

Count Rumford observed that the process of boring cannon (drilling the hole in the middle of the brass cannon) produced a lot of heat, especially when the drill was dull or blunt. He showed that the heat produced was related to the amount of mechanical work done by the drill. Davy (mentioned earlier here) showed that even at 0°C, two ice cubes would melt when rubbed together. This frictional heating is also a way that people sometimes start fires in the wilderness.

Other scientists liked the fluid theory. Lavoisier thought heat was a fluid that caused the atoms it surrounded to separate (which is why, he said, density usually decreases as you heat a substance). One important contribution he made was to show that the heat generated by human or animal metabolism (oxidizing food with oxygen from breathing) produces the same amount of energy as combusting the food (which is often if not always true). Carnot, who will be very important later (in the development of the second law of thermodynamics), also thought that heat was a liquid, because like liquids it "flows downhill" from hot objects to cold objects. He thought that like power generation from a waterfall, the amount of heat that moves and the distance it falls (change in temperature) determine the available power. However, later he realized that some of the heat is lost when it is converted to mechanical energy (work), which means it can't be a fluid like water (water isn't lost when falling water is used to drive a motor).

Mayer used data other people collected on heat capacities of air at constant pressure or constant volume to calculate the relationship between the energy defined as force x distance (like the modern unit joule) and energy defined by change in temperature of a substance (like the modern unit calorie, the energy needed to raise the temperature of 1g of water 1°C). Imagine heating a sample of air in a fixed volume container or in a chamber with a piston, so that it is always at atmospheric pressure. One sample does work when heated (by expanding against atmospheric pressure) and the other does not. The difference in heat required to get the same temperature change in the 2 containers must be equivalent to the work done by the system with the piston. Mayer argued that heat, work, and chemical energy are all interconvertible, meaning they are all energy in different forms.

Joule (for whom the unit joule is named) was an English beer-brewer who did the studies mentioned earlier that lead to the first law. You might have learned Joule's law in a physics class, that heat produced by electricity, Q, is

$$Q \ \alpha \ I^2 R \tag{1}$$

where I is current and R is resistance. He compared heat produced by electricity and heat produced by mechanical work (heating water using a paddlewheel powered by a falling weight) and thus showed the equivalence of mechanical work and heat. In other words, Joule and Carnot had showed that heat can be used to generate work (like in a power plant) and work can be used to generate heat (like with the cannon drills or paddlewheel). Kelvin combined these ideas and used them to propose the Kelvin temperature scale (but the details of that can wait until we study Carnot's discoveries in more detail).

Contributors and Attributions

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Kinetic and Potential Energy

Learning Objectives

- Define energy and its two main types listed below
- Describe the conservation of energy

You are probably familiar with these types of energy from a physics class. **Energy** is the capacity (ability, sort of) to do work. You have a sense of what work is from regular life, it's things that require effort. Energy and work have the same units. **Kinetic energy** is the energy that comes from motion. The equation for kinetic energy is

$$KE = \frac{1}{2}mv^2 \tag{1}$$

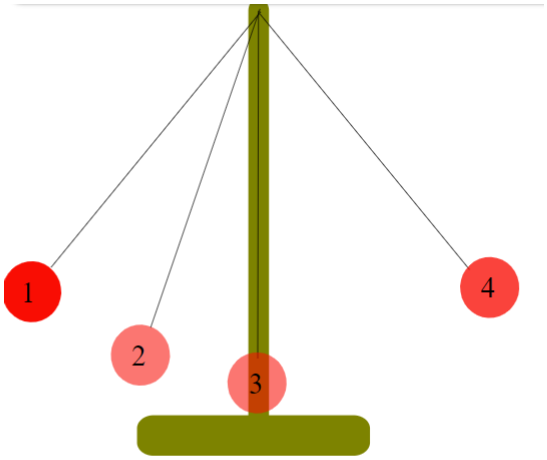
where KE is kinetic energy, m is mass, and v is velocity. This definition should make sense: big things moving fast have the most energy, the most ability to shove other things or knock them over, etc. **Potential energy** is energy that comes from position and a force. For instance, gravitational potential energy is the energy that things have if they are high up. If they fall, their potential energy will turn into kinetic energy because they are accelerated by gravity. The equation for potential energy from gravity is

$$PE = mgh \tag{2}$$

where PE is potential energy, m is mass, g is the acceleration of gravity, and h is the height. This makes the units of energy very clear: mass x distance x acceleration, or force x distance, which comes to kg•m^{2}s^{-2}. In chemistry, the force that leads to potential energy is almost always the Coulomb force, not gravity. In this case, the potential energy from 2 charges near each other is

$$PE = \frac{kQq}{d} \tag{3}$$

where q and Q are the 2 charges, d is the distance between them, and k is a constant, 8.99 x 10^9 J•m•C^{-2}. (Joules, J, are the SI unit of energy, and coulombs, C, are the SI unit of charge.) When the charges have the same sign, they repel and will accelerate away from each other if allowed to move; the potential energy has a positive sign. When the charges have the opposite sign, they attract each other and have negative potential energy. If they are allowed to get closer together, the potential energy will get more negative. If they are separated, d gets bigger and the potential energy approaches zero.



A pendulum. The red ball is raised to Position 1 and released; it swings through Positions 2 and 3 to Position 4 on the other side.

Conservation of Energy

You probably learned about **conservation of energy** already in a physics class. For instance, if you have a pendulum as shown, at Position 1 the weight has some potential energy, but no kinetic energy. When you release the weight, the weight falls, moving through Position 2. At Position 2, some of the potential energy has been converted to kinetic energy. Finally, at Position 3, all the potential energy has been converted to kinetic energy. As it passes 3, the process is reversed, and kinetic energy is converted to potential energy. When the weight reaches Position 4, all the kinetic energy has been converted back to the same amount of potential energy it started with at 1. This is just one example of conservation of energy. It is a general observation that the amount of energy in the universe doesn't change, and the amount of energy in a particular system doesn't change unless there is a flow of energy in or out.

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The First Law of Thermodynamics

Skills to Develop

- Develop applications of the First Law of Thermodynamics
- Calculate internal energy and elaborate on the results

The **First Law of Thermodynamics** is equivalent to the law of conservation of energy, which was described previously here. However, instead of describing a system in which energy changes form (KE to PE and back) but the total amount doesn't change, now we will describe a system in which energy can move in and out. The 2 ways it can do this are work and heat.

Imagine we have a system that is approximately isolated, like a thermos of water, and we do work on it in various ways. First we use the energy from a falling weight to mix it very vigorously, and we see what happens to the temperature of the system. Then we run some electric current through a resistor dipped in the system, and see what happens to the temperature of the system. And we observe that the same amount of work always raises the temperature the same amount. If we do the same experiments on a cup of water that isn't isolated like the thermos (but is otherwise the same), we find that the temperature doesn't increase as much when we do the same amount of work without the insulating thermos. As the system got warmer, some energy moved from the system to the surroundings. Without the thermos, heat leaves the system when it gets warmer than the surroundings, so we have to do more work to get the same increase in temperature.

Energy is the capacity to do work. Any system can do work. Perhaps it can heat a gas, causing it to expand against a force, or fall, compressing a spring, etc. But an isolated system's capacity to do work won't change. For instance, if we use a system to do work, then wait a long time, the system won't regain its original ability to do work. More concretely, if we use a falling weight to do some other work, like lifting another weight or driving a motor, the weight won't be able to do more work until we lift it to its original height. It won't float back up by itself, ready to fall again. If we use a very hot block of metal to boil water and drive motors, the block will get cooler. And if we leave it isolated and wait, it won't heat back up again by itself so we can boil more water. The capacity of a system to do work is called its **internal energy**. The internal energy of a system can change if work is done on or by the system, or if heat enters or leaves the system. If no work is done and no heat flows, then the internal energy of the system can't change. We can write this as an equation:

$$\Delta E = q + w \tag{1}$$

where ΔE is the change in internal energy (some people use U instead), q is heat, and w is work. Heat q is positive when it flows into the system, and negative when it flows out. Work w is positive when it is done to the system and negative when it is done by the system. (Actually, some people use the opposite signs for work, in which case the equation is E=q-w) This should make sense. The internal energy of the system increases when we put energy in; it decreases when we take energy out.

Molecularly, internal energy means all the kinetic and potential energy of each particle in the system. Internal energy is a state function, like temperature and pressure. Work and heat are not state functions: they depend on processes. You can't look at an object and determine how much work or heat it has because that doesn't make sense, but you can measure what its temperature is, what its volume is, and what its internal energy is.

Outside Links

- Khan Academy: First Law of Thermodynamics (18 min)
- Khan Academy: More on Internal Energy (14 min)
- Khan Academy: Work from Expansion (13 min)
- CrashCourse Chemistry: Energy and Chemistry (9 min)

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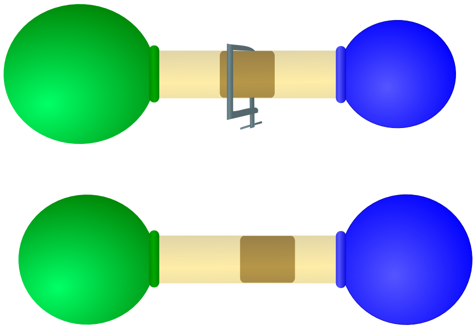
The Zeroth Law of Thermodynamics

Skills to Develop

- Define the Zeroth Law of Thermodynamics

Equilibria Again

We discussed equilibrium reactions before, especially in the stoichiometry section. We mentioned chemical equilibria, between reactants and products. We also mentioned solubility equilibria in the precipitation section. Now let's introduce some other types of equilibrium. Suppose we put a partially-filled balloon on each end of a tube with a piston. Initially the piston is clamped in place. If we remove the clamp so the piston can move, it will move until the pressure on each side is equal. At this point, the balloons will probably also be the same size (unless they are different size balloons), because pressure determines the size of the balloons. The changes the volume on each side until the pressures are equal, and then the system reaches mechanical equilibrium, because the piston won't move any more. Pressure is the property that tells us whether systems will be at mechanical equilibrium; if we clamp the piston and put on a new balloon, if it's at the same pressure as the other balloons then the piston won't move when the clamp is removed.



A balloon and piston system.

Top: initial position. Bottom: after reaching mechanical equilibrium.

Now we can introduce **energy** can flow in and out; maybe they have metal walls, or some other wall that conducts heat). We set them in contact, so they are touching each other. Maybe we can observe some sort of change in the systems, like that the pressure inside one increases and the other decreases. This might mean that one was hotter and the other colder, so the pressure inside changed as they approached the same temperature once they were touching. If no change happens when they touch, we could say that they were in thermal equilibrium. (If we leave them in contact long enough, they will reach thermal equilibrium, but that is different from being in thermal equilibrium when they first touch.) If we have a system A, and we find that it is in thermal equilibrium with another system B, and also with another system C, then we know without doing the experiment that B and C are also in thermal equilibrium with each other. That statement is the **Zeroth Law of Thermodynamics**. The property that tells us if 2 systems are already at thermal equilibrium is the **temperature**. This is a familiar word, but technically this concept of thermal equilibrium is how it is defined: the Zeroth Law introduces the concept and property of temperature.

We measure temperature using a **thermometer**. In science we use 2 scales to measure temperature, the Celsius or centigrade scale, on which water freezes at 0 °C and boils at 100 °C; and the Kelvin scale, on which water freezes at 273.15 K and boils at 373.15 K. The Celsius scale is probably what you are used to from regular life (although I am used to the Fahrenheit scale), and it is convenient because it focuses on water, which is very important for our lives. The Kelvin scale is good for science and thermodynamics especially, because 0 K is the lowest possible temperature.

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Work and Heat

Skills to Develop

- Compare and contrast work and heat

In physics, **work** is defined as motion over some distance against an opposing force. (A force is an acceleration multiplied by a mass.) For instance, lifting an object against the force of gravity. The amount of work is the opposing force multiplied by the distance the object moved. The amount of work done in lifting an object is the force of gravity (the mass of the object times the acceleration of gravity) times the height you lifted it. There are lots of other ways systems can do work: a stretched spring can expand and lift a weight, a battery or burning gas can drive a motor and move a car up hill or forward against friction and wind.

In chemistry, work is often defined in terms of a change in volume against a pressure. (Pressure is force divided by area, so convince yourself that P x V has the same units as F x d.) For instance, atmospheric pressure is constant at ~1 atm. If you have a sample of gas at higher pressure, and you let it come to mechanical equilibrium with the atmosphere, it will expand to some new volume. The work it does expanding against atmospheric pressure is (1 atm)(ΔV), where ΔV is (final volume - initial volume). In general, the work done by gases expanding is called pV work, and is

$$w = \int p dV \tag{1}$$

For our purposes, we won't be dealing with integrals, so we won't calculate work this way unless the pressure is constant, in which case we can use the simpler equation

$$w = -P\Delta V \tag{2}$$

where P is the constant pressure and ΔV is the change in volume of the system. The negative sign accounts for the fact that if the system is compressed, ΔV is negative, and work was done to the system, so w is positive.

There are several different definitions of heat. For instance, we can heat water to make tea, or enjoy the heat when we enter a warm room in the winter. In thermodynamics the meaning of heat is more precise: it is a process, a way energy can move. **Heat** is energy that moves from a hot object to a cold object. When heat leaves the system, it has a negative sign, and when it enters the system, it has a positive sign.

Heat and work are the ways that energy can move between objects. When you think about the molecules, the difference between work and heat is very simple. Work involves an orderly motion of molecules, like all the molecules in an object moving the same direction. Heat involves disorderly or random motions of molecules.

Outside Links

- Khan Academy: Introduction to Work and Energy (9 min)
- Khan Academy: Work and Energy (Part 2) (9 min)
- Khan Academy: Conservation of Energy (10 min)
- Khan Academy: Work from Expansion (13 min)

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CHAPTER OVERVIEW

Valence Bond Theory

Valence bond theory is one of two basic theories, along with molecular orbital theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory has orbitals that cover the whole molecule.

Topic hierarchy

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3-D Structures of Molecules

Skills to Develop

- List the common 3-D structures and their characteristics

Why do 3-D Structures Matter?

3D structures are important because they can have big effects on the properties of molecules. For instance, water has a dipole moment because it is bent, not linear. If it were linear, it would not be a great solvent for polar compounds, and all life would be completely different. In general, shapes of molecules will influence how they react, because they determine polarity (which can help pull molecules together to react) and fit (whether the reactive parts can get close to each other). Shapes of molecules can have other effects as well. Consider the following:

Formula	NaF	MgF_2	AlF_3	SiF_4	PF_5	SF_6
Melting Point (°C)	980	1400	1040	-77	-83	-55

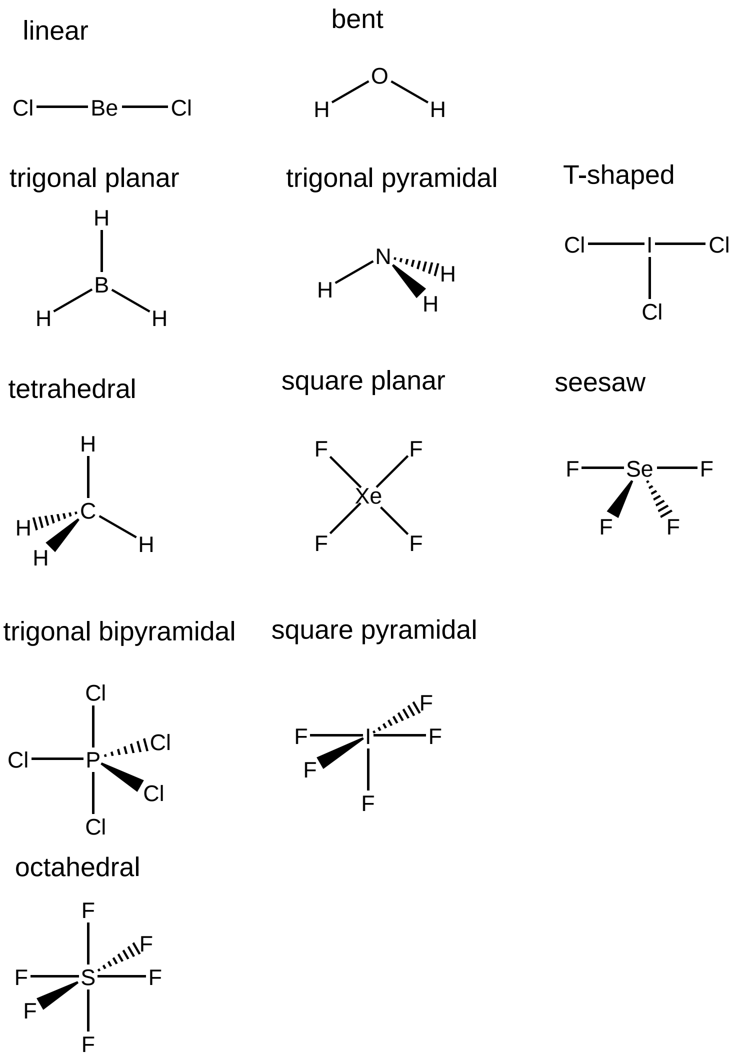
Notice that there is an abrupt change in the melt point between $AlF_3$and SiF_4. You might take this as the change from an ionic compound to a covalent compound, but the difference in electronegativity between Al and Si isn't that large, and both are much less electronegative than F. We can explain the change better using molecular structure than bond type. In the first 3, the structure is typical of ionic compounds. Instead of clearly-defined molecules, there is an alternating lattice of positive and negative ions. Each cation is surrounded by 6 fluoride ions, and each fluoride ion is surrounded by 6, 3, or 2 cations (depending on the formula). All the ion-ion attractions must be loosened to melt the solid, which requires high temperature. In SiF_4, however, each Si is surrounded by 4 "fluoride ions" (because radius decreases across the periodic table) which naturally makes a tetrahedron, and thus clearly separated molecules. When the molecules pack in the solid, the F atoms touch other F atoms, not Si atoms, and are not attracted much at all. This is only more true for PF_5 and SF_6, in which the F atoms surround the central atom even more completely. Thus, these 3 compounds are molecular gases.

How do we Measure 3-D Structures?

We can measure 3D structures with several different techniques, but X-ray crystallography is probably the most common. For small molecules, it can usually tell you the exact positions of all the atoms as long as you can grow a good crystal. This data includes the bond lengths and bond angles.

Describing 3-D Structures

You'll need to learn the names of the common geometries, which describe the shape of bonds around each atom. They are organized in the following diagram based on how many bonds the atom makes. If the molecule only has one central atom, the geometry of the molecule is the geometry of the central atom. If there are several atoms that have bonds to 2 or more atoms, we can describe the geometry at each.

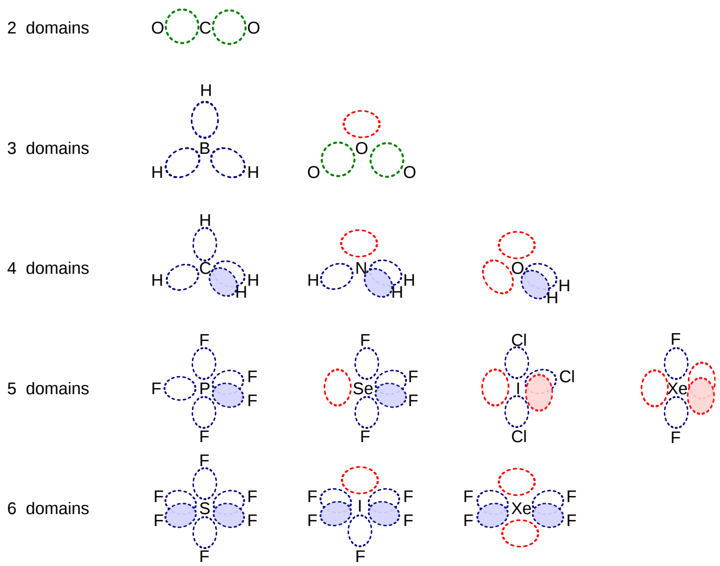


The names of different molecular shapes. Note that bonds shown with wedges are coming out of the page, and bonds shown dashed are going back behind the page.

Predicting Molecular Shapes (Bond Angles)

Lewis structures are a great way to predict the shapes of molecules. The basic idea is that while all electrons repel each other, electrons with the same spin repel each other even more. The 2 paired electrons with opposite spin that make up a bond can be in the same general area between the bonding nuclei (although they will still try to avoid each other within this area), but electrons with the same spin really have to give each other space. The result is that the bonding and non-bonding electron pairs each take up their own area and try to stay as far away from each other as they can. The area occupied by a lone pair or a bond is called a domain. (We only worry about the valence electrons. We can think of the core electrons having their own area closer to the nucleus, although it's actually a little more complicated than this.) For the same reason, the different parts of a molecule usually spread out also, so the different parts don't get too close and bump their electron pairs.

You can picture each pair of electrons as being a big soft balloon, as in the diagram. Bonding pairs are a little narrower because they are attracted to 2 nuclei and try to stay between them. Lone pairs are a little flatter and take up more space, because there's no other nucleus pulling them away in a specific direction. So we can expect bond angles are a little smaller than we might think, because lone pairs take up more space and push the bonds closer together. Multiple bonds also take up more space than single bonds, but still act like a single domain, because they are held by the same two atoms.



The electron domain model for predicting molecular shapes. Single bond domains are blue, multiple bond domains are green, and lone pair domains are red. Domains in front of other domains are shaded.

Bond Lengths

Bond lengths depend on the size of the atoms and the strength of the bonds. In general, bond length decreases going from single bond to double bond to triple bond.

Some Average Bond Lengths, in Å

Bond	r (Å)	Bond	r (Å)	Bond	r (Å)
C—C	1.54	C=C	1.34	C≡C	1.20
C—N	1.47	C=N	1.38	C≡N	1.16
N—N	1.45	N=N	1.25	N≡N	1.10
C—O	1.43	C=O	1.20	C≡O	1.13

Outside Links

- CrashCourse Chemistry: Orbitals (10 min)
- Khan Academy: VSEPR I (8 min)
- Khan Academy: VSEPR III (13 min)
- Khan Academy: VSEPR IV (15 min)
- Khan Academy: VSEPR V (11 min)
- Khan Academy: VSEPR VI (13 min)

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Dipole Moments

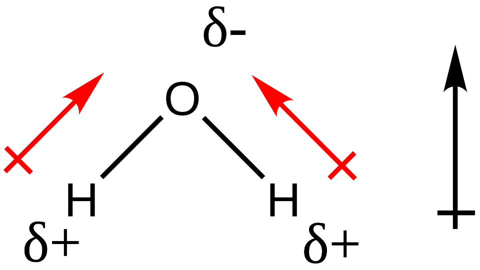
Skills to Develop

- Describe the significance of dipole moments

Dipole moments are a measure of how much how much charge separation exists in a bond or a molecule. We have talked about similar ideas before, because molecular dipole moments are important for solvation. We defined dipoles here when introducing magnetism, and discussed polarity also. To review, the electric dipole moment is defined as

$$\mu = q \times d \tag{1}$$

where q is the partial charge on each end and d is the distance between the charges. "Each end" could mean each end of a bond (each atom), or each end of a molecule, like water. The total dipole moment of a molecule is the vector sum of all the bond dipoles.



The bond dipole moments (red) and total dipole moment (black) in water, shown pointing from positive to negative.

Why do Dipole Moments Matter?

Dipole moments tell us, on average, where the electrons in a molecule are. They can also tell us the shape of molecules. For instance, if H_2O were linear, the 2 O-H bond dipoles would cancel each other out, and the whole molecule would be non-polar. Since we know water is polar, it has to have a bent shape.

Also, molecular dipole moments are very important for many properties, such as ability to dissolve solutes, melting and boiling points, and reactivity in general. Dipole moments (actually, change in dipole moments due to molecular vibration) are also involved in whether molecules absorb certain energies of light, which is important for the greenhouse effect. CO_2 and methane cause climate change because they can absorb IR light. Although these molecules are too symmetrical to have permanent dipole moments, vibrations can produce small temporary dipole moments that allow them to absorb light.

How do we Measure Dipole Moments?

We can measure molecular dipole moments by measuring the dielectric constant of a material (how much the material weakens the Coulomb forces when it is between the charges). Generally, materials with large dipoles have **high dielectric** constants. In Coulomb's law, the dielectric constant D reduces the force between charges.

$$F = \frac{kQq}{Dr^2} \tag{2}$$

Bigger D means less force. To measure bond dipole moments, we can measure the dielectric constants of diatomic molecules (in the gas phase, if the diatomic molecule doesn't exist as a solid or liquid).

Outside Link

- CrashCourse Chemistry: Polar and Non-Polar Molecules (11 min)

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Electronegativity

Skills to Develop

- Describe and explain the periodic trend for electronegativity
- Discuss the significance of electronegativity

Electronegativity is a measure of how much an atom attracts electrons. For instance, a more electronegative atom will be easily reduced, while a less electronegative atom will be easily oxidized. In covalent bonds, more electronegative atoms "pull harder" on the bonding electrons, so the shared electrons may spend more than half their time with the more electronegative atom, giving it a partial negative charge. (For example, O in water has a partial negative charge because it is more electronegative than H.) This will also influence the bond dipole moment.

How do we Define Electronegativity?

One way we can define electronegativity is by saying it is proportional to the sum of ionization energy and electron affinity. If it's hard to take electrons away, and easy to add electrons, the electronegativity is big.

$$EN = constant \times (IE + EA) \tag{1}$$

We choose the constant so that F has EN=4, and then use the same constant for all other elements.

However, electron affinities are not known exactly for most elements, so the first definition (the Mulliken definition, we'll talk more about Mulliken in the next section) is limited. Pauling proposed a different definition, which gives similar results but uses easier measurements.

Pauling's electronegativity scale is based on ionic resonance energies. Consider 2 diatomic molecules A_2 and B_2. We can measure the bond energy of each. We can also describe the bonding using resonance between a covalent structure, A—A and ionic structures [A$^+$][A$^-$]. If we make the molecule AB, what is its bond energy? In this case, because A isn't the same as B, one of the ionic resonance structures will be more important, and contribute to increased resonance stabilization. We can model the bond in AB using resonance between the covalent and ionic structures, A—B, [A$^+$][B$^-$], and [A$^-$][B$^+$]. We can guess that the pure covalent A—B bond strength is the average of the A—A and B—B covalent bonds, because this depends on factors like distance between the nuclei and repulsion between the electrons. The extra resonance energy from increased stability of one of the ionic structures should make the A—B bond energy bigger than the average of the A—A and B—B bonds, and this is observed. (Convince yourself using the data in the previous section.) The bigger the difference between the elements, the more stable the ionic structure becomes, and the greater the resonance energy is. The difference between the average of the A—A and B—B bonds and the experimental A—B bond energy is used as the basis of Pauling's electronegativity scale.

Predicting Relative Electronegativities

It pretty much follows the same pattern you would expect based on ionization energy and electron affinity. Thus, in general, electronegativity is big in the upper right of the periodic table and decreases down and to the left. It's good to know that H's electronegativity is between B and C. (Even though H is written on the far left of the periodic table, it is sort of in between an alkali metal and a halogen.)

Look at EN for yourself!

Go to Ptable's electron affinity page. See the general trend (bigger up and right) with some relatively high electronegativities among the heavy transition metals, like gold, as well.

An illustration of the general trend for electronegativity throughout the periodic table.

Using Electronegativity

We can use electronegativity as a convenient way to predict the polarization of covalent bonds (in other words, how ionic they are). At the extreme, we can use it to predict whether compounds are covalent or ionic, which suggests also that it correlates roughly with metallic or non-metallic character. We can also use it to predict good Lewis structures, which usually have the negative formal charges on the more electronegative atoms. (If you follow this rule consistently, you'll predict much more ionic bonding than you might expect, which is actually consistent with more sophisticated models.)

The Pauling definition of electronegativity leads us to the conclusion that "combination of elements" reactions should always or nearly always be exothermic if only single bonds are present in the products and reactants. For N_2 and O_2 the multiple bond energy is greater than 2 times or 3 times the single bond energy. For this reason, compounds between N and O and elements of similar electronegativity like Cl might have positive heats of formation, meaning that they can exothermically decompose to the elements. Many reactive compounds that decompose to form elemental gases, such as explosives and bleaches, are compounds of Cl, N, and O.

Outside Links

- CrashCourse Chemistry: Polar and Non-Polar Molecules (11 min)
- Khan Academy: electronegativity (12 min)

Contributors and Attributions

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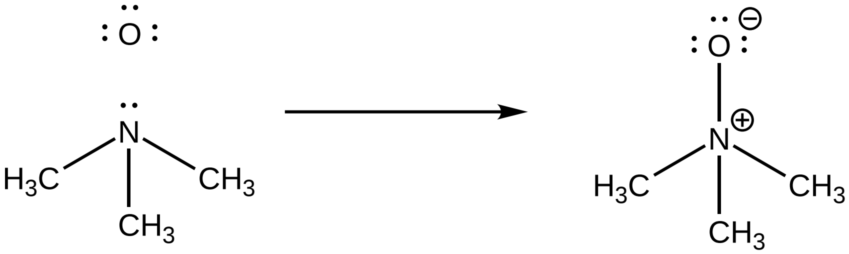
Formal Charges in Lewis Structures

Skills to Develop

- Determine and illustrate formal charges for Lewis structures

When you draw Lewis structures, sometimes the electrons are shared in a way which seems "unfair." For instance, in $(CH_3)_3NO$, to give N 8 electrons (and not more, since N can't have more than 8), you have to draw a single bond to oxygen. If you imagine a reaction between $(CH_3)_3N$ and an oxygen atom, both electrons that form the bond to O come from N (the former lone pair). (This is a rare example of a reaction that is both a Lewis acid-base reaction and a redox reaction.) However, once the bond is made, these electrons are shared. If you imagine that they are shared equally, then there is a single positive charge on N and negative charge on O. These are called **formal charges**.



The Lewis acid-base reaction to form trimethylamine oxide, a molecule with formal charges.

How are Formal Charges Different from Oxidation Numbers?

You might remember oxidation numbers from the discussion of redox chemistry earlier. Oxidation numbers are found by assuming that the bonding electrons are entirely owned by the atom that pulls hardest. Formal charges, in contrast, are calculated by assuming that the bonding electrons are shared evenly between the two atoms. The truth is usually somewhere in between. Both formal charges and oxidation numbers are used for "bookkeeping" or counting purposes. They don't tell you much about the real position of the electrons in the bond.

How Should You Find Formal Charges?

To find formal charges in a Lewis structure, for each atom, you should count how many electrons it "owns". Count all of its lone pair electrons, and half of its bonding electrons. The difference between the atom's number of valence electrons and the number it owns is the formal charge. For example, in NH_3, N has 1 lone pair (2 electrons) and 3 bonds (6 electrons total, so count 6/2 =3), so it owns 5 electrons, which is the same as the number of valence electrons. The formal charge is 0. For each H atom, it has 1 bond and thus 1 electron, so its formal charge is also 0. This is good, because all the formal charges of each atom must add up to the total charge on the molecule or ion. For the ammonium ion, NH_4^+, each H is still 0. Now N has 4 bonds and no lone pairs, so it owns 4 electrons. 5 - 4 = +1, so N has a +1 charge. This matches the +1 charge of the whole ion.

What Do You Need to Do with Formal Charges?

When you write Lewis structures, you should include formal charges next to each atom with a formal charge that isn't 0. (Usually, you circle the charge so it's clear.) This can also help you tell which Lewis structures are good. Usually negative formal charges should be on atoms that pull electrons strongly (like O or F, elements from the top right of the periodic table that have high ionization energies and high electron affinities). Positive formal charges should be on elements that pull electrons less. Big formal charges (more than 2) are usually bad. And it's better to have opposite formal charges right next to each other (so you get a formal "ionic bond"), and like formal charges farther from each other.

Outside Links

- CrashCourse Chemistry: Atomic Hook-ups (10 min)
- Khan Academy: Formal charges and dot structures (12 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Hybrid Orbitals

Skills to Develop

- Describe how to construct hybrid orbitals

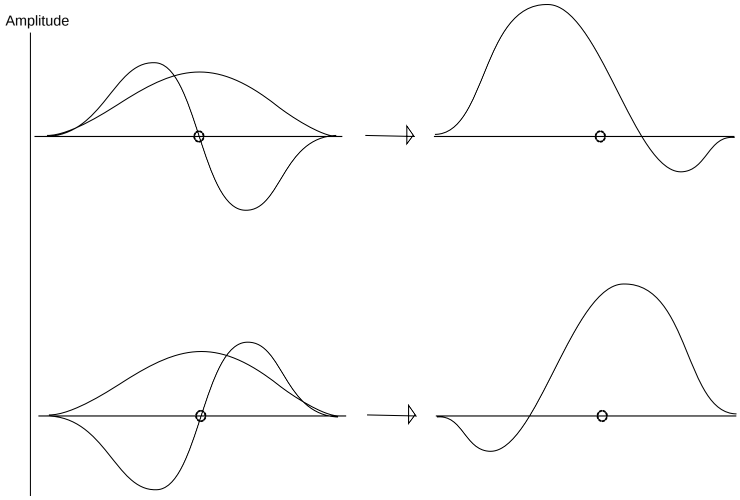
Hybrid orbitals are combinations of atomic orbitals that fit well with the 3D structures of molecules (that point in the same directions as the bonds or lone pairs). Because chemical bonding is based on Coulomb forces between electrons and nuclei, we expect that bonding electrons should spend a lot of their time between the nuclei. This is what makes a chemical bond. But what orbitals are they in when they do this? Because of the observed shapes of molecules, it seems like valence electron pairs each occupy their own area, called a domain. But the positions of these areas that we learned in the previous section don't match the positions of the atomic orbitals we studied before. We can fix this by making combinations of the atomic orbitals that have new shapes, called **hybrids**.

When are Hybrids Useful?

We mostly use hybrid orbitals to describe the bonding in organic chemistry, for compounds composed mainly of C and H. Hybrids aren't so good for molecules like SF_6.

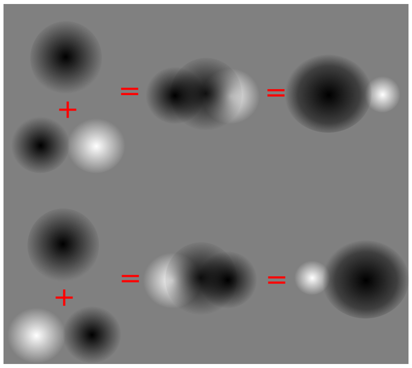
Building Hybrid Orbitals

We can build hybrid orbitals using wave interference. First, let's think about a molecule like BeF_2 (in the gas phase, where it is a molecule and not an ionic solid). This molecule is predicted to be linear, so how do we put the 4 bonding electrons into 2 orbitals pointed the right directions? We can imagine taking the Be 2s orbital and $2p_z$ orbital, and combining them in 2 ways, adding and subtracting. This gives us 2 new orbitals. (Any time you combine orbitals, you get as many out as you put in.) This is first shown using "1-D" waves, where the x-axis is radius and the y-axis is Ψ. It's important to think about the phases of the orbitals during this combination, and think about constructive and destructive interference.



The formation of sp hybrid orbitals, illustrated with approximate 1-D waves, showing Ψ vs radius. The small circle shows the position of the nucleus. We add the 2 waves on the left to get the total wave on the right.

Once you are comfortable with the wave mixing pattern in the diagram above, look at the 2-D version.

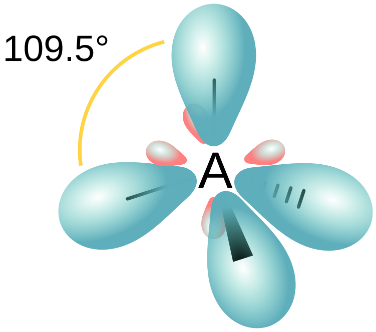


The formation of sp hybrid orbitals, illustrated with approximate 2-D drawings of atomic orbitals. Positive amplitude of Ψ is shown with black, negative amplitude of Ψ is shown with white, on a gray background. Where positive and negative amplitude waves overlap, the sum approaches zero (gray background).

You can see that by combining an s orbital and a p orbital on the same atom, we get 2 new orbitals, which point opposite directions. These orbitals are good for making 2 bonds in a linear shape, like in the molecule BeF_2. Each of the big black lobes with make a bond with an orbital or hybrid orbital on F. In the same way, we can mix 1s orbital and 2p orbitals to get sp^2 hybrids, or 1 s and 3 p orbitals to get sp^3 hybrids, shown below. We use sp^2 hybrids for trigonal planar molecules like BH_3 and sp^3 orbitals for tetrahedral shapes like in CH_4.

Important Hybrids

Although other hybrids are sometimes mentioned, the most important ones are sp, sp^2 and sp^3. (Hybrid orbitals using d orbitals are usually not a good or useful description of what's going on.) Just remember the general shape of each of these, and what geometry molecule they match.



Important hybrid orbitals, showing the number of hybrid orbitals and the angle between them. (Left to right or top to bottom, sp, sp^2, sp^3.) Positive amplitude of Ψ is blue and negative amplitude of Ψ is pink. Shapes are approximate. Modified from originals by Jfmelero via Wikimedia Commons.

Outside Links

- CrashCourse Chemistry: Orbitals (10 min)
- Khan Academy: Sp hybridization (11 min)

Contributors and Attributions

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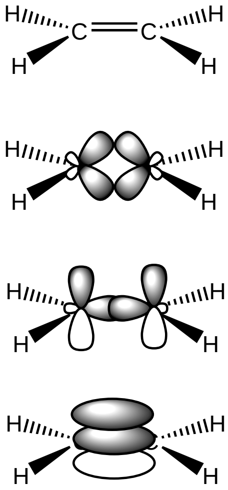
Multiple Bonds

Skills to Develop

- Define multiple bonds (name, characteristics)
- Describe and draw resonance structures
- Predict hybridization and numbers of σ and π bonds

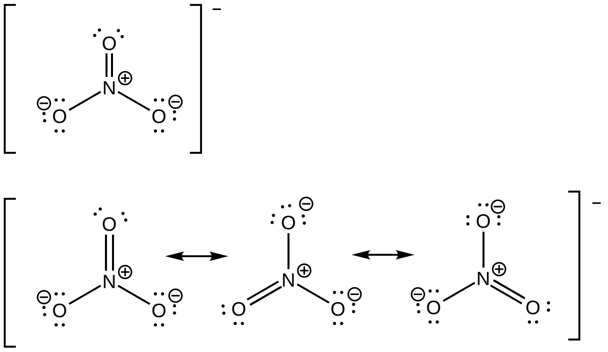
You already know that sometimes we have to use multiple bonds (double or triple bonds) to draw good Lewis structures. Lewis' idea of multiple bonds suggests that they should be shorter than single bonds (because the tetrahedra share an edge or a face, not just a point). This turns out to match the data from crystal structures. In the previous section, we used hybrid orbitals to show how we can make bonds using overlapping orbitals. This actually matches Lewis' image of the tetrahedra pretty well! So we could think about multiple bonds being made with hybrid orbitals just in the way that Lewis pictured, which are now called "bent bonds" because the electron density doesn't seem to be on the line between the nuclei. This isn't a bad way to think for some molecules. However, it becomes very confusing in cases of multiple bond resonance!



Ethylene (C_2H_4) shown (top to bottom) as a Lewis dot structure, using "bent bonds" and sp^3 hybridization, and using σ and π bonds with sp^2 hybridization (σ and π bonding orbitals shown separate, then combined).

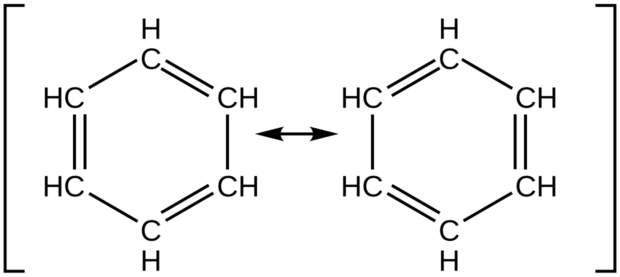
Multiple Bond Resonance

Let's think about Lewis structures for the nitrate ion, NO_3^-. We have to draw 1 double bond and 2 single bonds between N and O to give N exactly 8 electrons. This suggests that there should be 1 short bond and 2 long bonds in nitrate ion. However, there is no difference between the O atoms, so how would we choose which one gets the double bond? We could put it in any position, giving 3 different structures with the same energy. If you remember the idea of resonance energy you might expect that the availability of 3 different structures with the same energy allows resonance between the structures, so that each bond is actually 4/3 of a bond, and the molecule is much more stable because of the resonance energy.



Two Lewis structure descriptions of nitrate ion. Top: nitrate with 1 short double bond and 2 long single bonds. Bottom: nitrate shown using resonance structures, indicating that each bond is equivalent, with the double bond shared over all 3 oxygens.

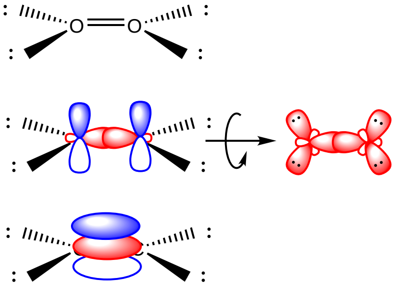
When we study the structure of nitrate, we can't find any difference between the oxygens. If we do X-ray crystallography on $CsNO_3$, say, we can check what all the bond lengths and bond angles are, and they appear equal. Other methods give the same result. Molecules or ions in which multiple bond resonance is important (just like bonds in which ionic resonance is important) are more stable than we would otherwise predict, and they appear to have "fractional" bonds. Benzene, an another important example of resonance, is shown in the figure. Other examples include the sulfate and phosphate ions. Try drawing resonance structures for these ions, using the "resonance arrow" ↔.



Resonance structures for benzene, C_6H_6

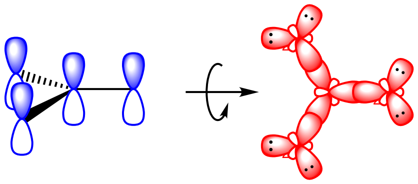
Orbitals for Multiple Bond Resonance

It's hard to imagine how multiple bond resonance can happen using the "bent bond" idea. However, we can use a different model of multiple bonds that makes it much clearer. Think about a molecule of oxygen. Each atom makes 2 bonds and has 2 lone pairs. We could think about doing this with sp^3 hybrids, but there's another way as well if we assume that the second bond is different from the first. Imagine using sp^2 hybrids on each atom. One p orbital is leftover, perpendicular to the 3 hybrids. We make a normal straight bond with one hybrid from each atom, which we will call a σ bond. We put the lone pairs in the other hybrids. The last bond pair goes in a bond made of the leftover p orbitals. This is called a π bond. This is illustrated in the figure.



Formation of σ and π bonds in O_2. The σ bond and lone pairs use sp^2 hybrids, shown in red. The π bond is made of the leftover p orbital, shown in blue.

Now imagine orbitals for nitrate ion. N makes 4 bonds and has no lone pairs. We want to make 3 normal bonds, and one more bond shared over all 3 oxygen atoms. Each oxygen atom has a normal bond to N, and 2 or 3 lone pairs. Let's use sp^2 hybrids on each atom. N makes 3 σ bonds using the sp^2 hybrids and has 1 p orbital leftover. Each O makes a normal σ bond with one hybrid and puts lone pairs in the other 2. All the hybrid orbitals on each atom are in the same plane, and the leftover p orbitals on each atom are sticking up and down from this plane. The 4 leftover p orbitals hold 3 electron pairs, and all these orbitals can mix together. We can't easily tell from this model which electrons are lone pair electrons and which are bonding electrons, but we can see that the bond is shared equally over all 3 O atoms.



Orbitals in nitrate ion. Left: the π system, using p orbitals, shown in blue. Right: the σ system, including σ bonds and lone pairs, using sp^2 hybrids, in red.

Ethylene, C_2H_4, is a planar molecule (all atoms are in the same plane). This makes sense using either the bent bond description or the σ and π bond description. In the latter case, if we twist the molecule around the double bond, the p orbitals won't line up with each other, so the double bond would break. Because double bonds can't rotate easily, the molecule can be different if there are different groups attached to each end of the double bond. These are called **isomers**.

Predicting Hybridization and Numbers of σ and π Bonds

Only 1 σ bond can be made between 2 atoms. If more bonds or partial bonds are present, they must be π bonds. So it's easy to count the number of σ and π bonds in a Lewis structure. Once you've done that, you can easily find what type of hybrids each atom makes (only for atoms with 8 total electrons; you shouldn't use hybrids for atoms that have more than 8). Each π bond needs a p orbital. The hybridization will be sp^x, where

$$x = 3 - (number\ of\ \pi\ bonds) \tag{1}$$

For example, an atom that makes 2 double bonds makes 2 π bonds, so it will be sp hybridized, just like an atom that makes 1 triple bond. An atom that makes 1 double bond is sp^2 hybridized.

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Overview of Pauling and Valence Bond Theory

Skills to Develop

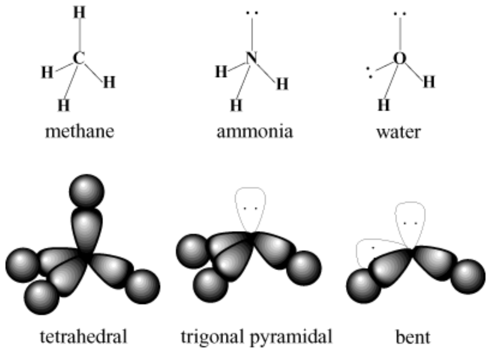
- List some of Pauling's contributions to chemistry
- Describe some of the limitations of valence bond theory

Pauling's father died when he was young and his mother had some medical and psychological problems, so he started working to support the family when he was 13. His mother wanted him to keep working to support her instead of going to college, but he didn't listen. He worked over the summer to earn tuition, but before his third year his mother took the money he had saved for tuition. Luckily, the college gave him a job to cover his tuition. He read Lewis and Langmuir's papers on chemical bonding, and applied to graduate school at Berkeley, where Lewis was. Unfortunately, Berkeley lost his application letter, so he went to Caltech. (After that, Lewis changed the graduate admission process so there would be no more mistakes!)

Linus Pauling

In graduate school, Pauling studied X-ray crystallography, which gave him a good understanding of the structures of molecules, such as bond lengths and bond angles, that was very useful for his later work. However, he had some trouble because he didn't want to give the usual credit to his teachers when he published papers. Pauling wanted to work with Lewis after he finished his doctorate, but the head of Caltech's chemistry department, Noyes, convinced him to go to Europe instead. The reason was that Noyes wanted Pauling to be a professor at Caltech, and was afraid Lewis would give him a job at Berkeley if they were allowed to meet. In Europe, Pauling studied the new quantum mechanics.

Pauling's big contribution to chemistry was valence bond theory, which combined his knowledge of quantum mechanical theory with his knowledge of basic chemical facts, like bond lengths and and bond strengths and shapes of molecules. Valence bond theory, like Lewis's bonding theory, provides a simple model that is useful for predicting and understanding the structures of molecules, especially for organic chemistry. Later Pauling applied his understanding of molecular shapes and bonding to a pretty good explanation of protein structures. Later still, he became famous for peace activism and promoting ascorbic acid (vitamin C) as a cure for colds and cancer.



Examples of using valence bond theory to predict the structures of molecules.

Valence bond theory is good for explaining the "ground state" properties of molecules, or the properties of molecules that only involve the lowest energy states. However, just like a hydrogen atom can be "excited" by light, moving the electron from n = 1 to n = 2, 3, 4... states, molecules have excited states that can be very important for reactions, colors, etc. Valence bond theory is not good for anything involving excited states, so we will talk about Molecular Orbital Theory as our next big topic.

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Resonance

Skills to Develop

- Describe the 3 types of resonance

We previously discussed a different kind of resonance, which is the tendency of some systems, such as the strings of instruments, to vibrate easily at particular frequencies. Now we will talk about **quantum mechanical resonance**. First, it may be easier to understand if you think about Fourier analysis. Perhaps you have heard before that any function can be written as a sum of sin and cos waves, like this:

$$f(x) = \Sigma_n a_n sin(nx) + \Sigma_m b_m cos(mx) \tag{1}$$

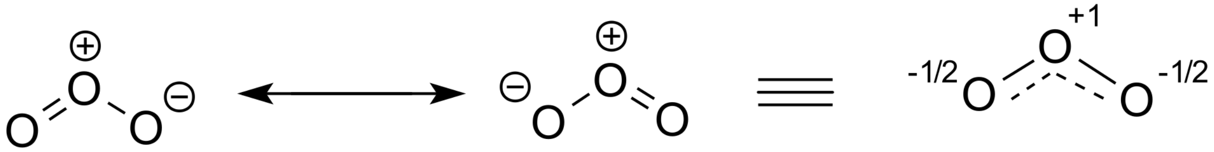
When we try to find wavefunctions for real chemical systems, it is too complicated to find an exact solution like the solutions for single hydrogen atoms. Instead, we usually describe the real wavefunction ψ(x,y,z,t) using series of functions (call them φ(x,y,z,t)) like a Fourier transform.

$$\Psi = \Sigma_n a_n \varphi_n(x,y,z,t) \tag{2}$$

Often the functions φ_n used to build the real wavefunction ψ are the hydrogen wavefunctions we talked about before, including s, p, d, and f orbitals in each shell. There is a principle that says that if you choose the coefficients (a_n) so that the energy of the total wavefunction is minimized, those are the best coefficients that get closest to the real wavefunction ψ. In other words, real life finds the lowest possible energy (highest stability), so the lowest energy we can find is the closest to the real thing. If we imagine a system that might be described by φ_1 or φ_2,

$$\Psi = a\varphi_1 + b\varphi_2 \tag{3}$$

we can calculate the ratio a:b that minimizes the energy of ψ. If a:b is very big, φ_1 is a good description of the system (at least compared to φ_2). If a:b is very small, φ_2 is a good description. If a:b is close to 1, then the real system is somewhere in between. The system is described as **resonating** between the two states. This doesn't mean that it alternates between them. It's like the difference between blue and yellow stripes (alternating between colors), and green (resonance, a mix of blue and yellow). The energy calculated for the combination will be lower than either single energy, and this difference is called the **resonance energy**.



An example, O_3, depicting how a resonating structure is not alternating between two similar structures, but is actually one structure at a lower energy state than either of the two similar structures.

Example

We can use different Lewis structures to represent the trial wavefunctions φ. For instance, imagine the formation of a bond between a H atom and a H^+ ion (H nucleus). We can consider 2 trial wavefunctions corresponding to the following structures:

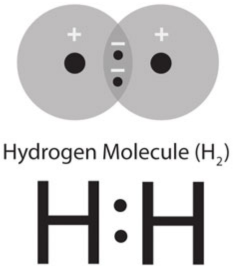
Structure 1: $H_A{}^+ \bullet H_B$

Structure 2: $H_A \bullet H_B{}^+$

If we calculate energy as a function of distance between the nuclei, for either structure 1 or structure 2 we don't predict a bond to form (instead, we expect the nucleus and atom to repel each other). If we allow resonance between structure 1 and structure 2, then we find that at a certain distance, 1.06 Å, the energy is a minimum. This means a bond can form. The resonance between the 2 structures means that the electron spends time near both nuclei. Since it has to move back and forth (very quickly, but maybe in a random motion, we don't know exactly), it must spend more of its time between the nuclei. When it is between them, we can expect that both nuclei are attracted to the electron, so it holds them together in a bond.

Ionic Resonance in H_2

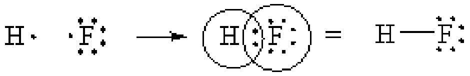
In the hydrogen molecule, we can use a similar model. We use the 2 structures $H_A(1) \bullet H_B(2) + H_A(2) \bullet H_B(1)$ (where H_A and H_B are the 2 nuclei, and 1 and 2 are the electrons) to represent the normal covalent bond, H—H. We get closer to the experimental data when we include the ionic structures $[H_A^+][:H_B^-] + [:H_A^-][H_B^+]$. At the normal bond length, the Coulomb attraction between the ions makes these structures stable enough to contribute about 2% to the full description of the molecule.



An ionic structure for H_2 would be one hydrogen atom having both electrons while the other atom has no electrons.

Ionic Resonance in Other Bonds

Ionic resonance structures are much more important in cases where the bond is between different elements. For instance, in HF, we expect the structure $[F^-][H^+]$ to be very important, perhaps as important as H—F, because F pulls much harder on electrons. We will keep discussing this in the next sections.



Outside Links

- Khan Academy: Resonance (12 min)
- Khan Academy: Resonance and dot structures (6 min)

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

Strengths of Covalent Bonds

Skills to Develop

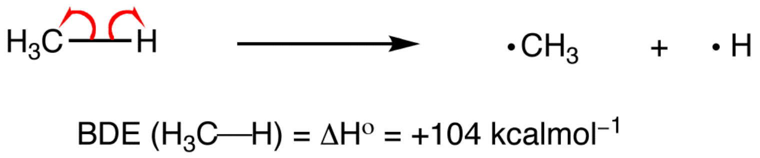
- Describe the significance of bond dissociation energy

Bond dissociation energy or bond energy is the energy required to break a bond. Usually we mean bond dissociation enthalpy, the enthalpy change for this reaction:

$$A—B \rightarrow A(g) + B(g) \tag{1}$$

For example, H—Cl → H• (g) + Cl• (g)

The • represents an unpaired electron, called a **radical**. When measuring the bond enthalpy, we break the bond so that half the bonding electrons go to each atom. Breaking a bond is always an endothermic process, so the bond energy is always positive. We use the symbol D(A—B) to represent the bond enthalpy of an A—B bond.



Another example of bond dissociation energy (BDE) where BDE(H_3C—H) = D(H_3C—H)

Bond energy is similar, but is the average energy required to break all the bonds in a molecule. For instance, C-H bond energy is the enthalpy of atomization of methane divided by 4. This is different from the energy required to break the first C-H bond in CH_4 because breaking the second bond might be easier or harder than breaking the first.

Some Approximate Average Bond Enthalpies (kcal/mol)

Bond	D (kcal/mol)	Bond	D (kcal/mol)
H-H	103	H-F	135
H-Cl	102	H-Br	87
H-I	70	H-C	98
H-O	110	H-N	92
C-C	83	C-F	116
C-Cl	78	C-Br	68
C-O	86	C-N	73
N-N	40	O-O	34
C=C	144	C≡C	200
C=O	191	C=N	147
O=O	118	N≡N	225
Cl-O	52	Cl-N	72
N-O	48	N=O	145

How do we Measure Bond Dissociation Energy?

As you might guess from the discussion above about bond energy vs. bond dissociation energy, it's actually quite complicated to measure these! There are a lot of complications to consider, and you can't always measure directly the heat of reaction that you want.

Why does Bond Dissociation Energy Matter?

Having a general knowledge of bond strengths lets us understand the structures of molecules and predict reactions. For instance, when we guess the arrangement of atoms to make a Lewis structure, we will probably do better if we avoid making weak bonds. N-N and O-O single bonds are pretty weak, so usually we try not to put them in Lewis structures, unless nothing else makes sense. The structure will be better if we can make a multiple bond or put some other atom in between.

We can also use bond strength knowledge to predict what direction reactions will go and how fast they will go. Recall that we can calculate the enthalpy of a reaction by comparing the atomization energies of the reactants and products. (This is the same idea as when we calculated enthalpies of reaction using standard enthalpies of formation.) If the product has stronger bonds than the reactants, the reaction is likely to be exothermic, and exothermic reactions often go forward. If the reactant has strong bonds, you might need to use a lot of energy to get the reaction started, even if it is exothermic. Combustion reactions are an example: C-C and C-H bonds are pretty strong, so we need a spark or a match to start the burning. Another example is "nitrogen fixation": we need N to make proteins and other important molecules in our bodies, but it is very hard to get N from N_2 because of the strong triple bond. This is why we have to use fertilizer in agriculture, and making nitrogen fertilizer uses roughly 1% of the world's energy. Another example is teflon or PTFE, which makes a very slippery and non-reactive coating that is used in non-stick pans, containers for reactive chemicals, etc. PTFE has only C-C and C-F bonds, both of which are very strong, so it doesn't easily react even at high temperature when you cook with it. In contrast, if a reactant has some very weak bonds, it might be very easy to start a reaction. For instance, hydrogen peroxide (HOOH) can be used as a bleach or disinfectant because the weak O-O single bond can easily break, helping it oxidize whatever is nearby. Hydrogen peroxide and hydrazine (N_2H_4) can both be used as rocket fuel because they react easily and exothermically (they have weak bonds, and they form products with stronger bonds).

Contributors and Attributions

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