CHEM 1402: GENERAL CHEMISTRY I



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Chem 1402:

General Chemistry I

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Licensing

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CHAPTER OVERVIEW

1.A: Basic Concepts of Chemistry

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1A.1: Chemistry and its Methods
1A.2: Sustainability and Green Chemistry
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1A.1: Chemistry and its Methods

Learning Objectives

- Differentiate between a theory, law, and hypothesis
- Distinguish between qualitative and quantitative information
- Introduce the four paradigms of science
- Critique the integrity of scientific practices

What is Chemistry

Let's start with Webster's Dictionary:

> *a science that deals with the composition, structure, and properties of substances and with the transformations that they undergo (*"Chemistry." *Merriam-Webster.com*. Merriam-Webster, n.d. Web. 16 May 2016.)

And Oxford's Dictionary:

> *The branch of science that deals with the identification of the substances of which matter is composed; the investigation of their properties and the ways in which they interact, combine, and change; and the use of these processes to form new substances. (*chemistry. Oxford Dictionaries. Oxford University Press, n.d. Web. 17 May 2016.)

So Chemistry is a Science.

What distinguishes a Science from other types of academic disciplines?

This is a good question, and I would say the **Scientific Method**.



Figure 1*A*.1. 1: Democritus (left, public domain) Greek amphitheatre, Siracusa (right, cc-by-2.0 Andrea Schaffer)

Democritus of pre-socratic Greece came up with an ancient atomistic theory that viewed mater as being based on two fundamental entities, atoms and the void. This ancient theory was similar in principle to the modern atomistic theory and is in fact where the name "atom" came from. The fundamental difference is that it was not based on the Scientific Method and the rigorous verification based on empirical (measurable) data. In essence, many philosophies could produce understanding and frameworks for understanding that gained societal acceptance through oration and debate, but just because they were widely accepted, did not mean they were correct. The scientific method places faith on measurable entities and the repeatability of the causal relations between them.

So what is the scientific method?

The Scientific method is a philosophy based on the process of making observations, forming hypothesis that could explain the observations, and testing the hypothesis through experimentation.

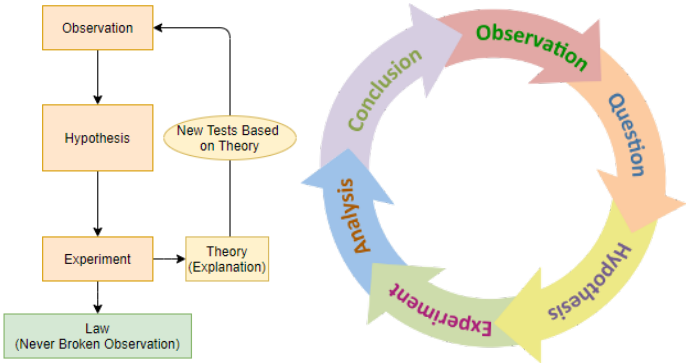


Figure 1A.1.1: Two flowcharts of the Scientific Method (left by Belford, right cc.10 by Thebiologyprimer). The flow chart on the left shows the role of theory and how scientific laws can evolve while the one on the right emphasizes the continual evolving nature of scientific knowledge.

A **theory** is a mental construct or model that explains what is happening, and is often the basis for further hypothesis to test with additional experiments. A theory can be right for the wrong reason. A scientific **law** is a refined result of this process that can never be broken and allows us to predict what will happen, but does not explain why. For example, the first law of thermodynamics says that the energy of the universe is constant, so if heat is transferred from one object to another in an isolated system, the heat lost by one will be the same quantity as the heat gained by the other. If a process occurs where energy is not conserved, the first law of thermodynamics would be invalidated, and it would no longer be a law.

The Scientific Method is sort of the philosophy of which scientific knowledge is based upon

What is the difference between Qualitative and Quantitative Information?

Qualitative information is based on observables, like ice floats on water, or chlorophyll is green, or the patterns of the lines on your fingerprint. Qualitative data can be used to identify what something is.

Quantitative information relates to a measurable quantity. Quantitative data may be a number like the number of seats in a room, but it also may have a number and a unit, like the number of grams a dime weighs. Quantitative data tells you how much of an observable you have.

How Old is Chemistry as an Applied Science?

As an applied science, chemistry dates to antiquity.



Figure 1A.1.3: Possibly 52,000 year old painting of bovine from Lubang Jeriji Saléh cave (right, public domain)

Primitive man learned how to make and keep fire that allowed him to cook and keep warm. Primitive man learned how to extract pigments from minerals that were used to paint their caves, and some of these have lasted multiple thousands of years. There were often religious overtures to their use of applied chemistry as shamans used these technologies to interact with their spirit world.

How old is Chemistry as a Modern Science?

Let's compare the text on two documents, one from 1776 and one from 1808.

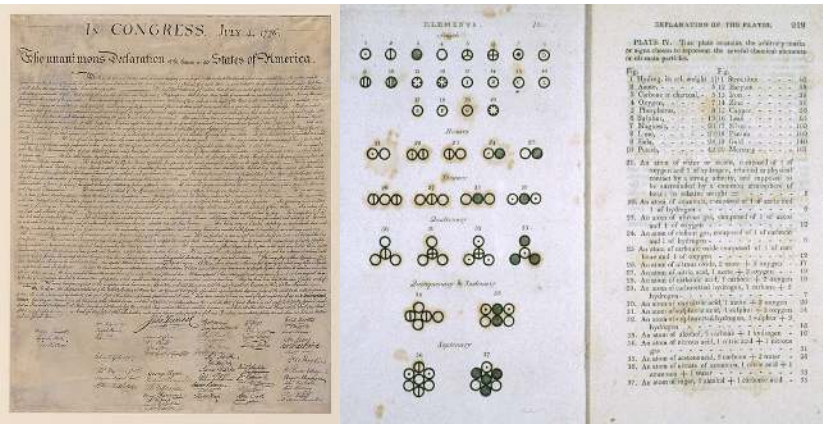


Figure 1.A.1.4: On the left is an image of the U.S. Declaration of Independence written in 1776, and on the right an image from John Dalton's 1808 book, "A New System of Chemical Philosophy" (both images in Public Domain).

The image on the left is the U.S. Declaration of Independence, while the image on the right comes from John Dalton's 1808 book, "A New System of Chemical Philosophy", which was written 32 years after the United States Declaration of Independence. Note that even in these recent times, hydrogen was not "H" but a circle with a dot in the middle of it, and Oxygen was a circle, and water was the two next to each other. The symbols of the periodic table that are so common today did not even exist when George Washington was president!

Is Chemistry as a Science Evolving?

Yes! Microsoft Research has a free online book, the Fourth Paradigm: Data Intensive Scientific Discovery, that postulates 4 paradigms of science. The scientific method evolved out of the first two paradigms but is still valid as a philosophical underpinning of the application of the latter paradigms. These paradigms can be summarized as follows.

- **Empirical Science-1st Paradigm:** This is the oldest and is experimental based employing qualitative and quantitative analysis of the physical world around us.
- **Theoretical Science-2nd Paradigm:** This involves algebraic and often calculus based mathematical relationships that are based on theories that evolved out of the scientific method. This class will mostly involve the first two paradigms, and it is important that students learn how to write algebraic relationships in contrast to arithmetic equations.
- **Computational Science-3rd Paradigm:** This is only several decades old and involves the use of computers to solve complex equations that humans alone could not compute. These may be **"ab-initio"** (latin for from the beginning) in that they are entirely based on theoretical relationships, or **"semi-empirical",** where they also employ empirical data. An example would be the application of QSAR (Quantitative Structure Acitivy Relationships) techniques in drug discovery to identify molecules that would be good candidates for the analysis in experimental (empirical) work.
- **e-Science-4th Paradigm:** This is the newest form of science and is only now emerging. As data becomes open and more accessible relationships between datasets can lead to new discoveries. An example would be the use of the International Monitoring System data of the global Comprehensive Nuclear-Test-Band Treaty (CBCT) that was set up to detect nuclear explosions for tracking ice-bergs and understanding climate change (note link is to the Way Back Machine of the Internet Archive) Unfortunately, unlike biology, much of the data in chemistry is not public but proprietary and subscription based, which limits its accessibility. But public compound databases are emerging that will bring chemistry into the fourth paradigm, like the National Institute of Health (NIC) National Center for Biotechnology Information (NCBI) PubChem , which as of May 2016 has information on over 89,000,000 unique chemical compounds.

Although this course will focus on the fundamentals of the first two paradigms of science, you will be entering a world and a workforce where the latter two paradigms will be gaining importance in the pursuit of science. It needs to be realized that all of these complement each other, and fit within the framework of the scientific method.

Chemistry is an exciting topic and full of discovery. It is the study of matter, of stuff. What is stuff? Why do some things react? Why are some things stable? With sciences like chemistry man has great control over the world around him. He can create new materials to wear, new energy sources, new drugs, and yes, he can also create toxins that pollute the earth, chemical weapons that kill and maim, and often chemistry gets a bad reputation because of the detrimental effects of its use. In the next section, before we get deep into this class we will briefly look at green chemistry.

Test Yourself

Contributors and Attributions

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1A.2: Sustainability and Green Chemistry

Learning Objectives

- consider a chemical's life cycle and how it impacts the environment
- evaluate the impact of a chemicals life in a market driven society that runs on a cost-benefit analysis
- Outline the 12 principles of Green Chemistry and give examples of each
- Assess how the principles of Green Chemistry relate to sustainability

The science of chemistry has had a profound impact on the quality of life in today's world. Look around you, and you see products that were created by man through the application of chemistry. The computer monitor, or cell phone/tablet screen you are looking at, or the piece of paper you printed this to, are all man-made through the industrial application of chemistry.



What is a Cost-Benefit Analysis?

We live in a market driven economy, and when a corporation decides if it is going to market a new product it invariably undergoes some sort of Cost-Benefit Analysis. That is, how much will it cost to produce and market the product, and what will be the benefit of that endeavor. For the corporation to survive it must bring in enough revenue to cover the cost of production and marketing and make a profit. Typically, this analysis covers the discovery, manufacture and sale of the chemicals that make the product, and does not account for what happens to the chemicals after it has been purchased by the consumer.

What is a chemical's life cycle?

Some use the term "from cradle to grave" to describe the life cycle of a chemical, which tracks the chemical from it's synthesis to its disposal. One of the problems with Cost-Benefit Analysis when dealing with chemicals is an accurate accounting of the chemicals life-cycle. In the eyes of a corporate revenue stream, once the chemical is sold it is no longer their responsibility and the cost-benefit analysis does not take in costs associated with the disposal of the chemical

What is the Law of Unintended Consequences?



This is not a scientific law, in fact the term was coined in the social sciences, but of relevance to the use of chemicals is that once a chemical has been disposed of, there can be unintended consequences. For example, DDT showing up in Penguins in Antarctica, or pharmaceuticals disposed down the sewer serve as endocrine disrupters that result in male fish acquiring female organs.

Do Cost-Benefit Analysis take into account the unintended consequences of a chemical's true life cycle?

So What is Green Chemistry?

Green chemistry is a philosophical approach to reduce the unintended consequences associated with the use of chemicals. Paul Anastas and John Warner developed 12 principles of green chemistry that can help lead to a sustainable science. This principles do not deal with cleaning up pollution, but avoiding it. You may download a bookmark on the 12 Principles of green chemistry from the EPA by clicking here.

In the following video Paul Anastas discusses the 12 Principles of green chemistry to a class at Yale



https://youtu.be/1cxXAeQn-M4

12 Principles of Green Chemistry

1. Prevent Waste
2. Design Safer Chemicals and Products
3. Design Less Hazardous Chemical Syntheses
4. Use Safer Solvents/Reaction Conditions
5. Increase Energy Efficiency
6. Use Renewable Feedstocks
7. Design Chemicals and Products that Degrade After Use
8. Minimize the Potential for Accidents
9. Analyze in Real Time to Prevent Polution
10. Use Catalysts, Not Stoichiometric Reagents
11. Maximize Atom Economy
12. Avoid Chemical Derivatives

In this video, the "Future of Sustainable Chemistry", John Warner discusses his role as a chemist and how the chemistry curriculum omits teaching students how to do science in an environmentally benign and safe way.



https://youtu.be/LnAbLi08OVM

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1A.3: Classifying Matter

Learning Objectives

- Identify the four states of matter
- Compare and contrast the characteristics of solids, liquids, and gases
- Classify substances as pure substances or mixtures
- Classify substances as homogenous and heterogeneous, or as elements or compounds

What are the Three Attributes of Matter?

1. Matter has Mass
2. Matter has Volume
3. Matter has Energy

What are the states of matter?

Matter has mass, occupies space and exists in different states that are determined by its energy. There are four fundamental states of matter that are observable in everyday life: solid, liquid, gas, and plasma. However, other states are known to exist in extreme situations (e.g., low or high energy states, as discussed in this Wikipedia article). In this class we will study the first three, but you need to be aware of all four of the fundamental states.

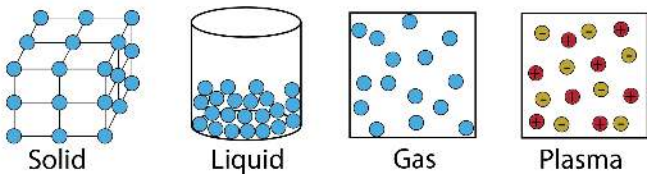


Figure 1A.3.1: Four phases of matter

Solid

Incompressible Rigid State: Constituent atoms or molecules do not move with respect to each other, but can vibrate in their positions.

- Resists change in density (density is typically constant).
- Maintains shape (structural rigidity).

Liquid

Incompressible Fluid State

- Resists change in density (denisty is typically constant).
- Not rigid, will flow and take shape of container.

Gas

Compressible Fluid State

- Variable density.
- Fills entire container.

Is a gas a Fluid?

Yes, a gas is a fluid.

Plasma

- High energy state where atoms can lose an electron and both species coexist.
- Most of the matter of the universe is in the plasma state.

The following video gives a good description of the plasma state.



Video 1.A.3.1: YouTube Video (3:32 min): "Plasma, The Most Common Phase of Matter in the Universe", uploaded by SciShow (https://youtu.be/AVEGJZxglIg).

What Factors Determine the Stable Phase of Matter?

This is a rather complicated question that we will deal with as the course proceeds. Essentially, it is an interplay between the cohesive forces of attraction which hold the particles together and the kinetic energy of motion. We will learn later that the Kinetic Molecular Theory states that the Kinetic Energy is proportional to the temperature, so as you increase the temperature you increase the kinetic energy of matter. At "low temperatures" the cohesive forces dominate and the solid phase is stable. As you add heat the temperature rises until you reach the melting point. Continued heat causes melting, and once you have melted the entire substance the liquid phase increases its temperature until it reaches it's boiling point. At the boiling point continued head causes vaporization and the temperature does not increase until it is all a gas. So the stable phase depends on the temperature, and the forces holding a substance together.

Mixtures and Pure Substances

Homogenous Matter - of same form. From Greek *homos* (same) and *genos* (race/kind)

Heterogeneous Matter - of different form. From Greek *heteros* (other) and *genos* (race/kind)

What is the Difference Between a Pure Substance and a Mixture?

A pure something has one entity, it could be an element or a compound. Pure water, pure table salt (sodium chloride) or pure gold are all pure substances. But a combination of water and salt or water and gold are mixtures. Note, if all the salt dissolves it is a homogeneous mixture, but a mixture of water and gold (which is insoluble) is heterogeneous.

Which is a Solution, a Homogenous or Heterogeneous mixture?

A solution is a homogenous mixture. Examples are milk, wine and ocean water. But a mixture of sand and water is not a solution because the sand does not dissolve, and so is a heterogenous mixture.

Can a pure Substance be Heterogenous?

Yes, for example ice water is heterogeneous with the two phases having distinctly different properties like density, although based on the definition many chemists use, it is not a mixture, as both ice and water are the same substance, the molecule H_2O. But even if it is treated as a pure substance, it is still heterogenous. Note this two phase system is an unstable mixture at any temperature above or below the melting point, as above the melting point the ice will melt, and below the melting point the water will freeze. At the melting point the system is stable if it is energetically isolated from the environment, which if you think about it, is a very hard thing to do. If heat enters enters the system at the melting point, some of the ice will melt, and if it leaves, some of the liquid water will freeze.

Note, the above discussion leads one to ask, is a mixture of ice and water a mixture? I personally say yes, as they have distinct properties, but I know of other chemists who say no, as they are both the same substance, water. This shows that even simple schema for classifying matter as a pure substance or mixture can lead to confusion, and you might want to ask your instructor what they think, and what definition of a pure substance they use.

Schema for Classification of Matter

The following flow chart breaks matter down into pure substances and mixtures, and note that it does not take into the account that a pure substance can exist as a mixture of phases with distinct properties.

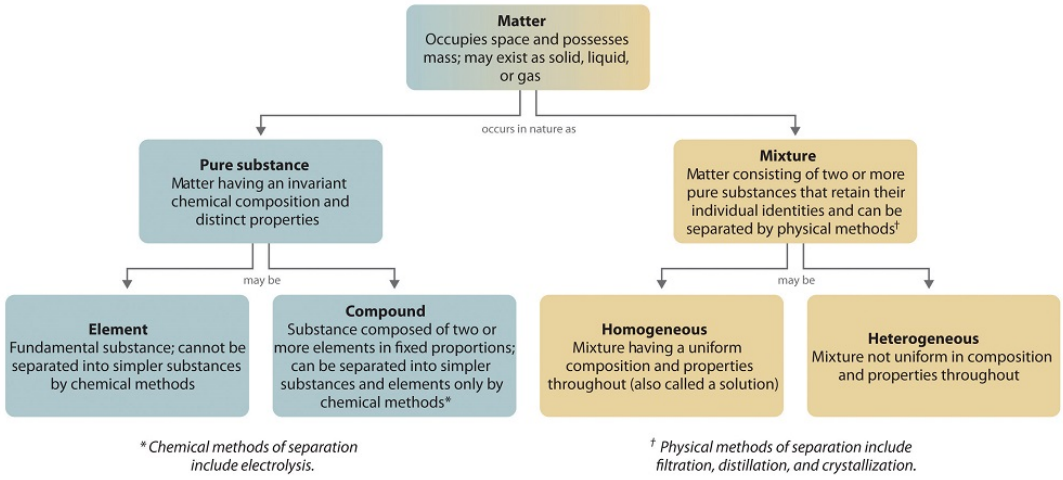


Figure 1.A.3.2: Schema for classifying matter.

How can you Separate a Heterogeneous Mixture?

- Filtration- allows an insoluble solid to be separated from a liquid phase.

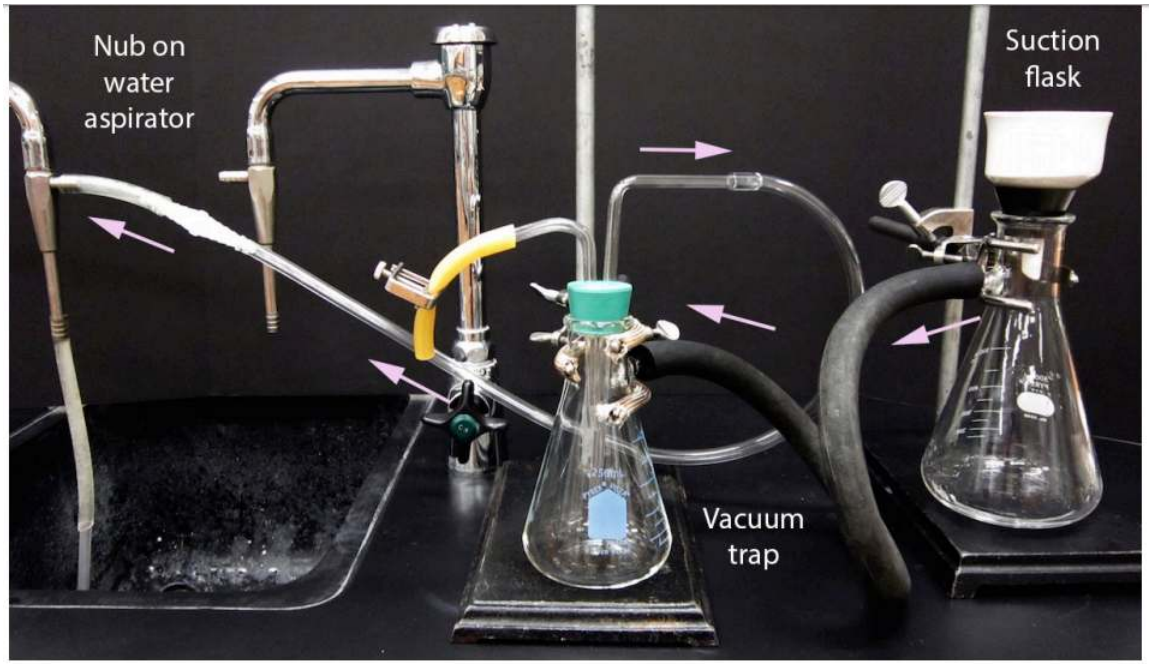


Figure 1.A.3.3: Illustration of suction filtration lab set up for organic chemistry, that allows separation of precipitate (solid) from a solvent/solution that it was formed in.

- Magnets - if one substance is magnetic and the other not, a magnet will separate them.



Video 1.A.3.2: YouTube showing how to separate iron from cereal (https://youtu.be/oQ5lzpAw2qE) uploaded by BBC Science Focus Magazine

How can you Separate a Homogenous Mixture?

Distillation

if one substance has a different boiling point than the other, it will boil off first. A still is as a device that can be used to separate two substances. Note, if both substances are volatile, like in an alcohol still where ethanol and water can be separated, the ethanol which has the lower boiling point boils off first, but the distallate (material collected in the receiving flask) will have a small amount of water, because water does have a vapor pressure below its boiling point (that is why water in an open container evaporates). If you want really pure ethanol you would double or triple distil.

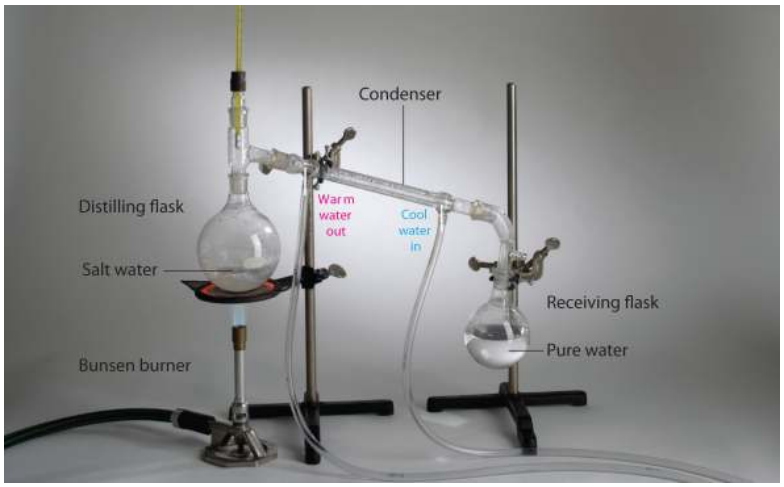


Figure:1.A.3.4 Distillation apparatus for separating two soluble liquids. The liquid with the lower boiling point boils first and is collected in the receiving flask.

Chromatography

Chromatography was developed around the turn of the last century and originally used to identify the pigments in plants. In the following video the girl breaks up plant leaves and soaks them in alcohol (a heterogeneous mixture). She then strains them and has a green homogenous mixture (solution). She then places a strip of filter paper into the solution with most of the strip above the surface. As the solvent moves up the filter paper it drags the pigments with them, but due to their different chemical properties they travel at different rates and breakup into bands.



Video 1A.3.3 YouTube showing how to separate plant pigments using chromatography. Uploaded by Alex Dainis (https://youtu.be/qH-AJDqsSII)

In the next sections we will look at elements and compounds.

Test Yourself

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1A.4: Elements

Learning Objectives

- Identify the name of the element given the symbol and vice versa
- Differentiate between atoms, elements, and molecules

Introduction

Atoms of the various elements can be considered to be the fundamental chemical entity of matter. There are 118 confirmed elements that can be arranged in the periodic table in a manner that allows chemists to predict behavior. Below is an official periodic table of the International Union of Pure and Applied Chemists (IUPAC). More information on the elements will be provided in Chapter 2.

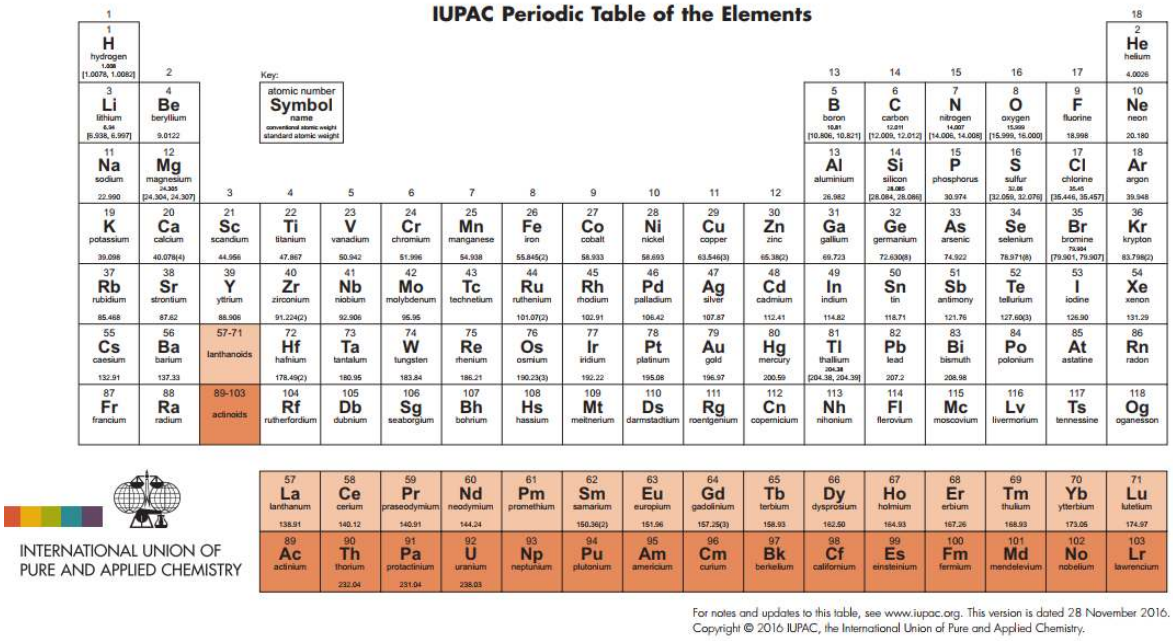


Figure 1A.4.1: If you click on the above image a printable PDF from IUPAC will open in a new window.

Who is Responsible for Naming the Elements?

IUPAC, the International Union of Pure and Applied Chemistry. Here is a December 30, 2015 Press Release on the **"Discovery and Assignment of Elements with Atomic Numbers 113, 115, 117 and 118."** To give you a feel for the challenges involved, here is a quote from the above Press Release:

> *"A particular difficulty in establishing these new elements is that they decay into hitherto unknown isotopes of slightly lighter elements that also need to be unequivocally identified" commented JWP chair Professor Paul J. Karol "but in the future we hope to improve methods that can directly measure the atomic number, Z."*

Note, isotopes and atomic numbers will be covered in Chapter 2.

What is the Difference Between an Atom and an Element?

An atom is a fundamental entity of matter that has a nucleus with one or more protons and zero or more neutrons, and containing electrons in orbitals around the nucleus. **An element is** a type of atom that is defined by the number of protons in the nucleus (see Chapter 2). The Atomic number is the number of protons in an atom. So all atoms with 6 protons are atoms of the element carbon.

Can Different Atoms of the Same Element have Different Masses?

Sure, if they have different numbers of neutrons. We call those Isotopes. Hydrogen has three isotopes, with all nuclei containing 1 proton and 0, (protium), 1 (deuterium) or 2 (tritium) neutrons.

Why Aren't Protons, Neutrons and Electrons Considered the Fundamental Chemical Entity?

Of course they are more fundamental than atoms, but they do not predict the behavior of the substance. An atom has a distinct number of protons and neutrons in its nucleus, and a specific number of electrons in identified orbitals. The chemical behavior is mostly determined by how many electrons the atom has, and what types of orbitals they are in (see Chapter 7). In chemical reactions the atoms of each element are conserved, and this will used to balance chemical equations in Chapter 3.

Are Atoms of a Type of Element Always Conserved in a Reaction?

No, some radiative process change the number of protons, and so an atom of one element becomes an atom of another element. These will be called Nuclear reactions, and will be covered in Chapter 23. Several of these radioactive decay processes will also be discussed in Chapter 2. **But in chemical reactions, we will say yes, the atoms of each type of element are conserved.**

UALR students in my class are required to know name and symbol of all the elements in this periodic table that are not shaded.

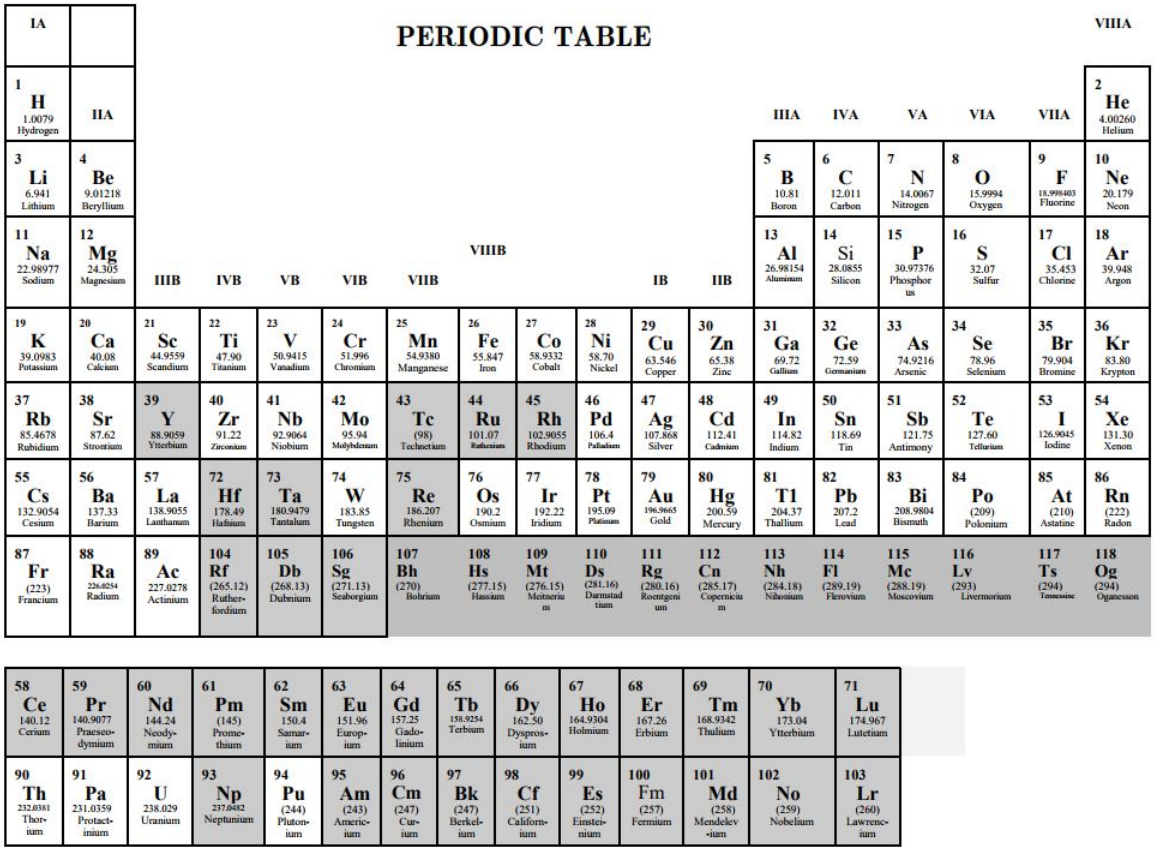


Figure 1A.4.2: UALR students are required to know unshaded elements of this table, so start memorizing them early!

Click here for a Downloadable PDF

Test Yourself

The following Flash Cards require you to type the names of 22 elements that are commonly misspelled.

For additional practice on names you can do the following quiz.

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1A.5: Compounds

Learning Objectives

- Define compound
- Recognize the different types of compounds (ionic and molecular compounds)

Introduction

Compounds occur when two or more atoms combine into a pure substance. These can be broken down into their constituent atoms. In chemical reactions the atoms of the reactants interact to form new substances. The reacting species are called reactants, and those produced are products. Reactant and products can be either elements or compounds. Compounds are held together by chemical bonds.

The following video shows the formation of the compound, Sodium Chloride from the elements sodium and chloride from Nile Red's YouTube Channel.



Video 1A.5.1: Youtube showing the formation of an ionic compound from its constituent elements. Uploaded by NileRed (https://youtu.be/ji_25I_q4LQ)

What is the difference between CO and Co?

The first letter of an element must be capitalized and the second is never capitalized. CO is the compound carbon monoxide, Co is the element cobalt.

Are all compounds molecules?

No, molecules are discrete entities where two or more nuclei from different atoms have shared electrons, and this type of bond is called a covalent bond. Water (H_2O) is a molecule with an oxygen connected to two different hydrogens through covalent bonds. Another common type of compound is an ionic compound like sodium chloride or table salt, NaCl. Ionic compounds form crystal lattices with each positive ion (cation) surrounded by multiple negative ions (anions).

Are all compounds either molecules or ionic compounds?

No, although in this class we will focus on ionic and molecular compounds. But there are many types of forces holding chemical species together. Metals have metalic bonds which can be of either the same element, or between different elements (brass metal is alloy, a mixture of zinc and copper held together through metallic bonds.) Ice is water held together through intermolecular forces. Diamond is a covalent network of carbon atoms (each carbon atom within the interior of the diamond is connected to 4 other carbon atoms) and there is no real formula, as the number of carbon atoms depends on the size of the diamond.

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1A.6: Physical Properties

Learning Objectives

- Define physical properties and give examples of common physical properties used to identify a substance
- Differentiate between extensive and intensive properties and give examples of each
- Define density as a way to relate the mass of a substance to its volume
- Apply the concept of density to environmental hazard such as plastics in bodies of water

Introduction

Physical properties are are typically observable properties that describe the physical state of matter. In contrast, **chemical properties** describe the chemical arrangement, composition and reactivity of matter.

Physical Properties can be Extensive or Intensive.

What are Extensive Properties?

Extensive Physical Properties are those that depend on the "extent" of the system. Volume and mass are extensive, and two gallons of water at 20 deg C have twice the volume and mass as one gallon of water at 20 deg C.

What are Intensive Properties?

Intensive physical properties do not depend on the "extent" of the system. Density and temperature are intensive, when you combine 2 gallons of water the temperature stays at 20 deg (it does not become 40) and the density stays at approximately 1g/ml. Intensive properties are often constants and can be used to identify a substance.

Table 1A.6.1: Common Physical Properties

Texture	Color	Temperature
Shape	Luster	Malleability
Ductility	Density	Viscosity
Solubility	Mass	Volume

Description of Some Physical Properties

Luster

The **luster** of an element is defined as the way it reacts to light in a glowing sort of reflective manner. Luster is a quality of a metal. Almost all of the metals, transition metals, and metalloids are lustrous. The non-metals and gases are not lustrous. Metallic luster can be attributed to the fact that metals have lots of loosely bound electrons that can interact with light particles (photons) of many different energies.

Malleability

Malleability is also a quality of metals. Metals are said to be malleable. This means that the metals can deform under an amount of stress. For example, if you can hit a metal with a mallet and it deforms, it is malleable. Also, a paperclip can be shaped with bare hands. In contrast a toothpick is not malleable and would snap if you applied a stress to it. This is also related to the metallic bond and its loose electrons, that allow for bonds to form in many different directions. Non-metals tend to have bonds defined by specific geometric orientations, and thus they break if the atoms are moved out of those orientations.



2:05 min YouTube uploaded by Uniclass Content showing difference between malleable and brittle materials



0:39 YouTube animation uploaded by Julian Yu

Ductility: Ability to be drawn into a thin wire

In materials science the ability to be drawn into a thin wire is called **ductility**. For example, raw copper can wrapped into a cord. Once again, this property is characteristic of mainly metals, nonmetals do not possess this quality.



0:39 YouTube animation uploaded by Julian Yu

Density

The **density** of an object is its mass divided by its volume. A substance will have a higher density if it has more mass in a fixed amount of volume. For example, take a ball of metal, roughly the size of a baseball, compressed from raw metal. Compare this to a baseball made of paper. The baseball made of metal has a much greater weight to it in the same amount of volume. Therefore the baseball made out of metal has a much higher density. The density of an object will also determine whether it will sink or float in a particular liquid. Water for example has a density of $1 g/cm^3$. Any substance with a density lower than that will float, while any substance with a density above that will sink.



Image courtesy of Wikimedia commons

Note that much of the ice is below the water, but because ice is less dense then water if floats and does not sink. The mass of the water displaced is equal to the mass of the iceberg, and since the iceberg is less dense and has a larger volume, some if it floats above the surface and therefor it does not sink to the bottom. In the winter the ice on a lake acts as an insulator and protects the deep water from freezing, if water was more dense than ice and lakes froze from the bottom up, they could solidify in the winter and not support aquatic life as we know it.

Table 1.A.6. 1: Density of Several Substances at 20°C.

Substance	Density g/cm^{-3}
Helium gas	0.000 16
Dry air	0.001 185
Gasoline	0.66-0.69 (varies)
Kerosene	0.82
Benzene	0.880
Water	1.000
Carbon tetrachloride	1.595
Magnesium	1.74
Salt	2.16
Aluminum	2.70
Iron	7.87
Copper	8.96
Silver	10.5

Substance	Density g/cm^{-3}
Lead	11.34
Uranium	19.05
Gold	19.32

Therefore, a column in a table or the axis of a graph is conveniently labeled in the following form:

As of 2015 there was an estimated 5.25 trillion pieces of plastics debris in the ocean, which represents a grave threat to the health of the ocean and earth's ecosystems. Of that, 269,000 tons floats while there are huge amounts (4 billion plastic microfibers/sq kilometer) that sink.



Video 1.A.6.2: Video show plastics problem in waterways. The fact that some plastics sink and some float can easily be understood by looking at a table of densities. Note, although a PETE 1 water bottle may initially float (because it is full of air), it will eventual degrade (physical change) to very small particles (micro-particles) and sink.

Table 1.A.6.2: Density of common plastics

Plastic Symbol	name	Density/g/cm^3	Uses
5 PP	Polypropylene	0.90 - 0.92	yogurt cups, plasticware
4 LDPE	Low Density Polyethylene	0.91 - 0.93	squeezable bottles
2 HDPE	High Density Polyethylene	0.94 - 0.96	milk bottles, bags
6 PS	Polystyrene	1.03 - 1.06	egg cartons, packing peanuts
1 PETE	Polyethylene Terephthalate	1.35 - 1.38	water bottles
3 PVC	Polyvinyl Chloride	1.32 - 1.42	juice bottles, cling wrap
7 O	Often Polycarbonate or Acrylonitrile butadiene styrene (ABS)	1.3 1.06	bottles auto body parts

In fact, we can sort plastic particles by placing them into different solvents of different densities, as shown in this Youtube. Note, these solvents must not mix with each other (so one phase must be like an oil, and the next like water, as oil and water do not mix), and the particles will aggregate in the solvent whose densities are closest to them (they sink in lighter density solvents and float in heavier density solvents).



2:19 Min YouTube uploaded by Chemical Thinking Laboratory on Separation of Plastics by Density

Viscosity

Viscosity is defined as the resistance to flow. The substance on the left has a lower viscosity and quickly flows to the walls of the table, while the substance on the right flows slower. Water has a lower viscosity than honey or magma. Viscosity is influenced by temperature.



Figure 1A.6.2: Viscosity demonstration. The fluid on the left has a lower viscosity than the fluid on the right. Image used with permission (CC SA-BY 4.0; Synapticrelay).

Q and A

Physical Properties describe the physical state of matter. Examples include the state of matter, odor, color, volume, denisty, melting point, boiling point, temperature, electrical conductivity,...

What is the Difference Between Extensive and Intensive Properties ?

Extensive properties depend on the amount of matter (extent of the system), while Intensive do not depend on the amount of system. Mass and Volume are extensive, while temperature and density are intensive. If you add one gallon of gasoline at 25^0C to a car's gas tank that contains a gallon of gasoline at 25^0C, you double the mass, volume and distance you could drive (energy of the gas), but the temperature does not double, and the density is the same.

Can intensive properties be used to identify what a substance is?

Not always, but often they can. For example, if a substance is incompressible (solid and liquid) the density is considered constant at a given temperature and pressure, and can be used to identify a substance (gold has a density of 19.3g/ml, and if a gold ring does not have that density, it is not pure gold (note the inverse is not necessarily true, just because the density is 19.3g/ml does not mean it must be gold, but that it could be gold). But a Gas is compressible, and fills the container, so density alone can not indicate what the gas is.

Can extensive properties be used to identify what a substance is?

Not directly, as they change as the system changes..

Do you measure intensive of extensive properties?

You usually measure extensive properties. To measure the density of something you measure it's mass and volume, and then take the ration (d=m/v).

Doesn't a thermometer measure temperature, an intensive property?

No, you actually measure something else that changes as the temperature changes. For example, if you know how the density of mercury (or alcohol) changes as a function of temperature, you can construct a thermometer where you measure the height of the column. What you are really measuring is the change in volume as the tube has a constant cross area V=Area time height, and you mark the height in units of temperature. So in reality, you are measuring the change in volume, an extensive property

How about an electric thermometer like a thermocouple, doesn't that measure the change in voltage across a junction as a function of the temperature change, and isn't voltage an intensive property? Yes, voltage is an intensive property, but the device that measures the voltage, like the voltmeter, is not really measuring voltage, but current across a fixed resistor. It uses Ohm's Law where the voltage = current times resistance (V=IR), and the current is an extensive property. This can be done with where a needle is deflected by the magnetic field produced by the current as it goes through a coil, and since the resistance the device can be calibrated in units of voltage. But it is really the current that is changing.

Test Yourself

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1A.7: Physical and Chemical Changes

Learning Objectives

- Differentiate between physical and chemical changes at the particulate level
- Classify changes as physical or chemical

Change is happening all around us all of the time. Just as chemists have classified elements and compounds, they have also classified types of changes. Changes are either classified as physical or chemical changes.

Physical & Chemical Change

Chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different types of changes that they study - physical changes and chemical changes.

Physical Change

Physical changes are changes in which no bonds are broken or formed. This means that the same types of compounds or elements that were there at the beginning of the change are there at the end of the change.Physical changes involve moving molecules around, but not changing them. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa)
- Separation of a mixture
- Physical deformation (cutting, denting, stretching)
- Making solutions (special kinds of mixtures)



Figure 1A.7.1: Ice Melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. Image used with permission (Public Domain; Moussa)

For the most part, physical changes tend to be reversible - in other words, they can occur in both directions. You can turn liquid water into solid water through cooling; you can also turn solid water into liquid water through heating. However, as we will later learn, some chemical changes can also be reversed.

Chemical Change

Chemical changes occur when bonds are broken and/or formed between molecules or atoms. This means that one substance with a certain set of properties (such as melting point, color, taste, etc) is turned into a different substance with different properties. Chemical changes are frequently harder to reverse than physical changes.



Figure 1A.7.1: Burning of wax to generate water and carbon dioxide is a chemical reaction. Image used with permission (CC-SA-BY-3.0; Andrikkos)

One good example of a chemical change is burning paper. In contrast to the act of ripping paper (physcial change), the act of burning paper actually results in the formation of new chemicals (carbon dioxide and water, to be exact).

Evidence of Chemical Change

We can't actually see molecules breaking and forming bonds, although that's what defines chemical change. We have to make other observations to indicate that a chemical change has happened. What kind of macroscopic observations can indicate a chemical change?

Observations that help to indicate chemical change include:

- Temperature changes when no energy is added or removed (it can increase or decrease)
- Light is given off
- Unexpected color changes (a substance with a different color is made, rather than just mixing the original colors together)
- Bubbles are formed (but the substance is not boiling - you made a substance that is a gas at the temperature of the beginning materials, instead of a liquid)
- Different smell or taste (do not taste your chemistry experiments, though!)
- A solid forms if two clear liquids are mixed (look for *floaties* - technically called a precipitate)

Example 1.7.1

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

a. Boiling water
b. A nail rusting
c. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
d. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

Solution

a. Physical: boiling and melting are physical changes. When water boils no bonds are broken or formed. The change could be written: $\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$
b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $\mathrm{Fe} + \mathrm{O_2} \rightarrow \mathrm{Fe_2O_3}$
c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.
d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

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1A.8: Energy: Some Basic Principles

Learning Objectives

- Define energy and differentiate between kinetic and potential energy
- Define chemical and thermal energy
- Differentiate between heat and work

What is Energy?

Energy is one of the most fundamental and universal concepts of physical science, but one that is remarkably difficult to define in a way that is meaningful to most people. This perhaps reflects the fact that energy is not a “thing” that exists by itself, but is rather an attribute of matter (and also of electromagnetic radiation) that can manifest itself in different ways. It can be observed and measured only indirectly through its effects on matter that acquires, loses, or possesses it.

The concept that we call energy was very slow to develop; it took more than a hundred years just to get people to agree on the definitions of many of the terms we use to describe energy and the interconversion between its various forms. But even now, most people have some difficulty in explaining what it is; somehow, the definition we all learned in elementary science ("the capacity to do work") seems less than adequate to convey its meaning.

Although the term "energy" was not used in science prior to 1802, it had long been suggested that certain properties related to the motions of objects exhibit an endurance which is incorporated into the modern concept of "conservation of energy". In the 17th Century, the great mathematician Gottfried Leibnitz (1646-1716) suggested the distinction between *vis viva* ("live force") and *vis mortua* ("dead force"), which later became known as kinetic energy (1829) and potential energy (1853).

Kinetic energy and potential energy

Whatever energy may be, there are basically two kinds.

Kinetic energy is associated with the **motion** of an object, and its direct consequences are part of everyone's daily experience; the faster the ball you catch in your hand, and the heavier it is, the more you feel it. Quantitatively, a body with a mass m and moving at a velocity v possesses the kinetic energy $mv^2/2$.

Example 1A.8.1

A rifle shoots a 4.25 g bullet at a velocity of 965 m s^{-1}. What is its kinetic energy?

Solution

The only additional information you need here is that

$$1\ J = 1\ kg\ m^2\ s^{-2}:$$

$$KE = ½ \times (.00425\ kg)\ (965\ m\ s^{-1})^2 = 1980\ J$$

Potential energy is energy a body has by virtue of its *location*. But there is more: the body must be subject to a "restoring force" of some kind that tends to move it to a location of lower potential energy. Think of an arrow that is subjected to the force from a stretched bowstring; the more tightly the arrow is pulled back against the string, the more potential energy it has.

More generally, the restoring force comes from what we call a *force field*— a gravitational, electrostatic, or magnetic field. We observe the consequences of *gravitational* potential energy all the time, such as when we walk, but seldom give it any thought.

If an object of mass m is raised off the floor to a height h, its potential energy increases by mgh, where g is a proportionality constant known as the *acceleration of gravity*; its value at the earth's surface is 9.8 m s^{-2}.

Example 1A.8.2

Find the change in potential energy of a 2.6 kg textbook that falls from the 66-cm height of a table top onto the floor.

Solution

$$PE = m\,g\,h = (2.6\ kg)(9.8\ m\ s^{-2})(0.66\ m) = 16.8\ kg\ m^2\ s^{-2} = 16.8\ J$$

Similarly, the potential energy of a particle having an electric charge *q*depends on its location in an electrostatic field.

"Chemical energy"

Electrostatic potential energy plays a major role in chemistry; the potential energies of electrons in the force field created by atomic nuclei lie at the heart of the chemical behavior of atoms and molecules. "Chemical energy" usually refers to the energy that is stored in the chemical bonds of molecules. These bonds form when electrons are able to respond to the force fields created by two or more atomic nuclei, so they can be regarded as manifestations of electrostatic potential energy. In an **exothermic** chemical reaction, the electrons and nuclei within the reactants undergo rearrangement into products possessing lower energies, and the difference is released to the environment in the form of heat.

Interconversion of potential and kinetic energy

Transitions between potential and kinetic energy are such an intimate part of our daily lives that we hardly give them a thought. It happens in walking as the body moves up and down. Our bodies utilize the chemical energy in glucose to keep us warm and to move our muscles. In fact, life itself depends on the conversion of chemical energy to other forms.



Figure: Conservation of energy applied to a bicyclist and a hill.

Energy is conserved: it can neither be created nor destroyed. So when you go uphill, your kinetic energy is transformed into potential energy, which gets changed back into kinetic energy as you coast down the other side. And where did the kinetic energy you expended in peddling uphill come from? By conversion of some of the chemical potential energy in your breakfast cereal.

Thermal energy

Kinetic energy is associated with motion, but in two different ways. For a macroscopic object such as a book or a ball, or a parcel of flowing water, it is simply given by $\frac{1}{2}mv^2$. However, when an object is dropped onto the floor, or when an exothermic chemical reaction heats surrounding matter, the kinetic energy gets dispersed into the molecular units in the environment. This "microscopic" form of kinetic energy, unlike that of a speeding bullet, is completely random in the kinds of motions it exhibits and in its direction. We refer to this as "thermalized" kinetic energy, or more commonly simply as *thermal energy*. We observe the effects of this as a rise in the temperature of the surroundings, or a phase change (like melting). The temperature of a body is direct measure of the quantity of thermal energy is contains.

Energy units

Energy is measured in terms of its ability to perform work or to transfer heat. Mechanical work is done when a force f displaces an object by a distance *d*:

$$w = f \times d \tag{1A.8.1}$$

The basic unit of energy is the *joule*. One joule is the amount of work done when a force of 1 newton acts over a distance of 1 m; thus 1 J = 1 N-m. The newton is the amount of force required to accelerate a 1-kg mass by 1 m/sec^2, so the basic dimensions of the joule are kg m^2 s^{-2}. The other two units in wide use. the *calorie* and the *BTU* (British thermal unit) are defined in terms of the heating effect on water. Because of the many forms that energy can take, there are a correspondingly large number of units in which it can be expressed, a few of which are summarized below.

Heat and Work

Heat and work are both measured in energy units, so they must both represent energy. How do they differ from each other, and from just plain “energy” itself? In our daily language, we often say that "this object contains a lot of heat", but this is gibberish in thermodynamics terms, although it is ok to say that the object is "hot", indicating that its temperature is high. The term "heat" has a special meaning in thermodynamics: it is a *process* in which a body (the contents of a tea kettle, for example) acquires or loses energy as a direct consequence of its having a *different temperature* than its surroundings. Hence, thermal energy can only flow

from a higher temperature to a lower temperature. It is this flow that constitutes "heat". Use of the term "flow" of heat recalls the incorrect 18th-century notion that heat is an actual substance called “caloric” that could flow like a liquid.

Test Yourself

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CHAPTER OVERVIEW

1.B: Review of the Tools of Quantitative Chemistry

1B.1: Units of Measurement
1B.2: Making Measurements: Experimental Error, Accuracy, Precision, Standard Deviation and Significant Figures
1B.3: Mathematics in Chemistry
1B.4: Problem Solving by Dimensional Analysis
1B.5: Graphs and Graphing
1B.6: Algebra Review

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1B.1: Units of Measurement

Learning Objectives

- Recognize different ways to quantity matter (measured, exact, ande defined numbers)
- Recognize English Units and Metric Units and SI units
- Understand the evolution of the definitions of units over time and their uses in society
- Convert between different units

Quantification of Matter

Scientists use three basic types of numbers when quantifying matter; counted numbers, measured numbers and defined numbers.

- **Counted Numbers:** A counted number is an exact number in the sense that you have an entity, and you count the number of entities. So an exact number has two parts, the entity, and the number of entities. If you have 16 rocks in your hand, you have sixteen rocks, not more, not less. If you break one of the rocks into two, you now have 17 rocks in your hand, not more, not less. These are exact numbers. Counted numbers are exact and there is no uncertainty about their value.
- **Measured Numbers:** Now the mass of the rocks is a measured number and requires a third aspect to describe, which is the unit, defined by the scale used to measure it. So a measured number has 3 parts; magnitude, unit and entity. Sixteen one pound rocks weighs less than one 500 pound rock, although the number 16 is more than the number one, and this is because different units are being used to describe the mass. If you break each of the sixteen one pound rocks in half, you have 32 rocks, but they still weigh the same. Measured numbers have uncertainty that is indicated by their number of significant digits (section 1B.2.2).
- **Defined Numbers:** A defined number has a value inherent in its definition, and like a counted number is an exact number, but it may, or may not have uncertainty. Defined numbers are often used in measurements, for example, twelve inches is defined to be one foot and there is no uncertainty in that equivalence.

$$12\text{inches} \equiv 1\text{foot}$$

- But not all defined numbers are integers, like the number π, which is defined to be ratio of the circumference to the diameter of a circle.

$$\pi \equiv \frac{circumference}{diameter}$$

π is an exact number in the sense that it is exactly the ratio of the circumference to the diameter of a circle, but it is an irrational number and like a measured number, when we write down the value of π we give it a precision (3.14, 3.142, 3.1416, 3.14159,...), which defines how precisely we express the number.

Understanding defined numbers is of importance, and as we shall learn, as of May 20, 2019, the basic units of the metric system became based on defined numbers (2019 SI unit definitions).

Metrology

Metrology is the science of measurement. There are two fundamental tenets to metrology, traceability and uncertainty. Traceability is the ability to relate a measurement to a standard through calibrations, where each calibration has an element of uncertainty, which relates to how precisely the measurement (calibration) was made (see Section 1B.2). Inherent in a standard are the definition upon which it is based, and the "method" used to put this definition into practice, which is often known by the French term "mise en pratique". In modern metrology the "mise en pratique" is a set of instructions that allows implementation of the standard into the practice of measurement, and results in the traceability and uncertainty of a measurement to the standard. The earliest standards were related to physical objects, and from these, tools like a ruler could be created that allowed the measurement of other objects in the unit of the standard. Early units included body parts, like the foot, which varied from person to person, and so a standard foot was required. A multitude of units could describe the same measurement (see Figure 1B1.1 for different ways to measure length).

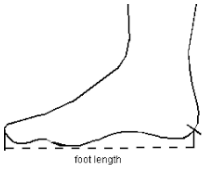


Figure 1B.1. 1: On the left are some of the units to describe length, some of which were based on human body parts (foot) or actions (pace).

Today science uses the metric system. In fact most countries in the world use the metric system as the normal units of measurement.



Figure 1B.1. 2: Areas of the world using the metric system.

The customary units of measurement in the US are the foot, inch and pound, even though most of the rest of the world uses the metric system, as does the scientific community. What may be surprising for most students is that a year after the civil war in 1866 the U.S. congress passed the **metric act,** which made the metric system legal for purpose of commerce.

Metric Units

Early Definitions

The Metric unit system evolved out of the French Revolutionary War, and was originally based on a unit of length, the meter. The earliest definition was the meridional definition, defining the meter as one ten-millionth of the distance from the north pole to the equator along the meridian going through Paris. This was done by surveying the distance from a belfry in Dunkirk France to Montjuic castle in Barcelona Spain, which was assumed to be one tenth the length of the Paris meridian. While the meridional metre survey was being conducted a series of prototype platinum bars were developed, and in 1799 the one that was closest to the meridional meter was chosen to be the standard meter (Wikipedia: History of the Metre). It should be noted that the original metric system was based entirely on this length, where the unit of mass was the gram, which was defined as the mass of a cube of water at 4^oC that was one hundredth of a meter on each side (1 cm^3). As this unit was very small compared to items that would be used in commerce, a prototype artifact of pure platinum was created that weighed 1000g, which became the first standard kilogram. This lasted until 1875 and the Treaty of the Meter.

Table 1B.1. 1: Early Metric Units.

Property	Unit	Symbol
length	meter	m
mass	gram	g
volume	liter	L

Note, one of the advantages of the metric system is the decimalization of the magnitude of units. This allowed easy conversion from small to large scale measurements. To go from centimeters to kilometers you simply multiple by 10,000, which is much easier to do than to convert the similar English units of inches to miles (see section 1B.3.5 Unit Conversions).

Treaty of the Meter

On May 20, 1875 the US was one of 17 nations to sign the "Treaty of the Meter" (the Metric Convention), which established the "Bureau International des Poids et Mesures" (**BIPM**), that was tasked to develop an international unified system of weights and measures. Through the BIPM's ongoing "*Conférence Générale des Poids et Mesures*" (**CGPM)**, the standards continue to be revised and redefined to the present time. In addition to defining the standards the BIPM is also responsible for producing the "*mise en pratique,"* which are published online. As a result of the metric convention 31 prototype meter standards of platinum/iridium

were built, and "National Prototype standard 27" was the U.S. reference standard for length until 1983. The mass standard was now an iridium/platinum alloy kept in a vault in Sèvres France, under conditions specified by the Treaty of the Meter.



Figure 1B.1. 4: prototype meter No. 27 (*Credit: NIST) and* International Prototype Kilogram (Credit BIPM)

Over time the metric unit system for measurement evolved into the SI or International System of Units.

International System of Units

In 1921 during the 6th meeting of the CGPM the scope and responsibilities of the BIPM was extended into other fields of physics (like temperature and time). In 1960 during during the 11th meeting of the CGPM, the International System of Units was established, and the system now officially became known as the **SI system** for its French spelling, *Système international d'unités*. The SI units are commonly called the metric units, they are the units used in scientific publications and as we shall see, are continually being revised and redefined through meetings of the CGPM.



Figure 1B.1. 5: Logo of *Bureau international des poids et mesures* (BIPM).

There are seven SI base units that underpin all SI measurements. Through proper combinations they can describe other measured phenomena, like volume and energy, whose units of liter and joule are classified as derived SI units (section 1B.3.3.2).

SI Base Units

The seven SI base units are listed in Table 1B.1. 2. These can be combined to form derived units that describe any measurable physical quantity. Thus by defining these seven SI base units, any physical measurement can be reproduced. In this class we will use the first five units extensively; the meter, kilogram, second, kelvin and mole (and general chemistry 2 will also use the ampere).

Table 1B.1. 2: Seven SI Base Units. General chemistry I (Chem 1402) students need to know the units in red.

length	**meter**	**m**
mass	**kilogram**	**kg**
time	**second**	**s**
temperature (absolute)	**kelvin**	**K**
amount of substance	**mole**	**mol**
electric current	ampere	A
luminous intensity	candela	cd

Note a kilogram is 1,000 g (SI prefixes section 1B.3.3.3), which is roughly the volume of one liter of water (with the liter being a derived unit for volume). The kilogram is the only SI base unit with an SI prefix.

A few special points about some of the SI base units are worth noting

- The base unit of **mass** is unique in that an SI Prefixe is built into it (k for 1,000); i.e., the base SI unit is not the *gram*, *but the **Kilogram***. This historically occurred because a gram is a real small quantity, and did not represent the magnitude of mass used in normal daily activities or commerce.
- Although the kilogram has an SI prefix in the base unit, you do not use Si prefixes on the kg, but on the gram (10^9 g is a gigagram, not a megakilogram).
- The base unit of **time** is the second, and time is not expressed as a decimalized metric number. Numerous attempts to make it so have never garnered any success; we are still stuck with the 24:60:60 system that we inherited from ancient times. The ancient Egyptians of around 1500 BC invented the 12-hour day, and the 60:60 part is a remnant of the base-60 system that the Sumerians used for their astronomical calculations around 100 BCE.
- Of special interest to Chemistry is the *mole*, the base unit for expressing the **quantity of matter**. It is now defined as exactly 6.02214076 x 10^{23} entities of anything.

1960-2019 Definitions

The following SI base unit definitions are adapted from NIST Special Publication 330 as obtained from the website, NIST Reference on Constants, Units and Uncertainty.

Table $1B.1.3$: Pre 2019 SI base unit definitions as adopted from NIST Special Publication 330.

meter	The distance of length traveled by light in a vacuum over the time interval of 1/299,792,458 of a second. (Note the speed of light in a vacuum is 299,792,458m/sec
kilogram	The mass the international iridium/platinum prototype kept in Paris France.
second	The duration of 9,192,631,770 periods of radiation corresponding to transitions on the cesium 133 atom (atomic clock)
kelvin	1/273.16 of the thermodynamic temperature of the triple point of water
mole	the number of atoms in 12 grams of carbon-12 (the symbol is mol)
ampere	constant current maintained by two straight parallel conductors of infinite length in a vacuum that are 1 meter apart and produce between them a force of 2x10^{-7}N/m
candela	the luminous intensity of a source of monochromatic radiation in a direction with a frequency of 540x10^{12} hertz in that direction with a flux of 1/683 watt per steradian.

The definitions in Table $1B.1.3$ are based on both artifacts and constants/phenomena. For example, the meter was originally based on an artifact in France, but in 1983 was changed to being defined by the speed of light (c) in a vacuum. In 1967 the second became defined by the cesium-133 atomic clock. In 1971 the mole was defined by the number of atoms in 12 grams of carbon-12, which required a sample of carbon-12. In 1954 the kelvin was defined by the triple point of water (a concept covered in general chemistry 2, section 12.7.3), which requires a sample of water (that has variable isotopic composition, a topic that will be on the first exam, section 2.3). But throughout this time, the definition of the kilogram never changed, it was still based on the standard kilogram in France.

There are some problems with the above definitions, the most obvious of which is the artifact-based definition of the kilogram. At the time of the creation of the original standard there were also "witness" standards made of identical mass, many of which became national prototypes. Over the years they would on occasion have their masses verified, and were shown to be changing (fig. 1B.1.6). The problem is, if a witness standard is getting "heavier", no one really know if it is really heavier, or if the prototype was getting lighter.

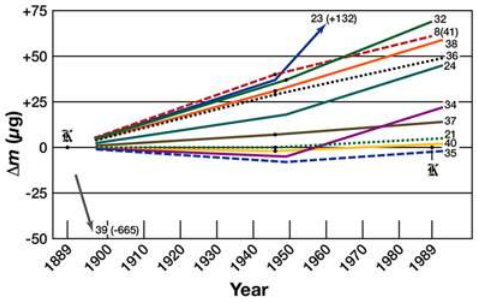
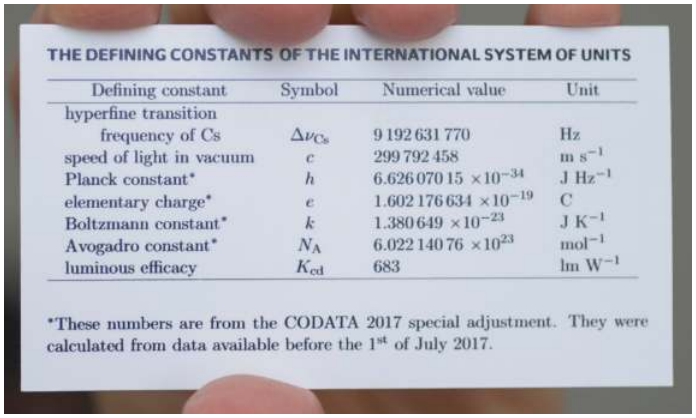


Figure $1B.1.6$: Graph showing relative changes in mass of the witness BIPM prototype Kilogram artifacts relative to the International Prototype Kilogram (NIST)

2019 Definitions

On May 20, 2019 the definitions of the SI Base units were changed, and instead of defining 7 base units, seven constants that are considered to be invariants of nature are defined as exact numbers with no uncertainty. These constants are defined numbers, and this is a fundamental change as what is being defined are constants of nature and not the base units. The base unit is then obtained by applying the constant to the *"mise en pratique"*. To do this, scientists first had to be able to measure these constants very accurately, and once done, they defined the constant based on the measurement as an exact (defined) number. Then to apply it they sort of reverse engineered the process of measuring the constant, with the constant now being treated as a defined (exact) number, and could measure the value of a sample based on the defined constant.

This sounds sort of complicated, but the process is actually easy to understand if we look at a constant we are familiar with, like density, the ratio of the mass of a substance to its volume. For an incompressible substance like water the density can be considered a constant, and if you define the density of water to be 1 g/ml as an exact definition, and have a device to measure volume, you can then use that to determine the mass. So the mass is determined by the defined value of the density as 1 g/mL (an exact number by definition). Of course the density of water as a constant is not an invariant of nature, and changes as temperature, pressure and other factors change. But the principle is the same.



THE DEFINING CONSTANTS OF THE INTERNATIONAL SYSTEM OF UNITS

Defining constant	Symbol	Numerical value	Unit
hyperfine transition frequency of Cs	$\Delta\nu_{Cs}$	9 192 631 770	Hz
speed of light in vacuum	c	299 792 458	m s^{-1}
Planck constant*	h	$6.626\,070\,15 \times 10^{-34}$	J Hz^{-1}
elementary charge*	e	$1.602\,176\,634 \times 10^{-19}$	C
Boltzmann constant*	k	$1.380\,649 \times 10^{-23}$	J K^{-1}
Avogadro constant*	N_A	$6.022\,140\,76 \times 10^{23}$	mol^{-1}
luminous efficacy	K_{cd}	683	lm W^{-1}

*These numbers are from the CODATA 2017 special adjustment. They were calculated from data available before the 1st of July 2017.

Figure $1B.1.7$: Card with SI defining constants (Stoughton/NIST). These values are considered as defined numbers.

Many of these constants will be encountered as we proceed through the material of this class and although students need to know the SI base units, they do not need to be concerned with deriving the SI base units from the 7 defined constants.

It is hoped that by the time this Chapter is finished students can understand the logic of the new definitions, and use units in their calculations. The key to this is that the constants must have the units of the base unit that they describe (density has units of mass over volume, so could be used to describe units of mass or volume). When you look at the card in Figure 1B.1.7 you see units like J/Hz for Planck's constant. Those are actually SI derived units (section 1B.3.2), and Planck's constant can be described in units of $\frac{kg \cdot m^2}{s}$, so it could be used to define the SI base units of Kilogram, meter and second. In sections 1B.3 Mathematics in Chemistry and section 1B.4 Dimensional Analysis, students will learn how to use units in calculations, and these type of math skills are what is required to mathematically relate the fundamental constants to the SI base units.

Optional: A Deeper Look

To get a better understanding of the change in definitions it may be prudent to look at the respective values of the new and old definitions. This information is obtained from The International System of Units, 8th ed. Section 2.1.1, BIPM (old definitions) and Appendix 3, Resolution 1 of 26th CGPM (new definitions).

- **Meter**
- **Kilogram**
- **Second**
- **Ampere**
- **Kelvin**
- **Mole**
- **Candela**

Reuse <> Embed

The kilogram is probably the unit whose definition has undergone the most radical change as it was the only previous definition that depended on one specific artifact, and now involves the use a a device called the Watt balance. The Watt balance essentially balances gravitational forces with electromagnetic to determine Planck's constant. Once Planck's constant was determined, new "secondary standard" kilograms can be created by sort of reverse engineering the use of the device, but even this is very complicated, as the Watt balance operates in a vacuum and cryogenic temperatures, and the secondary standard needs to be in atmospheric conditions where normal measurements occur. The article "A LEGO Watt balance: An apparatus to determine a mass based on the new SI", gives a pretty good walk though on how the Watt balance is used.

Students who wish to learn more about the new SI definitions are encouraged to look at the resources provided through NIST's SI Redefintion website. The American Scientist article "Weighing the Kilogram" by Paul Karol is also an easy to read article going over many of the issues associated with defining the kilogram and the mole.

Note: All students need to know what the SI Base units are, and if they see the definitions of the base units on an exam, they need to determine if they relate to the pre or post May 2019 revisions, as many textbooks and exam banks will still be using the old ones.

SI Derived Units

In the previous section we stated that the SI base units could be combined to measure different types of physical phenomena. Figure 1B.1.8 shows common units of measure that can be derived from the base units. There are two types, those that do not have special SI names and symbols, like area (m^2), and those that do, like pressure, work,... So for example, the SI unit of energy is the Joule, which is a "derived unit" and can be described in terms of the base units of mass, length and time:

$$\underbrace{1J = 1\frac{kg \cdot m^2}{s^2}}_{\text{SI Derived Unit of Energy in terms of SI Base Units}} \tag{1B.1.1}$$

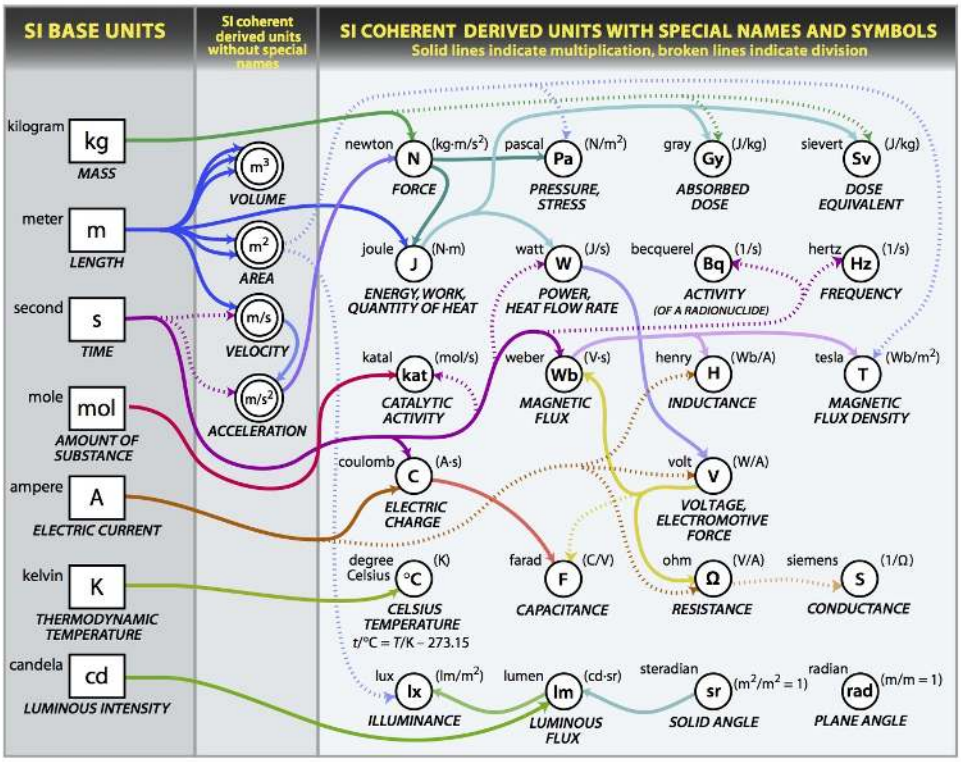


Figure 1B.1. 8: Flowchart showing how different derived SI units can be created from the base units (NIST).

Table represents common SI units:

Table 1B.1. 4: Derivied SI units and their dependencies on the SI bas units.

Quantity	Unit	Explanation
Work	N	Newton = kg m s^{-2}
Pressure	Pa	Pascal = N m^{-2}
Energy	J	Joule = N.m
Charge	C	Coulomb = A.s
Electric Potential	V	Volt = J/C
Power	Watt	1 watt = 1 J/s
Volume	L	1L = $1dm^3$
Volume	mL	1mL = $1cm^3$
Molarity	M	mol/L

Note, there are many non-SI units like the calorie, atm, foot, etc., which can also be described in terms of the SI base units. Conversions between units is covered in section 1B.3.5.

SI Prefixes

SI prefixs are commonly used to represent very large and small numbers. You need to memorize many of these and know how to convert between them.

Table 1B.1. 5: SI prefixes. Note Chem 1402 students need to memorize all the values in red.

Multiplier	Name	Abbreviation		Name	Multiplier
10^{+30}	quetta*	Q	q	quecto*	10^{-30}
10^{+27}	ronna*	R	r	ronto*	10^{-27}
10^{+24}	yotta	Y	y	yocto	10^{-24}
10^{+21}	zetta	Z	z	zepto	10^{-21}
10^{+18}	exa	E	a	atto	10^{-18}
10^{+15}	peta	P	f	femto	10^{-15}
10^{+12}	tera	T	p	pico	10^{-12}
10^{+9}	giga	G	n	nano	10^{-9}
10^{+6}	mega	M	m	micro	10^{-6}
10^{+3}	kilo	k	m	milli	10^{-3}
10^{+2}	hecto	h	c	centi	10^{-2}
10^{+1}	deca	da	d	deci	10^{-1}

*quetta, ronna, ronto & quecto were added in 2022 (https://www.bipm.org/en/cgpm-2022/resolution-3).

NOTE: The Angstrom is a common unit of length Å = 10^{-10}m). It is not an SI prefix, but is a common unit of length that is used when describing bond lengths and distances between atoms (and ions) in a crystal.

Use of SI prefixes

For real large or small numbers, the convention is to place a number with between 1 and 999 in front of the SI prefix, and use the appropriate prefix to show the value. So a memory stick with 1,200,000 bytes would be written as 1.2 Mbyte, not as 1,200 kbytes.

What is the ENG key on scientific calculators?



Figure 1*B*.1.8: Three display modes on TI 30 calculator.

The ENG key takes large or small numbers and expresses them as integer multiples of 10^3 or 10^{-3}, effectively converting them to values that can be expressed with SI prefixes. If you type 1,200,000 into your calculator and press ENG, it gives 1.2 x 10^6, so 1,200,000 bytes of memory on a memory stick would be 1.2 MBytes (you do not say 1,200 kBytes). If you try 0.12 and press ENG, it gives 120 x 10^{-3}, so 0.12g is 120 mg. So the ENG function quickly converts numbers to values that can easily be expressed with SI prefixes.

section 1B.3 we will go over mathematical operations using SI prefixes, and the conversions of units.

Vocabulary

Metric - decimal based unit of measure originally based on the meter, but evolved into SI.

Metrology - Science of Measurement

SI Base Unit - seven base units that all physical measurements can be derived from.

SI Derived Unit - a unit of measurment created by combining SI Base Units.

SI Prefixes - used to describe large or small values of SI units, usually of multiples of 10^3.

SI Unit - System international, unit of measure started in 1960 and evolving through the "Bureau International des Poids et Mesures" (**BIPM**), which was established by the Metric Convention of 1875. It is the established unit of measure for the practice of

science.

Test Yourself

Flash cards that go from SI prefix name to value. *NOTE: If you already know an answer you can just click "I got it right" and move on to the next. Everytime you reload these should rearrange.*

Flash cards that go from SI prefix value to name. *NOTE: If you already know an answer you can just click "I got it right" and move on to the next. Everytime you reload these should rearrange.*

Flash cards that go from SI prefix symbol to value. *NOTE: If you already know an answer you can just click "I got it right" and move on to the next. Everytime you reload these should rearrange.*

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:
- Ronia Kattoum (Learning Objectives)
- Elena Lisitsyna & Vincent Belford (H5P interactive modules)

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1B.2: Making Measurements: Experimental Error, Accuracy, Precision, Standard Deviation and Significant Figures

Learning Objectives

- Differentiate between precision and accuracy
- Explain what significant Figures are
- Know and apply the rules of significant Figures to measured numbers

Experimental Error

What is the difference between random and systematic error? There are two concepts we need to understand in experimental error, **accuracy** and **precision**. Accuracy is how close your value or measurement is to the correct (true) value, and precision is how close repeated measurements are to each other. If the targets below represent attempts to hit the bulls eyes in an archery contest, they represent two types of error. The ones in the left image represents systematic error as all hits are to the left of the bulls eye. This kind of error would occur if you use an old ruler to measure length, but the ruler was worn down over time so it was no longer twelve inches. If you average all measurements that contain systematic error, you still miss the true value. On the right the holes are scattered around the bulls eye in relatively equal directions, so the error is random. If you average the random error, you actually get a good estimate of where the bulls eye is. So to compensate for systematic error you need to recognize it, and adjust for it. You can compensate for random error by making multiple measurements and averaging them.

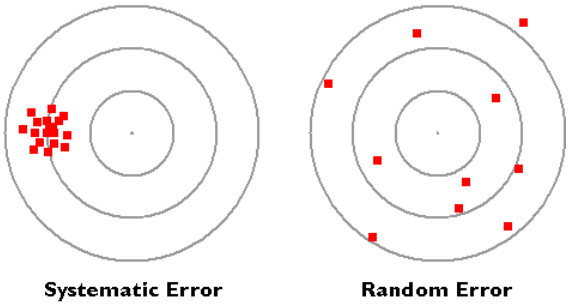


Figure $1B.2.1$: Systematic error has a bias where all measurements are offset, this is typically due to a flaw in an instrument, or how the operator uses it. Random error is evenly distributed around the true value.

Accuracy

The accuracy of a measurement is how close it is to the real value. If error is random, we can improve the accuracy by taking several measurements and using the average value. Thus, the average value of all the measurements on the right target of Figure 1.B.2.1 is very close to the center, but the average on the left side is not. We often use percent error to describe the accuracy of a measurement.

Percent Error

$$Percent\ Error = \frac{|Experimental\ Value - Theoretical\ Value|}{Theoretical\ Value}(100) \tag{1B.2.1}$$

Where the theoretical value is the true value and the experimental value is the measured value. Note, some texts omit the absolute value sign, which means some measurements would have a positive percent error and others would have a negative. The problem with that is if one wanted to know the average percent error for a series of random measurements, the positive and negative values would cancel and indicate a lower average value than is real. Note, that is a different question than what is the percent error of the average value, in which case you would calculate the average value, and base the error on that. The advantage of omitting the absolute value sign is a positive value means your reading is too high, and negative means it is too low. If you make multiple measurements, it is best to use the absolute value sign, and if only one, it does not really matter. It would probably be best to ask your instructor if you are in a lab class.

Precision

Precision is a measure of how close successive measurements are to each other. Precision is influenced by the scale, and when reporting a measurement, you report all certain values, and the the first uncertain one (which you "guesstimate"). This is illustrated in Figure 1B.2.2. The scale on the left is a cm scale because the smallest value you know is in cm, and marker (arrow) is clearly than 1 and less than 2 centimeters, and so would be reported as 1.6cm, or maybe 1.7cm (as you report all certain values, plus the first uncertain value). The scale on the right is a mm scale, and you know the marker is greater than 16 mm and less than 17mm, and you would report it as 1.67cm (which is the same as 16.7mm).



Figure 1B.2. 2: A cm scale (left) and mm scale (right).

So if 100 people measure the same object, they will come up with different values, and the closeness of those values is dictated by the scale they use. The mm scale is more precise because everyone would come up with values between 1.6 and 1.7 cm, while with the cm scale, their values would be between 1 and 2 cm.

So how do we describe the "spread" of successive measured numbers?

Standard Deviation

The standard deviation is a way of describing the spread of successive measurements. If you look at Figure 1B.2.2 you quickly realize that different people will read different values for the uncertain digit, and if multiple measurements are made of the same object by different people, there will be a spread of values reported. A normal (symmetric) distribution results in a bell shaped curve like in Figure 1B.2.3.

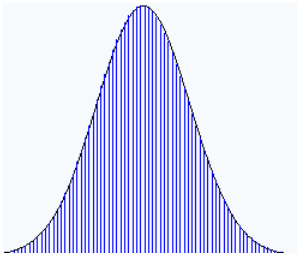


Figure 1B.2. 3: Normal Distribution curve

But how wide that distribution is spread depends on the precision of the measurement. In Figure 1B.2.4 we see two distributions based on the two scales in 1B.2.2, where on the left, the centimeter scale was used, and the values reported have a greater spread (between the certain values of 1 and 2cm), than on the right, where the more precise millimeter scale was used, and the spread is between the certain values of 1.6 and 1.7 cm. If the error is a true random error, they will have the same average value.

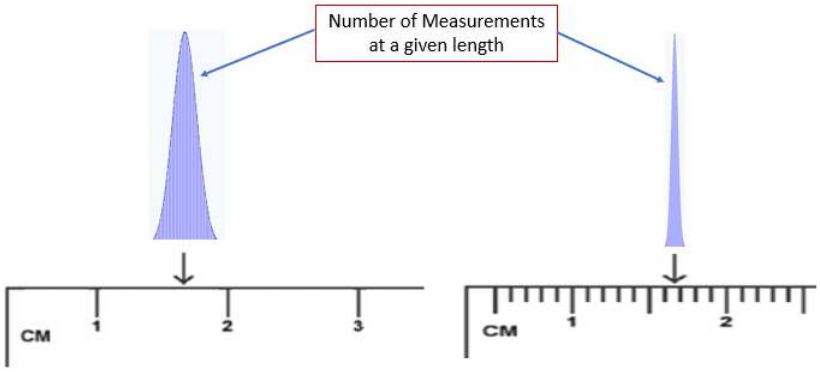


Figure 1B.2. 4: Normal Distribution curves for measurements made with different scales

Deeper Look

The **standard deviation**, σ, describes the spread of a data set's individual values about its mean, and is given as

$$\sigma = \sqrt{\frac{\sum_i (X_i - \overline{X})^2}{n-1}} \tag{4.1}$$

where X_i is one of n individual values in the data set, and $\overline{X}$ is the data set's mean (average) value.

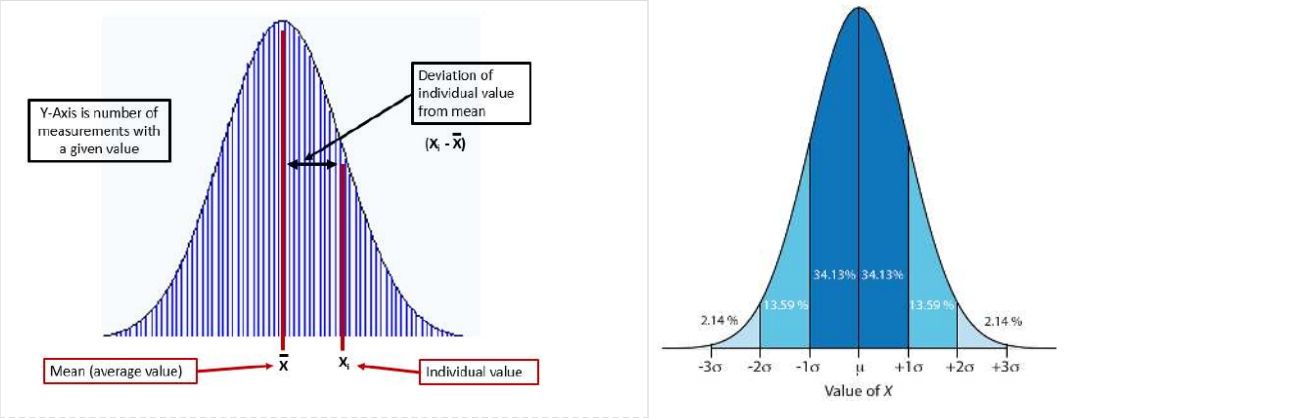


Figure $1B.2.5$: Figure on left illustrates the deviation of an individual value from the mean (average), and on the right, the percent of the total number of measurements within one to three standard deviations from the mean.

Note from the right side of the above Figure, 68.2% of data is within one standard deviation, 95.4% is within two standard deviations and 99.7% is within three standard deviations from the mean. So the standard deviation is a measure of the spread of your data, that is, the precision of your measurement.

So when writing an individual measurement, how to we show the precision with which we know the value of the number?

Significant Figures

Significant Figures are a set of conventions to express numbers where clearly indicate all certain and the first uncertain digit. The goal is to:

- Report all certain values
- Report first uncertain value
  - Uncertain Value is a "guess" between smallest unit of scale
  - Successive Measurements will vary by uncertain value

The rules for significant Figures are:

Significant Figure Rules

1. Non Zeros are always significant
2. Leading Zeros are never significant
3. Captive Zeros are always significant
4. Trailing Zeros are only significant if a number has a decimal point

We will go over why these rules are needed in the section on carrying significant Figures in mathematical calculations.

Significant Figures, Exact Numbers and Defined Numbers:

A counted number is an integer and thus is an exact number, for which there is no uncertainty. So it does not influence significant Figures. If one looks on the web one often sees people saying that a counted number has an infinite number of significant Figures, mathematically that may work, but it is incorrect, in that you do not need an infinite number of significant digits to exactly define a counted number. The fact is, there is no uncertainty in an exact number, 3 cows is 3 cows. Now defined number may or may not have significant digits. Twelve inches = 1 foot, there are no significant digits. But an irrational number like π, which is also a

defined number, would require an infinite number of significant digits to exactly define, and if you use pi in a calculation, you should use enough significant digits so that it does not determine the number of significant digits in your answer. Simply speaking, significant digits are a way to indicate the precision of measured values, and the above rules enable you to preserve them in calculations. Exact and defined numbers do not involve measurements, and so they do not influence the number of significant digits in a calculations (unless you do not use enough digits for a defined value like π.

Vocabulary

Accuracy - how close an answer is to the true value

Precision - how close repeated measurements are to each other

Percent error - measure of accuracy: $Percent\ Error = \frac{|Experimental\ Value - Theoretical\ Value|}{Theoretical\ Value}(100)$

Random error - error that is random

Significant Figures - all certain digits plus first uncertain (guess value that is smaller than smallest unit of scale)

Standard deviation - measure of precision

Systematic error - error with a bias

Test Yourself

Contributors and Attributions

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- Mark Tye (Diablo Valley College)
- Mike Blaber (Florida State University)
- Ronia Kattoum (Learning Objectives)
- Elena Lisitsyna (H5P interactive modules)

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1B.3: Mathematics in Chemistry

Learning Objectives

- Express numbers both in scientific notation and standard notation
- Carry out calculations with the correct number of significant Figures
- Convert between various units

Math Review: 4 Ways of Expressing Numbers

There are four common ways to express numbers, and some of these are preferable when the numbers are very large or very small.

1. Floating Number
2. Scientific Notation
3. SI Prefixes
4. Logarithms

Floating Numbers

Floating numbers are common numbers where the "magnitude" is determined by the position of the decimal point. Digits to the left of the decimal are larger than 1 and digits to the right are less than one, or a fraction. So 12.121200 and 121212.00 are two numbers of identical digits but the second is 10^4 times larger than the first . A fraction typically has a zero in front of the decimal, so 0.25 is $\frac{25}{100}$ or one quarter $\frac{1}{4}$.

Scientific Notation

Unlike a floating numbers scientific notation has two parts, first a number with only one digit to the left of the decimal and a variable number of digits to the right of the exponent, which is multiplied by 10 to a power, such that it equals the value of the desired number. We call the power of 10 its exponent.

$$\_ . \_ \_ \_ \times 10^n \tag{1B.3.1}$$

Where n is the power and the underscore represents the number of digits in the number. Note, due to this format, scientific notation always has an unambiguous number of significant digits.

Q&A: What is Exponentiation?

Exponentiation is the replication of multiplication the way multiplication is the replication of addition

$$10^0 = 1$$

$$10^1 = 10 \qquad 10^{-1} = \frac{1}{10} = 0.1$$

$$10^2 = 10(10) = 100 \qquad 10^{-2} = \frac{1}{10^2} = \frac{1}{100} = 0.001$$

$$10^3 = 10(10)(10) = 1000 \qquad 10^{-3} = \frac{1}{10^3} = \frac{1}{1000} = 0.0001$$

Q&A: Can the exponent have units?

No, the exponent can not have units, it is the number of times you multiplied or divided the number by 10, but you write the units behind the number expressed in scientific notation.

$$1.333 \times 10^4\ L = 13,333\ L \tag{1B.3.2}$$

Advantages of Scientific Notation

1. Allows Awkwardly Large and Small Numbers to Be Expressed in Term of Compact and Easily Written Numbers
2. Allows Accurate Representation of the Number of Significant Figures in a Number, That Is a Measurement's Precision, the "Certainty" of Our Measurements

SI Prefixes

SI prefixes are similar to scientific notation, where you express a number with between 1 and 3 digits to the left of the decimal point, times 10 to the power of 3, but use the appropriate SI prefix to represent 10 to the power of 3. Note, it is common to express floating numbers with a comma every three decimal places (power of 10^3). So the number

13,000,000,000g = 13 x10^9g or 13 gigagrams.

You need to know the SI prefixes from section 1B.1.3.3.

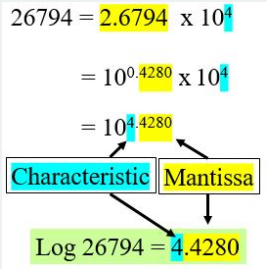
Logarithms

Logarithms are very similar to scientific notation, but the pre-exponential is expressed as 10 to the power of a fraction, and the log of a number, is the power of 10 that equals a number. Logarithms are often not covered in general chemistry 1, but they are extensively used in general chemistry 2.

Deeper Look: Logarithms

This is optional material for general chemistry 1, but you will need to understand this for general chemistry 2.

Let's consider the number 26794. It can be expressed in scientific notation or as a log



So logarithms are very similar to scientific notation, where the number being multiplied by 10 to a power is expressed as 10 to the power of a fraction. Please see the math review in Chapter 14 prelude for more information on logarithms, where there is a video relating logarithms to scientific notation

Significant Digits, Calculations and Rounding off Answers

It is important to be able to preserve the number of significant Figures in calculations based on the precision of the data used in those calculations, and there are two sets of rules, one for multiplication and division, and the other for addition and subtraction.

Multiplication and Division

The number of significant Figures in the product of multiplication or dividend of division is based on the valued used with the least number of significant digits.

Exercise $1B.3.1$

How many significant Figures are in the answer to the following problem?

$$\frac{(3.42)(127)}{1.6} = ?$$

Answer

Two, you do not even need to do the math to answer this question.

Addition and Subtraction

Here, the number of significant Figures is based on the least precise measured value. In this case you actually have to line the numbers up by the decimal point and do the math, and then limit the answer to the precision of the least precise value.

Consider:

$$\begin{array}{r} 1.2 \\ \underline{4.41} \\ 5.61 \end{array}$$

↑ limit final answer to the tenths column: 5.6

Exercise $1B.3.2$

How many significant Figures are in the answer for 99 + 1?.

Answer

3, the answer is 100. or 1.00 x 10^2 because both numbers are known to the "ones" place.

Note: in the above exercise, a number with two sig. figs was added to a number with one sig fig., and the answer had three sig. figs. Unlike multiplication and division, you must do the math to determine the number of sig. figs for addition and subtraction.

Rounding Off Answers

When you have to truncate an answer by removing numbers you may round up or round down. Truncation is removing a digit from the number, and all digits smaller than that digit.

- If truncated digit is less than 5, round down (use value of preceding digit)
- if truncated value is greater than 5, round up (add one to preceding value).
- if truncated value equals 5, look at the next digit.
  - if it is even, round down
  - if it is odd, round up*

*Note, when the truncated value equals 5 you round in the direction that makes the answer end in an even number

Contradictions of the Rules

Sometimes the rules break down and you need to be aware of it. For example, if you weight two nickels and each nickel weights 5.0 grams, what is the weight of both nickels? Well, multiplication is the repetition of addition and so you could multiply the weight of each nickel by two

$$2 \text{ nickels} \left(\frac{5.0 \text{ grams}}{\text{nickel}} \right) = 10. \text{ grams} \tag{1B.3.3}$$

or you could add the mass of the two nickels

$$5.0\,g + 5.0\,g = 10.0\,g \tag{1B.3.4}$$

So when you multiplied the answer would have two significant Figures because the number with the least was the measured mass (the 2 nickels was an exact counted number), but when you added, they were all known to the tenths position, and so your answer has 3 significant digits.

Converting Floating Decimal Point Numbers to Scientific Notation

A closer look at scientific notation shows that the number is being represented by two parts, the pre-exponential and the exponential (10 to a power). To convert a floating decimal point number to scientific notation you need to multiple or divide the pre-exponential by 10 to a power, until there is just one digit to the left of the decimal point. Because this changes the value of the number, you need to divide or multiple that pre-exponential by 10 to a power (the second term of the notation, noting that division is represented by 10 to a negative exponent), so that they combined expression equals the value of the floating decimal point number.

This is easy to see by looking at the solutions to the next two examples, where you convert a fraction and a number greater than (or equal to) 10 to scientific notation.

Convert the following floating numbers to scientific notation

Exercise $1B.3.3$

0.00456 (A number smaller than 1)

Answer

Step 1: Since this number is less than 1 you need identify the power of 10 which you can multiply it by and set one digit to the left of the decimal. Here, we can multiply by 1000 or 10^3 and force the original number to have one digit to the left of the decimal, but we have changed its value.

0.00456 x 10^3 = 4.56 (note, which is not equal to the original number)

Step 2: Since we multiplied it by 10^3 we must also divide by 10^3 (effectively multiplying the original number by 1 and not changing it's value). Than we express the factor in the denominator as a power of 10.

$$(0.00456) = (0.00456)\left(\frac{10^3}{10^3}\right) = \left(\frac{0.00456 \times 10^3}{10^3}\right) = \left(\frac{4.56}{10^3}\right) = 4.56 \times 10^{-3} \tag{1B.3.5}$$

Note, once you get the hang of this you can just count the number of digits you need to move the decimal to bring the original number to one digit to the left of the decimal and multiply that number by 10 to the negative value of those digits. Here we moved the decimal three positions to the right, so we multiply by 10^{-3} (ie., divide by 10^3).

Exercise $1B.3.4$

456.00, (A number larger than or equal to 10)

Answer

Since this number has more than one digit to the left of the decimal, we must divide it by a factor of 10 to make it smaller so that one digit is to the left of the decimal. Then we must multiply everything by 10 to the same power that we divided by 10 in the first step.

$$(456.00) = (456.00)\left(\frac{10^2}{10^2}\right) = \left(\frac{456.00 \times 10^2}{10^2}\right) = \left(4.56 \times 10^2\right) \tag{1B.3.6}$$

Note, once you get the hang of this you can just count the number of digits you need to move the decimal to bring the original number to one digit to the left of the decimal and multiply that number by 10 to the value of those digits. Here we moved the decimal two positions to the left, making it 100 times smaller, so we multiply by 10^2 to maintain the same value.

Significant Digits:

How can you express the number 400 to 2 significant digits?

You must use scientific notation.

4.0 x 10^2

As scientific notation always has a decimal point there is never a problem expressing significant digits.

Mathematical Operations with Scientific Notation

Multiplication and Division

Try plugging the following number into your calculator. Odds are you will get an error message, and you need to know how to solve calculations that are bigger or smaller than your calculator can handle.

$$\frac{\left(9.47 \times 10^{598}\right)\left(7.39 \times 10^{-98}\right)}{\left(1.432 \times 10^{-645}\right)\left(2.46 \times 10^{4}\right)} \tag{1B.3.7}$$

The trick is to break the above equation into two parts, one dealing with the pre-exponential, and one dealing with the powers of 10. The following video shows how to do this, and the above problem is solved in the exercise below the video.

Example $1B.3.1$: multiplication and division with scientific notation

Solve the following problem

$$\frac{\left(3.00 \times 10^{480}\right)\left(4.0 \times 10^{-20}\right)}{\left(2.00 \times 10^{-500}\right)\left(1.50 \times 10^{70}\right)}$$

Solution



Video $1B.3.1$: Scientific notation in multiplication and division. https://youtu.be/nIFIZkkNRAk

(4.0x10^{890})

Exercise $1B.3.5$

Solve the following problem.

$$\frac{\left(9.47 \times 10^{598}\right)\left(7.39 \times 10^{-98}\right)}{\left(1.432 \times 10^{-645}\right)\left(2.46 \times 10^{4}\right)}$$

Answer

$$= \left(\frac{9.47x7.39}{1.432x2.46}\right)\left(\frac{10^{598}\times 10^{-98}}{10^{-645}\times 10^{4}}\right)$$

$$= \left(19.86\times 10^{(598-98+645-4)}\right)$$

$$= \left(19.9\times 10^{1141}\right) = \left(1.99\times 10^{1142}\right)$$

Addition and Subtraction

This can easily be solved with your calculator, the challenge is how do you determine the number of significant Figures in the answer. To do this you need to line them up by multiplying everything by the same power of 10.

Consider the following problem

$$4.860 \text{ x } 10^{12} + 9.7 \text{ x } 10^{10} + 3.68\text{x}10^{11}$$

Would you believe the answer has four significant Figures? (The solution to this problem is below the following video.)

Example $1B.3.2$: Addition and subtraction with scientific notation

Solve the following problem and report answer to the correct number of significant Figures:

$3 \text{ x } 10^{23} + 3.00 \text{ x } 10^{25}$

Solution



Video $1B.3.2$: Scientific Notation in addition and subtraction. https://youtu.be/Ghe32OnScdI

$(3.00 \text{ x } 10^{25})$

Exercise $1B.3.4$

$4.860 \text{ x } 10^{12} + 9.7 \text{ x } 10^{10} + 3.68\text{x}10^{11}$

Answer

You first need to express all numbers to the same power so you can line up the decimal point. It is suggested that you choose the largest power and make everything else a fraction.

$$4.860 \text{ x } 10^{12}$$

$$+0.097 \text{ x } 10^{12}$$

$$\underline{+0.368 \text{ x } 10^{12}}$$

$$5.325 \text{ x } 10^{12}$$

Unit Conversions

As chemists have different ways of expressing measurements they need to be able to convert between different units. Central to this is the concept of an equivalence statement which says two ways of representing the same thing are equivalent. For example 12 in = 1 foot is an equivalence statement. An equivalence statement allows you to convert from one unit to the other, and this is done by creating a conversion factor. A conversion factor is

simply the ration of one part of the equivalence statement to the other, where the numerator has the unit you want to convert to, and the denominator has the unit you want to transform from.

12 in = 1 foot

has two conversion factors

1. to convert from feet to inches multiply by the conversion factor of

$$\left(\frac{12\ in}{1\ foot}\right) \tag{1B.3.8}$$

2. to convert from inches to feet multiply by the conversion factor of

$$\left(\frac{1\ foot}{12\ inches}\right) \tag{1B.3.9}$$

There are three fundamental types of conversions that you will need to be able to perform. The first involve different ways of expressing numbers within the same scale, which include transforming floating numbers to SI prefixes and scientific notation. The second involves converting from one scale to another, like the metric system to the English [read: American] system, and you are expected to know that 2.54 cm=1 inch [read: memorize that]. The third involves physical constants of specific substance, where you convert from one type of physical measurement to another. Density is such a physical constant, and it allows you to convert mass measurements to volume.

What is consistent with each of these three different types is that they all represent an equivalence statement, and from the equivalence statement you can generate a conversion factor.

Three Basic Types Conversions

A. Different prefixes of same base scale (cm -> Km)
B. Conversions between scales (cm -> in)
C. Physical Constants d=M/V

Conversions involving SI Prefixes

2 Basic Techniques:

1. **Basic Technique : Use two equivalence statements**
2. **Advanced Technique: Use one equivalent statement**

Basic Technique

How many micrograms are in a kilogram?

Set up conversion factors based on an equivalence statements.

1 kg = 10^3 g and 1 µg = 10^{-6} g

so, this gives two conversion factors

$$\left(\frac{10^3 g}{1 kg}\right) and \left(\frac{1 \mu g}{10^{-6} g}\right) \tag{1B.3.10}$$

You have two conversion factors. In the first you will convert kilograms to grams, and in the second you will convert the grams to micrograms.

$$(1 kg)\left(\frac{10^3 g}{1 kg}\right)\left(\frac{1 \mu g}{10^{-6} g}\right) = 10^{3-(-6)} \mu g = 10^9 \mu g \tag{1B.3.11}$$

In the advanced technique (below) you will solve this problem with only one conversion factor.

Example $1B.3.3$

3x10^{23}fsec = ? Gsec

Solution



Video $1B.3.3$: Basic technique for unit conversions. https://youtu.be/Jlfk7XjDnwM

(3x10^{-1} Gsec)

Exercise $1B.3.5$

Convert 32.4 ng to Mg.

Answer

$$(32.4ng)\left(\frac{10^{-9}g}{ng}\right)\left(\frac{Mg}{10^{6}g}\right)=32.4\times10^{(-9-6)}Mg=32.4\times10^{-15}Mg=3.24\times10^{-14}Mg \tag{1B.3.12}$$

Advanced Technique

How many micrograms are in a kilogram?

Set up a single conversion factor based on an equivalence statement.

The trick here is to multiple both SI prefixes by the number that makes them equal to one. That is, if a micro is one millionth, than there are a million micro in one, and and likewise if a kilo is a thousand, than a thousandth of a kilo is one, and so a million micrograms equals a thousandth of a kilogram.

$$1\mu g=10^{-6}g\therefore 1g=10^{6}\mu g \tag{1B.3.13}$$

$$1kg=10^{3}g\therefore 1g=10^{-3}kg \tag{1B.3.14}$$

so, this gives two conversion factors

$$\frac{10^{6}\mu g}{10^{-3}kg}=\underbrace{\frac{10^{9}\mu g}{1kg}}_{\text{converts kg to }\mu g}\leftarrow or\rightarrow\frac{10^{-3}kg}{10^{6}\mu g}=\underbrace{\frac{10^{-9}kg}{1\mu g}}_{converts\ \mu g\ to\ kg} \tag{1B.3.15}$$

(Use the ratio which has the starting unit in the denominator and ending unit in the numerator.)

See Video $1B.3.4$ for the advanced technique combined with scientific notation
(next video below)

Exercise $1B.3.6$

Convert 32.4 ng to Mg..

Answer

1 g = 10^{-6} Mg = 10^{9} ng

$$(32.4ng)\left(\frac{10^{-6}Mg}{10^{9}ng}\right)=\left(32.4\times10^{(-6-9)}Mg\right)=\left(32.4\times10^{-15}Mg\right)=\left(3.24\times10^{-14}Mg\right) \tag{1B.3.16}$$

SI Prefix Conversions & Scientific Notation

The following video shows you how to do SI conversions of numbers expressed in scientific notation. The trick is to write the SI prefix in terms of its power of 10.

Example $1B.3.1$

Convert: 3 x 10^{23} kiloseconds to nanoseconds.

Solution



Video $1B.3.4$: Advanced technique with SI notation. https://youtu.be/43wWTLB7GS0

(3 x 10^{35} nsec)

Exercise $1B.3.7$

Convert 3.57x10^{14} ml to ml

Answer

$$\left(3.57\times10^{14}\mu l\right)\left(\frac{10^{3}ml}{10^{6}\mu l}\right)=\left(3.57\times10^{(14+3-6)}ml\right)=\left(3.57\times10^{11}ml\right) \tag{1B.3.17}$$

Conversions Between Different Scales

You need equivalence statements between different units. These are the same techniques as the previous, just that the conversions are between different types of units.

Note

UALR students are required to memorize the following conversion factors

- 2.54 cm=1 in (exact) (Metric length to English Length)
- 1 ml = 1 cm^3 (Metric volume to Metric length cubed)

Exercise $1B.3.8$

How many dm are in an object which is 2.450 feet long?

given 12 in = 1 ft,

Answer

$$\left(2.450\ ft\right)\left(\frac{12\in}{1\ ft}\right)\left(\frac{2.54\,cm}{1\,in}\right)\left(\frac{10^{1}dm}{10^{2}cm}\right)=\left(7.4676\,dm\right)=\left(7.468\,dm\right) \tag{1B.3.18}$$

Example $1B.3.5$

What is the volume in Gallons of a 1.00 cubic foot object?

(Try this first, the answer is at the bottom of the video.)

Solution

Note, you are required to know a 1 ml =1 cm^3, 1 in = 2.54 cm, and of course the SI prefix conversions.



Video $1B.3.5$: Conversions between scales

(7.48 gal)

Exercise $1B.3.9$

How many gallons are in a cuboid can that is 2.05 ft wide, 12.4 inches long and 1.30 yards deep?

Given: 4 qt = 1 gal, 1.057qt=1L, 12in = 1 ft, 3 ft = 1 yd:

Answer

$$(2.05ft)\,(12.4in)\,(1.3yd)\left(\frac{3ft}{1yd}\right)\left(\frac{12in}{1ft}\right)^2\left(\frac{2.54cm}{1in}\right)^3\left(\frac{1mL}{1cm^3}\right)\left(\frac{1L}{1000mL}\right)\left(\frac{1.057qt}{1L}\right)\left(\frac{1gal}{4qt}\right)=61.8gal \quad (1B.3.19)$$

Conversions Involving Physical Constants

Many substances have physical properties showing a linear relationship that can be described by the equation of a straight line Y=mX+b. If these are extensive properties (section 1.6.1), then the Y intercept (b) equals zero and this takes the form of Y=mX, which is an equivalence statement, and allows one to convert measurements in the unit of X to those of the unit of Y. These are often tabulated by the constant m $\left(m=\frac{Y}{X}\right)$, which allows conversions of measurements between the units of X and Y.

This can be understood by looking at one such constant, density, which is the linear proportionality constant for the extensive properties of mass and volume, where m = dv (the y intercept is zero because if you have nothing, its mass and volume both equal zero - review extensive properties). So if you know the density of something, you can convert its mass to volume, or its volume to mass. Therefor it is common to compile tables of densities and other physical constants.

It should be stated that although these generate conversion factors, they are really describing relationships, that is, mass and volume describe completely different aspects of matter and density allows you to convert from one to another. This is completely different than definind 12 inches as a foot, where inches and feet are different units that describe the same thing.

Conversions Involving Density

Density is defined as

$$d=\frac{m}{v} \quad (1B.3.20)$$

This gives the equivalence statement

$$m=dv \quad (1B.3.21)$$

and there are thus two conversion factors

$$\underbrace{\frac{m}{d}}_{\text{converts mass to volume}} \leftarrow or \rightarrow \underbrace{dv}_{\text{converts volume to mass}} \quad (1B.3.22)$$

That is, dividing the mass by the density converts it to its volume, and multiply the volume by the density converts its volume to its mass

Example $1B.3.6$

How many liters is the volume of 12.140 kg of Iridium? Use 22.65 g/ml as the density of Iridium

(Please do this before looking up the answer at the bottom of the video.)

Solution



Video $1B.3.6$: Conversion Factors involving physical scales.

0.5360 L, note, the number of sig figs was determined by the density and not the starting mass.

Exercise $1B.3.1$

How many pounds would 61.8 gallons of water weight if at a given temperature the water has a density of 0.98g/mL?

Answer

$$(61.8gal)\left(\frac{4qt}{1gal}\right)\left(\frac{1L}{1.057qt}\right)\left(\frac{1000ml}{1L}\right)\left(\frac{0.98g}{mL}\right)\left(\frac{1lb}{453.6g}\right)=505.27lb=510lb \tag{1B.3.23}$$

Note the answer has 2 significant digits because of the density.

Fractions and Percentage

A fraction is a $\frac{Part}{Whole}$, with a value between 0 and 1. Percentage is simply the fraction x 100, where the 100 is a defined number. Fractions and percentages are commonly used to quantify a multicomponent system or mixture. In chemistry there are sort of two ways of quantifying matter, to count the number of particles or measure the mass of each type of particle. It is common (although not required) to use the fraction to represent the fraction of a sample based on the number of particles (mole fraction), and use % to represent the mass distribution (mass %).

Note:

$$\sum fractions=1 \tag{1B.3.24}$$
$$\sum percents=100$$

Exercise $1B.3.10$

What is the mass % water if 1 gram of a salt is added to 99.0 g of water?

Answer

99.0%. You may ask, why three significant digits?

$$\frac{99.0}{99.0+1}100=\frac{99.0}{100.}100=99.0 \tag{1B.3.25}$$

Vocabulary

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Ronia Kattoum (Learning Objectives)
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1B.4: Problem Solving by Dimensional Analysis

Learning Objectives

- Use dimensional analysis to solve problems

Introduction

In the section on unit conversions we came up with conversion factors that were based on equivalence statements, and through multiplying a measured number by the conversion factor we could convert a measured number in one set of units to another. For example, if we wanted to know how many feet are in 36 inches, we could multiply it by the conversion factor $\left(\frac{1\ foot}{12\ inches}\right)$, which would tell us that there are 3 feet in 36 inches. Because the value in the numerator equals the value in the denominator, using the conversion factor as a multiplier did not change the length of the object as we converted it from 36 inches to 3 feet. We also note from the unit conversion section that there were three types of conversion factors that we used; those relating different prefixes for the same units, those relating one type of unit to another for the same type of measurement, and those that used physical constants that relate one type of measurement to another. The last conversion factor is fundamentally different than the others in that it depends on the substance (different substances can have different densities).

Dimensional analysis is based on the use of conversion factors to solve problems and the term "dimensional analysis" is probably a misnomer in that the name originates from its use to relate different fundamental dimensions of physical objects like mass, volume and length to each other based on equivalence statements, but it can be used with any equivalence statement, even ones that are not based on physical dimensions. What needs to noted here is that many equivalence statements are conditional, for example the price of gasoline is a conditional equivalence statement. One day it may be $2.49/gallon, when another day it may be $4.20/gallon, so clearly the price of a gallon of gas is not a constant, but when you go to the gas pump, you can use the equivalence statement to calculate how much you need to pay for a gallon of gas, and thus it can be used in dimensional analysis.

Setting Up Equations

The Trick to Dimensional Analysis is to keep your units in your conversion factors, and set them up so all units cancel except the units you want in your answer. This is easiest seen by looking at a problem.

General Strategy:

1. Write down what is given.
   - You must have a conversion factor with the unit of the answer you want
   - You must have two values (inital condition or conversion factor) for each unit you wish to cancel, and these will be set up so one of those is on the denominator and the other on the numerator.
2. Start with either the given quantity or the conversion factor that has the value you want (in the numerator) and stepwise add conversion factors until the units are the units of the desired answer

Example $1B.4.1$

How much does it cost to drive a car from Little Rock to Memphis (137 miles) if a car gets 21 mpg and the price of gas is $2.54/gal

Solution

Given Information:

There are two equivalence statements here, along with the distance needed to be travelled

$$137\ miles$$
$$21 miles = 1 gallon$$
$$\$2.54 = 1 gallon$$

Lets solve this two ways

First Way: Start with the distance you need to travel.

$$137 miles$$

you need to get rid of miles, so you need a conversion factor with miles in the denominator

$$137\ \cancel{miles}\left(\frac{1\ gallon}{21\ \cancel{miles}}\right)$$

Solving the above equation would tell you how many gallons you need, but you want to convert gallons to dollars, so you need a conversion factor that has gallons and dollars, and you need dollars in the numerator and gallons in the denominator.

$$137\ \cancel{miles}\left(\frac{1\ \cancel{gallon}}{21\ \cancel{miles}}\right)\left(\frac{\$2.54}{\cancel{gallon}}\right)=\$16.57$$

Second Way: You want to know how much it costs and only one of the given data has cost, so start with that conversion factor, placing cost in the numerator, and cancel everything else out.

$$\left(\frac{\$2.54}{gallon}\right)$$

get rid of gallons

$$\left(\frac{\$2.54}{\cancel{gallon}}\right)\left(\frac{1\ \cancel{gallon}}{21\ miles}\right)$$

get rid of miles and solve

$$\left(\frac{\$2.54}{\cancel{gallon}}\right)\left(\frac{1\ \cancel{gallon}}{21\ \cancel{miles}}\right)\left(137\ \cancel{miles}\right)=\$16.57$$

The advantage of the second method is sometimes you may be given more than one starting value and may not know what to start with. The important thing here is to keep units in the calculations.

Exercise $1B.4.1$

What is the value of a gold bar with dimensions of 1.5cm x 2.5cm x 2.0cm if gold sells for $300/oz and has a density of 19.32g/ml? (16 oz = 1 lb)(1 lb = 453.59 g)(19.32 g = 1 mL)

Answer

Note: you were not given the conversion factor to go from cm^3 to ml, and this is because you are expected to know that 1 cm^3 = 1 mL.

$$\left(\frac{\$300}{oz}\right)\left(\frac{16oz}{1lb}\right)\left(\frac{1lb}{453.59g}\right)\left(\frac{19.32g}{1mL}\right)\left(\frac{1mL}{1cm^3}\right)(1.5cm)\,(2.5cm)\,(2.0cm)=\$1500 \qquad (1B.4.1)$$

.

Exercise $1B.4.2$

Give the volume in liters of a box which is 2.4 yards by 2.4 inches by 2.4 feet in size? (3 ft = 1 yd)(12 in = 1ft)

Answer

Note: in addition to knowing 1 cm^3 = 1 mL, you are also expected to know that 1 in = 2.54 cm.

$$(2.4yd)\,(2.4in)\,(2.4ft)\left(\frac{3ft}{1yd}\right)\left(\frac{12in}{1ft}\right)^2\left(\frac{2.54cm}{1in}\right)^3\left(\frac{1mL}{1cm^3}\right)\left(\frac{10^{-3}L}{1mL}\right)=98L \qquad (1B.4.2)$$

Be Aware: area has the units of length squared and so conversion factors involving area in the dimensions of length need to be squared, and volume is length cubed, and so conversions of volume expressed by length cubed must be cubed. Not mL

is not a unit of length, but of volume.

.

The following video shows the solution of a more complex problem involving going from English to metric units and the use of physical constants.

Example $1B.4.1$

What is the mass of 1.0000 cubic feet of water?

Solution



Video $1B.4.1$: Dimensional Analysis Problem

(28.28 kg)

Note, the physical constant density had significant Figures, and those were what determined the number of significant Figures in the final answer.

Important

1. Always Include Units in Calculations

2. Check All Solutions for Proper Dimensions

Reverse Engineering Eqs from Constants

When you are given a constant you must be given the units, or it makes no sense. For example the density of water is 1.00 g/ml but also 62.4 lb/ft^3, so you can't have a density of water without units. From the units you can back calculate the equation, although sometimes you need to analyze it to make sure it makes sense, for example temperature and temperature change can have the same units, but mean different things. If your constant is a linear proportionality constant, than you can say

Y = mX + b, where m is your constant, and the units of m must be the units of $\left(\frac{Y}{X}\right)$

so if Density has the units of $\left(\frac{g}{mL}\right)$, then

- Y must be something that has the unit of g, and thus mass would work
- X must be something that has the unit of mL, and thus volume would work

Of course you need to think about these, as sometimes different things can have the same units. For example, a change of one degree kelvin equals a change of 1 degree Celsius, but 1 degree kelvin = 273.15 degrees Celsius, and so you do not know if the equation is T or ΔT/ Likewise time and frequency (Hz) have the units of time, where frequency if the cycles per second (and so has units of reciprocal time).

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Ronia Kattoum (Learning Objectives)
- Elena Lisitsyna (H5P interactive modules)

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1B.5: Graphs and Graphing

Learning Objectives

- Define independent and dependent values
- Recognize the different types of functions
- Generate an algebraic expression for data from a graph
- Recognize units of temperature and how they were derived graphically
- Convert between different scales of temperature

Introduction

A graph can be used to show the relationship between two related values, the dependent and the independent variables.

- **Dependent Variable:** A measurable variable whose value depends on the independent variable. Often represented by the algebraic symbol y.
- **Independent Variable:** A measurable variable of which when changed, the value of the dependent variable changes. Often represented by the algebraic symbol x.

$$y = \text{function of x} \quad (1B.5.1)$$
$$or$$
$$y = f(x)$$

Such a relationship would be the maximum amount of table salt (sodium chloride) you can dissolve in water as a function of temperature, which is represented by the data in table 1B.5.1. This represents a saturated solution, and what you notice is that if you raise the temperature of the water more table salt can dissolve. That is, if you have 26.1 g salt at 20.0 ºC dissolved in 100 grams of water (which is the maximum amount that can dissolve in 100 grams of water), and add another 2 grams, it just falls to the bottom of the solution and the temperature does not change. If you then raise the temperature the solid at the bottom starts to dissolve and somewhere around 70 degrees all the salt dissolves. So the solubility is the dependent variable, and its value depends on the temperature, the independent variable. You noted in the above example that changing the dependent variable (solubility) had no effect on the temperature (independent variable).

In this case Equation 1B.5.1 could be expressed as

$$Solubility = f(Temperature) \quad (1B.5.2)$$

Table $1B.5.1$: Solubility of table salt as a function of water. In this graph 6 measurements of the solubility were made at different temperatures. Here, the solubility is the maximum amount of salt that can be dissolved in 100 grams of water, and any extra salt beyond that falls to the bottom of the container as a precipitate (solid).

Data Measurement number	Temperature (^{o}C)	Solubility (g NaCl/100 g water)
1	0.00	35.2
2	20.0	36.1
3	40.0	37.0
4	60.0	37.7
5	80.0	38.4
6	100.0	39.0

A plot can then be made of the data where the dependent variable (y) is plotted on the vertical axis (ordinate axis) and the independent variable(x) is plotted on the horizontal axis. Figure 1B.5.1 represents a plot of the data from table 1B.5.1, where each point represents one of the data measurements, with the values typically expressed in terms of (x,y). So the third data point would have values of (60.0,37.0) representing the temperature and solubility.

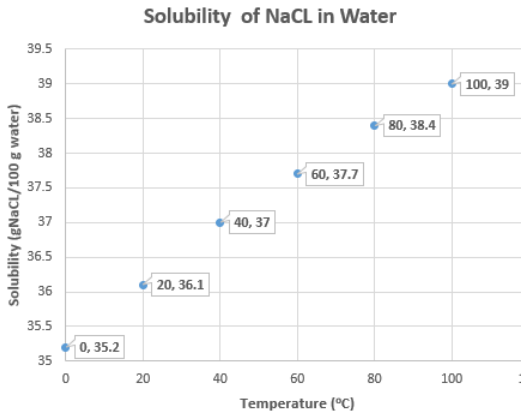


Figure $1B.5.1$: Data from table 1B.5.1 plotted with temperature along the x-axis and solubility along the y Axis

It should be noted that not all plots involve dependent and independent variables, and that sometimes both variables are dependent on another entity, which is not being plotted. This is the case for temperature conversions from Fahrenheit to Celsius, where both scales are measuring an intensive property, the temperature of some object or substance, and it is the temperature that changing. Or a plot of mass vs. volume for a pure incompressible substance, which are both extensive properties that depend on the amount of substance being measured.

Types of Functions

In science there are many types of functions, and general chemistry makes extensive use of three types; linear, power and exponential.

1. Linear Function:

$$y = mx + b \tag{1B.5.3}$$

2. Power Function:

$$y = ax^m \tag{1B.5.4}$$

(which is linear in the logarithmic form)

$$logy = mlogx + loga \tag{1B.5.5}$$

3. Exponential Function:

$$y = ae^{mx} \tag{1B.5.6}$$

(which is linear for a plot of the natural log of the dependent variable against the independent variable)

$$lny = mx + lna \tag{1B.5.7}$$

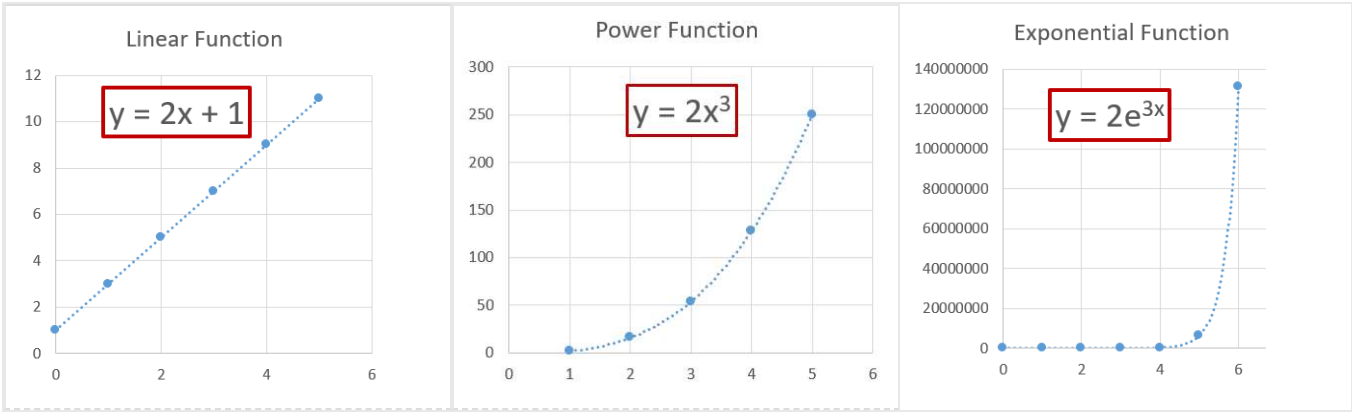


Figure $1B.5.2$: Plots of the three types of functions that are commonly used in general chemistry.

We will not use the power function or exponential function until the second semester of general chemistry, when students will be using these extensively. There is a review of logarithms in the prelude to Chapter 14, and this Chapter we will only cover linear functions.

Graphing Linear Functions

Equation 1B.5.3 is a linear equation

$$y = mx + b$$

- m is called the slope of the line, which is the ratio of the change in y (the rise) to the change in x (the run). Since the line is linear, the slope is the same between any two points along the line.
- b is called the y-intercept, which is the value of y when x=0.

Steps for Graphing a Linear Function

1. Pick your range and scale: In graphing a linear function the first step is to identify the range and scale for each axes. The range is defined by the minimum and maximum value along each of the axes. The scale is defined by the values of each line in the grid, which is used both to plot the data points, and once graphed, to read values from the graph. There are often minor and major marks given to the grid, where the major marks show the numerical value of that position.
    - Choosing the Range: There are two approaches. The first is to use the highest and lowest data value as the lower and upper bound of the range, although you may want the actual bounds to be some easy number to read, like a multiple of ten. The second approach is to look at the data, and see if the data is bounded by some real limit. For example, in the above data we are looking at the solubility of a salt in liwuid water, so the temperature range may want to be defined by the temperature range where water is a liquid, even if your highest data point is not at the boiling point, and your lowest is not at the freezing point.
    - Choosing the Scale: Here you want the grid line to be easy to read. If possible, multiple's of 10 are very useful, but you need to look at the data. Want you want to avoid is where each mark is some hard to read value.
2. Plot data: Mark each data point on the graph (like in Figure 1B.5.1, but do not write down the x,y coordinate values, just mark a point on the graph to indicate where there is a data value.
3. Hand draw a best fit line that has an even distribution of points on both sides of the line. If the data is truly a linear function, there will be a random distribution of points along the line. Figure 1b.5.3 shows such a "best fit line".

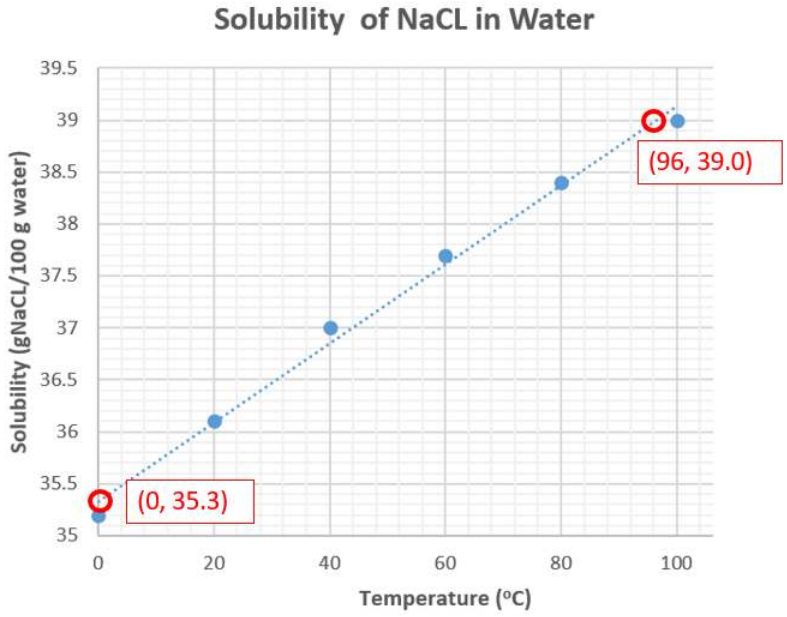


Figure \(\PageIndex{3}]): Best fit line that evenly describes the data. Not we do not connect the points, and some of the points are not on the line.

4. Pick two points to calculate the slope from. Start at the left side and find the point on the line with the smallest values where the line crosses the grid lines, here it is point (0,25.50), and then starting at the right end pick the point with the highest values

(96,39.00).

- Note the precision is defined by both the data and the scale on the grid lines.
  - For the y-axis the precision is defined by the data, and although we have a mark every 0.1 values, so it looks like we could report solubility to the .01 value, the original data was only known to the 0.1 value (table 1B.5.1). So so even though the scale on the graph is more precise, we can only use that precision to read from the scale, and not report the value. That is from the scale we could read to a value of 35.30 and not 35.3, but we must use 35.3 in our calculation
  - For the x-axis the original data has a precision to the 0.1 digit, that is, we have values like 20.0 ^{o}C. But the smallest value on the minor grid axis is 4 ^{o}C, and so we have to "guess" between them to report the uncertainty, and thus choose the precision to be to the "ones" position.
- Note, if we choose points near to each other, we can lose significant digits. For example, if the second point was (4,35.5) the change in temperature would be 4-0 or 4 degrees (1 significant digit), while using the value on the graph give 96-0, or 96 degrees, which has two significant Figures.
- That is, we report all certain, and the first uncertain data point, as read off the graph. A graph scale should never have a smaller scale than the raw data, that is, it can't add to the precision

5. Now calculate the slope

$$\text{slope} = m = \frac{\text{rise}}{\text{run}} = \frac{(y_2 - y_1)}{(x_2 - x_1)} = \frac{(S_2 - S_1)}{(T_2 - T_1)} = \frac{(39.0 - 35.3)}{(96 - 0)} = 0.039 \ \frac{g\ NaCl}{100 g H_2O \cdot\ ^{o}C} \tag{1B.5.8}$$

6. Now calculate the y intercept. Since the graph goes through zero, you can just read it from the graph

- Since the x-axis includes zero, you can simply read it from the graph, b=35.3(gNaCl/100g water).
- If your graph does not include the zero point, you can extrapolate backwards from a given value.
  We know that:

$$m = \frac{\Delta y}{\Delta x} = \frac{\Delta S}{\Delta T} \tag{1B.5.9}$$

If we define S_{20}=solubility when T=20, and S_0=solubility when T=0, then b= S_0, and S_{20} comes from the graph on Figure 1B.5.3 where, **S_{20}=36.1(gNaCl/100g water)**.

$$m = \frac{S_{20} - S_0}{20 - 0} = \frac{S_{20} - b}{\Delta T_{(=20)}} \tag{1B.5.10}$$

Where $\Delta T_{(=20)}$ means the value of ΔT= 20,

solving for b and including units in numerical calculation gives:

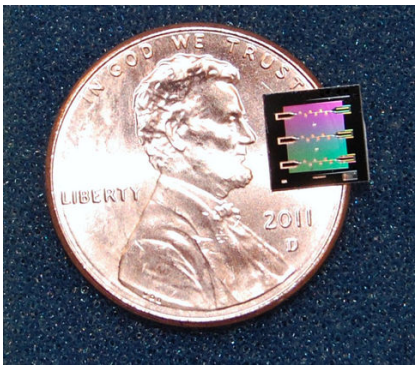
$$b = S_{20} - m(\Delta T_{(=20)}) = 36.1 \left(\frac{g\ NaCl}{100 g H_2O}\right) - 0.039 \ \frac{g\ NaCl}{100 g H_2O \cdot\ ^{o}C} (20\ ^{o}C) = 35.3 \left(\frac{g\ NaCl}{100 g H_2O}\right) \tag{1B.5.11}$$

Temperature Scales

There are three temperature scales you need to be familiar with, Celsius, Kelvin and Fahrenheit. It should also be noted that the term temperature is used in two contexts, the actual temperature of an object, or the temperature change an object undergoes. As we shall see, the temperature of an object in Celsius is different than in Kelvin, but a temperature change in Celsius equals the temperature change in Kelvin.

Kelvin Scale

The kelvin Scale, which is one of the 7 SI base units, and is now defined by four of the SI defining constants (k, h,c & $\Delta\nu_{Cs}$). Kelvin is a thermodynamic temperature scale, and the lowest possible temperature is 0K, absolute zero.



1B.5. 1: Scientists at NIST cooled a "micro drum" fabricated on a sapphire chip like the one on this penny to the lowest possible energy of the "quantum ground state", which was below 400 μ kelvin.

Celsius Scale

The Celsius scale is named after the Swedish astronomer Anders Celsius, who in 1742 created a temperature scale based on the normal (1 atm) melting and boiling points of water. The original Celsius thermometer actually had the boiling point at 0 deg C and the freezing point at 100. A year later this was reversed, with zero being the freezing point and 100 being the boiling point. This early scale was often called the centigrade scale as there were 100 degrees between the normal (1 atm) freezing and boiling points. Today, this is not a valid definition, and the degree Celsius is defined by the Kelvin scale, where the normal boiling point of water (at 1 atm pressure) is 273.15K.

$$T_{Celsius} = T_{kelvin} + 273.15 \tag{1B.5.12}$$

Fahrenheit Scale

This scale was introduced in 1724 by Daniel Gabriel Fahrenheit and there are several stories on how this scale originated, but zero was essentially defined by how cold a salt water solution could be lowered (salt lowers the freezing point of water), and 96 degrees was defined by the human temperature. In 1776 this scale was redefined by two exact points, 32 degrees being the freezing point of water, and 212 being the boiling point.

Temperature Conversions

Figure 1B.3.2 shows the relationship between the three commons scales with values given for absolute zero and the boiling and freezing points of water.

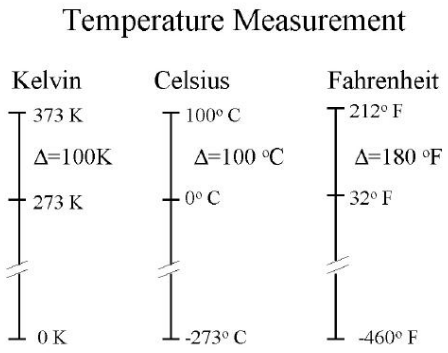


Figure 1B.5. 2: Relationship of the three common temperature scales

Celsius/Kelvin Conversions

Because the kelvin defines the Celsius scale, the conversion is simple.

Celsius to kelvin

$$T_{Celsius} = T_{kelvin} + 273.15 \tag{1B.5.13}$$

Kelvin to Celsius

$$T_{kelvin} = T_{Celsius} - 273.15 \tag{1B.5.14}$$

Celsius/Fahrenheit

Both Celsius and Fahrenheit are linear scales and a plot of data from the freezing point to the boiling point of water can show the relationship. In Figure 1B.3.3 we plot the Fahrenheit values along the ordinate (y-axis) and Celsius along the abscissa (x-axis) and we note there are multiple ways of writing the equation relating Celsius and Fahrenheit.

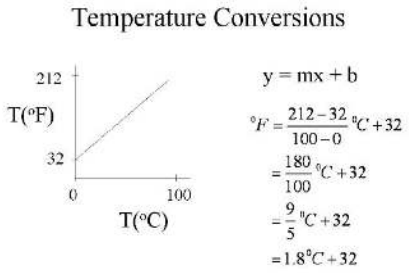


Figure $1B.5.3$: plot of T(F) as a function of T(C)

We note that the above equation has two forms

Celsius to Fahrenheit

$$T_F = 1.8T_C + 32 \tag{1B.5.15}$$

Fahrenheit to Celsius

$$T_C = \frac{T_F - 32}{1.8} \tag{1B.5.16}$$

These equations are much more complicated than the density equation because the y-intercept is not zero. In the following videos we will develop a quick technique for converting between these temperature scales called the Plus 40/minus 40 technique. So first, lets look at the difference between the linear plots of Fahrenheit vs. Celsius and mass vs. volume.



Video $1B.5.1$: Graphing Part 1 - In this video we compare the plot of Fahrenheit and Celsius to that of mass and volume, and see that the density plot is simpler to use because the y-intercept is zero

So what we do is find the temperature at which $T_F = T_C$ and make that value equal to zero

Exercise $1B.5.1$

At what temperature does $T_F = T_C$?

Answer

We start by setting them equal to a common T,

$$T_F = T_C = T$$

Then substitute into the equation and solver for T

$$T = \frac{9}{5}T + 32$$
$$T(1 - \frac{9}{5}) = 32$$
$$T(\frac{-5}{5}) = 32$$
$$T = 32(\frac{-5}{4})$$
$$T = -40$$

.

So the scales converge at -40 degrees.

Plus Forty/Minus Forty Technique

The strategy of the plus forty/minus forty techniques is to make the value where the two scales intersect equal to forty, then the y-intercept is zero, and so you can just multiple or divide by the slope. This is a three step process

1. Add 40 to the number (since the intersected at -40, that value is now zero)
2. multiple or divide by the slope
   - If going from Fahrenheit to Celsius, divide by 1.8
   - If going from Celsius to Fahrenheit, multiply by 1.8
3. Subtract the 40If going from Fahrenheit to Celsius, divide by 1.8

This technique is explained in the following video.

Plus forty/minus forty explained

This video derives the plus forty/minus forty technique



Derivation of the plus forty/minus forty technique

Video $1B.5.2$: Graphing Part 2: temperature conversions

Example $1B.5.7$: Celsius to Fahrenheit

Convert 184K to Fahrenheit

Solution



Note, this video needs to be redone when I get back to AR, as I forgot to write down the negative sign (although I stated it), and the date was wrong, as it was really 1983.

Ans: -128ºF

Video $1B.5.3$: Temperature conversion Plus 40 minus 40 method (C to F)

Exercise $1B.5.1$

Add exercises text here.

Answer

Add texts here. Do not delete this text first.

Example $1B.5.8$: Fahrenheit to Celsius

136 ºF =? ºC

Solution



58ºF

Video $1B.5.4$: Temperature conversion Plus 40 minus 40 method (F to C)

Contributors and Attributions

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1B.6: Algebra Review

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CHAPTER OVERVIEW

2: Atoms, Molecules, and Ions

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2.1: Atoms: Their Composition and Structure
2.2: Isotopes: Atomic Number and Atomic Mass Unit
2.3: Isotope Abundance and Atomic Weight
2.4: The Periodic Table
2.5: Chemical Compounds
2.6: Ionic Compounds and Formulas
2.7: Nomenclature
2.8: Atoms and the Mole
2.9: Calculations Determining the Mass, Moles and Number of Particles
2.10: Percent Composition
2.11: Empirical and Molecular Formulas
2.12: Hydrates

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2.1: Atoms: Their Composition and Structure

Learning Objectives

- Describe the structure of the atom
- Summarize the evolution of atomic theory based on landmark experiments by various scientists
- Define the properties of the subatomic particles including mass and charge

The Nuclear Atom- Overview

The precise physical nature of atoms finally emerged from a series of elegant experiments carried out between 1895 and 1915. The most notable of these achievements was Ernest Rutherford's famous 1911 alpha-ray scattering experiment, which established that

- Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense) *nucleus* which carries a positive electric charge whose value identifies each element and is known as the *atomic number* of the element.
- Almost all of the *volume* of an atom consists of empty space in which electrons, the fundamental carriers of negative electric charge, reside. The extremely small mass of the electron (1/1840 the mass of the hydrogen nucleus) causes it to behave as a quantum particle, which means that its location at any moment cannot be specified; the best we can do is describe its behavior in terms of the probability of its manifesting itself at any point in space. It is common (but somewhat misleading) to describe the volume of space in which the electrons of an atom have a significant probability of being found as the *electron cloud*. The latter has no definite outer boundary, so neither does the atom. The radius of an atom must be defined arbitrarily, such as the boundary in which the electron can be found with 95% probability. Atomic radii are typically 30-300 pm.

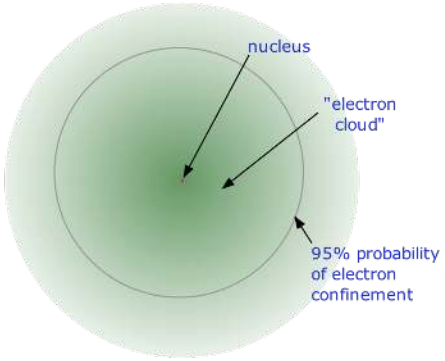


Figure 2.1.1: The structure of the nuclear atom with a central nucleus and surrounding electrons.

The nucleus is itself composed of two kinds of particles. *Protons* are the carriers of positive electric charge in the nucleus; the proton charge is exactly the same as the electron charge, but of opposite sign. This means that in any [electrically neutral] atom, the number of protons in the nucleus (often referred to as the *nuclear charge*) is balanced by the *same* number of electrons outside the nucleus. The other nuclear particle is the *neutron*. As its name implies, this particle carries no electrical charge. Its mass is almost the same as that of the proton. Most nuclei contain roughly equal numbers of neutrons and protons, so we can say that these two particles together account for almost all the mass of the atom.

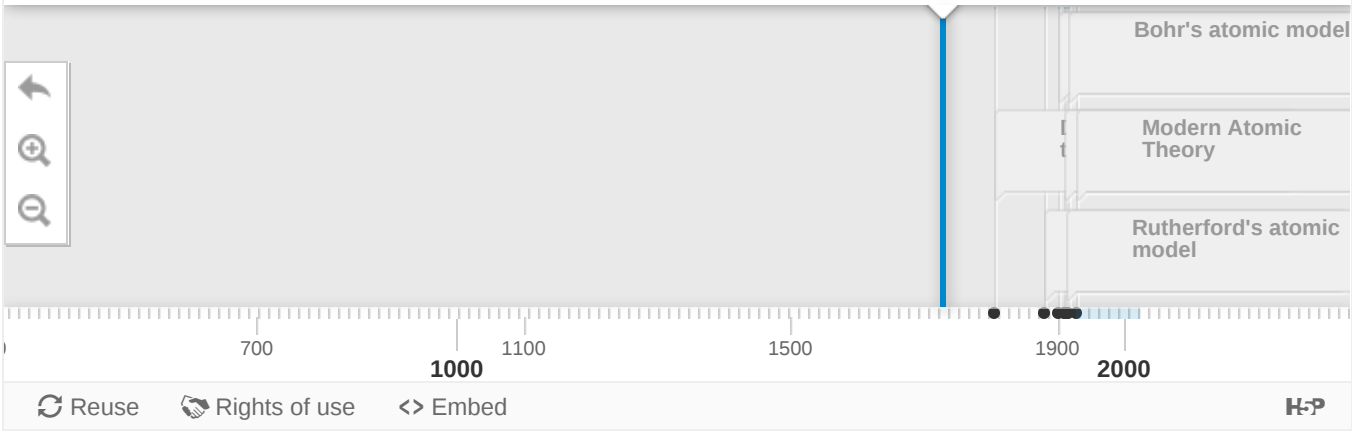
Note

Because the electrons of an atom are in contact with the outside world, it is possible for one or more electrons to be lost, or some new ones to be added. The resulting electrically-charged atom is called an *ion*.

Atomic Theory through the Nineteenth Century

Atomic Theory

Atoms were once thought to be the smallest pieces of matter. However, it is now known that atoms are made up of protons, neutrons, and electrons.



Early Greek Atomistic Philosophers

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for “indivisible.” They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four “elements”—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and “elements” as philosophical concepts, in contrast to the modern scientific method.

John Dalton's Atomic Theory

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton’s hypotheses about the microscopic features of matter are still valid in modern atomic theory.

Five Postulates of Dalton's Atomic Theory

1. **Matter is composed of exceedingly small particles called atoms**. An atom is the smallest unit of an element that can participate in a chemical change.
2. **An element consists of only one type of atom,** which has a mass that is characteristic of the element and is the same for all atoms of that element A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

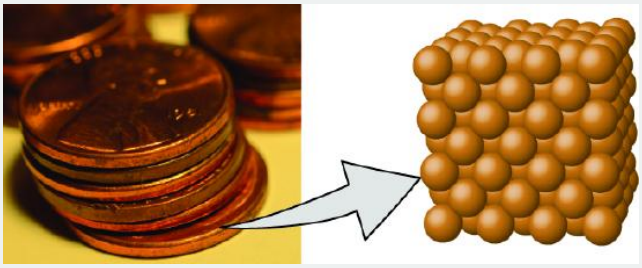


Figure 2.1.2: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by “slgckgc”/Flickr)

3. **Atoms of one element differ in properties from atoms of all other elements**.
4. **A compound consists of atoms of two or more elements combined in a small, whole-number ratio**. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio .
5. **Atoms are neither created nor destroyed during a chemical change**, but are instead rearranged to yield substances that are different from those present before the change.

Atomic Theory late Nineteenth Century and Beyond

Discovery of the Electron

J.J. Thomson: Cathode Ray Tube

If matter is composed of atoms, what are atoms composed of? Are they the smallest particles, or is there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with one of the most significant discoveries being made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms .

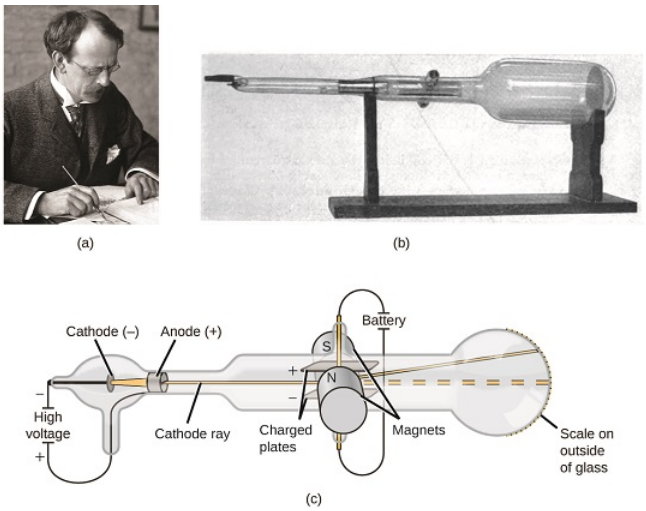


Figure 2.1.3: J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons).

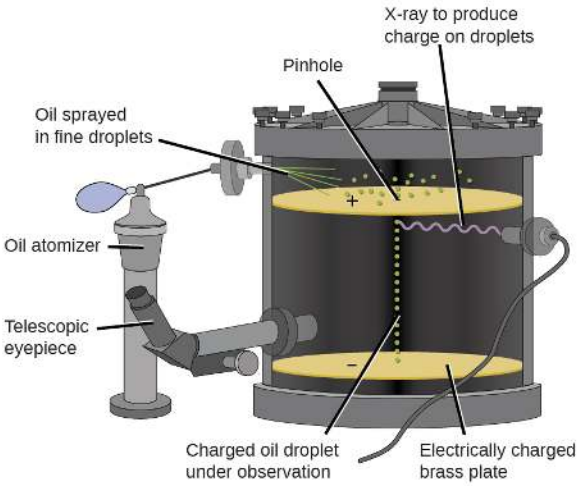
Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we now call an electron, a negatively charged, subatomic particle with a mass less than a thousandth that of a proton. The term "electron" was coined in 1891 by Irish physicist George Stoney, from "electric ion."

Robert Millikan Oil Drop Experiment

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his "oil drop" experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops.



Video 2.1.1: Youtube animation of Millikan's Gold Foil uploaded by HerrPingui



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure 2.1.4: Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

$$\text{Mass of electron} = 1.602 \times 10^{-19} \ \cancel{\text{C}} \times \frac{1 \text{ kg}}{1.759 \times 10^{11} \ \cancel{\text{C}}} = 9.107 \times 10^{-31} \text{ kg} \tag{2.3.1}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the "plum pudding" model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons.

Figure 2.1.5: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "Man vyi"/Wikimedia Commons; credit b: modification of work by "NASA"/Wikimedia Commons).

Radioactivity

The second line of investigation began in 1896, when the French physicist Henri Becquerel (1852–1908) discovered that certain minerals, such as uranium salts, emitted a new form of energy. Becquerel's work was greatly extended by Marie Curie (1867–1934) and her husband, Pierre (1854–1906); all three shared the Nobel Prize in Physics in 1903. Marie Curie coined the term radioactivity (from the Latin *radius*, meaning "ray") to describe the emission of energy rays by matter. She found that one particular uranium ore, pitchblende, was substantially more radioactive than most, which suggested that it contained one or more highly radioactive impurities. Starting with several tons of pitchblende, the Curies isolated two new radioactive elements after months of work: polonium, which was named for Marie's native Poland, and radium, which was named for its intense radioactivity. Pierre Curie carried a vial of radium in his coat pocket to demonstrate its greenish glow, a habit that caused him to become ill from radiation poisoning well before he was run over by a horse-drawn wagon and killed instantly in 1906. Marie Curie, in turn, died of what was almost certainly radiation poisoning.



Figure 2.1.6: Radium bromide illuminated by its own radioactive glow. This 1922 photo was taken in the dark in the Curie laboratory.

Building on the Curies' work, the British physicist Ernest Rutherford (1871–1937) performed decisive experiments that led to the modern view of the structure of the atom. While working in Thomson's laboratory shortly after Thomson discovered the electron, Rutherford showed that compounds of uranium and other elements emitted at least two distinct types of radiation. One was readily absorbed by matter and seemed to consist of particles that had a positive charge and were massive compared to electrons. Because it was the first kind of radiation to be discovered, Rutherford called these substances α particles. Rutherford also showed that the particles in the second type of radiation, β particles, had the same charge and mass-to-charge ratio as Thomson's electrons; they are now known to be high-speed electrons. A third type of radiation, γ rays, was discovered somewhat later and found to be similar to a lower-energy form of radiation called x-rays, now used to produce images of bones and teeth.

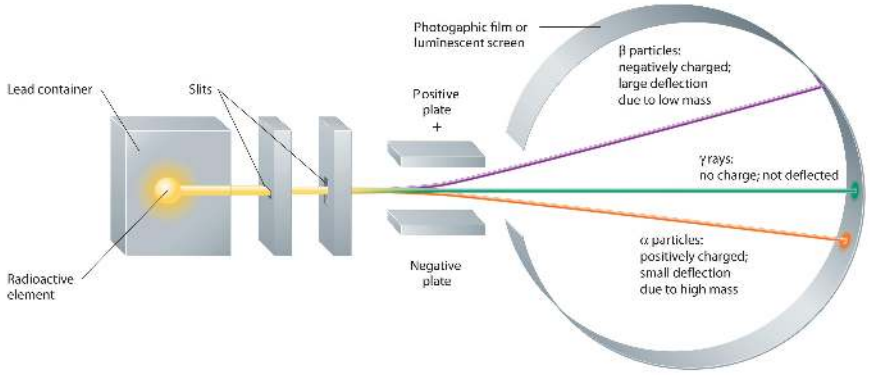


Figure 2.1.7: Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.)

These three kinds of radiation—α particles, β particles, and γ rays—are readily distinguished by the way they are deflected by an electric field and by the degree to which they penetrate matter. As the Figure above illustrates, α particles and β particles are deflected in opposite directions; α particles are deflected to a much lesser extent because of their higher mass-to-charge ratio. In contrast, γ rays have no charge, so they are not deflected by electric or magnetic fields.

Three Common Types of Radiation

1. Alpha (α)- helium nuclei (first to be discovered by Rutherford), are [+] and attracted towards negative electrodes. Under an equivalent electric field α particles are deflected more than β particles and thus have a larger mass..
2. Beta (β) - electrons (second to be discovered), are [-] and attracted towards positive electrodes. Under an equivalent electric field β particles are deflected less than α particles and thus have a smaller mass..
3. Gamma (γ) - high energy light waves (photons), neutral and not attracted towards electrodes.

Rutherford's Gold Foil Experiment and the atomic atom

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged alpha particles (α particles) that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the Chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of

the α particles using a luminescent screen that glowed briefly where hit by an α particle. What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure 2.1.4). Rutherford described finding these results: “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." (Nobel Laureates in Chemistry, 1901-1992, James Laylin, p. 57).

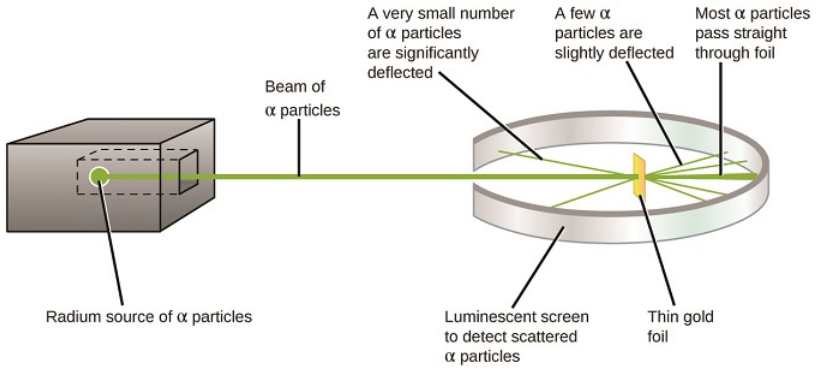
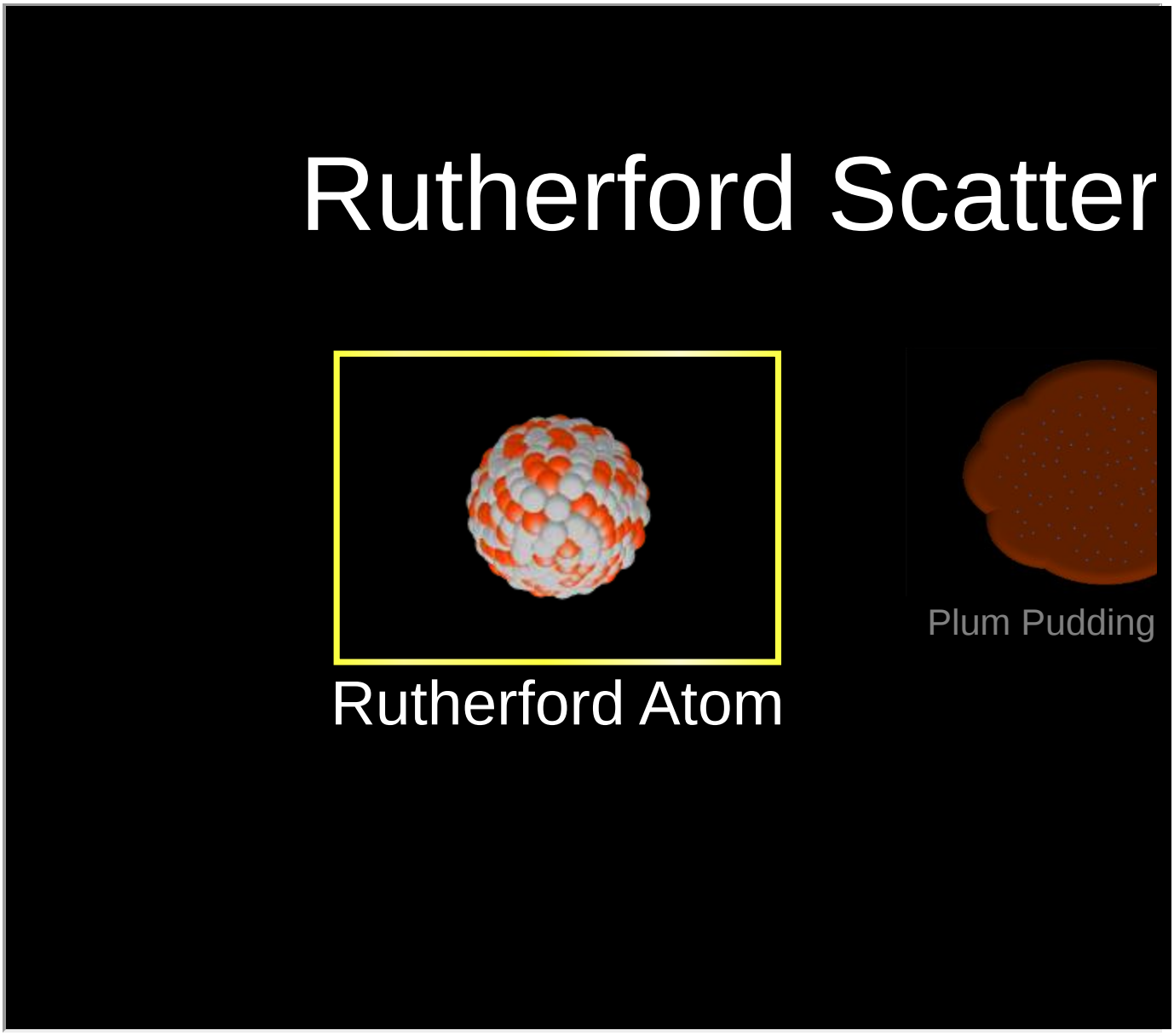


Figure 2.1.8: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

The following Phet simulation allows you to investigate Rutherford's gold foil experiment. At a minimum, you should run this simulatioin in both modes (Rutherford Atom and Plum Pudding), and understand how this experiment changed the scientific view of the atom, and led to the modern atomic model where most of the mass of matter is in the nucleus (neutrons and protons), and most of the volume is the void where the electron orbitals reside.



Simulation 2.1.1: PhET Rutherford Scattering Simulation. On the bottom of the simulation you can switch between the two models of the atom, the Rutherford model and the plum pudding model. If you click on the blue button of the Alpha particles on the left you will start the simulation. On the top left are two ways of viewing the simulation, atomic orbital (default setting), or nuclear view. On the right you can change the energy of the alpha particle, the identity of the material deflecting the alpha particle (number of protons), or the isotope (number of neutrons).

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, **Rutherford drew two conclusions:**

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the nucleus, must be at the center of each atom.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral . After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a

“building block,” and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

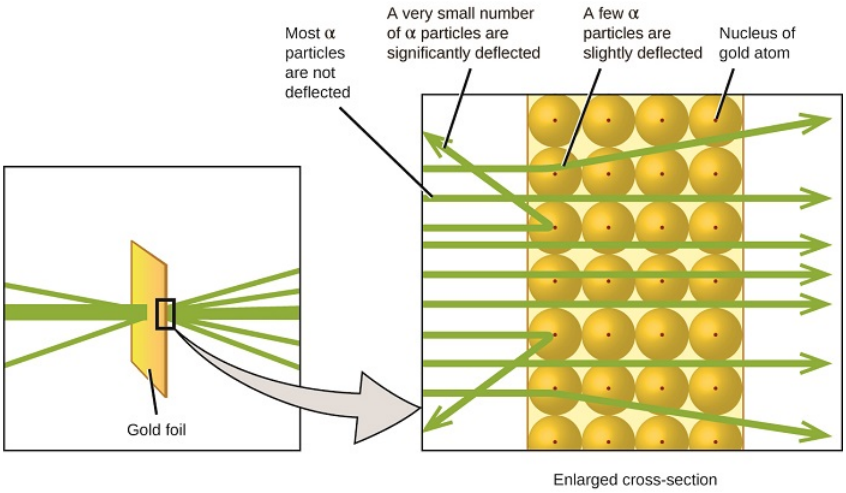


Figure 2.1.9: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.



Video 2.1.2: Youtube video of Rutherford's Gold Foil experiment uploaded by HerrPingui

The Elements

To date, 118 different elements have been discovered; by definition, each is chemically unique. To understand why they are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of its components. Atoms consist of electrons, protons, and neutrons. Although this is an oversimplification that ignores the other subatomic particles that have been discovered, it is sufficient for discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 2.1.1, which illustrates three important points:

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. Relative charges of −1 and +1 are assigned to the electron and proton, respectively.
2. Neutrons have approximately the same mass as protons but no charge. They are electrically neutral.
3. The mass of a proton or a neutron is about 1836 times greater than the mass of an electron. Protons and neutrons constitute the bulk of the mass of atoms.

The discovery of the electron and the proton was crucial to the development of the modern model of the atom and provides an excellent case study in the application of the scientific method. In fact, the elucidation of the atom’s structure is one of the greatest detective stories in the history of science.

Table 2.1.1: Properties of Subatomic Particles (values from NIST Reference on Constants, Units, and Uncertainty).

Particle	Mass (g)*	Atomic Mass (amu)*	Electrical Charge (coulombs)	Relative Charge
electron	$9.1093837015\times10^{-28}$	0.0005485799090	$-1.602176634 \times 10^{-19}$	−1
proton	$1.67262192369 \times10^{-24}$	1.007276466621	$+1.602 \times 10^{-19}$	+1
neutron	$1.67492749804\times10^{-24}$	1.00866491595	0	0

In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties [such as radium (Ra) for its radioactivity], for the native country of the scientist(s) who discovered them [polonium (Po) for Poland], for eminent scientists [curium (Cm) for the Curie], for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to indicate their origin. Examples are Fe for iron, from the Latin *ferrum*; Na for sodium, from the Latin *natrium*; and W for tungsten, from the German *wolfram*. Examples are in Table 2.1.2.

Table 2.1.2: Element Symbols Based on Names No Longer in Use

Element	Symbol	Derivation	Meaning
antimony	Sb	stibium	Latin for "mark"
copper	Cu	cuprum	from Cyprium, Latin name for the island of Cyprus, the major source of copper ore in the Roman Empire
gold	Au	aurum	Latin for "gold"
iron	Fe	ferrum	Latin for "iron"
lead	Pb	plumbum	Latin for "heavy"
mercury	Hg	hydrargyrum	Latin for "liquid silver"
potassium	K	kalium	from the Arabic al-qili, "alkali"
silver	Ag	argentum	Latin for "silver"
sodium	Na	natrium	Latin for "sodium"
tin	Sn	stannum	Latin for "tin"
tungsten	W	wolfram	German for "wolf stone" because it interfered with the smelting of tin and was thought to devour the tin

Vocabulary

Test Yourself

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Elena Lisitsyna (H5P interactive modules)
- Anonymous
- Material adapted from Open Stax

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2.2: Isotopes: Atomic Number and Atomic Mass Unit

Learning Objectives

1. Differentiate between atomic number and mass number
2. Define isotopes
3. Compare characteristics of varying isotopes
4. Define the atomic mass unit
5. Convert between amu's and grams

Atomic Number and Mass Number

When you study the periodic table, the first thing that you may notice is the number that lies above the symbol. This number is known as the **atomic number**, which identifies the number of protons in the nucleus of ALL atoms in a given element.

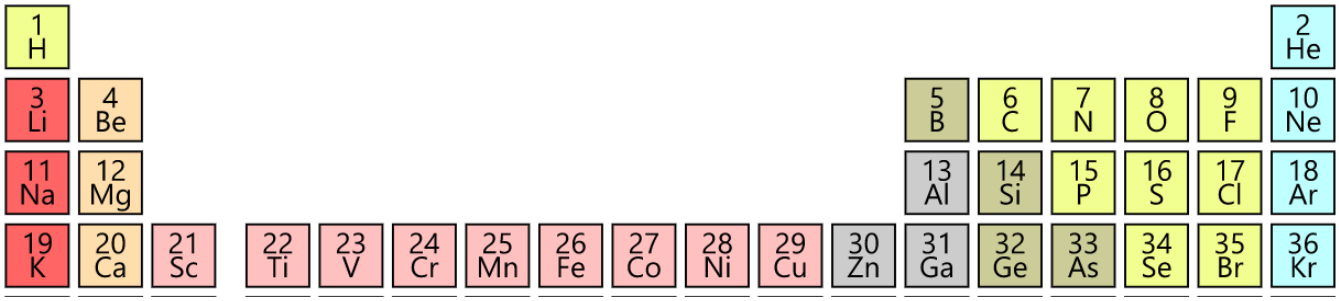


Figure 2.2.1: First four rows of the periodic table showing the atomic number Z for each of the elements, which is the number of protons an atom of that element contains.

The symbol for the atomic number is designated with the letter **Z**. For example, the atomic number (z) for sodium (Na) is 11. That means that all sodium atoms have 11 protons. If you change the atomic number to 12, you are no longer dealing with sodium atoms, but magnesium atoms. Hence, the atomic number defines the element in question.

Recall that the nuclei of most atoms contain neutrons as well as protons. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called **isotopes**. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemical behavior. Because different isotopes of the same element haves different number of neutrons, each of these isotopes will have a different **mass number(A)**, which is the sum of the number of protons and the number of neutrons in the nucleus of an atom.

Mass Number(A) = Number of Protons + Number of Neutrons

The element carbon (C) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of 12. An isotope of any element can be uniquely represented as $^{A}_{Z}\mathbf{X}$, where X is the atomic symbol of the element, A is the mass number and Z is the atomic number. The isotope of carbon that has 6 neutrons is therefore $^{12}_{6}\mathbf{C}$. The subscript indicating the atomic number is actually redundant because the atomic symbol already uniquely specifies Z. Consequently, it is more often written as $^{12}\boldsymbol{C}$, which is read as "**carbon-12**." Nevertheless, the value of Z is commonly included in the notation for nuclear reactions because these reactions involve changes in Z.

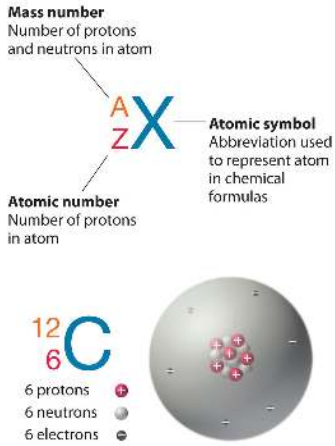


Figure 2.2.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

Atomic Mass Unit (Dalton)

The atomic mass unit (u, amu or Da) is a relative unit based on a carbon-12 atom with six protons and six neutrons, which is assigned an exact value of 12 amu's (u's). This is the common unit for atomic or molecular mass, and 1 amu is thus $1/12^{th}$ the mass of a ^{12}C atom. Using this definition, and relating it to the standard mass of the kilogram, one sees the obvious, that the amu is a very small number.

$$\mathbf{1\ amu = 1.66054x10^{-27}Kg = 1.66054x10^{-24}g = 1.66054\ yoctograms}$$

The amu is also called the Dalton and large molecules like proteins, nucleic acid and large polymers are often expressed in Kilo Daltons ($1kDA=10^3$ Da) or Mega Daltons ($1MDa=10^6$ Da).

As a result of this definition, the mass of all other elements on the periodic table are determined relative to carbon-12.

Isotopes

Isotopes are different atoms of the same element that contain different numbers of neutrons in their nucleus, and therefore they have different atomic masses. There are essentially two types of isotopes, stable isotopes and radioactive isotopes. A radioactive isotope or radioisotope is an isotope that undergoes a radioactive decay where the number of protons changes over time and when this occurs an atom of one element is transmuted into another element. This is called a nuclear transmutation. Three types of radioactivity were described in the previous section, α, β amd γ (section 2.1.3). When an atom undergoes α decay it looses two protons and when it undergoes β decay it gains a proton, and thus these two types of radiation cause nucelear transmutations. γ radiation does not affect the elemental identity of an atom. The rate at which a radioisotope decays is often described by its half life, which is the amount of time it takes for half of a sample to undergo a nuclear transmutation. There are more than 3,000 natural and artificial known isotopes, with many of them having short half lives (less than a month). Note, some radioisotopes have very long half lives (billions of years) and so are essentially stable on human time lines.

Example 2.2.1

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

Given: number of protons and neutrons

Asked for: element and atomic symbol

Strategy:

1. Refer to the periodic table and use the number of protons to identify the element.
2. Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.
3. Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

Solution:

A The element with 82 protons (atomic number of 82) is lead: Pb.

B For the first isotope, A = 82 protons + 124 neutrons = 206. Similarly, A = 82 + 125 = 207 and A = 82 + 126 = 208 for the second and third isotopes, respectively. The symbols for these isotopes are $^{206}_{82}Pb$, $^{207}_{82}Pb$, and $^{208}_{82}Pb$, which also can also be symbolized as Pb-206, Pb-207, and Pb-208.

Exercise 2.2.1

What is the mass number of a phosphorous atom with 16 neutrons

Answer

31

Exercise 2.2.2

How many protons, neutrons, and electrons are in As-74 atom?

Answer

33 protons, 41 neutrons, 33 electrons

Exercise 2.2.3

The actual mass of As-74 is 73.924 amu's.

A) What is the mass of As-74 in grams?

B) What is the mass of the arsenic atom relative to the carbon-12 atom?

Answer

A) Mass of As-74 = (73.924 amu) x (1.66054×10^{-24} g/amu) = 1.2275×10^{-22} g

B) Mass of As-74/Mass of C-12 = 73.924 amu/12.000 amu= 6.1603 ... so, the mass of an As-74 atom is 6,1603 times more than a C-12 atom.

Vocabulary

Test Yourself

Contributors and Attributions

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2.3: Isotope Abundance and Atomic Weight

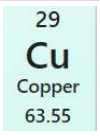
learning objectives

1. Define atomic weight
2. Calculate atomic weight from percent abundance
3. Manipulate the atomic weight equation to calculate various unknown variables
4. Distinguish between atomic weight, atomic number, and mass number

Atomic Weight

The atomic weight is the mass of an atom, typically expressed in atomic mass units (amu). For an isotope, it is the mass of the nucleus, that is the mass of the protons and neutrons, as the mass of the electrons are considered negligible. In their natural state only 21 elements exist as single isotopes, that is a sample has nuclei of only one isotope, and these are called the mononuclidic elements. Most elements exist as a mixture of nuclei from multiple isotopes, and these are labeled as the polynuclidic elements. The atomic weight of a monuclidic element is that mass of that nuclide.

For a polynuclidic element the atomic weight is the average weight based on the fractional abundance of each isotope, and this is the value given on the periodic table. Copper has two isotopes, ^{63}Cu (69.15%, mass=62.9300 amu) and ^{65}Cu (30.85%, mass = 64.928 amu), and so the respective mole fractions are 0.6915 and 0.3085, resulting in an average atomic weight of 63.55 amu, even though there is not a single atom that weighs 63.55 amu.



$$\underbrace{0.6915}_{fraction\ ^{63}Cu}\ \underbrace{(62.9300\,amu)}_{mass\ ^{63}Cu} + \underbrace{0.3085}_{fraction\ ^{65}Cu}\ \underbrace{(64.928\,amu)}_{mass\ ^{65}Cu} = \underbrace{63.55\,amu}_{\text{average mass}}$$

$$note:\ 0.6915 + 0.3085 = 1$$

Figure 2.3.1: Natural samples of copper contain two isotopes, and its atomic weight is to four significant digits is 63.55 amu, even though there is not a single atom of copper that weights 63.55 amu.

Exercise 2.3.1

The atomic weight of chorine is _____and the atomic number of chlorine-35 is_____.

a. 35, 17
b. 17, 35
c. 35.4527; 17
d. 35.4527; 35

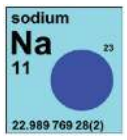
Answer

C) the atomic weight is the average of mass of all isotopes of chlorine atoms and found below the symbol on the periodic table. The atomic number is the number of protons in all chlorine atoms and is found on the top of the symbol in the periodic table.

Mononuclidic Elements

There are 21 elements with natural occurring samples that have only have one nucleus and are thus classified as mononuclidic. Nineteen of these are stable and two are radioactive (Bi & Th). The term monoisotopic refers to having only 1 stable nucleus, of which there are 26, ninteen of which are mononuclidic, but seven of the monoisotopic elements also have radioactive isotopes and so are not mononuclidic, but polynuclidic.

For a mononuclidic element, the atomic weight is the weight of its isotope. Sodium is a stable mononuclidic element that consists of just one isotope, ^{23}Na.



Stable Isotope	Relative Atomic Mass	Mole Fraction
^{23}Na	22.989 769 29	1

Figure 2.3.1: Sodium only has one isotope, and note, the uncertainty of this value is expressed by the (2) in 22.989 769 28(2), indicating that the last value has an uncertainty of +/- .000 000 02. Adapted from 2018 IUPAC Technical Report - IPTEI for Education Community, (cc. 4.0), p. 1864.

The following lists the 21 stable mononuclidic elements:

Table 2.3.1: List of the Mononuclidic elements, note, ^{232}Th has a half life of $1.4x10^{10}years$, while ^{209}Bi has one of $2x10^{19}years$, and so even though they are radioatcive, natural samples only have one isotope (Th is 99.98% ^{232}Th and 0.02% ^{230}Th) .

$^{27}_{13}Al$	$^{75}_{33}As$	$^{9}_{4}Be$	$^{209}_{83}Bi^{*}$	$^{133}_{55}Cs$	$^{59}_{27}Co$	$^{19}_{9}F$

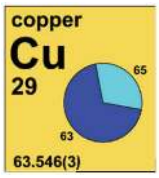
$^{197}_{79}Au$	$^{165}_{67}Ho$	$^{127}_{53}I$	$^{55}_{25}Mn$	$^{93}_{41}Nb$	$^{31}_{15}P$	$^{141}_{59}Pr$
$^{103}_{45}Rh$	$^{45}_{21}Sc$	$^{23}_{11}Na$	$^{159}_{65}Tb$	$^{232}_{90}Th^{*}$	$^{169}_{69}Tm$	$^{89}_{39}Y$

Polynuclidic Elements

The vast majority of elements are polynuclidic, that is, a sample contains a mixture of nuclei from different isotopes. For some samples the fraction of each isotope is constant, while for others itf varies between samples. So there are two types of polynuclidic elements, those with invariant isotopic distributions, and those with variable isotopic distributions.

Constant Isotopic Distributions

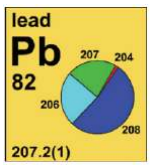
For example, copper has two stable isotopes, and is approximately 69% ^{63}Cu and 31% ^{65}Cu by number (not mass). This ratio is constant from sample to sample and so it is invariant. The atomic weight of copper is based on this isotropic distribution and comes out to 63.546 amu, even though there is not a single atom of copper that weighs 63.546 amu (69% of them weigh 63 amu and 31% weigh 65).



Stable Isotope	Relative Atomic Mass	Mole Fraction
^{63}Cu	62.929 597	0.6915
^{65}Cu	64.927 790	.3085

Figure 2.3.3: Copper has two stable isotopes as indicated in the pie diagram. *Adapted from 2018 IUPAC Technical Report - IPTEI for Education Community, (cc. 4.0), p. 1901.*

Lead has 4 stable isotopes as shown in Figure . Lead is a fairly large element and has many radioisotopes, in fact it has 29 isotopes with a half life of less than one hour, seven between an hour and a year, and two with half lives over a year (^{202}Pb = 5.25x10^{4} years & ^{210}Pb = 22.3 years), but these are insignificant to the thousandth position (note the four mole fractions add to one).



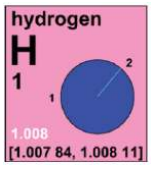
Stable Isotope	Relative Atomic Mass	Mole Fraction
^{204}Pb	203.973 043	0.014
^{206}Pb	205.974 465	0.241
^{207}Pb	206.975 897	0.221
^{208}Pb	207.976 652	0.524

Figure 2.3.4: Lead has 4 stable isotopes. Adapted from 2018 IUPAC Technical Report - IPTEI for Education Community, (cc. 4.0), p 2007.

Variable Isotopic Distributions

Until recently, it was thought that the isotopic composition of an element was constant, but now it is realized that these can vary across samples. To date, the following 13 elements have been identified to have a range of isotopic distributions; hydrogen, lithium, boron, carbon, nitrogen, oxygen, magnesium, silicon, sulfur, chlorine, argon, bromine, and thallium. In 2009 the IUPAC Commission on Isotopic Abundances and Atomic Weights introduced an interval notation on atomic weights that expressed the natural occurring variability in the isotopic composition of the elements.

Hydrogen consists of two isotopes, protium (^{1}H, a single proton) and deuterium (^{2}H, a proton and a neutron). The isotopic composition of different samples vary within the defined ranges, so the percent protium ranges from 99.999% to 99.972%. There is a third naturally occurring radioactive isotope of hydrogen, ^{3}H (tritium), which is very rare and has a mole fraction that is so small that it is insignificant compared to protium and deuterium.



Stable Isotope	Relative Atomic Mass	Mole Fraction
^{1}H	1.007 825 0322	[0.999 72, 0.999 99]
^{2}H	2. 014 101 7781	[0.000 01, 0.000 28]

Figure 2.3.5: Hydrogen's Isotopic distribution can vary from sample to sample and so IUPAC introduced an interval notation. *Adapted from 2018 IUPAC Technical Report - IPTEI for Education Community, (cc. 4.0)*, p 1839.

These differences can actually show up in the hydrogen atomic weight in river water, where for example, water in the mountains will have a higher proportion of the heavier isotope, and this makes sense, as the heavier isotope would condense into rain easier than the lighter, and water at lower

elevations would tend to have more of the lighter isotope. This can be seen in Figure 2.3.6.

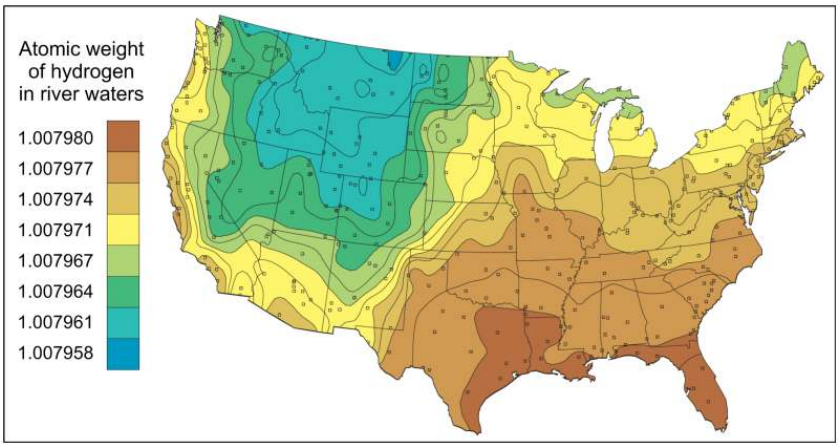


Figure 2.3.6: This map shows the variance of hydrogen's isotopic distribution from various water samples across the U.S.. Adopted from 2018 IUPAC Technical Report - IPTEI for Education Community, (cc. 4.0), p. 1840.

Note: The sum of the percent natural abundances of all the isotopes of any given element must total 100%.

Some naturally occurring and artificially produced isotopes are radioactive. All atoms heavier than Bismuth ($^{209}_{83}Bi$) are radioactive. However, there are many lighter nuclides that are radioactive. For example, hydrogen has two naturally occurring stable isotopes, ^{1}H and ^{2}H (deuterium), and a third naturally occurring radioactive isotope, ^{3}H (tritium).

Measuring Isotopic Abundances

The Mass Spectrometer is an instrument that allows us to measure the mass of atoms, or more accurately, the mass to charge ratio. In Figure 2.3.8 you can see chlorine gas entering an mass spectrometer. The chlorine has multiple isotopes and is hit with a stream of ionizing electrons which break the bond of Cl_2 and strip electrons off the chlorine atoms causing monatomic ions. These are then accelerated down the chamber until they reach a magnetic field that deflects the particles. The angle of deflection depends on both the mass of the particle and the magnetic field strength, with the lighter particles being deflected more for a constant magnetic field strength (*the lighter $^{35}Cl^{+}$ ions are deflected more than the heavier $^{37}Cl^{+}$ ions*.) At the end of the chamber is an exit hole with a detector, and as the magnetic field intensity is increased the deflection angle changes, which separates the particles. Note, the mass spectrum in Figure 2.3.8 (b) gives the relative abundance of each isotope, with the peak normalized to the isotope with the highest abundance. So if this ratio was 3:1 that means there are 3 particles of ^{35}Cl for every particle of ^{37}Cl, and the fractional abundance would be 0.75 for ^{35}Cl and 0.25 for ^{37}Cl.

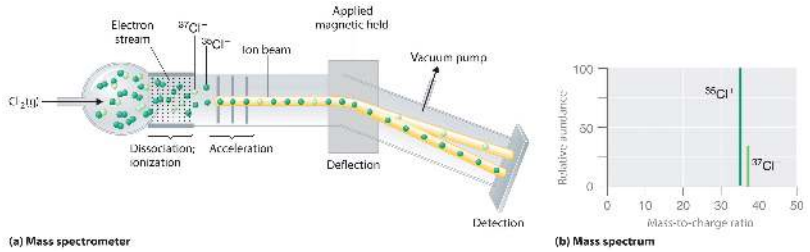


Figure 2.3.8: Determining Relative Atomic Masses Using a Mass Spectrometer. Image used wtih permission (CC BY-SA-NC; Anonymous by request).

Below is a video from YouTube describing the mass spectrometer



Video 2.3.1: 2:43 YouTube uploaded by Evagating on how a mass spectrometer works.

Here is a bar chart showing the relative abundance of 4 isotopes of strontium

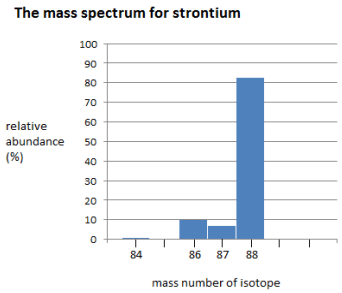


Figure 2.3.9: Bar chart showing the relative isotopic percent abundance for the four isotopes of strontium.

The mass spectrum of strontium has four different peaks, varying in intensity. The four peaks indicate that there are four isotopes of strontium. The four isotopes of strontium have isotopic mass numbers of 84, 86, 87, and 88, and relative abundances of 0.56%, 9.86%, 7.00%, and 82.58%, respectively. The intensity of the peak corresponds to the abundance. ^{84}Sr has the smallest peak, which corresponds to its relative abundance of 0.56%, whereas ^{88}Sr has the largest peak, which corresponds to its relative abundance of 82.58%. This indicates that ^{88}Sr is the isotope that occurs in highest amounts.

Exercise 2.3.2

Nitrogen has two isotopes, the first isotope has a mass of 14.004amu, while the second isotope has a mass of 15.000 amu, which isotope has the greatest natural abundance? Tip, you need to look at the periodic table.

a. ^{14}N
b. ^{15}N
c. There are equal amounts.
d. Not enough information provided.
e. none of the above

Answer

A)The average atomic weight is 14.007 amu which is much closer to 14 then 15, so 14 is the most abundant isotope. In the next section you will use this kind of data to calculate fractional abundances.

Isotopic Abundance Calculations

For elements with more than one isotope there are a variety of problems you need to be able to solve. You not only need to be able to calculate the average mass from the isotopic abundance and masses, but go backwards, using the atomic weight on the periodic table as the average atomic mass. Rewriting eq. 2.3.1 in terms of algebraic variables gives us a feel for the types of problems. Consider an element with two isotopes A & B, each having a mass of m_A or m_b and a mole fraction of X_A or X_bb .

$$\underbrace{X_A}_{\text{fraction A}}\ \underbrace{(m_A)}_{\text{mass A}} + \underbrace{X_B}_{\text{fraction B}}\ \underbrace{(m_B)}_{\text{mass B}} = \underbrace{m_{ave}}_{\text{average mass}} \tag{2.3.2}$$

In general the equation for an element with [n] isotopes is:

$$\sum_{i=1}^{n} X_i m_i = m_{ave} \tag{2.3.3}$$

Note, the equation for two isotopes has 5 unknowns, and you can get m_{ave} from the periodic table, so you need to be given three of the other variables to solve the equation (one equation can only be solved for one unknown). But there is another equation we can use to reduce the number of unknowns. That is the sum of the fractions equals 1

$$X_A + X_B = 1 \tag{2.3.4}$$

or in general

$$\sum_{i=1}^{n} X_i = 1 \tag{2.3.5}$$

In the following problem we look

you not only need to be able to calculate the average atomic mass, but also need to be use the average mass on the periodic table to work backwards and calculate percent

Example 2.3.1: Calculating Average Atomic Mass

What is the average atomic mass of Neon, given that it has 3 isotopes with the follow percent abundances;

^{20}Ne = 19.992 amu (90.51%), ^{21}Ne = 20.993 amu (0.27%), ^{22}Ne = 21.991 amu.

What we know: since you know what the element is, you can solve this without doing any math by using the periodic table, but you need to be able to do the math because it might be an unknown, and that is the only way you can Figure out the correct significant Figures.

Since Ne-20 has the greatest percent abundance, it should have the most impact on your average. Therefore, we expect the average atomic mass to be closer to the mass of Ne-20 (about 19.992 amu). Click the following video tutor to see if we estimated correctly.



Video 2.3.2: 4:53 minute YouTube solving above problem.

Answer According to the correct number of significant Figures, we came up with 20.18 amu as the average atomic weight even though the average atomic weight from the periodic table is 20.179 amu. However, it is still a good check to make sure that you are on the right path.

Check Yourself: We predicted earlier that our answer should be closer to the mass of Ne-20 (19.992 amu) instead of Ne-21 or Ne-22 because it has the greatest natural abundance, and thus, impacts the average more. We can see that the math does align with our logic!

Example 2.3.1: Isotopic Mass Calculation

Chlorine has two isotopes, with 75.53% being ^{35}Cl with an isotopic mass of 34.969 amu, what is the mass of the other isotope?

What we know: In this case, you have the average atomic mass (from the periodic table). You are trying to find the mass of the individual isotope. You also know that the individual isotopes have to add up to 100%.



Answer: The correct answer is 36.9 amu.

After watching the following two YouTubes, you should do the following worksheets, which were designed as in class activities for the prep course, and so give more step-by-step instructions than we are using. You will want to be able to bypass many of the "steps" in the handouts as these were designed for the preparatory chem 1300 class, which spent more time on this material. Also, note the handouts are posted as PDF files, and you can use the hypothes.is annotation system to comment on them, and if you tag them with the tag **f19c1402c2**, they will appear on the table of contents for this Chapter.

Isotope Abundance Worksheets:

Isotope Abundance Worksheet

Key to Isotope Abundance Worksheet

Vocabulary

Test Yourself

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Anonymous
- Ronia Kattoum & November Palmer (UA Little Rock)
- Elena Lisitsyna (H5P interactive modules)

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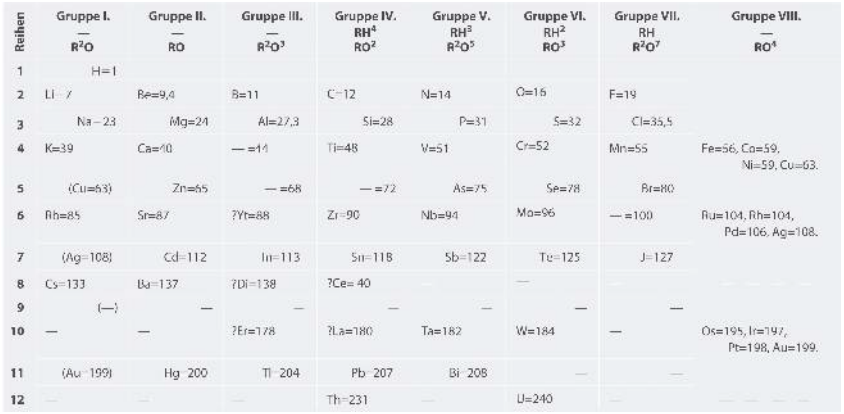
2.4: The Periodic Table

Learning objectives

1. Describe the evolution of the periodic table
2. Memorize terminology used to describe the periodic table (periods, groups, group numbers, and group names).
3. Locate elements on the periodic table and classify them as metals, nonmetals, metalloids
4. Infer likely properties of elements based on their position on the periodic table.

Mendeleev's Periodic Table

Mendeleev, who first published his periodic table in 1869 (Figure 2.4.1), is usually credited with the origin of the modern periodic table. One key difference between his arrangement of the elements and that of others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.



Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140				
9								
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208			
12				Th=231		U=240		

***Figure* 2.4.1** *Mendeleev's Periodic Table, as Published in the German Journal* Annalen der Chemie und Pharmacie *in 1872. The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.*

The groups in Mendeleev's table are determined by how many oxygen or hydrogen atoms are needed to form compounds with each element. For example, in Group I, two atoms of hydrogen, lithium, Li, sodium, Na, and potassium form compounds with one atom of oxygen. In Group VII, one atom of fluorine, F, chlorine, Cl, and bromine, Br, react with one atom of hydrogen. Notice how this approach has trouble with the transition metals. Until roughly 1960, a rectangular table developed from Mendeleev's table and based on reactivity was standard at the front of chemistry lecture halls.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Figure 2.4.1). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, eka-aluminum and eka-silicon (from the Sanskrit eka, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of eka-aluminum and eka-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.



Video 2.4.1: 4:24 min YouTube by TED-Ed on Mendeleev's periodic table, https://youtu.be/fPnwBITSmgU

The Modern Periodic Table

Since Mendeleev's development of the first periodic table and various scientists working to fill in the gaps, the modern periodic table now has 118 known elements. You may click on any element in the following periodic table for every known detail about every element that has been discovered or synthesized.

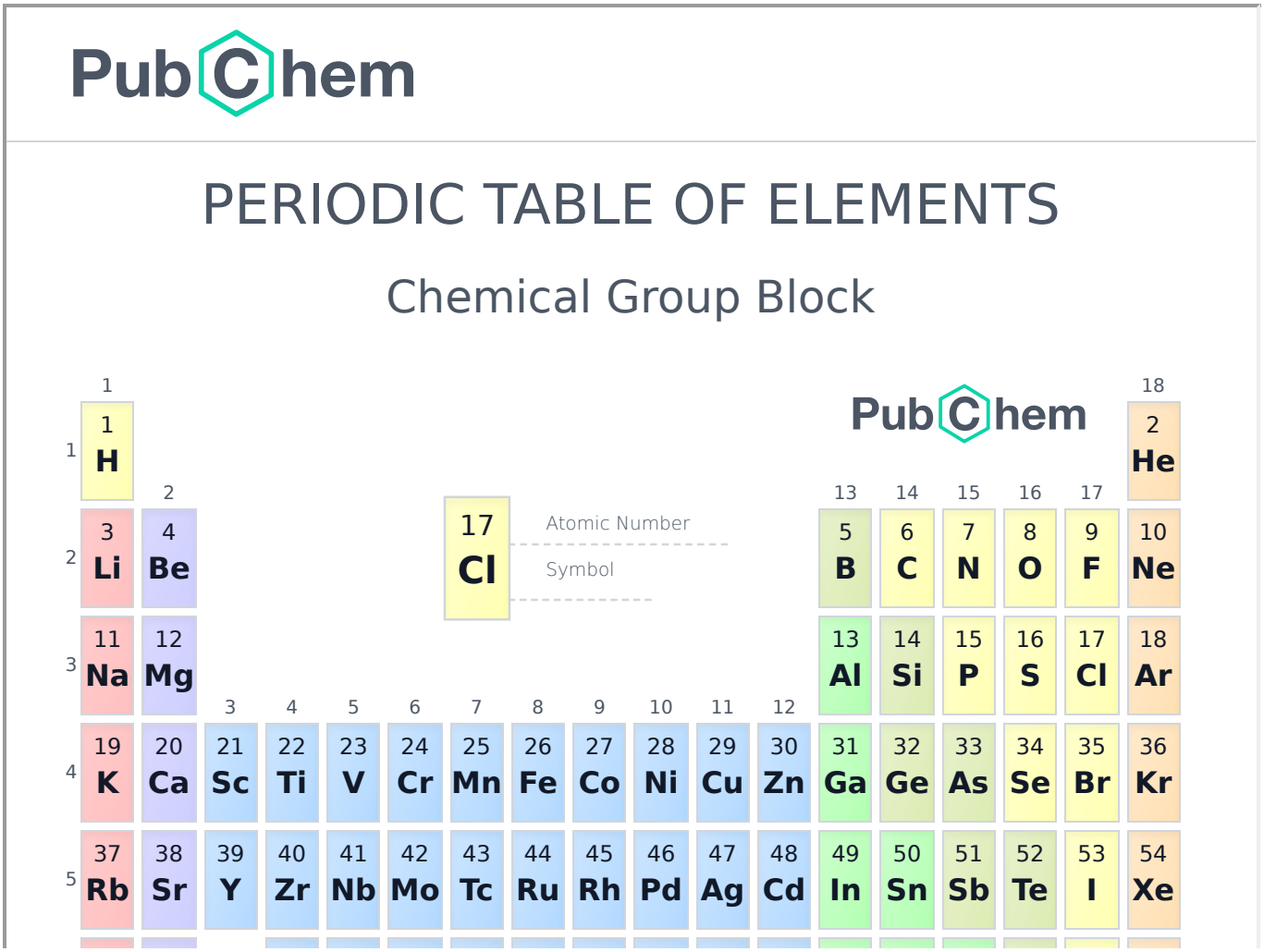




Figure 2.4.2: PubChem's Interactive periodic table of the elements, https://pubchem.ncbi.nlm.nih.gov/periodic-table/. This table is color coded: alkali metals, alkaline earths, transition metals, post transition metals, metalloids, nonmetals, noble gasses actinides and lanthanides

Note, if you click on an element information appears, along with a link to that element's page. Clicking that link takes you to PubChem's datapage for that element. PubChem is part of the U.S. National Institute of Health's Library of Medicine, and aggregates data from multiple resources. There is a link within PubChem to the actual data source for each element. So note, if you click on carbon and go to section 2.1 (Atomic Weight) of its data page, you see values from IUPAC, The U.S. Department of Energy (Jefferson Lab and Los Alamos) and NIST. IUPAC and NIST provide interval values, will the DOE does not. If you then click on IUPAC, it sends you to the Commission on Isotopic Abundances and Atomic Weights page for Carbon. Note that for carbon-12 the atomic weight is exactly 12 Da (Daltons). The fact that PubChem maintains the data provenance makes it a very important resource, as it is important to know the source of your information. This periodic table also has a dropdown box that allows you to display various properties (like atomic size, chemical groups,...)

Classification of the Periodic Table

If you tried to click on any of the above elements, the details of each element may seem overwhelming and it may seem incredibly difficult to find patterns. However, the beauty of the periodic table is found in it's *periodicity*, repeating patterns that help us predict

physical and chemical properties of various elements. Thus the periodic table can also be split into seven rows, known as **periods** (Figure 2.4.4). At first glance, it may seem like the two lone rows at the bottom of the period table, known as the **actinide and lanthanide series** should be periods 8 and 9. However, if you look carefully, these two row should actually be wedged in the 6th and 7th period, respectfully, in order to follow the order of increasing atomic number. Those rows are kept at the bottom to decrease the width of the periodic table and are also known as the **inner transition metals.**

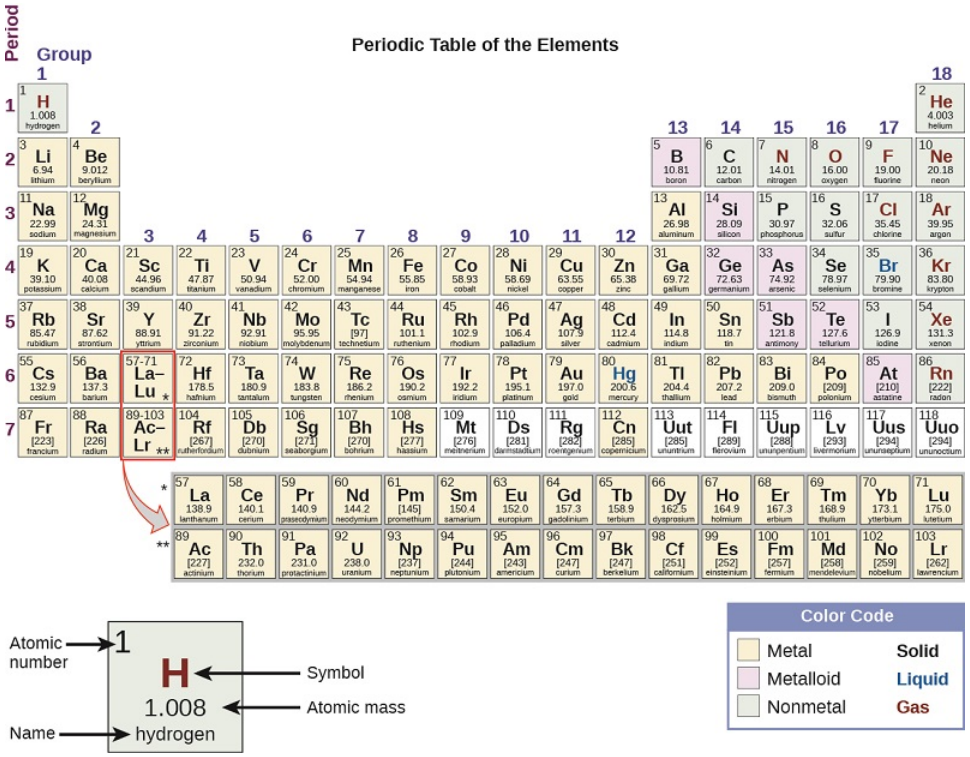


Figure 2.4.3: The periodic table is split into seven periods(rows) with the **inner transition metals** shown separately on the bottom to decrease the width of the periodic table. It can also be broadly divided into metals, nonmetals, and metalloids(semimetals). The states of the elements is also indicated at room temperature of 25° C.

Groups can be numbered as 1-18 (Figures 2.4.3 or 2.4.4) or they can be numbered 1-8 followed by "A" or "B" (Figure 2.4.5). The "A" designation represents the **main group elements** (Columns 1-2, and Columns 13-18) The "B" designation represents **transition elements** (Columns 3-12). Either group numbering system is acceptable, but we will see later that there is a benefit for knowing the group numbers with the "A" and "B" designation. In addition, some of the individual groups have a particular group name. For example, Group 17 or 7A elements are also known as the **halogens.** Group 2 or 2A elements are known as the **alkaline group metals.** Group names are commonly used by chemists and are worth knowing. But, most importantly, elements in the same groups tend to have similar chemical and physical properties. We will also discuss the reason behind such patterns later in this text. Figure 2.4.4 provides the common names of the groups.

Exercise 2.4.1

Which of the following elements will most likely have similar chemical properties to fluorine?

A) neon

B) nitrogen

C) iodine

D) sulfur

Answer

C) iodine. Elements in the same **group** have similar chemical properties, not the same periods.

The Families of the Periodic table

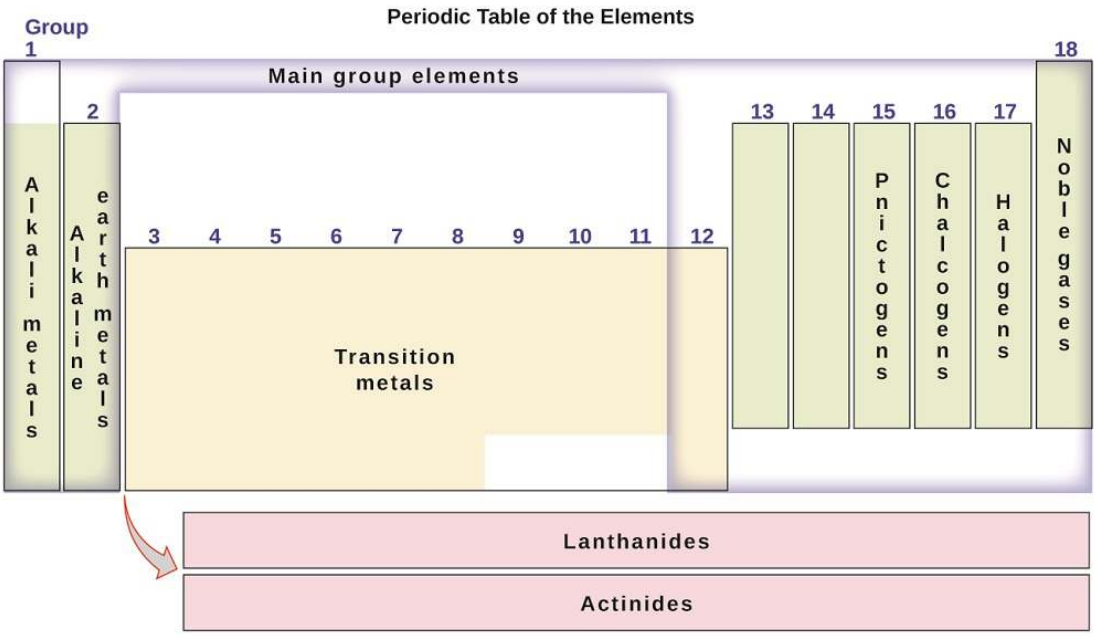


Figure 2.4.4: Families or groups of the Periodic Table

Exercise 2.4.2

What alkali metal is found in period 4?

A) carbon

B) potassium

C) calcium

D) Titanium

Answer

B) Potassium is in Group (Column) 1A and is in the 4th period (row).

Figure 2.4.4: Modern Family or group numbering system for the Periodic Table along with the names of the families.

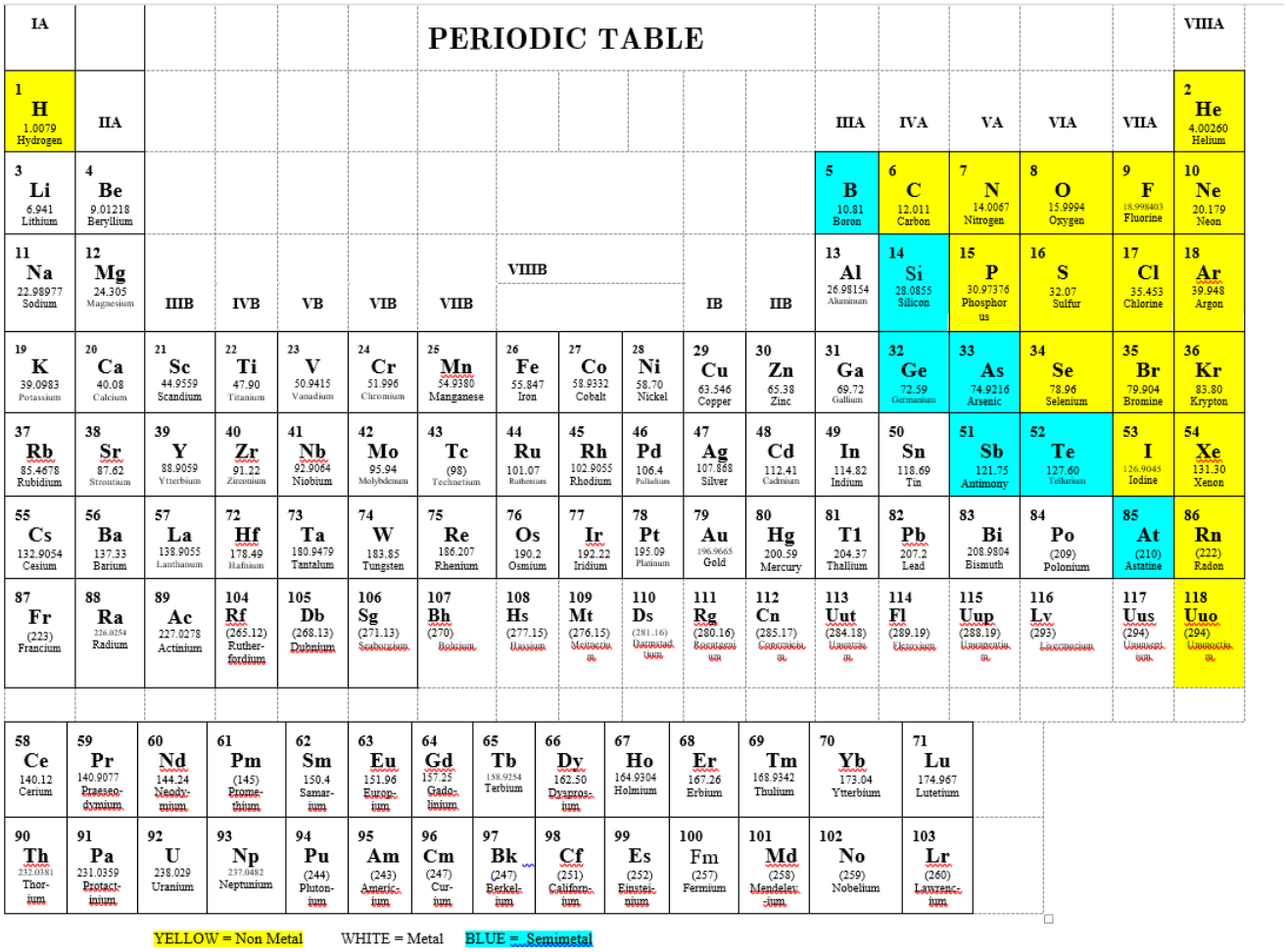


Figure 2.4.5: The older method of numbering the families or groups. Note the color coding of this table indicates metals, metaloids (semi-metals) and non-metals. These will be discussed below.

Exercise 2.4.3

What is the group number for oxygen?

A) 16

B) 6

C) 16A

D) Both A and B

Answer

Figures 2.4.3 and 2.4.5. If you start at boron and draw "stairs" down to astatine, the seven elements that are "on" are the **metalloids or semi-metals.** Everything to the left of the "stairs" with the exception of hydrogen is a **metal**. Everything to the right of the "stairs", in addition to hydrogen, is a **nonmetal.** This is essential for describing common physical properties for each of the three categories and will be used in nomenclature of chemical compounds.

Exercise 2.4.4

What is true regarding the classification of the following silicon? (select all that apply)

A) group 4A

B) metalloid

C) main group element

D) period 14

E) nonmetal

Answer

A, B, and C are all correct. D is incorrect. The period (row) is 3. The group is 13. E is incorrect because silicon sits on the stairs and is one of the metalloids.

Physical Properties of Metals:

Note, these can be related to the fact that electrons in metallic bonds are loosely bonded between multiple core atoms and freely flow from one atom to another.

1. Conduction (heat and electricity)
2. Malleability (can be hammered into thin sheets)
3. Ductility (can be pulled into wires)
4. Lustrous (Shiny appearance)

Physical Properties of Non-Metals:

Note, nonmetals are held together by directional covalent bonds of shared electrons, and this relates to their properties.

1. Poor Conductors
2. Nonlusterous
3. Nonmalleable
4. Brittle
5. Brightly colored

They have both properties of metals and non-metals. One of the most important physical properties of metalloids is their semi-conductive properties.

Natural States of Atoms

If you go to the Pubchem periodic table and click "standard state, you will see 2 elements are liquid, 11 are gasses, and one (Og) is "expected" to be a gas. If you click on Og and go to it's PubChem elemental page you see the most stable isotope has a half life of 0.89 millliseconds, and only a few atoms have ever been produced. You are required to know these, and note, several elements like Ga, Cs and Fr melt at very low temperatures and so may actually be liquids at room temperature

Liquids: **Hg, Br_2,** (Ga, mp=85.58^oF; Cs, mp=83.3^oF; Fr, mp=80.6^oF and Rb, mp=103.1 ^oF)

Gasses: Noble Gasses and Lighter diatomics, **H_2, N_2, O_2, F_2, & Cl_2**

Solids: All other elements

Vocabulary

Test Yourself

Query 2.4.1

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has

both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Anonymous
- Modifications by Ronia Kattoum
- Elena Lisitsyna (H5P interactive modules)

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2.5: Chemical Compounds

learning objectives

1. Differentiate between ionic compounds and molecular compounds in the way the bonds form and varying characteristics
2. Identify elements that exist as diatomic molecules
3. Define allotropes
4. Interpret different types of formulas including molecular formulas, structural formulas, and condensed structural formulas

Introduction

Chemical compounds occur when 2 or more atoms are bonded together. We will consider two basic types of bonds, covalent and ionic, and thus focus on two basic kinds of chemical compounds, covalent and ionic. Each of these compounds is associated with a chemical formula, and it is important to note that there is a third type of bond that is very common and which we are not considering here, and that is the metallic bond. A pure metal, or an alloy like Brass, (a mixture of copper and zinc) is neither an ionic or covalent compound. Brass does not form a "compound" in the classical sense of Dalton's theory, where there is a constant ratio of copper to zinc that leads to a specific formula. In fact brass can be considered to be a solid solution, and the different grades of brass depend on the ratio of copper to zinc. So we do not associate a typical chemical formula with metals and alloys.

Chemical bonds are the result of Coulombic (electrostatic) interactions between charged particles, where like charges repel and opposite charges attract. In the case of covalent bonds, these are between electrons and the nuclei of one atom with the electrons and nuclei of another. In the case of ionic bonds, these are between cations ([+] charged ions) and anions ([-] charged.

Coulombic interactions can be described by the following equations

$$E = k\frac{q_1 q_2}{r} \qquad F = k\frac{q_1 q_2}{r^2} \tag{2.5.1}$$

- **E is the potential energy**
- **F is the force**
- **r is the distance** of separation (note that the potential goes to zero when they are separated by infinity)
- **q is the charge** of the ions

What is important to understand is that the charge is in the numerator and the distance is in the denominator. This means that the greater the charge (at constant distance), the greater the force, and the less the distance (the closer the ions are to each other), the greater the force. So simply speaking, highly charged particles that are close to each other have stronger interactions than weak particles that are far apart. In fact, the concept of zero Coulombic energy equates to particles separated by infinity. It should also be noted that this force can be attractive or repulsive.

Covalent Bonds and Molecules

Covalent bonds occur when two or more atoms *share* valence (outer shell) electrons resulting in the formation of **molecular compounds**, which typically involve nonmetals. These come about as a result of the Coulombic forces of attraction and repulsion between the [+] nuclei and the [-] valence (outer shell) electrons of different atoms. It is easiest to see this in the simplest molecule, the diatomic hydrogen. On the left of the diagram below, you have two isolated atoms that are so far away that the blue electron does not feel an attraction to the red nucleus, and the red electron does not feel an attraction to the blue nucleus, and so no bond forms. As they get closer together the electrons of each atom begin to feel an attraction to the nucleus of the other atom and they move closer together.

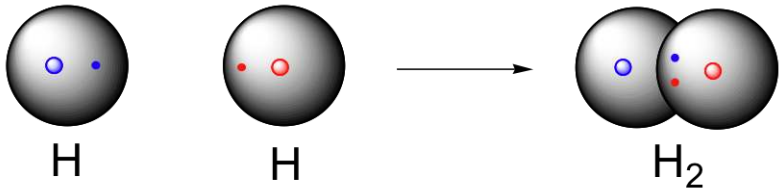


Figure 2.5.1: Simplified picture showing hydrogen as two isolated atoms (left) and as a diatomic covalent molecule (right)

Figure 2.5.2 represents a potential energy (well) diagram showing the energy as a function of the distance between two two hydrogen atoms. Now if you think about it, zero energy is when they are separated by infinity, and there is no attraction. As they come together a bond is formed as the electrons of each atom are attracted to the nucleus of the other [opposite charges attract], which is lower in energy than zero, because you must add energy to break the bond. But at some point they get so close that the nuclei begin to repulse each other [like charges repel], which forces them to move apart. So in reality, a covalent bond is not static with a fixed bond length, but a sort of vibration, as in a spring, with the atoms oscillating back and forth.

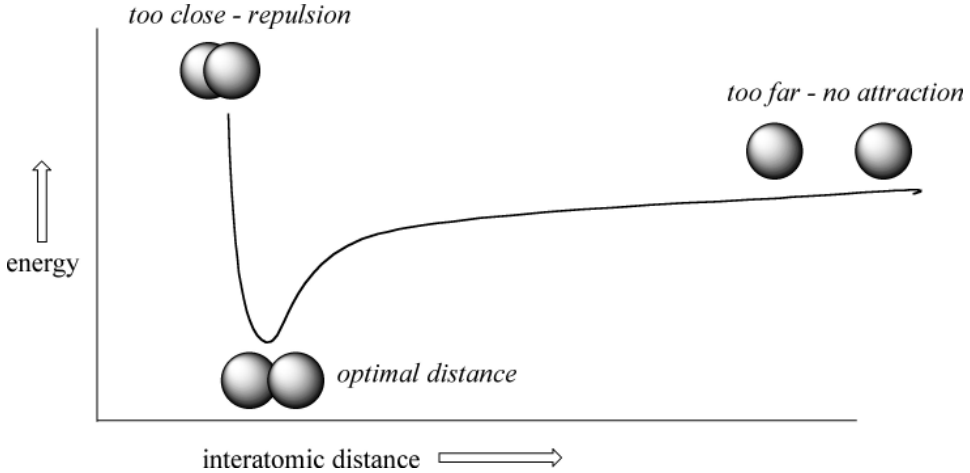


Figure 2.5.2: Potential well diagram explaining why a bond is not static, but oscillating, as the molecules alternate between [+/+] nuclear/nuclear repulsions (when they are real close), and [+/-] nuclear/electron attractions (as they start to separate). The bottom of the curve is considered to be the bond length. Video \(*PageIndex{1}\) has an animation that demonstrates this.



Video 2.5.1: *If you advance this 3*:07 Youtube to 1:20 you can see the formation of a covalent bond as two atoms approach each other, and at 2:06 the animations shows how the bond is not static, but oscillates. https://youtu.be/Wl5QHeS2UXE?t=128. Uploaded by Dr. Amal Kumar.

Diatomics

Atoms of some elements form molecules by forming bonds with themselves, and if there are two atoms, they are called the diatomic elements, and you need to know the seven diatomics.

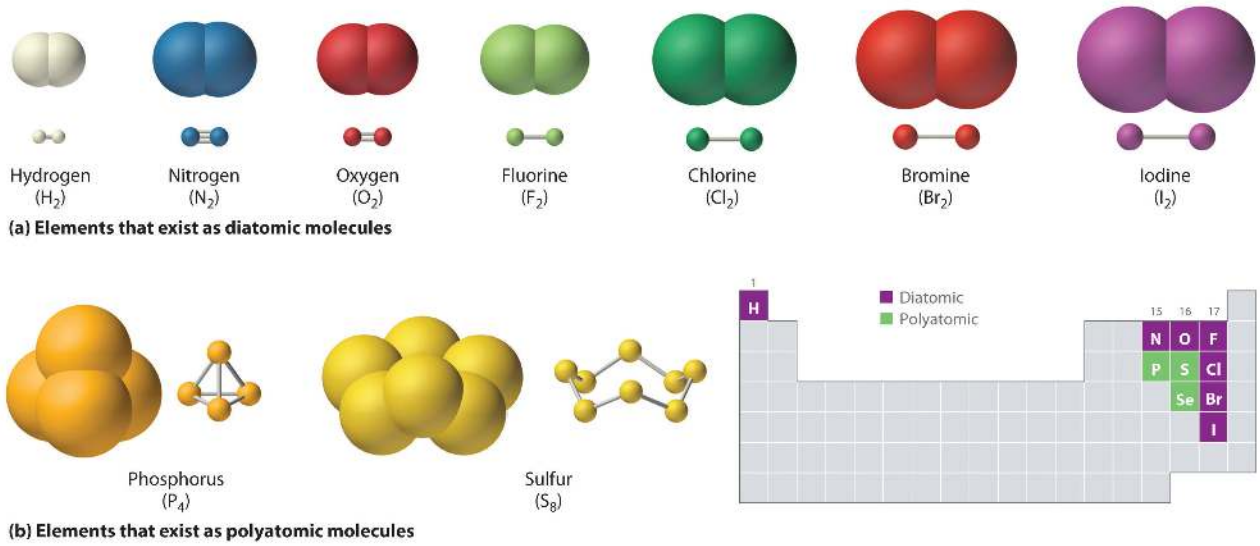


Figure 2.5.3: Elements that form diatomic and polyatomic molecules in their natural state (CC BY-SA-NC; Anonymous).

The ones on the periodic table that are purple form diatomic molecules, the ones in green form polyatomic molecules.

NOTE: When we say "oxygen" (or any diatomic molecule), we may mean monatomic oxygen O, or diatomic oxygen, O_2. We have to look at the context of the statement. If we are describing it as a substance, like "he breathes oxygen", we mean O_2, but if we are describing it as part of a compound, like how many atoms of oxygen are in 3.00 grams of water, we mean O.

Allotropes

Allotropes are when atoms of an element can form more than one stable compound. For example, oxygen can form O_2 (diatomic oxygen) and O_3 (ozone), which are allotropes. (Not to be confused with isotopes, which are different nuclides of the same element containing different numbers of neutrons). Selenium forms several allotropes including Se_2, Se_6 and Se_8. Note, the most stable allotrope can change as you change the temperature and pressure, for example, at high T (900 ^oC) Se_2 is the most stable, but at lower temperature the larger ones became more stable.



Video 2.5.2: *1:51 min YouTube on Allotropes of Carbon uploaded by Elearnin (https://youtu.be/sUqr6Uk29Z8).*

Molecular Formula

When multiple atoms are held together by covalent bonds they form a single chemical entity, which we call a molecule. As postulated in Dalton's atomic theory, the ratio of the atoms of the different elements are whole numbers, and this can be described

by the molecule's molecular formula. So each water molecule (H_2O) has two atoms of hydrogen and one of oxygen, while each molecule of aspirin ($C_9H_8.O_4$) has 9 carbon, 8 hydrogen and 4 oxygen.

Representations of Molecular Structures

Molecular formulas tell you how many atoms of each type of element are in a bond, but they do not necessarily tell you which atoms are bonded to which other atoms, or their orientation in space. In contrast, **structural formulas** show which atoms are bonded to one another and, in some cases, the approximate arrangement of the atoms in space. Knowing the structural formula of a compound enables chemists to create a three-dimensional model, which provides information about how that compound will behave physically and chemically.

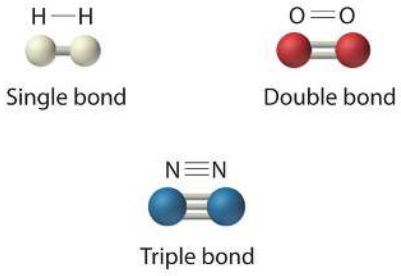


Figure 2.5.4: Molecules That Contain Single, Double, and Triple Bonds. Hydrogen (H_2) has a single bond between atoms. Oxygen (O_2) has a double bond between atoms, indicated by two lines (=). Nitrogen (N_2) has a triple bond between atoms, indicated by three lines (≡). Each bond represents an electron pair. *(image from LibreText core content.)*

The structural formula for H_2 can be drawn as H–H and that for I_2 as I–I, where the line indicates a single pair of shared electrons, a single bond. Two pairs of electrons are shared in a double bond, which is indicated by two lines, for example O_2 is O=O. Three electron pairs are shared in a triple bond, which is indicated by three lines, for example, N_2 is N≡N (see Figure 2.5.3 pr 2.5.4). Carbon is unique in the extent to which it forms single, double, and triple bonds to itself and other elements. The number of bonds formed by an atom in its covalent compounds is not arbitrary. Hydrogen, oxygen, nitrogen, and carbon have very strong tendencies to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Table 2.5.1).

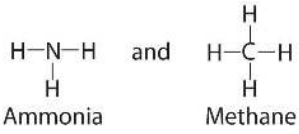
Table 2.5.1: The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

Atom	Number of Bonds
H (group 1)	1
O (group 16)	2
N (group 15)	3
C (group 14)	4

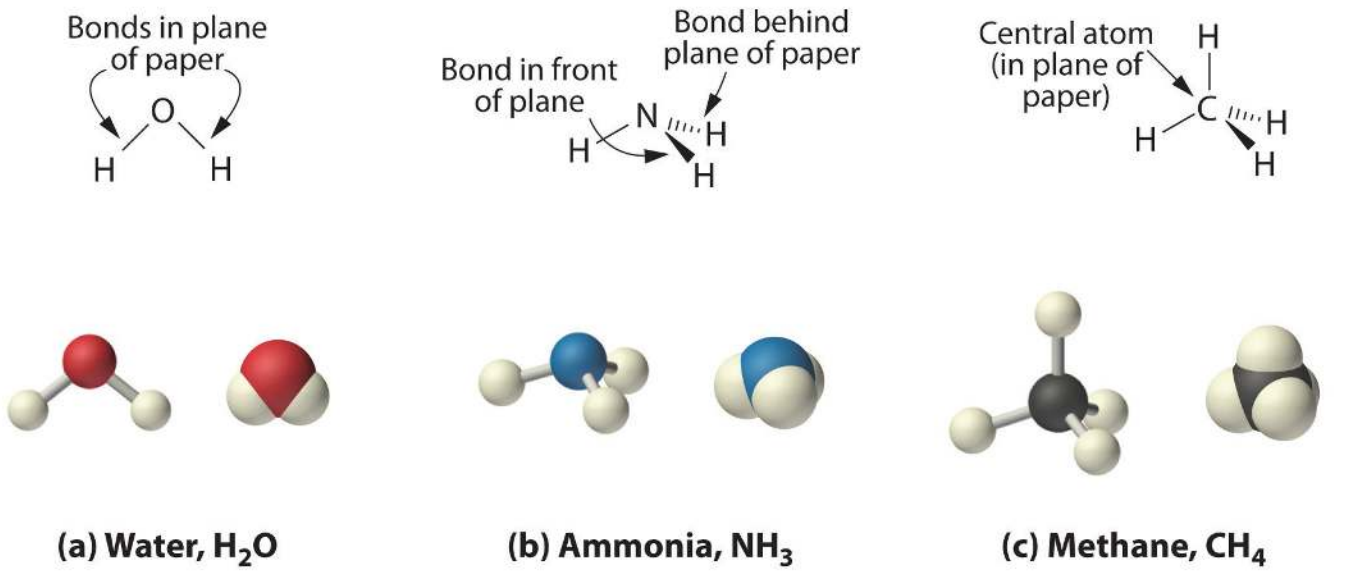
The structural formula for water can be drawn as follows:



Because the latter approximates the experimentally determined shape of the water molecule, it is more informative. Similarly, ammonia (NH_3) and methane (CH_4) are often written as planar molecules, even though they are not planar:



As shown in Figure 2.5.5, however, the actual three-dimensional structure of NH_3 looks like a pyramid with a triangular base of three hydrogen atoms. The structure of CH_4, with four hydrogen atoms arranged around a central carbon atom as shown in Figure 2.5.3, is tetrahedral: the hydrogen atoms are positioned at every other vertex of a cube. Many compounds—carbon compounds, in particular—have four bonded atoms arranged around a central atom to form a tetrahedron.



The Three-Dimensional Structures of Water, Ammonia, and Methane. (a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center. *(image from LibreText core content.)*

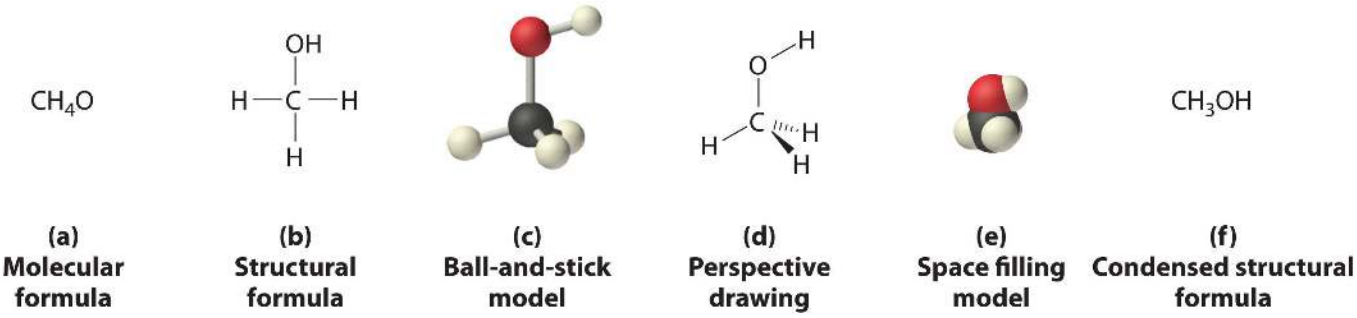


Figure 2.5.6: Different Ways of Representing the Structure of a methane (a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule. *(image from LibreText core content.)*

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a condensed structural formula (part (f) in Figure 2.5.5), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is CH_3OH, which indicates that the molecule contains a CH_3 unit that looks like a fragment of methane (CH_4). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

Example 2.5.1

Write the molecular formula of each compound.

a. The phosphorus-sulfur compound that is responsible for the ignition of so-called strike anywhere matches has 4 phosphorus atoms and 3 sulfur atoms per molecule.
b. Ethyl alcohol, the alcohol of alcoholic beverages, has 1 oxygen atom, 2 carbon atoms, and 6 hydrogen atoms per molecule.
c. Freon-11, once widely used in automobile air conditioners and implicated in damage to the ozone layer, has 1 carbon atom, 3 chlorine atoms, and 1 fluorine atom per molecule.

Given: identity of elements present and number of atoms of each

Asked for: molecular formula

Strategy:

- Identify the symbol for each element in the molecule. Identify the compound is an organic or an inorganic compound.
- For inorganic compounds, list the elements beginning with the one farthest left in the periodic table. List elements in the same group starting with the lower element and working up. For organic compounds, list carbon first, the hydrogen, then any other element in alphabetical order.
- From the information given, add a subscript for each kind of atom to write the molecular formula.

Solution

a. The molecule has 4 phosphorus atoms and 3 sulfur atoms. Because the compound does not contain mostly carbon and hydrogen, it is inorganic. Phosphorus is in group 15, and sulfur is in group 16. Because phosphorus is to the left of sulfur, it is written first. Writing the number of each kind of atom as a right-hand subscript gives P_4S_3 as the molecular formula.

b. Ethyl alcohol contains predominantly carbon and hydrogen, so it is an organic compound. The formula for an organic compound is written with the number of carbon atoms first, the number of hydrogen atoms next, and the other atoms in alphabetical order: CHO. **C** Adding subscripts gives the molecular formula]C_2H_6O.

c. Freon-11 contains carbon, chlorine, and fluorine. It can be viewed as either an inorganic compound or an organic compound (in which fluorine has replaced hydrogen). The formula for Freon-11 can therefore be written using either of the two conventions. According to the convention for inorganic compounds, carbon is written first because it is farther left in the periodic table. Fluorine and chlorine are in the same group, so they are listed beginning with the lower element and working up: CClF. Adding subscripts gives the molecular formula CCl_3F. We obtain the same formula for Freon-11 using the convention for organic compounds. The number of carbon atoms is written first, followed by the number of hydrogen atoms (zero) and then the other elements in alphabetical order, also giving CCl_3F.

Exercise 2.5.1

Write the molecular formula for each compound.

a. Nitrous oxide, also called “laughing gas,” has 2 nitrogen atoms and 1 oxygen atom per molecule. Nitrous oxide is used as a mild anesthetic for minor surgery and as the propellant in cans of whipped cream.

b. Sucrose, also known as cane sugar, has 12 carbon atoms, 11 oxygen atoms, and 22 hydrogen atoms.
c. Sulfur hexafluoride, a gas used to pressurize “unpressurized” tennis balls and as a coolant in nuclear reactors, has 6 fluorine atoms and 1 sulfur atom per molecule.

Answer

A) N_2O

B) $C_{12}H_{22}O_{11}$

C) SF_6

Example 2.5.2

Write the molecular formula for each compound. The condensed structural formula is given.

a. Sulfur monochloride (also called disulfur dichloride) is a vile-smelling, corrosive yellow liquid used in the production of synthetic rubber. Its condensed structural formula is ClSSCl.
b. Ethylene glycol is the major ingredient in antifreeze. Its condensed structural formula is $HOCH_2CH_2OH$.
c. Trimethylamine is one of the substances responsible for the smell of spoiled fish. Its condensed structural formula is $(CH_3)_3N$.

Given: condensed structural formula

Asked for: molecular formula

Strategy:

- Identify every element in the condensed structural formula and then determine whether the compound is organic or inorganic.
- As appropriate, use either organic or inorganic convention to list the elements. Then add appropriate subscripts to indicate the number of atoms of each element present in the molecular formula.

Solution:

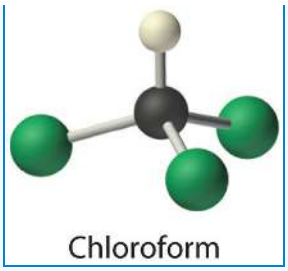
The molecular formula lists the elements in the molecule and the number of atoms of each.

a. Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula S_2Cl_2.
b. Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and hydrogen atoms, so it is organic. As with all organic compounds, C and H are written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $C_2H_6O_2$.
c. The condensed structural formula shows that trimethylamine contains three CH_3 units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. According to the convention for organic compounds, C and H are written first, giving the molecular formula C_3H_9N.

Exercise 2.5.2

Write the molecular formula for each molecule.

a. Chloroform, which was one of the first anesthetics and was used in many cough syrups until recently, contains one carbon atom, one hydrogen atom, and three chlorine atoms.



a. Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is H_2NNH_2.
b. Putrescine is a pungent-smelling compound first isolated from extracts of rotting meat. Its condensed structural formula is $H_2NCH_2CH_2CH_2CH_2NH_2$. This is often written as $H_2N(CH_2)_4NH_2$ to indicate that there are four CH_2 fragments linked together.

Answer

a. $CHCl_3$

b. N_2H_4

c. $C_4H_{12}N_2$

Ionic Bonds and Ionic Compounds

If the number of protons in an atom or molecule is not equal to the number of electrons it has a net charge and is called an ion. Note, if it is an atom, it is called a monatomic ion, and if it is a molecule, it is called a polyatomic ion. There are obviously two types of ions, positive and negative, which are called cation and anion respectively. The charge of the ion is the number of protons minus the number of electrons.

Cation: Net positive charge, the number of protons is greater than the number of electrons
Anion: Net negative charge, the number of protons is less than the number of electrons.

The following Youtube video goes over some concepts we will study later (electronegativity, and polar bonds), but if you watch between eleven seconds and 49 seconds you get a good visualization of the difference between a ionic and covalent bond.



Video 2.5.3: 1:26 YouTube, watch between 11 and 48 seconds for a good visualization, we will learn about electronegativity and polar bonds later.

Formula for Ionic Compounds.

When writing the formula of an ionic compound we use the lowest whole number ratio of cations ([+] ions) to anions ([-] ions). If you look at a salt crystal you will see that each positive ion is surrounded on all 6 sides by negative ions, and that a crystal lattice

forms. So it makes no sense to have a "molecular formula" for an ionic compound, because the number of atoms will grow as the crystal grows.

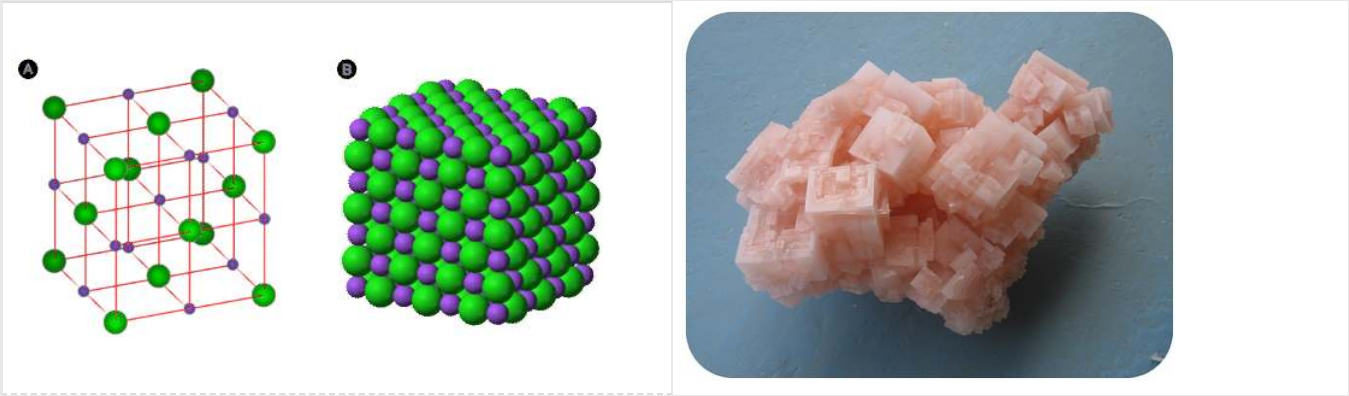


Figure 2.5.7 On the left is a crystal lattice of NaCl table salt, which is also shown on the right, where it forms Halite crystals. Because the number of ions depends on the size of the crystal, we use the lowest ratio of positive to negative ions that results in a neutral structure.

The concept of ionic bonds will be further developed in the next section.

Vocabulary

Test Yourself

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Anonymous
- Modifications by Ronia Kattoum
- Elena Lisitsyna (H5P interactive modules)

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2.6: Ionic Compounds and Formulas

Learning objectives

- Relate the stability of ionic compounds to Coulomb's Law
- Recognize properties of ionic compounds
- Recognize that metals lose electrons to form cations and that nonmetals gain electrons to form anions
- Predict the charge of monatomic main group elements based on their group number.
- Name monoatomic anions and cations
- Memorize polyatomic ions
- Write formulas for ionic compounds using monatomic and polyatomic ions by applying the principle of charge neutrality.

Introduction

In the preceding section we discussed covalent bonds of molecules and introduced the concept of ionic bonds. In this section we will develop a deeper understanding of ionic compounds. We will see that to be stable an ionic compound must be neutral, and that there is not a discrete formula as there is with covalent compounds, in fact we use the lowest ratio of positive to negative charged ions that results in a neutral formula. In the previous section we did introduce the concept of cations (positive ions) and anions (negative ions). In the next section we will go over nomenclature, the naming of compounds.

Coulomb's Law

Coulomb's Law is a mathematical formula that describes the electrostatic interaction between two charged particles that was first proposed by the French physicist Charles Coulomb (1736–1806). Coulomb's law is often called an inverse square law, as the force decreases as a function of the square of the distance between the two particles.

$$E = k\frac{q_1 q_2}{r} \qquad F = k\frac{q_1 q_2}{r^2} \tag{2.6.1}$$

- E is the potential energy
- F is the force
- r is the distance of separation (note that the potential goes to zero when they are separated by infinity)
- q is the charge of the ions
- k is a constant

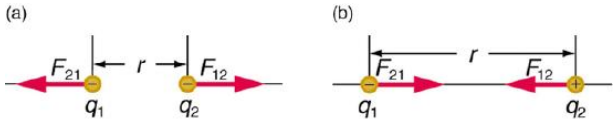


Figure 2.6.1: In (a) the like charges repel each other, while in (b) the opposite charges attract each other (CC BY; OpenStax).

The electrostatic interactions can be understood by the above image, where in (a), like charges repel and in (b), opposite charges attract. If you look at Coulomb's law, you note that in (a) the force is positive (because both q_1 and q_2 are negative), while in (b) the force is negative (because q_1 is negative while q_2 is positive). That is, attractive interactions result in a lowering of the energy

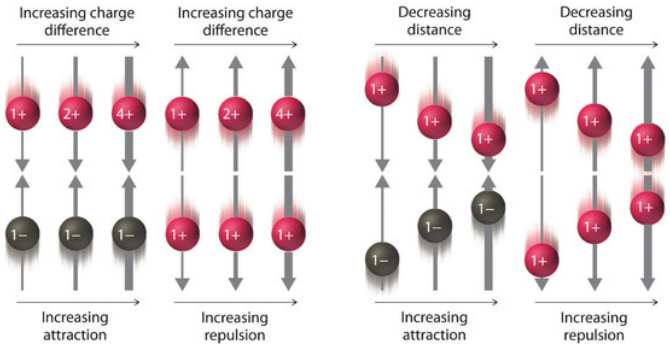


Figure 2.6.2: Here we see the effect of both magnitude and the sign of charge on electrostatic interactions between ions (CC BY-SA-NC; anonymous).

In the above diagram the width of the arrows indicate the magnitude of the forces of electrostatic interaction. You should be able to look at the algebra associated with Coulomb's Law and see how it results in these interactions. In the numerator is the charge, and so the greater the charge, the greater the interaction. In the denominator is the distance between the charges, and so the larger the distance, the weaker the interaction.

NOTE: It is very important that you learn how to "read" algebraic equations like Coulomb's Law. Math is actually a universal language and being able to read equations is one of the most important skills you can learn in this class. That is, it makes no difference what language you study in, the math is still the same, and being able to read equations is a fundamental skill you should gain from this class.

Exercise 2.6.1

Using the principle of Coulombs Law, would you expect KCl or Al_2O_3 to have a greater melting point, noting that the stronger the forces of attraction the higher the temperature required to melt the compound?

Answer

According to Coulombs Law, the greater the charge, the stronger the interaction between ions and the greater energy (temperature) needed to separate the ions, so Aluminum oxide would be predicted to have a higher melting point than potassium chloride.

Crystal Lattice and Principle of Charge Neutrality

Why must ionic compounds be neutral?

An ionic bond is not between two ions, but the result of the interaction of multiple cations ([+] ions) and anions ([-] ions) as the coordinate with each other and form an ionic crysta. Salts are typical ionic compounds. That is, a salt crystal has +/+ and -/- repulsions (increasing the energy), and +/- attractions (decreasing the energy, and making the compound more stable), and if the attractive forces are greater than the repulsive, an ionic compound is formed. In the following diagram we see how a crystal forms which maximizes the attractive interactions of the opposite charges while minimizing the repulsive interactions of the like charges. If the compound was not neutral, but had more cations, or more anions, the like/like repulsive forces would be larger and the material would become unstable and break apart. Therefore, ionic compounds must be neutral.

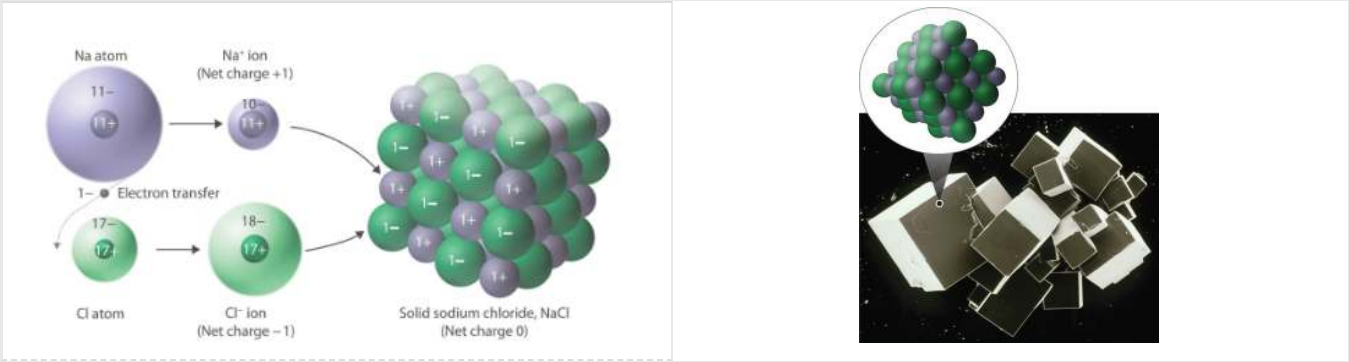


Figure 2.6.3: In the above image the sodium (a metal) loses and electron (becoming smaller) while the Chlorine atom (nonmetal) gains an electron (becoming bigger). A crystal lattice results where the cations and anions pack in three dimensional space that can result in a macroscopic crystal that is visible to the naked eye (CC BY-SA-NC; anonymous).

The salt crystals seen to the naked eye are the result of the way cations and anions pack to form a stable crystal structure that minimizes like/like repulsions and maximizes opposite charge attractions as defined by Coulomb's Law. The following video from YouTube describes the formation of sodium chloride.



Video 2.6.1: 2:10 min YouTube video describing formation of sodium chloride, table salt. Uploaded by Salvatore Lombardo, https://youtu.be/c-nMmwfTV-w.

Properties of Ionic Compounds

Because of the arrangement of cations and anions in a the crystal lattice, these ions are held tightly into their position. Although the ions can vibrate and oscillate about their position, it take much more energy than room temperature for one ion to break free of the lattice structure. This results in very high melting points and boiling points for ionic compounds. Therefore, ionic compounds are crystal solids at room temperature. They are not malleable or soft. When struck sharply, they do shatter cleanly, with layers of ions breaking off at once.

Monatomic Ions

Metals tend to form cations and nonmetals tend to form anions. The following periodic table shows some of the common ions formed by common elements. Note, the noble gasses (turquoise) do not tend to form ions.

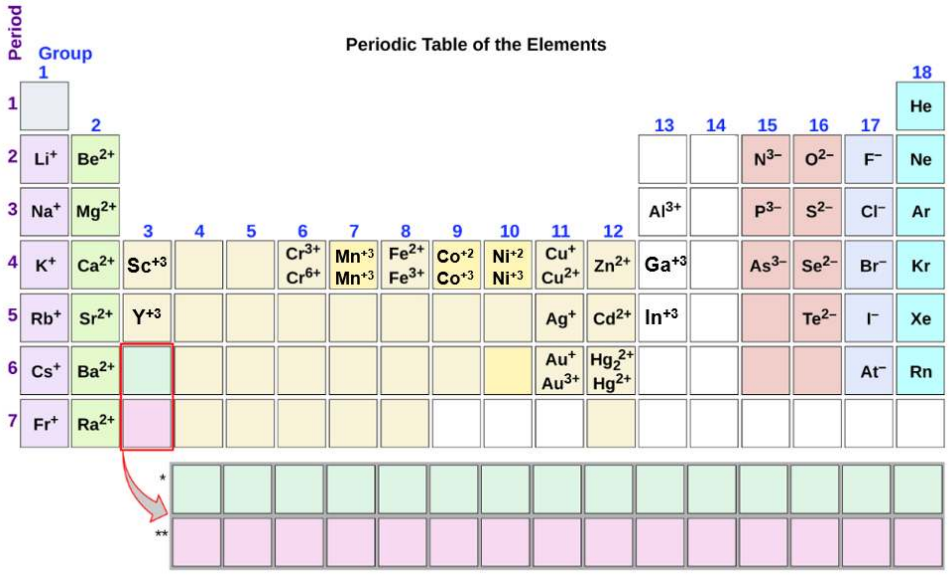


Figure 2.6.4: Note some metals form more than one type of monatomic cation (this table is not complete), and Hg_2^{2+} is not really a monatomic ion, but a diatomic ion.

Figure 2.6.4 should not be considered to be a comprehensive Figure and this topic will be brought up again in the next section. There are several things you can note from this table though. First, metals tend to from cations and nonmetals tend to form anions, while the noble gasses do not tend to form ions. Second, the nonmetals have only one charge state, which represents the number of electrons that need to be added for them to have the same number as a noble gas. Third, there are two types of metals, those that have only one charge state (like the nonmetals), and those that have multiple charge states. These different types of ion forming metals will be discussed more in the next section on naming compounds (section 2.7.3).

Monatomic Cations:

When atoms (typically metals) lose one or more electrons the become positively charged cations. For example, when a neutral sodium atom loses one electron, it becomes the sodium ion, Na^+ as shown in the following shorthand notation:

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + \mathrm{e}^- \tag{2.6.2}$$

Another example shows the formation of the magnesium ion from the neutral magnesium atom losing 2 electrons to pick up a +2 charge.

$$\mathrm{Mg} \longrightarrow \mathrm{Mg}^{2+} + 2\,\mathrm{e}^- \tag{2.6.3}$$

Can we predict the stable charge of a monoatomic cation?

Yes, it is easy for non-transition metals that have only one charged state (alkali metals, alkaline earth and post-transition metals - see Figure 2.4.2). The trick is to remove enough electrons so that the cation has the same number of outer shell electrons as a noble gas, that is, it is isoelectronic to the noble gas. This is easy if we use the atom's group number's in terms of the "A" designation (remember there are two conventions for numbering the groups), as the group number effectively tells you how many electrons are needed to be removed. So Sodium (Group 1A) has 11 electrons and so if it looses one it has 10, like Neon (a noble gas). Magnesium has 12, so it looses 2 to become like Neon, and Aluminum has 13 and so looses 3 to become like Neon.

Note: Why does hydrogen not form a +1 cation?

Although hydrogen has one electron in its outer shell (like all the alkali metals), it only has one electron and so completely removing it would leave behind a bare nucleus, a subatomic particle the proton, which would not be stable. Consequently hydrogen does not form a cation, but can result in an acid, which is a polar covalent bond. In the above video sodium with 11 electrons gave an electron to chlorine, forming the Na^+ cation and the Cl^- anion, which then formed the crystal table salt NaCl. If chlorine was to try and remove the electron from hydrogen, it would not be able to as the resulting nucleus would pull it back, this results in the molecular acid HCl, where the chlorine can not completely remove the electron from the hydrogen. This is called a "polar covalent bond" and will be discussed later this semester.

Monatomic Anions:

*W*hen atoms (typically non-metals) gain one or more electrons they become negatively charged anions. For example, when a neutral fluorine atom gains one electrons, it becomes the fluoride ion as shown by the following shorthand notation:

$$\mathrm{F} + \mathrm{e}^- \rightarrow \mathrm{F}^- \tag{2.6.4}$$

Another example is the formation of the sulfide ion when a neutral sulfur atom gains two electrons picking up a -2 charge.

$$\mathrm{S} + 2\,\mathrm{e}^- \rightarrow \mathrm{S}^{2-} \tag{2.6.5}$$

Can we predict the stable charge of a monoatomic anion?

Yes, just as with the monatomic cations, stable monatomic anions are isoelectronic to the nearest noble gas, but in this case you add electrons instead of subtract. Once again, if we use the "A" designations for numbering the groups, we simply add the number of electrons required to be the same as a noble gas. So chlorine gains 1, oxygen gains 2 and nitrogen gains 3. This number can be determined by taking the group number 5, 6 or 7 from groups 5A, 6A and 7A and subtracting from 8 (for group 8A).

Exercise 2.6.2

Based on the position of the periodic table, predict the charge of the following elements if they are to produce ions. (do not look at periodic table above to come up with your answer)

a. Sr

b. Ga
c. P

Answer

A) Sr^{2+}. Sr is a group 2A main group metal. So, +2 charge.

B) Ga^{3+}. Ga is a group 3A main group metal. So, +3 charge.

C) P^{3-}. P is a group 5A main group nonmetal. So, 5-8 = -3 charge.

Polyatomic Ions

Many ions contain more than one nuclei and these are labeled at polyatomic Ions. There are different types of polyatomic ions. We will look at two common types, oxyanions and carboxyanions. Students need to memorize the polyatomic ions in Figure 2.6.5 by the time the get to then next section as they will be using this in naming ionic compounds.

When forming a stable crystal, these compounds have both covalent bonds (holding the polyatomic ions together), and ionic bonds (holding the cations and anions together in a stable neutral lattice).

Polyatomic Ions

NH_4^+	Ammonium	$C_8H_4O_4^{-2}$	Phthalate
CH_3COO^-	Acetate	SO_4^{-2}	Sulfate
NO_2^-	Nitrite	SO_3^{-2}	Sulfite
NO_3^-	Nitrate	CrO_4^{-2}	Chromate
OH^-	Hydroxide	$Cr_2O_7^{-2}$	Dichromate
ClO_4^-	Perchlorate	PO_4^{-3}	Phosphate
ClO_3^-	Chlorate	PO_3^{-3}	Phosphite
ClO_2^-	Chlorite	AsO_4^{-3}	Arsenate
ClO^-	Hypochlorite	CN^-	Cyanide
MnO_4^-	Permanganate	SCN^-	Thiocyanide
CO_3^{-2}	Carbonate	$C_2O_4^{-2}$	Oxalate
HCO_3^-	Bicarbonate	O_2^{-2}	Peroxide
OH^-	Hydroxide	$S_2O_3^{-2}$	Thiosulfate

Figure 2.6.5: Common polyatomic ions general chemistry students need to know.

What you may notice is there are several types of structural features to these ions, and we will look at two, the oxyanions and the carboxyanions.

Oxyanions

Oxyanions have a central nonmetal with oxygens covalently bonded to them. The atoms of the same periodic family tend to from analogous oxyanions

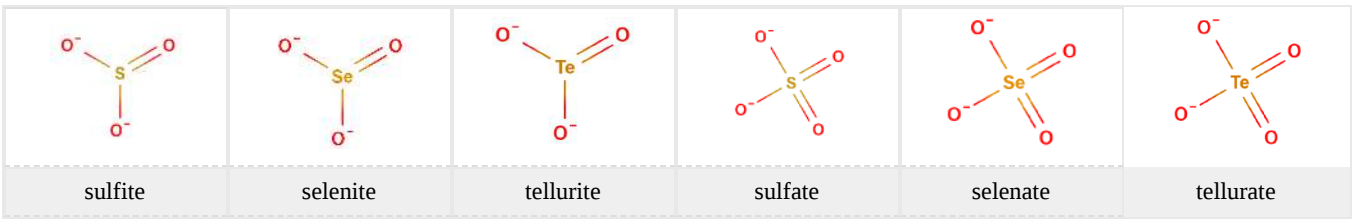


Figure 2.6.6: Polyatomic ions of group VIA, -ites on the left, -ates on the right.

The larger halogens (chlorine, bromine and iodine) form four types of oxyanions, as exemplified by chlorine here.

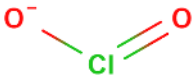
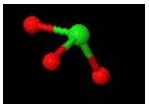
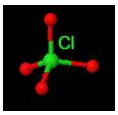
			
hypochlorite	chlorite	chlorate	perchlorate

Figure 2.6.7: The four oxyanions of chlorine. Note that in all cases, the oxygens have covalent bonds to the chlorine, which is the central nonmetal ion. The other halogens form similar types of oxyanions.

Carboxylate ions

Carboxylate is a functional group that gives can hold a negative charge in an organic compound. The left most box of Figure 2.6.8 shows the generic structure of a carboxylate ion, where R represents some organic compound, and the carboxylate is also attached to two oxygens which"share" the electron. There are three carboxylate ions students are required to memorize and their structures are represented in Figure 2.6.8:

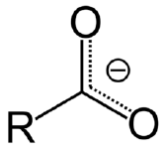
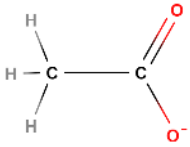
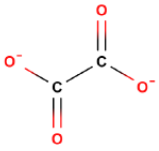
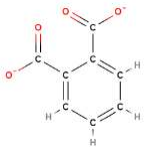
			
generic carboxylate ion	Acetate	Oxalate	Phthalate
Formula	$CH_3(CO_2^-)$	$(CO_2^-)_2$	$C_6H_4(CO_2^-)_2$
Description	Attached to carbon	two attached to each other	attached to benzene ring

Figure 2.6.8: Recognizing that these ions have carboxylate groups makes it easier to remember their formula, as they are all similar in structure

Right now the important thing is to understand what a polyatomic ion is. In the next section on nomenclature we will build up on this structural information to come up with some tricks to make memorizing names easier.

Ionic Compound Formula and the Principle of Charge Neutrality

The Principle of Charge Neutrality simply states that for matter to be stable it must be neutral. If an ionic compound had a formula of Na_2F, and you had 10,000 of those units, then there would be 20,000 positive things and 10,000 negative things, meaning an excess of 10,000 positive things repelling each other, and so it would not be stable, and so would not form (and realize that real substances on macrosocopic scales that we can measure have in the order of 10^{23} entities.

You might ask, if something is neutral, why are the ion-ion attractions greater than the repulsion, that is, why isn't the energy of interaction neutral? The reason that the attractions are greater than the repulsions is because opposite ions tend to be closer together (they are attracted) than the ions of same sign (they are repulsed), and according to Coulomb's law, the closer they are the greater the force, and so a neutral compound has a net attractive force and forms a stable compound.

The formula of an ionic compound represents the lowest whole number ratio of cations to anions, it is as simple as that. Most cations have charges of [+1] through [+6] while most ions have charges of [-1] through [-3].

Trick:
Set # of Anions = Charge of Cation and
set # of Cations = Charge of Anion
Beware that this must be the Lowest Whole # Ratio of cation to anion.

Strategy:

1. **Identify charge of each ion**
2. **multiply charge of each ion by absolute value of the charge of the counter ion.**

3. **Make sure resulting ratio is the lowest whole number ratio, if not, divide by common denominator so all values are integers.**

Watch video 2.6.2 to see how to perform this calculation



Video 2.6.2: (6'15") Video on using Principle of Charge Neutrality to determine formula of Ionic Compound

Exercise 2.6.3

What is the formula for the ionic compound that forms when the calcium ion reacts with the oxide ion?

Answer

CaO. Ca^{2+} and O^{2-}. You need one calcium ion for every one oxide ion for the compound to be charge neutral.

s

Exercise 2.6.4

What is the formula for the ionic that forms when the lead(IV) (Pb^{4+}) ion reacts with the sulfate (SO_4^{2-}) ion?

Answer

Add $Pb(SO_4)_2$. Pb^{4+} and SO_4^{2-}. For every one Lead(IV) ion, you need two sulfate ions to be charge neutral. 1(+4) + 2(-2)=0. You may use the criss-cross rule, but you must make sure that you reduce to the simplest whole number ratio.

Determining Ion Charges from Formula

If given a formula like NaCl or FeO or Fe_2O_3 you need to be able to calculate the charge of the ions. In the case of NaCl it is easy as Na is always [+1] and Cl is always [-1]. But iron can have multiple charges and so needs to be Figured out.

Fortunately, the anion is always of known charge and so you can use that to algebraically reverse engineer the principle of charge neutrality. that is for a general formula C_xA_y where C is the Cation with charge [+m] and there are x of them, and A is the Anion with charge of [-n] and there are y of them, we know from the principle of charge neutrality that

$$\begin{gathered} x(+m)+y(-n)=0 \\ \therefore \\ x=\frac{0-y(-n)}{x} \end{gathered} \tag{2.6.6}$$

So for FeO we know the charge of the oxygen is -2, so 1(charge of Fe) +1(charge of O) = 0, so Fe=+2 as)=-1

for Fe_2O_3 we have

2(charge of Fe) + 3(charge of Oxygen) = 0

so

$$2(+m)+3(-2)=0 \tag{2.6.7}$$
$$\therefore$$
$$+m=\frac{0-3(-2)}{2}=3$$

that is: 3x2 -2x3=0, which makes sense.

Exercise 2.6.5

What is the the charge for the cation in each of the following comounds?

a. V_2O_5

b. Pb_3N_4

Answer

a. V^5 because oxygen is minus 2.

b. Pb^4 because nitrogen is minus 3.

Test Yourself

Contributors

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:
- Elena Lisitsyna (H5P interactive modules)

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2.7: Nomenclature

learning objectives

1. Recognize ionic compound, molecular compounds, and acids.
2. Give the names and formulas for ionic compounds
3. Give the names and formulas for molecular compound s
4. Give the name and formula for acidic compound

Introduction

Nomenclature, the naming of chemical compounds is of critical importance to the practice of chemistry, as a chemical can not only have many different names, but different chemicals can have the same name! S o how can you do science if you do not know what you are talking about??? In this section we will look at nomenclature of simple chemical compounds. The rules we use depends on the type of compound we are attempting to name.

Overview of Nomenclature

The rules we use in nomenclature depend on the types of bonds the compound has and these are outlined in Figure 2.7.1 and the video lecture in video 2.7.1. That is, before we do anything we have to ask what kind of compound are we trying to name?

- The first question we ask is if the compound is ionic or covalent?
  - **If it is covalent**, which is typically between 2 or more nonmetals, we need to ask, is it a simple molecule, or is it an acid.
    - If it is **a simple molecule we use Greek prefixes** to identify the number of atoms of each type of element in the molecule.
    - If it is **an acid, we base it's name on the ionic compound it would form if hydrogen could be a cation**. Note, hydrogen can not lose its only electron as then it would be a subatomic particle and the charge density would be too high, so it forms a covalent bond.
  - **If it is ionic**, we **use the principle of charge neutrality to name the compound**.

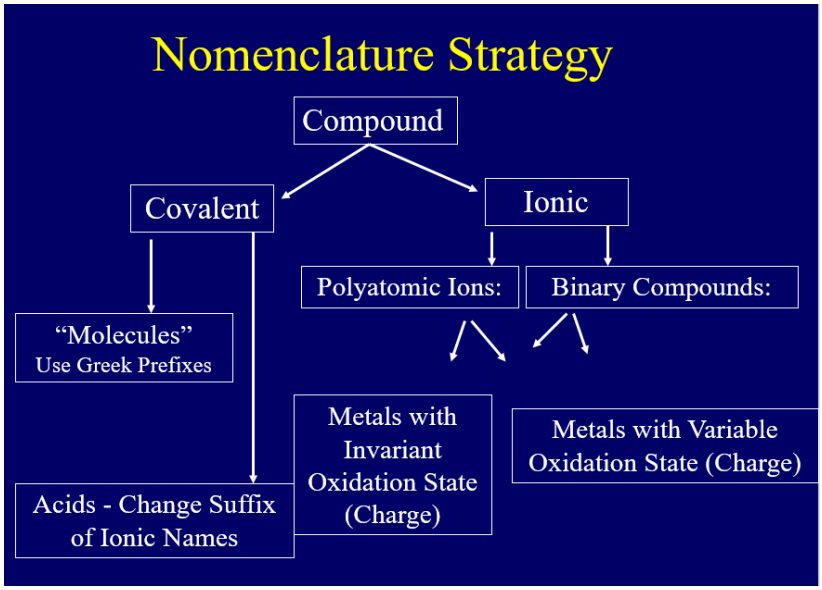


Figure 2.7.1: Outline of strategy for naming molecules (watch the Youtube immediately below for a lesson on how to use this outline)



Video 2.7.1: YouTube (2'17") describing the logic of the flow diagram for (https://youtu.be/4Ikom9GjAhE)

The following lesson will start with naming ionic compounds, then naming covalent compounds and then acids. After that, we will look at some special types of compounds, hydrated compounds (which are ionic compounds that contain water in their structure) and acid salts, which are salt's with acidic anions.

Ionic Compounds

When naming an ions the cation uses the metal's elemental name followed by the word ion or cation and the nonmetal anion uses the elemental name with an ide ending. So the metal sodium (Na) forms the sodium ion or sodium cation (Na^+), while the nonmetal chloride (which exists as Cl_2) is called chloride (Cl^-), and you do not need to indicate that it is an ion (there is nothing wrong with the terms chloride anion or chloride ion, but they are providing redundant information).

Exercise 2.7.1

Give the symbol and name for the ion with 34 protons and 36 electrons. Is it a cation or an anion?

Answer

Se^{2-}, selenide. In it an anion since there are more electrons than protons.

Ionic compounds have a [+] cation and a [-] anion. We use the **Principle of Charge Neutrality,** that is, for an **ionic compound to be stable its chemical formula MUST BE NEUTRAL.** So **you do not need to state the number of cations and anions**, you **only need to state what they are** (and what their charge is). You then Figure the formula based on the lowest whole number ratio of cations to anions that produces a neutral formula.

We will start with binary ionic, which are between monatomic anions and cations. We note that there are two types of metals, those that have only 1 charge (Type 1), and those that can have more than one stable charge. Finally, polyatomic ions often form which are covalently bonded atoms where the total number of protons is not equal to the total number of electrons.

Binary Ionic

Binary ionic compounds are between a metal and nonmetal. This does not mean there are two atoms, but two types of atoms, so Al_2S_3 is a binary ionic compound. The rules are simple, name the cation first and the anion second, giving the anion the -ide suffix.

- **Cation (metal) first**
- **Anion (nonmetal) second with -ide suffix**

The problem is some metals have more than one stable charge state, and so for those metals (type 2 metals), we need to identify the charge in the name.

Two Types of Monatomic Cations

There are two types of monatomic cations, those of metals that form only one charge state, and those that can form multiple charged states, but there is only one type of monatomic anion as none of them form multiple charged states (review section 2.6.4.1)

For simplicity, we are going to label the metal cations as Type 1 (invariant charge) and type 2 (variable charge)

Type 1: Invariant Charge (Oxidation State)

Remember metals lose electrons to form cations and nonmetals gain electrons to form anions. Figure 2.7.2 lists the ions (cations and anions) that have invariant charges. All the anions are of this type, gaining the number of electrons required to fill the valence shell and become isoelectronic with the nearest noble gas.

There is a pattern to the metals if you use the A/B block notation in that 1A & 1B tend to form [+1] , IIA & IIB tend to form [+2], while IIIA & IIIB tend to form [+3]. It is easy to see how the alkaline metals (1A) lose one electron as that gives them the same as a noble gas, but you need to get to Chapter 7 and understand the orbitals before you can understand why silver (1B) behaves the same. The alkaline earths (IIA) each lose 2 and gain the same electron configuration of a noble gas, while Zinc and Cadmium (IIB) also lose two electrons, but once again, we need to get to Chapter 7 to understand why. As for the [+3] forming ions, these are IIIA and IIIB. Now the B block are easier to see, as they simply loose three electrons, one from the IIIB, IIA and IA block of a period, and then they have the same number of electrons as a noble gas. As for the IIIA, we need to understand Chapter 7, but imagine that all of the orbitals of the transition metals are filled (B block) and the ones lost are from IA, IIA and IIIA.

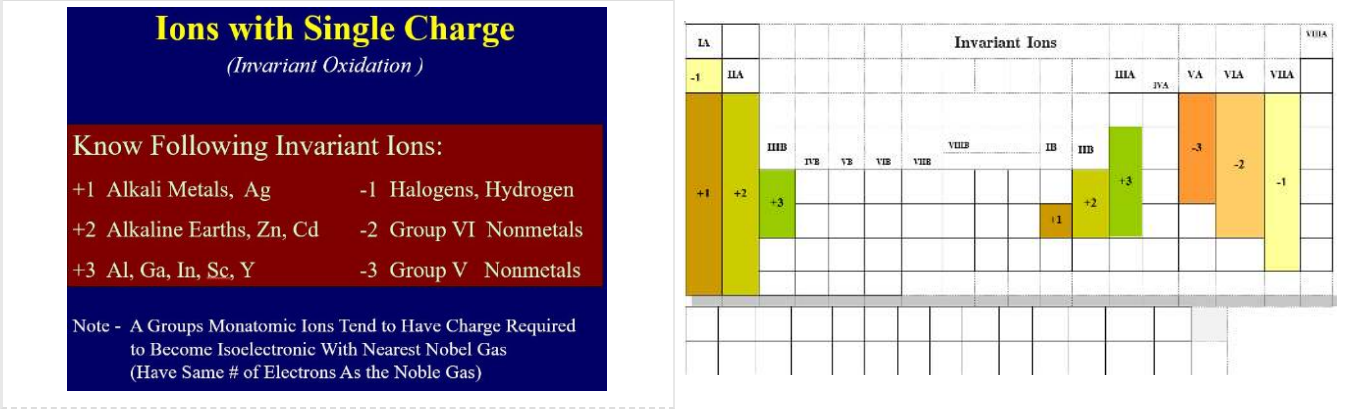


Figure 2.7.2 The elements in the above table form only one stable charged state. Can you see the pattern for the cations in relation to the A/B block notation. Note, we often refer to the charge of a monatomic ion as its oxidation state.



Video 2.7.2: 3:10 min YouTube on nomenclature for binary ionic compounds (with type I metal cations).

Using the Principle of Charge Neutrality (section 2.6.6) and knowing the charge of the ions allows you to determine the formula.

For type 1 metals is is very simple, you just name the metal, then the nonmetal, giving the nonmetal an -ide ending. So table salt (NaCl) is sodium chloride.

Exercise 2.7.2

What is the formula for Barium Chloride?

Answer

Barium is an alkaline earth and always corms a cation of charge of [+2], while chlorine is a halogen and always form the chloride ion of [-1]. For barium chloride to be neutral you would need two chlorides for every barium, and so the formula is $BaCl_2$.

Exercise 2.7.3

Name $AlBr_3$

Answer

Aluminum is always [+3] and bromide is always [-1] so it is aluminum bromide. The name does not have to tell how many cations and anions there are, as we know there are three [-1] bromides for every one [+3] aluminum ion, as otherwise it would not be neutral (review section 2.6.5.1)

Type II: Cations with Variable Charge (Oxidation State)

Most transition metals form multiple stable cations with different charges, and so you have to identify the charge state, which is done by writing the charge in Roman numerals and placing it in parenthesis after the name of the metal. So Fe^{+2} is iron(II) and Fe^{+3} is iron(III). Some of the metals form very common ions which have latin names that are in common use, and you need to be familiar with those in the following table. Note, **"-ic" stands for the higher oxidation state** (charge), and **"-ous" stands for the lower oxidation state.**

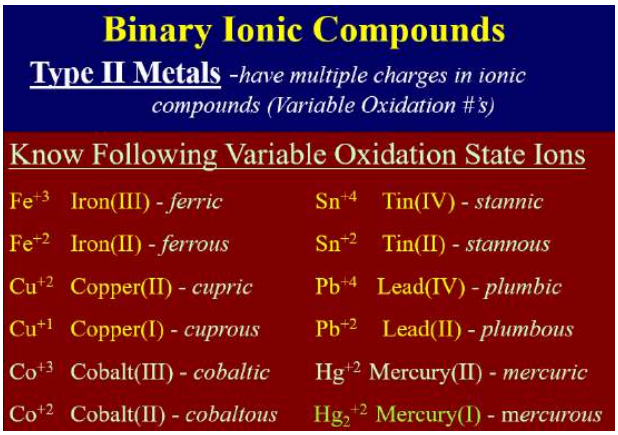


Figure 2.7.3: Some common type 2 metal and their stable ions.

Note the latin convention is to use:

- ***-ous*** ending for the **lower** oxidation state (charge)
- ***-ic*** ending for the **higher** oxidation state (charge)

Note **mercury(1) is not a monoatomic cation**, but is really a diatomic cation of two mercury atoms bound to each other, both having lost one electron. Polyatomic ions will be covered in the next section

Exercise 2.7.4

What is the formula of mercury(I) chloride?

Answer

Hg_2Cl_2, for every one Hg_2^{-2} cation there must be two Cl^- anions. So Hg_2Cl_2 it the lowest whole number ratio of cation to anion.

Example 2.7.1

Give the names and formula of the two chloride salts that from with the common cations of iron.

Solution

NOTE: Review section 2.6.5 and Video 2.6.2 if you have problems calculating the formula in this example or the next exercise.

Example 2

Ions:	Fe^{2+} and Cl^-	Fe^{3+} and Cl^-
Compound:	$FeCl_2$	$FeCl_3$
Nomenclature	Iron (II) Chloride or Ferrous Chloride	Iron (III) Chloride or Ferric Chloride

Exercise 2.7.5

Give the names and formula of the two nitride salts that from with the common cations of lead.

Answer

Ions:	Pb^{2+} and N^{-3}	Pb^{4+} and N^{-3}
Compound:	Pb_3N_2	Fe_3N_4
Nomenclature	Lead (II) nitride or Plumbous nitride	Lead (IV) nitride or Plumbic Nitride

Polyatomic Ions

Polyatomic ions are covalent units (molecules) where the total number of protons ≠ to the total number of electrons and they were introduced in section 2.6.4.2. They end in [-ide], [-ate] and [-ite]. Many of these are oxyanions with oxygen being bonded to a nonmetal and others are carboxylate ions. It should be noted that ionic comounds like ammonium acetate are composed entirely of nonmetals, but they form a crystal structure of cations and anion.

Table 2.7.1: List of Polyatomic ions freshmen chemistry students are required to know

Formula	Name		Formula	Name
NH_4^+	Ammonium		SO_3^{2-}	Sulfite
Hg_2^{2+}	Mercury (I) ion		SO_4^{2-}	Sulfate
ClO^-	Hypochlorite		$S_2O_3^{2-}$	Thiosulfate
ClO_2^-	Chlorite		CrO_4^{2-}	Chromate
ClO_3^-	Chlorate		$Cr_2O_7^{2-}$	Dichromate
ClO_4^-	Perchlorate		CN^-	Cyanide
NO_2^-	Nitrite		SCN^-	Thiocyanate
NO_3^-	Nitrate		OH^-	Hydroxide
CO_3^{2-}	Carbonate		O_2^{2-}	Peroxide
HCO_3^-	Bicarbonate		MnO_4^-	Permanganate
PO_4^{3-}	Phosphate		$C_2O_4^{2-}$	Oxalate
PO_3^{3-}	Phosphite		$C_8H_4O_4^{2-}$	Phthalate

Naming Oxyanions: Oxyanions are polyatomic ions where oxygen is attached to a nonmetal and as was discussed in section 2.6.4.2.1, nonmetals of the same periodic group from homologous oxyanions. Lets look at the 4 oxyanions of bromine

- perbromate (BrO_4^-)
- bromate (BrO_3^-)
- bromite (BrO_2^-)
- hypobromite (BrO^-)

These all end with -ate or -ite, and the real reasoning deals with the oxidation state of the nonmetal, sort of its hypothetical charge within the covalently bonded polyatomic ion. We will cover that in a later Chapter, but right now we note that the "-ate" ions have more oxygens and the "-ites" have less, with "per____ate" having the most, and "hypo___ite" having the least.



Video 2.7.3: YouTube video going over how to remember the names, formulas and charges of oxyanions (https://www.youtube.com/embed/AOtrIEjZd4c).

Overview of video:

- Oxyacids have same charge as central atom's monatomic ion (except for the first period)
  - nitride, phosphide,arsenide = [-3] so oxyanions of phosphorous & Arsenic = [+3], but of nitrogen = [+1]
  - oxide, sulfide, selenide, telluride = [-2] so oxyanions of sulfur, selenium & tellurium = [-2], oxygen does not form same kind of anions
  - fluoride, chloride, bromide, iodide = [-1], so oxyanions of chlorine, bromine, & iodine = [-1], fluorine's also = [-1] but I think only hypofluorite really exits, although I have seen the others on exams. For example, a search of PubChem for perfluorate gives no hits.
- ate implies more oxygens
  - hyper___ate implies even more oxygen
- ite implies less oxygens
  - hypo___ite implies even fewer oxygen.

Naming Carboxylate ions: Carboxylate ions were introduced in section 2.6.4.2.2. The following YouTube uses the structure of the carboxylate functional group as a tool to assist in remembering the formulas.



Video 2.7.4: Nomenclature of oxalate, phthalate and acetate, all of which have the carboxylate functional group.

Exercise 2.7.6

Name the following compounds:

A) $NiCO_3$

B) $Sr(NO_2)_2$

C) NH_4NO_3

Answer

A) **Nickel(II) carbonate**. Nickel is a Type II cation, so you need a Roman Numeral. To Figure out that charge "x", we need take a look at what we know. There is one carbonate ion at a charge of -2. There is one Nickel ion at unknown charge "x". 1(x) + 1(-2) = 0. To be charge neutral, x=+2.

B) **Strontium nitrite.** Strontium is a type I cation and there is no need for a Roman Numeral. NO_2^- is the nitrite ion.

C) **Ammonium nitrate.** both are polyatomic ions, so you simply state the name of cation followed by the name of the anion.

Covalent Compounds

Molecules are compounds held together by covalent bonds. In the overview of this Chapter (section 2.7.2) it was pointed out that there are two types of covalent compounds, what we are calling "classical molecules", and acids. Hydrogen like all the alkali metals only has one electron in its outer shell, but unlike the other elements of the first period (group 1A) you can not remove the electron and make an ion because all that is left would be a proton, which is a sub-atomic particle. This creates a class of molecules called acids, where hydrogen effectively takes the place of the cation, and the resulting bond is a polar covalent bond where the electron is unequally shared. Classical molecules occur when nonmetals form covalent bonds with each other and this can get very complicated. Organic chemsitry is based on the study of carbon based molecules and uses IUPAC nomenclature which is beyond the level of this course (the IUPAC Nomenclature book for organic compounds is 1568 pages long!).

Simple Molecules

In this class we will look at the nomenclature of very simple small molecules that form when two or more nonmetals share covalent electrons and form a classical molecule. In a molecule the formula represents the chemical entity, where as in an ionic compound, it is the lowest whole number ratio of cation to anion. So molecules like P_2O_5 and P_4O_{10} have the same ratio of phosphorous to oxygen, but they are different molecules, and so we need a nomenclature system that tells how many atoms of each element are in the compound.

The rules are simple, before each atom we place a Greek prefix indicating the number of those atoms in the formula. If there is only on atom, we often omit the prefix "mono". In this class we will name molecules with no more than 10 atoms of each type and you need to memorize the 10 prefixes in table 2.7.1.

Table 2.7.1: Common greek prefixes used in naming simple molecules

# of Atoms	1	2	3	4	5	6	7	8	9	10
Prefixes	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Deca-

There are some rules we need to follow,which are:

1. If there are two atoms, place the more "metallic" first (furthest to the left on the periodic table)
2. is there is a central atom, place it first, and the atoms attached after.
3. If there are more than two atoms, place in order of bonds

Example 2.7.2

Give the names for: CO, BCl_3

Give the formula for: carbon dioxide, dinitrogen pentoxide

Solution

CO = carbon ***mon***oxide BCl_3 = boron***tri***chloride

carbon dioxide= CO_2 dinitrogen pentoxide = N_2O_5

Exercise 2.7.7

Name each molecule.

a. SF_4
b. P_2S_5
c. N_2O_4
d. P_4S_{10}

Answer a

sulfur tetrafluoride

Answer b

diphosphorus pentasulfide

Answer c

dinitrogen tetraoxide

Answer d

tetraphosphorus decasulfide

Exercise 2.7.8

Give the formula for each molecule.

a. disulfur difluoride
b. iodine pentabromide
c. nitrogen trifluoride
d. diphosphorous pentaoxide

Answer a

S_2F_2

Answer b

IBr_5

Answer c

NF_3

Answer d

P_2O_5

Acids

In a binary ionic compound an alkali metal typically loses an electron to a nonmetal forming an [+1] cation while the nonmetal forms an anion. The resulting cation has core (inner shell) electrons that give it volume and surround the nucleus with electrons resulting in a stable ion, even if the net charge is positive. Hydrogen is also in group IA but has no inner shell electrons, and so it can't form a cation, as that would be a subatomic particle and the charge density would be so great that it would attract the electron back. So what happens is an unequal sharing of the electron and hydrogen forms an acidic bond with anions that is of the same formula as the other group 1A alkali metals would form. So acid nomenclature is based on that of an ionic compound.

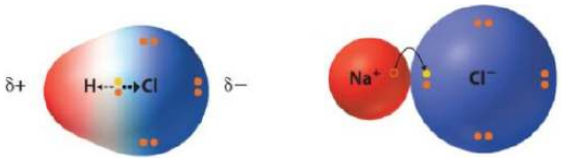


Figure 2.7.5: Hydrogen forms acids of the same "formula" as other alkali metals. On the left is the acid with chloride, HCl and on the right the salt of chloride NaCl.

When an acid dissolves in water the proton is transferred to a water forming hydronium ion H_3O^+ and thus dissociates forming the same anion as the analogous salt.

$$HCl(aq) \rightarrow H^+ + Cl^- \qquad (2.7.1)$$
$$NaCl(aq) \rightarrow Na^+ + Cl^-$$

where H^+ really exists as H_3O^+ in the water.

So we could say sodium chloride is a salt with a common ion to HCl. Because of this, we base the name of the acid on it's salt. Since there are three endings to salts (-ide, -ite, -ate), there are three correlating names for acids.

- **-ide** becomes **hydro** [anion stem]**ic acid**
- **-ite** becomes [anion stem]**ous acid**
- **-ate** becomes [anion stem]**ic acid**

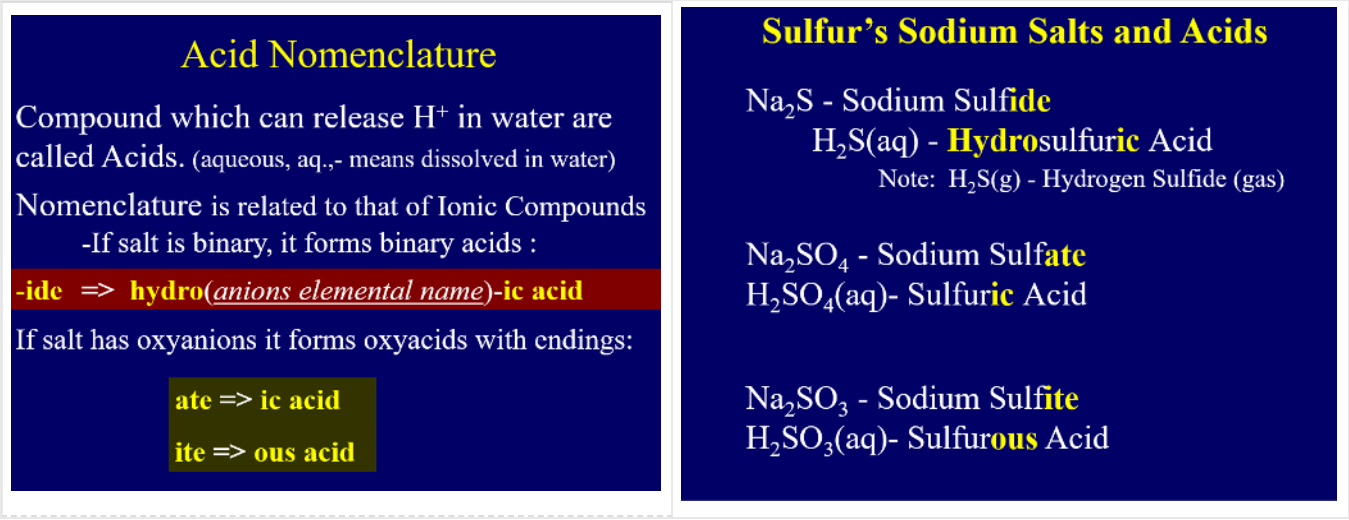


Figure 2.7.6: The rules for acid nomenclature as based on the nomenclature of ionic compounds

Compare the questions and answers of exercise 2.7.9 and 2.7.10 to so this relationship for the salts and acids of chlorine

Exercise 2.7.9

Name the five sodium salts of chlorine.

a. NaCl
b. NaClO
c. $NaClO_2$
d. $NaClO_3$
e. $NaClO_4$

Answer a

Sodium chloride

Answer b

Sodium hypochlorite

Answer c

Sodium chlorite

Answer d

Sodium chlorate

Answer e

Sodium perchlorate

Exercise 2.7.10

Name the five acids of chlorine.

a. HCl
b. HClO
c. $HClO_2$
d. $HClO_3$
e. $HClO_4$

Answer a

Hydrochloric acid

Answer b

Hypochlorous acid

Answer c

Chlorous acid

Answer d

Chloric acid

Answer e

Perchloric acid

Acid Salts

In the discussion of acids it became clear that an anion can make one of two kinds of bonds, either an ionic bond to a cation, or a covalent bond to hydrogen forming an acid. If an acid has a charge of [-2] or [-3], it could make both kinds of bonds, in which case it forms an acid salt. Lets look at the different species carbonate ion forms

$$\begin{gathered} Na_2CO_3 \text{ (the salt)} \\ NaHCO_3 \text{ (the acid salt)} \\ H_2CO_3 \text{ (the acid)} \end{gathered} \tag{2.7.2}$$

- Na_2CO_3 has 3 ions, two are [+1] and one is [-2]
- $NaHCO_3$ has 2 ions, one is [+1] and the other is [-1]
- H_2CO_3 has no ions

HCO_3^- is an acidic ion and there are two names for it, hydrogen carbonate or bicarbonate

So the three species are

$$\begin{gathered} Na_2CO_3 \quad \text{sodium carbonate} \\ NaHCO_3 \quad \text{sodium bicarbonate} \\ H_2CO_3 \quad \text{carbonic acid} \end{gathered} \tag{2.7.3}$$

Video 2.7.5 goes over the nomenclature of the salts of carbonate and Video 2.7.6 goes over the nomenclature of the salts of phosphate.



Video 2.7.5 Nomenclature of the compounds of carbonate (https://youtu.be/xSvTg9iPbbY)

Note that for phoshate with a [-3] charge that there are two acid salts

$$\begin{gathered} Na_3PO_4 \text{ (the salt)} \\ Na_2HPO_4 \text{ (the first acid salt)} \\ NaH_2PO_4 \text{ (the second acid salt)} \\ H_3PO_4 \text{ (the acid)} \end{gathered} \tag{2.7.4}$$

When there are more than one hydrogen taking the place of a cation you use greek prefixes, so the second acid salt is call sodium dihydrogenphosphate.



Video 2.7.6 Nomenclature of the compounds of phosphate (https://youtu.be/zOQRb01gN8Y)

Hydrated Salts

A hydrated salt has water as part of the crystal lattice structure. A real crystal has empty space between the ions and the water molecules help reduce the repulsive forces of like charges and so actually become part of the crystal geometric structure, but they are not the cation or the anion. These waters are so important that certain types of crystals will not grow without them. Cobalt(II) chloride hexahydrate is a hydrated salt



Figure 2.7.7: Cobalt(II) chloride hexahydrate crystals, image credit: http://en.Wikipedia.org/wiki/File:Cobalt(II)-chloride-hexahydrate-sample.jpg

Formula Convention: Follow ionic formula with a dot, and then indicate the number of waters followed by H_2O.

$$[Anhydrous\ Formula] \cdot [Number\ of\ Water]\ H_2O$$
$$CoCl_2 \cdot 6H_2O$$

Naming Convention: Append salt's name with the word "hydrate" that is preceeded by the number of waters of hydration,
Cobalt(II) chloride hexahydrate

Note, these are the same prefixes that are used in naming covalent compounds (table 2.7.1).

Problem Sets

- Worksheet 2.6: Nomenclature (and key)
- Homework 2.7 Nomenclature

Test Yourself

Graded Assignment: Section 4.5

The following set has 24 questions and randomly loads 10

The following set has 31 questions and randomly generates 10

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- November Palmer, Ronia Kattoum & Emily Choate (UALR)
- Elena Lisitsyna & Vincent Belford (H5P interactive modules)

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learning objectives

1. Define the mole
2. Differentiate molar mass from molecular weight
3. Calculate molar mass of a compound from its formula

The Mole

The mole is a unit of measurement that defines quantity as a counted number. It is the value of Avogadro's constant, one of the seven SI base units (review section 1B1.3.1) and the modern definition is the number of entities defined by , 6.02214076 x 10^{23} . This may not be intuitive, but this is an exact definition and there is no uncertainty to it.

1 dozen of eggs = 12 eggs

1 mole of eggs = 6.02214129 x10^{23} eggs

Note, the symbol for mole is mol and not M (which means mol/liter).

To appreciate the magnitude of Avogadro's number, consider a mole of pennies. Stacked vertically, a mole of pennies would be 4.5 × 10^{17} mi high, or almost six times the diameter of the Milky Way galaxy. If a mole of pennies were distributed equally among the entire population on Earth, each person would have more than one trillion dollars. The mole is so large that it is useful only for measuring very small objects, such as atoms.

Students need to memorize this number to 4 significant digits (6.022 x 10^{23}) but may need more if they use it in a calculation where using 4 significant digits determines the wrong number of significant digits in the answer. So if you multiply a six digit number like 1.00000 by Avogadro's number, you should use 7 digits for avagadro's number, ie., 6.022140 x 10^{23} .and the answer is 6.02214 x 10^{23} and not 6.022 x 10^{23}.



Video 2.8.1 Ted-Ed video on "How big is a mol?" by Daniel Dulek

Molar Mass

The molar mass is the mass of 6.022x10^{23}) atoms or compounds (molecules or ionic formula).

Substance (formula)	Atomic, Molecular, or Formula Mass (u)	Molar Mass (g/mol)	Structure
Helium (He)	4.0026 (atomic mass)	4.0026	 Pixabay

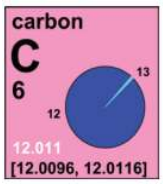
Substance (formula)	Atomic, Molecular, or Formula Mass (u)	Molar Mass (g/mol)	Structure
ethanol (C_2H_5OH)	46.069 (molecular mass)	46.069	
calcium phosphate $[Ca_3(PO_4)_2]$	310.177 (formula mass)	310.177	 wikimedia commons

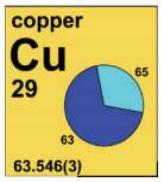
Figure 2.8.1: Comparison of atomic and molar mass for atom, molecule and ionic compound

The molar mass is often called the molecular weight or the formula weight (*fw*). Technically speaking, molecular weight only works for molecules, where it is the weight of one mole of molecules, where each molecule is a particle. For ionic compounds you could have one piece of crystal that has a mole of its constituent elements as defined by the ionic formula, but there is only one particle, and so it is better to consider its formula mass, or formula weight. We will use the symbold fw to indicate formula weight

Molar Mass of Elements

The importance of a mole is that if you have one mole of an element, the mass of the mole in grams is the same as the average mass of each element in Daltons (u). So if the average isotopic mass of an atom in a sample of carbon weights 12.011 u, then one mole of a sample of carbon weights 12.011 grams.







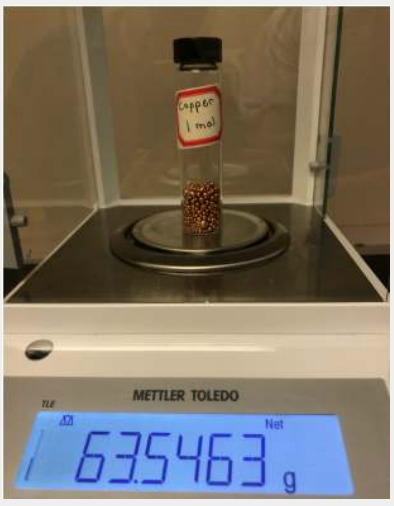


Figure 2.8.2: The two samples of carbon (left) and copper (right) have the same number of molecules (1 mol or 6.022×10^{23}) but different masses and volumes. Note, these are tared weights, that is, the weight of the container was subtracted from the displayed value (see use of analytical balances).

Exercise 2.8.1

Which has a greater number of particles? Which of the following has a greater mass?

A) 2.5 moles of He

B) 2.5 moles of Ar

Answer

Both have the same number of particles because there are 2.5 moles of each. That is similar to saying 2.5 dozen of donuts is the same number of items as the 2.5 dozen of cars. However, 2.5 moles of cars is going to have a larger mass than 2.5 dozen of trucks. By the same token, 2.5 moles of Ar is going to have more mass than 2.5 moles of He, even if they have the same number of particles.

Molar Mass of Compounds

Molecular

Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.114
O	2	×	16.00	=	32.00
				Molecular mass	206.27

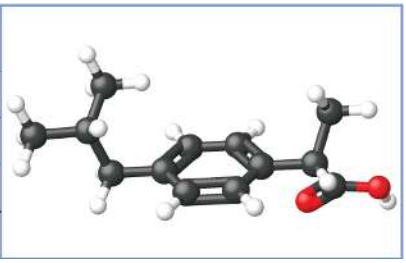


Figure 2.8.3: Calculation of molar mass of molecule (ibuprofen) (adopted from OpenSTAX)

Ionic

Remember Ionic compounds are discrete cations and anions combined to form a neutral crystal lattice. The formula for an ionic compound is the lowest whole number ratio of cations to anions and is not defined by the bonds, and there is no discrete "molecule" like there was for ibuprofen. Sodium chloride for example has the formula of NaCl, even though each sodium is bonded to 6 chlorines, while each chlorine in turn if bonded to 6 sodiums forming a lattice in 3 diensional space. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (Figure 2.8.4), even though a real sample has many more sodium and chloride ions within its crystal structure.

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

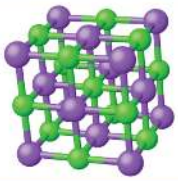


Figure 2.8.4: Calculation of molar mass of ionic compound (table salt, NaCl) (adopted from OpenSTAX)

You can also calculate the molar mass of polyatomic ions. This is often called molecular weight or formula weight.

Example: The molar mass of sulfate (SO_4^{-2})

1 mole S (1)(32.07) = 32.06g
4 mole O (4)(16.00) = 64.00g
1 mole SO_4^{-2} = 96.06g

Practice

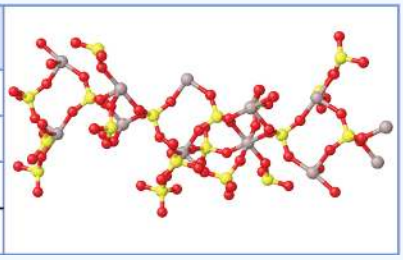
Exercise 2.8.2

What is the molar mass for each of the following molecules?

a. Aluminum Sulfate
b. Benzene (C_6H_6)
c. Acetylene (C_2H_2)
d. Water
e. Hydrogen Peroxide

Answer a

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14



Aluminum Sulfate ($Al_2(SO_4)_3$) = **342.14g/mol** (Image adopted from OpenSTAX)

NOTE: we could have used the molar mass of sulfate that was calculated above

$$3x96.06 + 2(26.98) = 241.14$$

Answer b

Benzene (C_6H_6) = **78.12g/mol**

Answer c

Acetylene (C_2H_2) = **26.04g/mol**

Answer d

Water (H_2O) = **18.02g/mol**

Answer e

Hydrogen Peroxide (H_2O_2) = **34.02g/mol**

Exercise 2.8.3

What is the molar mass for each of the following molecules?

a. Sodium Bicarbonate
b. Ammonium Nitrate
c. Potassium Perchlorate
d. Silver Chloride
e. Acetic Acid

Answer a

Sodium Bicarbonate ($NaHCO_3$) = **84.02g/mol**

Answer b

Ammonium Nitrate (NH_4NO_3) = **80.08g/mol**

Answer c

Potassium Perchlorate ($ClKO_4$) = **138.54g/mol**

Answer d

Silver Chloride (AgCl) = **143.32g/mol**

Answer e

Acetic Acid (CH_3COOH) = **60.06g/mol**

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- November Palmer, Ronia Kattoum & Emily Choate (UALR)
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2.9: Calculations Determining the Mass, Moles and Number of Particles

learning objectives

- Convert grams of a substance to moles
- Convert moles of a substance to grams

Counting by Measuring

In this section we will learn to "count" the number of particles of a solid substance by measuring its mass. This is building off of section 2.8.2.2, molar mass of a compound and Dimensional analysis (section1B.4), where the molar mass is considered an equivalent statement that allows you to convert from a measured value of mass to a counted value of number of particles. As such, it is like a unit conversion based on a physical constant (section 2B.3.5.3), the molar mass of a compound.

We will use the following symbols

m = mass (g)

n = moles (mol)

Formula Weight is defined as

$$fw = \frac{m(g)}{n(mol)} \tag{2.9.1}$$

$$mass = moles\ times\ formula\ weight$$

This formula weight is an equivalence statement that depends on the identity of the chemical and converts between its mass and its number of moles. For water

$$1\ molH_2O = 18\ grams \tag{2.9.2}$$

$$fw(H_2O) = 18\frac{g}{mol}$$

$$m = n(fw) \tag{2.9.3}$$

and there are thus two conversion factors

$$\underbrace{\frac{m}{fw}}_{\text{converts mass to mols}} \quad \leftarrow or \rightarrow \quad \underbrace{n(fw)}_{\text{converts mols to mass}} \tag{2.9.4}$$

That is, dividing the mass by the formula weight converts it to the number of moles, and multiply the molese by the formula weight converts its moles to mass. The formula weight relates mass to moles the way density relates mass to volume, and it is a constant that for any element or compound that can be determined from the periodic table.

Grams to Moles

Figure 2.9.1 shows the flow chart for converting mass to moles. I

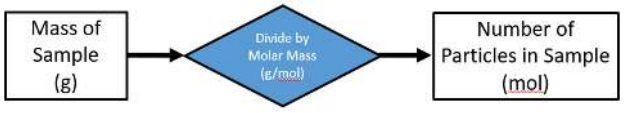


Figure 2.9.1: Flowchart for converting mass to moles.

The best way to solve these problems is to set up a conversion factor based on the equivalence statement (Equation 2.9.2), and then multiply by a conversion factor based on this equivalence statement, where you put the mass in the denominator (which is the same as dividing by the molar mass).

When Using Conversion Factors Keep Units in Equations

Example 2.9.1

How many molecules are in 3.00g of ibuprofen?

Solution

We calculated the molar mass of ibuprofen in section 2.8.2.2.1 to be 206.27 g/mol.

From the molar mass we can generate the equivalence statement:

$$206.27g\ C_{13}H_{18}O_2 = 1\ mole\ C_{13}H_{18}O_2 \tag{2.9.5}$$

We are converting a mass of 3.00 g, which has 3 significant Figures, and so will use one extra for the molar mass, and use 206.3 g/mol. From

$$3.00\ \cancel{g}\ C_{13}H_{18}O_2 \underbrace{\left(\frac{mol\ C_{13}H_{18}O_2}{206.3\ \cancel{g}}\right)}_{\text{converts mass to mol}} = 0.0145 \text{ mol or } 14.5\text{mmol} \tag{2.9.6}$$

or we can convert to actual molecules, but need a second equivalence statement

mole = 6.02214x10^{23} molecules ibuprofen

$$3.00\ \cancel{g}\ C_{13}H_{18}O_2 \underbrace{\left(\frac{\cancel{mol}\ C_{13}H_{18}O_2}{206.3\ \cancel{g}}\right)}_{\text{converts mass to mol}} \underbrace{\left(\frac{6.022x10^{23}\ C_{13}H_{18}O_2}{\cancel{mol}}\right)}_{\text{converts moles to molecules}} = 8.76x10^{21} \text{ molecules of ibuprofen} \tag{2.9.7}$$

NOTE: Either Answer is Correct.

Moles to Grams

Figure 2.9.2: shows the flow chart of converting number of particles to mass, but once again, we will use the conversion factor based on the equivalence statement.



Figure 2.9.2: Flow chart for converting number of particles to mass.

The Trick: The Molar Mass is a conversion factor like a Physical Constant, and so make a Equivalence Statement out of it.

Example 2.9.2

Using the molar mass of 206.27 g/mol, calculate the mass in grams of 10 molecules of ibuprofen?

Solution

To answer this we need two equivalence statements

- **1 mole = 206.27 g ibuprofen**
- **1 mole = 6.02214x10^{23} molecules ibuprofen**

Note: 10 molecules is an exact number and has no significant digits Since the molar mass was given with five significant digits, we would not use 6.022x10^{23} for Avogadro's number because that has 4, and so we have to decide how many to use with Avogadro's number. The rule of thumb (see below) when deciding how many to use is to use one more significant digit than the number you are working with, and so we choose six.

$$10\ \cancel{molecules}\ C_{13}H_{18}O_2 \underbrace{\left(\frac{mol\ C_{13}H_{18}O_2}{6.02214\ x10^{23}\ \cancel{molecules}}\right)}_{\text{converts molecules to moles}} \underbrace{\left(\frac{206.27g\ C_{13}H_{18}O_2}{\cancel{mol}}\right)}_{\text{converts moles to mass}} = 3.4252x10^{-21} \text{ g of ibuprofen} \tag{2.9.8}$$

Exercise 2.9.1

Answer the following Questions

a. How many moles is 12.2 g of Sodium Bicarbonate?
b. How many moles is 18.8 g of Ammonium Nitrate?
c. How many atoms is 30.8 g of Ammoium Nitrate?
d. What is the mass of 2.45 mole Silver Chloride?
e. what is the mass of 3.44 mole of benzene (C_6H_6) ?

Answer a

Sodium Bicarbonate ($NaHCO_3$) = **0.145 mol**

Answer b

Ammonium Nitrate (NH_4NO_3) = **0.235 mol**

Answer c

Potassium Perchlorate ($ClKO_4$) = **0.222mol**

Answer d

Silver Chloride (AgCl) = **351g**

Answer e

Benzene (C_6H_6) = 269**g**

Significant Digits in Molar Mass Calculations

The number of significant digits you use in calculating the molar mass depends on your data. The rule of thumb is use one more significant digit than the measured value that determines the number of significant digits in your final answer. There is no need to use more, but if you use less, then the significant digits of the molar mass determines the significant digits of your final answer.

You should redo equation 2.9.5 using a molar mass of 206.27 g/mol and you will see the final answer (to three significant digits) is the same. In making these conversions, you should always use a molar mass with one extra significant digit than your measured number. If you had uses 3.00000g of ibuprofen (6 significant digits), then if possible you should have used seven significant digits for the molar mass. If you had used five significant digits (206.27g/mol) your answer would have 5 significant digits, even though your measured value had seven.

Contributors and Attributions

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2.10: Percent Composition

learning objectives

1. Introduce Mass Percent and Mole Fraction
2. Calculate Mass Percent from Chemical Formulas

Introduction

Percent and fraction essentially tell you the same thing, they describe the ratio of a part of the whole. Because a chemical compound has a constant composition, which is defined by is molecular or compound formula, the fraction of each type of element must be constant. For example, water has 3 atoms, one hydrogen and two oxygens. So the fraction of oxygen is 1/3 (33.3%) and the fraction of hydrogen is 2/3rd (66.7%), as exemplified in the left pie chart of Figure 2.10.1. But water weights 16 times as much as hydrogen and so if you could weigh a water molecule, the mass of oxygen would be 16 Daltons, while that of the two hydrogens would be 2 Daltons, so on a mass basis, water if 88.9% oxygen and 11.1% hydrogen. So when we say the fractional or percent composition, we need to identify how we are determining it. Usually, but not always, chemists use percentage for mass and fraction for moles (number of particles).

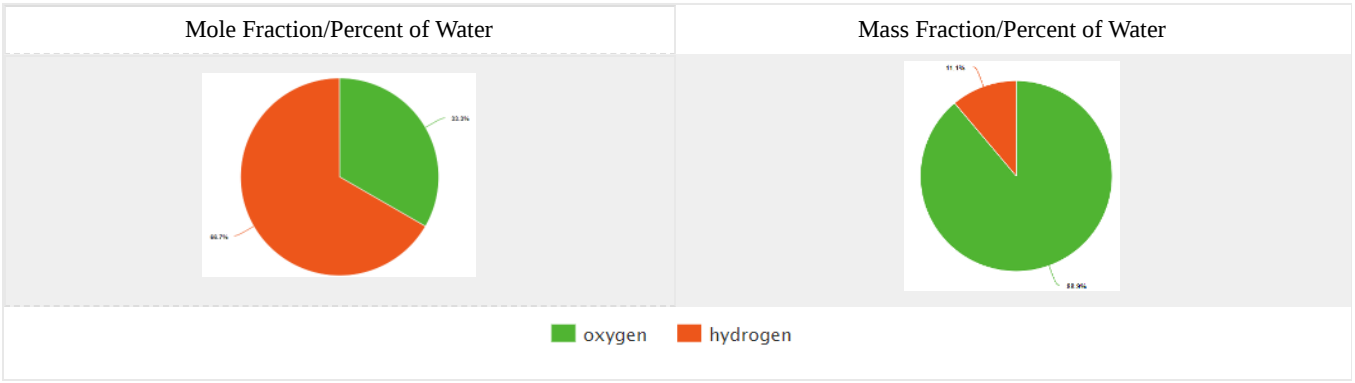


Figure 2.10.1: Mole (left) and mass (right) fractions (or percentages) of oxygen and hydrogen in water.

So, is water mostly oxygen or hydrogen? Well, that depends on how you look at it. If you are counting atoms, it is mostly hydrogen. If you are measuring the mass, it is mostly oxygen.

Mass Percent

Mass percent of any element in a compound is 100 time the mass of the element divided by the total mass

$$\text{Mass \% element} = \frac{\text{mass element}}{\text{mass compound}} \times 100\% \tag{2.10.1}$$

One mole of water weights 18 grams, with 2 grams being hydrogen and 16 being oxygen, so the fraction of hydrogen is 2/18 (0.1111) and the fraction oxygen is 16/18 (.8889), and note that the sum of the fractions is 1. The percentage of an element in a compound is 100 times the fraction, so for water the mass percent hydrogen is 11.11% and the mass percent oxygen is 88.89%.

$$\text{Mass \%H} = \frac{\text{mass H}}{\text{mass compound}} \times 100\% \tag{2.10.2}$$

$$\text{Mass \%O} = \frac{\text{mass O}}{\text{mass compound}} \times 100\% \tag{2.10.3}$$

for water

$$\text{Mass \%H} = \frac{2\text{g}}{18\text{g}} \times 100\% = 11.11 \tag{2.10.4}$$

$$\text{Mass \%O} = \frac{16\text{g}}{18\text{g}} \times 100\% = 89.99 \tag{2.10.5}$$

Equations 2.10.4 and 2.10.5 describe the right pie chart in Figure 2.10.1, and note they add to 100%.

Video 2.10.1 shows a technique to calculate the percent composition of a formula that minimizes the amount of work you need to do.



Video 2.10.1: Calculating the mass % composition of the elements in acetic acid.

NOTE: Even though mass has units, mass percent is unit-less, and so care needs to be taken to identify what the percent or fraction relates to. Also, because a sample of a pure substance consist of molecules or ionic compounds of the same formula, the percent or fractional value does not depend on the sample size. So one molecule of water has the same percent composition as a gallon of [pure] water.

It should also be noted that as the following two videos show, some formulas have the same percent composition, even though they are different molecules, like acetylene (C_2H_2) and benzene (C_6H_6).



Video 2.10.2: Comparing % Composition of acetylene with benzene.

Exercise 2.10.1

What is the mass percent of oxygen in dichlorine heptoxide?

Answer

Mass of Cl in 1 mol Cl_2O_7 , 2 Cl : 2 x 35.45 g = 70.90 g

Mass of O in 1 mol Cl_2O_7 , 7 O: 7 x 16.00 g = 112.00 g

Molar mass of Cl_2O_7 = 182.90 g/mol

$$\% \text{ O} = \frac{112.00 \text{ g O}}{182.90 \text{ g}} \times 100\% = 61.24\% \text{ O}$$

Mole Fraction

The mole fraction of each element in a sample is the number of moles of that in a sample divided by the total number of moles in the sample, and this can be determined by the chemical formula, where it is the number of atoms of that element in the formula divided by the total number of atoms in the formula.

$$\text{mole fraction of an element } = \frac{\text{moles of the element}}{\text{total moles in compound}} \tag{2.10.6}$$

shows the numbers of each type of element and so one mole of water (H_2O) has two moles of hydrogen and one mole of water. That is the mole fraction of hydrogen is 2/3 (.6667) and the mole fraction oxygen is 1/3 (.3333), meaning the mole fraction for water is 67% hydrogen and 33% oxygen.

$$\text{mole fraction H} = \frac{\text{mole H}}{\text{total mol in compound}} \tag{2.10.7}$$

$$\text{mole fraction O} = \frac{\text{mole O}}{\text{total mol in compound}} \tag{2.10.8}$$

for water

$$\text{mole fraction H} = \frac{2 \text{ mole H}}{3 \text{ mol}} = 0.667 \tag{2.10.9}$$

$$\text{mole fraction O} = \frac{1 \text{ mole O}}{3 \text{ mol}} = 0.333 \tag{2.10.10}$$

Equations 2.10.9 and 2.10.10 describe the right pie chart in Figure 2.10.1.

Exercise 2.10.2

What is the mole fraction of oxygen in dichlorine heptoxide?

Answer

Moles of Cl in 1 mol Cl_2O_7 = 2 mol Cl

Moles of O in 1 mol Cl_2O_7 = 7 mol

Total moles in Cl_2O_7 = 9

$$mole\ fraction \text{ O} = \frac{7 \text{ mol O}}{9 \text{ total moles}} = .778$$

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- Ronia Kattoum (Learning Objectives)

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2.11: Empirical and Molecular Formulas

learning objectives

1. Distinguish between empirical formula and molecular formula
2. Determine empirical formula and molecular formula using percent composition
3. Determine empirical formula and molecular formula using mass data

Introduction

Empirical measurements are based on a measurable (empirical) quantity like mass. Knowing the mass of each element in a compound we can determine its formula. There are two types of formulas, empirical and molecular.

Empirical Formula: Lowest whole number ratio of the elements in a compound

Molecular Formula: Actual whole number ratio of the elements in a compound.

The Empirical formula is the lowest whole number ratio of the elements in a compound. In (section 2.10), we discovered that benzene and acetylene have the same mass percent composition, and thus it is logical that they have the same ratio of elements to each other, that is, they have the same empirical formula.

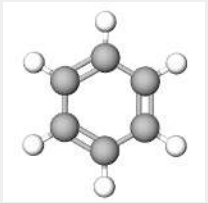
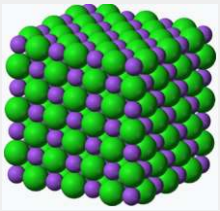
Compound	Acetylene	benzene	NaCl
Structure			
Empirical Formula	CH	CH	NaCl
Molecular Formula	C_2H_2	C_6H_6	not a molecule (use NaCl)

Figure 2.11.1: Empirical and molecular formulas of several simple compounds.

Empirical Formula

The Empirical formula is the lowest whole number ratio of the elements in a compound. In (section 2.10), we discovered that benzene and acetylene have the same mass percent composition, and thus it is logical that they have the same ratio of elements to each other, that is, they have the same empirical formula.

For salts that do not have homonuclear diatomic ions (like Hg_2^{+2} or O_2^{-2}) the empirical formula is the formula we write to describe the salt. Mercury(I)chloride has the empirical formula of HgCl, but the real compound formula is Hg_2Cl_2 (review table 2.7.3)

Multiple molecules can have the same empirical formula. For example, benzene (C_6H_6) and acetylene (C_2H_2) both of the empirical formula of CH (see Figure 2.11.1.

Calculating Empirical Formulas

Steps:

1. **Obtain Mass of Each Element (in grams)**
   - if given total mass you need the mass of all but one element (sum of masses equals total mass).
   - if given % composition assume 100 g and convert to mass.
     - if given % composition you need data for of all but one element (sum of percents equals 100%).
2. **Calculate # of moles of each element present** (from masses and atomic weights).
   - You now have a formula representing the mole ratio of the elements in the compound and you need to make these integers.

3. **Divide # of Moles of each element by the one with the smallest value** (forcing it to one and making all other values greater than one).
4. **Multiply the results of step 3 by the smallest integer which will convert them all to whole numbers.**

Note

The trick is to convert decimals to fractions and then multiply by the lowest common denominator (watch video 2.11.1)

$0.5=\frac{1}{2}$	$0.33=\frac{1}{3}$	$0.67=\frac{2}{3}$	$0.25=\frac{1}{4}$	$0.75=\frac{3}{4}$
$0.2=\frac{1}{5}$	$0.4=\frac{2}{5}$	$0.6=\frac{3}{5}$	$0.8=\frac{4}{5}$	$0.167=\frac{1}{6}$

The following video shows how to calculate the empirical formula for aspiring.

Calculate the empirical formula for aspirin:

Aspirin is made of H, O & C, and was analyzed to contain 60.0% carbon and 35.5% Oxygen.



Video 2.11.1: Empirical formula of aspirin

Example 2.11.1

A certain compound was found to contain 67.6% C, 22.5% O, and 9.9% H. What is the empirical formula?.

Solution

$$22.5gO\left(\frac{1molO}{16.00g}\right)=1.4\Rightarrow\frac{1.4}{1.4}=1 \tag{2.11.1}$$

$$67.6gC\left(\frac{1molC}{12.011g}\right)=5.63\Rightarrow\frac{5.63}{1.4}=4 \tag{2.11.2}$$

$$9.9gH\left(\frac{1molH}{1.007g}\right)=9.9\Rightarrow\frac{9.9}{1.4}=7 \tag{2.11.3}$$

$$\mathbf{C_4H_7O}$$

This Applet comes from the ChemCollective at Carnegie Mellon University. This link will send you to the video and tutorial associated with this applet. Every time you load the page a new problem will load, and there are a series of tiered hints to help you work through the problems.

Mineral Composition

A mineral sample is obtained from a region of the country that has high arsenic contamination. An elemental analysis yields the following elemental composition:

Element	Atomic Weight (g/mol)	Percent Composition
Zn	65.409	23.4%
As	74.9216	53.7%
O	15.9994	22.9%

What is the empirical formula of this mineral? (click here if you want step-by-step help to solve this problem)

Note that each time you load this page, you will get a new version of this problem. You may want to practice this problem until you can get the answer correct without using the step-by-step help.

Use the check button (Check) to submit your answer and the hint button (Hint) to get help with the problem.

Zn ☐ As ☐ O ☐ Check Hint

Exercise 2.11.1: empirical formula

Calculate the Empirical formula for the following

a. A 3.3700 g sample of a salt which contains copper, nitrogen and oxygen, was analyzed to contain 1.1418 g of copper and 1.7248 g of oxygen.
b. A compound of nitrogen and oxygen that contains 30.43% N by weight.
c. A 2.402-g sample of made of C, H, N and O contains 1.121 g of N, 0.161 g H, 0.480 g C, and an unspecified amount of oxygen.

Answer a

CuN_2O_6

Answer b

NO_2

Answer c

N_2H_4CO

Exercise 2.11.2: empirical formula

Given the empirical formula of the compound in part (a) of the above:

a. What could be the formula of the compound.
b. What would be the name of the compound, using the formula in the answer from part (a) of this question.

Answer a

$Cu(NO_3)_2$

Answer b

Copper(II) nitrate of cupric nitrate

Exercise 2.11.3: empirical formula

In section 2.10.2 we saw that benzene and acetylene both have the same mass percent composition (92.3% C and and 7.7% H), so calculate their empirical formulas

a. What is the empirical formula of acetylene (C_2H_2)?
b. What is the empirical formula of benzene (C_6H_6)? (Knowing (a) the empirical formula of acetylene and (b) that benzene and acetylene have the same mass % composition, cam you answer this without doing any math?)

Answer a

CH

Answer b

CH

Molecular Formula

To calculate the molecular formula we need additional information beyond that of the mass or mass percent composition, we need to know the molar mass of the substance. There are many experimental ways that can be determined, and we will learn some as the semester proceeds. The mass spectrometer that we used to determine the isotopic composition in section 2.3 of this Chapter could be used to determine the molar mass of many unknowns. But there are other techniques, and at this point in the semester, the molar mass will be treated as a given.

The empirical formula represents the lowest whole number ratio of the elements in a molecule while the molecular formula represents the actual formula of the molecule. So the molecular formula must be an integer multiple of the empircal formula, that is it is n times larger where n=1 or 2 or 3 or.... but it is an integer. This gives the following relationship

$$[\text{Molecular Formula} = \text{n}([\text{Empirical Formula})] \tag{2.11.4}$$

then if we have one mole

$$[\text{Molecular Weight} = \text{n}([\text{Empirical Weight})] \tag{2.11.5}$$

or

$$n = \frac{[\text{Molecular Weight}]}{[\text{Empirical Weight}]} \tag{2.11.6}$$

So you calculate the Empirical formula as above, then determine the weight of one mole, divide that into the molar mass, and that tells you how many times it is bigger, and then multiple the emprical formula by that number.

Let's compare Benzene to acetylene. In video 2.10.2 (section 2.10.2) we saw that benzene and acetylene had the same mass % composition and in exercise 2.11.3 we say they had the same empirical formula

Table 2.11.1: data setup for calculating molecular formula for empirical formula and molar mass for benzene and acetylene

name:	Benzene	Acetylene
Formula Weight	78.12g/mol	26.04g/mol
Empirical Formula	CH	CH
Empirical Formula Weight	13.017	13.017
$n=\frac{[\text{Molecular Weight}]}{[\text{Empirical Weight}]}$	$\frac{78.12}{13.017}=6$	$\frac{26.04}{13.017}=2$
Formula = n times empirical formula	6(CH) = C_6H_6	2(CH) = C_2H_2

Calculating Molecular Formulas

Example 2.11.2

A certain compound was found to contain 67.6% C, 22.5% O, and 9.9% H. If the molecular weight of the compound was found to be approximately 142 g/mol, what is the correct molecular formula for the compound?

Solution

C_4H_7O has a empirical weight of

(4)(12.01) + (7)(1.007) + (16.00) = 71.09g/mol

$$\left(\frac{142g/mol}{71.09g/mol}\right)=2 \tag{2.11.7}$$

multiply the coefficients by 2

$C_8H_{14}O_2$

Exercise 2.11.4: Molecular formula

Calculate the molecular formula for the following

a. A compound has an empirical formula of C_2HF has a molar mass of 132.06 g/mol.
b. 200.0 g sample of an acid with a molar mass of 616.73g/mol contains 171.36 g of carbon, 18.18g of nitrogen and the rest is hydrogen.
c. Strychine has a molar mass of 334 g/mol and percent composition of 75.42%C, 6.63%H and 8.38%N and the rest oxygen.

Answer a

$C_6H_3F_3$

Answer b

$C_{44}N_4H_{32}$

Answer c

$C_{21}N_2H_{22}O_2$

Contributors and Attributions

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- November Palmer & Emily Choate (UALR)
- Ronia Kattoum (Learning Objectives)

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2.12: Hydrates

learning objectives

- Define hydrates and identify common hydrates
- Outline properties of hydrates
- Determine formulas for hydrates

Introduction

Water, the most common chemical on earth, can be found in the atmosphere as water vapor. Some chemicals, when exposed to water in the atmosphere, will reversibly either adsorb it onto their surface or include it in their structure forming a complex in which water generally bonds with the cation in ionic substances. The water present in the latter case is called *water of hydration* or *water of crystallization*. Common examples of minerals that exist as hydrates are gypsum ($CaSO_4 \cdot 2\,H_2O$), Borax ($Na_3B_4O_7 \cdot 10\,H_2O$) and Epsom salts ($MgSO_4 \cdot 7\,H_2O$). Hydrates generally contain water in stoichiometric amounts; hydrates' formulae are represented using the formula of the anhydrous (non-water) component of the complex followed by a dot then the water (H_2O) preceded by a number corresponding to the ratio of H_2O moles per mole of the anhydrous component present. They are typically named by stating the name of the anhydrous component followed by the Greek prefix specifying the number of moles of water present then the word *hydrate* (example: $MgSO_4 \cdot 7\,H_2O$: magnesium sulfate heptahydrate).

Properties of Hydrates

It is generally possible to remove the water of hydration by heating the hydrate.

The residue obtained after heating, called the anhydrous compound, will have a different structure and texture and may have a different color than the hydrate.

Example:

$$\underbrace{CuSO_4 \cdot 5\,H_2O(s)}_{\text{Deep Blue}} \xrightarrow{\Delta} \underbrace{CuSO_4(s)}_{\text{Ashy White}} + 5\,H_2O(g) \tag{2.12.1}$$

$$\underbrace{CuSO_4(s)}_{\text{Ashy White}} \xrightarrow{H_2O(l)} \underbrace{CuSO_4(aq)}_{\text{Deep Blue}} \tag{2.12.2}$$

Any anhydrous compound from a hydrate generally has the following properties:

- Highly soluble in water
- When dissolved in water, the anhydrous compound will have a color similar to that of the original hydrate even if it had changed color going from the hydrate to the anhydrous compound.

Most hydrates are stable at room temperature. However, some spontaneously lose water upon standing in the atmosphere, they are said to be *efflorescent*.

Other compounds can spontaneously absorb water from the surrounding atmosphere, they are said to be *hygroscopic*. Some hygroscopic substances, such as P_2O_5 and anhydrous $CaCl_2$, are widely used to "dry" liquids and gases (see experiment on the Molecular Weight of CO_2); they are referred to as desiccants. Other hygroscopic substances, such as solid $NaOH$, absorb so much water from the atmosphere that they dissolve in this water, these substances are said to be *deliquescent*. Some compounds like carbohydrates release water upon heating by decomposition of the compound rather than by loss of the water of hydration. These compounds are not considered true hydrates as the hydration process is not reversible.

Formula of a Hydrate ($\text{Anhydrous Solid} \cdot x\text{H}_2\text{O}$)

The formula of a hydrate can be determined by dehydrating a known mass of the hydrate, then comparing the masses of the original hydrate and the resulting anhydrous solid. The mass of water evaporated is obtained by subtracting the mass of the anhydrous solid from the mass of the original hydrate (2.12.3):

$$m_{\text{H}_2\text{O}} = m_{\text{Hydrate}} - m_{\text{Anhydrous Solid}} \tag{2.12.3}$$

From the masses of the water and anhydrous solid and the molar mass of the anhydrous solid (the formula of the anhydrous solid will be provided), the number of moles of water and moles of the anhydrous solid are calculated as shown below (2.12.4, 2.12.5):

$$n_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{MM_{\text{H}_2\text{O}}} \tag{2.12.4}$$

$$n_{\text{Anhydrous Solid}} = \frac{m_{\text{Anhydrous Solid}}}{MM_{\text{Anhydrous Solid}}} \tag{2.12.5}$$

In order to determine the formula of the hydrate, $[\text{Anhydrous Solid} \cdot x\text{H}_2\text{O}]$, the number of moles of water per mole of anhydrous solid (x) will be calculated by dividing the number of moles of water by the number of moles of the anhydrous solid (Equation 2.12.6).

$$x = \frac{n_{\text{H}_2\text{O}}}{n_{\text{Anhydrous Solid}}} \tag{2.12.6}$$



Video 2.12.1: Youtube video uploaded by dcaulf (https://www.youtube.com/watch?v=KCuYQ3ayFNM)

Exercise 2.12.1

You weight out a 0.470-sample of hydrated nickel(II) chloride, $NiCl_2 \cdot xH_2O$. Upon heating, the mass of the anhydrous salt that remains is 0.256 grams. What is the formula of the hydrate? What is the name of the hydrate?

Answer

Mass of water: mass of hydrate – mass of anhydrous salt = 0.470 g – 0.256 g = 0.214 g of water

n (moles) of H_2O = 0.214 g H_2O x $\frac{1\ mole\ of\ H2O}{18.02\ g\ H2O}$ = 0.0118756 moles of H_2O

n(moles) of $NiCl_2$ = 0.256 g $NiCl_2$ x $\frac{1\ mole\ of\ NiCl2}{129.60\ g\ NiCl2}$ = 0.0019753 moles of $NiCl_2$

$\frac{n\ (moles)\ of\ H2O}{n(moles)\ of\ NiCl2} = \frac{0.0118756\ moles\ of\ H2O}{0.0019753\ moles\ of\ NiCl2} = 6.0$

So... $NiCl_2 \cdot 6H_2O$

Name: Nickel(II) chloride hexahydrate

Contributors

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- Original Article can be found here: 5: Properties of Hydrates (Experiment)
- Modified by Ronia Kattoum (UA of Little Rock)

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CHAPTER OVERVIEW

3: Chemical Reactions

Topic hierarchy

3.1: Introduction to Chemical Equations
3.2: Types of Chemical Reactions
3.3: Balancing Chemical Equations
3.4: Aqueous Reactions
3.5: Acid-Base Reactions
3.6: Redox Reactions

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3.1: Introduction to Chemical Equations

learning objectives

- Define terms used to represent chemical reactions including reactants, products, states, coefficients, and stoichiometry, reaction conditions.
- Apply the law of conservation of matter to balanced chemical reactions
- Differentiate between the liquid phase and the aqueous phase

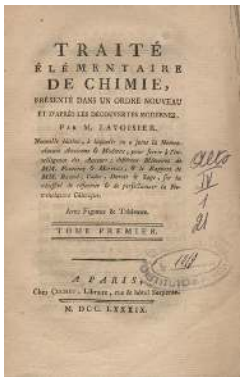
What are Chemical Equations?

Chemical equations are how chemists describe chemical reactions, the process by which one form of matter (reactants) turn into another form of matter (products). Below is the unbalanced chemical reaction for the combustion of methane (CH_4) with oxygen (the reactants) to produce carbon dioxide and water (the products).

$$CH_4(g) + O_2(g) \text{ ® } CO_2(g) + H_2O(g)$$

(unbalanced equation)

Law of Conservation of Mass: Balancing Reactions


TRAITÉ
ÉLÉMENTAIRE
DE CHIMIE,
TOME PREMIER.
A PARIS,
M. DCC. LXXXIX.

Antoine Lavoisier (1743-1794) is attributed to introducing the **Law of Conversation of Matter,** which states that during a chemical process mass is neither created or destroyed, and thus the total mass of the products equals the total mass of the reactants. This was first published in his 1789 "Traité Élémentaire de Chimie" and in France this was known as Lavoisier's Law, *"Rien ne se perd, rien ne se crée, tout se transforme. (Nothing is lost, nothing is created, everything is transformed."*). The Gutenberg Project offers a free English translation of the book (Elements of Chemistry)..

As matter is made of compounds and elements, and the compounds may change, this means the total number of atoms of each element must be conserved. In the above equation only atoms of carbon are conserved, and so the equation is not balanced. In the equation below, that atoms of each element are conserved, and so it is balanced.

$$CH_4(g) + 2O_2(g) \text{ ® } CO_2(g) + 2H_2O(g)$$

(balanced equation)

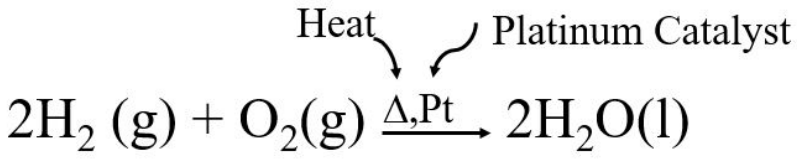
Stoichiometric Coefficients:

Once the reactants and products are written, you are not able to change the subscripts of the compound to balance the chemical reaction without changing the identity of the reactants and products. However, you may use stoichiometric coefficients in front of each chemical entity (molecule or element) to balance the equations. The word "stoichiometry" come from the Greek *stoicheion* (element) and *metrein* (to measure). We will learn more about this in section 4.1.

What other information can be included in a chemical equation?

- Phases
  - (s) - Solid
  - (l) - liquid
  - (g),(v) - gas, vapor
  - (aq) - aqueous
- Reaction Conditions (often indicated above the arrow)
  - (Δ) - Heat

- Catalyst



Aqueous vs. Liquid Phase:

Liquid is a phase, the condensed fluid phase (in contrast to a gas, which is the dispersed fluid phase). Aqueous is a solution where something is dissolved in water, the solvent. NaCl(l) is molten sodium chloride, that is obtained by heating it above the melting point. NaCl(aq) is aqueous sodium chloride, which is made by dissolving the salt into water. At one atm pressure and normal temperatures, you can have NaCl(aq) (salt water), but you can't have molten NaCl (l), because the melting point is 1,474^{o}F.

Catalysts:

Catalysts can be understood by looking at the mechanism of a reaction, that is, how it actually proceeds, and can be considered to be chemicals that function as both a reactant and a product. That is, the catalyst reacts with something and form a new chemical, an intermediate, and that intermediate also reacts, and reproduces the catalyst. Catalysts can speed up reactions, or make reactions happen which without the catalyst are so slow that they don't really happen.

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Ronia Kattoum

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3.2: Types of Chemical Reactions

learning objectives

- List and define the 5 types of reactions based on the rearrangement of atoms
- Match given reactions to their respective category of reaction type
- Relate combustion reactions of hydrocarbons to climate change
- Relate decomposition reactions to production of hydrogen fuel cells.

Some Basic Types of Chemical Reactions

We are going to identify 5 basic "types" of chemical reactions because they have characteristic equations that allow us to use different techniques when we balance them. That is, in the next section when we balance a reaction, the first thing we will ask is what type of reaction it is, and then we will use the technique that is appropriate to that type reaction. There are other ways of classifying reactions that may actually tell us more about the chemistry, like are electrons transferred between atoms when a reaction occurs, which we will discuss later in this Chapter, and are called oxidation-reduction (redox) reactions, or acid base reactions (which at this level, occur when protons are transferred between between reactants).

1. **Formation Reactions (synthesis reactions)**
2. **Decomposition Reactions**
3. **Single Displacement Reactions**
4. **Double Displacement Reaction**
5. **Combustion Reactions**

Formation or Synthesis Reactions

$$H_2(g) + Cl_2(g) \text{ ® } 2HCl(g)$$

As the name implies, two or more chemicals come together and form another chemical. Here, HCl is being formed from hydrogen and chlorine.

Decomposition Reaction

$$CaCO_3(s) \text{ --> } CaCO(s) + CO_2(g)$$

As the name implies, something decomposes into something else. Here Calcium Carbonate decomposes to calcium oxide and carbon dioxide

Single Displacement Reactions

$$Fe(s) + CuSO_4(aq) \text{ -> } FeSO_4(aq) + Cu(s)$$
$$F_2(g) + BaCl_2(aq) \text{ -> } BaF_2(g) + Cl_2(g)$$

In a single displacement reaction something that is "pure" displaces something in a compound. As a rule of thumb, we say metals form cations and nonmetals from anions. So a metal can exist in two forms, as a pure metal, or as a cation (in an ionic compound). Likewise, a nonmetal can exist as something pure, or as an anion (in an ionic compound). In the first of the above two equations, the metal iron displaces the cation Copper(II) and we call that a metal single displacement reaction, while in the second, the fluorine displaces the anion chloride, and so we call that a nonmetal single displacement reaction. Note, sometimes these are called single replacement reactions.

If you note, these reactions involve a change in the charge of the metal or nonmetal, and so they involve the transfer of electrons. We will pick these up again later in this Chapter when we get to section 3.6.2 and discuss these from the perspective of electron transfer.

Metal

$$Fe(s) + AuSO_4(aq) \text{ --> } FeSO_4(aq) + Au(s)$$

Some metals prefer to be ions, and other prefer to be pure. This can be understood by comparing iron ore with gold ore. Iron (pure) spontaneously rusts and iron ore that is mined must consists of compounds like hematite (Fe_2O_3) and magnetite (Fe_3O_4), while

gold, a noble metal, does not tend to form ionic compounds, and so pure gold can be found in gold ore. So the above reaction is logical, in the sense that iron as a pure metal is not stable, while gold is.

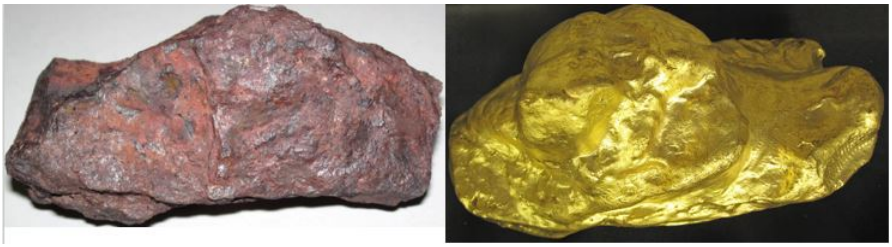


Figure 3.2.1: Hematite ore on left (image from flickr) and gold on right (image from wikicommons).

Since the above reaction proceeds, we can correctly predict that:

$$FeSO_4(aq) + Au(s) \text{ --> No Reaction}$$

Nonmetal

$$F_2(g) + BaCl_2(aq) \text{ -> } BaF_2(g) + Cl_2(g)$$

Single Displacement Reactions are actually a subset of another class (type) of reactions called Redox or Oxidation-Reduction Reactions, where electrons are transferred between species. We will cover those in section 3.6 of this Chapter, and at the time come up with a way to predict if a single displacement reaction will occur, or if there is no reaction.

Metal-Nonmetal

A metal can also displace hydrogen from an acid or even from water (look at water as H-OH, where the anion is hydroxide). For example

$$2Na(s) + 2H_2O(l) \text{ ->} H_2(g) + 2NaOH$$

Here the pure sodium metal becomes a cation, while a hydrogen is pulled off of each water to from hydrogen gas (a diatomic), and so hydrogen is behaving similar to a cation on the reactant side, but it is not a cation, it is an acidic hydrogen atom in a covalent bond. These reactions can give off heat which can then combust the hydrogen, as seen in Video 3.2.2.



Video 3.2.2. 1'09" YouTube uploaded by halosaqi showing alkali metals displacing hydrogen from water.

Double Displacement Reactions

$PbNO_3(aq) + NaS_2(aq)$ ® $PbS(s) + NaNO_3(aq)$

In a double displacement reaction, the ions of two ionic compounds swap counter ions.



Video 3.2.3: 22 " YouTube uploaded by Bob Belford showing lead(II)nitrate reacting with sodium sulfide to form the black lead(II)sulfide and sodium nitrate (https://youtu.be/X6BV8Av_UnU).

We will look at these in great detail in section 3.4.

Combustion Reaction

In a combustion reaction a compound reacts with oxygen and releases energy. Carbon dioxide and water are also released if the compound contains carbon.

$CH_4 + 2O_2$ --> $CO_2 + 2H_2O$ + energy

Today's society uses fossil fuels as an energy source and the carbon dioxide emission is a concern to many scientists. The following youtube video was created by the EPA to describe the consequences of our economic reliance on fossil fuels. You may wish to check the link at the end of the video,
www.epa.gov/climatechange/students .



Video 3.2.4: 2'37" youtube posted by EPA (https://youtu.be/ScX29WBJI3w)

Do combustion reactions always produce carbon dioxide and water?

No there are other types of combustion reactions, like the combustion of hydrogen and magnesium.

$2H_2 + O_2$ --> $2H_2O$ + energy
$2Mg + O_2$ -->MgO + energy



Video 3.2.5: RSC video of magnesium reacting with water from Peter Wothers lecture series (https://youtu.be/gAhsvOP5yaM)



Video 3.2.6: RSC video of magnesium reacting with sand (silicon dioxide) from Peter Wothers lecture series (https://youtu.be/J60J-g4ifXg)

The hydrogen economy is considered as an alternative to fossil fuels and an area of intense current chemistry research. The concept is simple, one can use electricity generated by methods like solar, hydroelectric, wind, geothermal to split water into hydrogen and oxygen. Then you can transport the hydrogen to a new location and recombine them to produce energy where you need it, and produce no carbon dioxide. There are obvious challenges, like the storage of the hydrogen. As we shall learn later this semester, energy is the capacity to do work and transfer heat. So any energy lost as heat can not be used for work. You have probably heard of fuel cells, and they operate like a battery that consumes fuel, and can be more efficient than a combustion engine because they do not produce as much heat. In the following video the person uses a reversible fuel cell kit to demonstrate the concept of a hyrdogen economy. Simply speaking, you split water into hydrogen and oxygen when you are near a power source (solar, geothermal, wind, hydroelectric) then you recombine them where you want to use the energy, and in the process, you produce no carbon dioxide.



Video 3.2.5: 4'18" YouTube Uploaded by Andrew Copeland showing basic concepts behind hydrogen economy as an alternative to the fossil fuel economy (https://youtu.be/qZhhnBfXP7I).

Practice Problems

Exercise 3.2.1

Identify the types of reactions for each equation

a. $AlCl_3(aq) + Na_2CO_3(aq) \rightarrow Al_2(CO_3)_3(s) + NaCl(aq)$
b. $C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$
c. $Li_2S + Br_2 \rightarrow 2LiBr + S$
d. $H_2CO_3 \rightarrow H_2O + CO_2$
e. $Ba(C_2H_3O_2)_2(aq) + 2HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2HC_2H_3O_2(aq)$

Answer a

Double Displacement

Answer b

combustion

Answer c

Single Displacement (non metal)

Answer d

Decomposition

Answer e

Double Displacement (involving acid)

Exercise 3.2.21

Identify the types of reactions for each equation

a. $H_2S(g) \rightarrow H_2(g) + S(s)$
b. $Pb + 2CuCl \rightarrow PbCl_2 + Cu$
c. $CH_2CO(g) + 2\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(g)$
d. $HCl + NaOH \rightarrow NaCl + H_2O$

Answer a

Decomposition

Answer b

Single Displacement (metal displacement)

Answer c

Combustion

Answer d

Double Displacement (neutralization)

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- November Palmer & Emily Chaote (UALR)
- Ronia Kattoum (Learning Goals)

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3.3: Balancing Chemical Equations

learning objective

- Balance chemical reactions based on reaction type

The first step is to identify reactants and products. Sometimes these will be given in the problem statement, and for certain types of problems, you will need to be able to predict the products.

Basic techniques for balancing equations

1. **Identify reactants and products**
   - Be sure to write correct formulas
   - Never change the subscripts in the formulas when balancing an equation
   - Read the question carefully. Problem statements may say "when molecule A is formed from the reaction of molecule B and C", and students will treat molecule A as a reactant, when it is really a product.
2. **Write Unbalanced Skeletal Equation**
   - Write Reactants to left of arrow.
   - Write Products to right of arrow.
   - Leave a space for stoichiometric coefficient.
     - placing a line in front of each chemical is a good way to do this

$$\_\_\text{Reacant(A)} + \_\_\text{Reactant(B)} \rightarrow \_\_\text{Product(X)} + \_\_\text{Product(Y)} \tag{3.3.1}$$

3. **Identify Type of Reaction**
   1. Single Displacement
      - Balance ions not atoms (Video 3.3a)
   2. Double Displacement
      - Balance ions not atoms (Video 3.3b)
      - Strategy is pick an ion, do its counterion, then do the counterion's counterion, and repeat, until all have been balanced (watch video).
   3. Combustion
      - Balance Carbon first, hydrogen second and oxygen last
   4. All other
      - Balance by inspection
      - If an element exists by itself, like Fe, O_2, S_8, balance it last.
4. **Check Work**

Single Displacement Reactions

$$Al(s) + FeSO_4(aq) \rightarrow ?$$

The trick is to balance the ions. In the following video, we do not balance Al, Fe , S and O, but aluminum and sulfate. You know from the previous section that the aluminum displaces the iron in the sulfate salt, and so you also need to be able to predict the products (aluminum and iron sulfate form iron plus aluminum sulfate)



Video 3.3.1: 44" video uploaded by Bob Belford showing how quickly you can balance a single displacement reaction by balancing the ions, not the atoms. (https://youtu.be/KTHURNRwd5Y)

Double Displacement Reaction

$$Al_2(SO_4)_3 + NH_4ClO_4 \rightarrow ? \tag{3.3.2}$$

In the double displacement reaction the ions swap partners. As long as the same ions exist on both sides of the equation (none convert to another compound or ion) you can simply balance the ions, not the atoms. So in this video we balance aluminum, sulfate, ammonium and perchlorate, and not Al, S, O, N, H and Cl.



Video 3.3.2: 1'12" youtube uploaded by Bob Belford on balancing double displacement reactions. Note the "path" used to go from ion pair to ion pair.

Combustion Reactions

Fire, the combustion reaction dates to the dawn of humanity.





Figure 3.3.1: Prometheus, a Titan of Greek mythology who was credited for creating man from clay and giving him fire. This caused the wrath of Zeus who bound him to a cliff where an eagle feed on his liver every day until he was saved by Heracles. (Images public domain, left Heinrich Friedrich Füger "Prometheus Brings Fire", center Salvator Rosa' s "Torture of Prometheus" (ca. 1646-1648), right, Pixabay image)

We typically think of fire as the combustion of organic compounds as they react with oxygen to produce carbon dioxide and water, but combustion is actually a broader class of reactions where compounds react with oxygen to produce oxides and release energy. In the following video you see magnesium metal combusts, not only in air, but in water.



Video 3.3.3: 1'26" video of the Royal Society of Chemistry showing a lecture demonstration with magnesium burning in air and water, (https://youtu.be/gAhsvOP5yaM).

In this class you need to know that carbon based compounds combust with oxygen and produce carbon dioxide and water. The general unbalanced equation is

$$C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O \tag{3.3.3}$$

In balancing carbon based combustion reactions there is a schema that makes things very easy.

1. Balance carbon
2. Balance hydrogen
3. Balance oxygen (you may need to use a fractional coefficient)
4. If you used a fractional coefficient, multiply by the denominator so all stoichiometric coefficients are integers.

The following video shows how to balance the combustion reaction for the hydrocarbon C_8H_{18}.



Video 3.3.4: 1'06" video balancing combustion reaction of octane. Note, Digital corrigendum: Octane is C_8H_{18} and I wrote C_8H_8 by mistake in the second step, but treated it as C_8H_{18} , and will redo when I have time, but the technique/answer is correct except for that typo (https://youtu.be/FfpRu2k23js).

The next video shows an even more complicate problem, the combustion of $C_9H_{17}O_3H$.



Video 3.3.5: 54" video showing the combustion of $C_9H_{17}O_3H$ (https://youtu.be/ulSV3b-MQRY).

Practice Problems

Exercise 3.3.1

Balance the following equations

a. $AlCl_3(aq) + Na_2CO_3(aq) \rightarrow Al_2(CO_3)_3(s) + NaCl(aq)$
b. $C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$
c. $Li_2S + Br_2 \rightarrow LiBr + S$
d. $C_8H_{18}O + O_2 \rightarrow CO_2 + H_2O$
e. $Ba(C_2H_3O_2)_2(aq) + HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + HC_2H_3O_2(aq)$

Answer a

$2AlCl_3(aq) + 3Na_2CO_3(aq) \rightarrow Al_2(CO_3)_3(s) + 6NaCl(aq)$

Answer b

$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

Answer c

$Li_2S + Br_2 \rightarrow 2LiBr + S$

Answer d

$C_8H_{18}O + 12O_2 \rightarrow 8CO_2 + 9H_2O$

Answer e

$Ba(C_2H_3O_2)_2(aq) + 2HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2HC_2H_3O_2(aq)$

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3.4: Aqueous Reactions

Learning Objectives

- Outline the differences between strong electrolyte, weak electrolyte, and a nonelectrolyte
- Predict the solubility of ionic compounds in water using solubility rules
- Memorize seven strong acids that are strong electrolytes
- Distinguish ways of writing aqueous reaction equations
  - General (molecular) ionic
  - Total (complete) ionic
  - Net Ionic

The objective of this section is to predict what will happen for single and double replacement reactions that occur in aqueous solutions. Note, if in a double displacement reaction two solutions combine and form a solid, you have a precipitation reaction. Many texts treat this as a type of reaction, but we will treat it as a subset of the double displacement reactions.

Electrolytes

Pure water does not conduct electricity, and it has been observed that when a substance dissolves in water, it may produce mobile ions that allow the water to conduct electricity, and we call that compound an electrolyte, or it may not, in which case we call it a nonelectrolyte.

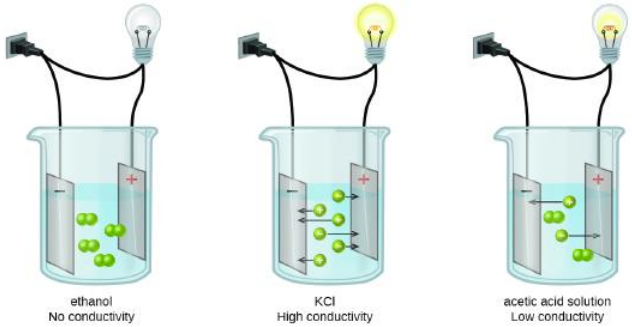


Figure 3.4.1: Ethanol on the left is a nonelectrolyte and does not conduct electricity. KCl is a strong electrolyte and the bulb is very bright. Acetic acid is a weak electrolyte, and although the image may not show it, if the concentrations are the same, the light is dimmer than for the KCl

Exercise 3.4.1

Both salt (NaCl) and table sugar, glucose ($C_6H_{12}O_6$) dissolve in water. Why is salt water a strong electrolyte, while sugar water is a non-electrolyte?

Answer

NaCl is an ionic compound that dissociates into ions that conduct electricity. $C_6H_{12}O_6$ is a molecular compound that does not break up into ions, and therefore, does not conduct electricity. The sugar molecule remains intact, but each sugar molecule is separated from the other when added to water. The reason it dissolves in water is because of the term "the like dissolves the like", meaning both sugar and water are polar molecules. We will discuss this in more depth later in the text.

There are two basic ways an aqueous compound can be an electrolyte; being a soluble ionic compound or a strong acid.

Soluble Ionic Compounds

- If ionic compounds dissolve and form a solution, the ions separate and are free to move about and conduct the electricity. But not all ionic compounds dissolve, and so they can be weak, strong or even nonelectrolytes. Typically, the nondissolved ionic compound forms a solid that falls to the bottom as a precipitate.

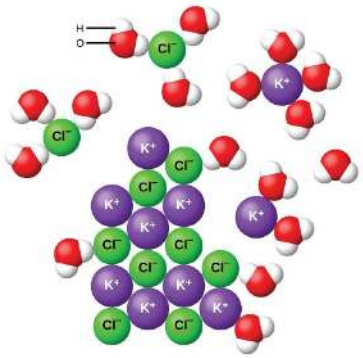


Figure 3.4.2: In the above image, the solid KCl is being surrounded by water molecules which cause the ions to leave the crystal and enter the solution. Once they enter the solution they are mobile and can conduct electricity, so KCl is an electrolyte (it is actually a strong electrolyte)

Covalent Compound that React with Water

Just as in the case with ionic compounds, covalent compounds can be weak, strong or nonelectrolytes. There are two types we will look at, acids and a type of bases called the amines.

Acids

The second way to produce an electrolyte happens when certain types of covalent molecules that react with the water. Acids give a proton to the water and so form ions as in the image below where HCl reacts with water to from chloride and hydronium ions (Figure 3.4.3) .

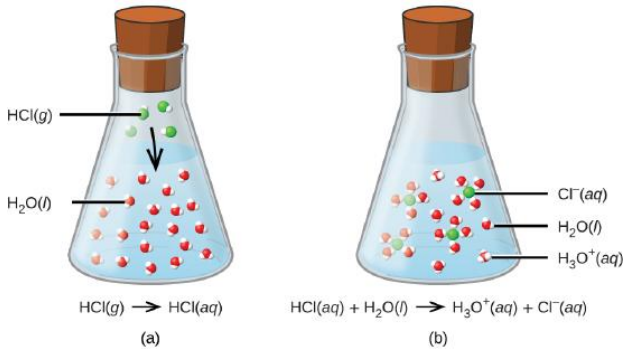


Figure 3.4.3: In *the above image the gaseous molecule HCl dissolves in water (a), where it then gives a proton to the water and forms the electrolyte with chloride and hydronium ions.*

Strong acids are acids that completely react with water to form hydronium and the acid's anion.

Note

You need to memorize 7 strong acids, which are acids that completely react with water to form hydronium ions and the anion of the acid, and so these are strong electrolytes.

1. **HCl**, **HBr**, **HI** (heavier binary halides, HF is weak)
2. $\mathbf{H_2SO_4}$ (sulfuric acid)
3. $\mathbf{HNO_3}$ (nitric acid)
4. $\mathbf{HClO_3}$, $\mathbf{HClO_4}$.

The above list is not comprehensive but in this class all other acids can be assumed weak unless they are called strong.

Amine Bases

Some bases are covalent compounds and the amines are an important group. They all have a nitrogen that can extract a proton from the water and form ions, as in the case below of ammonia, which grabs a proton from the water forming the weak electrolyte ammonium hydroxide (Figure 3.4.4).

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{3.4.1}$$

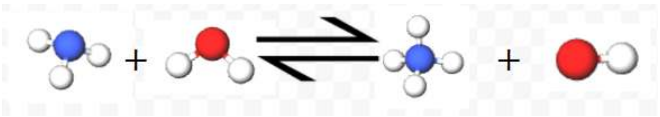


Figure 3.4.4: *In the above image, ammonia grabs a proton from water forming ammonium hydroxide.*

Types of Electrolytes

Compounds can be Strong, Weak, or Nonelectrolytes

1. **Strong Electrolytes** - Strong Conductors of Electricity due to formation of a large number of Mobile Ions
2. **Weak Electrolytes** -Weak Conductors of Electricity due to formation of a few Mobile Ions
3. **NonElectrolytes** –Non Conductors of Electricity as they do not form Ions in aqueous solutions

Strong Electrolytes

Ionic - Soluble Salts and Strong Bases

$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

Covalent - Strong Acids (protonate water)

$HCl(aq) + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq)$

$H_2SO_4(aq) + H_2O \rightarrow H_3O^+(aq) + HSO_4^-(aq)$

Weak Electrolytes

Ionic - Slightly Soluble Salts

$CoCl_2(s) \rightleftharpoons Co^{+2}(aq) + 2Cl^-(aq)$

Covalent - Weak Acids & Amine Bases (hydrolyze water)

$HF(aq) + H_2O \rightleftharpoons H_3O^+(aq) + F^-(aq)$

$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-$

NonElectrolytes

Ionic - Insoluble Salts

$CoS(aq) \leftrightarrow Co^{+2}(aq) + S^{-2}(aq)$

Covalent - Molecules which do not hydrolyze or protonate water

$C_{12}H_{22}O_{11}(s) + H_2O \rightarrow C_{12}H_{22}O_{11}(aq)$

The following animations gives an atomic scale visualization of strong, weak and nonelectrolytes



Video 3.4.1: 2'37" YouTube animation uploaded by Georgianna Allen giving an explanation for how some compounds can be weak, strong or non-electrolytes (https://youtu.be/B5mSet29qxA).



Video 3.4.2: 1'29" YouTube animation uploaded by BerkeleyChemDemos showing conductivity of various solutes. Note, the solid ionic compounds do not conduct because their ions are not mobile. You should pause the video before they add the light bulbs and try and predict if the bulb will come on.

Predicting Products for Double Displacement Reactions

Determine what the products will be for the following reactions. Initially we will ignore phases, but by the time we finish this exercise you will need to be able to identify phases as you write the equation. This process requires that you identify the ions in the reactants and for double displacement reactions swap partners and use the principle of charge neutrality to determine what the product are. For single replacement reaction you need to Figure which species (anion or cation) is gaining or losing charge and the other species is a spectator ion. Once that is done you need to balance the equations

Students frequently swap ions without thinking about the product formula and this leads to mistakes. It is suggested you follow these steps:

1. **Identify reactant ions and their charge**
2. **Swap Ions**
3. **Determine Product Formula based on principle of charge neutrality**
4. **Balance Equation**

Example:

$$Pb(ClO)_2\,(aq) + Na_2SO_4\,(aq) \rightarrow \tag{3.4.2}$$

1. **Identify reactant ions and their charge**

Pb^{+2}	ClO^-
Na^+	SO_4^{-2}

Table 3.4.1: Matrix showing the cations and ions for each of the two ionic compounds in the double displacement reaction

2. **Swap Ions**

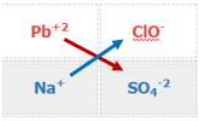


Table 3.4.2: Matrix of Table 3.4.1 showing the cations and ions swapping partners.

$$Pb^{+2} + SO_4^{-2} \rightarrow ?$$

$$Na^+ + ClO^- \rightarrow ?$$

Note: If dealing with a strong acid, treat the "H" as a cation (break the acid HA into H^+ and A^-, where A is any anion, noting the number of hydrogens equals the charge of the anion, as the acid must be neutral). We will cover acids in the next section.

3. **Determine Product Formula based on principle of charge neutrality**

$$Pb(ClO)_2\,(aq) + Na_2SO_4\,(aq) \rightarrow PbSO_4\,(?) + NaClO\,(?) \tag{3.4.3}$$

If you need help determining formulas review section 2.6

4. **Balance Equation**

$$Pb(ClO)_2\,(aq) + Na_2SO_4\,(aq) \rightarrow PbSO_4\,(?) + 2NaClO\,(?) \tag{3.4.4}$$

Exercise 3.4.2

Predict products for the following reactions

a. $Mg_3(PO_4)_2 + NaClO_3 \rightarrow ?$
b. $AlPO_4 + Na_2SO_3 \rightarrow ?$

Answer a

$Mg(ClO_3)_2 + Na_3PO_4$

Answer b

$Al_2(SO_3)_3 + Na_3PO_4$

The next step is is figuring out the phase of the product. There are 3 common phases for aqueous reactions, solid (precipitate), aqueous and gas. In the case of aqueous products resulting from mixing two solutions, we state there is no reaction. In general chemistry 2 we will use mathematical formula of solubility products, but in this class we will use the Solubility rules, which are a good "rule of thumb" to determine if a salt will dissolve or not. Now note, these are all relative values, and even a soluble salt will form a precipitate, if you add a lot of it. For example, you can dissolve around 140 grams of potassium iodide in 100 g of water at 32ºF, which makes it a very soluble salt, but a precipitate will occur if you try and add 200 g of KI to 100 g of water.

Solubility Rules

We saw that some compounds are soluble, other are partially soluble, and some are completely insoluble. How do we know determine this? We will start off with the simplest types, which are ionic compounds, and we will base these on the nature of the ions. There are sort of two opposing processes going on. Are the attractions of the ions in the crystal stronger than their attraction towards the water, or weaker? If the ionic attractions within the crystal are stronger, they do not dissolve and they form a precipitate. If on the other hand, the ions are more attracted to the water, they leave the crystal and the compound is soluble. We will use the solubility rules to determine if a salt is soluble or not.

What are the Solubility Rules?

These are what I am calling a "rule of thumb," and allow us to roughly predict if a salt will dissolve or not. It must be understood that the concept is relative, for example, table salt is considered a soluble salt and if you add table salt to water it will dissolve a lot, up to 359g per liter, but at that point it becomes saturated, and any more will form a precipitate. On the other hand silver chloride is an insoluble salt, and you can only dissolve 0.0019g into 1 liter, but any more will fall to the bottom as a precipitate.

Note, some textbooks give slightly different rules, and this set is incomplete. If your text is different, please discuss this with your instructor. When you get to general chemistry 2 you will learn a different approach, where we can quantify the amount dissolved for an insoluble salt, like the 1.9 mg/liter for silver chloride.

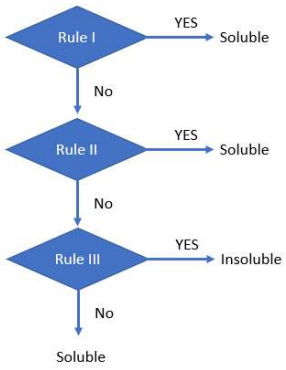
Is there a strategy to using the solubility rules?
Yes, for the ones I have set up below.

- We first look at the [+] cation, and ask if it is any one of the cations listed in step IA. If yes, we say it is soluble, and the question is answered. After this step we focus on the [-] anions. If it is not soluble from step 1A, we go to 1B, and if the anion is from this list, it is soluble.
- We now go to the compounds that are usually soluble, step II, and you need to memorize the exceptions, which are insoluble.
- We now go to the compounds that are usually insoluble, step III, and you need to memorize the exceptions, which are soluble.

Solubility Rules

Table 3.4.3: Solubility rules with schema showing flow diagram. NOTE: the exceptions in steps II and III have opposite meanings.

I. Soluble
  a. Group 1A & Ammonium (the only cations in this list)
  b. NO_3^-, ClO_4^-, ClO_3^-, $CH_3CO_2^-$
II. Usually Soluble
  a. Cl^-, Br^-, I^-, (Except those with Ag^+, Hg_2^{+2}, & Pb^{+2})
  b. F- (Except Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2} & Pb^{+2})
  c. SO_4^{-2} (Except those with Ca^{+2}, Sr^{+2}, Ba^{+2}, Ag^+ & Pb^{+2})
III. Insoluble (Except with cations from I.a)
  a. OH^- (Except those with Sr^{+2} & Ba^{+2})
  b. Everything else (this is not true, but will work in this class)



In the following video we will first predict the products for the double displacement reaction of aluminum sulfate and barium chloride, and then apply the solubility rules to determine the phases of the products.

$$Al_2(SO_4)_3 + BaCl_2 \rightarrow ?$$



Video 3.4.3: YouTube predicting products and phases for a double displacement reaction (https://youtu.be/e1gzOZxT51w).

Exercise 3.4.3

Use the solubility rules to determine if the following compounds are soluble or insoluble. Indicate answer by writing formula followed by (aq) for soluble and (s) for insoluble. (You may also want to write the names of the species)

a. $PbSO_4$
b. $NaClO_4$

Answer a

Insoluble. Sulfate ions are typically soluble, but lead(II) is an exception, so lead(II) sulfate is an insoluble solid. This means that **$PbSO_4$** (s) is not broken up into ions in water, but is a precipitate.

Answer b

Soluble. perchlorate ions and alkali metals are soluble, so sodium perchlorate is soluble, meaning that it breaks up into ions, $Na^+(aq) + ClO^-_4(aq)$ in water.

Exercise 3.4.4

Identify the following as a strong electrolyte, a weak electrolyte, or a non-electroylte.

a. $Ba(NO_3)_2$
b. H_3PO_4
c. $C_6H_{12}O_6$
d. HNO_3
e. AgBr

Answer a

strong electrolyte - Rule 1B

Answer b

weak electrolyte - weak acid (not one of the seven strong acids)

Answer c

non-electrolyte - molecular compound, not ionic

Answer d

strong electrolyte- strong acid (one of the seven strong acids)

Answer e

non-electrolyte - insoluble precipitate - Exception to Rule 2A

Mixtures of Multiple Solutions

Consider 3 aqueous salt solutions each with different cations and anions. For example, consider NaCl, $AgNO_3$ and $(NH_4)_2CO_3$. There are 3 cations and 3 anions which results in 3^2 or 9 combinations (of which 3 are the reactants). This seems like a very complicated problem (4 salts would result in 16 potential combinations and 5 salts would result in 25) and so we need to develop a technique to see the problem. This can be done through a matrix, where the rows represent the cations, the columns the anions and the cells the potential combinations:

Table 3.4.4 Seting up a matrix with cation in the column and anions in the row, and if you sequentially fill this, the diagonal is your reactants, and the off diagonal are the possible products.

	Cl^-	NO_3^-	CO_3^{-2}
Na^+	NaCl		
Ag^+		$AgNO_3$	

NH_4^+			$(NH_4)_2CO_3$

Now think about it for a minute. If you look at each row it starts with a cation, and if rule 1A says it is soluble, you can knock out the whole row, giving it XXX in table 3.4.5 to indicate no precipitate (all salts sodium and ammonium are solube), then then look at each column and according to rule 1B, you can knock out the middle column because all salts of nitrate are soluble. This reduced your workload to just two cells.

Table 3.4.5: Using the matric method to reduce the workload when calculating potential preciptiates for mixtures of multiple salts. Note, all sodium, nitrate and ammonium salts are soluble and so we can ignore them in identifying potential precipitates, so the answer is AgCl(s) and Ag_2CO_3(s).

	Cl^-	NO_3^-	CO_3^{-2}
Na^+	XXX	XXX	XXX
Ag^+	AgCl (s)	XXX	Ag_2CO_3(s)
NH_4^+	XXX	XXX	XXX

The following video shows how to solve these problems in the shortest amount of time for the following reaction:

$$NaCl + Na_3PO_4 + AgNO_3 + Pb(NO_3)_2 + Na_2SO_4$$



Video 3.4.4: 4'31" YouTube on calculating any precipitates formed when 5 soluble salts are mixed (https://youtu.be/hdO0hp6cDUk)

Exercise 3.4.3

Identify if any precipitates that would form if the following solutions are mixed:

a. $Pb(ClO_4)_2$(aq), K_2SO_4(aq), $AgCH_3CO_2$ (aq) + KCl(aq)
b. $Ba(ClO_3)_2$(aq), Li_2SO_4(aq), $NH_4CH_3CO_2$ (aq) + $BaCl_2$

Answer a

	ClO_4^-	SO_4^-	$CH_3CO_2^-$	Cl^-
Pb^{+2}	XXX	$PbSO_4$ (s)	XXX	$PbCl_2$ (s)
K^+	XXX	XXX	XXX	XXX
Ag^+	XXX	Ag_2SO_4 (aq)	XXX	AgCl (s)

K^+	XXX	XXX	XXX	XXX

So the answer is $PbSO_4$ (s), $PbCl_2$ (s) and AgCl (s), everything else is aqueous.

Answer b

d

	ClO_4^-	SO_4^{-2}	$CH_3CO_2^-$	Cl^-
Ba^{+2}	XXX	$BaSO_4$(s)	XXX	$BaCl_2$(aq)
Li^+	XXX	XXX	XXX	XXX
NH_4^+	XXX	XXX	XXX	XXX
Ba^{+2}	XXX	$BaSO_4$(s)	XXX	$BaCl_2$(aq)

So the answer is $BaSO_4$, everything else is aqueous.

Describing Aqueous Equations

There are three basic ways you will need to know that are used to describe aqueous chemical reactions. These are typically single and double displacement reactions. The difference between these lies in how you describe the ions of dissolved ionic compounds. Do you describe them as the separate ions, which are really what is floating around, or do you describe them by their neutral compound formula? That is, you can represent the solution as either the salt(aq) or its ions

$$NaCl(aq) \text{ means } Na^+(aq) + Cl^-(aq) \tag{3.4.5}$$

The General (Molecular) Equation uses the formula of the salt, the total ionic equations separates soluble salts (and strong acids) into their ions, while the net ionic equation cancels any ions that appear on both the reactant and product sides of the balanced equation, the "spectator ions", as they do not participate in the reaction. The net ionic equation typically describes the actual chemistry of the reaction, and what is going on.

1. General (Molecular)Equation
2. Total Ionic Equation
3. Net Ionic Equation

In solving these problems remember, (aq) = aqueous, (s) = solid, (g) = gas and (l) = liquid, and be sure the final equation is balanced.

General (Molecular) Equation

The General or Molecular Equation describes the reactions in terms of the formula of the salts, indicating the phase. These are often (incorrectly) called "molecular equations" because they use the formula of the neutral compound as if it was a molecule. The following equation is an example of a general double displacement reaction, and given the reactants, you need to be able to predict product compounds, balance the equation and predict the phases.

$$Pb(ClO_4)_2\,(aq) + Na_2SO_4\,(aq) \rightarrow PbSO_4\,(s) + 2NaClO_4\,(aq) \tag{3.4.6}$$

As indicated above, the aqueous ions separate on dissolution, and so we could write them out as separate entities, which is the Total or Complete Ionic Equation.

Total Ionic Equation

The Total or complete ionic equation writes soluble ionic compounds in terms of their ions. So if it is an ionic compound with (aq), you break it into its ions. If it is covalent, you do not break it into ions. If it is an acid, you only break it into its ions if it is strong, and that will be covered in the next section, but weak acids that are dissolved, like HF(aq) do not break into ions, while strong ones like HCl do.

Describing eq. 3.4.6 in terms of a net ionic equation gives:

$$Pb^{+2}\,(aq) + 2ClO_4^-\,(aq) + 2Na^+\,(aq) + SO_4^{-2}\,(aq) \rightarrow PbSO_4\,(s) + 2Na^+\,(aq) + 2ClO_4^-\,(aq) \tag{3.4.7}$$

Net Ionic Equation

The net ionic equation tells you what is happening, that is, what bonds (covalent or ionic) are being created. If you look at equation 3.4.7 you see there are two perchlorate and two sodium ions on both sides of the equation, and so we call them spectator ions because they did not react. If we cancel them the equation is still balanced and this gives the net ionic equation, which in this reaction results in the formation of the ionic compound, lead (II) sulfate.

$$Pb^{+2}\,(aq) + SO_4^{-2}\,(aq) \rightarrow PbSO_4\,(s) \tag{3.4.8}$$

This is often called a precipitate reaction as the lead (II) sulfate crashes to the bottom of the container, and some textbooks classify precipitation reactions as a class of reaction.

Example 3.4.1

Write the general, complete and net ionic equations for the reaction of **barium chloride** and **potassium sulfate**

Solution

$$\underbrace{BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(aq)}_{\text{General (Molecular) Equation}}$$

$$\underbrace{Ba^{+2}(aq) + \overbrace{2Cl^-(aq) + 2K^+(aq)}^{\text{Spectator Ions}} + SO_4^{-2}(aq \rightarrow BaSO_4(s) + \overbrace{2Cl^-(aq) + 2K^+(aq)}^{\text{Spectator Ions}}}_{\text{Complete Ionic Equation}}$$

$$\underbrace{Ba^{+2}(aq) + SO_4^{-2}(aq \rightarrow BaSO_4(s)}_{\text{Net Ionic Equation}}$$

Exercise 3.4.1

Write balanced net ionic equations to describe any reaction which occur when the following solutions below are mixed.

a. $Na_2CO_3 + Sr(NO_3)_2$
b. $Cu_2SO_4 + BaCl_2$

Answer a

$$Sr^{2+}(aq) + CO_3^{-2}(aq) \rightarrow SrCO_3(s)$$

Answer b

$$Ba^{2+}(aq) + SO_4^{2-}(aq) -> Ba(SO_4)(s)$$

Preci

Contributors and Attributions

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- November Palmer, Ronia Kattoum & Emily Chaote (UALR)

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3.5: Acid-Base Reactions

Learning Objectives

- Define the Arhennius acid/base and Bronsted-Lowry acid/base and differentiate between them
- Recognize if an acid or base is strong or weak.
- Identify the acid and base in chemical reaction
- Write molecular, complete ionic, and net ionic equations for acid-base neutralization reactions

Acids and Bases

What are acids and bases?

We will cover two definitions, the Arrhenius and Bronsted-Lowry definitions.

Arrhenius Acid/Base

Arrhenius Acid - Increases Hydronium ion to that of neutral water

Arrhenius Base - Increases hydroxide ion to that of neutral water.

This definition is based on the behavior of acids and bases when they are added to water. First we need to look at the autoionization of water. When two
water molecules bump into each other a proton can be transferred from one to the other forming hydronium and hydroxide ions (eq. 3.5.1).

$$H_2O(l) + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{3.5.1}$$

This is a very weak reaction and in neutral water (pH=7) the concentration of hydronium and hydroxide ions both equal 10 $^{-7}$ moles/liter. The concentration of pure water is is 55.56moles/liter (eq. 3.5.2)

$$\frac{1000g\ H_2O}{L}\left(\frac{mol\ H_2O}{18.02g}\right) = 55.6mol/l \tag{3.5.2}$$

This means that only one out of every 5.5x10^8 molecules of water is ionized (eq.3.5.3), which is such a small number that pure water is a nonelectrolyte.

$$\frac{55.6\frac{mol\ H_2O}{l}}{10^{-7}\frac{molH_3O^+}{l}} = 5.56x10^8\frac{mole\ H_2O}{mole\ H_3O^+} \tag{3.5.3}$$

Arrhenius Acid

These are compounds that donate a proton to water.

$$HC(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{3.5.4}$$

This is often written with the waters omitted, that is H$^+$(aq) represents hydronium ion and not a proton.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq) \tag{3.5.5}$$

Arrhenius Base

These are compounds that increase the hydroxide concentration. They can be soluble ionic compounds that have hydroxide ions, or compounds that remove a proton from water forming hydroxide, and the later can be molecules.

Sodium hydroxide is an ionic compound that is a strong base (you can it is soluble because of solubility rule IA)

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq) \tag{3.5.6}$$

Ammonia is a molecule that is a weak base, and it removes a proton from water forming ammonium and hydroxide. But it does not react much, so we use a two way arrow.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{3.5.7}$$

In the later case the ammonia took a proton from the water and this reaction is similar to the autoinoization of water, except that it is an ammonia and not another water molecule that acquires the second proton.

NOTE: Stong Acids and Bases are strong electrolytes

Bronsted-Lowry Acid/Base

The Bronsted-Lowry definition is broader than the Arrhenius. If you look at the Arrhenius Acid, it donates a proton to water, so the Bronstead expands that to donating a proton to anything, not just water. Likewise, the Arrhenius accepts a water from water, and the Bronstead expands that to accepting a Proton from anything.

Bronstead-Lowry Acid: A Proton Donor. Note the HCl gave a proton to the water molecule in the above example

Bronstead-Lowry Base: A Proton Acceptor. Note the ammonia above accepted a proton from the water.

Exercise 3.5.8

Identify the following as a Bronsted-Lowry acid, base, both, or neither

a. H_3PO_4
b. $CaCl_2$
c. SO_3^{-2}
d. NaOH

Answer a

Bronsted-Lowry acid - has 3 protons (H^+) to donate

Answer b

neither - ionic compound that is charge balanced. Neither gives nor accepts protons

Answer c

Bronsted-Lowry base - is an anion and so can accept a positive proton (in fact two of them).

Answer d

Bronsted-Lowry base - the hydroxide ion accepts a proton and so functions as a bronstead base

Neutralization Reactions

A reaction between an acid and a base is called a neutralization reaction, and these can be considered to be a type of displacement reaction, where the proton of the acid is being displaced as it is given to another species. You may have heard that a neutralization reaction is when an acid and a base react to form a salt plus water. That is not always true, but they do always form a salt, as the hydrogen is being "displaced" from the acid in the formation of the salt.

Neutralization reactions always give off heat, that is they are "exothermic" (a concept we will study in Chapter 5), but when a neutralization reactions forms salt and a soluble salt, the only observation may be the heat evolved.

There are 4 types of neutralization reactions, depending on whether the acid and base are strong or weak.

1. Strong Acids and Strong Bases
2. Strong Acids and Weak Bases
3. Weak Acids and Strong Bases
4. Weak Acids and Weak Bases

To identify which type reaction is going on, you need to know if the acid or base is strong. need to know the following strong acids and strong bases. There are others, and if a problem calls it a strong acid, treat it as a strong acid. Strong acids were covered in section 3.4.1.2.1 Acids and strong bases are covered by the solubility rules Ia and IIIa of section 3.4.2.1. Table 3.5.1 reviews them for you.

Strong Acids	Strong Bases

• HCl, HBr, HI • $HClO_3$, $HClO_4$ • HNO_3 • H_2SO_4 • others as specified	• Soluble alkali metal hydroxides (solubility rule 1a) ◦ LiOH, NaOH, KOH, RbOH, CsOH • Soluble heavier alkaline earth hydroxides (solubility rule 3a) ◦ $Sr(OH)_2$, $Ba(OH)_2$ ◦ $Ca(OH)_2$ should probably be considered as a strong base even though we are not calling it a soluble salt in rule 3a. A saturated solution has is 1.8 g/L) and thus strong, and we will cover these "border cases" in gen chem 2 when we get to solubility constants.

You need to know the general (molecular), total (complete) and net ionic equations for acid base neutralization reactions

Strong Acid and Strong Base

The result is a salt plus water; the anion of the acid and the cation of the base are spectator ions. Example: HCl and NaOH

General Molecular Equation:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \tag{3.5.8}$$

Total Ionic Equation

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l) \tag{3.5.9}$$

Net Ionic Equation

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{3.5.10}$$



Video 3.5.1: 1'35" YouTube predicting products and writing aqueous equations for a strong acid and a strong base, (https://youtu.be/-NfFjKwCDp4). *Digital corrigendum: "all" salts of sodium (not chloride) are soluble*

Strong Acid and Weak Base

The cation of the strong acid is a spectator ion. Example: HCl & NH_3.

General Equation:

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq) \tag{3.5.11}$$

Total Ionic Equation:

$$H^+(aq) + Cl^-(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq) \tag{3.5.12}$$

Net Ionic Equation:

$$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq) \tag{3.5.13}$$



Video 3.5.2: 1'06" Youtube on the reactions of strong acid and weak base (https://youtu.be/Yf2YQ6QvMEc).

Weak Acid and Strong Base

In the reaction of a Weak Acid and a Strong base the cation of the base is a spectator ion. Example: HF + NaOH.

General Equation

$$HF(aq) + NaOH(aq) \rightarrow NaF(aq) + H_2O \tag{3.5.14}$$

Total Ionic Equation

$$HF(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + F^-(aq) + H_2O(l) \tag{3.5.15}$$

Net Ionic Equation

$$HF(aq) + OH^-(aq) \rightarrow F^-(aq) + H_2O(l) \tag{3.5.16}$$



Video 3.5.3: 1'19" Youtube on the reactions of weak acid and strong base (https://youtu.be/bI0tolYG_s0).

Weak Acid and Weak Base

In the reaction of a weak acid and a weak base there is no spectator ion. Since there are no spectator ions, the total ionic and the net ionic are exactly the same. Example HF and NH_3.

General Equation

$$HF(aq) + NH_3(aq) \rightarrow NH_4F(aq) \tag{3.5.17}$$

Total Ionic Equation

$$HF(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + F^-(aq) \tag{3.5.18}$$

Net Ionic Equation

$$HF(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + F^-(aq) \tag{3.5.19}$$



Video 3.5.4: 0'57" Youtube on the reactions of weak acid and strong base (https://youtu.be/561IAx1lzKk)

Acids and Salt

Acids also react with ionic compounds, in fact many ways of leaching metals from ionic ores involves reactions with acids. These can be treated as a double displacement reaction where the hydrogen is being displaced by the cation. Realize hydrogen is not a cation, and the acid is a molecule, but just as we name it along nomenclature rules that use its salt (section 2.7.4.2), we can also treat it the way we would a cation, in predicting how it reacts. Example: H_2SO_4 + $NaCH_3CO_2$

General Equation:

$$H_2SO_4(aq) + 2NaCH_3CO_2(aq) \rightarrow Na_2SO_4(aq) + 2HCH_3CO_2(aq) \tag{3.5.20}$$

Total Ionic:

$$2H^+(aq) + SO_4^{-2}(aq) + 2Na^+(aq) + 2CH_3CO_2^-(aq) \rightarrow 2Na^+(aq) + SO_4^{-2}(aq) + 2HCH_3CO_2(aq) \tag{3.5.21}$$

Net Ionic:

$$2H^+(aq) + 2CH_3CO_2^-(aq) \rightarrow 2HCH_3CO_2(aq) \tag{3.5.22}$$

Notice how in this reaction a covalent bond was formed and we made the molecule acetic acid.



Video 3.5.5: 3'43" Youtube on the reaction of a salt and an acid

Exercise 3.5.2

Predict and Write Net Ionic Equations for the following

A) $AgCH_3CO_2$ (aq) + HCl(aq) -->

B) H_2SO_4(aq) + $Pb(NO_3)_2$ (aq) -->

C) H_2SO_3(aq) + $AgNO_3$ -->

Answer

A) Ag^+(aq)+ $CH_3CO_2^-$(aq) + H^+(aq)+ Cl^-(aq) ® AgCl(s) + HCH_3CO_2 (aq)

B) Pb^{+2}(aq) + SO_4^{-2}(aq) ® Pb SO_4(s)

C) H_2SO_3(ag) + $2Ag^+$(aq) ® Ag_2SO_3(s) + $2H^+$(aq)

Acid Reactions Evolving Gases

We have seen that acid-base reactions can produce gasses. Many of these can also produce gases, in fact, the acids of oxyanions can decompose into a nonmetal oxide and water upon heating.

Heating OxyAcids

Oxyacids are acids of polyatomic ions that are oxyanions. These can decompose under heat into a nonmetal oxide and water.

$$\underbrace{H_2SO_4(aq)}_{oxyacid} \overset{heat}{\rightarrow} \underbrace{SO_3(g)}_{\text{nonmetal oxide}} + H_2O(l) \tag{3.5.23}$$

$$\underbrace{H_2SO_3(aq)}_{oxyacid} \overset{heat}{\rightarrow} \underbrace{SO_2(g)}_{\text{nonmetal oxide}} + H_2O(l) \tag{3.5.24}$$

$$\underbrace{H_2CO_3(aq)}_{oxyacid} \overset{heat}{\rightarrow} \underbrace{CO_2(g)}_{\text{nonmetal oxide}} + H_2O(l) \tag{3.5.25}$$

Another name for the nometal oxide is the acid anhydride, as you have removed a water from the oxyacid, therefor it is the acid without the water, the acid anhydride.

Strong Acids and Salts of Oxyanions

These are actually two reactions, first a double displacement reaction, followed by a decomposition reaction. In the first step, the hydrogen of the strong acid displaces the cation of the salt containing a oxyanion, forming the oxyacid, which then decomposes. Consider the reaction of HCl and $CaCO_3$ (Calcium carbonate, but known as Calcite to geologists)

In the first step, we do a double displacement type of reaction forming carbonic acid. Note, when we say HCl(aq), we actually have a solution that is mostly water, and we are adding it to a solid rock, and so the products are also dissolved into the water (watch video 3.5.6 as geologists use this reaction to identify a rock vein.

$$2HCl(aq) + CaCO_3(s) \rightarrow H_2CO_3(aq) + CaCl_2(aq) \tag{3.5.26}$$

In the second step the carbonic acid decomposes into carbon dioxide and water

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(aq) \tag{3.5.27}$$



Video 3.5.6: 0'57" YouTube uploaded by Amanda Nicole showing how the reaction of HCl with carbonate rock to produce carbon dioxide gas can be used as an identification test. (Note, as indicated above, rocks of sulfate and sulfite would also produce gasses of sulfur oxides).

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- November Palmer, Ronia Kattoum & Emily Choate (UALR)

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3.6: Redox Reactions

Learning Objectives

- Use given guidelines to determine oxidation numbers of atoms in a compound.
- Differentiate between oxidation numbers and charges
- Use oxidation number to determine which species in a reaction is oxidized and which is reduced, which is the oxidizing agent and reducing agent.
- Recognize and identify redox reactions
- Determine if single displacement redox reactions are spontaneous or not based on activity series.

Introduction

Another way of classifying reactions is do they involve the transfer of electrons from one chemical species to another? If so, it is an oxidation/reduction reaction or **Redox Reaction** for short. The definitions for oxidation and reduction are:

Oxidation: the loss of electrons
Reduction: the gain of electrons

So far we have covered two types of reactions that must involve oxidation and reduction, the single displacement reaction and the combustion reaction. The single displacement reaction is easy to see as it involves neutral metals becoming ions. The combustion reaction is more complicated as elemental oxygen is forming covalent bonds and there are no ions to help us identify which species is gaining and which species is losing electrons, and so we will need to introduce the concept of oxidation numbers to tackle this.

Lets start by looking at a very simple reaction, that of iron and oxygen to form Iron(III) oxide.

$$2Fe(s) + 3O_2(g) \text{ --> } 2Fe^{+3} + 3O^{-2} = Fe_2O_3(s)$$

In this reaction the iron is getting oxidized because each iron atom loses three electrons and the oxygen is getting reduced because each oxygen gains two electrons. We call oxygen the **oxidant** (oxidizing agent) because it causes oxidation while becoming reduced ($3O_2 + 6e^-$ -> $3O^{-2}$), that is, it must grab the 6 electrons from the iron in order to get reduced. Iron is called the **reductant** (reducing agent) because it reduces the oxygen while becoming oxidized ($2Fe$ -> $2Fe^{+3} + 6e^-$). That is, it gives 6 electrons to the oxygen causing reduction (as it gets oxidized).

We will start with single displacement reactions because they are the easiest to understand.

Single Displacement Reactions

Single displacement reactions were introduced in section 3.2.1.3 and there were two types, metal single displacement reactions and nonmetal single displacement reactions. Metals exist in two common forms, as an elemental (pure) metal (Fe) or as a cation in an ionic compound (FeS). In a metal single displacement reaction a pure metal displaces the cation of another metal in an ionic compound. Nonmetals also exist as pure elements (Cl_2) and as anions in ionic bonds (the also commonly exist in many types of covalent compounds). In a nonmetal single displacement reaction, a pure nonmetal displaces the anion of another nonmetal in an ionic compound. The more active a metal or nonmetal, the more it wants to form an ion, the less active, the more it tends to exist in its elemental form.

Metal Displacement Reactions

The more active a metal, the more it wants to exist as an ion. The less active it is, the more it wants to stay as a pure element.

Lets look at the reaction fo Zinc metal with Copper(II) ions (in a $CuSO_4$ salt).

$$\underbrace{Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)}_{\text{Spontaneous Reaction, is actually used in batteries!}} \tag{3.6.1}$$

and compare that to the reaction of Copper metal with Zinc ions (in a $ZnCl_2$ salt).

$$\underbrace{Cu(s) + ZnSO_4(aq) \not\rightarrow ZnSO_4(aq) + Cu(s)}_{\text{No Reaction, nothing happens!}} \tag{3.6.2}$$

So Zinc is a more active metal than copper. The following video shows how an activity series can be developed that tells you which metals are the most reactive, and which are the least reactive.



Video 3.6.1: 2'19" YouTube from Kirkman Chemistry showing how the activity series could be determined (https://youtu.be/NyvETlgCx5A).

Activity Series

Table 3.6.1 shows the ranking of the activity of metals in aqueous solutions. A single displacement reaction will occur when the metalic form of a more active metal comes into contact with a solution containing cations of the less reactive metal. In table 3.6.1 Zinc is above copper, and so we would expect zinc metal to displace copper ions (eq. 3.6.1), and conversely, since copper is below zinc (less active) we would expect no reaction if copper was placed in a solution of zinc ions (eq. 3.6.2). So the reactivity series can be used to predict if a single displacement reaction will occur or not occur. NOTE: There are two activity series in this table. On the left are those of the metals and on the right the halogens. The higher something is on the table, the more it wants to be an ion.

d

Table 3.6.1: Activity Series

Table 3.6.1 Activity series of metals and nonmetals reacting in aqueous solutions.

Activity of Metals		**Activity of Halogens**
Elements	**Reaction Occurring**	**Elements**
Li K Ba Sr Ca Na	React with cold water, replacing hydrogen.	F_2 Cl_2 Br_2 I_2
Mg Al Zn Cr Fe Cd	React with steam, but not cold water, replacing hydrogen.	

Activity of Metals		Activity of Halogens
Co Ni Sn Pb	Do not react with water. React with acids, replacing hydrogen.	
H_2		
Cu Hg Ag Pt Au	Unreactive with water or acids.	

The above table can be used to predict if a single displacement reaction will occur. Note, the position of hydrogen. Metals that are more active than hydrogen will displace the hydrogen from an acid. The alkali metals and heavier alkaline earths on the very top are so reactive that they will displace hydrogen from water, and so are unstable in normal atmospheric conditions. Also note on the top right are the activity series for the halogens. These follow the same principles as the metals

Using the Activity Series

Lets take a closer look at eq. 3.6.3, the reaction of Zinc(s) with copper(II)Sulfate. The sulfate is a spectator ion and so the net ionic equation is

$$Zn(s) + Cu^{+2}(aq) \rightarrow Zn^{+2}(aq) + Cu(s) \tag{3.6.3}$$

That is the Zinc loses 2 electrons (oxidation)

$$Zn(s) \rightarrow Zn^{+2} + 2e^- \tag{3.6.4}$$

while the copper cation gains two electrons (reduction)

$$Cu^{+2} + 2e^- \rightarrow Cu(s) \tag{3.6.5}$$

These must occur concurrently, that is the electrons given by the species being oxidized must be given to the species being reduced and for the activity series states that the species with the higher activity will give electrons to a cation of a species of lower activity.

Since Zinc is above Copper, Zince will give two electrons to Cu^{+2}.

Video 3.6.2 goes over how to use the activity series to determine if a single displacement reaction involving metals is spontaneous or not.



Video 3.6.2: 3'13" YouTube showing how to use the activity series to determine if a single displacement reaction is spontaneous or not (https://youtu.be/_tyUhPILO14)

As for a non metal, the more active halogens prefer to be anions, and so iodide will react with fluorine, but fluoride will not react with iodine (see exercise below).

Exercise 3.6.1

Predict the products, determine if a reaction occurs, balance the equation and determine phase of all species.

a. $Al(s)+ Pb(NO_3)_4(aq) ->$
b. $Sn(s) + CaSO_4(aq) ->$
c. $Hg(s) + NiSO_4(aq) ->$
d. $NaCl(aq) + F_2(g) ->$

Answer a

$4Al(s)+ 3Pb(NO_3)_4(aq) -> 3Pb(s) + 4Al(NO_3)_3(aq)$

Answer b

No reaction, tin is less active than calcium

Answer c

No reaction, mercury is less active than nickle

Answer d

$2NaCl(aq) + F_2(g) ->2NaF(aq) + Cl_2(g)$

Food for Thought 3.6.1

In Video 3.6.3 below, we saw that the further down you go on the periodic table the more reactive the alkali metal with water, and yet according to the activity series (table 3.6.1) the trend in activity (Li>K>Na) does not follow a periodic trend . Does anyone want to venture a guess as to what is going on? (Why does the activity series not follow the reactivity with water trend in the video).



Video 3.6.2: 6'16" YouTube by the Royal Society of Chemistry on the reactivity of alkali metals with water. (https://youtu.be/eaChisV5uR0)

Solution

This is actually an important concept that will come up in general chemistry 2. The "reactivity" or "explosiveness" is a function of kinetics and how fast the reaction proceeds. The activity series describes the final state once the reaction is over, and is not a measure of how fast it occurs. So the trend on the video is not the trend of the activity series, but relates to how fast the reaction between water and different alkali metals proceeds. [Note: this is a thought provoking question, which we may come back and visit when we get to the second semester of this class.]

Other Redox Reactions

In a metal single displacement reaction it is very easy to see which reactant is getting oxidized (the pure metal) and which is getting reduced (the cation), but in many redox reactions it is not so clear.

Consider the combustion of methane, for which there are no cations or anions, but for which covalent bonds are being broken and formed, and so electrons are being transferred between species.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{3.6.6}$$

It is clear that on the left side oxygen is neutral, but has it "gained" or "lost" electron density when it goes from bonds between itself to bonds between carbon or hydrogen? To Figure this out we introduce the concept of oxidation state to indicate if an atom in a covalent bond is electron rich or electron poor, and we use oxidation numbers to keep track of this in a reaction and determine if an atom was oxidized or reduced, even when no ion was formed.

Oxidation Numbers

Oxidation numbers indicate an atoms "charge" state, even if it is not a charged ion. There are three fundamental oxidation states, neutral, positive or negative. If you have an atom that is not bonded to anything, its oxidation state is its charge. If it is covalently bonded, its oxidation state is an indicator of whether electron density has moved toward the atom or away from it

[0] Oxidation States indicate element is neutral

[+] Oxidation States indicate element is “electron poor”

[-] Oxidation States indicate element is “electron rich”

At this point we have a set of rules for determining Oxidation state. In Chapter 7 we will gain a deeper understanding of these rules, and in general chemistry 2 we will learn how to use oxidation numbers when we balance chemical equations for charge.

Rules for Identifying Oxidation Numbers

The following rules allow you to identify the oxidation state of each atom in a covalent bonded molecule or polyatomic ion. Note, the sum of the oxidation states of all species equals the charge of the compound, being zero if it is a neutral molecule.

1. Oxd # = 0 for pure elements
2. Oxd # = charge of monatomic ion
3. Oxd # of F = -1 in compounds with other elements
4. Oxd # of Cl, Br & I = -1 in compounds except with Oxygen & Fluorine
5. Oxd # of H= +1, except for Metal Hydrides (-1)
6. Oxd # of O = -2, except with fluorides, Peroxides (-1) and Superoxides (-1/2)
7. The Sum of the oxd # ‘s of all elements in a compound = 0, and = the charge of a polyatomic ion

Video 3.6.3 shows how to calculate the oxidation state for the atom in chlorine and sodium thiosulfate (which is also covered in example 3.6.1.

Example 3.6.2

Calculate the oxidation state for each atom in sodium thiosulate **$Na_2S_2O_3$**. (From the above rules you will know the oxidation state of every element except one, and can algebraically solve for that. See Video 3.6.3 if you need additional help).

Solution

$Na_2S_2O_3$

Given: [Na] = +1 [S] = x [O] = -2

Set up equation, not here the sum equals zero, but if it was a polyatomic ion, it would equal the charge of the ion:

(2)[Na] + (2)[S] + (3)[O] = 0

Solve Equation for unknown

(2)[1] + (2)[x] + (3)[-2] = 0

2 + 2x - 6 = 0

2x = 4

x = 2



Video 3.6.3: 3'33" YouTube on identifying oxidation numbers in covalent compounds (https://youtu.be/0ymQWY9Hqx4)

Exercise 3.6.9

Give the oxidation state of the central atom in the fallowing compounds or ions.

a. HClO
b. $HClO_2$
c. $HClO_3$
d. $HClO_4$
e. NH_4^+

Answer a

+1

Answer b

+3

Answer c

+5

Answer d

+7

Answer e

-5

Exercise 3.6.9

NGive the oxidation state of sulfur in the following compounds.

a. SO_3
b. SO_3^{-2}
c. H_2SO_3
d. SO_4^{-2}

e. H_2SO_4

Answer a

+6

Answer b

+4

Answer c

+4

Answer d

+6

Answer e

+6

Contributors and Attributions

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- November Palmer & Ronia Kattoum (UALR)
- anonymous

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CHAPTER OVERVIEW

4: Stoichiometry: Quantitative Information about Chemical Reactions

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Topic hierarchy

4.1: Stoichiometry
4.2: Limiting & Excess Reagents
4.3: Percent Yield
4.4: Measuring Concentrations of Solutions
4.5: pH scale for concentration of Acids and Bases
4.6: Stoichiometry of Reactions in Aqueous Solutions
4.7: Chemical Equations and Quantitative Analysis
4.8: Spectrophotometry

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4.1: Stoichiometry

Learning Objective

- Master Stoichiometric Relationships
  - Determine relationships of quantities of reactants consumed and products produced
  - express these in both number of chemical entities (moles) or masses of chemical entities

Introduction

A balanced chemical equation gives the identity of the reactants and the products as well as the accurate number of molecules or moles of each that are consumed or produced in a chemical reaction. **Stoichiometry** is a collective term for the quantitative relationships between the masses, the numbers of moles, and the numbers of particles (atoms, molecules, and ions) of the reactants and the products in a balanced chemical equation. The stoichiometric coeficient (section 3.1) represents the lowest whole number of each reactant or product consumed or produced as related to each other and the ratio of the coefficients represents the relative rates at which the species are consumed or produced. This, for each specific reaction, the coefficients represent an equivalence statement. Consider the following balanced equation describing the formation of Analine ($C_6H_5NH_2$) from from nitrobenzene ($C_6H_5NO_2$).

$$4C_6H_5NO_2 + 9Fe + 4H_2O \rightarrow 4C_6H_5NH_2 + 3Fe_3O_4^* \tag{4.1.1}$$

From the last Chapter we know this relates the number of particles to each other, but we can not count atoms or molecules. As stated in section 3.1 the word sotichiometry comes from the Greek words ***stoicheion*** (meaning “element”) and ***metron*** (meaning “measure”) and in this Chapter we will use the balanced chemical equation to relate measurable properties like the mass or volume of a sample to predict the quantities of other reactants or products consumed or produced. We will also be able to predict the maximum theoretical yield for a reaction and the quantities of any excess reagents.

*Note, Fe_3O_4 is the mineral magnetite, and would be called Iron(II,III) oxide as it has both Iron +2 and Iron +3 in its crystal structure (you will not be responsible for naming it in this class).

Counting by Measurement

So how do we "count" chemical entities involved in a chemical reaction?

We count chemical entities in a reaction by measuring macroscopic observables like mass, volume, temperature and pressure. What we measure depends on the state of matter, but we need to relate a measurable property to the number of particles. In this Chapter we will learn how to do this for solid substances and for solutes in a solution. In the gas phase Chapter we will use the ideal gas law (PV=nRT) to do this for gas phase reactants.

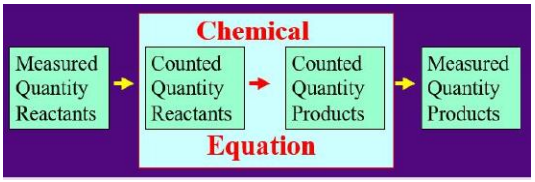


Figure 4.1.1: Flow chart showing three steps for using a balanced chemical equation to relate measured quantities of various reactants and products to each other.

We will start with the simplest types of stoichiometric equations, those involving masses.

Calculations Involving Mass Measurements

Mass measurements are the easiest as you use the molar mass to convert between grams and moles. In Figure 4.1.1 you see three arrows, two yellow and one red. Each of these involves a conversion factor. The yellow ones are conversions involving the molar masses, which relate the mass (grams) of a substance to its moles, and the red one involves the balanced chemical equation, which relates the stoichiometric coefficients of the various species to each other.

Technique: This is a three step process which should be done in one equation which uses three conversion factors.

- Conversion Factor #1: Use molar mass to convert **mass** of known material **to moles**.

- Conversion Factor #2: Use coefficients of balanced reaction equation to convert **moles** of known material **to moles** of desired material.
- Conversion Factor # 3: Use molar mass to convert **moles** of desired material **to mass** of desired material.

Set up as Dimensional Analysis Problem and solve with one equation (not three)!

How many grams of oxygen are produced when 4.0 g butane (C_4H_{10}) combusts?

Figure 4.1.2 solves this problem with one equation, where each step is a different conversion factor (equivalence statement). Each of these steps is detailied in the bullet list below

- Conversion Factor #1: **Mass** → **Mole**. Divide by molar mass of butane. Note, this has significant digits, and the units are included in the numerator and denominator as they are different, but the identity is the same and so not repeated in the denominator (it is implicitly understood that it is the same chemical entity, which in this case is butane)
- Conversion Factor #2: **Mole**→ **Mole**. Use coefficients of balanced reaction equation to convert moles of known material to moles of desired material. These are exact numbers that come from the balanced equation and so do not have significant Figures, but since they are relating two different entities, the identity of both the numerator and denominator are explicitly stated (oxygen in the numerator, butane in the denominator).
- Conversion Factor # 3: **Mole**→ **Mass**. Multiply by molar mass to convert moles oxygen to grams oxygen. Note, this has significant digits, and the units are included in the numerator and denominator as they are different, but the identity is the same and so not repeated in the denominator (it is implicitly understood that it is the same chemical entity, which in this case is oxygen butane)

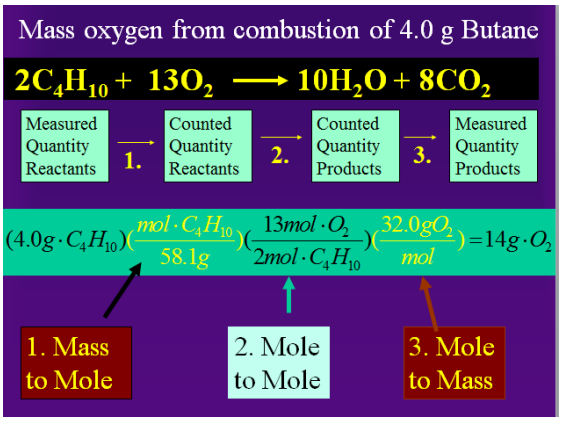


Figure 4.1.2: Solving a stoichiometric problem using all three conversions in one equation.

Cancel units in the above equation to be sure your answer has the desired units and only round off your final answer to the correct number of significant digits, do not round off during intermediate steps.

How many significant digits should your molar masses be? This can vary from instructor to instructor, but the rule of thumb is to use one more significant digit than the measured values of your problem statement. Since this problem had 4.0 g of butane, which has 2 significant digits, we used molar masses of 3 significant digits, but rounded the final answer to two. If at all possible, never use a molar mass with fewer significant digits than the measured values you are working with, as stated in the problem.

Do you Always start with the Mass-to-Mole step? ***NO!*** If the question was what mass of oxygen is produced if you combust 4 moles of butane, you do not need to do the first step. Note, both propane and carbon dioxide are gases at ambient conditions and so you can not measure their mass directly. Instead, you need to measure the pressure, temperature and volume of the gas to determine the number of moles. We will learn how to do this when we study gasses, but for now we will use masses in our calculations.

Worked Problems

Consider the formation of Analine ($C_6H_5NH_2$) from from nitrobenzene ($C_6H_5NO_2$), iron and water.

$$4C_6H_5NO_2 + 9Fe + 4H_2O \rightarrow 4C_6H_5NH_2 + 3Fe_3O_4 \qquad (4.1.2)$$

Lets look at some of the questions you could answer. (AND BE CAREFUL TO READ THE QUESTIONS!)

1. How many moles of iron would you need to produce 100 mole of analine?
2. How many grams of iron would you need to produce 100 mole of analine?

3. How many grams of iron would you need to produce 100 grams of analine?
4. How many grams of analine could 100 g nitrobenzene produce?
5. How many moles of Fe_3O_4 could 100 g of nitrobenzene produce?
6. How many moles of Fe_3O_4 would be produced if 100 g of analine was produced?
7. ...and many more permutations....SO READ THE QUESTION CAREFULLY!

Table 4.1.1; molar masses of chemicals in Equation 4.1.2

$C_6H_5NO_2$	Fe	H_2O	$C_6H_5NH_2$	Fe_3O_4
123.105g/mol	55.845g/mol	18.016g/mol	93.121g/mol	231.535 g/mol

Mol-to-Mol

Question 1: How many moles of iron is needed to produce 100.0 mol of Analine?

Implicit in this question is that nitrobenzene and water are in excess. Note: a good technique is to write down the equation and under each species identify what is given, and what is being asked

$$4C_6H_5NO_2 + \underbrace{9Fe}_{moles=?} + 4H_2O \rightarrow \underbrace{4C_6H_5NH_2}_{100\ moles} + 3Fe_3O_4 \tag{4.1.3}$$



Video 4.1.1: 1'25" YouTube solution to question 1 (https://youtu.be/Rt5S-wQ0FD8)

$$100\ mol\ \cancel{C_6H_5NH_2}\left(\frac{9\ mole\ Fe}{4\ \ mole\ \cancel{C_6H_5NH_2}}\right) = \tag{4.1.4}$$

Mass to Mass

Question 2: How many grams of analine could 100 g nitrobenzene produce?

We are now solving a problem where we can actually measure the quantity of reactants and products involved. We start by writing an equation, and under each species write the given values, while identifying what we are solving for.

$$\underset{\substack{mass=100.0g \\ fw=\frac{123.105g}{mol}}}{4C_6H_5NO_2} + 9Fe + 4H_2O \rightarrow \underset{\substack{mass=?g \\ fw=\frac{93.121g}{mol}}}{4C_6H_5NH_2} + 3Fe_3O_4 \tag{4.1.5}$$

We were given 100 g of nitrobenzene and wanted the mass of analine that could be produced, so the first thing I did was write that down under each species. I also needed the molar mass of nitrobenzene and analine, and so wrote that under those. Now on the equation I have everything I need to solve (Video 4.1.2



Video 4.1.2 3'03" Youtube solving question 2 (https://youtu.be/WQLgWy8O0u0)

$$100\ \ g\cancel{C_6H_5NO_2}\frac{mole\ \cancel{4C_6H_5NO_2}}{123.105\ \cancel{g}}\left(\frac{4\ \ mol\ \cancel{C_6H_5NH_2}}{4\ \ mol\ \cancel{C_6H_5NO_2}}\right)\frac{93.121g\ C_6H_5NH_2}{\cancel{mol}}= \tag{4.1.6}$$

Mass to Mole

Question 3: This time we want to know how many moles Fe_3O_4 would be formed from 100 g nitrobenzene. We start by writing down what we are given and what we are solving for (100g nitrobenzene given and moles of Fe_3O_4 sought for) and below that we right any additional information we need to solve this problem. That is, we need the molar mass of nitrobenzene in order to calculate the moles. We do not need the molar mass of Fe_3O_4 because the question is looking for how many moles, not how many grams.

$$\underbrace{4C_6H_5NO_2}_{\frac{mass=100g}{fw=\frac{123.105g}{mol}}}+9Fe+4H_2O\rightarrow 4C_6H_5NH_2+\underbrace{3Fe_3O_4}_{moles=?} \tag{4.1.7}$$



Video 4.1.3: 2'23" YouTube solving question 3 (https://youtu.be/kaE2FaFk260).

$$100\ g\ \cancel{C_6H_5NO_2}\frac{mole\ \cancel{C_6H_5NO_2}}{123.105\ \cancel{g}}\left(\frac{3\ mol\ Fe_3O_4}{4\ \ mol\ \cancel{C_6H_5NO_2}}\right)=? \tag{4.1.8}$$

Exercise 4.1.1

What is true regarding the following statements made for the following balanced chemical reaction?

4 Al(s) + 3 O_2(g) --> 2 Al_2O_3(s)

A) for every 8 moles of aluminum and 6 moles of oxygen consumed, 4 moles of aluminum oxide are produced.

B) for every 4 molecules of aluminum and 3 molecules of oxygen consumed, 2 molecules of aluminum oxide are produced.

C) for every 4 grams of aluminum and 3 grams of oxygen consumed, 2 grams of aluminum oxide are produced.

D) A and B only

E) A, B, and C

Answer

D) A and B only. Stoichiometric ratios in a balanced chemical equations represent a particles/particle ratio that can be scaled up to a mole/mole ratio. So, instead of looking at one molecule at a time, which is not very feasible, we can count by the mole (think by the dozen) of particles at time. Coefficients never represents a mass/mass to ratio because each species in a chemical reaction has a different molar mass. Note: A is still true. We are just doubling the amount of moles, but the ratio is still the same.

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- Anonymous
- Ronia Kattoum (exercise & learning goals)

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4.2: Limiting & Excess Reagents

Learning Objectives

- Understanding Stoichiometric Proportions
- Understanding Limiting and Excess Reagents
  - Predict quantities of products produced or reactants consumed based on complete consumption of limiting reagent (on both mole and mass basis)
  - Predict quantities of excess reagents left over after complete consumption of limiting reagents.

Stoichiometric Proportions and Theoretical Yield

A balanced chemical equation describe the ratios at which products and reactants are respectively produced and consumed. That said, the coefficients of the balanced equation have nothing to do with the actual quantity of reactants you start with, as you can mix any amount you choose, but clearly the maximum yield **(theoretical yield)** must be limited by the reactant that gets consumed up first, the **limiting reagent**. Any reagents remaining after the complete consumption of the limiting reagent are know as **excess reagents.**



Video 4.2.1: 4/34" YouTube uploaded by "Professor Dave Explains", the first 2:47 goes over Limiting and excess reagents, and then it goes into Percent Yield (section 4.2.3)

Here is some common terminology used to describe reactions based on the concentrations of reactions.

- **Stoichiometric Proportions:** Reactants are mixed in the ratios defined by their stoichiometric coefficients. If a reaction proceeds to completion, everything is consumed.
- **NonStoichiometric Proportions**: Reactants are mixed in ratios that are different than the stoichiometric coefficients. One species runs out first (Limiting Reagent), while another is not completely consumed (Excess Reagent).
  - **Excess Reagent:** The quantity (mole or mass) left over after the complete consumption of the limiting reagent

    Quantity Excess = Initial Quantity - Consumed Quantity.
- **Theoretical Yield**: the maximum possible yield based on the complete consumption of the limiting reagent

Thought Question 4.2.1

Are the limiting reagents always completely consumed?

Answer

No, only if the reaction goes to completion. There can be many different reasons why the limiting reagent is not completely consumed, these can include:

- Products also react to form reactants causing an equilibrium of reactants of products to coexist, this will be covered next semester (see Chapter 15)
- Reactions may not be over (some reactions occur very slowly).

Limiting Reagent Problem Strategies:

1. **Identify moles of all reactants present.**
   If given mass, divide by formula weight to convert to moles (this is the mass to mole step from the section 4.1,3.
2. **Divide moles of each reactant by it's stoichiometric coefficient.**
   This is the denominator of the mole-to-mole step in section 4.1.3.
3. **Smallest number indicates limiting reagent.**
4. **Multiply by stoichiometric coefficient of species you are solving for, and answer the question .**
   This is the numerator of the mole-to-mole step in section 4.1.3. If you are after moles, you are finished, if you are after mass, you need to use the molar mass of product to convert moles product to grams mass product, which is the mass-to-mole step in section 4.1.

Limiting Reagent Problem

Silver tarnishes in the presence of hydrogen sulfide and oxygen due to the following reaction

$4Ag + 2H_2S + O2 \text{ ----> } 2Ag_2S + 2H_2O$

What is the Limiting Reagent and Theoretical Yield of Ag_2S if 2.4 g Ag, 0.48 g H_2S and 0.16g O_2 react?

Note in the video how we first wrote the balanced equation, and then under each species wrote down what we were given. In this problem there are 3 reagents, and this technique allows us to quickly identify the



Video 4.2.2: 6'07" YouTube calculating the theoretical yield of Ag_2S based on the complete consumption of the limiting reagent (https://youtu.be/26ieM_k0NOU) [Digital Corrigendum: @1'50" in the video the mass silver divided by its molar mass and stoiochiometric coefficient was written down to be 0.0556 but was 0.00556. at 2'22" the value of oxygen was determined to be 0.005, and so that was smaller and was the limiting reagent. Note: at 2:57 this problem is redone the long way, and this allows you to see how the shortcut works.

Excess Reagent

To calculate the excess reagent you determine how much is left over after the complete consumption of the limiting reagent

$$\text{Mass}_{\text{excess reagent}} = \text{Mass}_{\text{initial}} - \text{Mass}_{\text{consumed by complete consumption of limiting reagent}}$$

Now building on the last problem, calculate the mass of excess reagents for the reaction of 2.4 g Ag, 0.48 g H_2S and 0.16g O_2 to form $Ag_2S + H_2O$.



Video 4.2.3: 4'37" YouTube calculating the excess reagent concentrations when 2.4 g Ag, 0.48 g H_2S and 0.16g O_2 react.

Exercise 4.2.1

Consider the oxidation of glucose through respiration:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + Energy \tag{4.2.1}$$

What mass of carbon dioxide forms when 25.00 g of glucose reacts with 40.0 g of oxygen?

Answer

Step 1: Calculate moles of each reactant:

$$25.00 \text{ g} \times \frac{1 \text{ mol}}{180.06 \text{ g}} = 0.1388 \text{ mol } C_6H_{12}O_6$$

$$40.0 \text{ g} \times \frac{1 \text{ mol}}{32 \text{ g}} = 1.25 \text{ mol } O_2$$

Step 2: Divide each by its stoichiometric coefficient, smallest value is limiting reagent.

$$1.25 mol O_2 (\frac{1}{6 mol}) = 0.208 \tag{4.2.2}$$

$$0.1388 mol C_6H_{12}O_6 (\frac{1}{1 mol}) = 0.1388$$

So glucose is the limiting reagent.

Step 3: calculate the mass carbon dioxide based on the complete consumption of the limiting reagent.

$$0.1388 mol\ C_6H_{12}O_6 (\frac{6 mol\ CO_2}{1 mol\ C_6H_{12}O_6}) \left(\frac{44.011 g\ CO_2}{mol}\right) = 36.66 g\ CO_2 \tag{4.2.3}$$

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4.3: Percent Yield

Learning Objectives

- Differentiate between actual yield, theoretical yield, and percent yield
- Calculate percent yield

Percent Yield

Percent Yield is defined as the actual yield divided by the theoretical yield times 100.

$$\text{Percent Yield} = \left(\frac{\text{Actual Yield}}{\text{Theoretical Yield}}\right) \times 100\% \tag{4.3.1}$$

There are many reasons why the actual yield of a chemical reaction may be less than the theoretical yield, and these will be taken up during later Chapters of the course. Here are some reasons, most of which deal with topics that will be covered in the second semester of this course.

1. Equilibria between products and reactants, where the limiting reagent is not completely consumed (Chapter 15)

$$Ca_3PO_4(s) \leftrightharpoons 3Ca^{+2} + 2PO_4^{-3} \tag{4.3.2}$$

2. Kinetics, simply speaking, the reaction may be very slow and not over (Chapter 14).
3. Formation of Intermediates. A chemical equation does not represent the mechanism but the overall balance of mass. The mechanism tells how the reaction actually proceeds (section 14.6), and there are often intermediate chemical species that are not completely consumed. This is exemplified in the following reaction.

$$H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HClg \tag{4.3.3}$$

It is highly unlikely that this reaction takes place in one step where three molecules simultaneously collide. A more plausible way for the reaction to occur is in two steps as below, where HI is an intermediate.

$$H_2 + ICl \rightarrow HCl + HI \tag{4.3.4}$$
$$HI + ICl \rightarrow HCl + I_2 \tag{4.3.5}$$

In the first step HCl and the intermediate HI are formed from the bimolecular collision of H_2 and ICl. In the second step, the HI (intermediate) collides with another ICl to form HCl and I_2. If you add the two steps the intermediate cancels out and you get the balanced equation.

$$H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HClg \tag{4.3.6}$$

4. Competing or Parallel Reactions

You may have a secondary reaction competing with the reaction described, like the formation of hydroiodic acid and chlorine gas.

$$H_2 + ICl \rightarrow HI + HCl \tag{4.3.7}$$
$$HCl + ICl \rightarrow HI + Cl_2 \tag{4.3.8}$$

So any HI or Cl_2 formed would reduce the yield of the desired I_2 and HCl. A parallel or competing reaction could also involve a completely different reactant. For example, if oxygen was available the following reaction could compete ICl for the H_2.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \tag{4.3.9}$$

Percent Yield Problem

Phosphoric Acid can be synthesized from Phosphorous, Oxygen and water according to the following equations

$$4P + 5O_2 + 6H_2O \rightarrow 4H_3PO_4 \tag{4.3.10}$$

What is the percent yield if 50.3 g of phosphoric acid is created from 20.0 g phosphorous, 15.0 g of water and 30.0 g of oxygen?

First we set up the problem and it is suggested that we write down the given quantities under each species of the balanced equation (as that makes it easier to see the given information)

$$\underset{\substack{m=20.0g\\ fw=30.98g/mol}}{4P} + \underset{\substack{m=30.0g\\ fw=32.00g/mol}}{5O_2} + \underset{\substack{m=15.0g\\ fw=18.01g/mol}}{6H_2O} \rightarrow \underset{\substack{ActualYield=50.3g\\ fw=97.995g/mol\\ TheoreticalYield=?}}{4H_3PO_4} \tag{4.3.11}$$

After calculating the theoretical yield (based on the complete consumption of the limiting reagent) we calculate the percent yield. This problem is solved in video 4.3.1.



Video 4.3.1: 4'40" YouTube solving a percent yield problem (https://youtu.be/BCOdyr1QKj0).

Exercise 4.3.1

A chemist decomposes 1.006 g of $NaHCO_3$ and obtains 0.434 g of Na_2CO_3. What are the theoretical yield and the actual yield? What is the percent yield?

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\ell) + CO_2(g)$

Answer

theoretical yield = 0.6345 g; actual yield = 0.434 g

percent yield = 68.4%

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4.4: Measuring Concentrations of Solutions

Learning Objectives

- Define Molarity
- Differentiate between solute, solvent, and solution
- Calculate the molar concentration for solutes
- Outline the steps to make a solution of a desired concentration from a solid or aqueous solute
- Calculate the concentration of ions in a soluble ionic compound
- Perform stoichiometric calculations involving aqueous solutes
- Calculate the concentration of unknown solutes

Introduction

Up to this point we have used stoichiometry to "count" atoms, molecules and ions by measuring mass of pure substances and using molar masses to calculate the number of chemical entities (moles). Many of the reactions we have studied involve solutions, where we are interested in a solute that is dissolved in a solvent, and we can not measure the mass of the solute independent of the solvent. We also need to realize that many chemical reactions require the reactants to be mobile, where they can bump into each other, and this can occur when they are dissolved in a solvent. So it is very important that we can count chemical entities when the entity of interest is a solute dissolved in a solvent, and in which case we measure the mass of volume of the solution as a whole (solvent plus all solutes) of which volume is typically the easiest to measure.

Concentration of a Solute

There are two basic ways of reporting the concentration of a solute in a solvent, by reporting the mass of solute in a given volume, or the number of moles of solute in a given volume. These are effectively conversion factors that define the equivalent mass or moles of a solute to the volume of the solution.

- **Mass Concentration**: has typical units of g/L

$$\frac{mass\ solute}{vol\ solution} = \frac{m(g))}{V(L))} \tag{4.4.1}$$

- **Mole Concentration (Molarity)**: has units of mol/L or M

$$\frac{moles\ solute}{vol\ solution} = \frac{n(moles))}{V(L))} = M(mol/L) \tag{4.4.2}$$

So a 3.0M solution of sucrose has 3.0 mole of sucrose per liter

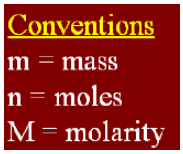


Figure 4.4.1: In order to avoid confusion we will use a small "m" to denote mass, and a large ""m" to denote Molarity.

How do we convert between mass and mole based concentration?

Simply by multiplying or dividing by the molar mass (g/mol). If you know the g/L, you simply divide by the molar mass, and if you know the moles/L and want the mass/L, you multiply by the molar mass (just use the molar mass as an equivalence statement).

How do we "count" solute molecules and ions?

By measuring the volume and knowing the molarity. This is analagous to measuring the mass and knowing the molar mass for a pure substance.

$$n(moles) = M(\frac{mol}{L})(V(L)) \tag{4.4.3}$$
$$n = MV$$

This can be contrasted to how we "count" chemical entities that are pure solids.

$$n(moles) = \frac{m(g)}{molar\ mass(\frac{g}{mol})} \tag{4.4.4}$$

$$n = \frac{m}{fw}$$

Making a Solution with a Solid Solute.

Step 1: Calculate Mass of solute needed for desired volume
Step 2: Quantitatively Transfer Mass to Volumetric Flask
Step 3: Dilute to volume with solvent, ensuring that all of the solid has dissolved.

Making 500.0 mL of 0.500 M Copper(II)Sulfate

Step 1: Calculate Mass $CuSO_4$(s) needed.

$$0.5000L\left(\frac{0.500molCuSO_4}{L}\right)\left(\frac{159.6gCuSO_4}{mol}\right) = 39.9gCuSO_4 \tag{4.4.5}$$

Step 2: Weight 39.9g $CuSO_4$(s) and quantitatively transfer to 500 mL graduated cylinder (which is calibrated to 500.0 mL), being sure all the salt is transferred.

Step 3: Fill half way and mix, then dilute to volume. Make sure all the solute is dissolved, and recheck that solution level is at bottom of meniscus.

Exercise 4.4.1

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer

1.57 M $C_6H_{12}O_6$

Why can't you just add 500.0mL of water to 39.9 g $CuSO_4$ to make 500.0 mL of 0.500M solution?
First, this is not taking into account the volume of the solute, and second, there is usually a change in volume when you dissolve a solute into a solvent, and in the case of ionic compounds this is a contraction.

Exercise 4.4.2

Using concentration as a conversion factor, perform the following calculation.

A) How many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

B) What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?

C) What volume of 1.50 M HCl solution contains 10.0 g of hydrogen chloride?

Answer

A) 1.74 L

B) 6.12 g

C) 183 mL or 0.183L

Ion Concentrations in Solution

When an ionic compound dissolves it breaks up into its ions.

$(NH_4)_2Cr_2O_7(aq) \rightarrow 2NH_4^+(aq) + Cr_2O_7(aq)$

Dissolving 252.07 grams of ammonium dichromate (fw = 252.07 g/mol) results in a solution that is 1M ammonium dichromate, but when an ionic salt dissolves, it breaks up into ions, and so what you really have is a solution that is 2 M ammonium ion (NH_4^+) and 1 M in dichromate ion ($Cr_2O_7^{+2}$)



Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

Example 4.4.1 Solution Concentration of Iron(II)chloride

Water is added to 2.16 g of the ionic compound ferrous chloride to make a solution with a total volume of 100.0 mL. Express the concentration of the salt solution, and that of its ions.

1. What is the salt concentration?
2. What are the ion concentrations?

Solution

Video 4.4.1 goes over this calculation.

Ans: 0.170M $FeCl_2(aq)$

0.170M $Fe^{+2}(aq)$

0.340M $Cl^-(aq)$

Yes, there are three answers! (that of the salt, and of the ions)



Video 4.4.1: 3'36" YouTube calculating the concentration of a Ferrous Chloride in example 4.4.1.

Exercise 4.4.3

You have a 1.50 M solution of Na_2CO_3. What is the concentration of:

A) sodium ions?

B) carbonate ions?

C) total ions?

Answer

A) $[Na^+]$ = 3.00 M

B) $[CO_3^{-2}]$= 1.50 M

C) $[Na^+]$ + $[CO_3^{-2}]$ = 4.50 M ; or you can choose think for every 1 mole of Na_2CO_3, there are 3 moles of ions (identify of the ions is irrelevant).

Preparing Solutions with Stock Concentrated Solutions (Dilution).

Many stockroom reagents come as concentrated solutions that can easily be diluted to a desired concentration by adding solvent. Adding a solvent does not change the moles of solute (n), so

$$n_{initial} = n_{final}$$
$$n_i = n_f$$
$$M_iV_i = M_fV_f$$

Step 1: Calculate initial volume of stock
Step 2: Transfer to volumetric flask with a volumetric pipette
Step 3: Dilute to Volume



(a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration.

(b) The measured volume of stock solution is transferred to a second volumetric flask.

(c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].

Example 4.4.2

How do you make 500.0 ml of 0.70M HCl solution from stock 11.6 M HCl?

Solution

Step 1: Calculate initial volume of 11.6 M hydrochloric acid needed.

$$M_iV_i = M_FV_F \tag{4.4.6}$$

$$V_i = V_f\left(\frac{M_f}{M_i}\right) = 500.0mL\left(\frac{0.70M}{11.6M}\right) = 30.2mL \tag{4.4.7}$$

Step 2: Quantitatively transfer this volume to a 500 mL volumetric flask (this has 4 significant Figures, that is, it is calibrated to 500.0 mL)

Step 3: Dilute with water to mark



Video 4.4.2: Dilution problem on creating 500.0 ml of a 0.700M HCl solutioin

Exercise 4.4.4

What is the concentration of an HCl solution if 598 mL of 0.778 *M* HCl is diluted to 1.00 L?

Answer

e. 5.23 * 10^2 mL

$M_i * V_i = M_f * V_f$

$M_f = \frac{(M_i * V_i)}{M_f} = \frac{0.778M(0.598L)}{1.00L} = 0.465M$

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4.5: pH scale for concentration of Acids and Bases

The pH Scale

What is pH?

The pH scale measures the concentration of hydronium ions in water. In section 3.5 we looked at the autoionization of water, which is when two water molecules collide and one gives a proton to another, resulting in the formation of hydronium and hydroxide ions.

$$H_2O(l) + H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq)$$

For neutral water the hydronium and hydroxide concentrations are equal, and this is a very small number, 10^{-7}M. As these are very small numbers we use a log scale to represent pH, which is a convenient way of expressing the hydronium ion concentration of a solution. It is fairly common knowledge that neutral water has a pH of 7, acids have a pH <7 and bases have a pH>7, but few people understand this in terms of the actual hydronium ion concentration. Our objective is to develop an understanding of logarithmic scales by developing a pH scale. First we will introduce the **convention of using brackets to describe concentration**, so $[H_3O^+]$ means the concentration of hydronium in moles per liter (M).

$$\mathbf{pH = -\log[H_3O^+]}$$

$$\mathbf{[H_3O^+] = 10^{-pH} = 1/10^{pH}}$$

So a $[H_3O^+]$ concentration of 1.0×10^{-7} M solution has a pH of 7.00. Note, in pH the significant Figures are given by the number of places to the left of the decimal, as it is not a number, but the number of times something has been divided (or multiplied) by 10. To understand this, consider a solution with a concentration of 1×10^{-12}, the number has 1 significant Figure and the pH is 12. Since 12 has two digits, we can't use the digits to the left of the decimal, and so we write it as 12.0, indicating it has 1 significant digit.

To get a feel for this we can use the following applet and the method of successive dilutions to develop a pH scale.

Developing pH Scale via Method of Successive Dilutions

Method of Successive Dilutions:

We have created a demonstration video, which describes the features and interface of the Virtual Lab.

In the virtual lab below:

Part 1: Setting up the lab for the method of successive dilutions.

- Open the stockroom and go to the strong acids
  - single click on 1 M HCl,
  - single click on the 3 L distilled water
- Click on "glassware" and move into the workbench a 100 mL volumetric flask
- Drag the water over the 100 mL volumetric flask and transfer 90 mL of water into the flask.
- right click on the volumetric flask and hit "duplicate". repeat this 7 times, so you have 8 100 mL flasks with each containing 90 mL of water.
- Click on 1 M HCl, and read the pH, which will be 0, because $1 = 10^{-pH} = 10^0 = 1$.

Part 2: Successive Dilutions.

- Click on the stock 1 M HCl and record the pH
- Transfer 10 ml of 1 M HCl to a volumetric flask with 90 mL water, so the total volume is 100 mL, and record the pH of the diluted solution, which represents 10 mL osf the stock dilute to 100 mL,
  - From the dilution equation, $M_iV_i = M_iV_i$ and

$$M_f = M_i\left(\frac{V_i}{V_f}\right) \tag{4.5.1}$$

    Note, the ratio of the volumes is unit-less and can be defined as the dilution factor, which in this case is 10:100 or 1 to 10, so the diluted solution is 1/10th the original.
  - If you successively dilute each solution 10 fold by pouring 10 mL into 90 mL of water, the pH of each solution is n, where n is the number of times you successively diluted the stock 1M solution.

- That is, each solution is $1/10^n$ the concentration of the original solution, where n is the number of times the original solution was successively diluted, and so the pH is the number of 1/10 dilutions.

Not Found

The requested URL was not found on this server.

Why after eight 10-fold dilutions does the pH not become 8, but stays at 7?

Neutral water is the result of one water molecule transferring a proton to another water molecule, and this results in a hydronium concentration of 10^{-7}. When the acid is diluted to a concentration of less than 10^{-7}, it is so dilute that it protonates fewer water molecules than the water does.

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4.6: Stoichiometry of Reactions in Aqueous Solutions

Introduction

At the beginning of this Chapter we covered stoichiometry of reactions where everything was a solid, and we used the mass and formula weight to calculate the moles of reactants or products consumed or produced. For a reaction where two chemicals interact with each other they must come into contact with each other if the reaction is going to proceed. One way of enabling this mobility is to dissolve the reactants into a solvent creating a solution. Unless you have a pure substance, you can not use mass to measure the number of particles, as you are weighting both the solvent and solute(s). So if you have a solution, you need to know the concentration, and the most common way of representing chemical concentrations is the molarity.

Solid phase:

$$n(moles) = \frac{m(g)}{fw(\frac{g}{mol})} \tag{4.6.1}$$

$$n = \frac{m}{fw} \tag{4.6.2}$$

Aqueous phase (solute concentration):

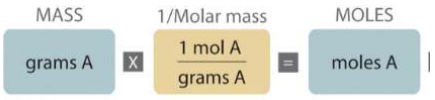
$$n(moles) = M\left(\frac{mol}{L}\right)V(L) \tag{4.6.3}$$

$$n = MV \tag{4.6.4}$$

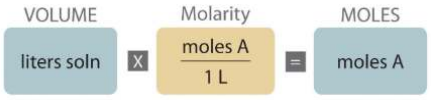
where,
n = moles
m = mass
V = Volume
fw = formula weight (molar mass)

So now we can calculate the moles of a pure substance if we weigh it's mass and know it's molar mass, or if we measure its volume and know it's concentration (Molarity).

If given a solid, you need to know its molar mass



If given a solute, you need to know its concentration (molarity)



Solution Stoichiometry

In sections 4.1 and 4.2 we calculated theoretical yield, limiting reagent and excess reagents for reactions where all chemical species were described as solids where we measured the mass. Now that we have a way to describe solute concentrations (Molarity) we can extend these to include solutions where we measure the volume. Lets look at the reaction of adding a solid soluble salt to an aqueous solution

Dissolving 10.0 g of Copper(II)sulfate into 500.0 mL of 0.100 M sodium phosphate

Exercise 4.6.1

What are the formulas of the reactants when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate? (see video 4.6.1)

Answer

$CuSO_4$(s) and Na_3PO_4(aq)

Exercise 4.6.2

What are the formulas and phases of the products when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate?(see video 4.6.1)

Answer

Na_2SO_4(aq) and $Cu_3(PO_4)_2$(s)

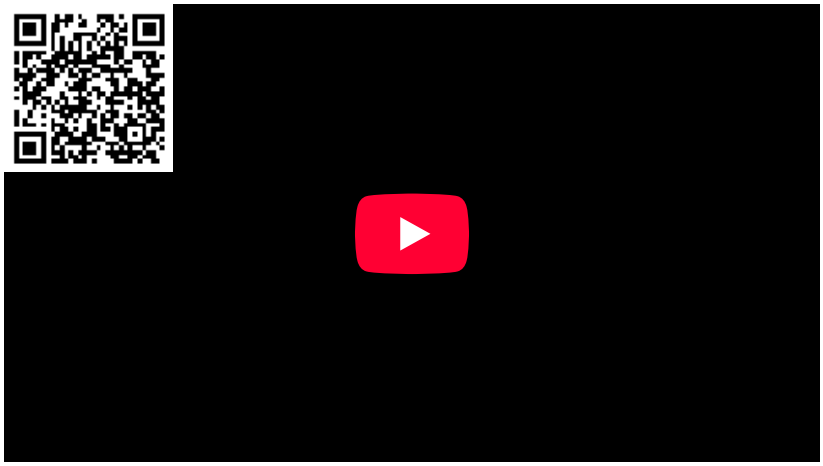
Exercise 4.6.3

Write the balanced equation when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate?(see video 4.6.1)

Answer

$3CuSO_4(aq) + 2Na_3PO_4(aq) \rightarrow 3Na_2SO_4(aq)$ and $Cu_3(PO_4)_2(s)$

NOTE: We added copper(II)sulfate as a solid, but it dissolved (see solubility rules, section 3.4.2.1), and so it should be treated as aqueous when writing the equation



Video: 4.6.1: 3'54" YouTube identifying reactants, products, phases and balancing the equation for the dissolution of 10 g of copper(II) sulfate into 500.0 mL of 0.100 M sodium phosphate (https://youtu.be/qdtiFATDMdU).

Calculating the Theoretical Yield for the mass of precipitate formed

Example 4.6.1

Calculate the theoretical yield for the mass of precipitate formed when 10.0 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate.

Solution

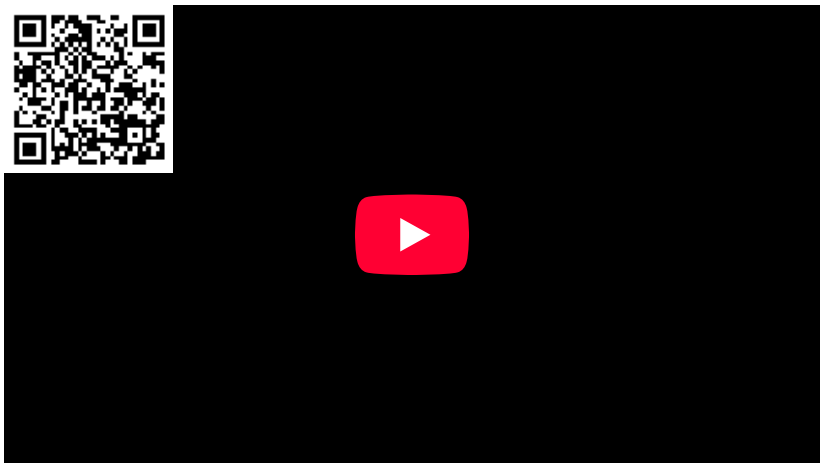
See video 4.6.2 for the solution of this problem, and video 4.6.3 for a deeper explanation of the fast technique used in video 2. Note how we set up the equation by writing out the given data under each species, along with the moles that we need to calculate with that data. We calculate for the moles of each reactant (n), divide by its storichiometric coefficient, and the smallest number is the limiting reagent. We then proceed and calculate the mass of copper(II)phosphate formed.

$$\underset{\substack{n=\\ m=10.0g\\ fw=159.61g/mol}}{3CuSO_4(s)} + \underset{\substack{n=\\ M=0.100mol/l\\ V=500.0ml}}{2Na_3PO_4(aq)} \rightarrow \underset{\substack{m=?\\ fw=380.58g/mol}}{Cu_3(PO_4)_2(s)} + 3Na_2SO_4(aq) \tag{4.6.5}$$

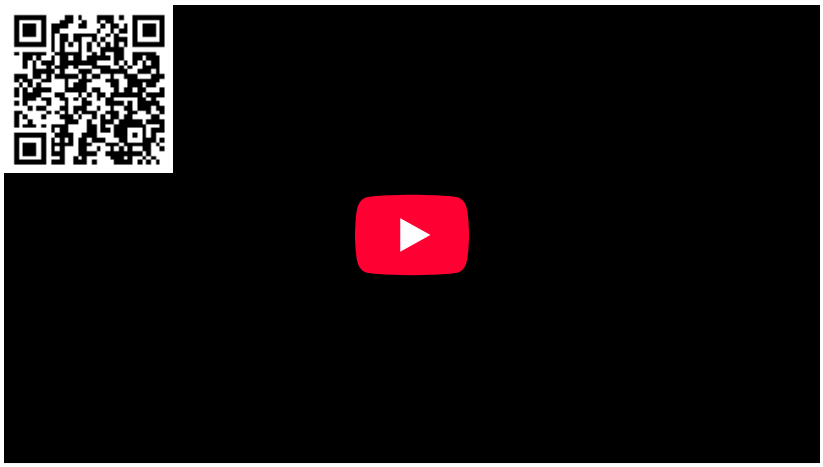
at 2'25" into video 4.6.2 we calculated the limiting reagent, which was copper(II)Sulfate and thus based the yield on its consumption. The overall equation is

$$10.0gCuSO_4(s)\left(\frac{molCuSO_4}{159.69g}\right)\left(\frac{1molCu_3(PO_4)_2}{3molCuSO_4}\right)\left(\frac{380.58gCu_3(PO_4)_2(s)}{mol}\right) = 7.95gCu_3(PO_4)_2(s) \tag{4.6.6}$$

Note, the above equation is not used in the fast technique, but is used in video 4.6.3 when we explain the fast technique



Video: 4.6.2: 3'30" YouTube video calculating the mass precipitate formed by complete consumption of the limiting reagent for the dissolution of 10 g of copper(II) sulfate into 500.0 mL of 0.100 M sodium phosphate (https://youtu.be/Vh3Je39bgQc)



Video: 4.6.3: The fast technique in video 4.6.2 explained in more detail (https://youtu.be/5Qlo1bi1uzE).

Calculating excess reagents

Since the copper sulfate is the limiting reagent we can calculate the amount of excess sodium phosphate

Example 4.6.2: Excess Reagent

Calculate the concentration (molarity) of excess phosphate when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate (note: the real reaction is expressed by the net ionic equation:

$$3Cu^{+2}(aq) + 2PO_4^{-3}(aq) \rightarrow Cu_3(PO_4)_2(s) \tag{4.6.7}$$

Solution

see Video 4.6.4

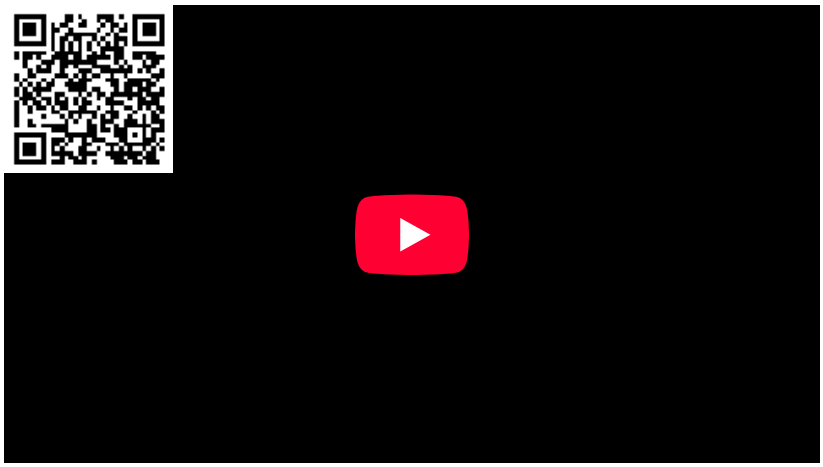
First calculate moles excess phosphate

$$\text{Initial moles} - \text{amount consumed by reaction with limiting reagent} \tag{4.6.8}$$

$$0.050 mol PO_4^{-3} - 0.06265 mol Cu^{+2}\left(\frac{2\ mol\ PO_4^{-3}}{3\ mol\ Cu^{+2}}\right) = 0.0082 mol PO_4^{-3}$$

then divide into total volume

\frac{0.0082mol PO_4^{-3}}{0.500l}= 0.016MPO_4^{-3}(aq)



Video 4.6.4: Determining the excess phosphate when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate https://youtu.be/xsp1_BADnqA).

Calculating Concentration of Spectator Ions

For the reaction that occurs when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate we have calculated the theoretical yield

Example 4.6.3 Spectator Ion Concentrations

Calculate spectator ion concentrations when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate

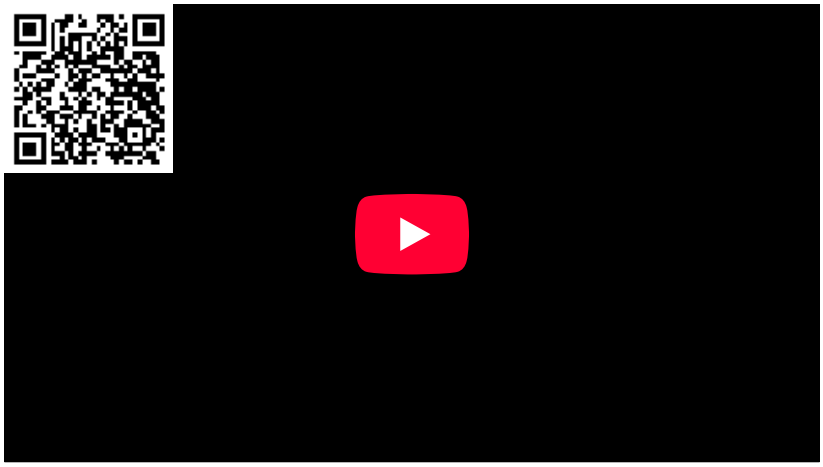
Solution

See video 4.6.5 for the solution to this problem. There are several ways you can set this up. In calculating the limiting reagent we determined the moles of each reactant and so that would be a logical place to start

$$\underset{\substack{n=\frac{m(g)}{fw(g/mol)}=\frac{10.0g}{159.61g/mol}\\ n=0.06265mol}}{3CuSO_4(s)} + \underset{\substack{n=MV=(0.100mol/l)(0.5000l\\ n=0.0500mol}}{Na_3PO_4(aq)} \rightarrow Cu_3(PO_4))2(s) + 3Na_2SO_4(aq) \tag{4.6.9}$$

$$\frac{molSO_4^{-2}}{V_{total}} = \frac{0.06265molCuSO_4\left(\frac{1molSO_4^{-2}}{molCuSO_4}\right)}{0.500l} = 0.125M \tag{4.6.10}$$

$$\frac{molNa^{+}}{V_{total}} = \frac{0.0500molNa_3PO_4\left(\frac{3molNa^{+}}{molNa_3PO_4}\right)}{0.500l} = 0.300M \tag{4.6.11}$$



Video 4.6.5: 2'44" YouTube calculating the spectator ion concentration when 10 g of copper(II) sulfate is dissolved into 500.0 mL of 0.100 M sodium phosphate.

Exercises

Exercise 4.6.4

Consider the reaction of sodium phosphate and barium chloride, where 25.00 ml of 0.8000M Na_3PO_4 is mixed with 25.00ml of 0.1000M $BaCl_2$ (and the final volume is 50.00 ml, that is there is no change in volume upon mixing).

a. What is the limiting reagent?
b. What is the identity and mass of precipitate formed?
c. What is the concentration of the sodium spectator ion?
d. What is the concentration of the excess phosphate?

Answer a

$BaCl_2$



Answer b

$0.5016 g Ba_3(PO_4)_2$

$$0.002500 mol BaCl_2 \left(\frac{1 mol Ba_3(PO_4)_3)}{3 mol BaCl_2}\right)\left(\frac{601.93 g Ba_3(PO_4)_2)}{mol}\right) = 0.5016 g Ba_3(PO_4)_2$$

Answer c

0.1200M

$M_f V_f = M_i V_i$

$M_F = \frac{M_i V_i}{V_f}$

$$\frac{0.8000 mol/L\ Na_3PO_4\left(\frac{3 mol Na^+}{mol Na_3PO_4}\right)0.02500 L\ Na_3PO_4}{0.02500 L + 0.02500 L} = 1.200 M Na^+$$

Answer d

$$mol_{excess}\ PO_4^{-3} = mole_{initial} - mol_{consumed}$$

$$0.8000 mol Na_3PO_4/L\left(\frac{1 mol PO_4^{-3}}{mol Na_3PO_4}\right)0.02500 L - \left(0.100 mol/L\ BaCl_2\left(\frac{1 mol Ba^{+2}}{mol BaCl_2}\right)0.02500 L\left(\frac{2 mol PO_4^{-3}}{3 mol Ba^{+2}}\right)\right) = 0.01833 mol PO_4^{-3}$$

$$Concentration = \frac{mol_{excess}\ PO_4^{-3}}{V_T} = \frac{0.01833 mol PO_4^{-3}}{0.02500 L + 0.02500 L} = 0.3667 M\ PO_4^{-3}$$

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

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- anonymous

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4.7: Chemical Equations and Quantitative Analysis

Learning Objectives

- Differentiate between quantitative and qualitative analysis
- Determine the amount of unknown solute in a solution using the gravimetric analysis technique
- Determine the empirical formula of a hydrocarbon or an organic compound using the combustion analysis technique

Quantitative Analysis is a branch of analytical chemistry where you determine the "quantity" of an unknown, which is often contrasted to qualitative analysis, which seeks to identify the identity of unknown. There are many types of quantitative techniques that are based on stoichometry, and many of these deal with solutions, and will be covered in the next several sections of this Chapter

Gravimetric Analysis:

The identification of the quantity of an unknown solute in a solution by making it the limiting reagent of precipitation reaction, weighing the mass of the resulting precipitate and then using the stoichiometry of the precipitation reaction to determine the moles of the unknown. This technique takes advantage of the solubility rules, and the strategy is to use a double displacement reaction where where one of the products is soluble, while the other forms a precipitate

For example, if you wanted to identify the moles of soluble barium chloride in a solution, you could add excess sodium sulfate, the complete ionic equation would be

$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
(limiting) (excess)

By adding excess sodium sulfate, you can force all the barium to form a precipitate, which can be filtered, dried, and weighed. Once the mass is known, the moles barium sulfate can be calculated, and from that the moles (or mass) of the barium chloride can be determined. For this to work, the unknown must be the limiting reagent.

Gravimetric Analysis of Lead (II) Nitrate

Lead was found in the drinking water at Flint Michigan, and one way of removing it is through the double displacement reaction with phosphate, to create lead(II) phosphate, which is an insoluble salt. Interestingly, this forms a protective coating in the pipe that prevents further corrosion. In fact, the city of Flint had removed phosphate from the treatment process, as it also prevents corrosion of iron, and that is when the lead started to dissolve in the first place, as described in the Chemical and Engineering News article of the American Chemical Society.





Figure 4.7.1: Images from Flint Michigan in response to lead in the drinking water. Left image of Texas National Guard from U.S. Department of Defense, right image uploaded to Flickr by Edward Kimmel.

By applying the solubility rules from section 3.4.2.1 one can not only see how phosphate can remove disolved lead from the water, but even be used in the lab to determine the concentration of lead in an unknown sample.

Example 4.7.1: Analysis of Lead in Water Sample.

What is the molar concentration of Pb^{+2} in contaminated water if 14.06 grams of $Pb_3(PO_4)_2$(s) precipitates out of 1.00 liter of a lead(II)chloride solution

Solution

The unbalanced equation is:

$$Pb(NO_3)_2(aq) + Na_3PO_4(aq) \rightarrow Pb_3(PO_4)_2(s) + NaNO_3(aq) \tag{4.7.1}$$

The net ionic equation is

$$\underset{unknown}{3Pb^{+2}(aq)} + \underset{excess}{2PO_4^{-3}(aq)} \rightarrow \underset{m=14.06g}{Pb_3(PO_4)_2(s)} \tag{4.7.2}$$

The general strategy is:

1. From mass of lead(II)phosphate calculate moles of lead phosphate that precipitated out of 1 liter of contaminated water.
2. From formula of lead(II)phosphate calculate moles of phosphate ion
3. Use net ionic equation to calculate moles lead(II)
4. Divide into the volume of sample the lead precipitated out of (1.00l) to calculate lead(II) concentration

This is solved in video 4.7.1, and in one equation is:

$$\frac{14.06g Pb_3(PO_4)_2 \left(\frac{1\ mol\ Pb_3(PO_4)_2}{811.543\ g}\right)\left(\frac{3\ mol\ Pb^{+2}}{mol\ Pb_3(PO_4)_2}\right)}{1.00\ L} = 0.0519M\ Pb^{+2} \tag{4.7.3}$$



Video 4.7.1: 4'31" YouTube showing the calculation of lead (II) ion concentration in a sample of water if 14.06 g of lead(II)phosphate precipitate out of 1.00 L (https://youtu.be/XIEs8l2xfuk).

Exercise 4.7.1 Arsenic in Ground Water

You wish to detect the concentration of arsenate in ground water. You add silver nitrate to a 100 mL sample. The following table shows the concentration of silver arsenate as you add the silver nitrate to the arsenate

Total mL silver nitrate added to 100 mL of water	mass precipitate
0	0
1mL	0.154g

2mL	0.308g
3mL	0.370g
4mL	0.370g

From the above data it can be deduced that after 3 mL of silver nitrate was added, all the arsenate was removed from the water, and arsenate was the limiting reagent. What is the concentration of arsenate in the original sample?

Answer

The net ionic equation for the reaction is

$$3Ag^{+}(aq) + AsO_4^{-3}(aq) \rightarrow Ag_3AsO_4(s) \tag{4.7.4}$$

The arsenate concentration is the number of moles arsenate in 100 mL of water, expressed in liters.

$$\frac{0.350g Ag_3AsO_4 \left(\frac{mol Ag_3AsO_4}{462.52g}\right)\left(\frac{1\ mole\ AsO_4^{-3}}{1\ mol\ Ag_3AsO_4}\right)}{0.100L} = 0.00757M = 7.57mM \tag{4.7.5}$$

Lead in Consumer Products

In 1980 lead(II)acetate was listed as safe for use in cosmetics like hair color products has been used in products like Grecian Formula (Figure 4.7.2), and the FDA repealed is approval for use on October 30, 2018 for health concerns with the ban supposed to go into effect on December 3, 2018. The ban had a 30 day appeal period for anyone "adversely affected" by the ban and the manufacturer, Combe company requested a hearing claiming it was safe, and now the ban is on hold until this is resolved (see the Jan. 4, 2019 Environmental Defense Fund and Jan. 9, 2019 Consumer Report).

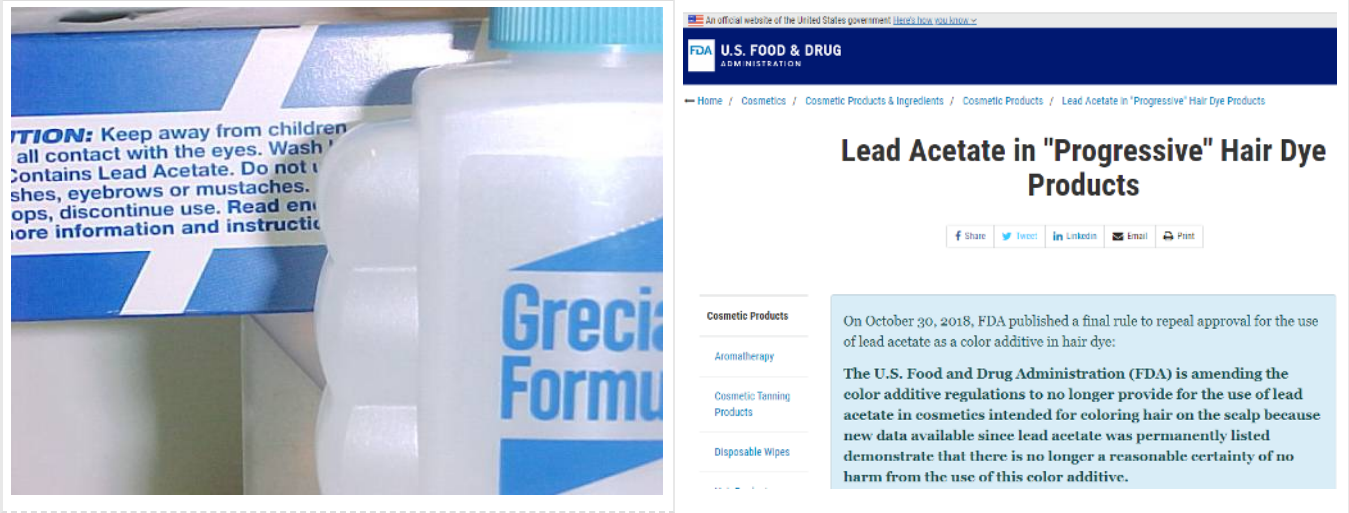


Figure 4.7.2 Image credit Bob Belford (left) and right the US FDA announcement repealing the approval of lead(II)acetate in hair products, https://www.fda.gov/cosmetics/cosmetic-products/lead-acetate-progressive-hair-dye-products.

Virtual Exercise 4.7.1

Using Virtual Lab 4.7.1 to design and run an experiment to determine the lead acetate concentration of your unknown. Please watch http://www.chemcollective.org/chem/common/vlab_walkthrouh_html5.php for a quick guide on how to run the virtual lab. The answer for Unknown A is given below. You should look at the logic of exercise 4.7.1 Arsenic in Ground Water to help with coming up with a strategy to solve this problem. Students at UALR will be given one of the other 5 unknowns as a homework assignment.

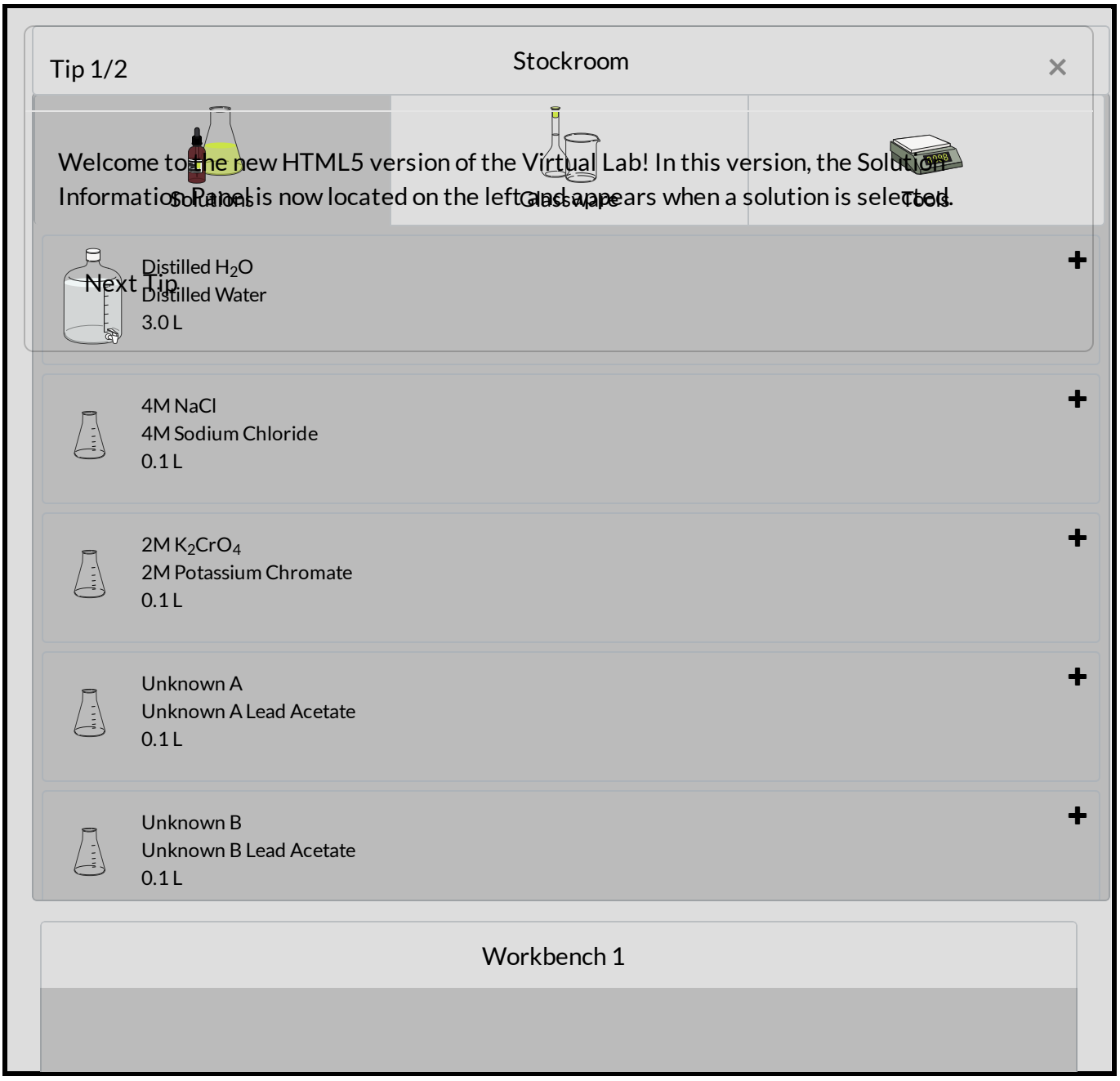
Answer

The reaction is:

$$Pb(C_2H_3O_2)_2(aq) + K_2CrO_4 \rightarrow PbCrO_4(s) + 2KC_3H_3O_2(aq) \tag{4.7.6}$$

Note we used the constant yield value of lead(II)chromate produced in excess potassium chromate for 100mL of unknown A

$$\frac{9.6966gPbCrO_4}{0.1000l}\left(\frac{1mol\ PbCrO_4}{323.2g}\right)\left(\frac{1mol\ Pb(C_2H_3O_2)_2}{1mol\ PbCrO_4}\right) = 0.3000M\ Pb(C_2H_3O_2)_2 \tag{4.7.7}$$



Virtual Lab 4.7.1: ChemCollective Virtual Lab developed by Dave Yaron of Carnegie Mellon University, (http://www.chemcollective.org/). NOTE: if the lab loads as "Default Lab Setup" (with a bunch of acids, bases and indicators), refresh the page . You want it to load the "Gravimetric Analysis of Unknown Leas Solutions", which contains sodium chloride, potassium chromate and six unknowns.

Acid Base Titration

Titrations are a very important analytical technique where you identify the quantity of an unknown (analyte) by reacting it with a titrant of known concentration until they are in stoichiometric proportions, and then use the balanced equation to determine the amount of the unknown analyte. These types of techniques often use visual indicators to indicate when they are complete, of which the indicators may be the reactants and products themselves, or other chemicals that react with the reactants and products. For example, an indicator in an acid-base neutralization reaction will have a color change over a specific pH range, and you choose an indicator that changes color at the pH indicative of where the acid and base are in stoichiometric proportions.



Video 4.7.2: 4'11" YouTube by Royal Society of Chemistry on performing an acid base titration. In this video the indicator is pink in a basic solution, and acid is added until it just goes clear. By knowing the volumen and concentration of the acid added we know the moles acid, then from the stoichiometric equation we can calculate the moles base, and dividing that by the initial volume of the base we can determine the base's initial concentration. (https://youtu.be/RI14t0R1wMY)

There are other types of titration, but the principle is the same.

Example 4.7.2: Acid Base Titration

A chemist needs to know the concentration of a 50 gallon drum of sulfuric acid. So the chemist uses a 25 mL volumetric pipette to transfer 25.00 mL of the unknown acid to an Erlenmeyer Flask and adds 2 drops of an indicator that changes color when the acid is neutralized. T his solution is then titrated with 0.100M sodium hydroxide and it takes 30.00 mL to neutralize the 25.00 mL of sulfuric acid. How concentrated is the sulfuric acid in the barrel?

Solution

Step 1: Write down the balanced equation and under each entity write what is given in the problem statement.

$$\underset{\substack{M=?\\V=25.00mL}}{H_2SO_4(aq)} + 2\underset{\substack{M=0.100M\\V=30.00mL}}{NaOH(aq)} \rightarrow Na_2SO_4(aq) + 2H_2O(l) \tag{4.7.8}$$

Step 2: Calculate moles acid neutralized by adding 30.00mL of 0.100M NaOH.

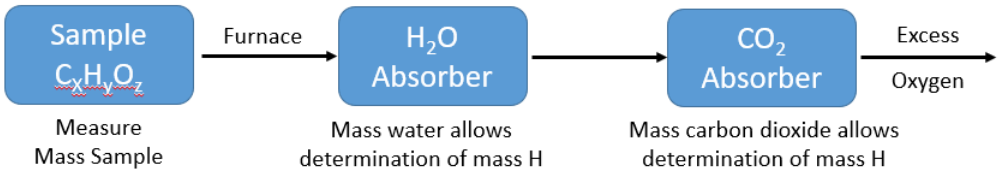
$$0.03000L NaOH \left(\frac{0.100 mol NaOH}{L}\right)\left(\frac{1\ mol\ H_2SO_4}{2\ mol\ NaOH}\right) = 0.0015\ mol\ H_2SO_4 \tag{4.7.9}$$

Step 3: Divide by the volume of acid titrated, and this gives the concentration of the acid in the 50 gallon drum

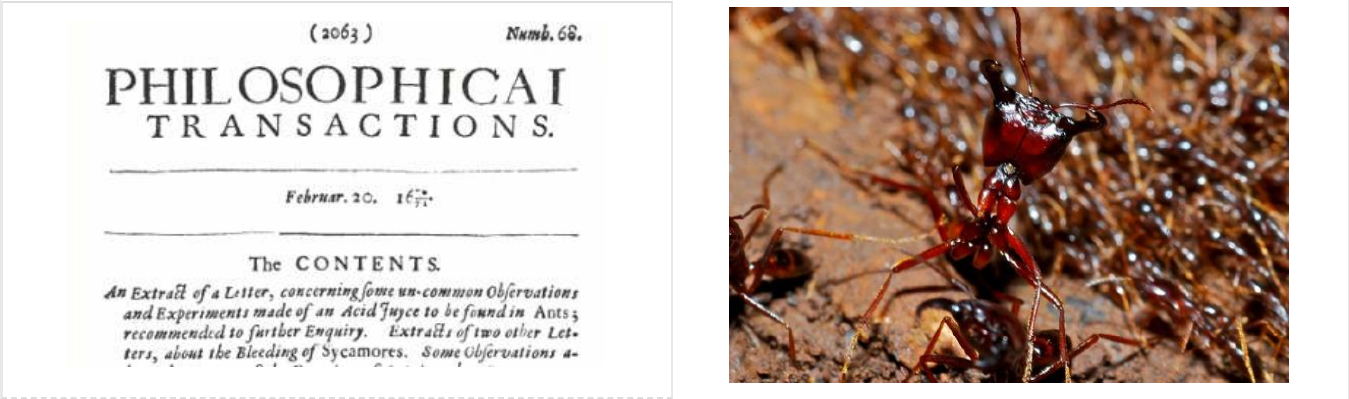
$$\frac{0.00150\ mol}{0.02500\ L} = 0.0600M = 60.0mM \tag{4.7.10}$$

Combustion Analysis

This is a type of qualitative analysis that can be used to determine the empirical formula of an unknown organic compound consisting of carbon, hydrogen and oxygen. In combustion analysis a sample of known mass is burned in excess oxygen. It is then passed through H_2O and CO_2 absorbers that collect the hydrogen and carbon that where in the original sample. As we know the mass percent of hydrogen in water (2.01/18.01 or 11.2%) and the mass percent of carbon in carbon dioxide (12.01/44.01 or 27.3%) we can identify their masses from the water and carbon dioxide produced. Once those masses are known, the mass of the oxygen can be determined by substracting them from the original sample mass, and this becomes an empirical formula problem like the ones is Chapter 2.



4.7.2: Schema for obtaining mass analysis data from combustion analysis to determine an empirical formula


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The CONTENTS.

An Extract of a Letter, concerning some un-common Observations and Experiments made of an Acid Juyce to be found in Ants; *recommended to further Enquiry. Extracts of two other Letters, about the Bleeding of* Sycamores. *Some Observations a-*

Figure 4.7.4: In 1670 John Wray published in the Philosophical Transactions of the Royal Society of London his observations and experiments dealing with the "Juyce to be Found in Ants" .doi:10.1098/rstl.1670.0052. Right, army ants in Uganda, image credit Bernard Dupont, Flickr

Example 4.7.3 Combustion Analysis of Acidum Formicum, Formic Acid

Formic acid, obtained through the distillation of Formica rufa (ants). What is the empirical formula of formic acid if 2.4527 g sample yielded 0.9696g water and 2.3482g carbon dioxide.?

Solution

Step 1: Calculate mass hydrogen in water

$$M_H = m_{H_2O}\,(\text{fraction of hydrogen in water}) \tag{4.7.11}$$

$$M_H = 0.9696g\ H_2O\left(\frac{2.016g\ H}{18.016g\ H_2O}\right) = 0.1067g\ H$$

Step 2: Calculate mass carbon in carbon dioxide

$$M_C = m_{CO_2}\,(\text{fraction of carbon in water}) \tag{4.7.12}$$

$$M_H = 2.3482g\ CO_2\left(\frac{12.011g\ C}{44.011g\ CO_2}\right) = 0.6404g\ C$$

Step 3: Calculate mass oxygen by subtracting mass hydrogen and carbon from mass of the sample

$$m_{oxygen} = m_{sample} - m_{hydrogen} - m_{carbon} \tag{4.7.13}$$

$$m_{oxygen} = 2.4527g - 0.1067g - 0.6404g = 1.7056g$$

Now this is an empirical formula problem and is solved in video 4.7.3, giving an empirical formula of CH_2O_2. Please see section 2.11 if you need to review empirical formula problems.



Video 4.7.3: 4'01" YouTube solving example 4.7.3, (https://youtu.be/QxugidpNaEA)

Exercise 4.7.3

Formaldehyde is composed of carbon, hydrogen and oxygen. If a 8.7355g sample undergoes combustion analysis and forms 12.806g of carbon dioxide and 5.2385g water, what is its empirical formula?

Answer

CH_2O

Test Yourself

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

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4.8: Spectrophotometry

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http://chemwiki.ucdavis.edu/Core/Physical_Chemistry/Kinetics/Reaction_Rates/Experimental_Determination_of_Kinetcs/Spectrophotometry

Spectrophotometry is a method to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through sample solution. The basic principle is that each compound absorbs or transmits light over a certain range of wavelength. This measurement can also be used to measure the amount of a known chemical substance. Spectrophotometry is one of the most useful methods of quantitative analysis in various fields such as chemistry, physics, biochemistry, material and chemical engineering and clinical applications.

Introduction

Every chemical compound absorbs, transmits, or reflects light (electromagnetic radiation) over a certain range of wavelength. Spectrophotometry is a measurement of how much a chemical substance absorbs or transmits. Spectrophotometry is widely used for quantitative analysis in various areas (e.g., chemistry, physics, biology, biochemistry, material and chemical engineering, clinical applications, industrial applications, etc). Any application that deals with chemical substances or materials can use this technique. In biochemistry, for example, it is used to determine enzyme-catalyzed reactions. In clinical applications, it is used to examine blood or tissues for clinical diagnosis. There are also several variations of the spectrophotometry such as atomic absorption spectrophotometry and atomic emission spectrophotometry.

A spectrophotometer is an instrument that measures the amount of photons (the intensity of light) absorbed after it passes through sample solution. With the spectrophotometer, the amount of a known chemical substance (concentrations) can also be determined by measuring the intensity of light detected. Depending on the range of wavelength of light source, it can be classified into two different types:

- **UV-visible spectrophotometer**: uses light over the ultraviolet range (185 - 400 nm) and visible range (400 - 700 nm) of electromagnetic radiation spectrum.
- **IR spectrophotometer**: uses light over the infrared range (700 - 15000 nm) of electromagnetic radiation spectrum.

In visible spectrophotometry, the absorption or the transmission of a certain substance can be determined by the observed color. For instance, a solution sample that absorbs light over all visible ranges (i.e., transmits none of visible wavelengths) appears black in theory. On the other hand, if all visible wavelengths are transmitted (i.e., absorbs nothing), the solution sample appears white. If a solution sample absorbs red light (~700 nm), it appears green because green is the complementary color of red. Visible spectrophotometers, in practice, use a prism to narrow down a certain range of wavelength (to filter out other wavelengths) so that the particular beam of light is passed through a solution sample.

Devices and mechanism

Figure 1 illustrates the basic structure of spectrophotometers. It consists of a light source, a collimator, a monochromator, a wavelength selector, a cuvette for sample solution, a photoelectric detector, and a digital display or a meter. Detailed mechanism is described below. Figure 2 shows a sample spectrophotometer (Model: Spectronic 20D).

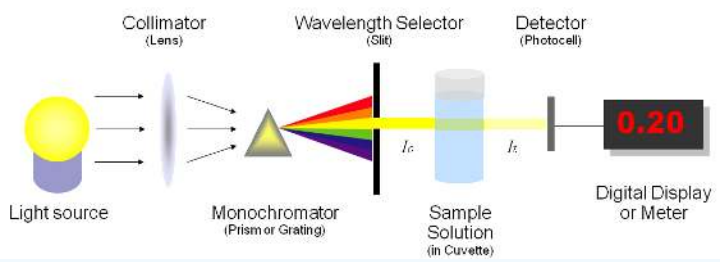


Figure 1: Basic structure of spectrophotometers (illustrated by Heesung Shim)

https://chem.libretexts.org/@go/page/52104

A spectrophotometer, in general, consists of two devices; a spectrometer and a photometer. A spectrometer is a device that produces, typically disperses and measures light. A photometer indicates the photoelectric detector that measures the intensity of light.

- **Spectrometer**: It produces a desired range of wavelength of light. First a collimator (lens) transmits a straight beam of light (photons) that passes through a monochromator (prism) to split it into several component wavelengths (spectrum). Then a wavelength selector (slit) transmits only the desired wavelengths, as shown in Figure 1.
- **Photometer**: After the desired range of wavelength of light passes through the solution of a sample in cuvette, the photometer detects the amount of photons that is absorbed and then sends a signal to a galvanometer or a digital display, as illustrated in Figure 1.



Figure 2: A single wavelenth spectrophotometer

You need a spectrometer to produce a variety of wavelengths because different compounds absorb best at different wavelengths. For example, p-nitrophenol (acid form) has the maximum absorbance at approximately 320 nm and p-nitrophenolate (basic form) absorb best at 400nm, as shown in Figure 3.

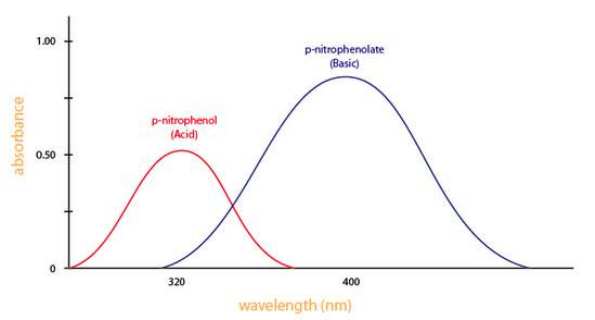


Figure 3: Absorbance of two different compounds

Looking at the graph that measures absorbance and wavelength, an isosbestic point can also be observed. An **isosbestic point** is the wavelength in which the absorbance of two or more species are the same. The appearance of an isosbestic point in a reaction demonstrates that an intermediate is NOT required to form a product from a reactant. Figure 4 shows an example of an isosbestic point.

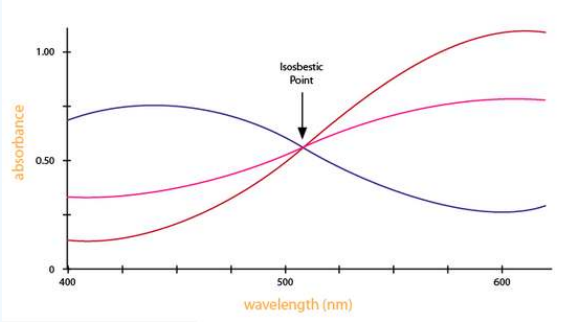


Figure 4: An example of isosbestic point

Referring back to Figure 1 (and Figure 5), the amount of photons that goes through the cuvette and into the detector is dependent on the length of the cuvette and the concentration of the sample. Once you know the intensity of light after it passes

through the cuvette, you can relate it to transmittance (T). Transmittance is the fraction of light that passes through the sample. This can be calculated using the equation:

$$Transmittance(T) = \frac{I_t}{I_o}$$

Where I_t is the light intensity after the beam of light passes through the cuvette and I_o is the light intensity before the beam of light passes through the cuvette. Transmittance is related to absorption by the expression:

$$Absorbance(A) = -log(T) = -log(\frac{I_t}{I_o})$$

Where absorbance stands for the amount of photons that is absorbed. With the amount of absorbance known from the above equation, you can determine the unknown concentration of the sample by using Beer-Lambert Law. Figure 5 illustrates transmittance of light through a sample. The length l is used for Beer-Lambert Law described below.

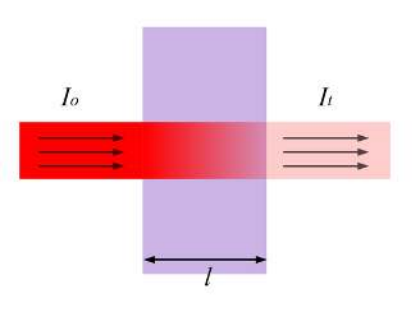


Figure 5: Transmittance (illustrated by Heesung Shim)

Beer-Lambert Law

Beer-Lambert Law (also known as Beer's Law) states that there is a linear relationship between the absorbance and the concentration of a sample. For this reason, Beer's Law can *only* be applied when there is a linear relationship. Beer's Law is written as:

$$A = \epsilon l c$$

where

- A is the measure of absorbance (no units),
- ϵ is the molar extinction coefficient or molar absorptivity (or absorption coefficient),
- l is the path length, and
- c is the concentration.

The molar extinction coefficient is given as a constant and varies for each molecule. Since absorbance does not carry any units, the units for ϵ must cancel out the units of length and concentration. As a result, ϵ has the units: $L \cdot mol^{-1} \cdot cm^{-1}$. The path length is measured in centimeters. Because a standard spectrometer uses a cuvette that is 1 cm in width, l is always assumed to equal 1 cm. Since absorption, ϵ, and path length are known, we can calculate the concentration c of the sample.

Example 1

Guanosine has a maximum absorbance of 275 nm. $\epsilon_{275} = 8400 M^{-1} cm^{-1}$ and the path length is 1 cm. Using a spectrophotometer, you find the that $A_{275} = 0.70$. What is the concentration of guanosine?

Solution

To solve this problem, you must use Beer's Law.

$$A = \epsilon l c \tag{4.8.1}$$

$$0.70 = (8400\ M^{-1}\ cm^{-1})(1\ cm)(c)$$

Next, divide both side by $[(8400\ M^{-1}\ cm^{-1})(1\ cm)]$

$$c = 8.33 \times 10^{-5}\ mol/L$$

Example 2

There is a substance in a solution (4 g/liter). The length of cuvette is 2 cm and only 50% of the certain light beam is transmitted. What is the absorption coefficient?

Solution

Using Beer-Lambert Law, we can compute the absorption coefficient. Thus,

$$-\log\left(\frac{I_t}{I_o}\right) = -\log(\frac{0.5}{1.0}) = A = 8\epsilon$$

Then we obtain that

$$\epsilon = 0.0376$$

Example 3

In example 2 above, how much is the beam of light is transmitted when 8 g/liter ?

Solution

Since we know ϵ, we can calculate the transmission using Beer-Lambert Law. Thus,

$$log(1) - log(I_t) = 0 - log(I_t) \quad = 0.0376 \text{ x } 8 \text{ x } 2 = 0.6016$$

$$log(I_t) = -0.6016$$

Therefore, I_t = 0.2503 = 25%

Example 4

In example 2 above, what is the molar absorption coefficient if the molecular weight is 100?

Solution

It can simply obtained by multiplying the absorption coefficient by the molecular weight. Thus,

$$\epsilon = 0.0376 \text{ x } 100 = 3.76 \text{ L·mol}^{-1}\text{·cm}^{-1}$$

Example 5

The absorption coefficient of a glycogen-iodine complex is 0.20 at light of 450 nm. What is the concentration when the transmission is 40 % in a cuvette of 2 cm?

Solution

It can also be solved using Beer-Lambert Law. Therefore,

$$-\log(I_t) = -\log(0.4) = 0.20 \times c \times 2 \tag{4.8.2}$$

Then c = 0.9948

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Contributors and Attributions

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CHAPTER OVERVIEW

5: Energy and Chemical Reactions

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5.1: Energy
5.2: Heat Capacity
5.3: Energy and Phase Transitions
5.4: First Law of Thermodynamics
5.5: Enthalpy Changes of Chemical Reactions
5.6: Calorimetry
5.7: Enthalpy Calculations

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5.1: Energy

Learning Objectives

- Define energy and work
- Define basic terms of thermodynamics like system and surroundings
- Describe the nature of energy transfers
- Compare and contrast exothermic and endothermic processes sign conventions associated with these process.

Introduction

In this Chapter we will introduce thermodynamics, the science of energy and its transformations. Energy can be considered to be the capacity to do work or transfer heat.

Definition: Energy

Energy is the capacity to do work (w) or transfer heat (q)

In Chapter 1 we introduced the concepts of kinetic and potential energy, and we will now take a deeper look at these. From a macroscopic perspective we sense objects as hot or cold as represented by the temperature, and recognize that heat will flow from hot to cold, but often mistake this to mean temperature is energy, which it is not. **Thermal energy** can be related to the random motion of molecules as they vibrate, rotate and translate in space.

Molecular Kinetic Energy

Translational Kinetic Energy

$E_k = \frac{1}{2}mv^2$, is the energy associated with the movement of a chemical entity's center of mass, where m is the mass of the chemical entity (molecule, atom or ion) and v is the velocity of its center of mass. In the fluid phases (gas and liquids) there will be a distribution of translational energies as different molecules randomly move around each other.

Vibrational Kinetic Energy

$E_k = \frac{1}{2}kx^2$, is the energy associated with atom's vibrational motion, which can be modeled as a oscillating spring with k being Hooke's law constant and x is the displacement from the equilibrium location. That is, even the atoms in a solid, be it a covalent bond or ionic bond (crystal lattice) are not static, and they vibrate back and forth around equilibrium positions like in a spring, with the the average distance being the "bond distance". Note, atoms oscillate because there are attractive and repulsive forces acting on them which change as their location changes. For example, in the diatomic hydrogen bond, the nuclei are accelerated towards each other if the attractive forces are greater than the repulsive, but as they get closer and closer, the nuclear/nuclear repulsion becomes stronger, and they start to be repulsed. As they move farther and farther apart, these forces become weaker, and the attractive forces once again begin to dominate, causing them to approach each other, with the resulting motion like the oscillation of a spring. Hooke's law equation actually describes the potential energy of the oscillator, when the distance is a maximum from the equilibrium, but as energy is conserved, this is equal to the kinetic energy that atoms feel in the midpoint of the oscillation. The hotter a substance the faster the vibrational frequency.



video 5.1.1. (4:38 min YouTube) from Open University. This is the first of 4 videos explaining how microwave ovens heat water. From 1:30 minutes to 3:40 minute an air puck attached to springs exemplifies oscillatory motion. In reality molecules are vibrating, rotating and translating.

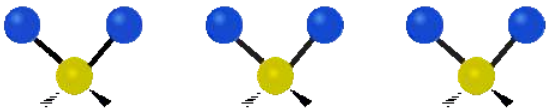


Figure 5.1.1: Three fundamental vibrational modes for water, images from Wikipedia article on Electromagnetic absorption by water.

Rotational Kinetic Energy

$E_\omega = \frac{1}{2} I\omega^2$, is the energy of a chemical entity associated with rotation, where ω is the rotational frequency (how fast the molecule spins) and I is the moment of inertia (in a sense, its resistance to spinning, the farther apart the hydrogen the greater I, the closer together, the smaller I. There can be multiple axis of rotation.

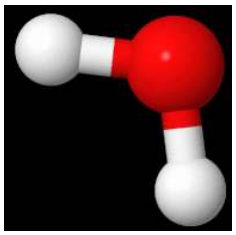


Figure 5.1.2: Water molecule spinning along axis that bisects H-O-H angle. (CC BY-SA 4.0 Internation; Darekk2 via Wikipedia)



Video 5.1.2 (0:17 min YouTube) showing a Figure skater reducing her moment of inertia by bringing her limbs close to her body with a resulting increase in rotational frequency to 308 RPMs. Not as she brings her arms and legs out she increases her moment of inertia, slowing down.

Molecular Potential Energy

Coulombic Energy is the energy between charged particles. There are both repulsive forces (between like charged particles) and attractive forces (between opposite charged particles).

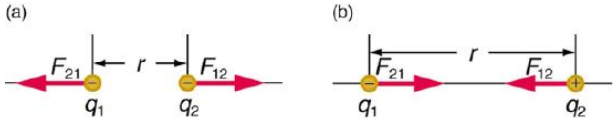


Figure 5.1.3 image showing repulsion of like charges and attraction of opposite

Atomic Coulombic Energy

The coulombic energy of attraction of the electron to the nucleus of an atom. These are weakest for outer shell electrons and strongest for core electrons.

Bond Coulombic Energies

The energies of covalent and ionic bonds. In the case of ionic compounds they are the attractive and repulsive interactions of the various cations and anions. For covalent, they are the +/- attractions of electrons to nuclei of different atoms, but there are also repulsive interactions of the -/- electrons and +/+ nuclei. The equilibrium distance is considered as the potential energy of the bond. As bonds are broken and formed during a chemical reaction energy the potential energy may be released or absorbed from the surroundings which either gain or lose kinetic energy.

Nuclear Energy

There are "strong" and "weak" forces holding the nucleus together and these will not be covered in this class.

Exercise 5.1.1

Identify the type of energy described by each of the following statements as potential or kinetic

a. Vibrational motion of atoms in a bond that are stimulated by infrared radiation
b. Energy of an electron in an atomic orbit
c. Energy of a covalent bond
d. Rotation of a molecule induced by microwave radiation

Answer a

Kinetic

Answer b

Potential

Answer c

Potential

Answer d

Kinetic

Units of Energy

Work based definition of energy

This is the SI unit of energy and one Joule is a Newton meter (J = N·m), where a Newton is the SI unit of force. The Newton (named after Isaac Newton) comes from classical mechanics and Newton's second Law of motion, F = ma (mass times acceleration), and acceleration is the change in velocity per unit time, $a = \frac{\Delta v}{\Delta t}$ and velocity is the vectorial change in displacement per unit time, $v = \frac{\Delta x}{\Delta t}$, where x is the displacement in a specific direction. So like any derived SI unit, the Joule can be described in terms of the SI base units, $1J = 1kg\frac{m^2}{sec^2}$

Calorie

Heat based definition of energy

Historically, the calorie is the energy required to raise one gram of water one degree celsius (from 14.5°C to 15.5°C), but today the calorie is considered to be a depreciated unit, and according to NIST Special Publication 1038, "*The International System of Units (SI)-Conversion Factors of General Use*", the definition of the calorie is based on the Joule:

1cal ≡ 4.184 Joules

Note, the above is a defined number and should not be treated as if it has significant digits. Also, the calorie is actually a very small unit of measurement and it should be noted that the nutritional Calorie (written with a capital C) is really a kilocalorie.

Exercise 5.1.2

The NIH provides a table of Estimated Calorie Requirements (kilocalories) for gender and age groups that indicates an active 19-30 year old male should needs around 3,000. calories. How many joules is this? Use appropriate SI Prefix in your answer.

Answer

12.55MJ

What is Work?

Work has many forms, of which mechanical(translational) work can be described as the energy used to displace an object a distance d when opposed against a force, like that of gravity.

$$w = Fd \tag{5.1.1}$$

where

- w is the work
- F is the opposing force
- d is the distance the object was displaced.

Note, there are other types of work, like the expansion of a gas and electric work (the work done to move a charged particle in an electric field). In this class we will mostly be interested in PV work, which can be visualized as the work done through the translational motion of molecules moving in three dimensional space.

Work of Expansion: Pressure-Volume (PV) Work

To fully understand this we need to have covered gasses, but we can imagine molecules in a gas as having translational motion, which could do work against the surroundings. If we could imagine a frictionless piston in a cylinder there would be three possibilities where the pressure inside is either equal to, greater than or less than the pressure outside. If the pressure inside is greater, the gas inside will expand moving the piston and doing work on the surroundings. If the pressure outside is greater, the piston will move inward compressing the gas inside as work is done on the system.

$P_{ext} = P_{int}$ The system is at equilibrium, no work is done
$P_{ext} > P_{int}$ The system contracts and work is done on the system
$P_{ext} < P_{int}$ The system expands and work is done on the environment

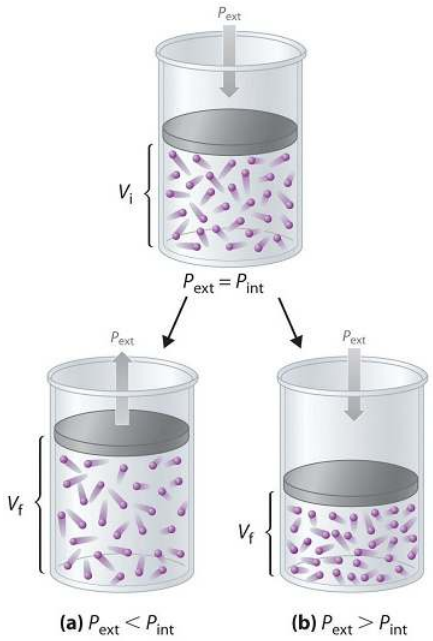


Figure 5.1.4 PV Work. Using a frictionless piston, if the external pressure is less than P_{int} (a), the gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. Alternatively, if the external pressure is greater than P_{int} (b), the gas will be compressed, and the surroundings will perform work on the system.

Pressure is defined as Force per unit area $P = \frac{F}{A}$, so F=PA, and if the external pressure in Figure 5.1.5 is greater than the internal pressure, work will be done on the system, causing it to contract by the volume AΔh, so ΔV = AΔh

$$w = Fd = P_{ext} A\Delta h \tag{5.1.2}$$

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is ΔV = AΔh, as shown in Figure 5.1.5. The work performed is thus

$$w = P_{ext} \Delta V \tag{5.1.3}$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)_{ext} (\Delta V) = \frac{\text{newton}}{\text{m}^2} \times \text{m}^3 = \text{newton} \cdot \text{m} = \text{joule} \tag{5.1.4}$$



Figure 5.1.5 Work Performed with a change in volume. The change in the volume (ΔV) of the cylinder housing a piston is ΔV = AΔh as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by w = P_{ext}ΔV.

Whether work is defined as having a positive sign or a negative sign is a matter of convention. In section 5.4 we will learn that positive work or heat is defined as when work or heat is added to the system, which in this case is the gas in the cylinder. So a contracting gas correlates to positive work (the system gains energy) and an expanding gas correlates to negative work, where the system does work on the surroundings. In the above case, the ΔV < 0, but it relates to a positive work flow with energy being added to the system. So based on this convention,

$$w = -P\Delta V \tag{5.1.5}$$

Exercise 5.1.3

A system containing oxygen gas is heated at a constant pressure of 40.0 atm so that its volume increases 177 L to 458 L. Express the amount of work that the system did in kilo-joules.

Answer

The formula for work from the expansion of a gas at constant pressure

$$w = -P_{ext}\,\Delta V$$

$$w = -40\ atm \times (458\ L - 177\ L) = -11240\ L\ atm$$

Convert from L atm to joules

$$-11240\ L\ atm \times 101.325\ \frac{J}{L\ atm} = -1138893\ J$$

Convert from J to kJ and round to get the final answer

$$-1138893\ J \times \frac{1\ kJ}{1000\ J} = -1140\ kJ$$

$$w = -1140\ kJ$$

Contributors and Attributions

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- Ronia Kattoum & Emily Choate (UALR)

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5.2: Heat Capacity

Learning Objectives

- Define heat capacity and specific heat capacity and differentiate between the two terms
- Deduce which substance will have greatest temperature changed based on specific heat capacities
- Calculate unknown variables based on known variables using the specific heat equation

Heat Capacitance

The heat capacity of a substance describes how its temperature changes as it absorbs or releases heat, it is the capacity of a substance to contain heat. This equation relates the heat absorbed (or lost) to the temperature change

$$\Delta q = q_{\text{transferred}} = q = C\Delta T \tag{5.2.1}$$

Please note this heat q is the amount of heat transferred to or from an object as its temperature is changed, and we call it q, not (\Delta q\). It is not the total heat energy of the object.

Rearranging the above Equation gives the definition of the heat capacitance of an object

$$C = \frac{q(J)}{\Delta T(K)} \tag{5.2.2}$$

This is an important equation because it relates the heat lost or gained by an object to its temperature change. A substance with a small heat capacitance cannot hold a lot of heat energy and so warms up quickly. We should note that the rate of heat transfer (how fast something heats up or cools down), is a function of the temperature difference. So as heat transfers from the hot object (which cools) to the cold object (which warms) the temperature difference reduces, and the rate of heat transfer slows down and finally stops when they reach the same temperature. The heat capacitance of a substance depends both on the material it is made of, and the mass of the substance.

Note: You can determine the above equation from the units of Capacity (energy/temperature). That is if a constant has units, the variables must fit together in an equation that results in the same units. So C equals something with energy in the numerator and temperature in the denominator. Now, you need to use some common sense here, as we are adding heat, not work, and adding heat changes the temperature, it does not make the temperature. So the right side is a ΔT, and not a T.

Exercise 5.2.1

The Heat Capacitance of a 10.0 g silver ring is 2.36J/^{o}C.

a. Convert this value to units of J/K.
b. Convert this value to units of cal/^{o}C.

Answer a

2.36J/K, these are the same value because the denominator is $DeltaT$ not T.

Answer b

0.564cal/^{o}C.

Specific Heat Capacitance

The specific heat capacitance is the heat capacitance per gram of a substance. This value depends on the nature of the chemical bonds in the substance, and its phase.

$$q = mc\Delta T \tag{5.2.3}$$

or

$$c = \frac{q(J)}{m(g)\Delta T(K)} \tag{5.2.4}$$

Note: Capital "C" is the **Heat Capacity** of an object, lower case "c" is the **specific heat capacity** of a substance. The heat capacity of an object made of a pure substance is:

$$C = mc \tag{5.2.5}$$

If the material of an object is made of uniform in composition you can use the specific heat capacity for that material to calculate the heat capacitance of the object. So doubling the mass of an object doubles its heat capacity, but does not change its specific heat capacitance.

Exercise 5.2.2

In exercise 5.2.1 we saw that a 10.0 g silver ring has a heat capacitance of 2.36J/ºC, what is the specific heat capacity of silver?

Answer

Assuming the ring is pure silver, the specific heat capacity of silver is 0.236J/g^{o}C.

Tip: Using Units of a Constant to the Identify equation

It should be noted that just as for heat capacity, the units of specific heat capacity must align with the units of the equation, and so you can calculate the equation from the units, as long as you realize J is a unit of energy (we are talking heat, not work), g is a unit of mass, and °C is a unit of temperature, although here, it stand for temperature change (ΔT). **Video 5.2.1 shows how we can use the units of a constant to determine the equation.**



Video 5.2.1: 5'32" YouTube on using constants to determine equations related to heat capacity and phase changes (https://youtu.be/mWj9pHQOyIc). **NOTE:** in this video the values of ΔH_v are for water, and so we use the molar mass of water to relate these. Some of these values are tabulated in table 5.3.1.

Is specific heat capacitance an extensive or intensive property?

The specific heat capacity is intensive, and does not depend on the quantity, but the heat capacity is extensive, so two grams of liquid water have twice the heat capacitance of 1 gram, but the specific heat capacity, the heat capacity per gram, is the same, 4.184 (J/g·K). So a table of specific heat capacitance based on the type of material can be used to allow us to calculate the heat capacitance of an object. **Note the heat capacity depends on the phase of the substance.**

Table 5.2.1: Specific Heat Capacities for common substances.

Substance	Symbol (state)	Specific Heat (J/g °C)	Substance	Symbol (state)	Specific Heat (J/g °C)

Substance	Symbol (state)	Specific Heat (J/g °C)		Substance	Symbol (state)	Specific Heat (J/g °C)
helium	He(g)	5.193		aluminum	Al(s)	0.897
water	$H_2O(l)$	4.184		carbon dioxide	$CO_2(g)$	0.853
ethanol	$C_2H_6O(l)$	2.376		Silicon	Si(s)	0.712
ice	$H_2O(s)$	2.093 (at −10 °C)		argon	Ar(g)	0.552
water vapor	$H_2O(g)$	1.864		iron	Fe(s)	0.449
nitrogen	$N_2(g)$	1.040		copper	Cu(s)	0.385
air	mixture	1.007		gold	Au(s)	0.129
oxygen	$O_2(g)$	0.918		lead	Pb(s)	0.128

Note: Metals have low heat capacities and thus undergo rapid temperature rises when heat is applied.

Exercise 5.2.3

If you add the same amount of heat to an equal mass of liquid water, solid gold, and solid iron, which would end up having the highest temperature?

Answer

Solid Gold. They all have the same mass and are exposed to the same amount of heat. So, the one with the lowest specific heat would have the highest temperature. It has the lowest resistance to temperature change when exposed to heat. If you ever reached into an oven to grab your food with a gold bracelet on, you may have experience the low specific heat capacity of gold. Metals have low heat capacities and thus undergo rapid temperature rises when heat is applied.

Example 5.2.1

What is the final temperature if 100.0 J is added to 10.0 g of aluminum at 25°C? $c)Al = 0.902\ J/(g.^o\ C)$. For extra help watch video 5.2.2, which solves this problem.

Solution

$$T_f = T_i + \frac{q}{mc} = 25^oC + \frac{100.0\ J}{10.0\ g(\frac{0.902\ J}{g\cdot^0C})} = 36.1^oC$$



Video 5.2.2: 1'18" YouTube solving example 5.2.2 (https://youtu.be/4hKfm4B-C6o).

Specific heat capacity can be used to identify an unknown substance

The specific heat capacity is a physical property of the material a substance is composed of and can be used to help identify the substance the way density can help identify an incompressible substance like a solid or liquid. It should be noted that two substances can have the same specific heat capacity just as two substances can have the same density, but for example, if the heat capacity of a clear liquid is not 1 cal/g^{o}C, the substance can not be pure water.

Example 5.2.2

You have an unknown metal that is either Al, Cu, Ag or Fe and want to identify it. Upon adding 51.26J to 10.0G of the metal its temperature is raised by 22°C

Solution

Calculate the specific heat capacity and relate to those on table Table 5.2.1. The metal is silver and this problem is solved in Video 5.2.3



Video 5.2.3: 1'12" YouTube using specific heat capacity calculations to help identify a metal (https://youtu.be/duAzx66-0TI)

Exercise 5.2.4

Can you use the specific heat capacity to tell the difference between lead and gold?

Answer

No, gold had a specific heat capacity of 0.129J/g^{o}C and lead of 0.128J/g^{o}C. The thousandths position is uncertain and so to three significant digits, you can not differentiate between these two samples (you report all certain and the first uncertain, so if you have a measurement of 0.128, you are not really sure of the 0.008 value.

Test Yourself

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:
- Ronia Kattoum & Emily Choate (UALR)

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5.3: Energy and Phase Transitions

Learning Objectives

- Define heat of fusion and heat of vaporization
- Relate heat of fusion and heat of vaporization to heat of freezing and heat of condensation
- Label various part of a heating curve
- Using a heating curve, calculate the heat input/output associated with phase changes and temperature changes using the proper equation(s)
- Using a heating curve, calculate the final temperature for a given quantity of heat input/out.

Energy and Phase Changes

When adding or removing heat from a system one of three things can occur:

1. Temperature Change within a phase (physical change)
2. Phase Change between two phases (physical change)
3. Adding heat can cause a chemical reaction (chemical change)

In this section we shall look at changes between two phases. In reality there are 4 states of matter, solid, liquid, gas and plasma, although in this class we will focus on the three common states, and their transitions.

Figure 5.3.1 shows the phase transitions between the various phases and not the enthalpy of the system is a measure of the heat energy at constant pressure and will be introduced in section 5.4.3 of this Chapter.

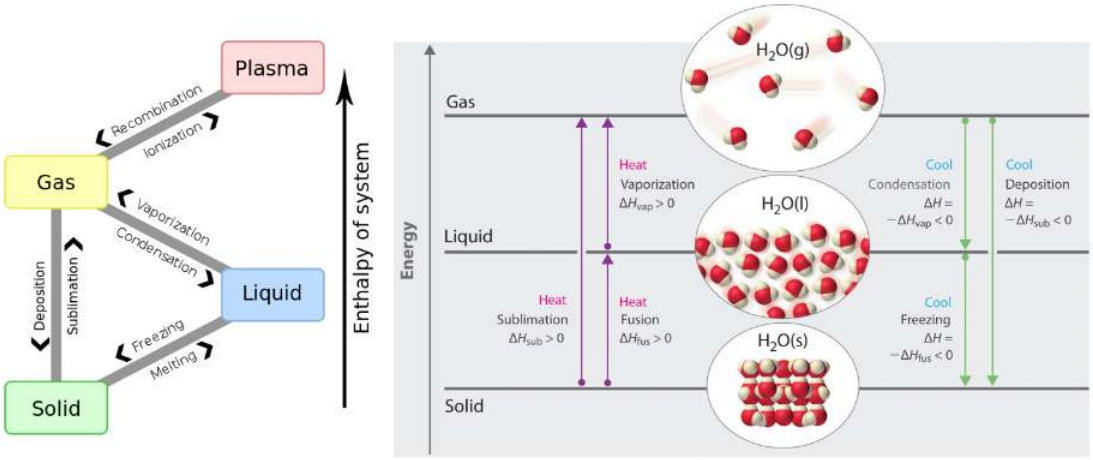


Figure 5.3.1: Energy diagrams showing phase transitions. The diagram on the left shows all 4 states, while the one on the right shows the three common states. This class will not be dealing with transitions to the plasma state, but you should be aware of it. There are several things to note on the right diagram.

1. Transitions going up (increased energy) are endothermic and require energy ,while those going down (decreased energy) are exothermic and release energy.
2. The energies absorbed in the endothermic steps are identical in magnitude to the energies released in the exothermic steps for the same transition.
   $\Delta H_{Fusion} = -\Delta H_{Freezing}$
   $\Delta H_{Vaporization} = -\Delta H_{Condensation}$
   $\Delta H_{Sublimation} = -\Delta H_{Deposition}$.
3. Energy is conserved
   $\Delta H_{Sublimation} = \Delta H_{Fusion} + \Delta H_{Vaporization}$
   $\Delta H_{Deposition} = \Delta H_{Condensation} + \Delta H_{Freezing}$

Note: Endothermic and Exothermic Reactions

We will formally introduce endothermic and exothermic reactions in the section 5.4 (the next section) when we discuss the First Law of Thermodynamics and define the direction of heat transfer (as being positive when something gains energy, and negative when something loses energy). So an exothermic process is one where energy is released to the environment and an

endothermic one is where energy is absorbed from the environment. We are introducing the concept early because all the process going in direction of increased energy (S->L ->G) are endothermic (you add energy to boil water), and those of decreasing energy (G -> L -> S) are exothermic

Exercise 5.3.1

Consider the process of water freezing.

a. Is it an endothermic or exothermic process?
b. Does it cool or warm the surroundings?

Answer a

Exothermic. It is easier for us to think about the opposite process of melting. It takes energy to melt ice, so heat is flowing into the system(the ice cube) and out of the surroundings (the air, let's say). So the surroundings (air) during the process of melting the ice. The opposite of melting ice is freezing water. So, you expect this process to be exothermic, releasing heat to the surroundings, and therefore, warming the surrounds.

Answer b

Warm

Sublimation

Students often have a hard time understanding sublimation. Carbon dioxide (dry ice) that you can buy at many grocery stores sublimes, that is, it goes directly from a solid to a gas without ever melting (which is why the call it "dry ice"). Video 5.3.2 demonstrates the sublimation and deposition of iodine.



Video 5.3.2: 1'39" YouTube uploaded by koen2all showing sublimation and deposition of iodine (https://youtu.be/jX9pskbKSw0).

Quantifying Phase Changes

We have seen how heat is either released or absorbed during phase changes. Now, we will study the quantity of energy associated with those phase changes. In order to carry out those calculations, we need to establish a standard bases for comparison, the **molar heat of the phase transition,** or the heat required for one mole of substance to change phase. Particularly, **molar heat of fusion,** refers to the amount of heat (in kJ) it take for one mole of substance to transition from the solid state to the liquid state (melt). The **molar heat of vaporization**, is the amount of heat (in kJ) it takes for one mole of a substance to transition from the liquid state to the vapor phase. Since we are not always working with exactly one mole of each substance, we will use this equation to Figure out the heat for the particular number of moles that we have according to the following equation:

$$\mathbf{q = n\Delta H_{transition}}$$

where n is the number of moles, and H is the heat or enthalpy required for one mole of a substance to go through the phase transition at the temperature where it occurs (which depends on the pressure). Unless otherwise noted, you can assume these are the boiling points and freezing point at 1 atm pressure. As you can see from Table 1, these values are usually given and tabulated.

Since, we typically deal with the mass of substance, there are some tables that also give you the heat of transition of a substance on a per gram bases (usually reported as J/g) Here is a link the following tables heat of fusion and heat of vaporization tables:

B2: Heats of Vaporization (Reference Table)

B3: Heats of Fusion (Reference Table)

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

Table 5.3.1: Enthalpies of Fusion (melting) and Vaporization for some common substances, and the transition temperature where they occur (at normal pressure of 1 atm).

Exercise 5.3.2

For a given substance, which is higher, $\Delta H_{Fusion} = \Delta H_{Vaporization}$ and why?

Answer

From table 5.3.1 it is clear that the enthalpy of vaporization is larger than fusion. This is because when you vaporize something you overcome all of the intermolecular forces and the material becomes a gas, filling up the entire container. It takes much more energy to vaporize a substance then to melt it.

Molar Heat of Freezing and Condensation

You may have wondered why table 5.3.1 only provides the molar heat of fusion and vaporization, and not the opposite processes of freezing and condensation. For example, if we wanted to quantify the amount of heat it takes to freeze a certain mass of N_2, what would be the molar heat of freezing? This is actually the negative of molar heat of melting or fusion, which is the heat energy required to melt one mole of a substance. So from the above diagram, it is - 0.71 kJ/mol. Note, this is a consequence of the First Law of Thermodynamics, the law of the conservation of energy, which we will discuss in detail in the next section. What it is stating is that the energy you must add to melt a mole of a substance is the same as the energy released when a mole freezes, because energy is conserved, but the energy flows in the opposite direction. Therefore, the above table not only gives you the enthalpies of fusion and vaporization, but also of freezing and condensation.

$$\Delta H_{Fusion} = - \Delta H_{freezing}$$

$$\Delta H_{vaporization} = -\Delta H_{condensation}$$

Molar Heat of Sublimation and Condensation

Table 5.3.1 also provides the heats of sublimation and condensation. Can you Figure them out?

$$\Delta H_{Sublimation} = \Delta H_{Fusion} + \Delta H_{Vaporization}$$
$$\Delta H_{Deposition} = - \Delta H_{Vaporization} - \Delta H_{Fusion}$$

Note: Quantifying Heat Transfer within a Phase

The heat being pumped into the system does not always go toward changing the phase of a substance. It may go into changing the temperature of a substance. For example, if you want to melt an ice cube that is at -10°C, you have to heat the ice to 0°C, before you can actually start the melting process. In order to quantity the amount of heat required to change the temperature (in the same phase, ice) from -10°C to 0°C, you can use the specific heat capacity equation that we covered in 5.2.

specific heat capacity, q = mCΔT (section 5.2) . Remember, the specific heat capacity (c), is different depending on which phase that the substance is in.

Heating Curves

A heating curve is a graph of the temperature of a substance as a function of the amount of heat added (moving to the right) or removed (moving to the left), as depicted in Figure 5.3.2. Note the flat regions represent phase changes, and the slope of the line in the rising regions is related to the capacitance of the sample being measured (it is actually the reciprocal, or 1/mc).

The concept of the heating curve is very important as it helps us Figure out what equation to use to quantify the heat associated with phase changes and temperature changes (watch the two videos below). At the beginning of this section, we stated that two of the three things that could happen when you add heat to a substance is that either it will undergo a phase change, or its temperature will rise. These are the two effects being described by the heating/cooling curve. The mathematical equations are:

q=mc ΔT (energy of a temperature change within a phase)
q=n $\Delta H_{transition}$ (energy of a phase transition)

It needs to be realized that if you add heat, you move to the right, and if you remove heat, you move to the left.

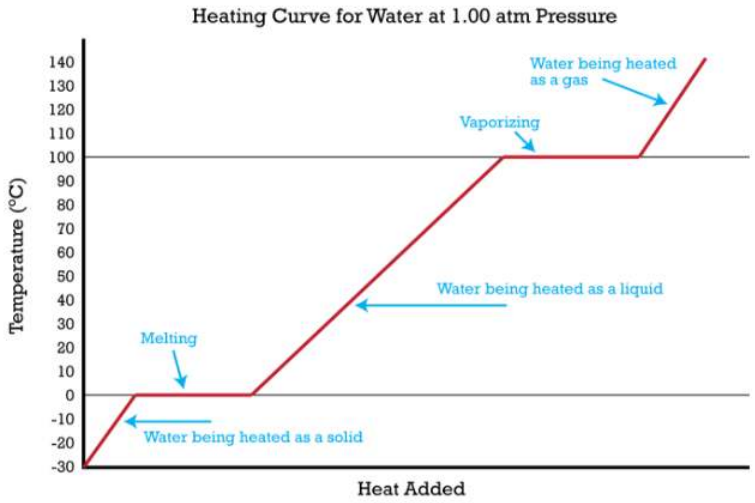


Figure 5.3.2: Cooling Curve for Water. Note, Increasing heat moves to the left, removing heat moves to the right.

What is wrong with the slopes of the lines in Figure 5.3.2?

For water c(liq) = 4.184(J/g-degC), c(ice) = 2.06(J/g-degC) and c(steam)=2.01(J/g-degC).

The slopes would be different, and the slopes of the ice and steam would roughly be twice as steep as the water. That is, it takes more energy to raise the temperature of liquid water by 1 deg than it does for either steam or ice.

What is wrong with the flat region of Figure 5.3.2?

They are roughly equal in length. In exercise 5.3.2 it was pointed out that $\Delta H_{Vaporization} >> \Delta H_{Fusion}$ and so the flat region for vaporizing should be much longer than the one for melting. As this is such an effect, a zig-zag is often drawn into the flat region to indicate that it is off the scale of the graph (see videos below).

Combined Temperate and Phase Change Problems

The following three examples deal with adding different amounts of energy to 100.0g of ice starting at -10.0°C.

Example 5.3.1 Calculation of Final Temperature

What is the final temperature when **1.6 kJ of heat** is added to 100.0 grams of ice at -10.0°C?

Solution

This problem requires you figuring out what phase the substance ends up in. Does 1.6kJ have enough enough energy to bring it to the freezing point? To melt it? To warm the liquid to its boiling point? To boil it? To raise the energy of a super heated steam?



Video 5.3.3: 5'35" YouTube showing the final temperature after adding 1.6kJ of heat to 100.0g ice at -10.0°C, (https://youtu.be/pjhZVhFjHGc).

Example 5.3.2 Calculation of Final Temperature

What is the final temperature when **25.00 kJ of heat** is added to 100.0 grams of ice at -10.0°C?

Solution

This problem requires you figuring out what phase the substance ends up in. Does 25.00kJ have enough enough energy to bring it to the freezing point? To melt it? To warm the liquid to its boiling point? To boil it? To raise the energy of a super heated steam?



Video 5.3.3: 3'08" YouTube showing the final temperature after adding 25.00kJ of heat to 100.0g ice at -10.0°C, (https://youtu.be/3cjSloZOsHQ).

Exercise 5.3.3

After all the ice has melted in the above problem, is there more ice, or liquid water?

Answer

Since it takes 33.24kJ to melt all the ice, and you have 22.94 left over after bring the supercooled ice to its freezing point, you have effectively applied the 22.94 kJ to the ice at zero degrees, and so the fraction melted is what you applied over what was required to melt it all. So 22.94/33.24 = 0.69, so it is 69% liquid water and 31% ice (69 grams of the 100 grams melted, and 31 are still frozen).

Example 5.3.3 Calculation of Final Temperature

What is the final temperature when **310.0 kJ of heat** is added to 100.0 grams of ice at -10.0°C?

Solution

This problem requires you figuring out what phase the substance ends up in. Does 310.0kJ have enough enough energy to bring it to the freezing point? To melt it? To warm the liquid to its boiling point? To boil it? To raise the energy of a super heated steam?

After adding 310 kJ you have enough energy to raise the super cooled water from -10.0^{o}C to its freezing point (2.06kJ), melt the ice (33.42kJ), heat the liquid water to its boiling point (41.84kJ) and boil all the water (225.37kJ) using a total of 303.7 kJ, with 7.3kJ left to raise the temperature of the super-heated steam to a final temperature of 136°C. Notice how the majority of the energy was used in the fourth step, the boiling of the the water (225.37kJ out of 310kJ, or 72.7% of the entire energy). This makes sense, as in going from a liquid to a gas you are overcoming all of the forces holding the water molecules together.



Video 5.3.3: 3'08" YouTube showing the final temperature after adding 310.0 kJ of heat to 100.0g ice at -10.0°C, (https://youtu.be/3cjSloZOsHQ).

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5.4: First Law of Thermodynamics

Learning Objectives

- Determine how heat and work are related to the overall internal energy of a system
- Calculate the work done by/on a system at constant pressure (PV work)
- Calculate changes in internal energy and enthalpy using the First Law of Thermodynamics
- Define a state function and determine which variables are state functions

Introduction

In the very first Chapter of this book we described three attributes of matter.

- Matter has Mass
- Matter has Volume
- Matter has Energy

Thermodynamics comes from the Greek words *therme* (heat) and *dynamis* (power) and deals with the third attribute of matter, energy. In section 5.1.2 we defined energy as the capacity to do work or transfer heat. The **first law of thermodynamics** states that energy can not be created or destroyed, that is, the energy of the universe is constant. This allows us to define a thermodynamic system, which in the case of chemistry is a reaction, with the surroundings being everything else.

So what do we mean the reaction is a thermodynamic system? Lets consider the combustion of hydrogen

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \tag{5.4.1}$$

During a chemical reaction the energy of the system changes as bonds in reactants are broken and the atoms rearrange to form the new bonds of the products. These new bonds are typically higher or lower in energy. If the products store more energy in their bonds, that energy must come from somewhere, and so it is transferred into the system from the surroundings. In the case of combustion, the products are lower in energy and so that energy is transferred to the surroundings. The key point here is as a reaction proceeds energy flows into or out of the system, depending on whether energy is absorbed or released as the products are formed. So what is positive energy flow?

Convention for Energy Flow

The convention thermodynamics use is that positive energy is when the system gains energy, which is when either heat is transferred to, or work is done on the system. This requires differentiating the system from the surroundings. In chemical thermodynamics, the system represents the internal energy of the atoms of the reactants as they become products.

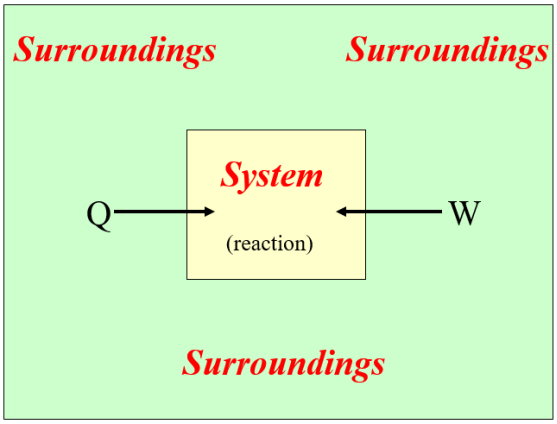


Figure 5.4.1: Diagram showing the convention for the flow of positive energy.

- Positive Energy Flow is when heat is added and/or work done to the system. (the system gains energy)
  - $\Delta E_{reaction} > 0$
- Negative Energy Flow is when the system releases work to the surroundings and/or does work on the surroundings. (the system looses energy).

- $\Delta E_{reaction} < 0$

From the perspective of a thermodynamic system we can view the universe to consist of the system and the surroundings

$$Universe = System + Surroundings \tag{5.4.2}$$

The first law states that the energy of the universe is a constant and so the change in the energy of the universe must equal zero.

$$\Delta E_{Universe} = 0 \tag{5.4.3}$$

Since the Universe is the system and the surrounding this means the change in energy of the system and surrounding must also equal zero

$$\Delta E_{Universe} = \Delta E_{System} + \Delta E_{Surrounding} = 0 \tag{5.4.4}$$

therefore,

$$\Delta E_{System} = -\Delta E_{Surrounding} \tag{5.4.5}$$

This is logical and means any energy lost by the system must be gained by the surroundings, and vice-versa, any energy gained by the system must be lost by the surroundings.

We define the energy of the system as the internal energy and give it the symbol U.

$$\Delta U = -\Delta E_{Surrounding} \tag{5.4.6}$$

Note: Direction of Heat Transfer

Students often confuse heat and temperature. If two objects are in thermal contact with each other and are different temperatures, heat will transfer from the higher temperature object to the one at the lower. So the temperature difference defines the direction of heat transfer, but not the energy of the ojbects. To understand this we need to look at the Second Law of Thermodynamics and another state function called entropy, which is covered in the second semester class.

Exercise 5.4.1

Does heat always flow from the object with more energy to the one with less?

Answer

No, it transfers from the one with the higher temperature to the one at a lower temperature. A lake at 30°C has more energy than a cup of water at 35°C, but if you add the water to the lake, it will cool as energy flows from the water to the lake.

Enthalpy

Enthalpy (H) comes from the Greek *enthalpein*, meaning (“to warm”). which is the measure of the heat of a system. From above we know the change in internal energy (U) of a system is equal to the heat and work done on the system.

$$\Delta U = Q + W \tag{5.4.7}$$

From section 5.1 we know the work of expansion is PV work, which for a system at constant pressure is

$$W = -P\Delta V \tag{5.4.8}$$

Enthalpy ΔH is defined as the heat transferred at constant pressure Q_p,

$$\Delta H = Q_p \tag{5.4.9}$$

substituting the definitions of work (Equation 5.4.8) and heat (Equation 5.4.9) into Equation 5.4.7 at constant P gives,

$$\Delta U = \Delta H - P\Delta V \tag{5.4.10}$$

rearranging to solve for enthalpy gives:

$$\Delta H = \Delta U + P\Delta V \tag{5.4.11}$$

a more general definition of enthalpy (which can be extended to conditions that are not at constant pressure is

$$H = U + PV \tag{5.4.12}$$

Note: relating enthalpy to work of expansion

In section 5.1.4 we introduced PV work as the work of expansion. That is, an expanding gas does work against the environment, and it takes work to compress a gas. According to the First Law, Positive work is when work is done on the system, which is that of compression, where Δ V is negative. so -PΔV is positive work, and equation 5.4.11 becomes

$$\Delta H = \Delta U - W \tag{5.4.13}$$

That is the enthalpy of a reaction is the heat transferred minus the work done on the system by a change in the volume of the system. That is, some of the energy change in going from reactants to products can be consumed by the system as it changes volumes, and this is most noticeable in gas phase systems.

Exercise 5.4.2

Calculate the Enthalpy change for a gas phase reaction at 1.2 atm if the change in internal energy is 47kJ and the volume increase by 1.1 L to 41.0 L. Note 1L-atm =101.325J

Answer

$$\Delta H = 47kJ + 1.2atm(41.0L - 1.1L)\left(\frac{101.325J}{L \cdot atm}\right) = 52kJ \tag{5.4.14}$$

We often call enthalpy the Heat of Reaction and tabulate tables of enthalpies of reaction, which can be used to tabulate the heat given off during a reaction.

State Functions

Enthalpy and Internal Energy are state functions. A state function is a function whose value is defined by the state, its pressure, temperature, composition, and amount of substance, and not the process of how it was obtained. So the difference between two state functions is path independent. Thus any solution of NaCl at 25°C and 1 atm that contains a mixture of 1 mol NaCl and 100 mol H_2O has the same internal energy and the same enthalpy as any other solution with the same specifications. It does not matter whether the solution was prepared by simply dissolving NaCl(*s*) in H_2O, by reacting NaOH(*aq*) with HCl(*aq*), or by some other method.

Is work a state function? No, as work is path dependent. If you look at Figure 5.4.2 you have a nice analogy for understanding the state function. The gravitational potential energy difference between an object at a height of the summit of Mt. Kilimanjaro and it's base is the same, no matter how you made it to the summit. The green and red path "X" and "Y" represent different paths, and the work required does depend on the path.

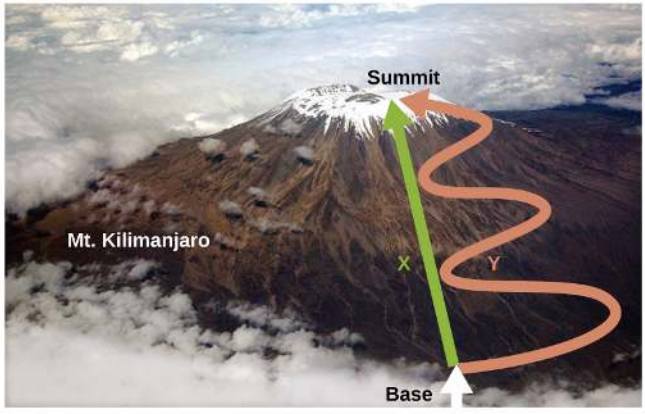


Figure 5.4.2: Diagram showing difference between path dependent function and a state function. The work required to reach the summit is not a state function, and depends on the path, but once you are on the top, the view is the same, no matter how you got there.

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5.5: Enthalpy Changes of Chemical Reactions

Learning Objectives

- Recognize that breaking bonds requires energy, and making new bonds releases energy
- Assess if the overall bond making and breaking process results in net energy input or output leading to overall exothermic or endothermic reactions
- Define standard reaction enthalpy and relate to stoichiometric coefficients in a a balanced chemical reaction
- Calculate the heat produced/consumed in chemical reaction based on amount of a reactants and products using standard reaction enthalpy and vice versa

Enthalpy of Reaction

When a reaction occurs, bonds in reactants break, the atoms rearrange and new bonds form as the products are created. If the bond energies of the formed bonds are different than the bond energies of the broken bonds, then the energy of the reactants is not equal to the energy of the products, and energy is either absorbed or released into the surroundings. There are a few things to note.

- Breaking bonds always requires energy, and so it is endothermic.
- Forming bonds is the opposite of breaking, and so it is exothermic.

Because enthalpy is a state function, we can energetically view a reaction as taking place in two steps (as illustrated in Figure 5.5.1. The first step is the endothermic step of breaking the reactant bonds and the second is the exothermic step of making the product bonds. The energy change of the reaction can be viewed as the sum of these two steps, and results in two possibilities,

1. The exothermic step (2) is greater than the endothermic step (1) and the reaction is exothermic.
2. The endothermic step (1) is greater than the exothermic step (2) and the reaction is endothermic.

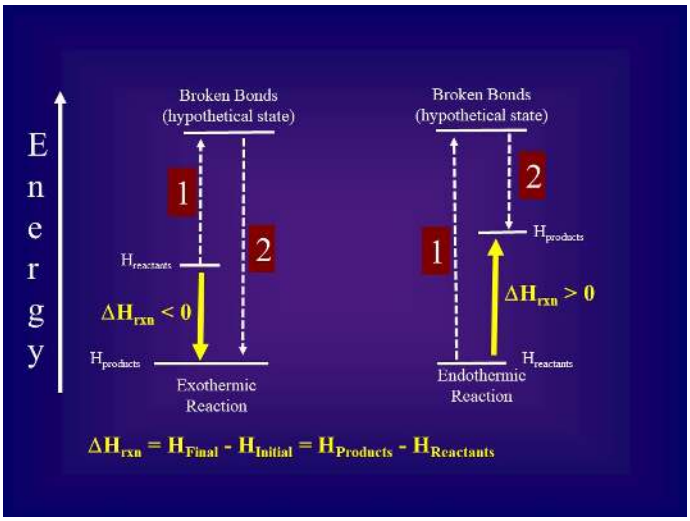


Figure 5.5.1: Energy cycle diagrams showing exothermic and endothermic reactions in terms of an initial endothermic step involving breaking reactant bonds, followed by an exothermic step involving making product bonds.

Note, we are interested in ΔH(reaction), which only depends on the initial (reactant) and final (product) state, because enthalpy is a state function this difference is path independent. What we do know is that the first step required energy and the second released energy. In Figure 5.5.2, we are only focusing on the energy difference between the initial and final states (yellow transition of Figure 5.5.1).

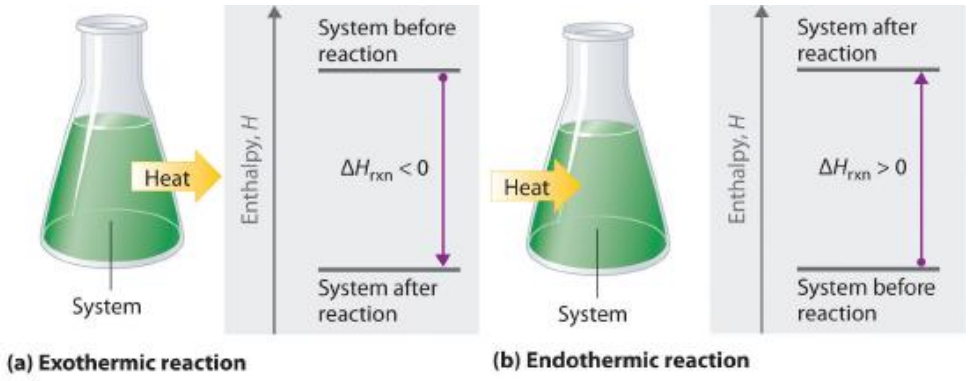


Figure 5.5.2: In this image we are only focusing on the reactant and product states, not the path. On the left side, the energy described the the enthalpy of reaction is released to the environment, and it warms the environment. On the right side, the system absorbs energy, cooling the environment.

Enthalpies of Reaction

In Chapter 3 (section 3.1) we learned about Lavoisier's "Law of Conservation of Matter", and from this we learned that chemical equation must be balanced. In the next Chapter 4, we applied stoichiometry to balanced equations and were able to predict reaction yields based on the complete consumption of the limiting reagent. In this section we are going to apply the First Law of Thermodynamics, the conservation of energy, to the balanced equation, and relate the energy of a chemical reaction to the stoichiometric coefficients of a reaction. The Enthalpy of Reaction is the energy evolved when the number of moles of each species is their coefficient, and this results in an equivalence statement that relates the stoichiometric number of each species to the enthalpy of reaction. The enthalpy of reaction is not written as per mole, but that information is implicit.

Enthalpy and Chemical Reactions

Endothermic Reactions: In endothermic reactions the heat is added to the system as reactants convert to products, and so the sign of ΔH is positive. Now the units of $\Delta H_{reaction}$ often confuse students, as there are actually implicit units of mole in the denominator, where it is based on the stoichiometric coefficient of the chemical you are interested in. The easiest way to look at this is as an equivalence statement, where the enthalpy of reaction is related to the coefficient of each species.

Reactants + Heat → Products, ΔH>0

Example:

$$4CO_2(g) + 2H_2O(l) \rightarrow 2C_2H_2(g) + 5O_2(g) \quad \Delta H_{reaction} = 2599kJ \tag{5.5.1}$$

The above equation is really saying 2599 kJ are being released for every 4 moles of CO_2, 2 moles H_2O, 2 moles C_2H_2 and 5 moles O_2.

This gives four equivalence statements

- 4 mole CO_2 = 2559kJ
- 2 mole H_2O = 2559kJ
- 2 mole C_2H_2 = 2559kJ
- 5 mole O_2 = 2559kJ

Example 5.5.1

Calculate the energy released when 88.0g C_2H_2 react with excess oxygen according to the above equation

Solution

Note: C_2H_2 is a product and in so the above equation needs to be written backwards, which changes the sign from endothermic (+) to exothermic (-).

$2C_2H_2(g)+5O_2(g) \rightarrow 4CO_2(g)+2H_2O(l)$ ($\Delta H_{reaction}$ = -2599 kJ)

$$88.0gC_2H_2\left(\frac{molC_2H_2}{26.0378g}\right)\left(\frac{-2559kJ}{2molC_2H_2}\right) = -4,324kJ \tag{5.5.2}$$

Exothermic reactions: In exothermic reactions heat is released from the system as reactants convert to products, and so the sign of ΔH is negative. Note, in example 5.5.1 1 we wrote the endothermic reaction of 5.5.1 backwards and it became exothermic. This is an important principle and a consequence of the First Law of Thermodynamics. That is, if a reaction is endothermic in one direction, it is exothermic in the other, and the amount of energy absorbed in the endothermic direction is equal to the amount released in the exothermic direction.

Reactants + Heat → Products + Heat, ΔH<0

Example:

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l) \quad \Delta H_{reaction} = -2599kJ \tag{5.5.3}$$

Looking at the energetics as a series of equivalence statements gives:

4 mole CO_2 = -2559kJ
2 mole H_2O = -2559kJ
2 mole C_2H_2 = -2559kJ
5 mole O_2 = -2559kJ

Exercise 5.5.1

According to Equation 5.5.3, how much heat is evolved if 88.0 g of oxygen reacts with excess C_2H_2?

Answer

$$88.0gO_2 \left(\frac{molO_2}{32.00g}\right)\left(\frac{-2559kJ}{5molO_2}\right) = -1,410kJ \tag{5.5.4}$$

Exercise 5.5.2

Consider the following reaction:

$$\mathrm{CO + 2\,H_2 \rightarrow CH_3OH + 128\,kJ}$$

a. Is the reaction endothermic or exothermic?
b. If 12.2 g of hydrogen gas are reacted _____kJ are _____(produced/consumed).
c. If 455 kJ of energy is produced, what was the mass of CO that was reacted?

Answer a

Exothermic. Since the heat is written on the right side of the equation, it can be thought of as heat produced or generated. So, it is an exothermic reaction. This reaction can also be written in this format, where the enthalpy is represented as having a negative value.

Answer b

387 kJ are produced:

Answer c

99.6 grams of CO reacted:

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:
- Ronia Kattoum (UALR)
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5.6: Calorimetry

Learning Objectives

- Apply the First Law of Thermodynamics to calorimetry
- Compare heat flow from hot to cold objects in an ideal calorimeter versus a real calorimeter
- Calculate heat, temperature change, and specific heat after thermal equilibrium is reached between two substances in a calorimeter
- Calculate the molar heat of enthalpy for a reactions using coffee cup calorimetry
- Compare and contrast coffee cup calorimetry and bomb calorimetry

Calorimetry

Calorimetery is an application of the First Law of Thermodynamics to heat transfer, and allows us to measure the enthalpies of reaction or the heat capacities of substances. From the first law we can state

$$\Delta E_{Universe} = \Delta E_{System} + \Delta E_{Surrounding} = 0 \tag{5.6.1}$$

therefore,

$$\Delta E_{System} = -\Delta E_{Surrounding} \tag{5.6.2}$$

A calorimeter is an instrument that has a thermally isolated compartment that is designed to prevent heat flow to the surroundings. Technically, this is called an adiabatic surface in that no heat flows in and out of the calorimeter, which is in contrast to isothermal, which means constant temperature. In truth, there is no such thing as a thermally isolated system, but we can design systems that approach it on the time scale of a measurement. We will consider two types of calorimeters, ideal calorimeters, where the calorimeter does not absorb heat itself, and real calorimeters, where the calorimeter absorbs heat. We will apply calorimetry to two different thermodynamic processes, that of transference of heat across objects at different temperatures, and that released or absorbed by a chemical reaction. We will look at two ways of measuring this heat, either the temperature change of the calorimeter, or the mass of a substance that undergoes a phase change within the calorimeter at a constant temperature.

If we consider the work in a calorimeter to be zero, and noting that Δ E = Δ Q + W, the above equation becomes

$$\Delta Q_{system} = -\Delta Q_{Surrounding} \tag{5.6.3}$$

If we can measure the heat absorbed or lost by the surroundings we can use the above equivalence statement to calculate the heat lost or absorbed the system, and this is the basis for calorimetry. Figure 5.6.1 shows the basic layout of an ideal calorimeter where the gray shaded box acts as a surface that prevent any heat entering or leaving the solution, and so the solution functions as the surroundings. In the first exothermic process heat is released by the system and the temperature rises, while in the second endothermic process heat is absorbed by the system and the temperature decreases.

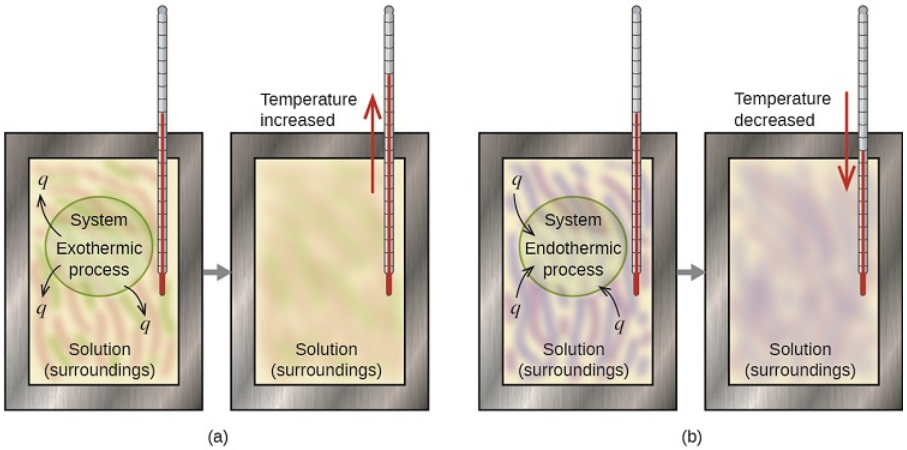


Figure 5.6.1: In part a, and exothermic process occurs and the calorimeter's temperature rises, while in part b an endothermic process occurs and the temperature falls.

Heat Transfer Between Hot and Cold Objects in an Ideal Calorimeter

When a hot object (T_H) is placed in thermal contact with a cold object (T_C) energy is transferred between the two, but the rate of heat transfer from the hot to the cold is greater, so it cools down while the cold object heats up, until they reach the same temperature (T_F). Once they are at the same temperature the system is at thermal equilibrium and the rate of transfer of energy from the hot to cold is the same as cold to hot. That is, energy is a vectoral flow, and even at the same temperature, there is a flow of energy across the boundary of two objects, but the flow is the same.

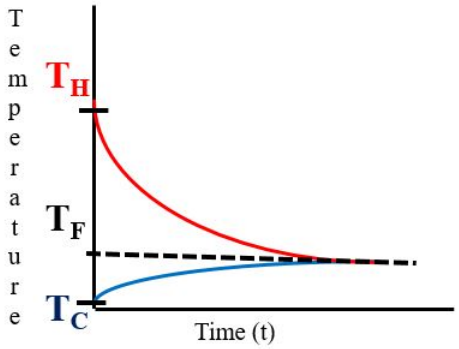


Figure 5.6.2: Graph showing temperature change as a function of time after a hot object is put in thermal contact with a cold object. Note, that in this case the capacity of the cold object to hold heat is greater, so the change in temperature of the cold object is less than the hot. Also note, $\Delta T = T_{Final} - T_{Initial}$ where $T_{Initial} = T_{Hot}$ for the hot object and $T_{Initial} = T_{Cold}$ for the cold object, so ΔT_{Hot} is a negative number (it cools, so $T_F < T_i$), while ΔT_{Cold} is a positive number (it heats, so $T_F > T_i$).

Starting with the first law for two isolated objects and considering no work, we have

$$q_{cold} + q_{hot} = 0 \tag{5.6.4}$$

so

$$q_{cold} = -q_{hot} = 0 \tag{5.6.5}$$

> The amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.

From section 5.2 we know that for a substance in a constant phase the heat relates to the temperature by equation 5.2.3 (q=mc\(\Delta|)T, which substituting into the above two equations give

$$m_C c_C \Delta T_C + m_H c_H \Delta T_H = 0 \tag{5.6.6}$$

or

$$m_C c_C \Delta T_C = -m_H c_H \Delta T_H \tag{5.6.7}$$

where

$$\Delta T_H = T_F - T_H \;\; and \;\; \Delta T_C = T_F - T_C \tag{5.6.8}$$

In an ideal calorimeter we consider the calorimeter to absorb no heat itself, so if we have material of a uniform composition, we can relate the heat transferred from the hot object to the cold object by eq. 5.6.7.

Example 5.6.1 Ideal calorimeter problem

What is T_F when 2.00g Au at 100.0°C is placed into 25.0 ml H_2O at 30.0°C? You can obtain the specific heat capacities for gold and water from table 5.2.1.

Solution

You are solving 5.6.7 for T_F.

$$T_F = \frac{m_H c_H T_H + m_c c_c T_c}{m_H c_H + m_c c_c} = 30.17^o C \tag{5.6.9}$$

The solution to this problem is worked out in video 5.6.1



Video 5.6.1: 7'05" YouTube solving example 5.6.1 (https://youtu.be/Htqzz9TAfrQ)

Heat Transfer Between Hot and Cold Objects in a Real Calorimeter

In a real calorimeter the calorimeter itself will absorb some of the heat, even if it transfers no heat to the surroundings. That is, the calorimeter itself has a heat capacitance. This usually needs to be measured for each calorimeter, and following the conventions of section 4.2, we use a capital C to represent the capacitance of an object, or the calorimeter constant. That is, the calorimeter constant is the calorimeter's heat capacitance.

Consider dropping a hot object into cold water that has been sitting in a calorimeter long enough to have the same temperature as the calorimeter.

From eq. 5.6 we know that $Q_{Cold} = -Q_{Hot}$,

But now there are two cold objects, the water and the calorimeter, so

$$Q_c = m_c c_c \Delta T_c + C_{cal} \Delta T_c \tag{5.6.10}$$

where C_{cal} is the heat capacitance of the calorimeter.

Exercise 5.6.1

Example 5.6.2 (below) is the same problem as Example 5.6.1 (above) but it is in a real calorimeter. Do you think T_F in a real calorimeter will be hotter or colder than in the ideal?

Answer

It will be colder because in example 5.6.1the 2 g Au was transferring its heat to 25 mL water, while in example 5.6.2it is transferring the heat to 25 mL of water AND the calorimeter itself.

is the same problem as Example 5.6.1 but it is in a real calorimeter. Before solving this or looking at the answer,

Example 5.6.2 Real calorimeter problem

What is T_F when 2.00g Au at 100.0°C is placed into 25.0 ml H_2O at 30.0°C? The calorimeter constant for the calorimeter is 36.0 J/°C and you can obtain the specific heat capacities for gold and water from table 5.2.1.

Solution

You are solving eq. 5.6.10 for T_F, but there are two entities absorbing the heat

$$Q_c + Q_H = 0 \tag{5.6.11}$$
$$(m_c c_c \Delta T_c + C_{cal} \Delta T_C) + m_H c_H \Delta T_H = 0$$

$$T_F = \frac{m_H c_H T_H + (m_c c_c + C_{cal}) T_c}{m_H c_H + C_{cal} + m_c c_c} = 30.12^o C \tag{5.6.12}$$

The solution to this problem is worked out in video 5.6.2 below.



Video 5.6.2: 7'16 YouTube calculating the final temperature for the problem in example 5.6.1 in a real calorimeter with a calorimeter constant of 36.0°C. (Video corrigendum: the calorimeter constant term was not shown in the numerator of the video but was taken into consideration when calculating the final answer, as is shown in eq 5.6.12)

Exercise 5.6.2

Calculate the calorimeter constant if **150.0 g** of lead at **100.0°C** were placed in a calorimeter with **50.0 g** of water at **22.0°C** and the resulting temperature of the mixture was **26.2°C**, you can obtain the specific heat capacities for lead and water from table 5.2.1.

Answer

As in example 5.6.2 we start with the first law (for a system that does no work).

$$Q_c + Q_H = 0 \tag{5.6.13}$$
$$(m_c c_c \Delta T_c + C_{cal} \Delta T_C) + m_H c_H \Delta T_H = 0$$

solve for C_{cal}.

$$c_{cal} = \frac{m_c c_c \Delta T_c + m_H c_H \Delta T_H}{\Delta T_c} \tag{5.6.14}$$
$$= \frac{50.0g \left(4.184 \frac{J}{g^o C}\right) (4.2^o C) + 150.0g \left(0.128 \frac{J}{g^o C}\right) (-73.8^o C)}{4.2^o C} = 550J$$

Calorimetry and Enthalpies of Reaction

Calorimeters can also measure the molar enthalpy of reaction, by simply equating the heat absorbed/lost by the calorimeter to the heat lost/absorbed by the reaction. That is, the system is the reaction. To come up with the heat of reaction, you need to know what the limiting reagent is, and calculate it from that.

Starting with the first law and considering there to be no work

$$Q_{system} = -Q_{surrounding} \tag{5.6.15}$$
which becomes
$$Q_{reaction} = -Q_{calorimeter}$$

- $Q_{calorimeter}$ represents the calorimeter and everything in it. That is, all the heat exchanged with the reaction is absorbed or released by the calorimeter and its contents.
- $Q_{reaction}$ is the enthalpy of reaction (ΔH_r) for a system at constant pressure. If we know the moles of the limiting reagent, we can divide by that and come up with the molar enthalpy of reaction

The following example shows how to calculate the molar enthalpy of reaction for the reaction between sulfuric acid and sodium hydroxide.

Example 5.6.3

Calculate ΔH_r for the neutralization of sodium hydroxide by sulfuric acid if 100.0 mL of 1.00M H_2SO_4 reacts with 100.0mL of 1.00M NaOH if all reactants were at 25.0^{o}C before reaction and reached a final temperature of 32.0$_o$C after the reaction. Treat the solutions as if they had the same specific heat capacity and density of pure water,

Solution

Step 1: Identify limiting reagent so we can identify moles reacted.

$$\underset{\substack{V=100.0mL\\M=1.00M}}{H_2SO_4} + \underset{\substack{100.0mL\\M=1.00M}}{2NaOH} \rightarrow Na_2SO_4 + 2H_2O \tag{5.6.16}$$

Sodium hydroxide (NaOH) is the limiting reagents (calculate moles of each reactant and divide by stoichiometric coefficient, review section 4.2 in necessary)

$$n_{NaOH} = 1.00\frac{molNaOH}{L}(0.1000L) = 0.100mol\ NaOH \tag{5.6.17}$$

Step 2: Calculate heat of reaction based on the first law of thermodynamics

We note the heat transferred from the reaction is abosorbed by the calorimeter and its contents, noting that the calorimeter itself is ideal and so its calorimeter constant is zero (C_{cal}=0).

$$\begin{aligned} Q_R &= -Q_{calorimeter} \\ &= -m_{contents}c_{H_2O}\Delta T \\ &= -200.0g\left(4.184\frac{J}{g^oC}\right)(32.0^oC - 25.0^oC) \\ &= -5.9kJ \end{aligned} \tag{5.6.18}$$

Step 3: Relate this to the moles of the limiting reagent

You know know that when 0.1000 M of NaOH completely reacted that -59.kJ of heat was released, so use the stoichiometric equation to calculate the heat of reaction.

$$\frac{\Delta H_r}{mol\ NaOH} = \frac{-5.9kJ}{0.100mol} = -59kJ/mol\ NaOH \tag{5.6.19}$$

Step 4: Relate this to the balanced equation to get the enthalpy of reaction

Remember, the enthalpy of reaction is the energy related to the balanced equation, not each reactant or product. So for the neutralization fo sulfuric acid by sodium hydroxide it is per mole sulfuric acid consumed, per 2 moles sodium hydroxide consumed, per mole sodium sulfate produced and per two moles sodium chloride produced.

So

$$\Delta H_{reaction} = -59\frac{kJ}{mol\ NaOH}(2\ mol\ NaOH) = -120kJ \tag{5.6.20}$$

Lets do a quick review of what the enthalpy of reaction means. So for the reaction

H_2SO_4(aq) + 2NaOH(aq) --> Na_2SO_4(aq) + 2 NaCl

it means is that for each mole of H_2SO_4 consumed or Na_2SO_4 produced- 120kJ of energy is released, while for each mole of NaOH consumed or NaCl produced -59kJ of energy is released when sodium hydroxide reacts with sulfuric acid.

Constant-Volume Calorimetry: Combustion Data

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter(A device used to measure energy changes in chemical processes. shown schematically in Figure 5.6.3). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the "bomb"). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

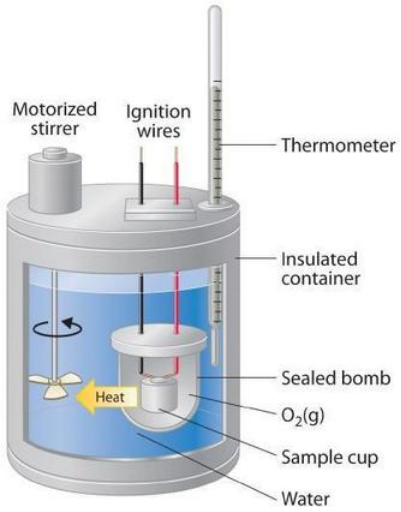


Figure 5.6.3: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.

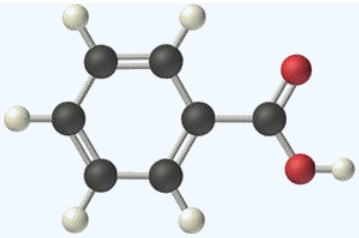
Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔU) rather than the enthalpy change (ΔH); ΔU is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 5.6.21, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{5.6.21}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its $\Delta H_{comb} = -26.38\ kJ/g$). This value and the measured increase in temperature of the calorimeter can be used in Equation 5.6.21 to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 5.6.4.

Example 5.6.4: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08 °C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation 5.6.21 to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.

B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 5.6.21 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$\begin{aligned} q_{comb} &= \left(0.579\ \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) \\ &= -15.3\ kJ \end{aligned}$$

From Equation 5.6.21,

$$\begin{aligned} -C_{bomb} &= \frac{q_{comb}}{\Delta T} \\ &= \frac{-15.3\ kJ}{2.08\ ^oC} \\ &= -7.34\ kJ/^oC \end{aligned}$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$\begin{aligned} q_{comb} &= -C_{bomb}\Delta T \\ &= (-7.34\ kJ/^oC)\,(3.64\ ^oC) \\ &= -26.7\ kJ \end{aligned}$$

Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

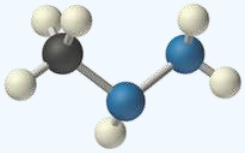
$$\begin{aligned} \Delta H_{comb} &= \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) \\ &= -2780\ kJ/mol \\ &= 2.78 \times 10^3\ J/mol \end{aligned}$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb} = -2803\ kJ/mol$ that calculated using enthalpies of formation.

Exercise 5.6.4: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75 °C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64 °C. Calculate the ΔH_{comb} of

methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer

-1.30×10^3 kJ/mol

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Ronia Kattoum
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5.7: Enthalpy Calculations

Learning Objectives

- Define Hess's Law and relate it to the first law of thermodynamics and state functions
- Calculate the unknown enthalpy of a reaction from a set of known enthalpies of combustion using Hess's Law
- Define molar enthalpy of formation of compounds
- Calculate the molar enthalpy of formation from combustion data using Hess's Law
- Using the enthalpy of formation, calculate the unknown enthalpy of the overall reaction
- Calculate the heat evolved/absorbed given the masses (or volumes) of reactants.

Hess's Law

Hess's Law states that if you can add two chemical equations and come up with a third equation, the enthalpy of reaction for the third equation is the sum of the first two. This is a consequence of the First Law of Thermodynamics, the fact that enthalpy is a state function, and brings for the concept of coupled equations.

Coupled Equations: A balanced chemical equation usually does not describe how a reaction occurs, that is, its mechanism, but simply the number of reactants in products that are required for mass to be conserved. In reality, a chemical equation can occur in many steps with the products of an earlier step being consumed in a later step. For example, consider the following reaction phosphorous reacts with oxygen to from diphosphorous pentoxide ($2P_2O_5$)

$$P_4 + 5O_2 \rightarrow 2P_2O_5 \tag{5.7.1}$$

and then the product of that reaction in turn reacts with water to form phosphorus acid

$$2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4 \tag{5.7.2}$$

In the above equation the P_2O_5 is an intermediate, and if we add the two equations the intermediate can cancel out. Hess's law states that if two reactions can be added into a third, the energy of the third is the sum of the energy of the reactions that were combined to create the third.

$$\begin{array}{lll} \text{equation 1:} & P_4 + 5O_2 \rightarrow 2P_2O_5 & \Delta H_1 \\ \text{equation 2:} & 2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4 & \Delta H_2 \\ \\ \text{equation 3:} & P_4 + 5O_2 + 6H_2O \rightarrow 3H_3PO_4 & \Delta H_3 \end{array} \tag{5.7.3}$$

Enthalpy is a **state function** which means the energy change between two states is independent of the path. Since equation 1 and 2 add to become equation 3, we can say:

$$\Delta H_3 = \Delta H_1 + \Delta H_2 \tag{5.7.4}$$

Hess's Law says that if equations can be combined to form another equation, the enthalpy of reaction of the resulting equation is the sum of the enthalpies of all the equations that combined to produce it.

t ΔH_f° epwise Calculation of

Using Hess's Law Determine the enthalpy of formation, ΔH_f°, of $FeCl_3(s)$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\mathrm{Fe}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) \quad \Delta H^\circ = -341.8\ \mathrm{kJ}$$

$$\mathrm{FeCl_2}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H^\circ = -57.7\ kJ$$

Solution

We are trying to find the standard enthalpy of formation of FeCl3(s), which is equal to ΔH° for the reaction:

$$\mathrm{Fe}(s) + \frac{3}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H_\mathrm{f}^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find $\Delta H°$ is the sum of the two reactions with known ΔH values, so we must sum their ΔHs:

$$\begin{aligned} \mathrm{Fe}(s) + \mathrm{Cl_2}(g) &\longrightarrow \mathrm{FeCl_2}(s) \qquad \Delta H^\circ = -341.8\ \mathrm{kJ} \\ \mathrm{FeCl_2}(s) + \frac{1}{2}\mathrm{Cl_2}(g) &\longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H^\circ = -57.7\ \mathrm{kJ} \\ \hline \mathrm{Fe}(s) + \frac{1}{2}\mathrm{Cl_2}(g) &\longrightarrow \mathrm{FeCl_3}(s) \qquad \Delta H^\circ = -399.5\ \mathrm{kJ} \end{aligned}$$

The enthalpy of formation, $\Delta H_\mathrm{f}^\circ$, of $\mathrm{FeCl_3}$(s) is −399.5 kJ/mol.

Exercise 5.7.1

Calculate ΔH for the process:

$$\mathrm{N_2}(g) + 2\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g)$$

from the following information:

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \Delta H = 180.5\ \mathrm{kJ}$$

$$\mathrm{NO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H = -57.06\ \mathrm{kJ}$$

Answer

66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of ΔH) if they are difficult to determine experimentally.

A More Challenging Problem

Using Hess's Law Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

$$\text{(i) } \mathrm{ClF}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{ClF_3}(g) \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH° for reaction (i):

$$\text{(ii) } 2\,\mathrm{OF_2}(g) \longrightarrow \mathrm{O_2}(g) + 2\,\mathrm{F_2}(g) \quad \Delta H^\circ_{(ii)} = -49.4\ \mathrm{kJ}$$

$$\text{(iii) } 2\,\mathrm{ClF}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{Cl_2O}(g) + \mathrm{OF_2}(g) \quad \Delta H^\circ_{(iii)} = +205.6\ \mathrm{kJ}$$

$$\text{(iv) } \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \longrightarrow \tfrac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \quad \Delta H^\circ_{(iv)} = +266.7\ \mathrm{kJ}$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that $\mathrm{ClF}_{(g)}$ is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$, which means that the ΔH° change is also multiplied by $\frac{1}{2}$:

$$\mathrm{ClF}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{1}{2}\mathrm{OF_2}(g) \quad \Delta H^\circ = \frac{1}{2}(205.6) = +102.8\ \mathrm{kJ}$$

Next, we see that $\mathrm{F_2}$ is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the ΔH° changes sign and is halved:

$$\frac{1}{2}\mathrm{O_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{OF_2}(g) \quad \Delta H^\circ = +24.7\ \mathrm{kJ}$$

To get $\mathrm{ClF_3}$ as a product, reverse (iv), changing the sign of ΔH°:

$$\frac{1}{2}\mathrm{Cl_2O}(g)+\frac{3}{2}\mathrm{OF_2}(g)\longrightarrow \mathrm{ClF_3}(g)+\mathrm{O_2}(g)\quad \Delta H^\circ=-266.7\ \mathrm{kJ}$$

Now check to make sure that these reactions add up to the reaction we want:

$$\begin{array}{ll}
\mathrm{ClF}(g)+\frac{1}{2}\mathrm{O_2}(g)\longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g)+\frac{1}{2}\mathrm{OF_2}(g) & \Delta H^\circ=+102.8\ \mathrm{kJ}\\
\frac{1}{2}\mathrm{O_2}(g)+\mathrm{F_2}(g)\longrightarrow \mathrm{OF_2}(g) & \Delta H^\circ=+24.7\ \mathrm{kJ}\\
\frac{1}{2}\mathrm{Cl_2O}(g)+\frac{3}{2}\mathrm{OF_2}(g)\longrightarrow \mathrm{ClF_3}(g)+\mathrm{O_2}(g) & \Delta H^\circ=-266.7\ \mathrm{kJ}\\
\hline
\mathrm{ClF}(g)+\mathrm{F_2}\longrightarrow \mathrm{ClF_3}(g) & \Delta H^\circ=-139.2\ \mathrm{kJ}
\end{array}$$

Reactants $\frac{1}{2}\mathrm{O_2}$ and $\frac{1}{2}\mathrm{O_2}$ cancel out product O_2; product $\frac{1}{2}\mathrm{Cl_2O}$ cancels reactant $\frac{1}{2}\mathrm{Cl_2O}$; and reactant $\frac{3}{2}\mathrm{OF_2}$ is cancelled by products $\frac{1}{2}\mathrm{OF_2}$ and OF_2. This leaves only reactants ClF(g) and F_2(g) and product ClF_3(g), which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH° values will give the desired ΔH°:

$$\Delta H^\circ=(+102.8\ \mathrm{kJ})+(24.7\ \mathrm{kJ})+(-266.7\ \mathrm{kJ})=-139.2\ \mathrm{kJ}$$

Exercise 5.7.2

Aluminum chloride can be formed from its elements:

$$\text{(i)}\ 2\ \mathrm{Al}(s)+3\ \mathrm{Cl_2}(g)\longrightarrow 2\ \mathrm{AlCl_3}(s)\quad \Delta H^\circ=?$$

Use the reactions here to determine the ΔH° for reaction (i):

$$\text{(ii)}\ \mathrm{HCl}(g)\longrightarrow \mathrm{HCl}(aq)\quad \Delta H^\circ_{(ii)}=-74.8\ \mathrm{kJ}$$

$$\text{(iii)}\ \mathrm{H_2}(g)+\mathrm{Cl_2}(g)\longrightarrow 2\ \mathrm{HCl}(g)\quad \Delta H^\circ_{(iii)}=-185\ \mathrm{kJ}$$

$$\text{(iv)}\ \mathrm{AlCl_3}(aq)\longrightarrow \mathrm{AlCl_3}(s)\quad \Delta H^\circ_{(iv)}=+323\ \mathrm{kJ/mol}$$

$$\text{(v)}\ 2\ \mathrm{Al}(s)+6\ \mathrm{HCl}(aq)\longrightarrow 2\ \mathrm{AlCl_3}(aq)+3\ \mathrm{H_2}(g)\quad \Delta H^\circ_{(v)}=-1049\ \mathrm{kJ}$$

Answer

−1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available.

Calculating Enthalpy of Reaction from Combustion Data

In section 5.6.3 we learned about bomb calorimetry and enthalpies of combustion, and table 5.7.1 contains some molar enthalpy of combustion data. In this section we will use Hess's law to use combustion data to calculate the enthalpy of reaction for a reaction we never measured. In fact, it is not even a combustion reaction.

Compound	Heat of Combustion (kJ/mol)
Hydrogen (H_2)	-286
Methane (CH_4)	-889
Ethane (C_2H_6)	-1,560
Propane (C_3H_8)	-2,220
Carbon	-393.5
Ethylene (C_2H_4)	-1411

Table 5.7.1 Heats of combustion for some common substances. Note, these are negative because combustion is an exothermic reaction. They are often tabulated as positive, and it is assumed you know they are exothermic. Also, these are not reaction

enthalpies in the context of a chemical equation (section 5.5.2), but the energy per mol of substance combusted.

Note: tips for hess's law calculations

The following tips should make these calculations easier to perform

1. Write the equation you want on the top of your paper, and draw a line under it.
2. From data tables find equations that have all the reactants and products in them for which you have enthalpies.
3. If an equation has a chemical on the opposite side, write it backwards and change the sign of the reaction enthalpy.
4. If the equation has a different stoichiometric coefficient than the one you want, multiply everything by the number to make it what you want, including the reaction enthalpy

Watch Video 5.7.1 to see these steps put into action while solving example 5.7.1.

Example 5.7.3 Calculating enthalpy of reaction with hess's law and combustion table

Using table 5.7.1 Calculate the enthalpy of reaction for the hydrogenation of ethene into ethane

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

Solution

Hess's Law is a consequence of the first law, in that energy is conserved.

We want the enthalpy for the reaction

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

From table 5.7.1 we obtain the following enthalpies of combustion

$$\begin{array}{lll} \text{eq. 1:} & H_2 + 1/2O_2 \rightarrow H_2O & \Delta H_1 = -286kJ/mol \\ \text{eq. 2:} & C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O & \Delta H_2 = -1411kJ/mol \\ \text{eq. 3:} & C_2H_6 + 3/2O_2 \rightarrow 2CO_2 + 3H_2O & \Delta H_3 = -1560kJ/mol \end{array} \quad (5.7.5)$$

Video 5.7.1 shows how to tackle this problem. The trick is to add the above equations to produce the equation you want. So, identify species that only exist in one of the given equations and put them on the desired side of the equation you want to produce, following the Tips above. Your final answer should be -131kJ/mol



Video 5.7.1: 7'00" YouTube applying Hess's law to calculate the enthalpy of hydrogenation of ethene from combustion data (https://youtu.be/-t20lkJTQYs)

Enthalpy as a State Function

What is important here, is that by measuring the heats of combustion scientists could acquire data that could then be used to predict the enthalpy of a reaction that they may not be able to directly measure. This is a consequence of enthalpy being a state function, and the path of the above three steps has the same energy change as the path for the direct hydrogenation of ethylene. We can look at this in an Energy Cycle Diagram (Figure 5.7.2).

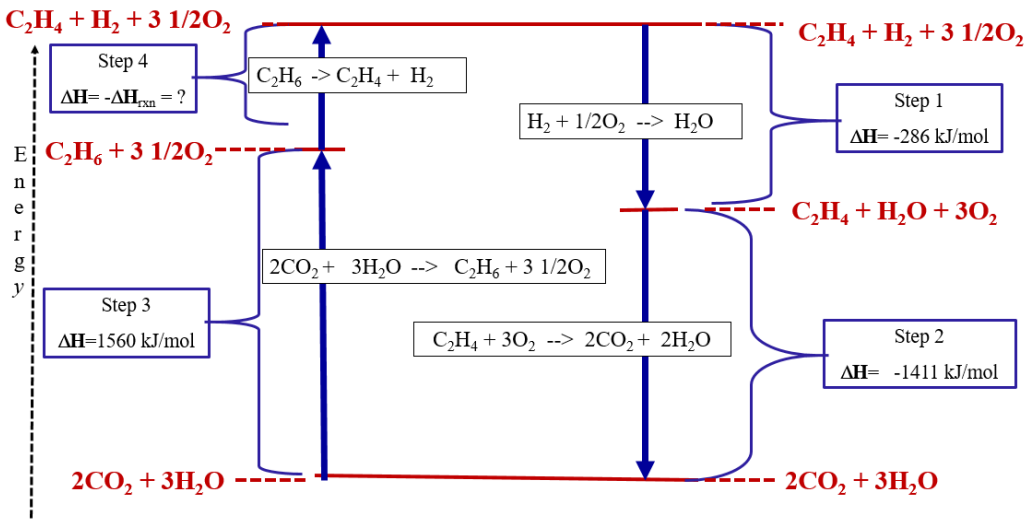


Figure 5.7.2: The steps of example 5.7.1 expressed as an energy cycle.

Because enthalpy is a state function, a process that involves a complete cycle where chemicals undergo reactions and are then reformed back into themselves, must have no change in enthalpy, meaning the endothermic steps must balance the exothermic steps.

$$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = 0 \tag{5.7.6}$$

That is, the energy lost in the exothermic steps of the cycle must be regained in the endothermic steps, no matter what those steps are.

Exothermic Steps

1. ΔH_1 = -296kJ/mol
2. ΔH_2 = -1411kJ/mol Total Exothermic = -1697 kJ/mol

Endothermic Steps

3. ΔH_3 = + 1560kJ/mol
4. ΔH_4 = - ΔH^*_{rxn} = ? J/mol Total Endothermic = + 1697 kJ/mol

Note, step 4 shows C_2H_6 -- > C_2H_4 +H_2 and in example 5.7.1 we are solving for C_2H_4 +H_2 --> C_2H_6 which is the reaction of step 4 written backwards, so the answer to 5.7.1 is the negative of step 4. This problem is solved in video 5.7.1 above.

Standard Enthalpies of Formation

The **standard molar enthalpy of formation ΔH^0_f** is the enthalpy change when **1 mole of a pure substance**, **or a 1 M solute** concentration in a solution, **is formed from its elements in their most stable states under standard state conditions**. In this class, **the standard state is 1 bar and 25°C.** Note, if two tables give substantially different values, you need to check the standard states. One of the values of enthalpies of formation is that we can use them and Hess's Law to calculate the enthalpy change for a reaction that is difficult to measure, or even dangerous. We can look at this as a two step process.

Note the enthalpy of formation is a molar function, so you can have non-integer coefficients. For example, the molar enthalpy of formation of water is:

$$\begin{aligned} H_2(g) + 1/2O_2(g) &\rightarrow H_2O(l) \quad \Delta H_f^o = -285.8\ kJ/mol \\ H_2(g) + 1/2O_2(g) &\rightarrow H_2O(g) \quad \Delta H_f^o = -241.8\ kJ/mol \end{aligned} \tag{5.7.7}$$

This equation says that 85.8 kJ is of energy is exothermically released when one mole of liquid water is formed by reacting one mole of hydrogen gas and 1/2mol oxygen gas (3.011×10^{23} molecules of O_2). Note, ΔH_f^o =of liquid water is less than that of gaseous water, which makes sense as you need to add energy to liquid water to boil it.

Compound	Enthalpy of Formation (kJ/mol)
Hydrogen (H_2)	0
Methane (CH_4)	-74.6
Ethane (C_2H_6)	-84.0
Ethylene (C_2H_4)	52.4
Carbon Dioxide	-393.5
Water (l)	-286
Water (g)	-241.8

Table 5.7.2: Standard enthalpies of formation for select substances. A more comprehensive table can be found at the table of standard enthalpies of formation , which will open in a new window, and was taken from the CRC Handbook of Chemistry and Physics, 84 Edition (2004).

Example 5.7.4: Writing Reaction Equations for ΔH_f°

Write the heat of formation reaction equations for:

a. $C_2H_5OH_{(l)}$
b. $Ca_3(PO_4)_{2(s)}$

Solution

Remembering that ΔH_f° reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $2\,C(s,\ \text{graphite}) + 3\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$
b. $3\,Ca(s) + \frac{1}{2}P_4(s) + 4\,O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Exercise 5.7.3

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_{5(l)}$
b. $Na_2CO_{3(s)}$

Answer a

$$4\,C(s,\ \text{graphite}) + 5\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OC_2H_5(l)\ ;$$

Answer b

$$2\,Na(s) + C(s,\ \text{graphite}) + \frac{3}{2}O_2(g) \longrightarrow Na_2CO_3(s)$$

Calculating Enthalpy of Reaction from Standard Enthalpies of Formation

Because enthalpy of reaction is a state function the energy change between reactants and products is independent of the path. We can choose a hypothetical two step path where the atoms in the reactants are broken into the standard state of their element (left side of Figure 5.7.3), and then from this hypothetical state recombine to form the products (right side of Figure 5.7.3). Note the first step is the opposite of the process for the standard state enthalpy of formation, and so we can use the negative of those chemical species's $\Delta H_{formation}$.

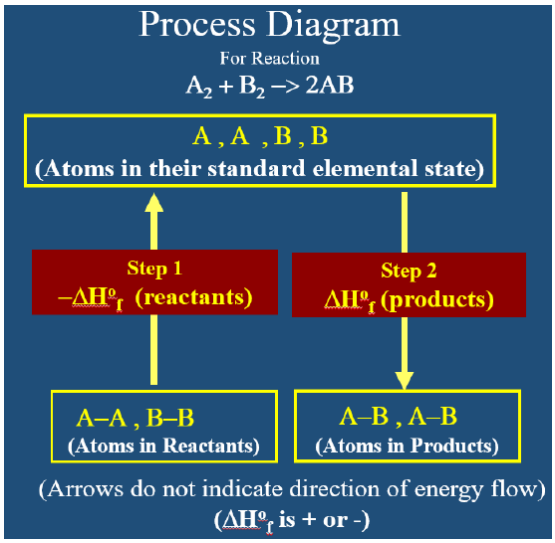


Figure 5.7.3: Process diagram showing the general process for using enthalpies of formation to calculate enthalpies of reaction. In essence we break apart the reactants into their atoms at standard state (the opposite of formation) in the first step, and then form the products from those atoms in the second step. This is not an energy diagram, but a process diagram, and either step may be endothermic or exothermic.

Note: Enthalpy vs. Molar Enthalpy

Enthalpy, q_p, is an extensive property and for example the energy released in the combustion of two gallons of gasoline is twice that of one gallon. As such, enthalpy has the units of energy (typically J or cal). Molar enthalpies of formation are intensive properties and are the enthalpy per mole, that is the enthalpy change associated with the formation of one mole of a substance from its elements in their standard states. Thus molar enthalpies have units of kJ/mol or kcal/mol, and are tabulated in thermodynamic tables. Also not that the equations associated with molar enthalpies are per mole substance formed, and can thus have non-interger stoichiometric coeffiecents. That is, you can have half a mole (but you can not have half a molecule.

The molar enthalpy of reaction can be used to calculate the enthalpy of reaction if you have a balanced chemical equation. This is described by the following equation, where where m_i and n_i are the stoichiometric coefficients of the products and reactants respectively.

$$\Delta H_{reaction} = \sum m_i \Delta H_f^o(products) - \sum n_i \Delta H_f^o(reactants) \tag{5.7.8}$$

$where\ m_i\ and\ n_i$ are the stoichiometric coefficients of the products and reactants respectively

If we look at the process diagram in Figure 5.7.3 and correlate it to the above equation we see two things.

1. **Reactants break apart** into their atoms that take their elemental standard state forms. This is the opposite of forming them, so this step is the negative of their enthalpy of formation.
2. **Products form** from their atoms in their elemental standard state forms. This is their enthalpy of formation

In both cases you need to multiply by the stoichiomertic coefficients to account for all the species in the balanced chemical equation. This allows us to use thermodynamic tables to calculate the enthalpies of reaction and although the enthalpy of reaction is given in units of energy (J, cal) we need to remember that it is related to the stoichiometric coefficient of each species (review section 5.5.2 enthalpies and chemical reactions).

So the equation

$$\Delta H_{reaction} = \sum m_i \Delta H_f^o(products) - \sum n_i \Delta H_f^o(reactants)$$

describes the enthalpy change as reactants break apart into their stable elemental state at standard conditions and then form new bonds as they create the products.

Let's apply this to the combustion of ethylene (the same problem we used combustion data for).

$$C_2H_4 + H_2 \text{ --> } C_2H_6$$

using the above equation, we get,

$\Delta H_{reaction} = \Delta H_f^o (C_2H_6) - \Delta H_f^o (C_2H_4) - \Delta H_f^o (H_2)$

ΔH -84 -(52.4) -0= -136.4 kJ

while above we got -136, noting these are correct to the first insignificant digit.

Example 5.7.5

Calculate the enthalpy of formation for acetylene, C_2H_2(g) from the combustion data (table 5.7.1, note acetylene is not on the table) and then compare your answer to the value in table 5.7.2

ΔH_{comb} (C_2H_2(g)) = -1300kJ/mol
ΔH_{comb} (C(s)) = -394kJ/mol
ΔH_{comb} (H_2(g)) = -276kJ/mol

Note, in the following video we used Hess's Law to calculate the enthalpy for the balanced equation, with integer coefficients. It is important that students understand that $\Delta H_{reaction}$ is for the entire equation, so in the case of acetylene, the balanced equation is

$2C_2H_2$(g) + $5O_2$(g) --> $4CO_2$(g) +2 H_2O(l) $\Delta H_{reaction}$ (C_2H_2) = -2600kJ

But when tabulating a molar enthaply of combustion, or a molar enthalpy of formation, it is per mole of the species being combusted or formed. That is, the equation in the video and the one above have the exact same value, just one is per mole, the other is per 2 mols of acetylene.

Solution

Watch the video below to get the tips on how to approach this problem.

Step 1: Write out each eq.

$$\begin{aligned} 2C_2H_2(g) + 5O_2(g) &\rightarrow 4CO_2(g) + 2H_2O(l) \quad & \Delta H_{comb} = -2600kJ \\ C(s) + O_2(g) &\rightarrow CO_2(g) \quad & \Delta H_{comb} = -393kJ \\ 2H_2(g) + O_2 &\rightarrow 2H_2O(l) \quad & \Delta H_{comb} = -572kJ \end{aligned} \tag{5.7.9}$$

Step 2: Write out what you want to solve (eq. for the formation of C_2H_2).

$$H_2(g) + 2C(s) \rightarrow C_2H_2(g) \tag{5.7.10}$$

Step 3: Combine given eqs. so they add into desired eq.

- If you reverse Equation change sign of enthalpy
- if you multiply or divide by a number, multiply or divide the enthalpy by that number

$$2\cancel{CO_2(g)} + \cancel{H_2O(l)} \rightarrow C_2H_2(g) + \cancel{5/2O_2(g)} \quad \Delta H_{comb} = -(-\frac{-2600kJ}{2})$$

$$2C(s) + \cancel{2O_2(g)} \rightarrow \cancel{2CO_2(g)} \quad \Delta H_{comb} = 2(-393kJ)$$

$$H_2(g) + \cancel{1/2O_2(g)} \rightarrow \cancel{H_2O(l)} \quad \Delta H_{comb} = \frac{-572kJ}{2} \tag{5.7.11}$$

Step 4: Sum the Enthalpies: 226kJ (the value in the standard thermodynamic tables is 227kJ, which is the uncertain digit of this number)

See video 5.7.2 for tips and assistance in solving this.



Video 5.7.2: 6:16 YouTube solving Example 5.7.2 (https://youtu.be/57v2DiU6HjM)

Enthalpies of Reaction and Stoichiometric Problems

Example 5.7.5

Determine the heat released or absorbed when 15.0g Al react with 30.0g Fe_3O_4(s).

Solution

There are three Tasks to this problem

1. Balance Equation and Identify Limiting Reagent
2. Calculate $\Delta H_{reaction}$ from enthalpies of formation
3. Calculate the heat given off by the complete consumption of the limiting reagent

Step 1:

$$\underset{\substack{15.0g\ Al\\ 26.98g/mol}}{8Al(s)} + \underset{\substack{30.0g\\ 231.54g/mol}}{3Fe_3O_4(s)} \rightarrow 4Al_2O_3(s) + 9Fe(3) \tag{5.7.12}$$

$$15gAl\left(\frac{molAl}{26.98g}\right)\left(\frac{1}{8molAl}\right) = 0.069 \tag{5.7.13}$$

$$30.0gFe_3O_4\left(\frac{1molFe_3O_4}{231.54g}\right)\left(\frac{1}{3molFe_3O_4}\right) = 0.043 \tag{5.7.14}$$

So Fe_3O_4(s) is the limiting reagent.

Step 2:

From T1: Standard Thermodynamic Quantities we obtain the enthalpies of formation

ΔH_f^o (Fe_3O_4)	ΔH_f^o (Al_2O_3)	ΔH_f^o (Al)	ΔH_f^o (Fe)
-1118.4kJ/mol	-1675.7kJ/mol	0	0

Using

$$\Delta H_{reaction} = \sum m_i\ \Delta H_f^o \text{ (products)} - \sum n_i\ \Delta H_f^o \text{ (reactants)}$$

gives

$$\Delta H_{reaction} = 4(-1675.7) + 9(0) - 8(0) - 3(-1118.4) = -3363.6kJ$$

Step 3:

Base heat released on complete consumption of limiting reagent.

$$30.0gFe_3O_4\left(\frac{1molFe_3O_4}{231.54g}\right)\left(\frac{-3363kJ}{3molFe_3O_4}\right)=-145kJ \tag{5.7.15}$$

Note, you could have used the 0.043 from step 2,
0.043(-3363kJ)=-145kJ

Example 5.7.7

Using enthalpies of formation from T1: Standard Thermodynamic Quantities calculate the heat released when 1.00 L of ethanol combustion.

Solution

See video 5.7.3

Energy and Stoichiometry.

Pure ethanol has a density of 789g/L. Using the tables for enthalpy of formation, calculate the enthalpy of reaction for the combustion reaction of ethanol, and then calculate the heat released when 1.00 L of pure ethanol combusts.



Video 5.7.3: 4:53min YouTube solving example 5.7.7: Calculating heat released by combustion of 1 L of ethanol (https://youtu.be/57v2DiU6HjM)

Exercise 5.7.4

How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25×10^3 kJ

Contributors and Attributions

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- Paul Flowers, et al. Open Stax (examples and exercises)
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CHAPTER OVERVIEW

6: The Structure of Atoms

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Topic hierarchy

6.1: Electromagnetic Radiation
6.2: Quantization: Planck, Einstein, Energy, and Photons
6.3: Atomic Line Spectra and Niels Bohr
6.4: Wave-Particle Duality
6.5: The Modern View of Electronic Structure
6.6: The Shapes of Atomic Orbitals
6.7: Electron Spin and the Pauli Exclusion Principle

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6.1: Electromagnetic Radiation

Learning Objectives

- Describe the characteristics of light and how it relates to matter
- Define electromagnetic radiation and give examples of electromagnetic radiation
- Differentiate between transverse and compressional waves
- Relate the wavelength and frequency of a electromagnetic radiation to the speed of light
- Rank the various types of electromagnetic radiation in order of increasing/decreasing frequency and wavelength

Introduction

Light interacts with matter, and it is through studying this interaction that scientists have learned a lot of what they know about the structure of matter. Light is electromagnetic radiation, and the nature of the interaction of light and matter is influenced by the energy of the light. For example, light of the proper energy can cause an electron to move from one orbital to another that has a different energy. There are two basic process, absorption and emission.

- Absorption: This is an endothermic process where matter absorbs the light energy.
- Emission: This is an exothermic process where light energy is emitted, and leaves the system (matter).

What are some characteristics of light?

1. Light travels through space.
2. Light has color.
3. Light has energy.
4. Light energy is quantified.

What is Light?

Light is electromagnetic radiation, which travels through space in light waves.

Properties of Waves

There are two basic types of waves, transverse and compressional. A transverse wave induces periodic oscillation perpendicular to the direction of the wave front, like a wave traveling across the surface of water causes an object to oscillate up and down. Light waves (electromagnetic radiation) are transverse waves. Compressional or longitudinal waves cause oscillating motion along the direction of the wavefront, where the particle density oscillates as they are compressed and expanded. Acoustic waves are longitudinal, as indicated by the vibrating speaker.

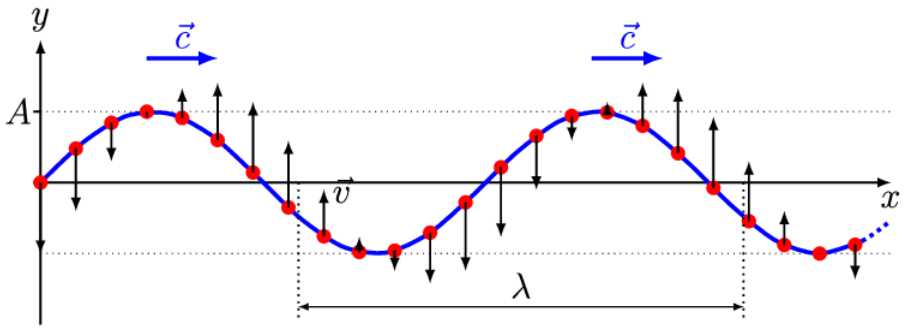


Figure 6.1.1: (a) Translational (transverse) wave (CC BY-SA 4.0 Internation; And1mu via Wikimedia Commons)

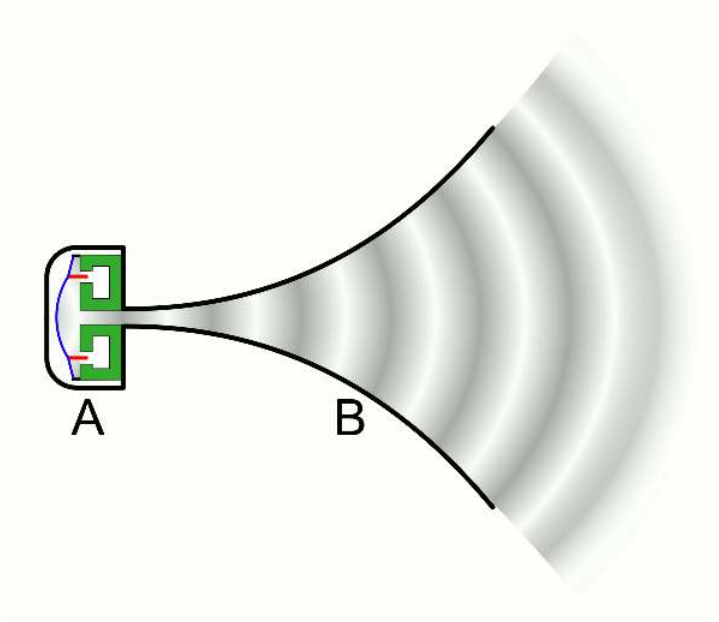


Figure 6.1.1: (b) Compression (longitudinal) wave (courtesy of Chetvomo, Wikimedia Commons)

Figure 6.1.1: Animated Gifs of transverse and longitudinal waves. Light waves are transverse waves while acoustic are longitudinal.

Wave Properties for Transverse Waves

- **Amplitude**- maximum displacement from undisturbed position during a complete oscillation, (units depend on what is oscillating).
- **Wavelength (λ)** -The distance between two peaks (units of length,typically nm for visible light).
- **Frequency (ν)**- Oscillations per unit of time (Hertz is cycles per second, and has units of sec^{-1}, your AC house electricity is 60Hz, meaning the frequency of oscillation is 60 times a second).
- **Wave Speed** - how fast the wave front propagates through the medium (units of distance per time). Use c for light waves.

$$\begin{aligned} \text{Wave Speed} &= \lambda\nu \\ &= (\text{wavelenth})(\text{frequency}) \end{aligned} \tag{6.1.1}$$

Electromagnetic Radiation

Light travels through space as an oscillation of electric and magnetic fields that are orthogonal (at right angles) to each other and the direction of propagation. So there are three vectors associated with a light beam, each that could be described by a Cartesian coordinate system axis. If the light in Figure 6.1.2 moves in the direction of the Z-axis, that would be the direction of the propagation and it is moving at the speed of light. (Note, speed is a scalar, how fast something moves, but does not tell you in what

direction. Velocity is a vector, and tells you both the speed and direction of motion). This motion would then induce concurrent oscillations of an Electric Field along the X-axis and the magnetic field along the Y-axis, but osciallating in phase and at the same frequency.

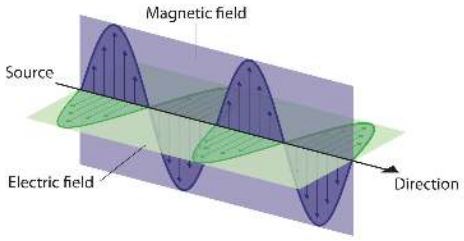


Figure 6.1.2: Diagram of an electromagnetic wave. The light wave is moving in the direction of propagation while the electric and magnetic fields are oscillating along horizontal and vertical planes respectively.



Video 6.1.1: 5:19min YouTube from BestOfScience describes electromagnetic radiation and relates the electromagnetic spectrum to many application in the modern world (https://youtu.be/cfXzwh3KadE).

As the above video show clearly shows, in today's modern world we are surrounded by electromagnetic energy coming from devices of anthropogenic origins.

The Electromagnetic spectrum

The electromagnetic spectrum describes light across a range of frequencies. Video 6.1.1 gives a good feel for the types of applications the different regions of the spectrum are used for. In the next section we discuss energy, and the higher the frequency (the lower the wavelength), the higher the energy.

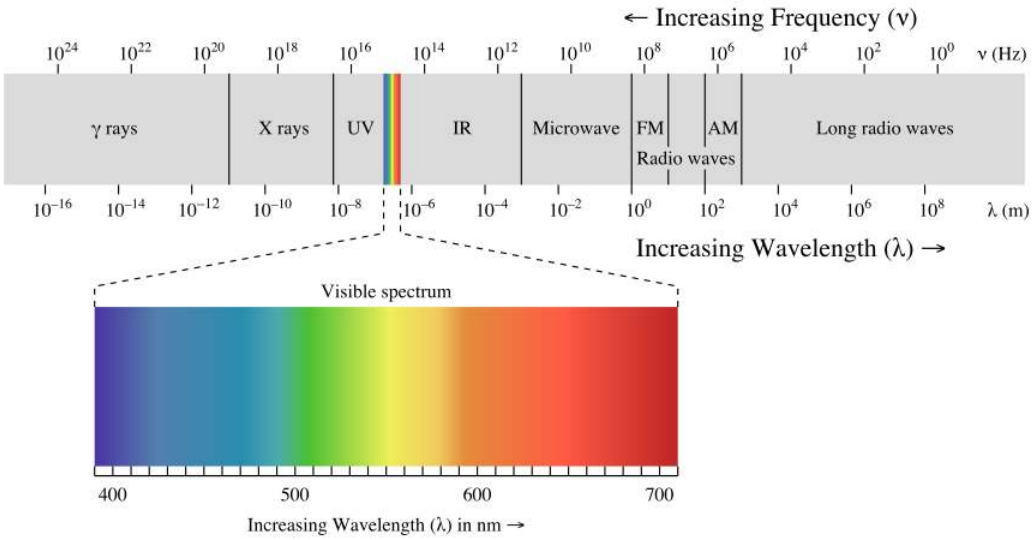


Figure 6.1.3: Regions of the electromagnetic spectrum.

Exercise 6.1.1

Is the wavelength of the UV radiation longer or shorter than microwaves?

Answer

Shorter. Gamma radiation has the shortest wavelength (greatest frequency). As you move from gamma rays to radio waves, the wavelength increases and frequency decreases.

Properties of Electromagnetic Radiation

$$c = \lambda\nu \tag{6.1.2}$$

- **c= 3.00 ×10^8 m/s** (2.99792458 × 10^8 m/s), which is 1.86 × 10^5 mi/s and about a million times faster than the speed of sound.
- **λ** - Wavelength, unit depends on the part of the Electromagnetic Spectrum you are interested in. Typically use SI prefixes and meters, so that the number is between 1 and 999. So in the visible region, we would use nm, with the range roughly being between 400 and 400 nm.
- **ν**- Frequency (Hz, or cycles per second)

Example 6.1.1

A sodium streetlight gives off yellow light that has a wavelength of 589 nm ($1nm = 1 \times 10^{-9} m$). What is the frequency of this light?

Solution

We can rearrange the Equation 6.1.2 to solve for the frequency:

$$v = \frac{c}{\lambda}$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$v = \left(\frac{2.998 \times 10^8 \ \cancel{\text{m}}\,\text{s}^{-1}}{589 \ \cancel{\text{nm}}}\right)\left(\frac{1 \times 10^9 \ \cancel{\text{nm}}}{1 \ \cancel{\text{m}}}\right) = 5.09 \times 10^{14}\,\text{s}^{-1}$$

Exercise 6.1.2

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer

0.353 m = 35.3 cm

Exercise 6.1.3

What is the frequency of a wave with a wavelength of 500 pm?

Answer

$6.0 \times 10^{17}\ Hz$

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Ronia Kattoum (UALR)
- Paul Flowers, et al. Open Stax (examples and exercises)
- anonymous

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6.2: Quantization: Planck, Einstein, Energy, and Photons

Learning Objectives

- Explain how the study of Blackbody Radiation lead to the understanding of quantized energy
- Relate wavelength and frequency to the energy associated with electromagnetic radiation
- Summarize the photoelectric effect and its impact on discovering the photon

Introduction

In the last section we saw that $c=\lambda\nu$, which means the frequency and wavelength of light are inversely related, that is $\nu = \frac{c}{\lambda}$, and so doubling the wavelength halves the frequency. In this section, we shall define the concept of a photon of light and see how planck's equation relates the frequency and wavelength to the energy of light.

Planck's Equation and Black Body Radiation

A black body is an object that absorbs light of all frequencies, and if heated, a black body will emit light of a characteristic spectrum. It could be experimentally observed that both the frequency (color) and the intensity (amount) of the light emitted by a black body is a function of its temperature, as indicated in Figure 6.2.1. By intensity, we mean how much light of a given color, so as the temperature goes from 3000K to 6000K we see that not only is more light given off, but that its color has shifted from the red to the blue.



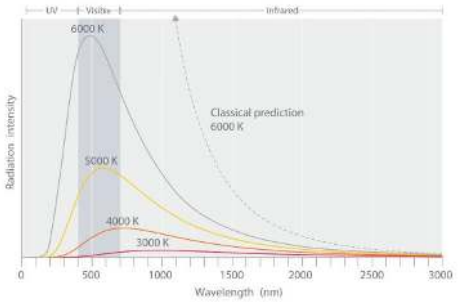
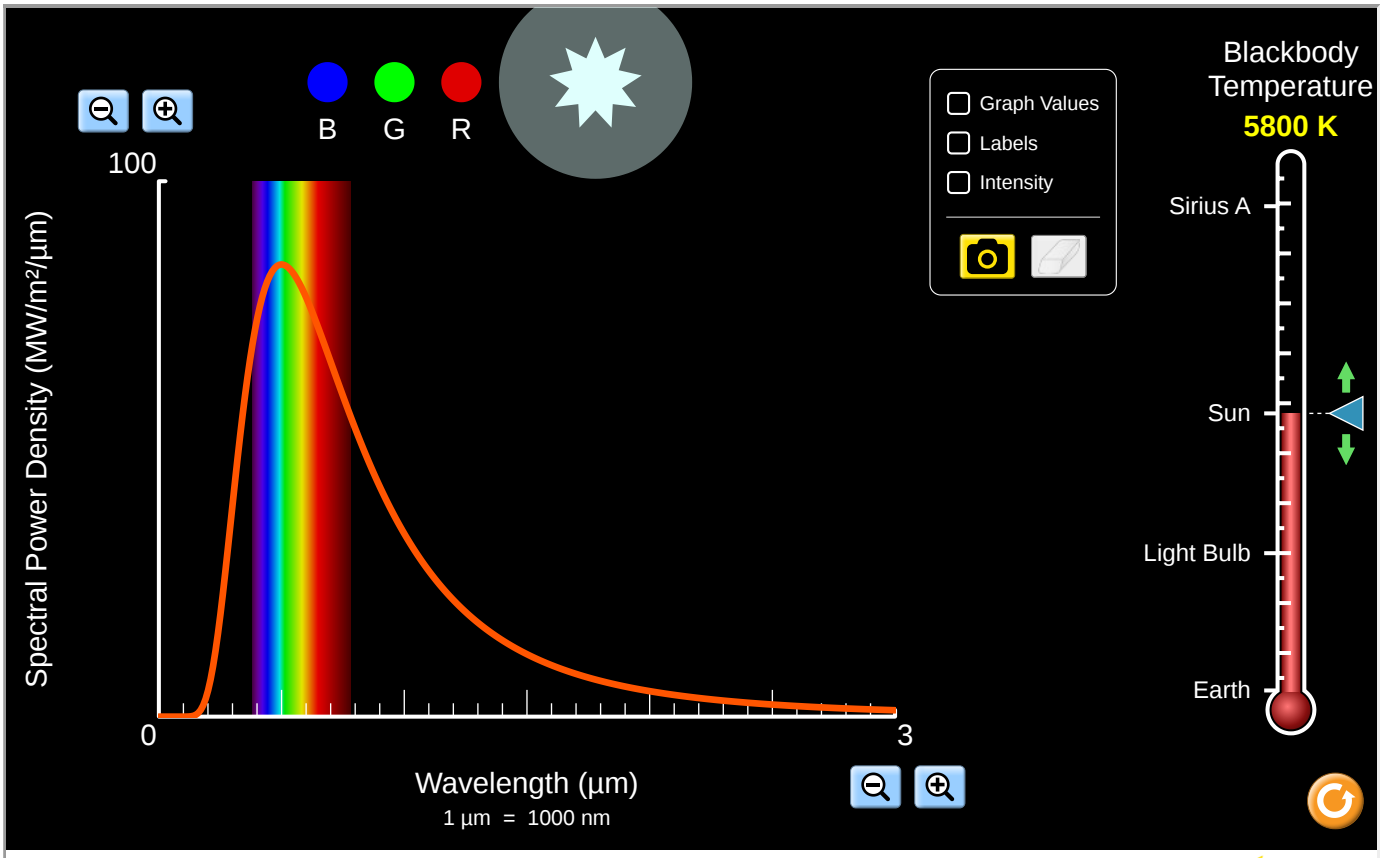


Figure 6.2.1: The intensity of light being emitted by a black body is a function of the temperature. As the temperature goes up two things happen. First, the intensity of light increases, and second, there is a blue-shift. That is, at low temperatures the light is red, and as it heats up, it moves towards the ultraviolet. Image on right from Wikipedia.



Phet Simulation 6.2.1: Interactive black body spectrum showing how the both the intensity and peak wavelength are a function of temperature.

It can be observed that as the energy goes up the intensity goes down, and around 1900 Max Planck accounted for this by considering the light to be emanating from oscillations that he associated with atoms of a specific frequency ν. He recognized that different particles could oscillate at different frequencies, and the energy of the oscillation was proportional to the frequency, as given by Planck's Law.

$$E = h\nu \tag{6.2.1}$$

Today Planck's constant is considered to be a fundamental physical constant (section 1B.1.3) and is in fact used in the modern definition of the kilogram. The current defined value of the Planck's constant is:

$$h \equiv 6.626070040(81) \times 10^{-34} J \cdot s (joule \cdot seconds) \tag{6.2.2}$$

In this class we will typically use it to 4 significant digits.

$$h = 6.626 \times 10^{-34} J \cdot s \tag{6.2.3}$$

Planck actually related the intensity of light to an integer times this value, but to truly understand this equation we need to look at the photoelectric effect, where we will see that n is related to the number of particles oscillating at the frequency ν.

$$I = nh\nu \tag{6.2.4}$$

To understand blackbody radiation and Figure 6.2.1 we need to rewrite Planck's law in terms of wavelength

$$E = h\nu = h\frac{c}{\lambda} \tag{6.2.5}$$

$$I = nh\nu = nh\frac{c}{\lambda} \tag{6.2.6}$$

.

The blue shift in the wavelength is because as E goes up, λ goes down. The increase in intensity is because as the temperature rises, n goes up.

Example 6.2.1

A ruby laser, a device that produces light in a narrow range of wavelengths emits red light at a wavelength of 694.3 nm (Figure 6.2.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A. Use Equation 6.2.1 and the relationship between wavelength and frequency to calculate the energy in joules.

Solution:

The energy of a single photon is given by

$$E = h\nu = \frac{hc}{\lambda}. \tag{6.2.7}$$

Exercise 6.2.1

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

a. What is the energy in joules of a single photon?
b. How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

Answer a

$1.287 \times 10^{-15}\ J/photon$

Answer b

4497 times

Exercise 6.2.2

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?.

Answer

We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

$$E = \frac{hc}{\lambda} onumber \tag{6.2.8}$$

$$E = \frac{(6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}})(2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}})}{(640\ \cancel{\text{nm}})\left(\frac{1\ \text{m}}{10^{9}\ \cancel{\text{nm}}}\right)}$$

$$E = 3.10 \times 10^{-19}\ \text{J}$$

Exercise 6.2.3

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3×10^9 Hz. What is the energy of one photon in these microwaves?

Answer

2×10^{-24} J

Photoelectric Effect

The photoelectric effect was the observation that an electric current can be generated if light of certain frequencies hits the surface of a metal object, but that light of only certain colors can do this. In fact, for each type of metal there was a maximum wavelength that could eject an electron, and any light with a longer wavelength would have no effect, even if you increased its intensity. Einstein recognized that this could be explained by Planck's equation where one could define a "particle of light" or photon as having a fundamental energy of hν.

$$E_{photon} = h\nu \tag{6.2.9}$$

Einstein was able to use Planck's quantization hypothesis to explain the photoelectric effect. As indicated in Figure 6.2.2 a minimum energy of 2.0 eV is required to eject a photon off of potassium, and so red light would not work, while green and purple would.

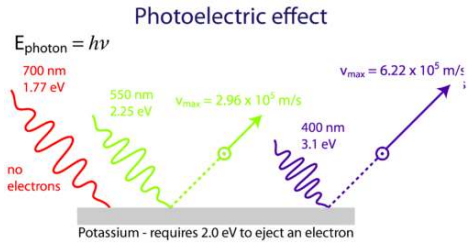


Figure 6.2.2: Potassium requires 2.0eV to eject an electron, and a photon of red light (700nm) only has 1.77eV and so no matter intense the red light is, it can not kick of an electron. Green and purple light have more energy, and when you shine them on the potassium you can kick off an electron.

The following video shows the photoelectric effect,



Video 6.2.1: 1'35" YouTube demonstrating the photoelectric effect. Credits go to College of Chemistry, University of California, Berkeley
Developed by Professor Alex Pines and Dr. Mark Kubinec with the support of The Camille & Henry Dreyfus Foundation (https://youtu.be/kcSYV8bJox8)

This second video by BestOfScience is a bit long, but summarizes this Chapter



Video 6.2.1: 9'36" YouTube titled "A Brief History of Quantum Mechanics" uploaded by BestOfScience. There are several sections of this video that may be useful. Around 20 seconds it starts going over spectrum. At around 2:25 it goes over black body radiation. At 5:40 it describes Planck's quantization hypothesis, and at 7:30 the photoelectric effect. (https://youtu.be/B7pACq_xWyw)

Exercise 6.2.4

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Answer a

False, brightness is related to the intensity of light and a bright light has a lot of photons, not the energy of each photon. If the light has enough energy to eject an electron this will increase the current (the number of electrons), but not the energy of each electron. If the photon does not have enough energy to eject an electron, increasing the brightness of that color of light will have no effect.

Answer b

False, increasing the frequency, how fast the wave oscillated increases the energy. In fact the effect is the opposite, and a long wavelenght oscillates slower and so this would decrease the energy.

Answer c

True, a bright light has a large flux (number of photons per unit surface area), and so with more photons striking the metal surface the number of electrons ejected increases.

Answer d

True and False. If the initial frequency is below the threshold value, then initially no current flows and as the frequency is increased a current starts to flow once that threshold energy is reached. But after that value is reached, further increasing the frequency does not increase the flow of electrons (the current), but it does increase the energy of each ejected electron.

Exercise 6.2.5

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is $9.87 \times 10^{14}\ Hz$.

Answer

$3.94\ kJ/mol$

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

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6.3: Atomic Line Spectra and Niels Bohr

Learning Objectives

- Define the ground state ground state and excited state of electrons
- Explain the difference between line spectra for absorption and emission of electrons
- Calculate the energy associated with the electron at specified energy state
- Calculate the energy difference with electron transition from a higher energy to lower energy, and vice versa
- Calculate the wavelength of light emitted as a result of a particular energy transition
- Differentiate between the Balmer, Lyman, and Paschen Series
- Describe the limitation of the Bohr Model

Line Spectra

There are two types of line spectra, emission and absorption. In an emission spectra electrons are excited to an excited state by thermal or electrical means and then relax back to a lower state and emit a photon of light at a specific energy, which is seen as at a specific wavelength. That is, electrons transfer from high to low energy and give off a photon of light with an energy equal to the difference in energy between the two electronic states. In an absorption spectra the opposite occurs and a sample is radiated with white light of multiple wavelengths, and if there is a wavelength of the same energy as the energy gap between two electronic states, that photon can be absorbed as an electron goes from the lower to higher (excited) energy state. Emission is an exothermic process in that a photon of energy leaves the system, while absorption is an endothermic process as a photon of energy is gained by the system.

Atomic Absorption Line Spectra

The following YouTube of the Sodium Absroption Lines from the Harvard Natural Sciences Lecture Demonstrations shows how an absorption line can be seen with rather primitive equipment.



Video 6.3.1 1'24" *YouTube uploaded by Harvard Natural Sciences Lecture Demonstrations showing an absorption line for sodium in the yellow region of the spectrum. (https://youtu.be/7u3rRy97m9Y)*

In video 6.3.1 you see what appears to be a single line but there are actually two lines known as the Sodium D-lines, at 588.9950 and 589.5924 nm. What is clear is that with very low technology these lines can be seen, and where they occur is unique for each element.

Hydrogen's absorption line spectra is shown in Figure 6.3.1. Here we see five black lines indicating that light at these wavelengths is being absorbed. The colored background is light that was transmitted through the sample because there was no allowed transition where the energy gap between two orbitals equaled the energy of the photon ($h\nu$) .



$\lambda = 656nm$ $\lambda = 486nm$
$\lambda = 434nm$; $\lambda = 410nm$

Figure 6.3.1: *Hydrogen Absorption Spectra, as would be observed if a continuous spectra was passed through hydrogen gas that was not excited, along with the 4 visible wavelengths (the line on the far left is at 397nm not really visible)*

Atomic Emission Line Spectra

In a gas discharge tube energy is added to a gas which is adsorbed by electrons. These excited electrons enter high energy orbitals and then fall back to their lower energy and can give off a photon of light of a specific wavelength that can be seen by a diffraction grating or prism. These type of spectra are called line spectra (in contrast to continuous spectra like the colors of the rainbow) and each element has a unique line spectra that can be used to identify it.

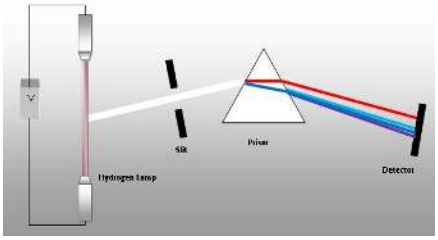


Figure 6.3.2: Prism showing light being emitted from hydrogen being separated into discrete wavelengths (colors), in contrast to the continuum of white light, as in the rainbow.

The following YouTube from Flinn Scientific goes over handling a gas discharge tube and shows the line spectra for several



Video 6.3.2: 1'07" YouTube by Flinn Scientific on the use of gas discharge tubes (https://youtu.be/J7w2EKfytvw)

.



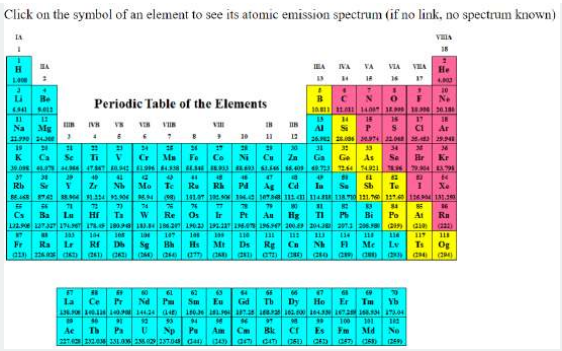
$\lambda = 656nm$ $\lambda = 486nm$
$\lambda = 434nm$; $\lambda = 410nm$

Figure 6.3.3: *Hydrogen Emission Spectra that would be observed if the light from a gas discharge tube filled with hydrogen was passed through a filter or prisim.*

Before proceeding Figures 6.3.1 and 6.3.3 should be compared, and noted that for lines occur at the same wavelengths.

Note: Interactive periodic table with atomic emission spectra

The following image is a link to an interactive periodic table hosted by Alan Jircitano at Penn State Behrend. If you click on an element, on that table it will pull up an emission spectra, if one exits



http://chemistry.bd.psu.edu/jircitano/index.html

Spectra of Hydrogen

With only one electron and one proton hydrogen is the simplest atom and early studies of its line spectra lead to some of the first theories with an experimental foundation for our understanding of the atom. The earliest equations were empirical in nature, that is, they dealt with mathematical formulas that could explain experimental observations, even if there was no understanding of why or what was going on. Although unknown in these early times, what we now know is that a photon of light can exchange energy with an electron, with the electron changing orbitals, where each orbital is of a different energy, and it is the difference in energy of the electron orbitals that must equal the energy of an emitted or absorbed photon in a manner that conserves energy.

Balmer Equation

Based on empirical data measured by Anders Angstrom, Johann Balmer (1825- 1898) was a Swiss mathematician who developed an equation for computing the wavelengths of the line spectra. It needs to be emphasized that although this equation could account for the line spectra it was based on empirical (experimental) data.

$$\lambda = B\left(\frac{n^2}{n^2 - 2^2}\right) \tag{6.3.1}$$

Balmer Equation describing the visible spectrum for hydrogen atom, where B = 364.56 nm, and n is an integer larger than 2.

Rydberg Equation

Johannes Rydberg came up with a more general equation of which the Balmer equation is a specific example for n

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{6.3.2}$$

R is the Rydberg constant, R= $1.097 \times 10^7 m^{-1}$ and $n_1 < n_2$. The following image shows the line spectra in the ultraviolet (Lyman series), visible (Balmer series) and various IR series that are described by the Rydberg equation.

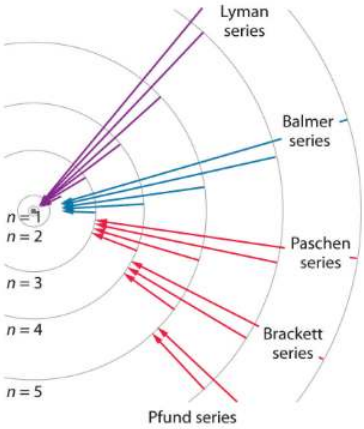


Figure 6.3.4: The different emission transitions for the hydrogen atom. Note, the red ones are of low energy (infrared) and the purple are high (ultraviolet) and the Balmer series are the ones that are visible.

Example 6.3.1: Algebra challenge

Can you derive the Balmer Equation from the Rydberg equation and using the Rydberg constant of R= $1.097 \times 10^{7} m^{-1}$ come up with a value for the Balmer constant?

Solution

B= 364.5 nm. See video 6.3.4 for the solution of this problem



Video 6.3.3: The above video derives the Balmer constant from the Rydberg equation and is good practice. There is also an issue with the camera on autofocus and tracking the person instead of the white board, and this will be redone when time allows. (https://youtu.be/WEh2LEulw1w)

Bohr Model

The advance of the Bohr model is that it related energy to the observations Rydberg and Balmer's equations described, and it introduced the concept of the quantization of the energy level of an electron in an orbit. Where it failed was that it viewed electrons to reside in a classical orbit that in principle could be defined by a radial distance. Before reading any more watch Video 6.3.3 and note that this video treats the electrons as residing in orbitals, not orbits. Orbitals will be discussed in sections 6.5 and 6.6.



Video 6.3.4: 3'49" YouTube uploaded by Wendell Thomas going over atomic line emission spectrum of hydrogen. (https://youtu.be/5aCWCn9Dhqs)

The Bohr model provides a theoretical framework for understanding line spectra. If a photon of light is absorbed, its energy ($h\nu$) is transferred to an electron which jumps from a low energy orbit to a high energy orbit, and the absorption spectral lines are correlated to wavelengths associated with the frequency of that light ($c=\lambda\nu$). In an emission spectra electrons are excited to upper energy states by some external energy source (thermally or electronically like in a discharge lamp), and then the excited electron spontaneously falls back to the lower energy ground state. This may happen through thermal or radiative means, and if it occurs through a radiative process, a photon of the energy associated with the electronic transition is emitted and this accounts for the lines in an emission spectrum. It is important to recognize that absorption is an endothermic process where the atom gains the energy of the photon, and emission is an exothermic process where the atom losses the energy of the emitted photon.

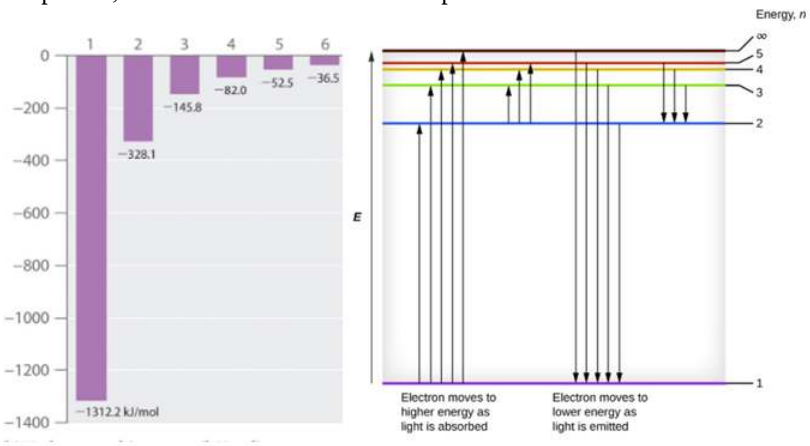


Figure 6.3.5: Energies of quantized orbitals (left) and absorption and emission transitions of electrons between orbitals (right), with infinity correlating to ionization (removal of an electron from the atom). Those transitions between orbits and that involve the n=1 state are high energy ultraviolet radiation and those involving the n=2 to or from higher n states are in the visible region (the n=2 to n=1 transition is ultravioloet)

The Bohr model is actually very simple to understand, in that it states the energy of the nth orbital is quantized, and inversely related to the square of the quantum number (n) times the energy required to ionize the electron, that is, to remove it from an orbit. This is described by the following equation and the reason it is negative is because zero energy is that when the electron and proton are separated by infinity, and noting that to remove an electron is an endothermic process (you add energy), means the energy of an electron in an orbital must be less than zero..

$$\boldsymbol{E_n = -R_\infty \left(\frac{1}{n^2}\right)} \tag{6.3.3}$$

Note: The above equation is a form of an inverse square law, except that unlike other inverse square laws, it is based on the value of an integer, $\frac{1}{n^2}$, giving it values of 1,1/4,/1/9,/16,1/25...

Other inverse square laws are like Coulomb's Law, $F = k\frac{Q_1 Q_2}{r^2}$ and Newton's Law $F = G\frac{m_1 m_2}{r^2}$. The difference is that the Bohr model is treating energy as a series of discrete (quantized) values inversely proportional to an integer, while Coulomb's and Newton's Law relates the force to the inverse square of the distance between two interacting particles, and is a continuum. That is, unlike Bohr's model, the particles can be separated by any distance (r is not restricted to discrete values).

$$E_{electron} = \Delta E_{n_i \to n_f} = E_{n_f} - E_{n_i} = -R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{6.3.4}$$

$$E_{photon} = h\nu = \frac{hc}{\lambda} \tag{6.3.5}$$

Absorption Spectrum

(this is endothermic and $n_f > n_i$)

The energy of the photon equals the energy of the electron transition as it absorbs the energy and goes to a higher level.

$$E_{photon} = E_{electron} \tag{6.3.6}$$

substituting $E_{photon} = h\nu$

$$h\nu = E_{n_f} - E_{n_i} \tag{6.3.7}$$

substituting $\nu = \frac{c}{\lambda}\ from\ c = \lambda\nu$ (eq. 6.1.2)

$$\frac{hc}{\lambda} = -R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{6.3.8}$$

Noting R_∞ is the minimum energy required to photo-ionize an electron in the lowest energy level, that is, to eject the electron from hydrogen so it is not longer in an orbital.

$$\frac{hc}{\lambda} = -R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{6.3.9}$$

To derive the Rydberg Equation we first divide by hc

$$\frac{1}{\lambda} = -\frac{R_\infty}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{6.3.10}$$

Then multiply by negative one

$$\frac{1}{\lambda} = \frac{R_\infty}{hc} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \tag{6.3.11}$$

And equate the Rydberg constant to R_∞/hc

$$R = \frac{R_\infty}{hc} \tag{6.3.12}$$

gives the Rydberg Equation

$$\frac{1}{\lambda} = R \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \tag{6.3.13}$$

Note **R = 1.097x10^{7}m^{-1}**
and is the historical Rydberg constant that predicted the wavelength of the hydrogen spectra.

What we are calling R_∞ is the minimum energy required to remove an electron from the ground state (lowest energy) orbital of hydrogen, and
R_∞ = 2.18x10^{-18}J

Note

The symbol R is often used to represent both the Rydberg constant and R_∞ and to know which is being defined you need to look at the units.

- If Given R = 1.097x10^{7}m^{-1}, use

$$\frac{1}{\lambda} = R\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \tag{6.3.14}$$

- If Given R = 2.18x10^{-18}J

$$\frac{1}{\lambda} = -\frac{R}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \tag{6.3.15}$$

noting that hc has units of $(J \cdot sec)\left(\frac{m}{sec}\right) = J \cdot m$



Video 6.3.4: 7'02" YouTube showing the deriviation of the above relations

Emission spectrum

In emission the system loses an energy as the photon is leaving (exothermic) and so the energy of the photon is negative ($n_i > n_f$)

$$-E_{photon} = E_{electron} \tag{6.3.16}$$

$$-\frac{hc}{\lambda} = -R_\infty\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{6.3.17}$$

Noting R_∞ is the minimum energy required to photo-ionize an electron in the lowest energy level, that is, to eject the electron from hydrogen so it is not longer in an orbital.

$$\frac{hc}{\lambda} = R_\infty\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{6.3.18}$$

To derive the Rydberg Equation we first divide by hc

$$\frac{1}{\lambda} = \frac{R_\infty}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{6.3.19}$$

or

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{6.3.20}$$

Note

If you are solving for a wavelength and you get a negative wavelength, you probably treated emission as if it was absorption, as there is no such thing as a negatative wavelength.

Practice Problems

Example 6.3.2

Using the Bohr model calculate the excited state an electron relaxes from for the blue line of the hydrogen emission spectra at $\lambda 486$ as seen in Figure 6.3.3.

Solution

For emission we know that

$$-E_{photon} = E_{electron} \tag{6.3.21}$$

and for visible radiation the final state is the n=2 state.

Using eq. 6.3.20 and solving for n_i gives:

$$n_i = \sqrt{\frac{1}{\frac{1}{n_f^2} - \frac{1}{\lambda R}}} \tag{6.3.22}$$

noting: $R = 1.097 m^{-1} = 0.01097 nm^{-1}$ and n_i=2 for visible radiation

gives

$$n_i = \sqrt{\frac{1}{\frac{1}{2^2} - \frac{1}{486 nm (0.01907 nm^{-1})}}} = 4 \tag{6.3.23}$$

And so the blue line is for light emitting from an electronic transition from the n=4 to n=2 state.

Exercise 6.3.1

What is the final quantum level in the absorption spectrum of Figure 3.6.1 for the purple band at 434 nm?

Answer

For absorption we know that

$$E_{photon} = E_{electron} \tag{6.3.24}$$

and noting for visible radiation the initial state is the n=2 state.

Using eq. 6.3.13 and noting for n_f.

$$n_f = \sqrt{\frac{1}{\frac{1}{n_i^2} - \frac{1}{\lambda R}}} \tag{6.3.25}$$

noting: $R = 1.097m^{-1} = 0.01097nm^{-1}$and n_i=2 for visible radiation

gives

$$n_f = \sqrt{\frac{1}{\frac{1}{2^2} - \frac{1}{434nm(0.01907nm^{-1})}}} = 5 \tag{6.3.26}$$

And so the purple absorption band at 434 nm is for light being absorbed as an electron jumps from the n=2 to the n=5 state.

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

- Ronia Kattoum (UALR)
- Material adopted and adapted from Paul Flowers, et al. Open Stax
- anonymous

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6.4: Wave-Particle Duality

Learning Objectives

- To understand the wave–particle duality of matter.
- To understand the uncertainty principle

A shortcoming of the Bohr model was that it could only predict the atomic spectra of hydrogen. It in essence treated an electron as a classical object in an orbit around the nucleus, where in reality an electron is a quantum particle that has wave-particle duality. This can be seen with Einstein's photoelectric effect where an electron interacts with a photon, which if it is of sufficient energy, ejects the electron out of an atomic orbital.

The Wave Character of Matter

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the following equation:

$$E = mc^2 \tag{6.4.1}$$

And from Planck's equation we know that

$$E = h\nu = h\frac{c}{\lambda} \tag{6.4.2}$$

equating these gives

$$E = h\frac{c}{\lambda} = mc^2 \tag{6.4.3}$$

$$or$$

$$\frac{h}{\lambda} = mc$$

rearranging give

$$\lambda = \frac{h}{mc} \tag{6.4.4}$$

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{\mathrm{mv}} \tag{6.4.5}$$

where

- h is Planck’s constant,
- *m* is the mass of the particle, and
- *v* is the velocity of the particle.

De Broglie extended this concept to all matter. This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie’s equation, which is an extremely small number. As you will calculate in Example 6.4.1, Planck’s constant (6.63×10^{-34} J•s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.

Note: in Plancks Equation $E = h\nu$ that ν is the frequency of a wavelengths oscillation while in de Broglie's Equation $\lambda = \frac{h}{mv}$ v is the velocity, and in fact mv is the momentum (p) and de Broglie's equation is often written as $\lambda = \frac{h}{p}$, where p is the momentum.

Example 6.4.1

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.
B. Substitute values into Equation 6.4.3 and solve for the wavelength.

Solution:

The wavelength of a particle is given by λ = *h*/*mv*. We know that *m* = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)\frac{min}{60 sec} = 44.69 m/sec$$

B Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626\times10^{-34}\ J\cdot s}{(0.149\ kg)\,(44.69\ m\cdot s^{-1})} = \frac{6.626\times10^{-34}\ \cancel{kg}\cdot m^{\cancel{2}}\cdot\ \cancel{s}^{\cancel{-2}}\cdot\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m}\cdot\ \cancel{s^{-1}}\right)} = 9.95\times10^{-35}\ m \qquad (6.4.6)$$

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

Exercise 6.4.1

Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer

1.32 Å, or 132 pm

Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that it can be bent or spread out by passing through a narrow slit as shown in the video below. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. Heisenberg's uncertainty principle for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. DeBroglie's idea of wave particle duality means that particles such as electrons which all exhibit wave like characteristics, will also undergo diffraction from slits whose size is of the order of the electron wavelength.



Video 6.4.1: 2'07" YouTube uploaded by bmoorbruins93 on Walter Lewin explaining Heisenberg's uncertainty principle (https://youtu.be/0FGo8mi-5w4).

This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that "at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation." Mathematically, the Heisenberg uncertainty principle is greater than or equal to Planck's constant *h* divided by 4π: states that the uncertainty in the position of a particle (Δ*x*) multiplied by the uncertainty in its momentum [Δ(*mv*)] is greater than or equal to Planck's constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{6.4.7}$$

Because Planck's constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie's equation to have measurable wavelengths.

If the precise position *x* of a particle is known absolutely (Δ*x* = 0), then the uncertainty in its momentum must be infinite (as dividing by zero equals infinity).

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{6.4.8}$$

Because the mass of the electron at rest (*m*) is both constant and accurately known, the uncertainty in Δ(*mv*) must be due to the Δ*v* term, which would have to be infinitely large for Δ(*mv*) to equal infinity. That is, according to Equation 6.4.8, the more accurately we know the exact position of the electron (as Δ*x* → 0), the less accurately we know the speed and the kinetic energy of the electron (1/2 mv^2) because Δ(*mv*) → ∞. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as Δ(*mv*) → 0], then Δ*x* → ∞ and we have no idea where the electron is.

Bohr's model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify **simultaneously** both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr's model.

Example 8.5.2

Calculate the minimum uncertainty in the position of the pitched baseball from Example 8.5.1 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A. Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 8.5.7) to solve for the minimum uncertainty in the position of an object (Δx).
B. Find Δv by converting the velocity of the baseball to the appropriate SI units: meters per second.
C. Substitute the appropriate values into the expression for the inequality and solve for Δx.

Solution:

A The Heisenberg uncertainty principle tells us that $(\Delta x)[\Delta(mv)] = h/4\pi$. Rearranging the inequality gives

$$\Delta x \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{\Delta(mv)}\right)$$

B We know that $h = 6.626 \times 10^{-34}$ J•s and $m = 0.149$ kg. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and $\Delta v = \pm 1$ mi/h. We have

$$\Delta v = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ m/s$$

C Therefore,

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right)$$

Inserting the definition of a joule (1 J = 1 kg•m^2/s^2) gives

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\left(\cancel{s^2}\right)}\right)\left(\frac{1\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)(0.4469\ \cancel{m})}\right)$$

$$\Delta x \geqslant 7.92 \pm \times 10^{-34}\ m$$

This is equal to 3.12×10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise 8.5.2

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

Answer: 6×10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

A Bit More on Waves

As de Broglie's equation states that all particles have wave-particle duality, it is prudent to discuss a bit more on the nature of waves.

Wave Interference

Two waves can interact with each other constructively or destructively.

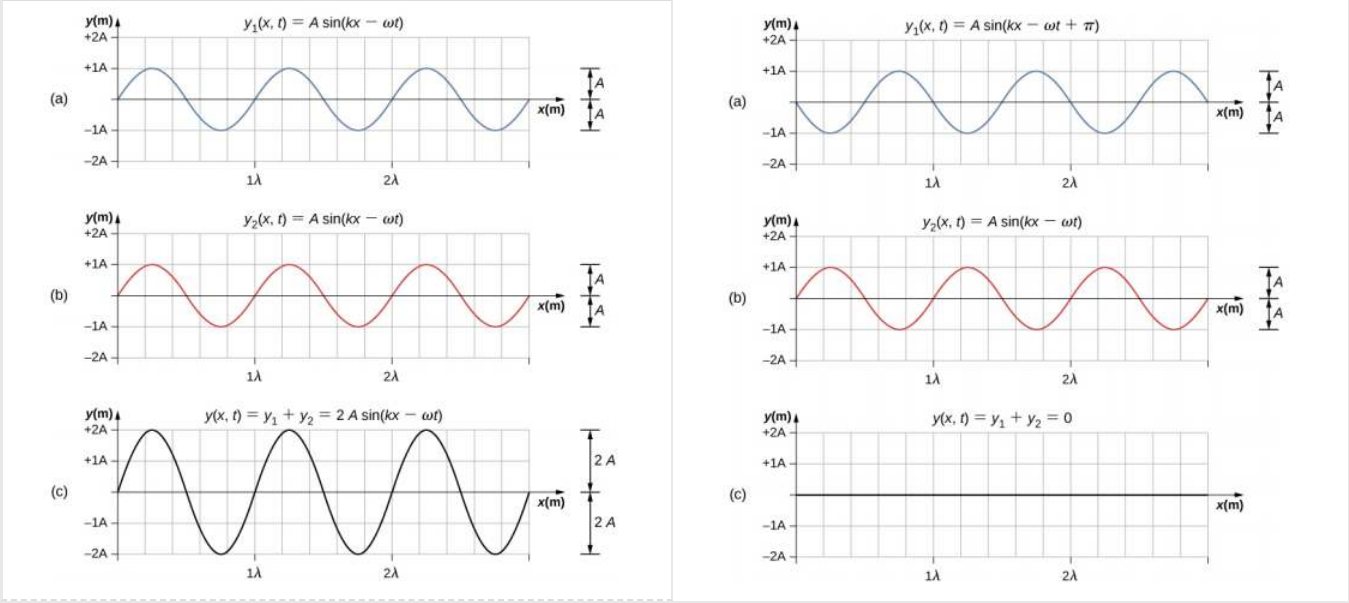


Figure 6.4.1: Constructive and destructive interference. Waves (a) and (b) are added together to form wave (c). Both waves are of the same frequency, the ones in the left are in phase and add to each other. The ones on the right are 180º out of phase, and annihilate each other.

A node is where the wave function equals zero and a standing wave has no amplitude.

Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a standing wave (a wave that does not appear to travel in space). A standing wave is easiest to visualize for a linear wave like the vibration along a string of defined length where the amplitude of motion at the ends of the string is restrained. As the wave front reaches the end of the string a second wave will reflect back towards the first and these two waves will interfere with each other, with all but a few wavelengths annihilating each other through destructive interference. The waves that do not annihilate each other resonate at quantized frequencies and result in standing waves. The first standing wave has a wavelength of twice the length of the string and is called the fundamental (lowest energy standing wave).

$$L = \frac{\lambda}{2} \quad \therefore \quad \lambda = 2L \tag{6.4.9}$$

Higher-energy vibrations are called overtones (the vibration of a standing wave that is higher in energy than the fundamental vibration) and are produced when the string is plucked more strongly; they have wavelengths given by

$$L = n\frac{\lambda}{2} \quad \therefore \quad \lambda = \frac{2L}{n} \tag{6.4.10}$$

where *n* has any integral value. Thus the resonant vibrational energies of the string are quantized. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. Notice in Figure 6.4.2 that all overtones have one or more nodes (the points where the amplitude of a wave is zero), points where the string does not move. The amplitude of the wave at a node is zero.

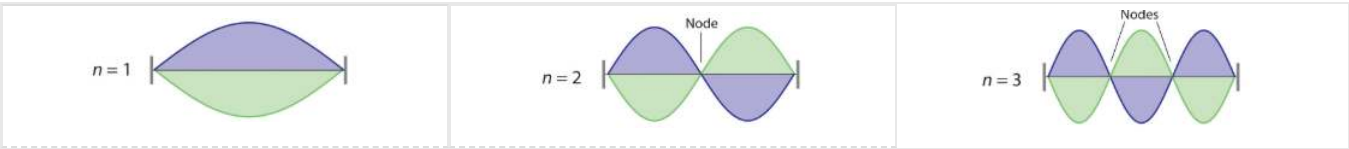


Figure 6.4.2: Fundamental and first two overtones for harmonic resonance frequencies along a string of length L Note the number of nodes are quantized as n-1 with n being an integer (the fundamental has no nodes).

Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 6.4.3). Here standing wave can only exist if the circumference of the circle is an integral multiple of the wavelength which would result in constructive interference, with all other wavelengths destructively annihilating themselves.

$$2\pi r = n\lambda, \quad n = 1, 2, 3... \tag{6.4.11}$$

where *r* is the radius of the circle.

De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to *n* = 1 where one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes

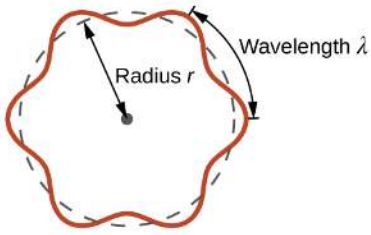


Figure 6.4.3: Standing waves around the circumference of a circle

The following YouTube goes over one, two and three dimensional standing waves and is worth watching.



Video 6.4.2: 4'49" YouTube uploaded by Physics Girl showing standing waves in one, two and three dimensional space. (https://youtu.be/wYoxOJDrZzw)

In reality atoms and their electrons exist in three dimensional space and Erwin Schrödinger extended the concept of standing waves to three dimensions and spherical harmonics, where the standing wave functions could be viewed as the harmonics of a fluid filled surface on a sphere. The Schrödinger wave equation lead to the modern quantum mechanical model of the atom and will introduced in the next section of this Chapter.

Contributors and Attributions

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6.5: The Modern View of Electronic Structure

Schrödinger Wave Equation

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies. This is a complex differential equation beyond the scope of this course that has the simplified form of

$$\hat{H}\psi = E\psi \tag{6.5.1}$$

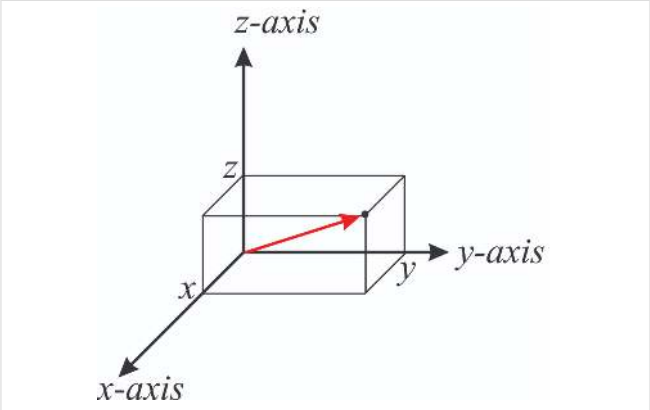
Where $\hat{H}$ is the Hamiltonian operator, which is a set of mathematical operations that work on the function ψ and can be used to determine the energy of the system. The Hamiltonian takes into account kinetic and potential energy interactions. When applied to the wave function solutions for spherical harmonics, which can be envisioned as standing waves of a fluid filled spherical object, the Schrödinger wave equation can be used to understand the different orbitals an electron can exist in a hydrogen-like atom (where one electron exists around a single nucleus).

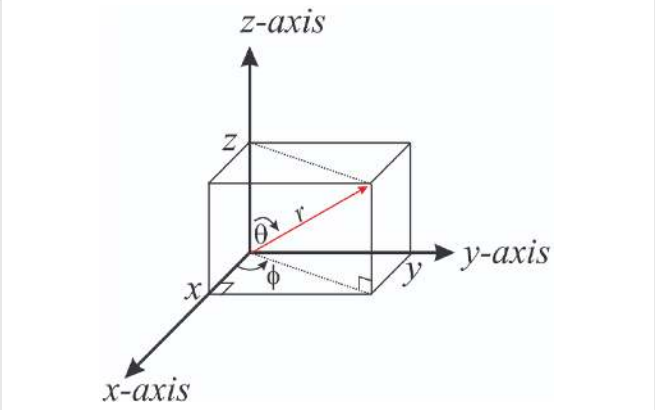


Video 6.5.1: 6'27" YouTube uploaded by "Professor Dave Explains" discussing the Schrödinger wave equation (https://youtu.be/O6g-7rUgrdg).

Note

The wave function ψ for the hydrogen like atom can have very complex forms involving sinusoidal and exponential functions that can include imaginary numbers like $\psi_{21\pm1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \rho e^{-\rho/2} \sin(\theta) e^{\pm i\phi}$. These wave functions are typically described by two coordinate systems, the Cartesian (x,y,z) or spherical (r,θ, ϕ).





Cartesian Coordinates	Spherical coordinates

Figure 6.5.1: The spherical coordinate system is easier than the Cartesian system to represent an electronic orbital. Note θ varies from 0 to 360º while ϕ varies from 0 to 180º.

Max Born set forth an interpretation of the square of these wave functions as probability density functions for the location of an electron, and we will define orbitals as regions in space where there is a 90% probability of finding an electron (as defined by the solutions to Schrödinger equation). It is important to distinguish the concept of orbita, which defines the location in space where one can find a tiny electron that shows wave-particle duality, in contrast to the orbit (of the Bohr) model that describes the location and trajectory of a macroscopic object like the moon in an orbit around a planet.

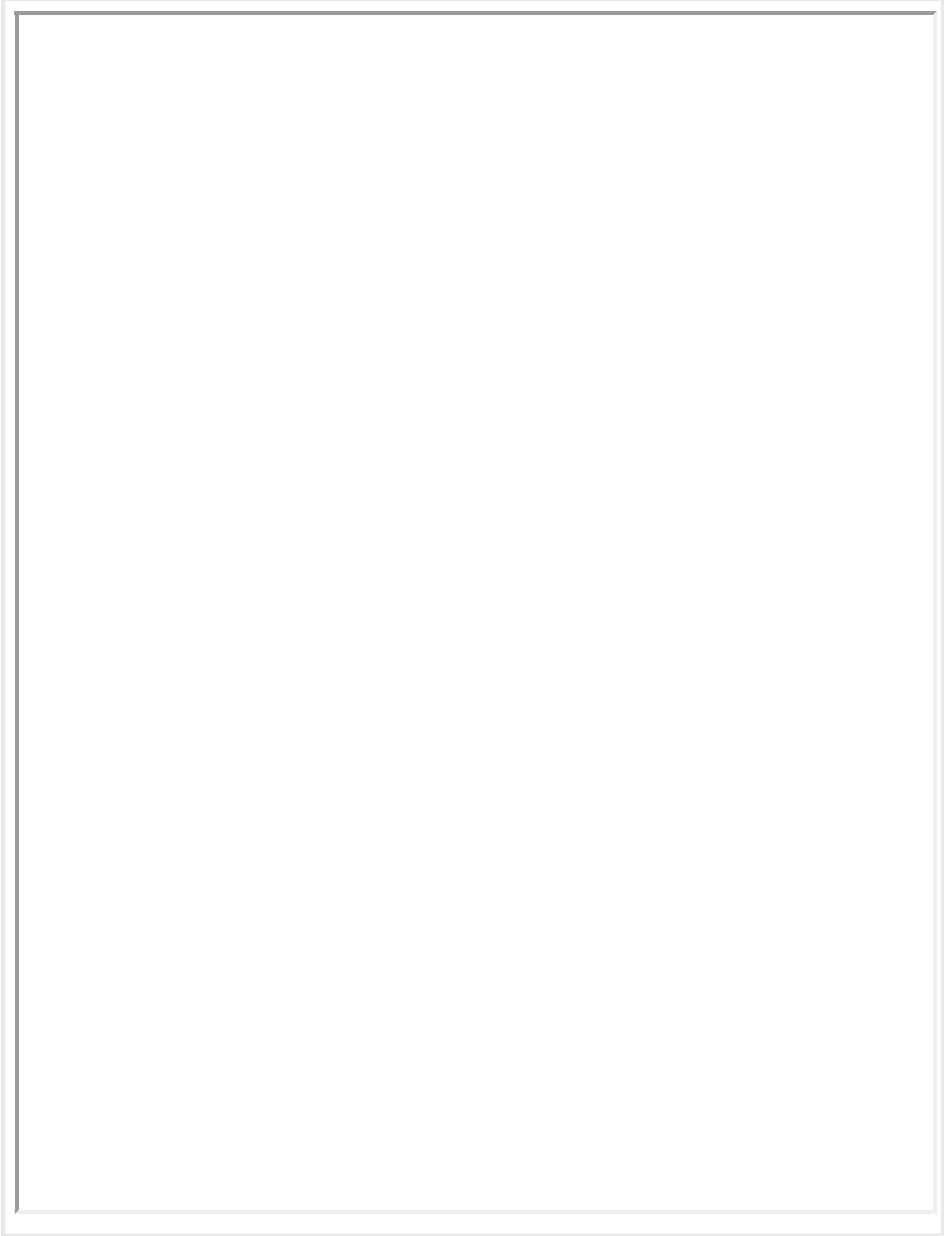
- **Orbit** - classical object in an orbit around another object, like the earth in an orbit around the sun. You can know both its position and momentum, that is, where it is and where it will be.
- **Orbital** - quantum object in an orbital where you have wave/particle duality and Heisenberg's uncertainty principle applies. You can not know both its position and momentum, and the orbital is a three dimensional probability function (ψ^2), which in this class we loosely define as where the electron has a 90% probability of being.



Video 6.5.2: 4'51" YouTube uploaded by Jared Owen on size of atoms and difference between an orbit and an orbital (https://youtu.be/ukGLH_NrFH8)

In this class we will define each orbital by a unique set of quantum numbers.

Phet Simulation



The above simulation can help us review the various approaches we have taken so far.

Quantum Numbers

Schrödinger's approach results in three quantum numbers that can be used to define an orbital (wave function), the principle (*n)*, azimuthal (*l*), and magnetic (m_l) quantum number. There is a fourth quantum number, the spin quantum number (m_s) and electrons can reside in orbitals that are defined by these four quantum numbers. Every electron in an atom must reside in an orbital that contains a unique set of quantum numbers.

Principle Quantum Number (n)

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{6.5.2}$$

As *n* increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of *n* are easier to remove from an atom. All wavefunctions that have the same value of *n* are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number *n* corresponds to the *n* used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels. As we will see, these can also be related to the periods of the periodic table.

Azimuthal Quantum Number (l)

The second quantum number is often called the **azimuthal quantum number (l)**. The value of *l* describes the *shape* of the region of space occupied by the electron. If you look at the standing waves in section 6.4.3.2 the value of l can be related to the number of nodes and so the first standing wave (n=1) has l=0 (there is no node).

The allowed values of *l* depend on the value of *n* and can range from 0 to *n* − 1:

$$l = 0, 1, 2, \ldots, n-1 \tag{6.5.3}$$

For example, if *n* = 1, l can be only 0; if *n* = 2, *l* can be 0 or 1; if n = 3, l can be 0,1, or 2; and so forth. For a given atom, all wavefunctions that have the same values of both *n* and *l* form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

In naming orbitals we often denote the azmuthial number with a symbol. l=0 is an s orbital, l = 1 is a p orbital, l=2 is a d orbital and l=3 is an f orbital.

Magnetic Quantum Number (m_l)

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field.

For each value of n there are 2l+1 values of m_l

The allowed values of m_l depend on the value of *l*: m_l can range from $-l$ to *l* in integral steps:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{6.5.4}$$

For example, if $l = 0$, m_l can be only 0; if *l* = 1, m_l can be −1, 0, or +1; and if *l* = 2, m_l can be −2, −1, 0, +1, or +2.

Each wavefunction with an allowed combination of *n*, *l*, and m_l values describes an atomic orbital, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

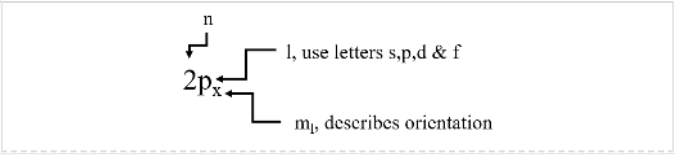
Spin Quantum Number

There is a fourth quantum number, which is the electron spin quantum number. The above three quantum numbers come from the solutions of the Schrödinger wave equation and describe the distance from the nucleus, the shape and orientation of the electronic orbitals that can exist for a hydrogen like atom. But there are actually two orbitals within each of these orbitals, and these result from the intrinsic spin of an electrons, which produces an intrinsic magnetic field. this will be covered in section 6.7 of this Chapter and is being mentioned now so that students realize up front, that there are really four quantum numbers that define the electronic orbitals of an atom.

It should be noted that in 1928 Paul Dirac developed a relativistic wave equation, the Dirac Equation, that was consistent with both quantum mechanics and the theory of special relativity, and not only accounted for all four quantum numbers, but even introduced the concept of antimatter. We will hold off on dealing with the spin quantum number until section 6.7.

Naming Orbitals

The first three quantum numbers define the geometric shapes of the orbitals and can be used to name them. The convention is to first indicate the principle quantum number (n), followed by a letter designating the azimuthal quantum number and then using a subscript to indicate the magnetic quantum number. The magnetic quantum number is often not specified. Note, the m_l value may be the true values (-3,-2,-1,0,+1,+2,+3), or as we will see in the next section, expressions within the x,y,z Cartesian coordinate system.



s: l=0
p: l=1
d: l=2
f: l=3

Number of Each Orbital

For each shell there are n orbitals. The following table shows the allowed orbitals for ground state configurations, for each shell (principle quantum number) you add an azimuthal orbital (the allowed values of l for each n are 0 to n-1), where l=0 is an s orbital, l=1 is a p, l=2 is a d....)

1s
2s, 2p
3s, 3p, 3d
4s, 4p, 4d, 4f
5s, 5p, 5d, 5f, 5g
6s, 6p, 6d, 6f, 6g, 6h
7s, 7p, 7d, 7f, 7g, 7h, 7i

As we shall see in the next Chapter, the structure of the periodic table is based on the filling of the orbitals in their lowest energy state, and the orbitals in orange (5g, 6g,6h,...) are of such high energy that electrons do not occupy them if the electron is in a ground state configuration.

Now because the are 2l+1 magnetic quantum numbers for each n, there are n2 potential orbitals for each principle quantum number

n= 1 as one s orbital = (1 total)
n=2 has one s and three p (4 total)
n=3 has one s, three p and 5 d (9 total)
n=4 has one s, three p, 5 d and 7 f (16 total)
....

***Table* 6.5.1:** *Values of n, l, and m_l through n = 4*

Table 6.5.1 summarizes the the first three quantum numbers for the values of n from 1 to 4.

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

Example6.5.1: n=4 Shell Structure

How many subshells and orbitals are contained within the principal shell with $n = 4$?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given $n = 4$, calculate the allowed values of l. From these allowed values, count the number of subshells.
B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n − 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of

m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to n^2:

Exercise 6.5.1

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer

3 subshells (s,p,d) and 9 orbitals (1 for l=0, 3 in p where l=1 and ml = -1, 0 and +1, and 5 for l=2 with ml = -2, -1, 0, +1 and +2)

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

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6.6: The Shapes of Atomic Orbitals

Introduction

In the previous section we learned that electrons have wave/particle duality, exist in orbitals that are defined by the Schrödinger wave equation that involves the complex coordinate system and imaginary numbers, and that they can be defined by quantum numbers n, l and m_l. We use the Greek symbol psi (ψ to represent a wave function. In this section we will look at the shapes of orbitals that have been transformed to the real coordinates of the x,y,z Cartesian coordinate system. The math of this transform is beyond the scope of this class, but for example, the $\Psi_{P_{+1}}$ and the $\Psi_{P_{-1}}$ orbitals can be combined in two ways that produce two new orbitals with real coordinates of the Cartesian coordinate system (the imaginary components of the wave functions cancel) the Ψ_{P_x} and Ψ_{P_y} orbitals. Since the original $\Psi_{P_{+1}}$ and $\Psi_{P_{+1}}$ were both solutions of the Schrödinger wave equation, their combinations are also solutions, and so we can visualize atomic orbitals as shapes along the x,y,z axes. All three quantum numbers influence the ultimate shape. The probability of finding an electron is ψ^2 and in the following representations we are implictily defining the orbitals as the square of the wavefunction.

$$1s \equiv \psi^2_{1s} \; and \; 2p_x \equiv \psi^2_{2p_x} \; and \; 3d_{xy} \equiv \psi^2_{3d_{xy}} \ldots .$$

So when we say 1s or $3d_{xz}$ we are orbital in terms of its location in space, and the images in Figure $6.6.1$ represents the shapes of some common orbitals where there is roughly a 90% probability of finding the electron that resides in that orbital.

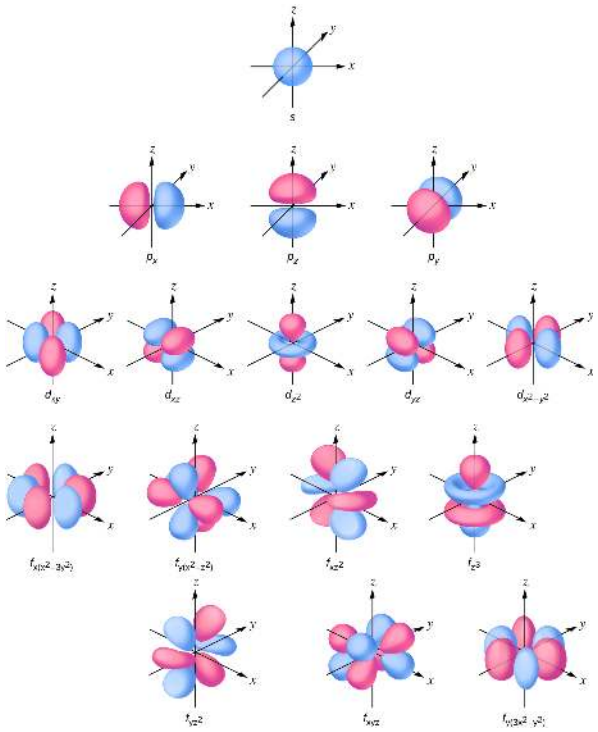


Figure 6.6.1: Select Cartesian coordinate visualizations of orbitals expressed in real space.

Note in Figure $6.6.1$ that there is one type of s orbital (l=0), three types of p (l=1), 5 types of d (l=2) and 7 types of d (l=3). These are not the orbitals described the the magnetic quantum numbers, but combinations of them that result in the x,y,z Cartesian coordinate system. It should also be indicated that these represent the geometry for the first principle quantum number where an azimuthal quantum number occurs, so for example, this is the s orbital of the first shell, the p orbital of the second shell, d orbital of the third shell and the f orbital of the fourth shell.

We will look at each of these in turn.

s-orbitals

For l=0 the electron density function is spherically symmetric and the 1s orbital has no nodes. Figure $6.6.2$ shows the square of the wavefunction

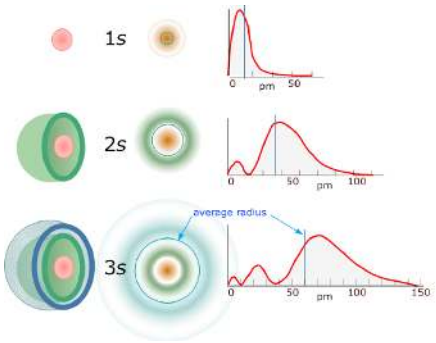


Figure 6.6.2: the radial distribution functions for the s orbitals of the first three principle quantum shells. This graph represents ψ_{ns}^2 for n=1,2 and 3 respectively.

As the principle quantum number increases both radial nodes occur and the average distance from the nucleus increases. The "onion skin" analogy has often been used to describe this where the flesh of the onion represents the probability of an electron exisiting (realize the greater r, the greater the surface area), and the nodes are the empty spaces between the layers of the onion. Of interest is that the higher principle quantum number has the peak of its inner peak closer to the nucleus (the first peak in the ψ_{3s}^2 is at a shorter radius than for the ψ_{2s} or ψ_{1s}.

Exercise 6.6.1

How many radial nodes would a 5s orbit have?

Answer

Four

p-orbitals

For the n=2 shell and greater there are three p orbitals. In the Cartesian coordinate the p_z correlates to the m_l=0 and the p_x and p_y are mathematical combinations of the m_l = +1 and m_l = -1. (Note, the terms p_x, p_y and p_z actually relate to the wavefunctions squared, as indicated above. For n=2 there is one node, in fact it is a nodal plane. If you look at the name, you can see that these are radially symmetric along one axis, which is the axis of the name, and the nodal plane is defined by the other two axes where they go through the origin.

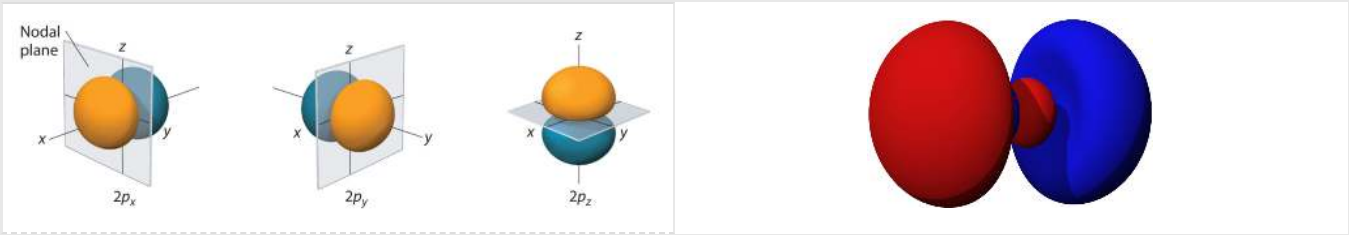
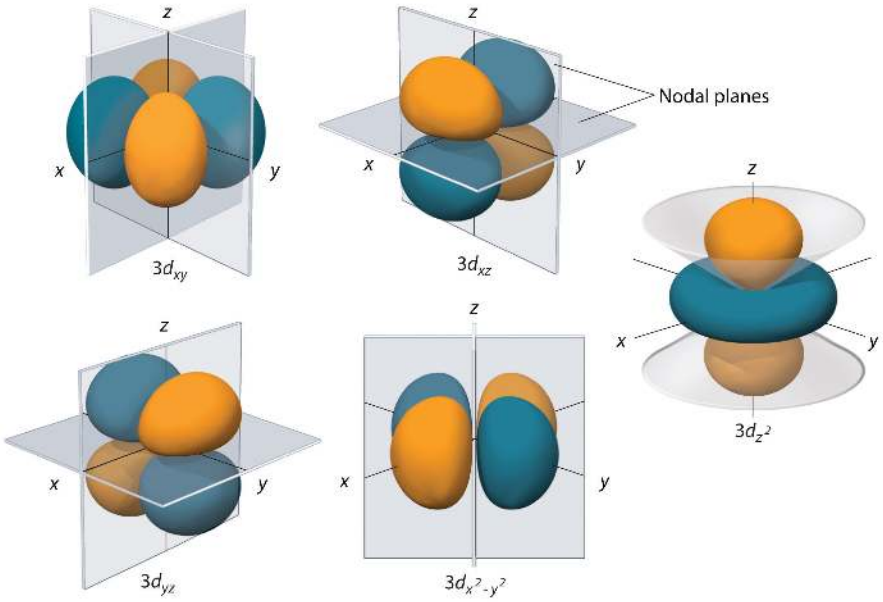


Figure 6.6.3: 2 p orbitals along the x, y and z axes (left) and a 3 p orbital (right).

Just as for s orbitals, as you move to higher principle quantum numbers the number of nodal surfaces increases, but they are no longer simple planar surfaces (see Figure 6.6.3).

d-orbitals

Starting with the third principle quantum number d orbitals form, and there are 5 of these. Once again we are looking at ones that are defined by the Cartesian coordinate system. You will note that the 3 d orbits have two nodal surfaces.



Three of the d-orbitals (d_{xy}, d_{xz}, and d_{yz}) have electron density between two axes, with the nodal planes being the plane defined by the axes in the name with the remaining axes. So in the case of d_{xy}, the nodal planes are the xz and yz planes. The $d_{x^2-y^2}$ has electron density along the x and y axes, with the nodal planes being at 45 degrees to those axes. The d_{z^2} orbital has to conical surfaces with electron density forming in a lobe like a P orbital along the z axes, and a donut-like ring around the xy plane. Just as with the other orbitals, as number of nodal surfaces increases as you increase n.

Exercise 6.6.2

What are the nodal planes for the d_{xy} orbital?

Answer

The xz and yz planes

f-orbitals

There are seven f orbitals and these are the most complicated. As you have probably Figured by now, the first f orbitals appear in the n=4 "shell," and they have three nodal surfaces. ULAR students will not be required to know the names or shapes of the F orbitals, and the following embedded application from ChemTube3D can give you a feel for the f orbitals .

Embedded Webpage from ChemTube 3D at the University of Liverpool. The direct link is https://www.chemtube3d.com/, if you click "Structure and Bonding/ atomic orbitals" you can look at the 3d structures of additional orbitals.

Contributors and Attributions

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6.7: Electron Spin and the Pauli Exclusion Principle

Introduction

In section 6.5.2.4 we introduced the spin quantum number and we now want to take a deeper look into why an electron needs one more quantum number to describe its wave function.

Stern-Gerlach Experiment

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n, l, and m_l. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart, as is demonstrated by the Stern-Gerlach apparatus of Figure 6.7.1.

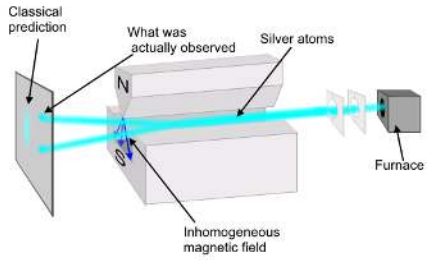


Figure 6.7.1: The Stern-Gerlach apparatus. Image used with permission from Wikipedi

In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called **electron spin**.

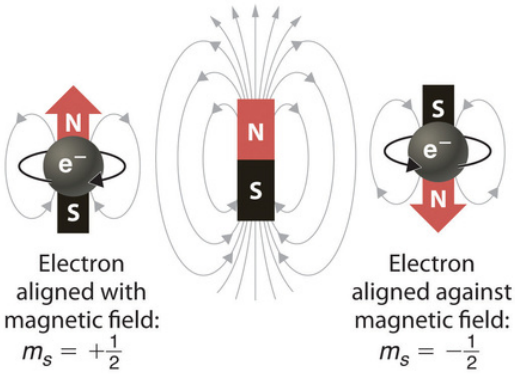


Figure 6.7.2: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure Figure 6.7.2). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated +½ (up) and −½ (down) to indicate that the two orientations are opposites; the subscript *s* is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

Pauli Exclusion Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principle: *No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).*

Note: Pauli Exclusion Principle

No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).

By giving the values of n, l, and m_l, we also specify a particular orbital (e.g., 1s with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or −½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

Example 6.7.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2p orbital and predict the maximum number of electrons the 2p subshell can accommodate.

Solution

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to an n = 2p orbital. List all allowed combinations of (n, l, m_l).
B. Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the 2p subshell can accommodate.

Solution:

A For a 2p orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1), \ldots, (l - 1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, −1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and −½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, −½), (2, 1, 0, +½), (2, 1, 0, −½), (2, 1, −1, +½), and (2, 1, −1, −½).

C Hence the 2p subshell, which consists of three 2p orbitals (2p_x, 2p_y, and 2p_z), can contain a total of six electrons, two in each orbital.

Exercise 6.7.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6s orbital, and predict the total number of electrons it can contain.

Answer

(6, 0, 0, +½), (6, 0, 0, −½); two electrons

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CHAPTER OVERVIEW

7: The Structure of Atoms and Periodic Trends

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Topic hierarchy

7.1: Orbitals of Polyelectronic Atoms
7.2: Electron Configurations of Atoms and Monatomic Ions
7.3: Atomic Properties and Periodic Trends

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7.1: Orbitals of Polyelectronic Atoms

Introduction

In the previous Chapter we learned that there are three types of orbitals for the Schrödinger wave equation solution of the hydrogen like atom that can be described by the three quantum numbers; n, l and m_l. We also learned that an electron in an orbital can have one of two spin states, which provided a fourth quantum number, the spin quantum number m_s. When there is only one electron the only interaction is between the electron and the nucleolus and so all the energies of a each principle quantum number are degenerate, that is of the same energy (left side of Figure 7.1.1). It is because of this that the Bohr model works for hydrogen atom, and each principle quantum number is often referred to as an electron shell, and in this text we will use these terms interchangeably. Once you have a multi-electron system though, you start to get electron - electron interactions in addition to electron-nucleus interactions, and all of these interactions are influenced by the shapes and of the orbitals. And so in the multi-electron system there is a lifting of the degeneracy of the azimuthal orbitals and the Bohr model no longer works (left side of Figure 7.1.1).

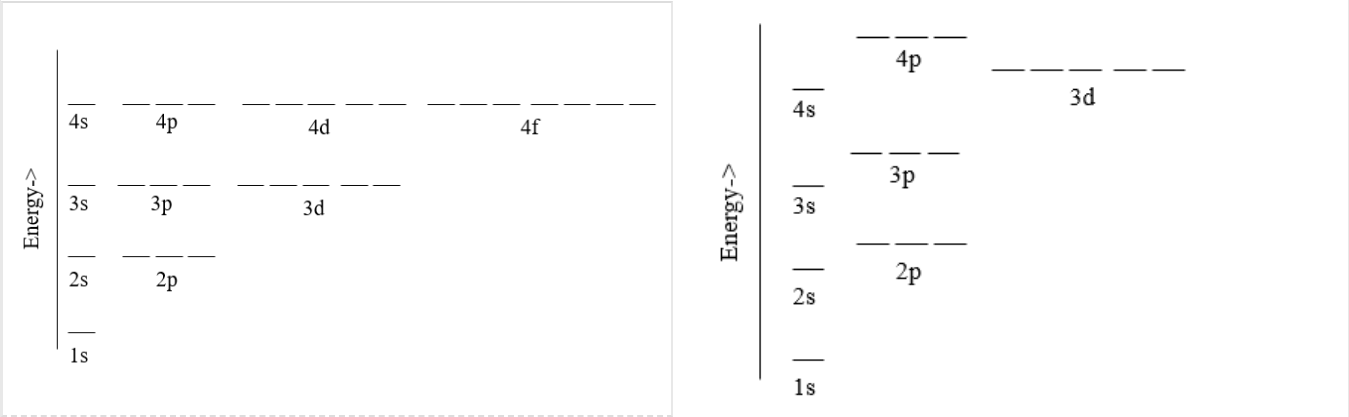


Figure 7.1.1: For hydrogen where there is only one electron all the azimuthal orbitals are degenerate (of equal energy) and so the Bohr model works. For the multielectron atom there are electron-electron interactions in addition to electron-nucleus interactions and these are influenced by the shapes of the orbitals and so the Bohr model breaks down due to a lifting of the degeneracy of the azimuthal orbitals.

This results in the different blocks of the periodic table (Figure 7.1.1. In the presence of an external magnetic field there is a further lifting of the degeneracy of the magnetic quantum numbers (m_l), with some showing no change in the energy of the azimuthal orbital (m_l=0), some showing an increase in energy as they align with the external magnetic field (m_l=+1, +2 ....), and others showing a decrease in energy as there align against the external magnetic fields (m_l=-1, -2, ...). It should be noted that due to conservation of energy, the amount of energy gained by the positive m_l is of the same magnitude as the amount lost by the respective negative m_l. This can be observed in the line spectra of the atoms when they are in the presence of an external magnetic field, and the magnitude of the split is dependent on the strength of the external field.

Periodic Table and Orbitals

The structure of the periodic table actually depends on the types of orbitals being filled with electrons for elements in the lowest energy electron configurations, which we call the ground state. We can define different regions by the types of orbitals electrons reside in, for example the alkali and alkaline earth metals are often referred to as the s-block as the outer (valence) shell electrons are filling the s orbitals of that shell (principle quantum number). So for Li and Be one and two electrons are filling the 2s orbital, while for Na and Mg they are filling the 3s orbitals. It should be noted that when you have more than one electron in an orbital they must have opposite spins (different spin quantum numbers). For these region each orbital can hold up to two electrons. Figure 7.1.1 shows the different blocks based on the azimuthal quantum numbers. Note, as discussed in section 6.5.5, the first s orbital is in the n=1 shell, the first p orbital is in the n=2 shell, the first d orbital is in the n=3 and the first f orbital is in the n=4 shell, where we are using the concept of "shell" to align with the principle quantum number. Also note, there are 1 type of s, 3 types of p, 5 types of d and 7 types of f orbitals, and as discussed above, since there are two spin quantum states (numbers) for each orbital, there can be up to two electrons in an orbital. Because of this there are two atoms for each shell in the s block, 6 atoms in the p block (that has 3 orbitals), 10 atoms in the d block (that has 5 orbitals) and 14 atoms in the f block (that has 7 orbtials).

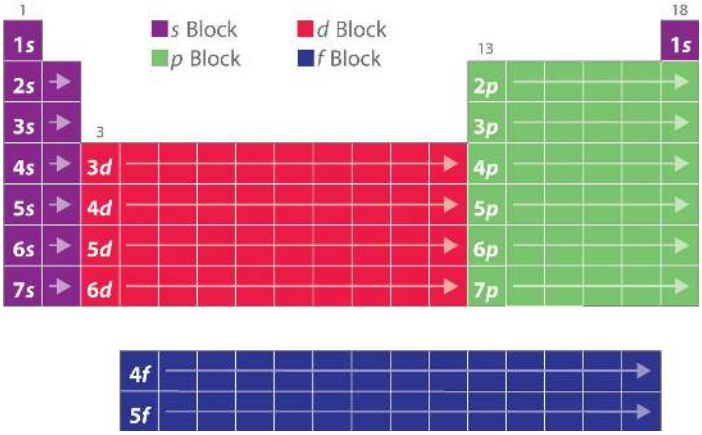


Figure 7.1.2: Color coding of the different blocks of the periodic table in terms of the types of orbitals being filled.

On closer inspection it can be noted that the 4s orbitals are filled before the 3d. Why is this, when electrons in shells of higher the principle quantum numbers are further away from the nucleus, and so feel less of an attraction? While it is true that a 4s orbital is further away from the nucleus, it is also closer. To understand this we must remember that an electron has wave-particle duality and we need to look at its radial probability function ψ^2 (Figure 7.1.3). What you see is that the 4s orbital has 3 nodes with 4 regions where there is a probability the electron can occur and the inner lobe is closer to the nucleus than the corresponding probability function for the d orbital. But note, most of the 4s orbital is farther away from the nucleus and so its average "radius" is farther away from the nuclues than the 3d.



Figure 7.1.3: radial distribution function shows 4s orbital penetrating 3d, and so an electron in the 4s orbital is both nearer and further from the nucleus than a 3d. (image cc 4.0 from chemistry stack exchange uploaded by orthocresol)

Now things get complicated real quick as for example 6p will penetrate a 4f, and a 7s penetrates both 5f and 6d orbitals.

n+1 Rule: Order of increasing energy for subshells. The order of filling orbitals is they go in order of increasing n+l value (remember l=0 for s, not one), and if two orbitals have the same value like 2p (2+1=3) and 3s (3+0=3), the one with the lower n is filled first. Fortunately there is an easy mnemonic device for remembering both which orbitals exist and their energies. In section 6.5.5 we built a table like that of Figure 7.1.4 and then moving diagonally downwards we come up with the way the orbitals are filled in the periodic table. So you see that the 4s are filled before the 3d, and for example the 5p is filled before the 4f.

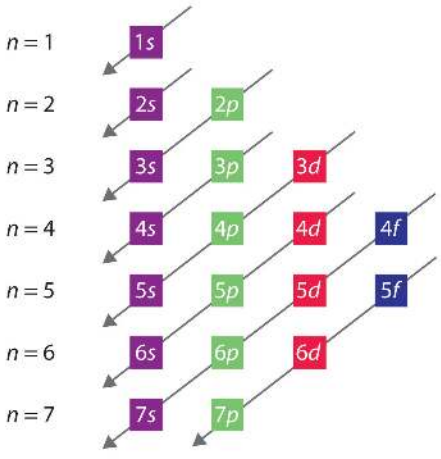


Figure 7.1.4: Mnemonic device for memorizing the energies of the orbitals by following the diagnols of the arrows as displayed.

Note how the color coding of the blocks in Figure 7.1.4 correlates to the structure of the periodic table as indicated in Figure 7.1.2

Exercise 7.1.1

Rank the following subshells in order of increasing energy, 3d,4s,4f,6s & 5d

Answer

3d = (3+2) = 5
4s = (4+0) = 4
4f = (4+3) = 7
6s = (6+0) = 6
5d = (5+2)=7

So: 4s<3d<6s<4f<5d note, both 4f and 5d have n+l values = 7, so 4f is filled first because it is the lower principle quantum number.

Representing Orbital Occupancies

In section 6.5.3 we introduced the convention for naming orbitals where the orbital represented by ψ^2_{1s} would be represented by 1s, and now we used post superscripts to indicate the number of electrons in an orbital. Figure 7.1.5 shows the ground state configuration of hydrogen, which would have only one electron in a 1s orbital

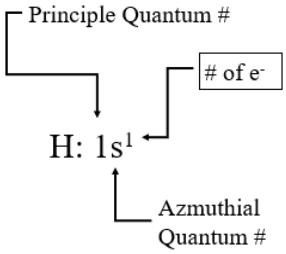


Figure 7.1.5: Convention for showing number of electrons in an orbital.

If the magnetic quantum number or the specific azimuthal orbital is indicated then the maximum number of electrons that can be in an orbital is two, but if just the azimuthal orbital is indicated, you can have more than two electrons (up to 6 for p, up to 10 for d and up to 14 for f orbitals). For example $4p^5$ means we have 5 electrons in the three 4p orbitals (p_x, p_y and p_z) of which two orbitals have paired electrons of opposite spin and one has a lone unpaired electron. If we wrote $4p^5{}_x$ it would be wrong and nonsense, as according to the Pauli Exclusion principle (section 6.7.3) there can only be one or two electrons in the px orbital, and they must have opposite spin.

So $4p^5$ implies one of three possible configurations, where the unpaired electron is expressed in red:

$$4p_x^2 4p_y^2 4p_z$$

or

$$4p_x^2 4p_y 4p_z^2$$

or

$$4p_x 4p_y^2 4p_z^2$$

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

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7.2: Electron Configurations of Atoms and Monatomic Ions

Introduction

In this section we shall assign electrons to orbitals and come up with some rules to determine the ground state electron configuration of atoms of the different elements. The ground state configuration is the lowest energy configuration, and the ground state electron configuration affects the behavior of atoms and results in the elemental structure of the periodic table. For example, all the alkali metals have "isoelectronic" valence shell electron configurations. That means their outer shells have similar numbers of electrons in similar orbitals, which for the alkali metals have a ns^1 electron configuration, where n is the outer (valence) shell. Because of this they behave similarly, and for example, can easily lose the outer electron and form a cation of charge [+1].

It should be emphasized that the electron configurations we are describing are the ground state or lowest energy state configuration. In real systems atoms contain energy and electrons can exist in excited states, so you will have populations of atoms in different states, and these atoms will be perpetually changing states as they exchange energy with each other and the surrounding. At higher temperatures there will be more atoms in excited states. These atoms will relax back to the ground state, by either transferring thermal energy to other atoms or giving off a photon (radiative relaxation), and it was these radiative process that resulted in the atomic line spectra of the last Chapter.

Rule of Determining Electron Configurations

The following rules allow us to determine the ground state electron configuration, which is what we imply when we say "electron configuration". That is, unless otherwise stated, an electron configuration implicitly refers to the ground state. You first determine the number of electrons in the atom (or ion) and then assign them to orbitals according to the following principles or rules.

1. Aufbau Principle
2. Hunds Rule of Maximum Multiplicity
3. Pauli Exlusion Priniciple

Aufbau Principle

Aufbau comes from the German "structure" or building up and *Aufbauprinzip*, is the "building up principle" where we assign electrons to the lowest energy orbitals first, and then successively add them to higher energy orbitals until we run out of electrons. This way the electron configuration is that of the lowest energy and so the Aufbau principle results in the ground state electron configuration. There are times when special attention needs to be given to the electron configurations and it may appear the Aufbau principle is not being obeyed, but it is. For example, it is for this reason that the 4s gets filled before the 3d, because as we noted in Figure 7.1.3 of section 7.1.2 the 4s orbital penetrates the 3d and although its average distance from the nucleus is greater than the 3d, when it's probability density is defined by the inner lobes of the wavefunction, it is closer to the nucleus and thus is of lower energy.

Hund's Rule

Hund's Rule of Maximum Multiplicity states that if you are filling degenerate orbitals that you put one electron in each before placing two electrons in one orbital, and they are assigned parallel spin (left configuration of Figure 7.2.1). There are two factors going on here. First, electron-electron repulsion will cause the orbitals to be as far apart as possible, and so the configuration on the right part of Figure is the highest energy because the electrons are in the same orbital. The image on the left is lower in energy than the middle one due to magnetic interactions (you can visualize the arrow to point in the direction the magnetic force would interact). In the middle image the two magnetic fields are in opposite directions and so are working against each other, making that a higher energy state. In fact, if you place two identical magnets on top of each other (right most image) they will cancel each other out. The image on the left is the lowest energy because the are both far apart and the magnetic fields of the intrinsic spin of the electron align, and so that is the ground state. The other two states are allowed, and are called excited states because they are at a higher energy level than the ground state.

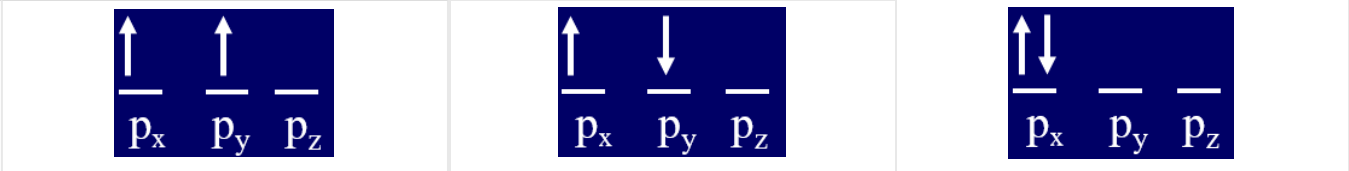


Figure 7.2.1: Three possible spin alignments for placing two electrons in the three degenerate p orbitals. The configuration on the left is the lowest energy state, the two on the right are allowed states, but are "excited states."

Hunds Rule is called Hunds Rule of Maximum Multiplicity because the spectral lines on the left configuration of Figure 7.2.1 will split into three lines in the presence of an external magnetic field. This is because for an ensemble of atoms some will have their magnetic moments perpendicular to an external magnetic field (no effect), some aligned with it, and others aligned against it, and Hunds rule states that the electron configuration that has maximizes the number of lines is the lowest energy state. So spin states of electrons can be seen through their interactions with magnetic fields and this shows in their spectra.

Note, there is a fourth possible configuration, which is with both electrons in the same orbital with the same spin, and that is not allowed because of the Pauli Exclusion principle.

Pauli Exclusion Principle

The Pauli Exclusion Principle states that no two electrons can have the same set of 4 quantum numbers, and thus if two electrons are in the same electronic they must have opposite spin quantum numbers

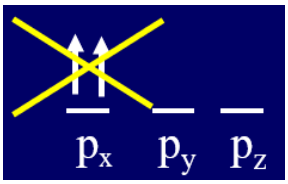


Figure 7.2.2: *A forbidden electron configuration due to the Pauli Exclusion Principle*

Note, the three configurations of Figure 7.2.1 are allowed, with the left-most one correlating with the ground state, while the configuration on 7.2.2 is forbidden and not allowed. So Hund's rule tells you which of these allowed states is lowest in energy, while the Pauli Exclusion principle defines configurations that can not exist, and excludes them as options.

Electron Configurations

Starting with the first row we get the following electron configurations for hydrogen and helium, noting how the coupled electrons in helium are spin paired (in opposite directions) according to the Pauli Exclusion principle

H: 2*p* ⎯ ⎯ ⎯ 2*s* ⎯ 1*s* ↑	He: 2*p* ⎯ ⎯ ⎯ 2*s* ⎯ 1*s* ↑↓
H: $1s^1$	H: $1s^2$

For the second period we start by filling the 2s orbitals, now the first shell is a core shell and the second is the valence, and we often use the Nobel gas to indicate the core electron configuration (which is that of Helium in this case). This second convention is often not used in the second period, but is used extensively when the number of core electrons becomes excessive.

Li: 2*p* ⎯ ⎯ ⎯ 2*s* ↑ 1*s* ↑↓	Be: 2*p* ⎯ ⎯ ⎯ 2*s* ↑↓ 1*s* ↑↓
Li: $1s^2 2s^1$ or [He]$2s^1$	Be: $1s^2 2s^2$ or [He]$2s^2$

After filling the 2s the 2p are filled, in accordance with the Aufbau principle and Hund's rule.

B: 2*p* ↑ ⎯ ⎯ 2*s* ↑↓ 1*s* ↑↓	C: 2*p* ↑ ↑ ⎯ 2*s* ↑↓ 1*s* ↑↓	N: 2*p* ↑ ↑ ↑ 2*s* ↑↓ 1*s* ↑↓
B: $1s^2 2s^2 2p^1$ or [He]$2s^2 2p^1$	C: $1s^2 2s^2 2p^2$ or [He]$2s^2 2p^2$	N: $1s^2 2s^2 2p^3$ or [He]$2s^2 2p^3$

O: 2p ↑↓ ↑ ↑ 2s ↑↓ 1s ↑↓	F: 2p ↑↓ ↑↓ ↑ 2s ↑↓ 1s ↑↓	Ne: 2p ↑↓ ↑↓ ↑↓ 2s ↑↓ 1s ↑↓
O: $1s^2 2s^2 2p^4$ or $[He]2s^2 2p^4$	B: $1s^2 2s^2 2p^5$ or $[He]2s^2 2p^5$	B: $1s^2 2s^2 2p^6$ or $[He]2s^2 2p^6$

We note above that in accordance with Hund's rule each of the degenerate p orbitals were given 1 electron until they were all filled, and we started pairing up electrons with oxygen. The next element would be sodium, the alkali metal of the third period. With an atomic number of 11 sodium has 10 electrons and at this point the value of using the shorthand notation where a Nobel gas represents the core electrons is of obvious values. That is, you could write Na: $1s^2 2s^2 2p^6 3s^1$ or $[Ne]3s^1$ noting that $[Ne]=1s^2 2s^2 2p^6$.

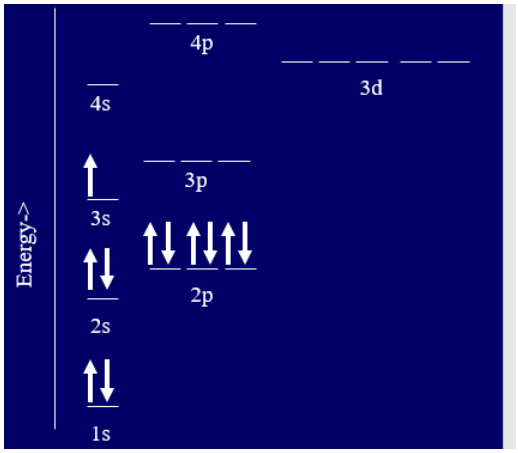


Figure 7.2.3: For sodium it is better to use the convention of expressing the core electrons with that of a Nobel gas.

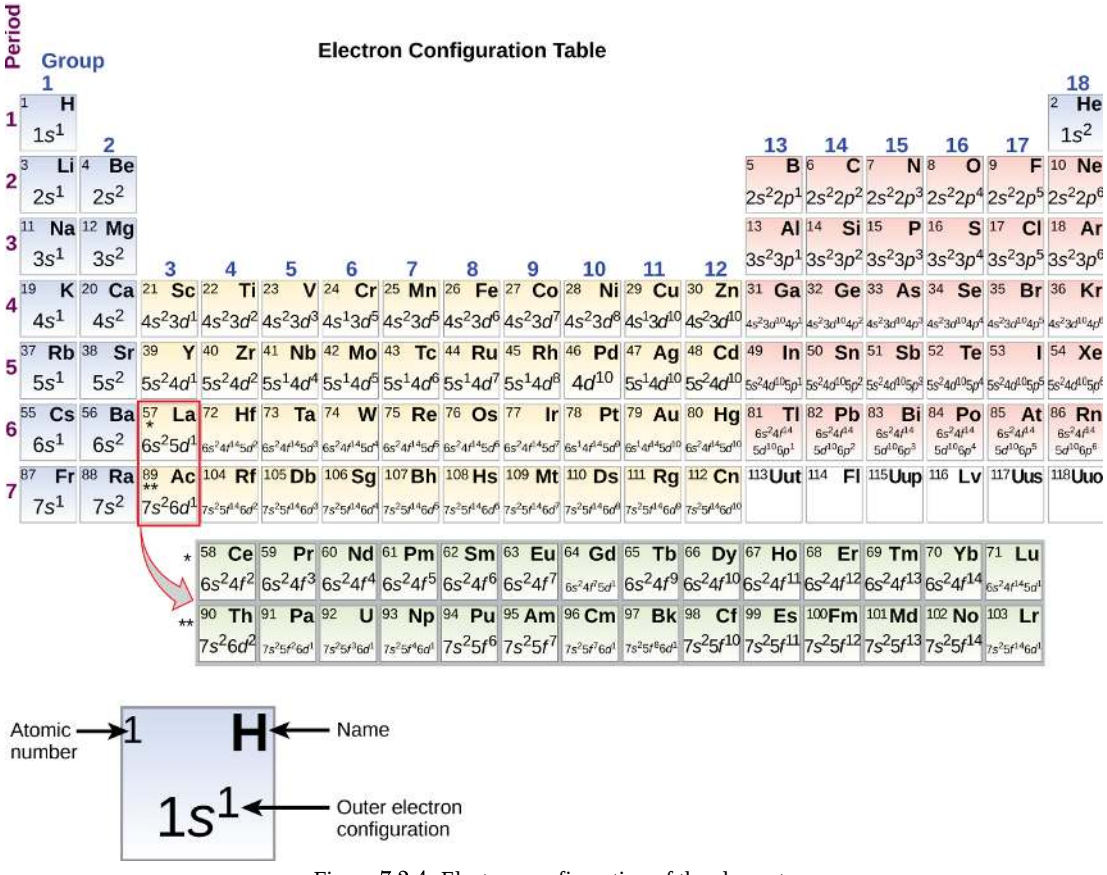


Figure 7.2.4: Electron configuration of the elements

Lets look at the electron configurations of the representative elements (s and p block)

Table 7.2.1: Electron configuration of representative elements

Group IIIA	Group IVA
[ ]$ns^2 2p^1$	[ ]$ns^2 np^2$

From table 7.2.1 [ ] indicates core electrons (not noble gas configuration) and it is clear that elements of a family have similar electron configurations for the outer shell, just a different principle quantum number.

Special Cases

Some of the transition elements have electron configurations that are not what you would expect based on the material presented in section 7.1.

Chromium:

$$Cr: \ [Ar]4s^1 3d^5 \tag{7.2.1}$$

This may seen strange, but if you look at the spin pairing energy all 6 spins are aligned, while if you just walked through the pattern, you would come up with $4s^2 3d^4$ and what is going on is that the gap between the 4s and 3d is so small that the spin pairing energy is greater. Also, this configuration is entirely symmetric which also influences its stability (there are no empty orbitals and they all have the one electron). The same logic goes for Molybdenium

Molybdenium:

$$Mo: \ [Kr]5s^1 4d^5 \tag{7.2.2}$$

Copper and Silver also show these kind of anomalies

Copper:

$$Cu: \ [Ar]4s^1 3d^{10} \tag{7.2.3}$$

Silver:

$$Ag: \ [Kr]5s^1 4d^{10} \tag{7.2.4}$$

Here there is extra stability being gained by having a completely filled subshell.

> **Note**
>
> UALR students are expected to know the electron configurations for chromium, molybdenium, copper and silver, and give a rough explanation of why the are not as would have been predicted if we just blindly followed the rules outline above.

Palladium has a filled 4d and empty 5s while Nickel has the configuration you would expect

Palladium:

$$Pd: \ [Kr]4d^{10} \tag{7.2.5}$$

Nickel:

$$Ni: \ [Ar]4s^{2}3d^{8} \tag{7.2.6}$$

Niobium is also not as would be predicted, and once again this is dealing with the fact that the 5s and 4d orbits are real close in energy, and the gap is of the order of the spin pairing energy.Niobium:

$$Nb: \ [Kr]5s^{1}4d^{4} \tag{7.2.7}$$

Exercise 7.2.1

Write the ground state electron configuration of yttrium in both the long format and the short nobel gas format.

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^1$
$[Kr]5s^2\ 4d^1$

Exercise 7.2.2

Write the electron configurations of:

a. Argon
b. Krypton
c. Radon
d. Silver

Answer a

$[Ne]\ 3s^2\ 3p^6$

Answer b

$[Ar]\ 4s^2\ 3d^{10}\ 4p^6$

Answer c

$[Xe]\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$

Answer d

$[Kr]\ 5s^1\ 4d^{10}$

Exercise 7.2.3

How many unpaired electrons are in:

a. Vanadium
b. Chromium
c. Iron
d. Copper

Answer a

Three in the 3d orbitals ($[Ar]\ 4s^2\ 3d^3$)

Answer b

six, 5 in the 3d and one in the 4s ($[Ar]\ 4s^1\ 3d^5$)

Answer c

four, in the 3d ([Ar] $4s^2$ $3d^6$)

Answer d

one in the 4s ([Ar] $4s^1$ $3d^{10}$)

Electron Configurations of Ions

Anions

Electron configuration of anions is pretty straight forward. You simply have additional electrons to the neutral atom, and add them the same way you would for an atom. Note, although monatomic anions are isoelectronic to a nobel gas, (chloride has the same electron configuration as Argon), you write down the electrons of its valence shell. So chloride's configuration is C^{l-}: [Ne]$3s^2 3p^6$ and not [Ar].

Cations

For cations you need to be careful and the electron comes from the highest principle quantum shell. So calcium and Titanium(II) have the same number of electrons, but they have different electron configurations (they are not isoelectronic).

Calcium (20 electrons):

$$Ca: \ [Ar]4s^2 \tag{7.2.8}$$

Titanium(II) (20 electrons):

$$Ti^{+2}: \ [Ar]3d^2 \tag{7.2.9}$$

The reasoning can be seen by the radial wavefunction density plot (Figure 7.2.5).



Figure 7.2.5: You note the 4s orbital has density that is both closer and farther from the nuclues than the 3d. For this reason the 4d gets filled before the 3d when building up an electron configuration along the lines of the aufbau principle. But when you remove an electron to form a cation, the 42 is also farther away from the nuclues, and so is easier to remove. This is a consquence that an electronic orbital is described by a wavefunction. (image cc 4.0 from chemistry stack exchange uploaded by orthocresol)

Exercise 7.2.4

Using noble gas shorthand notation, write the electron configurations of:

a. chloride
b. potassium cation
c. iron (II) and iron (III) (ferrous and ferric)
d. lead(II) and lead (IV) (plumbous and plumbic)

Answer a

[Ne] $3s^2$ $3p^6$

Answer b

[Ar]

Answer c

[Ar] $3d^6$ and [Ar] $3d^5 5$

Answer d

[Xe] $6s^2$ $4f^{14}$ $5d^{10}$ and [Xe] $4f^{14}$ $5d^{10}$

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

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7.3: Atomic Properties and Periodic Trends

Introduction

Now that we have an understanding of the electron configurations of the periodic table we are ready to tackle periodic trends in atomic properties. This is a very important section as it will allow us to predict behavior of atoms of the various elements. For example, if two ions have the same charge, the smaller ion forms a stronger bond because it can get closer to the counter ion. So knowing the radius of ions can help us predict ionic bond strengths.

Atomic Radius

The atomic radius is generally stated as being the total distance from an atom's nucleus to the outermost orbital of its electrons. In simpler terms, it can be defined as something similar to the radius of a circle, where the center of the circle is the nucleus and the outer edge of the circle is the outermost orbital of electron. As you begin to move across or down the periodic table, trends emerge that help explain how atomic radii change. With the exception of the 1s orbitals the nuclear charge the valence shell electrons feel is not the full nuclear charge (Z), but a reduced charge due to shielding caused by the negative charge of the inner shell (core) electrons. We call this the **effective nuclear charge**, (Z_{eff}).

$$Z_{eff} < Z_{real} \tag{7.3.1}$$

We shall see that this effective nuclear charge influences the size of an atom or ion.

Now determining the size of an atom is actually impossible because according to the Heisenberg Uncertainty Principle we never really know where an electron is, and is going at the same time. But if we look at two bonded atoms we can approximate the size by looking at the distances between the atoms, that is, by looking at bond lengths we can get an approximation of the size of the atoms. We will take two approaches based on the type of bond.

Covalent Radius

When a covalent bond is present between two identical atoms, the covalent radius can be determined. When two atoms of the same element are covalently bonded, the radius of each atom will be half the distance between the two nuclei because they equally attract the electrons. The distance between two nuclei will give the diameter of an atom, and the covalent radius is half this diameter.

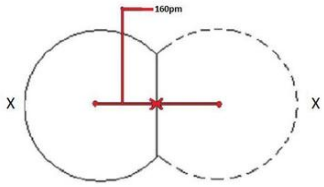


Figure 7.3.1: Covalent radii is one half the distance between two nuclei for a homonuclear bond.

Some compounds like the noble gasses do not form bonds and you can cool them down until they form a solid, and measure the difference between them, which is know as the Van der Waals atomic radius



Figure 7.3.2: On left is the covalent atomic radius of chlorine, on the right is the van der Waals atomic radi which comes from solid chlorine. These are not necessarily equal

Ionic Radius

Ionic radius are more complicated because the anion and cation are often of vastly different sizes. Now as we shall see, anions are larger than neutral molecules because they gain electrons, and metals are smaller than neutral atoms because they lose electrons. So

it is very common for the anion to be larger than the cation. As we shall see in Chapter 12 (section 12.2) of the second semester we can determine the size of ionic ions by looking at the structure of their crystal lattice. What is important to note here is that you can not use the internuclear distance as you can with covalent bonds, because the ion sizes are not equal.

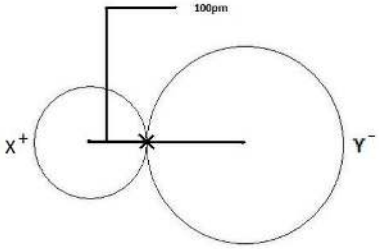


Figure 7.3.3: Ionic radii of cation and anion are not necessarily equal

Metallic Radius

At first glance you would think you could predict metallic radii the same way you do for covalent, that it would be one half the distance between two metal atoms. As we will learn in Chapter 12 (section 12.1) metals form a variety of different crystal lattice structures and in section 12.1.2 we will learn how to calculate the atomic radii of a metal atom for three different crystal structures. If the metals touch edge to edge along an axis then the atomic radius is one half the distance between the nuclei (as in Figure 7.3.1).

Periodic Trends in Atomic Radius

There are two general periodic trends in atomic radii. The radii increase as you go down a group, and decrease as you go across a period. These trends are shown in Figures 7.3.4 and 7.3.5

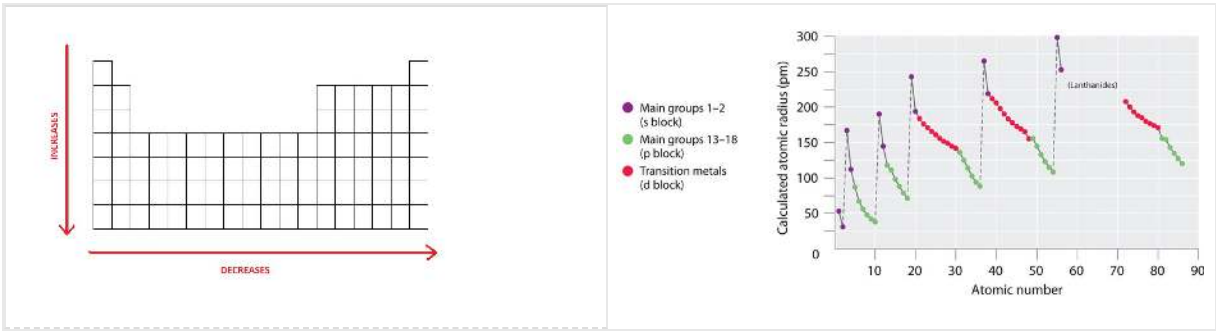


Figure 7.3.4: *On left is the general periodic trend for atomic radius and on the right are group trends.*

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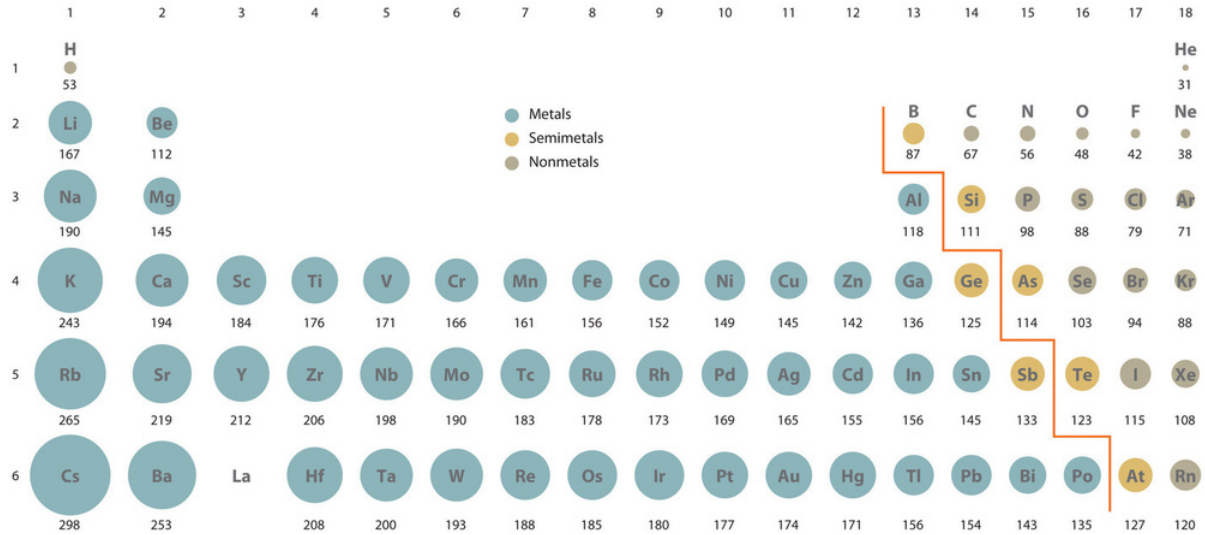


Figure 7.3.5: *Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: http://www.webelements.com. Web Elements is an excellent online source for looking up atomic properties.*

Trend 1: Increased radii going down a group. This one is easy to see, as in going down a group the principle quantum number goes up and you are effectively adding a new shell. It should be noted that valence shells have isoelectronic electron configurations (bottom row of table 7.2.1.) and you are increasing the number of filled core shells. This increase in the number of core electrons results in a larger radii for the valence electrons.

Trend 2: Decreased radii going across a period. This trend takes a bit more thought, but you are changing the valence shell electron configuration while maintaining the same core electron configuration. Core electrons spend more time between valence electrons and the nucleus and so are better at shielding. That is, when a core electron is between a valence electron and the nucleus the valence electron the magnitude of the positive charge the valence electron feels is diminished, and so the effective nuclear charge is decreased. Electrons in the same "shell" repel each other and so fill it in a manner where they are as far apart as possible, and so are not as effective at shielding each other as core electrons. So as you go across a period you increase both the number protons and electrons, but the electrons within a shell are dispersed in a manner that they do not shield each other effectively, and so the effective nuclear charge goes up.

$$\underbrace{Z_{Eff}}_{\substack{Effective\\Nuclear\\Charge}} = \underbrace{Z_{Real}}_{\substack{Actual\\Nuclear\\Charge}} - \underbrace{S}_{\substack{Shielding\\by\ core\\electrons*}} \tag{7.3.2}$$

*NOTE: This is not saying that valence shell electrons do not shield each other, you need to look at the shape of the wave function and you can see that valence electrons actually do penetrate core orbitals (Figure 7.3.6, but that core electrons are much better at shielding valence electrons, and so as you go across a periodic table the electrons feel a greater effective nuclear charge, which pulls them in tighter and decreases the radius.

Exercise 7.3.1

Arrange these atoms in order of decreasing radii and explain why; Si, Cl, Mg, F, Ca

Answer

Answer: Ca > Mg > Si> Cl>F.

Explanation:

- Ca > Mg because it has a higher principle quantum number (higher shell is further from nucleus)
- Mg > Si because Si has has greater Z_{Eff} and is thus smaller
- Si > Cl because Cl has greater Z_{Eff} and is thus smaller
- Cl > F because it has a higher principle quantum number (higher shell is further from nucleus)

When you change periods (add both a proton and an electron to a Nobel gas) you form an alkali metal and there is a huge increase in atomic size because now you have completely filled a shell). That is for example, The six 3p orbitals of argon do not effectively shield each other because they are in the valence shell, but they very effectively shield the 4s orbital of potassium, and so there is a huge increase in the radii as you move from argon to potassium.

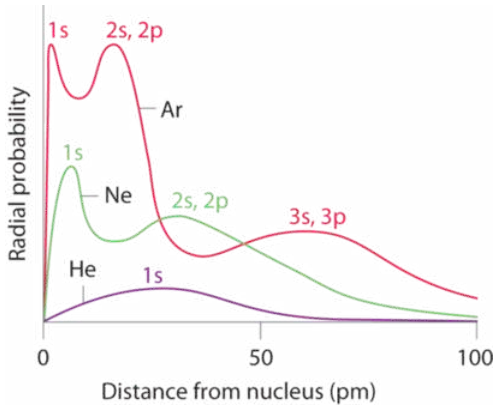


Figure 7.3.6: Radial *electron density functions for orbitals in He, Ne and Ar. Note the valence shell increases as the principle quantum number increases, but that the core electrons are pulled in tighter. The "size of the atom" is based on the valence electron probability distribution function.*

It should also be noted that as you increase the number of protons core shells are pulled in closer to the nucleus. This is shown in Figure 7.3.6 where the 1s orbital in Argon feels the nuclear charge of 18 protons and so is pulled in tighter than the 1s of Neon (10 protons), which in turn is much tighter than the 1s of helium. But only for helium is the 1s the valence electron.

$$\begin{gathered} 1s_{He} > 1s_{Ne} > 1s_{Ar} \\ but \\ 1s_{He} < 2s_{Ne} < 3s_{Ar} \\ and\ so \\ r_{Ar} > r_{Ne} > r_{He} \end{gathered} \tag{7.3.3}$$

So you have to be careful when reading questions.

Exercise 7.3.2

Indicate if the following are true, and if not, explain why

a. radius of K > radius Na because the 1s orbital of K is greater than the 1s orbital of Na.
b. radius of K > radius Na because the 1s orbital of K is greater than the 3s orbital of Na

Answer a

FALSE, the 1s orbital of K < the 1s orbital of Na because there is a larger nuclear charge.

Answer b

FALSE, the 1s orbital of K < the 3s orbital of Na, but the 4s orbital of K > than the 3s orbital of Na, and it is the valence shell that determines the "size" of the atom.

Atomic Radii of Monatomic Cations and Anions

Here you are changing the number of electrons of the parent atom without changing the number of protons, and the trend is simple. If you add electrons and form an anion, it is bigger because there are more electrons. If you remove electrons and make a cation it is smaller, because there are fewer electrons. This trend is observed in Figure 7.3.7.

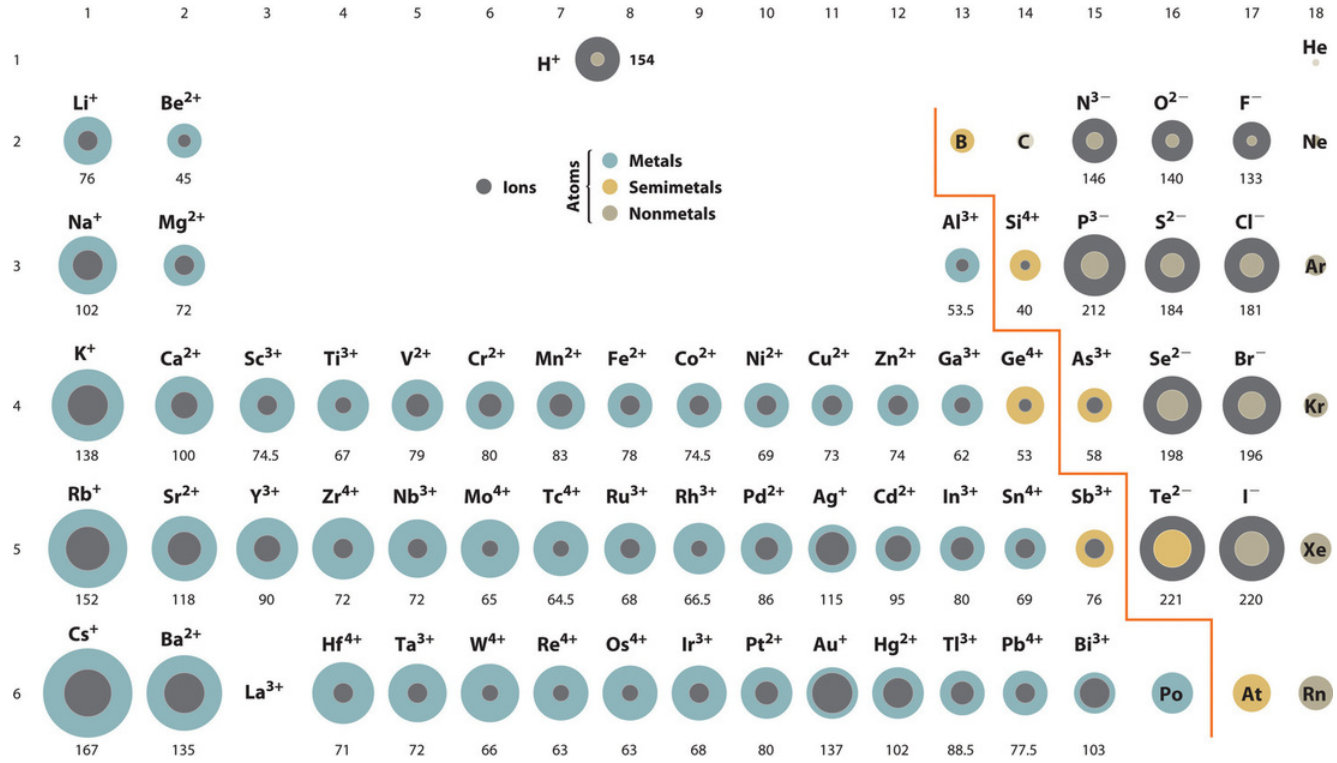


Figure 7.3.7: *Ionic Radii (in Picometers) of the Most Common Ionic States of the s-, p-, and d-Block Elements.Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.*

Isoelectronic Series

You note that many cations and anions are isoelectronic to a noble gas, with the nonmetal gaining electrons and the metal losing electrons until the have the same number as a nobel gas (they are isoelectronic to the nobel gas). This results in an isoelectronic series where the number of electrons is constant but the number of protons changes. So the more protons hold the electrons in tightest

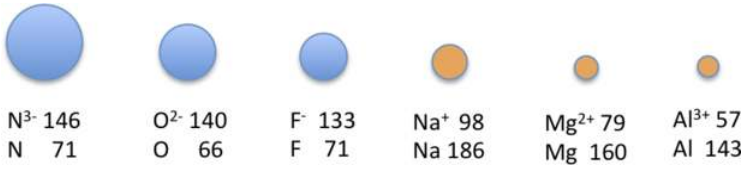


Figure 7.3.8: Anions and cations that are isoelectronic to the nobel gas Neon (the all have a [He]$2s^2 2p^6$ electron configuration).

Ionization Energy (I)

The ionization energy is the minimum energy required to remove an electron from an isolated gas phase chemical species in its ground (lowest energy) state. This is always an endothermic process. The removal of an electron from a neutral atom is its first ionization state, as indicated by the following equation:

$$X_{(g)} + Energy \rightarrow X^+_{(g)} + e^-_{(g)} \tag{7.3.4}$$

First Ionization Energy of Sodium (I_1) :

$$Na_{(g)} \rightarrow Na^+_{(g)} + e^-_{(g)} \quad I_1 = 496 kJ/mol \tag{7.3.5}$$

Any atom other than hydrogen can have successive ionization energies as you take off successively more electrons

Second Ionization Energy of Sodium

$$Na^{+}_{(g)} \rightarrow Na^{2+}_{(g)} + e^{-} \quad I_2 = 4,562 kJ/mol \tag{7.3.6}$$

Atoms that have low ionization energies are easy to ionize and so tend to form cations. It must be emphasized that these are for gas phase atoms where each atom is an isolated unit. Note, ionization energy has units of kJ/mol. In physics this is often treated as the ionization potential and expressed in units of electron volts.

$$1\ eV/atom = 96.49\ kJ/mol \tag{7.3.7}$$

Factors that Influence Ionization Energy

1. Effective Nuclear Charge: The greater the nuclear charge the greater the Coulombic attraction and the higher the ionization energy. Note, the effective nuclear charge is the true nuclear charge minus any shielding effects of core electrons (Z_{Eff} = Z-S)
2. Number of "Shells": The greater the number of shells the further the valence electron is from the nuclueus and the easier it is to remove, lowering the ionization energy.
3. Orbital Occupancy: Electron configurations can influence ionization energies, for example, filled s orbitals can have a shielding effect on p orbitals of the same period, and electron spin pairing energies can influence ionization energies. That is, if you have two electrons in the same orbital the electron-electron repulsion between them can reduce the ionization energy.

The Noble gasses have the highest ionization energies because they have filled outer shells and thus exeperience very high effective nuclear charges. Helium has the highest because it is the smallest and has no core electrons to shield its valence electrons. Elements in the lower left of the periodic table (Cesium and Francium) have the lowest ionization energies, and are the easiest to ionize.

There are two types of periodic trends we need to understand. Those of the first ionization energy, and those of higher order ionization energies.

Exercise 7.3.3

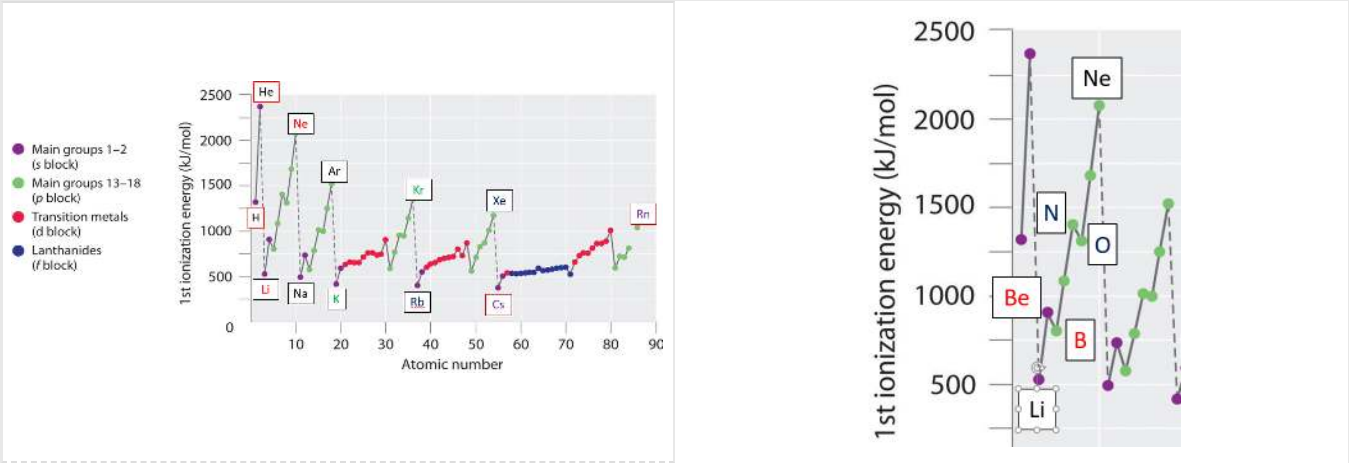
True/False and justify your answer: Elements with high ionization energies easily lose electrons and form cations

Answer

False, elements with low ionization energies are easy to ionize because it does not take much energy. Elements with high ionization energies, like the noble gasses take a lot of energy to ionize.

First Ionization Energy Trends

Going down a group is easy, there is an isoelectronic valence shell configuration and the ionization energy decreases because the electrons of each successive "shell" are further from the nucleus, and thus easier to remove. Going across a period requires looking at the electron configurations of each shell and taking into account electron-electron interactions. The general trend is increasing ionization energy because of increasing effective nuclear charge, but there are significant deviations from this that must be taken into account. Figure 7.3.9 shows the periodic trends in first ionization energies. The peaks are the noble gasses, which have the highest ionization potential



7.3.9: *Periodic trends in first ionization energy (left) with focus on second and third period (right)*

What is clear from Figure 7.3.9 is that there is not a linear increase in ionization ionization energy across each period, but some clear deviations. For the representative elements (s and p blocks) of the second and third period there is sort of a lightning bolt shape, and it is instructive to examine these in more detail.

Groups 2 and 3 (Be-B and Mg-Al) Exceptions

The explanation lies with the structures of boron and aluminum. The outer electron is removed more easily from these atoms than the general trend in their period would suggest.

Be		$1s^2 2s^2$		1st I.E. = 900 kJ mol^{-1}
B		$1s^2 2s^2 2p_x^1$		1st I.E. = 799 kJ mol^{-1}

You might expect the boron value to be more than the beryllium value because of the extra proton. Offsetting that is the fact that boron's outer electron is in a 2p orbital rather than a 2s. 2p orbitals have a slightly higher energy than the 2s orbital, and the electron is, on average, to be found further from the nucleus. This has two effects.

- The increased distance results in a reduced attraction to the nucleus and so a reduced ionization energy.
- The 2p orbital is screened not only by the $1s^2$ electrons but, to some extent, by the $2s^2$ electrons as well (remember, s orbitals penetrate and have inner lobes). That also reduces the pull from the nucleus and so lowers the ionization energy.

The explanation for the drop between magnesium and aluminum is the same, except that everything is happening at the 3-level rather than the 2-level.

Mg		$1s^2 2s^2 2p^6 3s^2$		1st I.E. = 736 kJ mol^{-1}
Al		$1s^2 2s^2 2p^6 3s^2 3p_x^1$		1st I.E. = 577 kJ mol^{-1}

The 3p electron in aluminum is slightly more distant from the nucleus than the 3s, and partially screened by the $3s^2$ electrons as well as the inner electrons. Both of these factors offset the effect of the extra proton.

Groups 5 and 6 (N-O and P-S) Exceptions

Once again, you might expect the ionization energy of the group 6 element to be higher than that of group 5 because of the extra proton. What is offsetting it this time?

N		$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$		1st I.E. = 1400 kJ mol^{-1}

O		$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$		1st I.E. = 1310 kJ mol^{-1}

The screening is identical (from the $1s^2$ and, to some extent, from the $2s^2$ electrons), and the electron is being removed from an identical orbital. The difference is that in the oxygen case the electron being removed is one of the $2p_x^2$ pair. The repulsion between the two electrons in the same orbital means that the electron is easier to remove than it would otherwise be. The drop in ionization energy at sulfur is accounted for in the same way.

Exercise 7.3.4

Rank the elements of the second period of the periodic table in order of increasing ionization energy

Answer

Li<B<Be<C<O<N<F<Ne

Higher Order Ionization Energies

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an *n*th ionization energy (I_n) according to the following reactions:

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_1 = \text{1st ionization energy} \tag{7.3.8}$$

$$E^+_{(g)} \rightarrow E^{2+}_{(g)} + e^- \qquad I_2 = \text{2nd ionization energy} \tag{7.3.9}$$

$$E^{2+}_{(g)} \rightarrow E^{3+}_{(g)} + e^- \qquad I_3 = \text{3rd ionization energy} \tag{7.3.10}$$

Values for the ionization energies of Li and Be listed in Table 7.3.1 show that successive ionization energies for an element increase steadily; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

Table 7.3.1: *Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).*

Reaction	Electronic Transition	I	Reaction	Electronic Transition	I
$Li_{(g)} \rightarrow Li^+_{(g)} + e^-$	$1s^2 2s^1 \rightarrow 1s^2 + e^-$	I_1 = 520.2	$Be_{(g)} \rightarrow Be^+_{(g)} + e^-$	$1s^2 2s^2 \rightarrow 1s^2 2s^1 + e^-$	I_1 = 899.5
$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^-$	$1s^2 \rightarrow 1s^1 + e^-$	I_2 = 7298.2	$Be^+_{(g)} \rightarrow Be^{2+}_{(g)} + e^-$	$1s^2 2s^1 \rightarrow 1s^2 + e^-$	I_2 = 1757.1
$Li^{2+}_{(g)} \rightarrow Li^{3+}_{(g)} + e^-$	$1s^1 \rightarrow 1s^0 + e^-$	I_3 = 11,815.0	$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^-$	$1s^2 \rightarrow 1s^1 + e^-$	I_3 = 14,848.8
			$Be^{3+}_{(g)} \rightarrow Be^{4+}_{(g)} + e^-$	$1s^1 \rightarrow 1s^0 + e^-$	I_4 = 21,006.6

The most important consequence of the values listed in Table 7.3.1 is that the chemistry of Li is dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li

$$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^- \tag{7.3.11}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be

$$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^- \tag{7.3.12}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^{+} and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2*s* valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

Table 7.3.1: Ionization Energies of certain elements (1st IE, 2nd IE, etc) in kJ/mol

Element	1st	2rd	3th	4th	5th	6th	7th
Na	496	**4562**					
Mg	738	1451	**7733**				
Al	577	1817	2745	**11580**			
Si	786	1577	3232	4356	**16090**		
P	1060	1903	2912	4957	6274	**21270**	
S	999.6	2251	3361	4564	7013	8496	**27110**
Cl	1256	2297	3822	5158	6542	9362	11020
Ar	1520	2666	3931	5771	7238	8781	12000

These are the ionization energies for the period three elements. Notice how Na after in the second I.E, Mg in the third I.E., Al in the fourth I.E., and so on, all have a huge increase in energy compared to the proceeding one. This occurs because the proceeding configuration was in a stable octet formation; therefore it requires a much larger amount of energy to ionize.

Exercise 7.3.5

An element in the second row of the periodic table shows the following trend in ionization energies

1st(kJ/mol)	2nd(kJ/mol)	3rf(kJ/mol)	4th(kJ/mol)	5th(kJ/mol)	6th(kJ/mol)
1086.45	2352.62	4620.47	6222.28	37831.0	47277.1

What is the identity of the element?

Answer

Carbon, because the jump from the 4th to the 5th ionization energy is huge, indicating the 5th electron is a core electron, and so there are 4 valence shell electrons., which would be carbon.

Electron Affinities (E_A)

Electron Affinity it typically described as the energy change in units of kJ/mol when an electron is added to a chemical species (atom in this case). A negative E_A indicates an exothermic reaction and the product state is lower in energy and thus favored. Most textbooks relate this energy change to the following equation:

$$\underbrace{A(g) + e^{-} \rightarrow A^{-}(g)}_{\text{Electron Affinity of A}} \tag{7.3.13}$$

The IUPAC goldbook definition is actually the "Energy required to detach an electron from the singly charged negative ion" for the process, which is actually the negative of the ionization potential (I) of the anion.

$$\underbrace{A^-(g) \rightarrow A(g) + e^-}_{\text{Ionization Potential of } A^-} \tag{7.3.14}$$

At first it seems like there are two different definitions but when you think about it, they make sense. If Equation 7.3.14 requires say that 73kJ/mol must be added to remove an electron from hydride (H^-), which is the ionization potential of hydride (not hydrogen), then the reverse reaction, the electron affinity of hydrogen 7.3.14 must be a negative 73 kJ/mol.

$$E_A(A) = -I(A^-) \tag{7.3.15}$$

If there is an affinity for an electron the reaction is exothermic (E_A<0) and this can become a tongue twister. To keep things straight you should always stick to the sign conventions of thermodynamics, realizing that things tend to go towards the lower energy state and so a negative E_A implies an affinity for the electron. That is why the Y-scale of Figure 7.3.10 is inverted (as you go up the numbers get more negative) with chlorine having the highest affinity for an electron with E_A=-348.6kJ/mol.

a

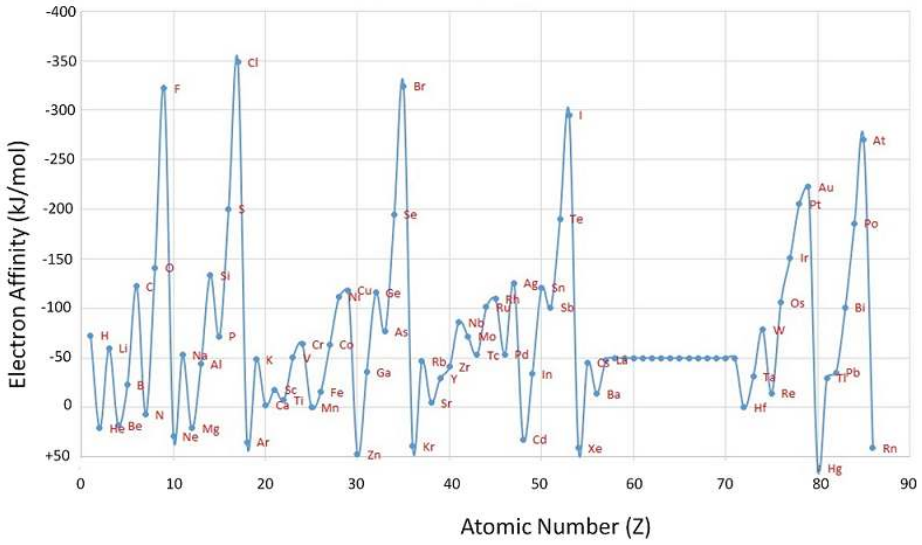


Figure 7.3.10: Chart of periodic trends in Electron Affinity (E_A). Note, the values of the Lanthanides are not given in this Figure.

w

A positive (endothermic) electron affinity means you must add energy to form the anion.

a

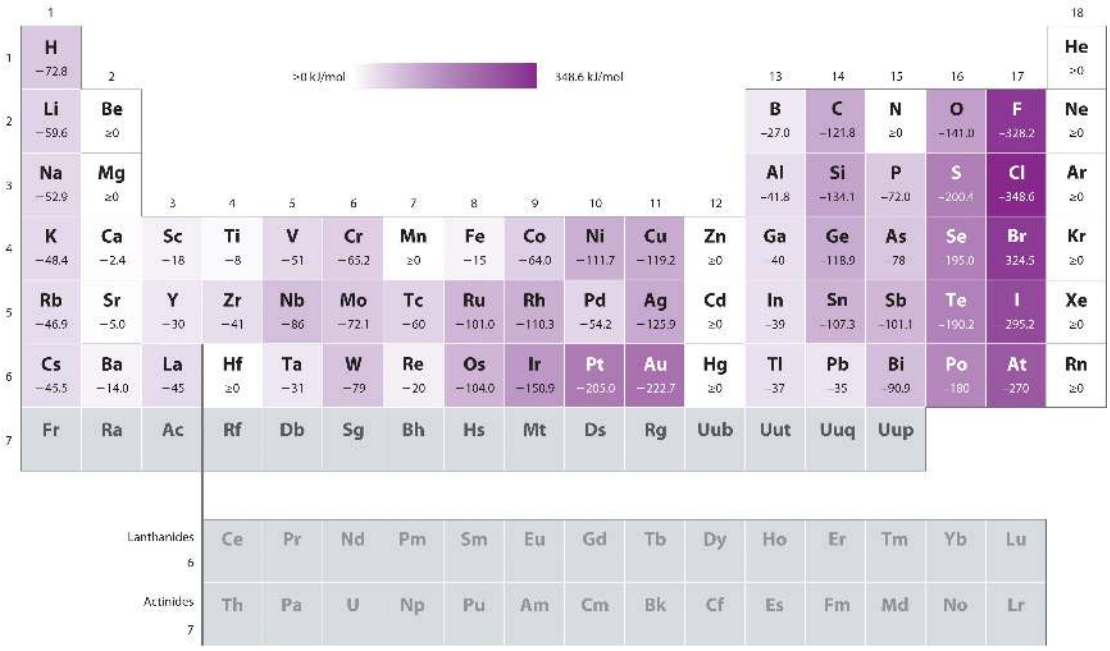


Figure 7.3.11: Values of Electron Affinity (E_A) for elements with exothermic values . In looking at Electron Affinities it needs to be understood that these are energy states for an isolated atom or ion where there is no interaction with any other chemical species. D*ata from Journal of Physical and Chemical Reference Data 28, no. 6 (1999).*

Note on Sign convention

The fact that the more exothermic the electron affinity the more an atom has an affinity for an electron has caused some confusion. Here is a table with the signs switched from the ones in Figures 7.3.10 and 7.3.11.

73 H 1312							He 2372
58 Li 520	−18* Be 899	29* B 801	121* C 1086	−58* N 1402	142 O 1314	331 F 1681	Ne 2080
52 Na 496	−54* Mg 738	48* Al 578	134* Si 786	75* P 1012	200 S 1000	348 Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	65 As 946	207* Se 941	324 Br 1140	Kr 1351
Rb 403	Sr 549	In 558	Sn 708	Sb 834	222* Te 869	296 I 1008	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 715	Bi 703	Po 812	At	Rn 1037

Figure 7.3.12: Table of ionization energies (black) and electron affinities (red). Note how the sign is changed from Figures 7.3.10 and 7.3.11. Values with asterisk (*) are theoretical calculations.

The truth is that there is inconsistent sign convention, and there is justification for both ways. Figure 7.3.12 give fluorine and chlorine positive electron affinities because they tend to grab an electron, and give nitrogen a negative one because it does not. In this class we will stick to the thermodynamic convention that a negative electron affinity means it is exothermic, and thus the affinity is higher. If you look closely at Figure 7.3.10 you will note that chlorine has the most negative value and is the highest on the chart, that means it has the highest electron affinity. So as you read through this, the more negative E_A, the greater the electron affinity.

Periodic Trends in E_A

Just like Ionization potentials you must look at the electron configurations to understand the periodic trends in E_A.

- Nonmetals other than the noble gasses tend to have negative (exothermic) E_As.

- Noble gasses all have endothermic electron affinities because they have a filled valence shell, and so the added electron is going to the next highest shell (principle quantum number), which is very well shielded and so it does not feel a strong Z_{eff} (Effective Nuclear Charge).
- There is a tendency for EA to increase going across a period (become more exothermic - negative) and this is due to increasing Z_{eff} (until you reach the noble gasses).
- Nitrogen has an endothermic E_A because of its electron configuration. As shown in Figure 7.3.12, in accordance with Hunds rule, nitrogen has one electron in all three of the p orbitals and their magnetic moments align. When you add the additional electron to make N-, it is not only being added to an orbital that is already occupied, but it magnetic field is against that of the other electrons.

N: 2p ↑ ↑ ↑ 2s ↑↓ 1s ↑↓	N^-: 2p ↑↓ ↑ ↑ 2s ↑↓ 1s ↑↓
N:[He]$2s^2 2p^3$	N^-: [He]$2s^2 2p^4$

Figure 7.3.12: Nitrogen has an endothermic electron affinity because you are starting to pair up electrons (there is a greater electron-electron repulsion term and all three of the other electrons have parallel magnetic fileds)

- The other group VA elements also show a dip, but are exothermic, and this is for the same reason as Nitrogen.
- Halogens decrease in electron affinity (become less exothermic) going down the group because the valence shell is further away from the nucleus and so the electron being added feels a weaker pull. Fluorine is the exception (it is not higher than chlorine) because it is so small that the electron-electron repulsions interfere with the pull towards the nuclues.
- Alkali metals have negative electron affinities because the s orbital is being filled

Second Electron Affinities

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{7.3.16}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{7.3.17}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is −141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{7.3.18}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{7.3.19}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{7.3.20}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) are energetically unfavorable in the gas phase.

Test Yourself

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has

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CHAPTER OVERVIEW

8: Bonding and Molecular Structure

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Topic hierarchy

8.1: Chemical Bond Formation: An Introduction
8.2: Covalent Bonding and Lewis Structures
8.3: Resonance
8.4: Formal Charge
8.5: Drawing Lewis Dot Structures
8.6: Molecular Geometries
8.7: Bond Polarity and Electronegativity (\(\chi\))
8.8: Bond and Molecular Polarity
8.9: Covalent Bond Properties: Order, Length, and Energy
8.10: DNA, Revisited

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8.1: Chemical Bond Formation: An Introduction

Three Broad Categories of Chemical Bonds

1. Covalent
2. Ionic
3. Metallic

To distinguish these we need introduce the concept of electronegativity (χ), which is a measure of how much an electron is attracted to an atom in a bond, and is covered in section 8.7 of this Chapter. In that section we will see that Fluorine is the most electronegative element with a value of 4, while Francium and Cesium are the least electronegative with a value of 0.7. A "rule of thumb" is that ionic bonds occur when $\Delta\chi$ is greater than 2, and either covalent or metallic occurs when it is less than 0.5, with Metallic occurring when the average is less than 2 and covalent when the average is greater than two. This can be explained by the van Arkel-Ketelaar diagram.

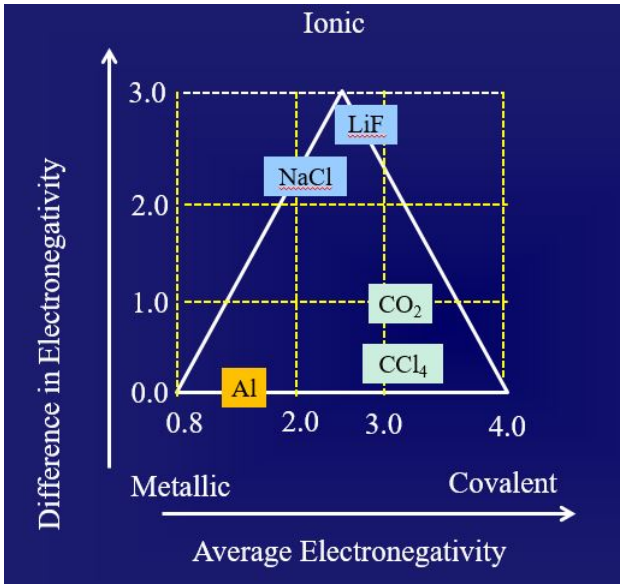


Figure 8.1.1: Van Arkel-Ketelaar diagram showing how electronegativity can be used to distinguish the three types of chemical bonds. The three corners of the diagram represent the extremes

- Bottom Left: Metallic bonds occur between atoms of low electronegativty
- Bottom right: Covalent bonds occur between atoms of high electronegativity
- Top middle: Ionic bonds occur between an atom of high and an atom of low electronegativity.

It needs to be understood that real bonds can be a mixture of these. For example, many covalent bonds are polar covalent, and we will cover this in section 8.7.



Video 8.1.1 (3:53 Youtube uploaded by Richard Thornley) goes over the van Arkel-Ketelaar diagram in more detail.

Most of this Chapter deals with covalent bonds, but it is important to realize that there are also ionic and metallic. In all of these cases, we consider the bonds to occur through interactions of the valence shell electrons, and that core electrons are held too tight to the parent nucleus to be involved with bonding.

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8.2: Covalent Bonding and Lewis Structures

Before proceeding do a quick review of "Covalent Bonds and Molecules", (section 2.5.2) of this LibreText. Note in that section we covered the potential well model and provided multiple ways of representing covalently bonded molecules. In this section we are going to develop a type of structural formula called the Lewis Dot Structure. In a Lewis Structure, you draw a molecular structure that accounts for the valence electrons of all the participating atoms, showing the connectivity (bonds) as lines between atoms, and lone electrons as dots. In section 8.6 you will use this lewis dot diagram to predict the three dimensional geometry of a molecule. Be sure to do the attached worksheets that will be at the end of this section

Valence Electrons and Lewis Symbols for atoms

In the last Chapter we recognized that electrons reside in orbitals and that the families of the periodic table had isoelectronic valence shell electron configurations. For the representative elements (s and p blocks) we have the following valence shell electron configurations.

Table: 8.2.1: (a) valence electron configurations and the number of valence electrons for the representative elements. (b) Lewis symbols and electron configurations for 2 period atoms.

Group Number	Valence Electron Configuration	Valence Electrons
1A	ns^1	1
2A	ns^2	2
3A	ns^2np^1	3
4A	ns^2np^2	4
5A	ns^2np^3	5
6A	ns^2np^4	6
7A	ns^2np^5	7
8A	ns^2np^6	8

Example	Electron Configuration	Lewis Symbol
Na	$[Ne]ns^1$	Na·
Mg	$[Ne]ns^2$	·Mg·
Al	$[Ne]ns^2np^1$	·Al·
Si	$[Ne]ns^2np^2$	·Si·
P	$[Ne]\ ns^2np^3$	:P·
S	$[Ne]ns^2np^4$	:S·
Cl	$[Ne]ns^2np^5$	:Cl·
Ar	$[Ne]ns^2np^6$	:Ar:

Note, the s and p-block elements have 4 orbitals (one-s orbital and three p-orbitals), and so the convention is to put one electron in each orbital before pairing them, and to only allow two electrons in an orbital (Pauli Exclusion principle). This means that there are 8 electrons around the central atom if we are filling S & p orbitals, which is the foundation of the octet rule (see below).

Lewis Dot Structure Conventions

There are two types of electrons, lone electrons and bonding electrons. The lone electron is only attracted to one nucleus, the bonding electrons are shared between two nuclei.

- Lone electrons are represented by a dot
- Bonding electrons are represented by a line connecting two nuclei

1. **Lone Electrons**
   - Single Electron X· (Single electron in orbit of nuclei X, note; this orbital could accept an additional electron)
   - Pair of Electrons X**:** or X| (spin coupled pair of electrons in an orbital of nuclei X)
2. **Bonding Electron Pairs**
   - Single bond X-Y (two electrons shared in a bonding orbital between nuclei X & Y)
   - Double bond X=Y (four electrons shared in two bonding orbitals between nuclei X & Y)
   - Triple bond X≡Y (6 electrons shared in three bonding orbitals between nuclei X & Y)

Lewis Dot Structures of Diatomics

Hydrogen:

Hydrogen has one electron and one proton. As each orbital would like two electrons, two hydrogens come together and share their electrons, providing the single bonded diatomic hydrogen molecule. **Note:** Hydrogen only forms one bond in most compounds.

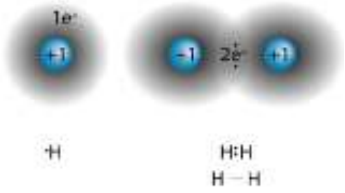


Figure 8.2.1: Diatomic hydrogen

Halogens:

X=F, Cl, Br, or I:

$$:\ddot{\underset{\cdot\cdot}{X}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{X}}: \rightarrow :\ddot{\underset{\cdot\cdot}{X}} - \ddot{\underset{\cdot\cdot}{X}}: \tag{8.2.1}$$

Oxygen:

$$:\dot{\underset{\cdot\cdot}{O}}\cdot + \cdot\dot{\underset{\cdot\cdot}{O}}: \rightarrow :\underset{\cdot\cdot}{O} = \underset{\cdot\cdot}{O}: \tag{8.2.2}$$

Nitrogen:

$$:\dot{\underset{\cdot}{N}}\cdot + \cdot\dot{\underset{\cdot}{N}}: \rightarrow :N \equiv N: \tag{8.2.3}$$

Octet Rule

The "octet rule" says that for many molecules the bonds are formed through interaction of the s and p orbitals of the atoms, and so the most stable (correct) electron configuration is when each atom of the molecule has 8 electrons (four filled orbitals) in the valence shell. There are many molecules that do not follow the octet rule, in fact we have already covered one, hydrogen, which can only have one bond (two electrons). There are **three types of exception to the octet rule, which are Lewis dot structures with atoms containing:**

a. less than 8 electrons.
b. more than 8 electrons
c. an odd number of electrons

Atoms that can have a Reduced Octet

One Electron Pair: Hydrogen always forms one bond and so has a duet (2 electrons). Note, there are cases like diboron (B_2H_6) that have "bridging hydrogens", which are covalently bonded to two boron. These are very uncommon and in this class, hydrogen always has a duet (two electrons).

Why does hydrogen never follow the octet rule and only has 2 electrons?

The valence orbitals of hydrogen (and helium) have a principle quantum number of 1, and so there is only one orbital available, the 1S. Since each orbital can contain up to two electrons (of opposite spin), hydrogen can have 2 electrons in its Lewis Dot Structure.

Two Electron Pairs: Group IIA atoms like Beryllium often have 4 valence electrons, as in the case of BeH_2 and BeF_2.



Figure 8.2.2: Lewis dot structure (left) and space filling diagram (right) of $BeCl_2$. Group IIA compounds can have stable structures with two electron pairs (4 electrons) .

Note: The above structure of Beryllium chloride is in the gas phase and the only structure this class is required to understand. In the solid phase Group IIA compounds form ionic not covalent compounds with halogens (and hydrogen). Beryllium, being so small, actually forms a chain like polymer in the solid phase. In this class we only need to be able to draw Lewis dot structures for compounds like the one in Figure Figure 8.2.2.

Three Electron Pairs: Group IIIA atoms like Aluminum can have 6 valence electrons

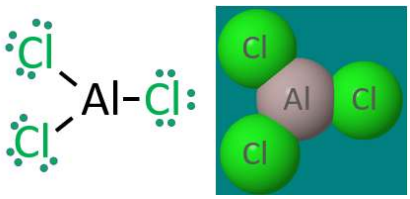


Figure 8.2.3: Lewis dot structure (left) and space filled diagram (right) of Aluminum chloride in the gas phase. Group IIIA compounds can have stable structures with three electron pairs (6 electrons).

Once again, this Lewis dot structure of covalent aluminum chloride is for the gas phase molecule, and in the solid phase this is an ionic compound and not covalent, in fact it forms a hydrated ionic crystal, aluminum chloride hexahydrate. But if you are asked to draw a Lewis dot structure for a group III halogen (or hydride), the central atom has 3 bonding pairs and not an octet.

Can atoms like Be (Group IIA) and Al (Group IIIA) have an octet?

Yes they can, but they do not need to.

Atoms that can have an Expanded Octet

To have an expanded octet (more than 8 electrons) you need more than 4 orbitals. In the next Chapter we will learn that molecular orbitals are different than atomic orbitals, but one way to describe molecular orbitals is by assuming they are the result of different atomic orbitals mixing with each other, and the number of molecular orbitals must equal the number of atomic orbitals that were mixed to create them. This means that you need to start using d-orbitals, and those are only available for atoms in the third period or above. So atoms in the third period or greater can have expanded octets.

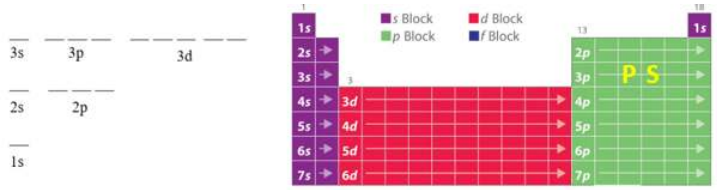


Figure 8.2.4: *On the left are the number of orbitals for each shell, and on the right they are assigned to the blocks of the periodic table as it is being filled for the ground state configuration. The important thing to note is the first two periods only have one and four orbitals respectively, and so atoms in those periods can not have an expanded octet. Atoms in the third period have d-orbitals and so atoms like phosphorous and sulfur can have more than an octet.*

Phosphorous often has 5 orbitals (10 electrons) and sulfur often has 6 orbitals (12 electrons) because they are in the third period (Figure 8.2.5), but nitrogen and oxygen can never have expanded octets because they are in the second period and there is not such thing as a 2d orbital.

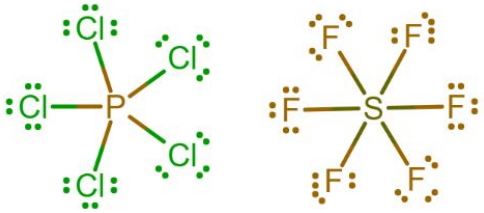


Figure 8.2.6: *Lewis dot structures of compounds of phosphorous and sulfur, which being in the third period have available d-orbitals, and so can have more than an octet of electrons.*

Exercise 8.2.1

Why can't elements if the second row have an expanded octet?

Answer

For the second row, the principle quantum number is 2, and so you have s and p orbitals in the valence shell. As there is one type of S, (2s) and three types of P, (p_x, p_y & p_z), there are only 4 available orbitals, which can take up to 8 electrons (an octet). NOTE: in the next Chapter we will study molecular orbitals, and the orbitals in molecules are not atomic orbitals (s,p,d,f), but are different. That said, the number of molecular orbitals is determined by the number of atomic orbitals in the valence shell, but they are different

---

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8.3: Resonance

Introduction

One of the postulates of the Lewis Dot Structure for representing molecules is that a bond is the result of a pair of electrons being shared between two different nuclei, and as such, can be represented as a line between the two nuclei (the letters that represent the elements involved). But what if the electrons are shared between more than two nuclei? When this happens, there is no one Lewis Dot Structure that accurately describes the molecule. When this happens you need to draw resonance structures, none of which accurately describe the bonds, with the real structure sort of being the average of all the resonance structures. In the next Chapter we will look at the types of bonds in molecules and learn that there are two fundamentally different types of bonds, σ bonds and π bonds. The sigma bonds can be described with Lewis dot structures as they represent bonding electrons shared between two nuclei, but sometimes the π bonds have electrons that are shared over more than two nuclei, in which case no single Lewis dot structure can accurately describe the bond. For example the organic solvent benzene (C_6H_6) has 6 electrons that are shared by all 6 carbons and can form a ring circuit, as depicted in video 8.3.1, and as we shall see, this requires two resonance forms of the Lewis dot structure.



Video 8.3.1: 0'30" YouTube uploaded by S.K. Sinha depicting the delocalized electrons of benzene (C6H6), which prevent one from being able to write one simple Lewis dot structure, and invoking the need for resonance structures. (https://youtu.be/7FyIQ6Sdrpg)

NOTE: Resonance structures represent different ways of placing electrons on the atoms in a molecule's Lewis dot structure. They do not describe different molecules and all resonance structures have the same connectivity. If you change the connectivity, you change the molecule, and that is not a resonance structure. In section 8.5 we will cover drawing Lewis dot structures and you will learn how to recognize if they exist while you are drawing them. But before we draw them, we want to define and describe them. So the following examples should help you identify and describe resonance structures.

Lets start with a look at the Lewis Dot Structure of Ozone

Illustration of Resonance: Ozone

Ozone (O_3) is an allotrope of oxygen, with diatomic oxygen (O_2) being the most common form of oxygen. Ozone is a very reactive form of oxygen that has detrimental health effects (which is why ozone alerts are posted along the highways of cities), but it also reacts with ultraviolet radiation in the upper atmosphere and thus shields the biosphere from the harmful effects of UV radiation. There are two ways of drawing the Lewis dot structure of ozone

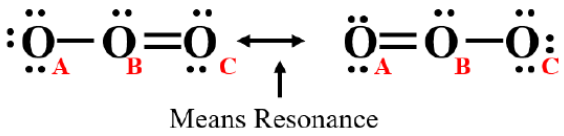


Figure 8.3.1: The two Lewis dot structures of ozone. Note, the two headed arrow means these are not real structures but resonance structures.

That is, from Figure 8.3.1 there is a choice of between which two atoms the double bond goes, oxygen B & C (left) or A & B (right), which is also demonstrated in the video 8.3.2.



Video 8.3.2: 1'15" YouTube uploaded by Selenium demonstrating that there is no single way to draw the Lewis dot structure of Selenium (https://youtu.be/YAyhIo3DnPc)

Figure 8.3.2 shows another way of drawing ozone that indicates the electrons of the second bond in the double bond are actually shared over all three oxygen atoms

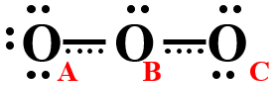


Figure 8.3.2: This image is sort of a mixture of the two resonance structures in Figure 8.3.1, where the electrons of the second bond of the double bond are shared by all three oxygen atoms.

The problem with Figure 8.3.2 is that it does not tell you how many electrons there are (you can't count dots and bars).

Resonance Structures vs. Isomers

It is important to denote the difference between resonance structures and isomers. Resonance structures are not real molecules, but a shortcoming of the postulates that Lewis dot structures are based on, that is, a covalent bond is formed when electrons are shared by two atoms, and thus can be represented by a line between the atoms. In the case of ozone above, the bonding electrons are shared by three atoms, and so no one Lewis dot structure could accurately represent ozone. Isomers are real molecules, Figure 8.3.3 shows two different isomers, hydrogen cyanide (HCN) and hydrogen isocyanide (HNC) and a chemical reaction can occur where these molecules interconvert into each other.

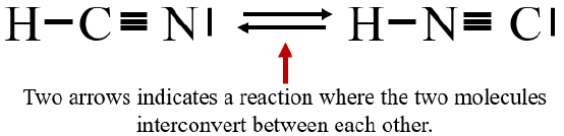


Figure 8.3.3: These are not resonance structures but different molecules, and the two opposing arrows indicates a reaction in both directions occurs.

Note

$A \leftrightarrow B$ - A & B are not two different molecules but different ways of writing the same molecule, **they are resonance structures.**

$A \leftrightharpoons B$ - A & B are two different molecules that can interconvert between each other and form an equilibrium mixture.

Bond Order

Bond order is a way of describing the magnitude of a bond; a single bond has a bond order of 1, double bond 2 and triple bond 3. An individual Lewis dot structure can only have integer bond orders.

Note

For bonds between identical nuclei, the higher the bond order the stronger the bond and the shorter the bond length.

If there are resonance structures, the bond order of the bonds in the resonant structure is the average bond order, which can be determined from any individual resonant structure, and it need not be an integer value.

$$\text{Bond Order} = \frac{\sum \text{bond order of all bonds in a resonance structure}}{\text{number of bonds in resonance structure}} \tag{8.3.1}$$

- Bond Order = 1: Single Bond
- Bond Order = 2: Double Bond
- Bond Order = 3: Triple Bond
- Bond Order = 1.5: Combination of Single and Double Bond
- Bond Order = 1.33: Combination of Two Single and one Double Bond

Example 8.3.1

What is the bond order of the oxygen-oxygen bond in ozone.

Solution

$$\text{Bond Order} = \frac{1 \text{ single} + 1 \text{ double}}{2 \text{ bonds}} = \frac{3}{2} = 1.5 \tag{8.3.2}$$

Both bonds in Ozone have a bond order of 1.5 and are the same length, which is longer than a double bond (because the double bond is a stronger bond) and shorter than a single bond (because a single bond is a weaker bond).

Nitrate Ion

The Lewis dot structure of nitrate has three resonance structures. Because it is an ion, it must be in brackets and the charge shown outside the Lewis dot structure.

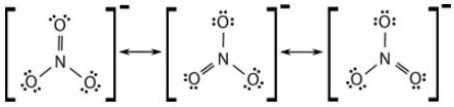


Figure 8.3.4: Three resonance structures of nitrate ion. Note, for ions, we place the Lewis dot structure in brackets and the charge as a superscript on the outside of the bracket. In section 8.3.5 we will learn how to draw Lewis dot structures, but it needs to be noted that you have extra electrons for anions, and fewer for cations.

If we were to merge the Lewis dot structure into one Figure like we did in fig. 8.3.4 for ozone

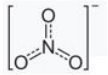


Figure 8.3.5 *In this Figure we have mixed the three resonance structures in Figure* 8.3.4 *like was done for ozone in Figure* 8.3.2.

Exercise 8.3.1

What is the bond order for the nitrogen=oxygen bond in nitrate?

Answer

$$\text{Bond Order} = \frac{2 \text{ single} + 1 \text{ double}}{3 \text{ bonds}} = \frac{4}{3} = 1.33 \tag{8.3.3}$$

So the bond order of nitrogen is 1.33, that is, it is 2/3 single bond and 1/3 a double bond.

Exercise 8.3.2

Would you expect the nitrogen-oxygen bond length of nitrate to be closer to the N-O single bond or the N=O double bond?

Answer

It is closer to the single bond in length because a bond order of 1.33 is closer to 1 than it is to 2.

Benzene

Benzene (C_6H_6) is a ring structure that is common in organic compounds known as aromatics and is represented in video 8.3.1 at the beginning of this Chapter. There are two resonance structures for benzene as indicated in Figure 8.3.5.

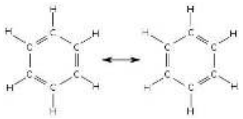


Figure 8.3.5: *Lewis dot structure of benzene explicitly showing the hydrogens*

Note, as carbon is in the second period of the periodic table there are no d-orbitals and so carbon can not have an expanded octet, nor is it in group IA, IB or IC, which allow it to have less than an octet. Thus carbon can be considered to follow the octet rule and needs 8 valence electrons in its Lewis dot structure. This allows us to remove the hydrogens from the Lewis dot structure and implicitly infer them. That is, each carbon needs 8 electrons and if the drawing omits 2, we assume there is a hydrogen present.



Figure 8.3.6: *Lewis dot structure of benzene with implicit hydrogens*

Figures 8.3.5 and 8.3.6 are two ways of drawing benzene and it is important that students become familiar with the convention of Figure 8.3.6. The reason this convention is so common is that the bonds to hydrogen are terminal, in the sense that hydrogen can only have one bond, and this convention of not drawing the hydrogen is common in chemistry, especially organic chemistry.

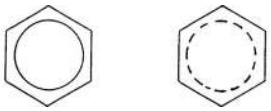


Figure 8.3.7: *Lewis dot structure of benzene showing the delocalization of the electrons across all the carbons.*

Exercise 8.3.3

a. What is the bond order of the carbon-carbon bond in benzene?.
b. Do resonance structures always add up to non-integer bond orders?

Answer a

$$\text{Bond Order} = \frac{3 \text{ single} + 3 \text{ double}}{6 \text{ bonds}} = \frac{9}{6} = 1.5 \tag{8.3.4}$$

Answer b

FALSE, look at carbon dioxide, the next example.

Carbon Dioxide

The Lewis dot structure of carbon dioxide is shown in Figure 8.3.8.

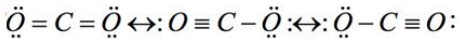


Figure 8.3.8: Three resonance structures of carbon dioxide

In the above Figure we see the second and third resonance structures average out to the first, and so the average of all the resonance structures is a double bond. Thus it is common to write carbon dioxide as having two double bonds, and that resonance structure is the correct structure of carbon dioxide.

Exercise 8.3.4

Calculate the bond order of carbon dioxide from the Lewis dot structures on the left and right of Figure 8.3.8.

Answer

For the structure on the left:

$$\text{Bond Order} = \frac{0 \text{ single} + 2 \text{ double}}{2 \text{ bonds}} = \frac{4}{2} = 2 \tag{8.3.5}$$

For the structure on the right:

$$\text{Bond Order} = \frac{1 \text{ single} + 1 \text{ triple}}{2 \text{ bonds}} = \frac{4}{2} = 2 \tag{8.3.6}$$

From exercise 8.3.8 it is clear that no matter which resonance structure you use, the bond order is the same. Now even though carbon dioxide has two double bonds, if you are asked to draw it's Lewis dot structure, you should include the two with the single and triple bonds, and this will be covered in section 8.5.

Summary

So what we have seen is that one of the shortcoming of Lewis dot structures comes from the concept that a line represents a bond between two nuclei, but sometimes this is false and the bond is between more than two nuclei. In that case you need to write multiple Lewis dot structures, the resonance structures, and use an arrow with two heads to indicate that each of the individual structures are resonance structure, and the true molecule is a combination of them all. If, as in the case of carbon dioxide, all the resonance structures average out to one of the resonance structures, then it can be treated as the real structure, and you have an integer bond order. If not, the real structure is none of the resonance structures, and the bond order is of non-integer order, often indicated with a dotted line.

It must be emphasized that resonance structures do not show the true bond order and thus do not represent the true structure of the molecule, which results from the combination of all the resonance structures.

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8.4: Formal Charge

Introduction

The concept of formal charge is actually very simple. It relates the number of electrons around an atom in a molecule's Lewis dot structure to the number of electrons that atom donated to the Lewis dot structure. In the next section we will cover drawing Lewis dot structures, and the first step is to calculate the number of electrons each atom donates to the molecule, and then to essentially draw a structure based on those electrons, placing them in either bonding or nonbonding orbitals. In formal charge calculations electrons in bonding orbitals are considered to be evenly split between the two bonding atoms, (one is assigned to each atom), while those in lone pair (non bonding orbitals) are assigned to the atom they are placed on.

A negative formal charge means there are more electrons around an atom than it donated, a positive means there are fewer electrons around an atom then it donated, and a neutral formal charge means the number it donated is the same as in the structure.

Some Important Things to Note about Formal Charges

1. Formal charges are not real charges, they are a way of looking at electron distributions in a Lewis dot structure. In section 8.7 we will cover electronegativty and molecular polarity, and then we will look at the actual charge distribution in real molecules, which does not always reflect the formal charge distribution.
2. The sum of the formal charges of all the atoms in a neutral molecule equals zero
3. The sum of the formal charges of all the atoms in an ion equals the charge of the ion.

Uses of Formal Charges

1. Formal charges can help identify the more important resonance structures, that is, hitherto we have treated all resonance structures as equal, but this is not always the case.
   - The Resonance Structure with the most atoms having Formal charges closest to zero is usually the preferred resonance structure
   - Negative formal charges are preferred on more electronegative atoms (see section 8.7: Bond Polarity and Electronegativity)
2. Formal charges can help identify the more likely of two isomers, that is, two different structures made from the same set of atoms, like HCN and HNC.
   - RULE of THUMB: The best Lewis dot structure has the most atoms with zero formal charge, or the closest to zero.

Calculating Formal Charge:

The following equation determines the formal charge for each atom in a molecule or polyatomic ion. The first part is the number of valence electrons the atom donates to the Lewis dot Structure. From this is subtracted the lone electrons around that atom, and then half the bonding electrons, as they are split between both nuclei of the bond. If this is zero, then the electrons the atom donated to the structure are around the atom. If it is positive, that means the atom contributed more electrons than are around it, and some of "its" electrons are around other atoms. If it is negative, that means there are more electrons around it than it contributed to the Lewis dot structure.

$$\text{Atoms Formal Charge} = [\text{valence electrons}] \text{ - } [\text{lone pair electrons}] - \frac{\text{bonding electrons}}{2} \tag{8.4.1}$$

Example 8.4.1

Calculate the formal charge of all atoms in H-C≡N: and H-N≡C:

Solution

For hydrocyanic acid(H-C≡N:) we get the formal charges of:
H=1-0-1/2(2)=0
C=4-0-1/2(8)=0
N=5-2-1/2(6)=0

For hydrogen isocyanide (H-N≡C:), we get the formal charges of
H=1-0-1/2(2)=0

N=5-0-1/2(8)=+1
C=4-2-1/2(6)=-1

So from the above example, HCN is the preferred structure (isomer) to HNC.

Intuitive Visualization:

Let's use different symbols to represent the electrons and show the bonds as electron pairs (next to each other) instead of lines. In Figure 8.4.1 we see that hydrogen donates one electron (the star), diamond donates 4 (the diamonds) and nitrogen donates 5 (the circles)

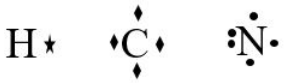


Figure 8.4.1: *Using stars (hydrogen), diamonds (carbon) and circles (nitrogen) to represent the electrons each atom donates.*

From Figure 8.4.1 it is clear the there are 10 valence electrons in a compound made from H,C and N, with hydrogen donating 1, carbon 4 and nitrogen 5. Since hydrogen must be terminal (it can't have two bonds and connect two other atoms), there are only two possible isomers, HCN and HNC. Figure 8.4.2 shows the ways these electrons can combine to form the bonds and lone pairs.

Using the above symbols we get the following Lewis dot structures.

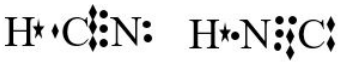


Figure 8.4.2: Lewis dot structures using stars, diamonds and circles to represent the electrons donated from Hydrogen (1 star), Carbon (4 diamonds) and Nitrogen (5 circles) respectively.

Example 8.4.1 showed that all atoms of the left structure of Figure 8.4.2 (hydrogen cyanide) had zero formal charge, while for the right structure (hydrogen isocyanide) the nitrogen had a +1 and the carbon a -1. This is clear to see in Figure 8.4.2, where one of the dots on the right side is near a carbon, meaning one of the electrons nitrogen donated is near the carbon.

Exercise 8.4.1

Which would be predicted to be more stable, hydrogen cyanide or hydrogen isocyanide

Answer

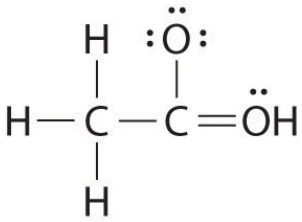
Hydrogen cyanide because all the atoms have zero formal charges.

It must be emphasized that there are limitations to applying formal charges in determining the stabilty of a compound. It is logical that Lewis dot structures that place electrons near the atom that donates are more likely than structures that place them far away on other atoms.

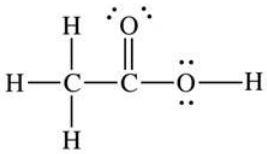
Exercise 8.4.2

Consider the two possible structures of acetic acid, CH_3COOH

a.



b.



a. For structure (a), what is the formal charge on the oxygen with three lone pairs?
b. For structure (a), what is the formal charge on the oxygen with the hydrogen atom?

c. For structure (b), what is the formal charge on the oxygen with no hydrogen?
d. For structure (b), what is the formal charge on the oxygen with the hydrogen atom?
e. Which is the better Lewis dot structure for acetic acid?

Answer a

-1

Answer b

+1

Answer c

0

Answer d

0

Answer e

Structure (b) because all the formal charges are zero

Formal Charge and Free Radicals

A free radical is a molecule that has one electron. Free radicals are very reactive and there are very few stable free radicals. For example, atomic chlorine is a free radical, $:\ddot{\underset{\cdot\cdot}{\text{Cl}}}\cdot$, and two of them will combine to form a bond, which is why chlorine is a diatomic

$$:\ddot{\underset{\cdot\cdot}{\text{Cl}}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\text{Cl}}}: \rightarrow :\ddot{\underset{\cdot\cdot}{\text{Cl}}} - \ddot{\underset{\cdot\cdot}{\text{Cl}}}:$$

Lets look at two resonance structures of NO_2.

$$\ddot{\underset{\cdot\cdot}{\text{O}}} = \ddot{\text{N}} - \ddot{\underset{\cdot\cdot}{\text{O}}}\cdot \longleftrightarrow \ddot{\underset{\cdot\cdot}{\text{O}}} = \dot{\text{N}} - \ddot{\underset{\cdot\cdot}{\text{O}}}:$$

In the left resonance structure, all the atoms have zero formal charge, while on the right structure, the nitrogen has a +1 formal charge, and the oxygen with the single bond has a -1 formal charge.

Can you draw two additional resonance structures for the above molecules?

Yes, just switch the single and double bonds for the above two structures (with the oxygens and their lone electrons).

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8.5: Drawing Lewis Dot Structures

Introduction

There are multiple ways to draw Lewis dot structures. We will follow a flow chart that allows you to identify exceptions to octet rules and resonance structures. You start by counting the number of electrons the atoms donate to the structure, and you need to take into account charge if you are drawing an ion. Then draw a hypothetical structure where every atom except hydrogen has an octet, and then count the number of electrons in the structure. It is either less than, equal or greater than the number of electrons donated. These are outlined in the following flow chart and step-by-step rules are given below.

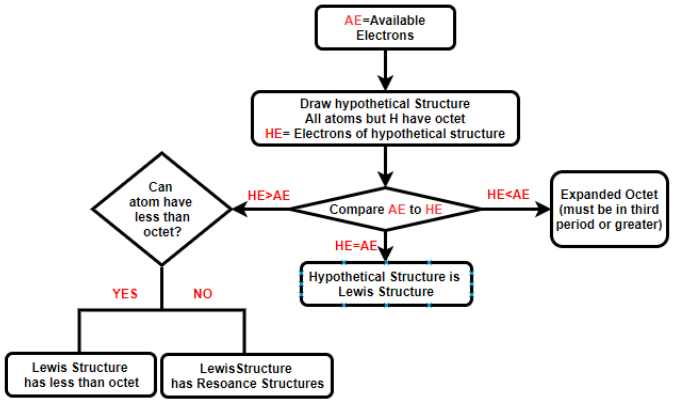


Figure 8.5.1: Flow chart for logic involved in the Lewis dot structure technique (below)

Lewis Dot Structure Technique

The following handout has these instructions: http://chemwiki.ucdavis.edu/@api/deki/files/60817/vsepr-1-Review.pdf

1**. Determine total number of available valence electrons.**

- Determine the total number of valence electrons available, each atoms of the representative elements contributes the number of electrons equal to it's group number (IA – VIIA).
- If there is an odd number of electrons, the structure will be a free radical, which has a lone electron in an orbital. This electron will exist in a nonbonding orbital or a multiple bond.
- If the compound is an ion,
  - add one electron for each negative charge
  - subtract one electron for each positive charge

2. Determine structural connectivity.

- First atom is central atom (unless Hydrogen, which can never be central)
- If more than 2 types of atoms, set up in order of formula
- Organic compounds often contain multiple carbons connected to each other, you will need to be able to identify functional groups.

3. Draw hypothetical structure with each atom surrounded by 8 electrons in pairs.

- Place two electrons forming a single bond between bonded atoms by drawing a line between the two atoms.
- For each atom not surrounded by an octet of electrons (4 bonds), add lone pairs of electrons (two dots to a lone pair) until all atoms are surrounded by an octet.
- Note, hydrogen can only have 2 valence electrons.

4. Count the total number of electrons in the hypothetical structure.

a. If it is **EQUAL** to the number of available electrons from step 1, **this is the correct Lewis Dot Structure**.
b. If it is **GREATER** than the number of available electrons from step 1, **go to step 5.**
c. If it is **LESS** than the available number of electrons from step 1**, go to step 7.**

5. Determine if any atoms can have less than an octet.

If not, proceed to step 6, if so, decrease the number of loan pairs around these atoms until the total number of electrons in structure equals the number from step 1.

a. Hydrogen always has a duet (one bond – 2 electrons)

b. Group IIA can have a quartet (4 electrons)

c. Group IIIA can have a sextet (6 electrons)

6. Combine adjacent lone pairs into multiple bonds

Place multiple bonds into structure by replacing two loan pairs from two adjacent atoms with a bonding pair. **Resonance structures result if you have more than one option for doing this.** Repeat this until the structure has the same number of electrons as determined in step 1. Be sure to generate all resonance structures

7. Expanded Octets

If any atoms have d orbitals available (3rd period or greater), they can have an "expanded octet", that is more than 8 valence electrons. Add lone pairs to these atoms until the number of electrons equals the number from step 1.

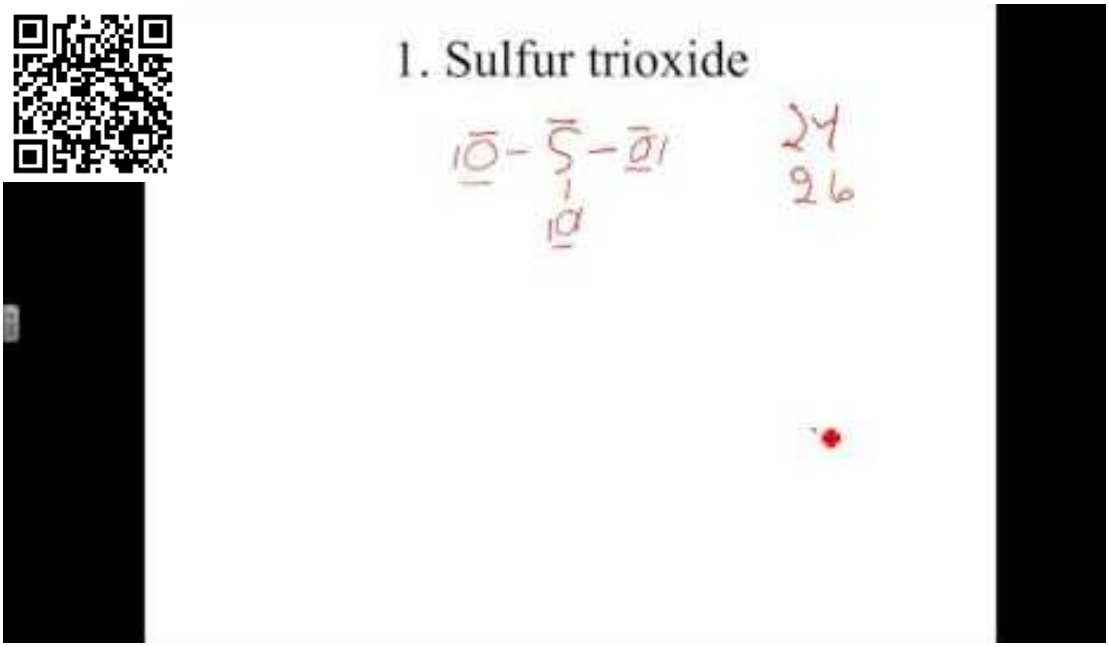
8 RESONANCE STRUCTURES: Check step 6 to see if additional electron configurations can be drawn by changing the position of multiple bonds, these represent resonance structures. The best configurations will be typically be the ones where the atoms are assigned the formal charges closest to zero (step 9). In the event that no resonance structure has a zero formal charge, assign negative formal charges to the most electronegative elements.

9. FORMAL CHARGES: These correlate the electron locations in the molecule to the atom that donates them. The formal charge (FC) for each atom can be determined by the following equation. The sum of the formal charges equals the charge of the species.

Examples

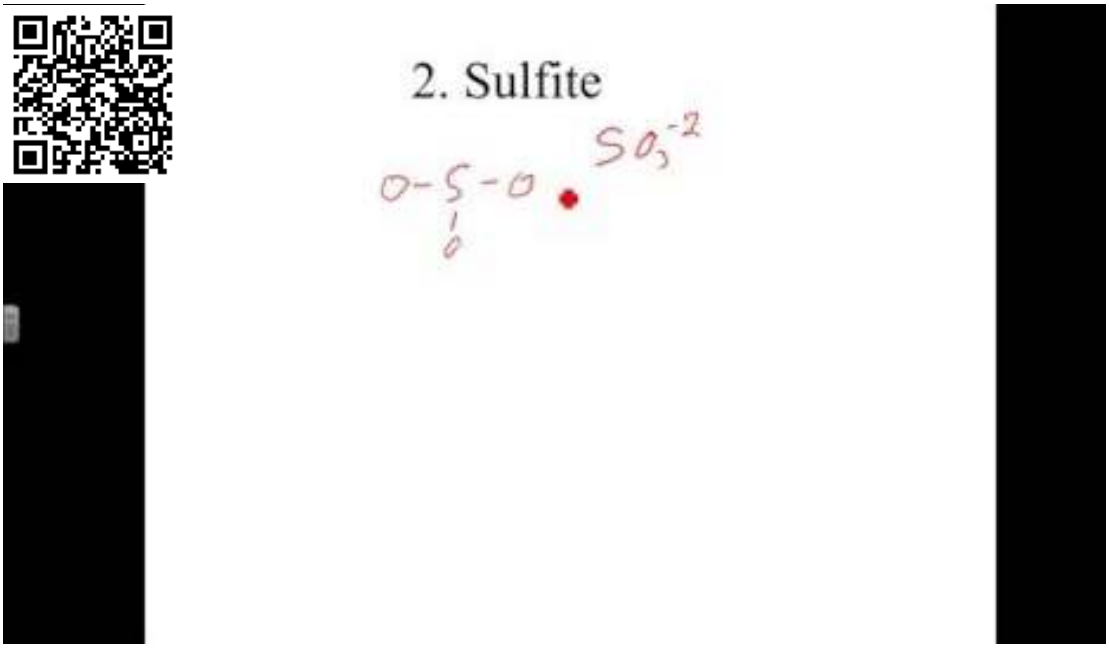
The following YouTubes follow the worksheet above, which should be downloaded and followed as you watch the YouTubes.

Sulfur Trioxide



Video 8.5.1: *Please look at Handout 1: Lewis dot structure technique while watching this video. Note steps 1 and 2 are switched but all the rest are the same.*

Sulfite



Video 8.5.1: Please look at Handout 1: Lewis dot structure technique while watching this video. Note steps 1 and 2 are switched but all the rest are the same.

Worksheet

The following worksheet should be downloaded and filled out. This is the first of two companion worksheets and in the molecular geometry we will start with the Lewis dot structures of these molecules and determine their geometry's, polarity's and the types of molecular orbitals involved in the bonds.

Handout 1.2: Lewis Dot Structure Worksheet:

http://chemwiki.ucdavis.edu/@api/deki/files/61154/vsepr1_WorkSheet.pdf

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8.6: Molecular Geometries

Introduction

There is a three step approach to determining the geometry of a molecule.

1. Determine the Lewis dot structure of the compound.
2. Determine the Electron geometry from the Lewis dot structure.
3. Determine the molecular geometry.

It is very important from the onset that students understand the difference between electronic geometry and molecular geometry. In calculating electronic geometry we use the Valence Shell Electron Pair Repulsion (VSEPR) model, which states that the lowest geometry for electronic orbitals around a positive nucleus is for the orbitals to be as far away as possible. Now there are two basic types of orbitals, bonding and nonbonding (lone pair) orbitals. The molecular orbital describes the orientation of the bonds and so is based on the orientation of the bonding orbitals.

VSPER

VSEPR (Valence Shell Electron Repulsion Theory) is used to determine the geometry of the orbitals around a nucleus. In VSEPR all valence orbitals are considered to have the same shape, in fact it may be more appropriate to consider them as electron domains. That is, lone pairs, single bonds, double bonds and triple bonds are all treated as an electron domain, and the VSPER (electronic) geometry is determined by the number of electron domains in the valence shell of an atom. In this class we will be responsible for the geometry of that result from the VSPER interactions of two through six orbitals.

Video 8.6.1 is a very short video showing the five VSPER electronic geometries for atoms with between 2 and 6 electron domains, the steric number. In watching video 8.6.1 you should note how the geometry changes as the steric number changes and additional orbitals are successively added to the central atom. The five geometries are summarized in table 8.6.1.

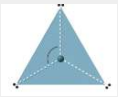
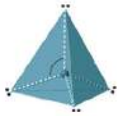
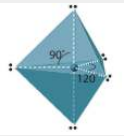
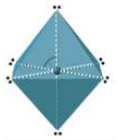


Video 8.6.1: *1'01" YouTube uploaded by Piti Treesukol showing the 5 VSEPR electronic geometries for steric numbers 2-6, there is no audio on this YouTube and you should look at how bringing in successive orbitals perturbs the geometry of the existing ones. (https://youtu.be/uwkmOVvnK4Q)*

The five VSEPR geometries are summarized in table 8.6.1.

Table 8.6.1: The 5 VSEPR Geometries.

# Electron Domains (Steric Number)	VSEPR Geometry	Angle Between Electron Domains	

# Electron Domains (Steric Number)	VSEPR Geometry	Angle Between Electron Domains	
2	linear	180°	
3	trigonal planar	120°	
4	tetrahedral	109.5^o	
5	trigonal bipyramidal	90°, 120°	
6	octahedral	90°	

Molecular Geometry

After calculating the electronic geometry from VESPR we can determine the molecular geometry based on the bonding orbitals. If there are no lone pairs and all orbitals are bonding, then the molecular geometry is the electronic geometry. Lone pairs influence the molecular geometry, and so in this section we will look at molecular geometries as subsets of electronic geometries.

Before proceeding, please watch the follow YouTube



Video 8.6.2: 6'20" youtube uploaded by Van Wyk describing the determination of molecular geometry from VESPR electronic geometries (https://youtu.be/TNzaVw9_GCY)

Figure 8.6.1 shows the various molecular geometries for the five VESPR electronic geometries with 2 to 6 electron domains. When there are no lone pairs the molecular geometry is the electron (VESPR) geometry. When there are lone pairs, you need to look at

the structure and recognize the names and bond angles. Note, this work ignores the trivial geometry of two atoms like HCl or H_2, as they must be linear, but when you have three atoms, they can be linear or bent.

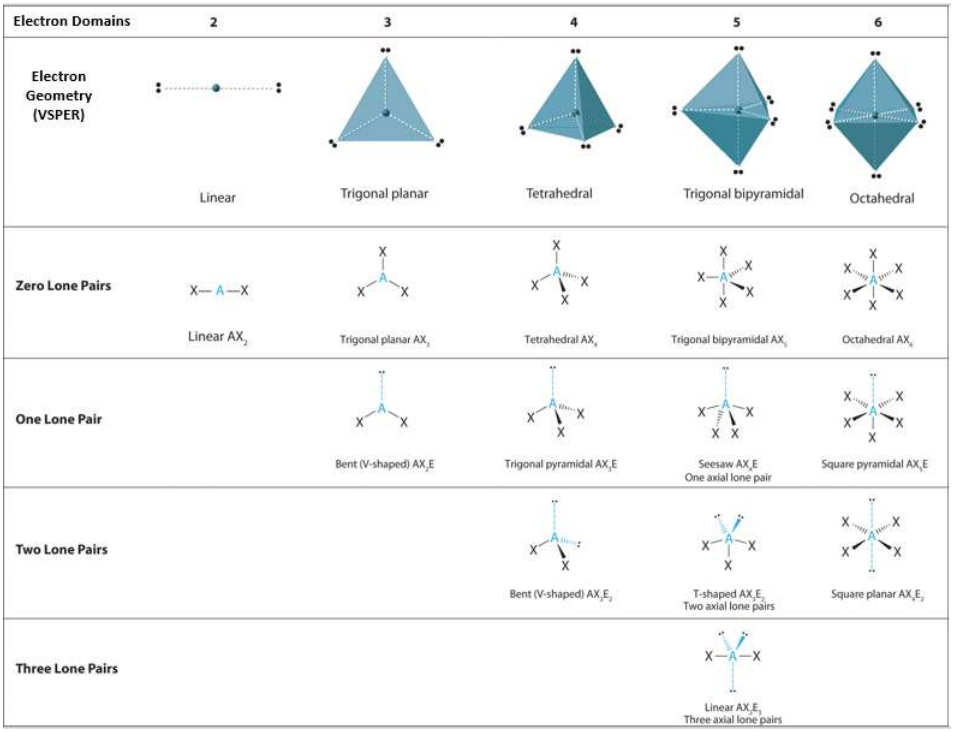


Figure 8.6.1: Overview of molecular geometries based on bonding orbitals of VSEPR electronic structures.

Two Electron Domains

Three atoms result in two electron domains and the structure is linear. There are three common types of molecules that form these structures, molecules with two single bonds (BeH_2), molecules with a two double bonds (CO2) and molecules with a single and triple bond (HCN).

H-Be-H	O=C=O	$H-C\equiv N$
BeH_2	CO_2	HCN

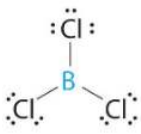
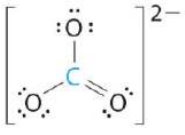
Note, Beryllium can have less than an octet, while carbon can not. Also note that the double bond in carbon dioxide and the triple bond in hydrogen cyanide are both treated as a single electron domain

Three Electron Domains

There are two molecular geometries that can come out of three electron domains, trigonal planar (no lone pairs) and bent with ≈120° bond angle (one lone pair) .

0 lone pairs

These are of the form AX_3, where X represents an atom that is bonded to three other atoms, and for which there are no lone pairs.

	
BCl_3 (Group IIIA can have less than an octet)	CO_3^{-2} (note there are resonance structures for carbonate)

1 lone pair

These are atoms of the form AX_2E, where E represents a lone pair. Examples are SO_2 and O_3. Note, the lone pair takes up more space than the bonding pair, so the bond angle is less then the ideal 120°.

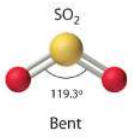


Figure 8.6.3: Note the bond angle in sulfur dioxide is less than the ideal 120° of its trigonal planar electronic geometry

-

Four Electron Domains

All atoms with four electron domains have tetrahedral electronic geometry

0 Lone Pairs

These are of the form AX_4 and the molecular geometry is the same as the electronic geometry

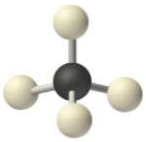


Figure 8.6.4: Molecules like methane (CH_4) have tetrahedral molecular geometry with 109.5° bond angles

1 Lone Pair

These are of the form AX_3E and have trigonal pyramidal molecular geometries. Note the bond angle is less than the ideal because the lone pair take up more space

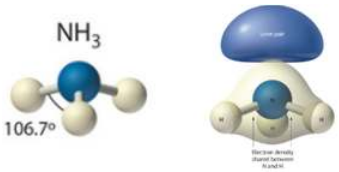
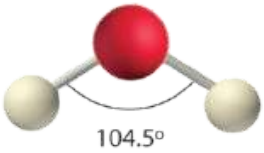


Figure 8.6.5: Molecules like ammonia have tetrahedral electronic geometry but trigonal pyramidal molecular geometry. Note the lone pair orbital takes up more space than the bonding orbitals and so the bond angle is less than the ideal 109.5°.

2 Lone Pairs

These are of the form AX_2E_2 and have bent angles, which in the case of water are 104.5°C



8.6.6: Molecules like water have tetrahedral electronic geometry and bent molecular geometry

These are of the form AX_2E_2 and have bent angles, which in the case of water are 104.5°C

> **Note**
>
> There are two bent geometries based on trigonal planar electronic geometry with one lone pair as exemplified by sulfur dioxide that has a bond angle a bit less than 120°C, and by tetrahedral electronic geometry with two lone pairs, as exemplified by water with 104.5°C bond angle.

Five Electron Domains

All molecules with 5 electron domains have trigonal bipyramidial electronic geometry. The central atom of these molecules must be in the third or higher period of the periodic table.

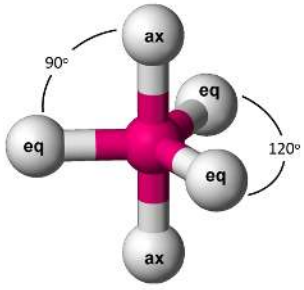


Figure 8.6.7: trigonal bipyramidal geometry has two types of bond angles, axial-equatorial (90°) and equatorial-equatorial (120°).

In Figure 8.6.7 you note that the two axial positions are linear to each other and if we define this axis as the z axis of the cartesian coordinate system, then the equatorial positions have a trigonal planar geometry in the xy plane. So the trigonal bipyramidal geometry is a superposition of linear and trigonal planar geometries. It is important to note that the bond angle between equatorial and axial positions (90°) is different than between two equatorial positions (120°).

0 Lone Pairs

As in the above cases, if there are no lone pairs, the electronic geometry is the molecular geometry.

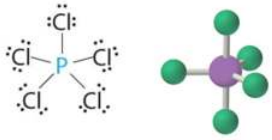


Figure 8.6.8: Phosphorous pentachloride has trigonal bipyramidal moleculare geometry.

1 Lone Pair

These are of the form AX_4E and have a "See-Saw" geometry, which is also classified as a distorted tetrahedron. Sulfur tetrafluoride (SF_4) has such a structure.

> **Note**
>
> The Lone pair can take two positions, axial or equatorial. **The lone pair goes into the equatorial position** because it takes up more space, and there is more room in the equatorial positions. This can be seen from Figure 8.6.7, where it is clear that the 90° bonds bring the atoms closer than the 120° bonds, and each axial position has three 90° bond interactions while each equatorial has two (and two 120°) bond interactions. As the lone pairs take up more space, they move into the equatorial positions.

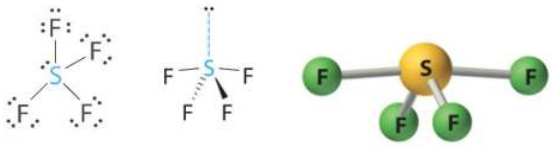


Figure 8.6.9: SeeSaw (distorted tetrahedron) geometry of sulfur tetrafluoride

2 Lone Pairs

These are of the form of AX_3E_2 have trigonal bipyramidal electronic geometry and "T-shaped" molecular geometry. Bromine triflouride (BrF_3) is an example of a molecule with 5 electron domains and two lone pairs (Figure .

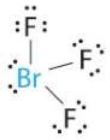


Figure 8.6.10: Lewis dot diagram of bromine trifluoride showing two lone pairs.

There are three ways of distributing the lone pairs between the axial and equatorial positions and the lone pairs always go on the equatorial positions because these are the least confined. This can be seen in Figure 8.6.11

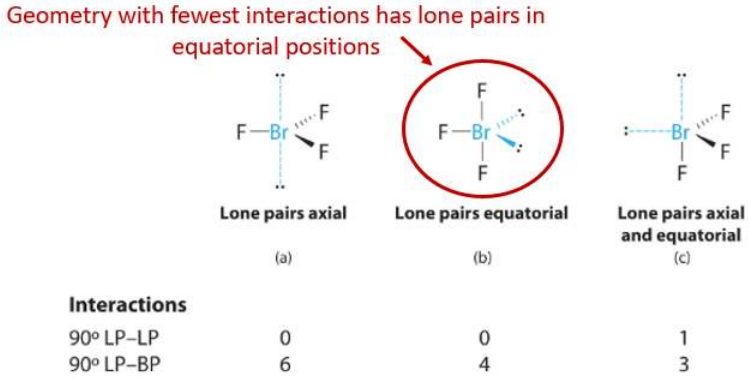


Figure 8.6.11: Configuration (b) and (c) both have 4 interactions, and the 90o LP-LP is greater than the 90o LP-BP interaction and so the middle configuration is the least confined.

Once again, the **lone pairs go into the equatorial positions.**

3 Lone Pairs

These are of the form AX_2E_3 and and the trigonal bipyramidal electronic structure results in a **linear molecular structure**. Triiodide (I_3^-) is an example of this geometry.

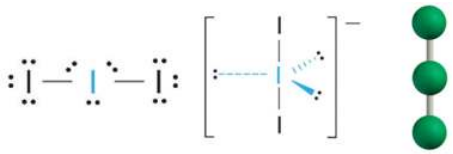


Figure 8.6.12: Note the lone pairs go into the equatorial positions and the molecule is linear because the bonds are along the axial positions

---

Six Electron Domains

Six electron domains form an *octahedron*, a polyhedron with 8 faces, but the electron pair geometry has linear orientations along the 3 Cartesian coordinate axis. Therefore the octahedral represents 6 electron domains along the Cartesian axis (Figure 8.6.13).

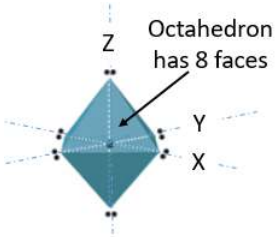


Figure 8.6.13 : Six domains has electron pairs oriented along the 3 Cartesian coordinate axes

0 Lone Pairs

- These are of the form AX_6 and the molecular geometery is the same as the electronic geometry. The central atom must be on the third period or greater of the periodic table as this structure has an extended octet. Sulfur hexafluoride is an example of a hexagonal molecular geometry.

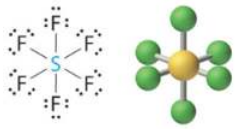


Figure 8.6.14: Lewis dot structure and octahedral geometry of sulfur hexafluoride.

1 Lone Pair

- These molecules are of the form of AX_5E and form square pyramid structures. Bromine pentafluoride (BrF_5) has this structure.

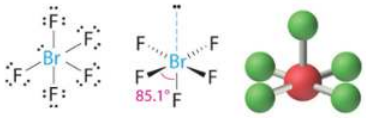


Figure 8.6.15: Lewis dot structure and square pyramidial geometry of bromine pentafluoride.

2 Lone Pairs

These structures are of the form $AX_4E_2$and form square planar structures. Iodine tetrachloride ion (ICl_4^-). T

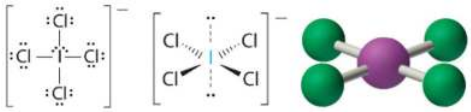


Figure 8.6.16: Lewis dot structure and square planar geometry of

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Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate (CH_3–N=C=O), as linked AX_mE_n fragments beginning with the left carbon, followed by the nitrogen and then the second carbon

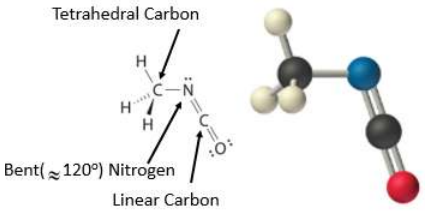


Figure 8.6.17: Geometric structure of methyl isocyanate (CH_3–N=C=O), note there is no rotation around the double bonds only the single CN bond can rotate.

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has

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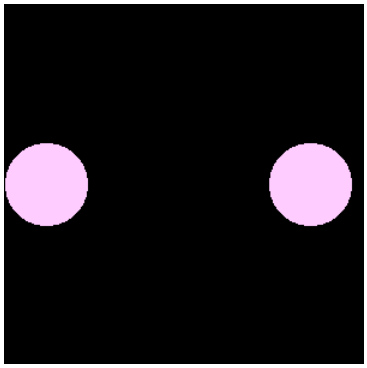
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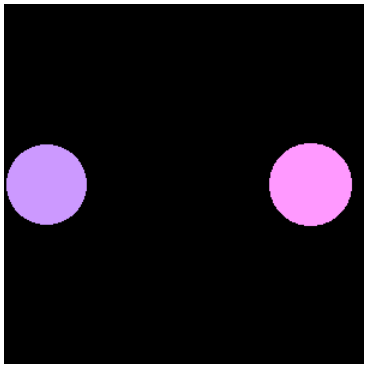
8.7: Bond Polarity and Electronegativity (χ χ)

Introduction

In a covalent bond electrons are shared in a bonding orbital between two nuclei. If it is a homonuclear bond (between atoms of the same element like in H_2, N_2, O_2, Cl_2,...), the bonding electrons are shared equally and the charge distribution around the bond is symmetric (left animation of Figure 8.7.1). If it is a heteronuclear bond like H-Cl or H-C, the electrons may or may not be shared equally. Equally shared electrons result in a non-polar bond and unequally shared electrons result in a polar bond, where one atom feels a partially positive charge (δ^+) and the other atom feels a partially negative charge (δ^-). In this Chapter we will introduce the concept of electronegativity (χ, pronounced "ky" as in "sky") to help identify if a bond is polar or not. In a bond with atoms of different electronegativity, the bonding atoms with a higher electronegativity attracting electron density more than atoms with a lower electronegativity, and so it has a partially negative charge..



Orbitals of two atoms of similar electronegativity come together to form a symmetric nonpolar covalent bond



Orbitals of two atoms of dissimilar electronegativity come together and form an asymmetric polar covalent bond.

Figure 8.7.1 : The atoms of the left have equal electronegativity and so form a nonpolar bond with a symmetric electron distribution. The atoms on the right have different electronegativity, with the pink orbital having a higher electronegativity than the blue, and so the resulting bond is asymmetric, with there being a partial negative charge on the more electronegative atom and a partial positive on the less electronegative atom.

In Summary:

- A **nonpolar covalent bond** has a symmetric bonding orbital electron density function with equal sharing of the bonding electron.
- A **polar covalent bond** has an asymmetric bonding orbital electron density function with non-equal sharing of the bonding electrons

Electronegativity

Introduction

Electronegativity is not a thermodynamic property and has no units. The term "electronegativity" was introduced by Berzelius in 1811 and we will use the Pauling scale for electronegativities, developed by Linus Pauling, which ranges in value from 0.7 (Francium and Cesium) to 4.0 (Fluorine). Although we assign electronegativity values to element, they are not properties of an atoms per se, but of the atoms when in a bond. That is, if two atoms of different electronegativities form a bond, the more electronegative element will pull electron density from the less electronegative element, which can also be classified as the more electropositive element. It also needs to be noted that in a molecule where an atom is bonded to more than one other atom, the actual electron distribution is the result of all interactions.

Periodic Trends of Electronegativities

On a basic level, electronegativities can be correlated to ionization energies and electron affinities, although the later are thermodynamic properties of an isolated atom in the gas phase, while electronegativities are based on an arbitrary unitless scale. That said, atoms with low ionization energies (which are always endothermic) tend to be electropositive, because they do not

tightly hold onto their valence electrons. Likewise, atoms with exothermic electron affinities (release energy when they gain an electron) tend to have high electron energies as they like to gain electrons.

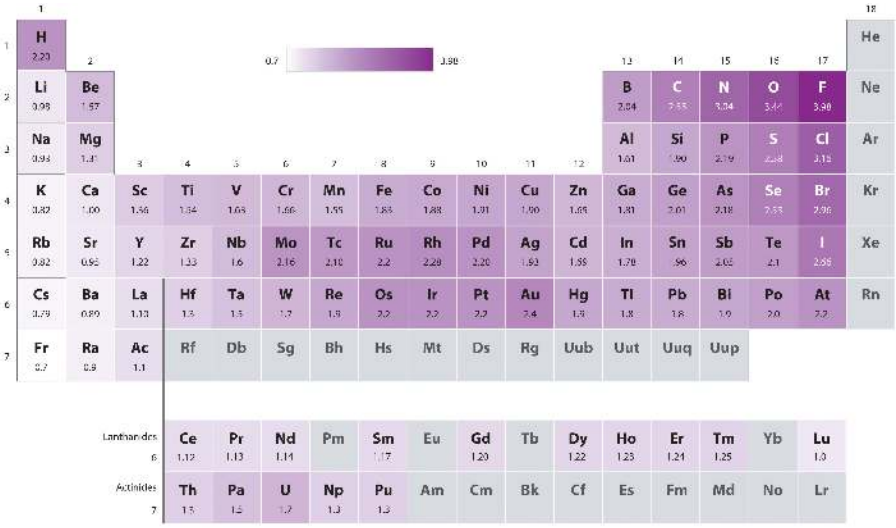


Figure 8.7.2: Paulings scale of electronegativity (chi) of the elements. When a bond forms between two elements, the more electronegative element has a stronger pull for electrons than the more electropositive element.

Exercise 8.7.1

Why do the Noble Gases in Table 8.7.1 not have a value for electronegativity?

Answer

Remember, electronegativity is not a thermodynamic property, but a relative value given to an atom in a bond, which indicates how strongly it pulls the shared electron density towards itself. The noble gasses tend to not bond with other elements, which is why we call them noble, and thus it does not make sense to give them a value.

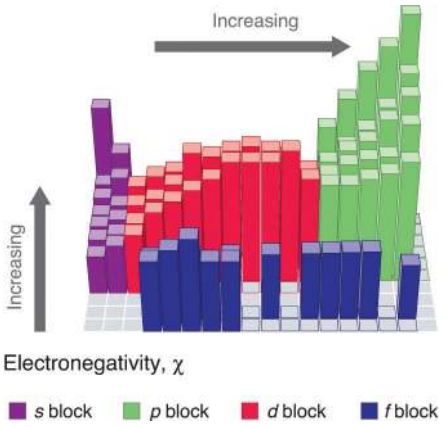


Figure 8.7.3: Diagram showing periodic trends in electronegativity. Note going up a group and across a period results in an increase in electronegativity.

Exercise 8.7.2

Why would going across (left to right) a period result in an increase in electronegativity?

Answer

Remember that the effective nuclear charge increases going across a period, and the size of the atoms get smaller. This means the pull on the electron would be stronger, and so the trend makes sense.

Why would going down a group result in increased electropositivity (decreased electronegativity).

Answer

Each element has an isoelectronic valence shell electron configuration, with the principle quantum number getting larger, meaning the valence electrons are farther away from the nucleus. This means they are less tightly held and so it would be less electronegative.

Without a table of electronegativities, would you be expected to know which would be greater

a). Mercury or Silver?
b). Mercury or Indium?

Answer

a) **No**, as going up the periodic table increases χ while going right to left decreases it. That is, (χ-{Cd}>(χ-{Hg} while (χ-{Ag}<(χ-{Cd}, and you do not know which effect is the greater. (The trends oppose each other.)

b) **Yes**, as going up and left to right both increase χ, (χ-{Cd}>(χ-{Hg} but going right to left decreases, (χ-{In}>(χ-{Cd}, so In must be greater than Hg

Rule of Thumb: Predicting Bond Types

As a "rule of thumb", electronegativity differences can be used to predict if a bond will be covalent, polar covalent or ionic. If the difference in χ between two bonding atoms is less than 1/2, they are of very similar electronegativity and it is a covalent bond. If it is greater than 2 they are substantially different and more electronegative atom completely removes a valence electron from the electropositive, forming an ionic compound, and if it is between 0.5 and 2.0 it is polar covalent.

Table 8.7.2: Rule of Thumb values for predicting bond types from electronegativity

Difference in Electronegativity (χ)	Bond Type	Example
<0.5	Covalent or metallic	Cl-Cl ($\Delta\chi$=0), C-H ($\Delta\chi$=0.35)
0.5-2.0	Polar Covalent	H-Cl ($\Delta\chi$=0.96)
>2.0	Ionic	Na-Cl ($\Delta\chi$=2.23)

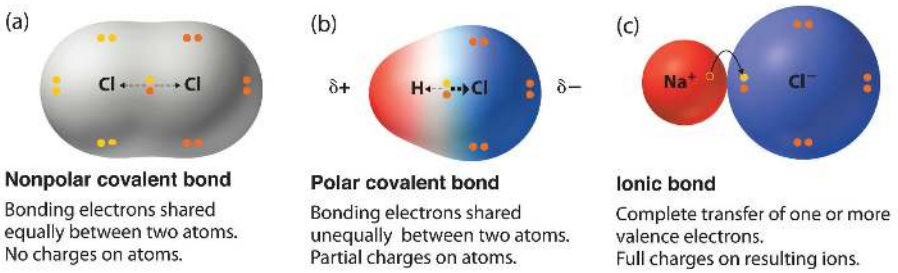


Figure 8.7.4: Illustration of different bond types between atoms of different electronegativities (see table 8.7.1 for χ values and table 8.7.2 for ($\Delta\chi$ values).

Van Arkel-Ketelaar (VAK) Diagram

Now that we have covered periodic trends in electronegativity it is a good time to revisit the Van Arkel-Ketelaar (VAK) diagram introduced in the introduction of this Chapter, although this is being done with the caveat that this Chapter focuses on covalent and polar covalent bonds. In the VAK diagram the X axis is the average electronegativity of the two atoms in a bond, which can only be a high value if they are both nonmetals and only be a low value if they are both metals, and so metallic bonds would be on the left and covalent bonds (between two nonmetals) on the right. The Y-axis is the difference in electronegativity, a value that can only be a high value if one is a metal and the other a nonmetal, which also results in an average value that is midway between the metal and a nonmetal, and this results in triangular structure where the top would represent ionic bonds between metals and nonmetals.

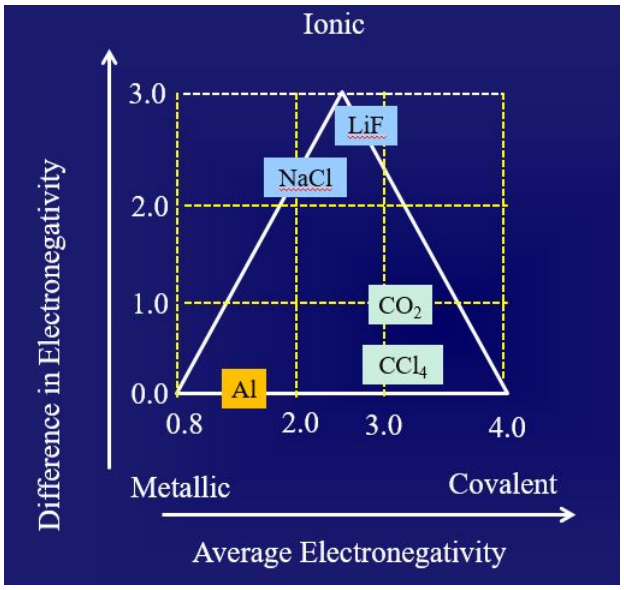


Figure 8.7.5: Van Arkel-Ketelaar diagram predicting the metallic, ionic or covalent nature of a bond between two atoms as a function of electronegativity differences and average values.

The following youtube is an animation that shows the difference between covalent, polar covalent and ionic bonds based on the difference in electronegativity of the bonding atoms.

Animated YouTube going over electronegativity and bond types



Video \(PageIndex1 3:32 min YouTube by professor Dave going over the basics of electronegativity (https://youtu.be/PoQjsnQmxok).

Second YouTube going over bonds types and electronegativity.



Video 8.7.2: 2'11" YouTube uploaded by RicochetScience going over electronegativity (https://youtu.be/09Vx5VHiMHA)

Dipole Moments of Diatomics

If the difference in electronegativity between the atoms of a bond are between 0.5 and 2.0 we can determine that the bond is polar, and if the atom is a diatomic, that must result in a polar molecule.

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl} \tag{8.7.1}$$

Polar molecules have a positive and negative end, which will align with an external electric field as shown in Figure 8.7.4

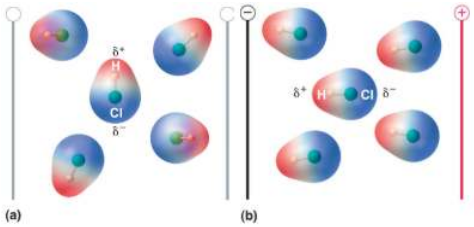


Figure 8.7.6: (a) polar HCl molecules randomly aligned in absence of an electric field, and (b) aligned in the presence of an electric field.

Figure 8.7.6 Shows the effect of an electric field on a polar molecule. In that absence of an external electric field (a) the molecules have random orientation, in the presence of an electric field (b) they align with the field as the δ^+ end of the polar molecule is attracted towards the negative plate of the external field and the δ^- end is attracted towards the positive plate of the external field. Since the molecule is being pulled in opposite directions it does not migrate to the plate the way an ion would, but aligns with the field.

It should be noted that there are attractive interactions between the red δ^+ end of one molecule with the blue δ^-, but in the gas phase these interactions are essentially negligible.

Dipole Moment

An electric dipole occurs when two equal charges are separated by a distance. The dipole moment is a vector $\vec{\mu}$, which is a measure of the electric dipole's strength and orientation and has the units of the Debye. The dipole moment of a molecule is a function of the partial charges of the polar bond, and the distance between them. Ignoring the vector aspects, this can be calculated by Equation:

$$\mu = qr \tag{8.7.2}$$

where

- μ is the dipole moment (really a vector)
- q is the magnitude of the partial charges q^+ or q^- (or the more commonly used terms δ^+ and δ^-), and
- r is the distance between the two charges of the dipole moment (which is also a vector).

The Debye is a very small unit, which in terms of SI base units has a value of 3.34×10^{-30} Amp meter seconds. Note, Yocto, (10^{-24}) is the smallest SI prefix and this is of the order of 10^6 times smaller!

Relating Dipole Moments to $\Delta\chi$ and bond lengths:

In table 8.7.2 we look at the diatomic molecules between H and the halogens. We note that as you go down the periodic table the bond length increases, which would result in a large dipole moment. But it goes down because the $\Delta\chi$ decreases to a greater extend. So the difference in electronegativity is the major factor in determining the strength of the polarity of a molecule.

Table **8.7.2:** *Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics*

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

Note:

In this class you will not be performing calculations with μ, but you do need a conceptual understanding, and you need to understand the difference between the charge of an ion, and the magnitude of the dipole moment of a polar molecule. So far we have kept to simple diatomics. In the next section we will move onto compounds with more than one polar bond, and see that the orientation of the bonds affects the polarity of a molecule, and that a symmetric molecule like carbon dioxide has polar bonds, but is in itself, nonpolar.

Contributors

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:
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8.8: Bond and Molecular Polarity

Introduction

Carbon dioxide and water have molar masses of 44 amu and 18 amu respectively, and from common sense, we know that if you apply an equal force to two different objects of different masses, the lighter one moves faster. Common sense also tells us that a gas moves faster than a liquid, so why at ambient conditions (room temperature and room pressure) is the heavier carbon dioxide a gas while the lighter water is a liquid?

The answer to this seeming paradox is that although both water and carbon dioxide have polar bonds (Table 8.8.1), only water is a polar molecule, and carbon dioxide is nonpolar because it is symmetric and its bond dipoles cancel. This can be visualized in Figure 8.8.1,

Table 8.8.1: χ and ($\Delta\chi$ data for water and carbon dioxide, showing that they both have polar bonds.

Atom	Electronegativity (χ)	Bond	($\Delta\chi$)	Molecule	Dipole Moment (D)
C	2.55	C-O	0.89	Water	1.85
O	3.44	O-H	1.44	Carbon Dioxide	0
H	2.20				

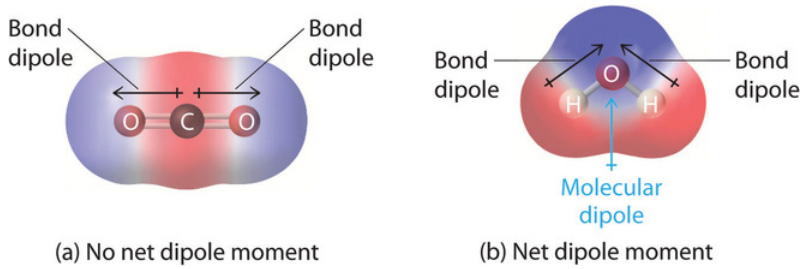


***Figure* 8.8.1**: *Both carbon dioxide and water have polar bonds, but only water is a polar molecule. Carbon dioxide is symmetric and the pull of the two oxygens on the carbon's electrons cancel out, so it is a nonpolar molecule with polar bonds.*



Video 8.8.1: *4'51" Youtube uploaded by Wendell Thomas going over bond polarity (https://youtu.be/DnRqqiLhdkM)*

Molecular Dipoles

The dipole moment of a molecule is the sum of all the bond dipoles within the molecule. These can be calculated by the following equation:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{8.8.1}$$

where

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

For simple molecules we can use visualizations and a few tricks to determine if a molecule with polar bonds is polar or not. The First question we ask is, is it symmetric. If it is symmetric, than the bond dipoles cancel out and the molecule is non polar.

Symmetric Geometries

In section 8.6 Molecular Geometries we learned that there are 5 VSPER geometries, which are indicated in Figure 8.8.2

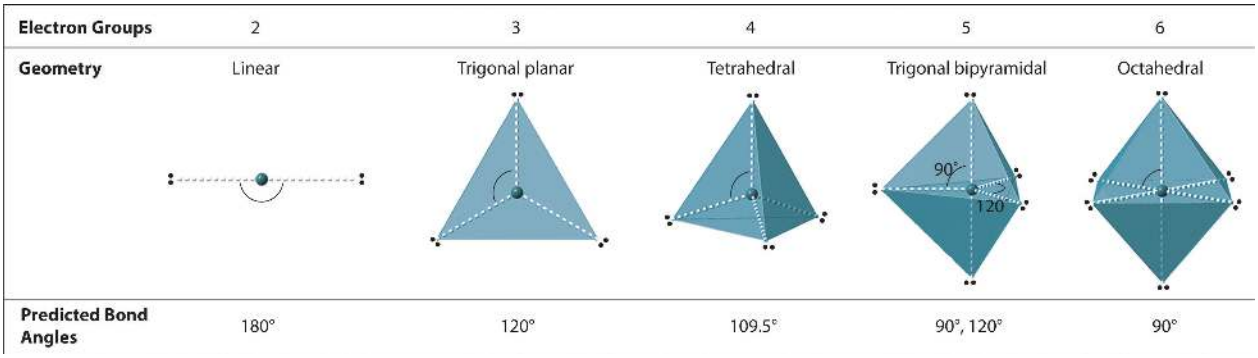


Figure 8.8.2: Five Symmetric Geometries from VSEPR theory.

If we take a closer look we see there are only three geometries, **linear**, **trigonal planar** and **tetrahedral**, with trigonal bipyramidal being a combination of linear along the axis and trigonal planaar along the equatorial plan, and with octahedral being linear along each of the 3 Cartesian coordinate axes (x,y,z).

Tip to Toe Technique for Vector Addition

One way to visualize the resultant vector from the addition of two (or more) vectors is to move the toe of the second vector to the tip of the first, with the resultant being the vector from the toe of the first to the tip of the second. In doing this, you can not change the orientation or the magnitude of the vector you moved. This is exemplified in Figure 8.8.3.

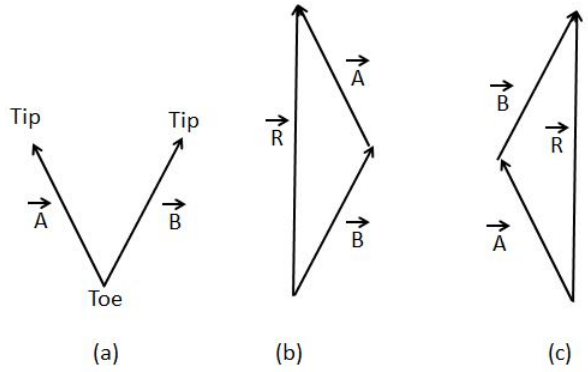


Figure 8.8.3: Visualization of vector addition using the tip to toe technique. We want $\vec{R}$, the resultant from the addition of adding $\vec{A}$ to $\vec{B}$ in (a). In (b) we move the toe of $\vec{A}$ to the tip of $\vec{B}$, while in (c) we move the toe of $\vec{B}$ to the tip of $\vec{A}$. $\vec{R}$ is the same in either case (b) or (c).

Applying this technique to carbon dioxide shows the dipole moment is zero



Figure 8.8.4: Here we show one of the C=O bonds in black and the other in red. When you move the toe of the red bond to the tip of the black, the resultant (toe of black to tip of red) is zero, as they are on top of each other.

Applying this technique to the trigonal planar structure of Aluminium chloride also creates a nonpolar molecule from the very polar Al-Cl bond χ_{Al}= 1.61, χ_{Cl}=3.16, so ($\Delta\chi$= 1.55, which is a highly polar bond. (Note: $AlCl_3$ is a crystal in the solid phase, but a trigonal planar molecule in the vapor phase).

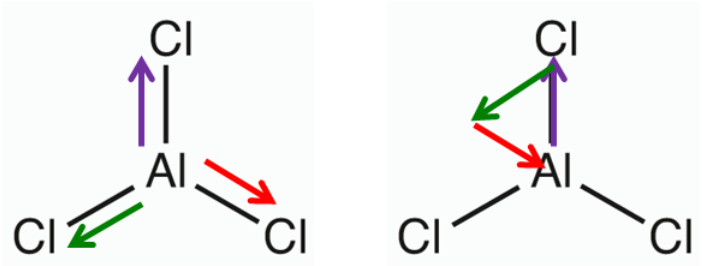


Figure 8.8.5: Here we show the three Al-Cl bonds in different colors, and when added, the resultant vector goes back to the central atom.

Summary of Symmetric Structures

A=central atom, B,C,D = atoms of type B,C or D, E=Lone pair electrons

1. sp hybrid
   - Linear
     - AB_2
2. sp^2 hybrid
   - Trigonal planar
     - AB_3
3. sp^3 hybrid
   - tetrahedral
     - AB_4
4. sp^3d hybrid
   - trigonal bipyramidal
     - AB_5
     - AB_2C_3 (B in axial positions, C in equatorial plane)
   - linear
     - AB_2E_3 (B in axial positions, E - lone pairs in equatorial plane)
5. sp^3d^2 hybrid
   - Octahedral
     - AB_6
     - AB_4C_2 (B along X & Y axes, C along Z axis)
     - $AB_2C_2D_2$ (B along X, C along Y and D along Z axes)
   - Square Planar
     - AB_4E_2 (B along X & Y axes, E - lone pairs along Z axis)

Contributors and Attributions

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8.9: Covalent Bond Properties: Order, Length, and Energy

Introduction

The covalent bond involves the electrostatic interactions of valence electrons and multiple nuclei of the atoms that form the bond. There are both attractive forces between opposite charges, and repulsive forces between like charges, and these can be described by Coulomb's law:

$$E = k\frac{q_1 q_2}{(4\pi\epsilon_0)r} \qquad F = k\frac{q_1 q_2}{(4\pi\epsilon_0)r^2} \tag{8.9.1}$$

- E is the bond energy
- F is the force
- r is the distance of separation between charged particles (note that the potential goes to zero when they are separated by infinity)
- q_1, q_2 are the charges of the respective species interacting

The potential well diagram of a homonuclear diatomic is a good way to understand a covalent bond as illustrated for hydrogen in Figure 8.9.1. It needs to be understood that a bond is dynamic, with the atoms oscillating around an equilibrium distance, which we call the bond length. This oscillation can be understood by looking at Figure 8.9.1. Region (1) shows the atoms completely separated. As they come closer together the electrons of each atom start being attracted to the nuclei of the other atom as in region (2), which lowers the energy and causes a bond. As the atoms keep moving closer the nuculear-nuclear repulsion start to become significant, and in region (4) the energy increases and the atoms move apart. Region (3) is the equilibrium bond length which represents the bottom of the potential well and is the length at which the molecules oscillate back and forth around.

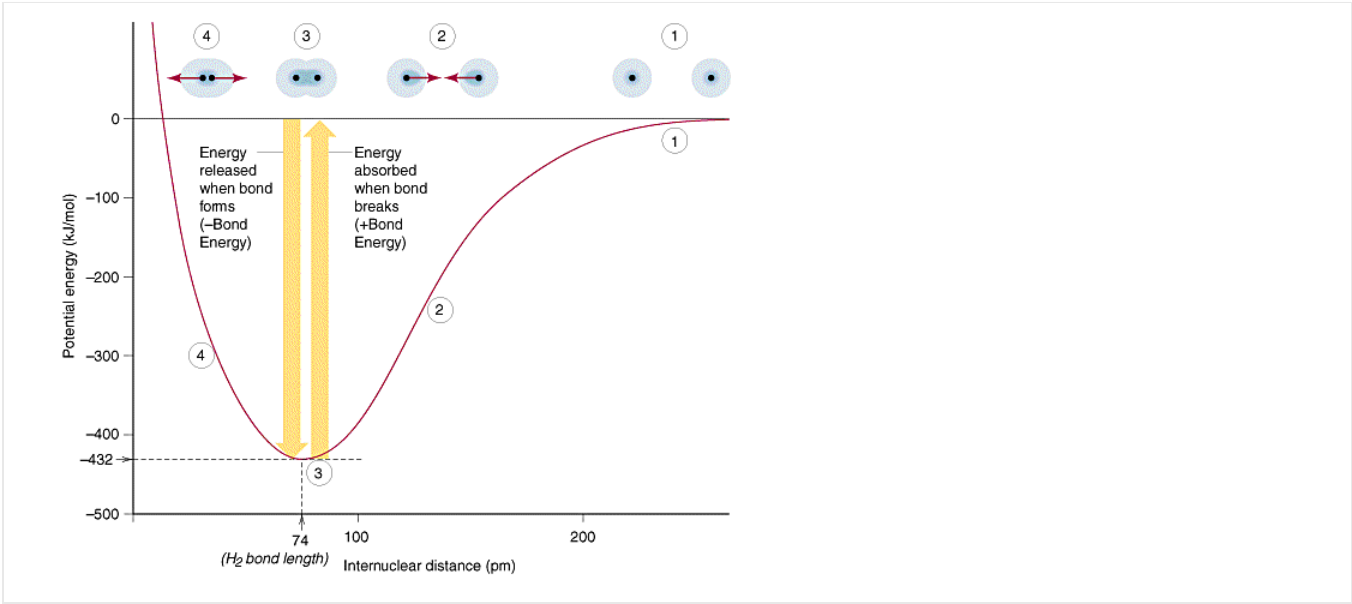


Figure 8.9.1: Potential Well Diagram for H_2, where the energy of the H-H bond is plotted as a function of the internuclear distance (radius)

From eq. 8.9.1 we note that when the atoms are separated by infinity (r=infinity) the energy is being divided by infinity, which means it is infinitesimally small and thus equals zero. This means the bond itself has a negative energy and the bond dissociation energy is the endothermic energy you must add to break a bond. Note, this also indicates why opposite charges attract, as that lowers the energy of the bonded particles when compared to the separated particles. It is important that you remember that any bond can be written as a "formation" (exothermic) or dissociation (endothermic) process.

Generic Bond Dissociation

If we look at a generic covalent bond as two electrons being represented as two shared electrons, we see there are two basic ways to break the bond, homolytically and heterolytically. In the former case, each of the separated species has one electron, making them

free radicals (species with a lone electron), while the second forms ions, with one species having both electrons and the other having none.

Homolytic bond cleavage

$$A - B \rightarrow A\cdot + B\cdot \tag{8.9.2}$$

Heterolytic bond cleavage

$$A - B \rightarrow A^{+} + B:^{-} \tag{8.9.3}$$
$$or$$
$$A - B \rightarrow A:^{-} + B^{+}$$

The potential well diagram in Figure 8.9.1 represents homolytic bond cleavage, which is the type we will discuss in this section. Remember, bond formation is the opposite of dissociation, and so can be visualized as the overlap of two orbitals on two different atoms that contribute one electron each (as indicated in fig. 8.9.1). There is another type of bond called the dative coordinate covalent bond, where one atom provides both electrons that are shared through the overlap with a vacant orbital on another atom.

Bond Order

The bond order is the number of covalent bonds in a chemical bond and the concept was introduced when we covered resonance structures.

Table 4.6.1 Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$H_3C–CH_3$	1	153.5	376	$H_3C–NH_2$	1	147.1	331
$H_2C=CH_2$	2	133.9	728	$H_2C=NH$	2	127.3	644
HC≡CH	3	120.3	965	HC≡N	3	115.3	937
$H_2N–NH_2$	1	144.9	275.3	$H_3C–OH$	1	142.5	377
HN=NH	2	125.2	456	$H_2C=O$	2	120.8	732
N≡N	3	109.8	945.3	O=C=O	2	116.0	799
HO–OH	1	147.5	213	C≡O	3	112.8	1076.5
O=O	2	120.7	498.4				

Table 8.9.1: Sources: Data from *CRC Handbook of Chemistry and Physics* (2004); *Lange's Handbook of Chemistry* (2005); http://cccbdb.nist.gov.

Fractional Bond Orders and Resonance Structures: Lewis dot structures represent a bond as a line between two atoms and sometimes Pi electrons are shared between more than two atoms and you need to draw multiple resonance strcutures to accurately describe the molecule. In these cases you can have fractional bond orders.

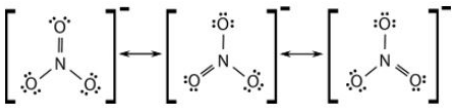


Figure 8.9.2: *Lewis dot structure of nitrate, where the actual bond order is 1.33*

In the case of nitrate (Figure 8.9.2) we see there are three resonance structures with each representing 2 single and one double bond, and if we look at each NO bond, two of the structures are single and one is double, for a total bond order of 4 across 3

structures, and so the bond order is 4/3 or 1.33. That is, the real molecule does not have two single and one double bond, but has three identical bonds of order 1.33.

What is the bond order of the CO bond in carbon dioxide?

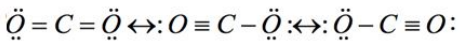


Figure 8.9.3: *Resonance structures for carbon dioxide.*

The CO bond order is two, as across the three resonance structures each bond is either 2, 3 or 1, for a total of 6. As there are 3 structures, the bond order of 6/3 or 2.

Bond Length

A bond is not static but dynamic with the atoms undergoing the attractive and repulsive forces as described in the potential well (fig. 8.9.1), where the bottom of the well represents the equilibrium position of the oscillating atoms, which we call the bond length. Table 8.9.1 shows bond lengths for a variety of bonds. Please note that this particular table is in picometers (10^{-12}), and that a common unit for bond length is the Angstrom Å (10^{-10}), so for example, the O=O bond is 1.207 Å.

Coulomb's law states that the bond energy is inversely related to the bond length (r), and so factors which influence a bond's strength influence its length. This can allow us to determine some trends in bond lengths.

Some trends in bond lengths for homologous series (where one atom is constant and another is changed)

- Bond length increases going down the periodic table. (smaller atoms make smaller bonds)
  H-F < H-Cl < H-Br < H-I
- Bond length decreases going across the periodic table. (smaller atoms make smaller bonds)
  C-C > C-N > C-O
- For bonds between equivalent atoms, the greater bond order the shorter the bond length
  C≡C > C=C < C-C
  Thus the NO bond of Nitrate, (fig. 8.9.2) is greater than N-O and less than N=O

Bond Dissociation Enthalpy

The IUPAC definition for bond dissociation energy, D, is "the enthalpy (per mole) required to break a given bond of some specific molecular entity by homolysis, e.g. for $CH_4 \rightarrow \cdot CH_{3)} + H\cdot$, (IUPAC Gold Book) and the "mean bond energy" is "the average value of the gas phase bond dissociation energies (usually at a temperature of 298K) for all bonds of the same type within the same chemical species.

Table 8.9.2 Energies for the successive breakup of C-H bonds in methane Source: Data from CRC Handbook of Chemstry and Physics (2004)K.

Reaction	D (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

Average bond energies can be tabulated as in table 8.9.3 and it needs to be emphasized that these values are average energies. One uese of these tables is that you can determine the enthalpy of reaction if you know the structure of all species in a balanced chemical equation.

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \qquad (8.9.4)$$

Single Bonds										Multiple Bonds	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835

Single Bonds										Multiple Bonds	
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327	S–F	284	Cl–I	208	N=N	418		
H–F	565	C–Br	285	S–Cl	255	Br–Br	190	N≡N	942		
H–Cl	428	C–I	213	S–Br	218	Br–I	175	N=O	607		
H–Br	362	Si–Si	222	I–I	149	O=O	494				
H–I	295	Si–O	452	S=O	532						

***Table* 8.9.3 :** *Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K. Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).*

Trends in Bond Dissociation Energy

There are 3 trends we can observe with bond energies. You should be able to relate these trends to the bond length trends (above).

1. Bonds with hydrogen (H-X) decrease in strength as we go down a column of the periodic table.

$$\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$$

2. Bonds between like atoms generally become weaker going down a column of the periodic table

$$\text{Cl-Cl} > \text{Br-Br} > \text{F-F} > \text{I-I}$$

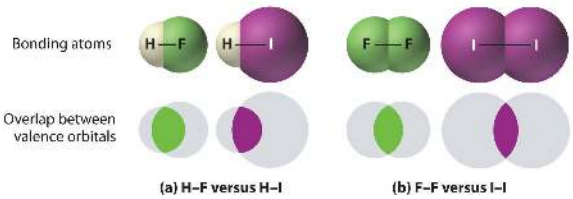


Figure 8.9.1 shows trends (1) & (2) as being results of the trends in atomic radii (as you move down a period atoms take up more volume), and since the bond energy from Coulomb's law is inversely proportional to the distance (1/r) between the atoms, the smaller atoms form stronger bonds. By being closer, a greater percent of the orbitals overlap and this results in stronger bonding interactions.

3. Bond Strength increases as Bond Order Increases

$$\text{C≡C} < \text{C=C} < \text{C-C}$$

Enthalpies of Reaction from Bond Dissociation Energies

Since enthalpy is a state function (path independent), we can choose a reaction path where we break all the bonds of the reactants and then form the reactants by creating new bonds. The first step is the summation of their Bond Dissociation Energies (D) for the reactants. The second step is the formation of the products, which is the opposite of their dissociation, so we subtract the sum of their dissociation records.

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed})$$

Why is subtracting the bond dissociation energies the same as their formation energies?

First Law of Thermodynamics states energy of the universe is conserved, and so if a process is endothermic in one direction (bond dissociation), it must be exothermic by the same quantity in the opposite direction (bond formation).

There is sort of a three step process, and you must draw Lewis dot structures in order to identify the bonds.

1. Balance equation
2. write Lewis dot structures of all species so you can identify bonds
3. Apply the equation:
   $\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed})$

Bond Dissociation Problem:

Using bond dissociation energies calculate the molar enthalpy of combustion for acetic acid.



Video 8.9.1: 7'49" YouTube going over bond dissociation energies

Contributors and Attributions

Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:

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8.10: DNA, Revisited

This Page is Under Construction

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http://chemwiki.ucdavis.edu/Core/Biological_Chemistry/Nucleic_Acids/DNA/DNA%3A_Double_Helix

The secondary structure of DNA is actually very similar to the secondary structure of proteins. The protein single alpha helix structure held together by hydrogen bonds was discovered with the aid of X-ray diffraction studies. The X-ray diffraction patterns for DNA show somewhat similar patterns.

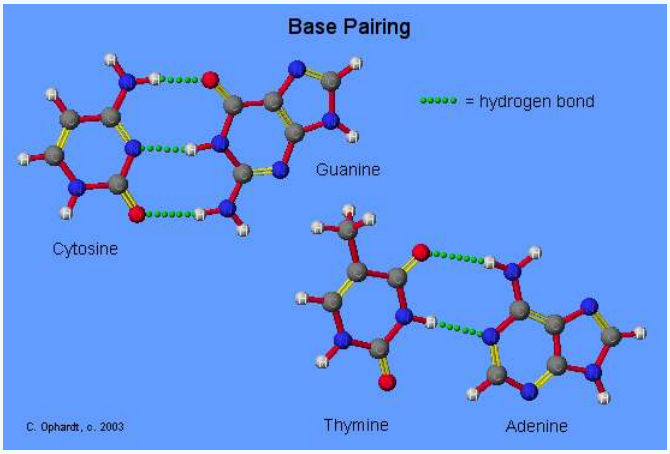
Introduction

In addition, chemical studies by E. Chargaff indicate several important clues about the structure of DNA. In the DNA of all organisms:

1. The concentration of adenine equals that of thymine.
2. The concentration of guanine equals that of cytosine.

Chargaff's findings clearly indicate that some type of heterocyclic amine base pairing exists in the DNA structure. X-ray diffraction data shows that a repeating helical pattern occurs every 34 Angstrom units with 10 subunits per turn. Each subunit occupies 3.4 Angstrom units which is the same amount of space occupied by a single nucleotide unit. Using Chargaff's information and the X-ray data in conjunction with building actual molecular models, Watson and Crick developed the double helix as a model for DNA.

The **double helix in DNA** consists of two right-handed polynucleotide chains that are coiled about the same axis. The heterocyclic amine bases project inward toward the center so that the base of one strand interacts or pairs with a base of the other strand. According to the chemical and X-ray data and model building exercises, only specific heterocyclic amine bases may be paired.

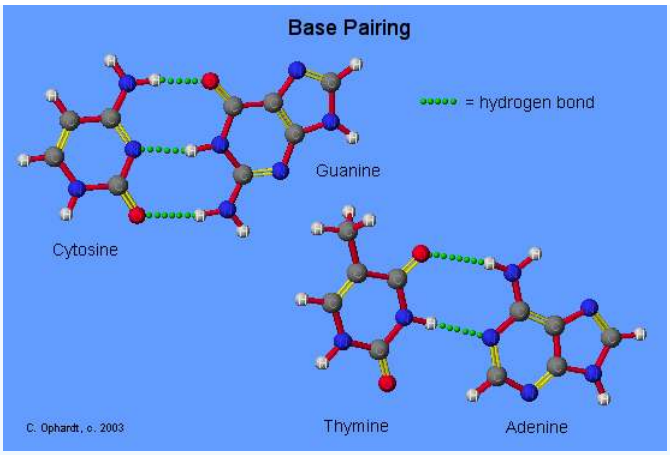


Base Pairing Principle

The Base Pairing Principle is that adenine pairs with thymine (A - T) and guanine pairs with cytosine (G - C)

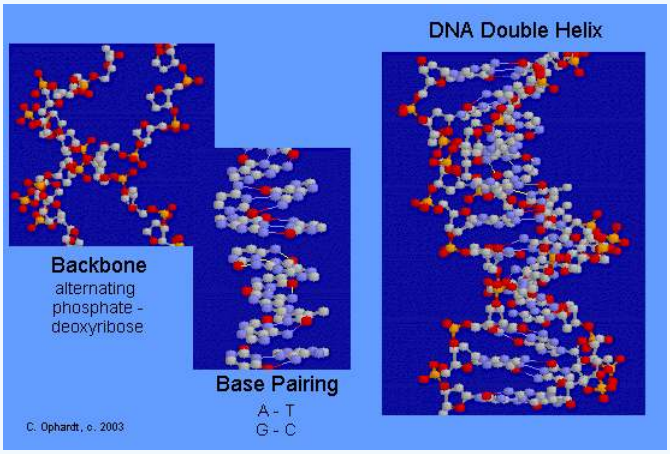
The base pairing is called complementary because there are specific geometry requirements in the formation of hydrogen bonds between the heterocylic amines. Heterocyclic amine base pairing is an application of the **hydrogen bonding principle**. In the structures for the complementary base pairs given in the graphic on the left, notice that the thymine - adenine pair interacts through two hydrogen bonds represented as (T=A) and that the cytosine-guanine pair interacts through three hydrogen bonds represented as (C≡G).

Although other base pairing-hydrogen bonding combinations may be possible, they are not utilized because the bond distances do not correspond to those given by the base pairs already cited. The diameter of the helix is 20 Angstroms.



DNA Double Helix

The double-stranded helical model for DNA is shown in the graphic on the left. The easiest way to visualize DNA is as an immensely long rope ladder, twisted into a cork-screw shape. The sides of the ladder are alternating sequences of deoxyribose and phosphate (backbone) while the rungs of the ladder (bases) are made in two parts with each part firmly attached to the side of the ladder. The parts in the rung are heterocyclic amines held in position by hydrogen bonding. Although most DNA exists as open ended double helices, some bacterial DNA has been found as a cyclic helix. Occasionally, DNA has also been found as a single strand.



Problems

QUES. Describe the structure of the double helix of DNA in your own words including the terms: backbone, heterocyclic amines, complementary base pairings, hydrogen bonding, deoxyribose, phosphate.

Quiz: In RNA, which base hydrogen bonds with uracil? Carefully compare the structure of uracil to the others to find the one that is most similar.	Answer

Quiz: If DNA is heated, what happens to the double helix? Hint: The result is similar to the denaturing of a protein by the same method. What type of bonding holds the secondary structure of both proteins and DNA?	Answer

Outside Links

- The structure of the 'Dickerson Dodecamer' was originally reported in: Drew, H. R., Wing, R. M., Takano, T., Broka, C., Tanaka, S., Itakura, K. & Dickerson, R. E. (1981). Structure of a B-DNA dodecamer: conformation and dynamics. Proc. Natl. Acad. Sci. USA 78, 2179-2183. and the coordinates were acquired from the Brookhaven Protein Data Bank. The filename is 1BNA.

Contributors

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CHAPTER OVERVIEW

9: Orbital Hybridization and Molecular Orbitals

9.1: Orbitals and Theories of Chemical Bonding
9.2: Valence Bond Theory
9.3: Molecular Orbital Theory

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9.1: Orbitals and Theories of Chemical Bonding

Introduction

In Chapter 7 we described atomic orbitals for the hydrogen-like atom, based on the wavefunction of an electron in a spherical harmonic orbital around a positive nuclei and then we extended it to the multi-electron atom. In each of these cases we were describing an isolated atom. In a molecule there is more than one nucleus, and so the wavefunction will be different. There are two basic approaches we will take to describing molecular orbitals, the valence bond approach and the molecular orbital approach. We will also identify two different types of molecular orbitals, σ and π.

σ orbitals: These are orbitals that have electron density along the internuclear axis, and the sigma bonding orbitals from valence bond theory account for the VSEPR orientations.

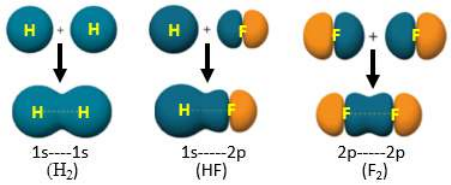


Figure 9.1.1: Sigma bonds have overlap along the internuclear axis. Here we see the sigma bonds formed from the overlap of two s orbitals (H_2), an s and a p orbital (HF) and two p orbitals (F2).

π orbitals: These orbitals result from the overlap of p orbitals and have a node along the internuclear axis. They are involved in multiple bonds. So a double bond is 1 σ and 1 π, while a triple bond is a σ and 2 πs.

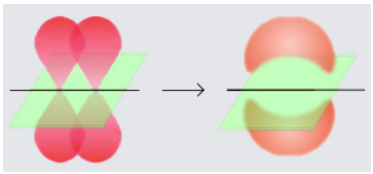


Figure 9.1.2: π bonds result from the overlap of p orbitals that are not oriented along the internuclear axis. If the green plane is the xy plane, then the red p orbitals could be the pz orbital and they could form a π bond with electron density above and below the axis. (image credit JoJan, commons.wikimedia.org/wiki/File:Pi-bond.jpg)

The above two images show the types of overlap involving atomic s and p orbitals. But in molecular systems these are often not appropriate to describe molecular orbitals, and so we are going to look at two different approaches to molecular orbitals, Valence Bond Theory and Molecular Orbital Theory

Valence Bond Theory

Valence Bond (VB) Theory: In section 9.2 we cover Valence bond theory, where we treat the molecular orbitals that result in the VSEPR orientations as being the result of the hybridization of atomic orbitals (s,p,d,...), that is, atomic orbitals mix to form molecular orbitals. There are several things to recognize for two orbitals to "mix". First, the number of molecular orbitals produced equals the number of atomic orbitals mixed. Second, the atomic orbitals being mixed need to be of similar energy. Third, the resulting molecular orbitals acquire the geometry, nodal features and orientation of the orbitals that are mixed. So if you mix an s orbital with a p, it will have a shape that is half S and half P in characteristics. Valence Bond Theory can account for VSEPR geometries, but fails on some more advanced topics like some magnetic properties, or the concept of antibonding orbitals. To understand these we need to take a more complicated approach, molecular orbital theory. But there is a lot of value to valence bond theory and chemists use it all the time.

Molecular Orbital Theory

Molecular Orbital (MO) Theory: Molecular orbital theory is the direct quantum mechanical solution to the multi-nuclei wave function. These result in two types of wave functions, bonding and antibonding orbitals. In section 9.3 we will look at this for the simplest case, the homonuclear and heteronuclear diatomic. We will also look at magnetic properties like paramagnetism and show how MO theory can account for these types of properties in molecules like diatomic oxygen, when valence theory does not.

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9.2: Valence Bond Theory

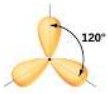
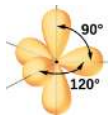
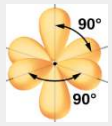
Introduction

Valence bond theory is an approach to bonding where molecular orbitals (wave functions) are considered to be the result of the mixing of pure atomic orbitals (section 6.6). These mixed or hybrid obritals are the orbitals used in VSEPR models of section 8.6 . The first period of the periodic table does not form hybrid orbitals because there is only one 1s orbital (to form a hybrid two or more things must mix). The second period can form up to four hybrid orbitals because there is one 2s orbital and three 2p orbitals and these are related to VESPR geometries of 2,3 and 4 electron domains. The third period (and higher) have d orbitals that can be involved in hybridization and so they can have expanded octets, and hybrid orbitals involving s,p and d orbitals result in 5 and 6 electron domain VSEPR geometries.

Hybrid Orbitals

These are the orbitals responsible for the VESPR geometries. There are five basic VESPR geometries and so there are five hybrid orbitals that we will look at, ranging from two to six electron domains. The name of the hybrid orbital indicates the number of atomic orbitals involved in the hybridization are outlined in table 9.2.1.

Table 9.2.1: Overview of the hybrid orbitals responsible for VESPR geometries

Hybrid Orbital	Number of Hybrid Orbitals	Atomic Orbitals Mixed	Hybrization Characterization	VSEPR (electronic) Geometry	Examples
sp	2	s,p	1/2s, 1/2p	 Linear	BeH_2, CO_2
sp^2	3	s,p,p	1/3s, 2/3p	 Trigonal Planar	SO_3, NO_3^-, $AlCl_3$, SO_2, O_3
sp^3	4	s,p,p,p	1/4s, 3/4p	 Tetrahedral	CH_4, NH_3, H_2O
sp^3d	5	s,p,p,p,d	1/5s, 3/5p, 1/5d	 Trigonal Bipyramidal	PF_5, SeF_4
sp^3d^2	6	s,p,p,p,d,d	1/6s, 1/2p, 1/3d	 Octahedral	SF_6,

Note, second period elements have no d orbitals and so can not have more than an octet of electrons, that is, only the third period and greater can form sp^3d and sp^3d^2

Requirements for Hybridization of Atomic Orbitals

1. Atomic orbitals need to be in similar regions of space
2. Atomic orbitals need to be of similar energy (a 1s will not hybridize with a 4p).
3. Energy is conserved
    - the two 2sp orbitals have an energy that is halfway between the 2s and 2p atomic orbitals.

- the three $2sp^2$ hybrid orbitals have an energy that is two thirds the distance between the 2p and 2s atomic orbitals (closer to the energy of the p).
- the four $2sp^3$ hybrid orbitals have an energy that is three fourths the distance between the 2p and 2s atomic orbitals (closer to the energy of the p).

4. Number of hybrid orbitals created equals number of atomic orbitals mixed.

Bond Formation and σ bonds

One way of looking at the formation of a bond is for two atoms with a free radical atomic orbital (atomic orbital with one electron) to come together and overlap and form molecular orbitals. This is the opposite of homolytic bond cleavage that was discussed in section 8.9 . In this model, we consider two atoms to approach from infinity with one electron in an orbital of each atom, and when they overlap a covalent sigma bond is formed. This can be expressed by the potential well diagram that we have looked at throughout this semester

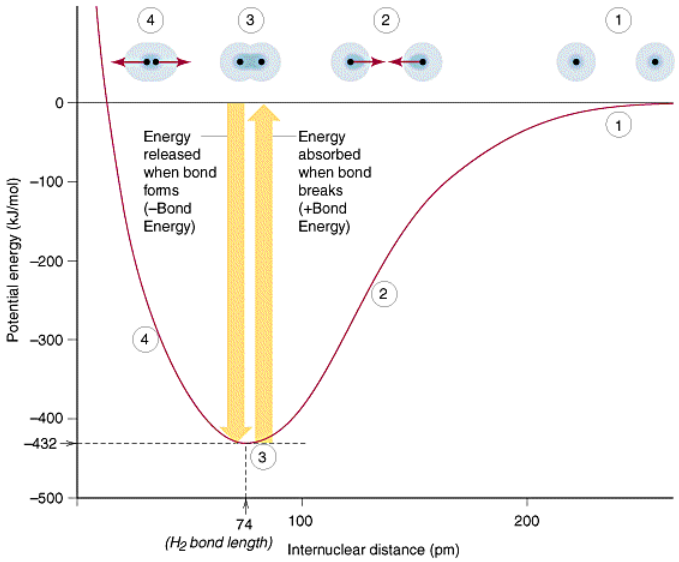


Figure 9.2.1: The potential well diagram for the formation of a sigma bond in diatomic hydrogen. What is important to note in this model is that when two atoms have an orbital with one electron it it, those orbitals can overlap and form a bonding orbital.

Now let's look at BeH_2, which we know has two single bonds. In the ground state beryllium has an electron configuration of Be: $[He]2s^2$, which means it does not have two orbitals with a single electron that could overlap with the single electron in hydrogen's orbital as occurs in Figure 9.2.1. Instead, what happens is the s orbital hybridizes with a p orbital and the two electrons in the 2s orbital are now shared by two orbitals, the two 2sp orbitals. Before proceeding watch video 9.2.1.



Video 9.2.1: 10'11" YouTube ukploaded by Van Wyk on molecular shapes and hybrid orbitals (*https://youtu.be/qraDpWX_msY*)

The Hybrid Orbitals

sp Hybrid

- Linear Geometry
- 180° bond angle
- molecules with sp hybrid orbitals may also be involved with π bonds (see section 9.2.4)

In Figure 9.2.2 we note that the p orbitals align along Cartesian axes, and so if we consider the s to hybridize with the p_x then the two sp orbitals face in opposite directions along the x-axis.

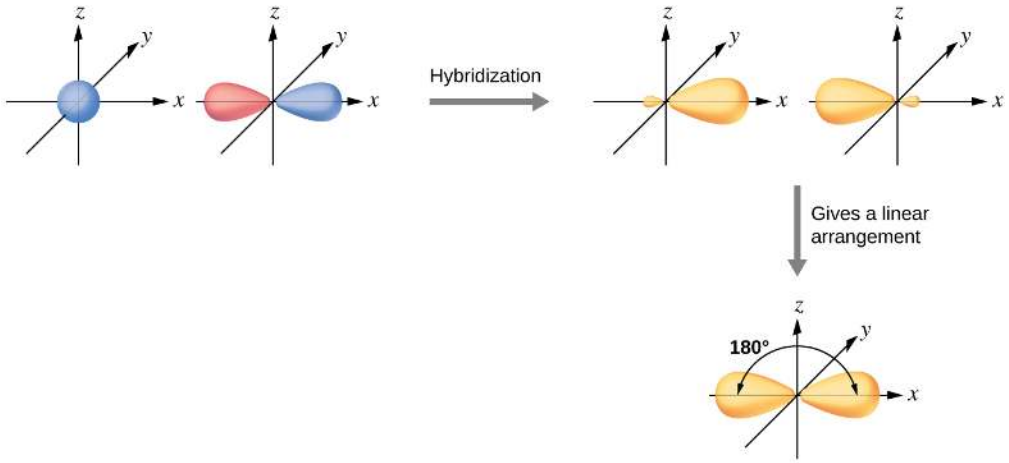


Figure 9.2.2: the S and p orbitals on the left hybridize to form two sp orbitals on the right. Note the p has a node at the nucleus while the S does not, and thus there is a minor lobe on each of the hybrids. The bottom image is showing the major lobe of both orbitals being aligned at 180 degrees.

Let's follow through with beryllium hydride mentioned above. The beryllium in beryllium hydride (BeH_2) is an example of an sp hybrid. If we look at the ground state electron configuration of Be, it is $[He]1s^2$, and so it has a filled valence orbital and as such, could not bond. This is shown on the left electron configuration of Figure 9.2.3, where on the right, the two red arrows are the Be sp orbitals which are equal in energy (half way between the 2s and sp) and with one electron in each, can overlap with the 1s orbitals of two different hydrogen atoms.

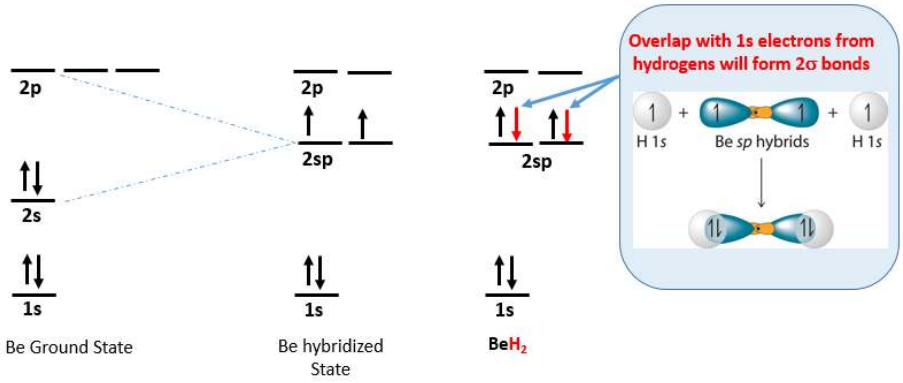


Figure 9.2.3: Electron configuration of beryllium (left), in hybridized state with two orbitals containing a lone electron (middle) and for beryllium hydride (right). The rightmost configuration is the linear molecule H-Be-H with and the right image is not showing the energy of the σ bond, but how it can be formed with the overlap of the H1s orbitals of two hydrogen atoms with the two Be hybrid 2sp orbitals.

Exercise 9.2.1

What is the orbital of the chlorine in $BeCl_2$?

Answer

it is a 3p orbital as chlorine has one free-radical orbital in it's valence state, and so there is no need to hybridize it.

sp^2 hybrid

- Trigonal planar geometry
- 120° bond angle
- molecules with sp^2 hybrid orbitals may also be involved with π bonds (see section 9.2.4)

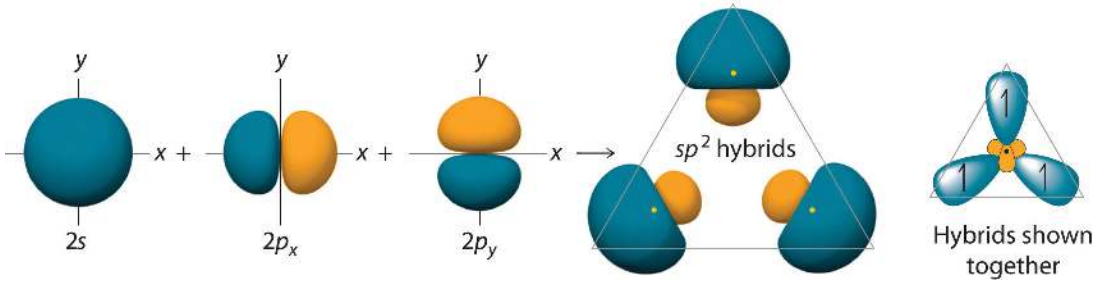


Figure 9.2.4: sp2 hybrids form a trigonal planar structure

Lets look at boron trihydride (BH_3)

The ground state of boron is $[He]2s^22p^1$ and so can not account for the three bonds in boron trihydride, and the valence bond approach it to hybridize the 2s with two of the 2p orbitals giving three sp^2 hybridized orbitals with one electron each, which can then bond with the lone electron in hydrogen's 1s orbital, as indicated in Figure 9.2.4. It should be noted that halogens form analogous structures like BFH_3 where the bonding electron from the halogen comes from the p orbital with a lone electron.

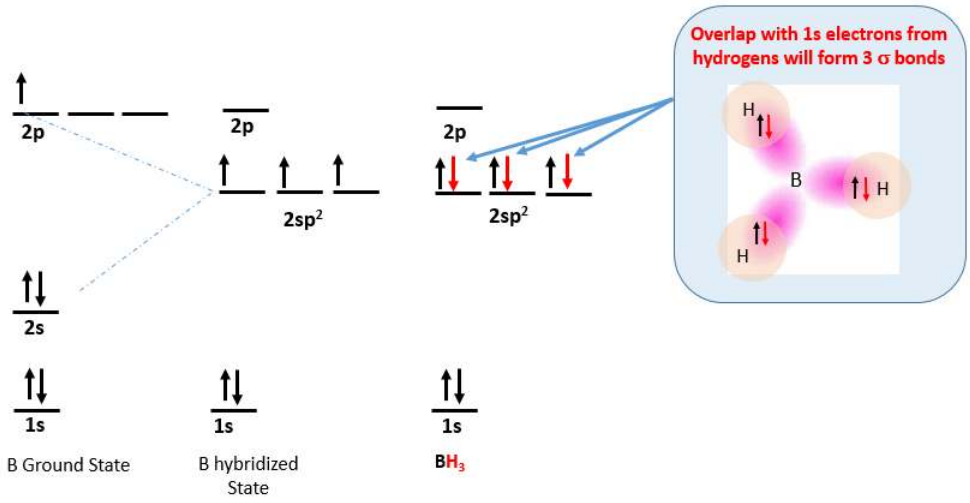


Figure 9.2.5: Boron can form three bonds when it has sp^2 hybrid orbitals

Fluorine forms an analogous structure where the lone electron is in a 2p orbital

sp^3 hybrid

- tetrahedral electronic geometry
- 109.5° bond angle

Molecules with 4 "electron domains" have sp^3 hybridized orbitals. The four sp^3 hybridized orbitals result from the mixing of 1 s orbital with 3 p orbitals orient in 3D space as they involve a p_x, p_y & p_z and according to VSEPR orient in a tetrahedral structure as shown in Figure 9.2.9

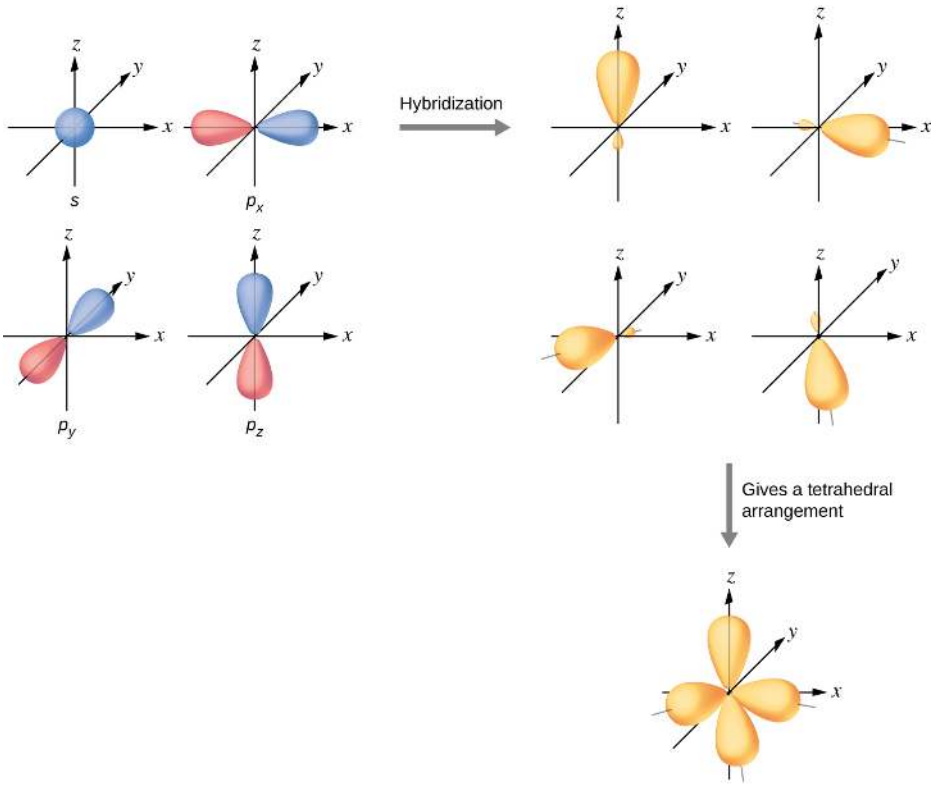


Figure 9.2.6: *Tetrahedral structure of the four sp^3 hybridized orbitals.*

Methane (CH_4) is from group IV and has 4 electrons in it's outer shell. This results in the following electron configuration and a tetrahedral molecule.

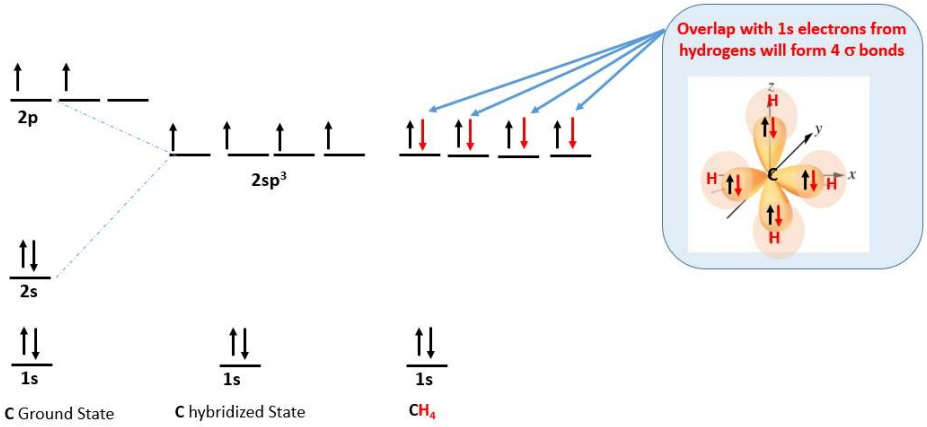


Figure 9.2.7: Hybridization of hydrogen-like atomic orbitals to produce sp3 hybrid orbitals responsible for tetrahedral VSEPR structure, with all orbitals being σ bonding orbitals. Note the energy of the hybrid is 3/4ths the difference between the one 2s orbital and the three 2p orbitals that hybridized.

Ammonia (NH_3) is from group V and has 5 electrons in it's outer shell. This results in the following electron configuration and a trigonal pyramidal molecule.

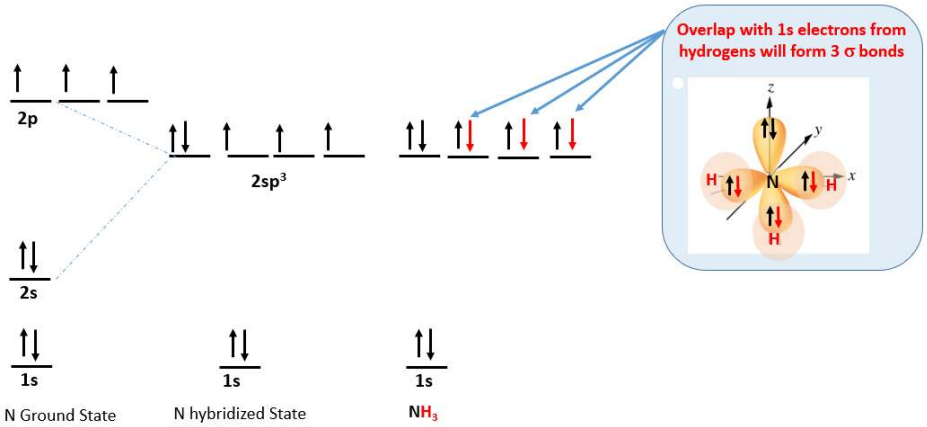


Figure 9.2.8: Ammonia has 5 electrons and so one of the hybrid orbitals has a lone pair, resulting in the trigonal pyramidal molecular geometry.

Water (H_2O) is from group VI and has 6 electrons in it's outer shell. This results in the following electron configuration and a bent ($104.5^{o)}$ molecule.

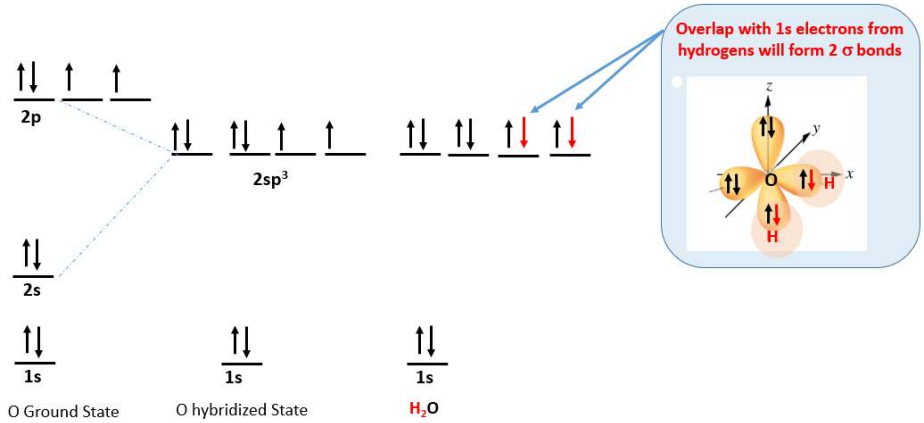


Figure 9.2.9: Water has six electrons and so two of the hybrid orbitals are filled (have lone pairs) and it forms a bent (104.5^{o}) molecule.

sp^3d hybrid

- trigonal bipyramidal electronic geometry
- 120° bond angle (equatorial-equatorial) and 90° bond angles (axial-equatorial)

Only elements in the third or greater period of the periodic table have d orbitals and so only those elements can have expanded octets.

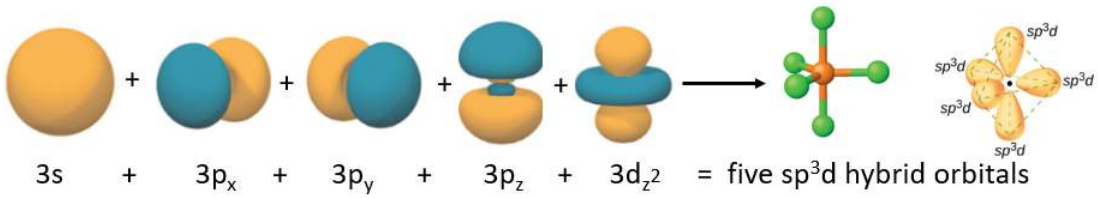


Figure 9.2.10: The five atomic orbitals that combine to form the five sp^3d hybrid obritals that result in a trigonal bipyramidal VSEPR structure

sp^3d^2 hybrid

- octahedral electronic geometry
- 90° bond angles

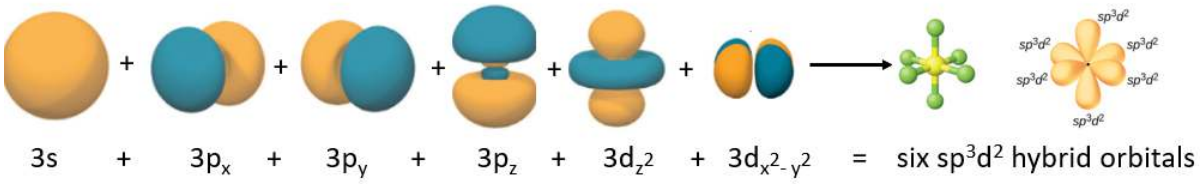


Figure 9.2.11: The six atomic orbitals that combine to form the six sp^3d^2 hybrid obrtals that result in an octahedral VSEPR structure

π Bonds

So far we have described single σ bonds where the orbitals of two atoms overlap to form a bonding orbital with electron density along the internuclear axis, and these are responsible for the VSPER geometric structures. In this section we will describe a second type of bond, the π bond, which results from the overlap of adjacent unhybridized p orbitals. π bonds are weaker then $\sigma bonds$ and have a node along the internuclear axis (actually a nodal plane), and thus π bonds have two regions of space where bonding occurs. If the π bond is formed by two p_z orbitals on adjacent atoms there is electron density on both sides of the xy plane (which becomes a nodal plane). π bonds combine with σ bonds to form multiple bonds, with a double bond consisting of one σ and one π) bond, and a triple bond consisting of one σ and two π bonds. Video 9.2.2 illustrates a π bond.s



Video 9.2.2: 0'27" YouTube uploaded by #BiotechReview showing a π bond in a compound forming a double bond. (https://youtu.be/hsuT4katVA4)

Double Bonds

A double bond consists of a σ and a π bond and these are common with adjacent atoms that have sp^2 hybrid orbitals. Lets look at the C=C bond of ethylene C_2H_4. Figure 9.2.12 shows the electron configuration the carbon atoms would be in after hybridization where two of the p orbitals (px and py in this case) hybridize with the s to form the trigonal planar geometry defined by the three σ bonds (two to hydrogens and one to the second carbon). The fourth valence electron of carbon resides in the unhybridized p orbital (red electron) and if both of the carbons have their trigonal σ structures in the same plane, the two pz orbitals can overlap, as illustrated in Figure 9.2.12

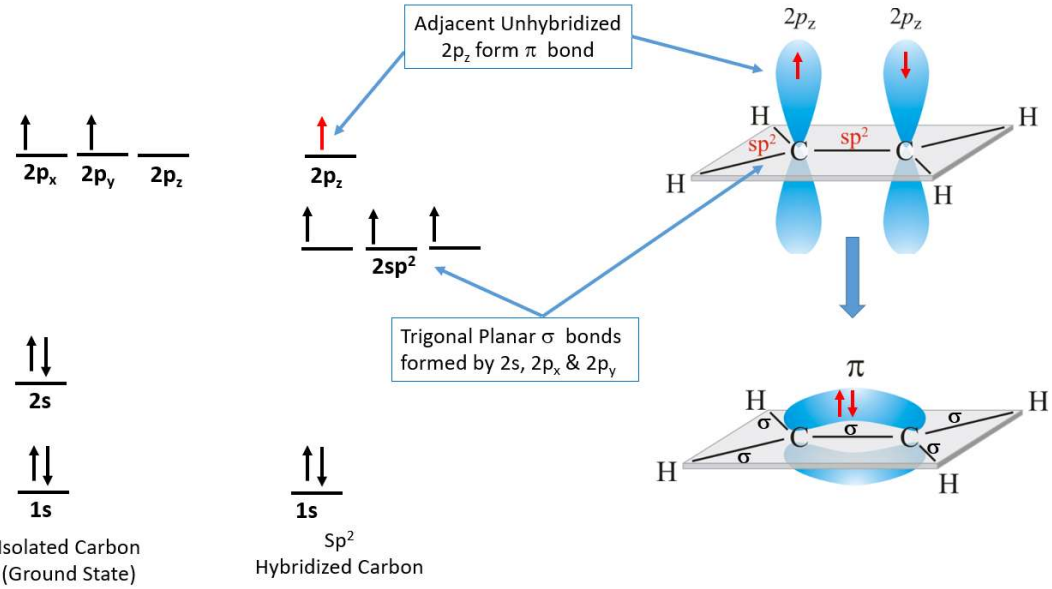


Figure 9.2.12: (modified image from: Eni Generalic, Chemistry Glossary)

There are several things to note about π bonds in double bonds.

1. The sp^2 framework of the sigma bonds must be in the same plane (ethylene is a planar molecule) and if you rotate one of the carbons 90° along the C-C axis, you break the pi bond.
2. For there to be efficient orbital overlap of the unhybridized p orbitals the nuclei of the atoms need to be close to each other. This occurs for atoms of the second period and nitrogen, carbon and nitrogen can form π bonds. Silicon, unlike carbon, does not form stable double bonds because it is a larger atom and there is insufficient overlap of the p orbitals responsible for π bonds.
3. π bonds prevent rotation. This is very important in biological systems as molecules freely rotate around single σ bonds but can not rotate around multiple bonds, which thus gives the molecule a fixed structure.
4.

Resonance structures.

If more than two adjacent atoms have sp^2 hybrid orbitals and they are all in a plane, the p orbitals of multiple atoms can overlap resulting in a π bond that extends across multiple atoms and this can not be drawn with a single Lewis dot structure, which is why we need resonance structures. Benzene (C6H6) is an example where the electrons in the π orbital are extended over 6 carbon atoms

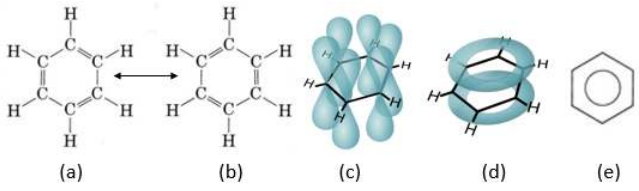


Figure 9.2.13: Benzene has a π ring system delocalized over 6 carbon atoms (images [c] & [d] obtained from wikimedia commons and were uploaded by Zlir'a)

That above image gives a good bearing on some of the issues associated with Lewis dot structures. (a) and (b) are the Lewis resonance structures, and these do not indicate that the electrons in the second (π bond are delocalized over all the carbons. (c) shows the unhybridized p orbitals and (d) shows these overlaping above and below the plane the atoms and σ bonds exist in.

The following two YouTube animations give a feel for how π bonds can spread out over multiple atoms.

Video 9.2.3: 0'32" YouTube uploaded by mtchemers quickly depicting the overlap of p orbitals to give the delocalized ring structure of benzene. (https://youtu.be/-EFEfVDUp6M)

Video 9.2.4: 0'22" YouTube uploaded by kwesiamoa showing π orbitals of nitrate (https://youtu.be/DnytqBRf3wA)

Triple Bond

In the triple bond there are two π bonds and one σ bond. These can occur when in acetylene (C_2H_2) where the carbon is sp hybridized leaving one electron in each of the two unhybridized p orbitals. This is shown in Figure 9.2.14 where each carbon forms two bonds, one with a hydrogen and one with the other carbon.

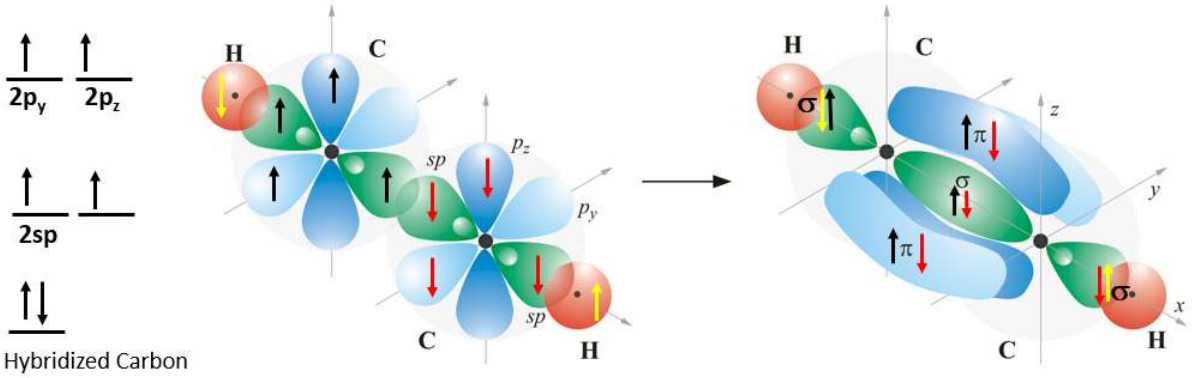


Figure 9.2.22: (image credit: modified from Eni Generalic, Chemistry Glossary)

On the left is the electron configuration of the hybridized carbons, in the middle, these electrons are assigned with one of the carbon's electrons being in black, and the other in red. The hydrogen's are in yellow. Each carbon is sp hybridized and so the molecule is linear. The bond between the carbons is a triple bond because it hast one σ and two π bonds. Note each of the pi bonds has two lobes, above and below the plane defined by the axis of the other two p orbitals. That is, for the π bond formed from the overlap of pz orbitals, the xy plane is the nodal plane, with the π bond having no electron density along the internuclear axis. Video 9.2.5 illustrates the bonding in Figure 9.2.14



Video 9.2.5: 1'28" YouTube uploaded by Gordon Watson showing the σ and π bonds of acetylene (https://youtu.be/yG1509YzKkI)

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9.3: Molecular Orbital Theory

Introduction

In valence bond (VB) theory we treat σ and π bonds as being the result of the overlap of atomic orbitals, that is, the bonding orbitals are the result of the overlap of the atomic orbitals of the bonding atoms. In molecular orbital (MO) theory we consider the orbitals to belong to the molecule, that is, the wavefunction is the quantum mechanical solution of the multinuclear molecule. Although MO calculations are beyond the scope this class we need to look at these for the simplest of molecules in order to understand the behavior of real molecules. For example, valence bond theory has no way of describing antibonding orbitals, which are very real and influence the behavior of molecules.

Chemists need both MO (Molecular Orbital) and VB (Valence Bond) theory. As we have seen in the last section, VB theory is very useful to predict the geometry of simple molecules based on the connectivity of atoms. It is easy to understand the concept of a bond as the overlap of half filled atomic orbitals between two different atoms, and VSPER correctly predicts the electronic geometry if there is more than one electron domain around an atom, which in turn allows the prediction of the molecular geometry. In this class we will tackle MO for the simplest of molecules, the diatomics, and use an easy to understand approach, LCAO-MO (Linear Combination of Atomic Orbital -Molecular Orbital). There are two types of diatomics, homonuclear like H_2, Cl_2 and and heteronuclear like HCl and HBr.

LCAO-MO Introduction

This describes molecular orbitals that are the result of the linear combination of atomic orbitals. A standing wave function (ψ) has a [-] negative and a [+] region (which is not charge, see Figure 9.3.1), which is why we used ψ^2 to describe the probability of finding an electron in a region of space (review section 6.6 for atomic orbitals). If two waves interact and they have the same sign (positive or negative amplitude) they add to each other, and if they have opposite sign, they subtract from each other. It must be emphasized that the [+] and [-] does not represent charge, but describe the region of the wavefunction.



Figure 9.3.1: Linear wave showing the concept of positive and negative region of a wave (this is not charge!) If this wave was added to another wave and the sign was the same, they would add, but if in a region of space the sign was different, they would subtract (destructive interference).

So in LCAO-MO of a diatomic, we look at the two wave functions, and how they can interact.

What are the factors involved with the mixing of atomic orbitals to produce a molecular orbital?

1. The number of molecular orbitals equals the number of atomic orbitals that are mixed.
2. The energies of the molecular orbitals equals the energies of the atomic orbitals that mixed them
   - Bonding orbitals are lower in energy than the atomic orbitals
   - Antibonding orbitals are higher in energy.
3. The energies of the atomic orbitals must be near each other.

Molecular Orbitals involving s orbitals

Let's look at H2. There are two ways 1s orbitals can add to each other, constructively to form bonding orbitals or destructively to form antibonding orbitals (noting with an asterisk [*]). This type of interaction forms a σ bond because s orbitals can only overlap along an internuclear axis, and result in σ and σ^* orbitals (Figure 9.3.2). Note, in these equations the wavefunctions of two 1 s orbitals ψ_{1s} combine to form a $\psi_{\sigma_{1s}}$ and $\psi_{\sigma^*_{1s}}$ orbitals and the σ_{1s} or σ^*_{1s} bond is the MO squared, $\psi^2_{\sigma_{1s}}$ or $\psi^2_{\sigma^*_{1s}}$

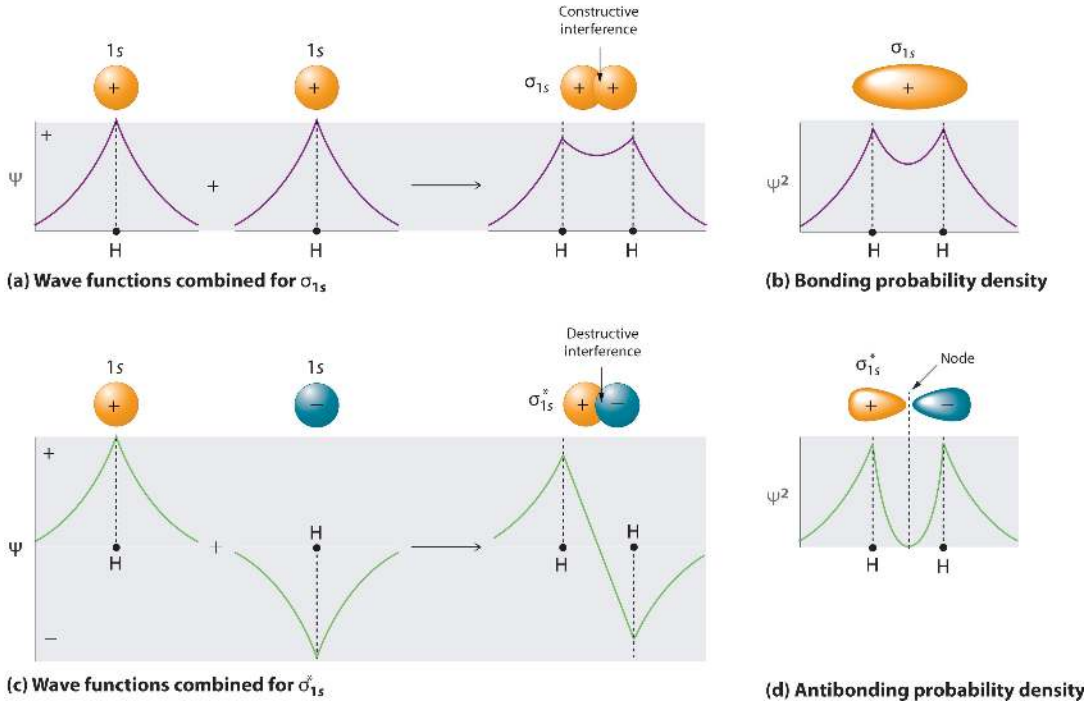


Figure 9.3.2: Constructive and destructive interferance of 1s orbitals that combine to form diatomic hydrogen.

Molecular Orbitals involving p orbitals

p orbitals can combine for form either σ bonds or π, and these can be either bonding orbitals or antibonding orbitals. In the following images the z axis is considered to be the internuclear axis. Overlap of p_z orbitals results in σ bonds and overlap of p_y or p_z orbitals results in π bonds

σ_p, σ_p^* orbitals

In the following images the color indicates the +/- regions of the wavefunction

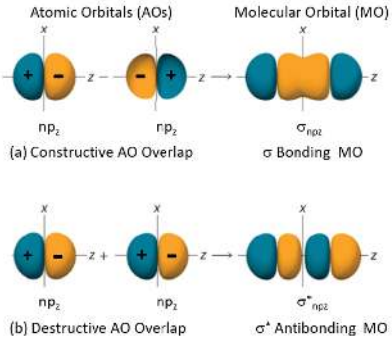


Figure 9.3.3: LCAO-MO approach for combining ψ_{p_z} along the internuclear axis (z) to form σ and σ^* bonds.

Note, we are NOT saying that the p_z of one atom overlaps the p_z of another atom along the internuclear axis and this overlap represents the σ bond, that is the valence bond approach. We are saying that there is a MO (molecular orbital) based on nuclear-nuclear, nuclear-electron and electron-electron interactions for the diatomic (two nuclei system), and the MO wavefunction can be described by combining the two AO wavefunctions.

π, π^* orbitals

The p orbitals that are orthoganal (perpendicular) to the internuclear axis (z in these drawings) can combine to form both bonding and antibonding orbitals

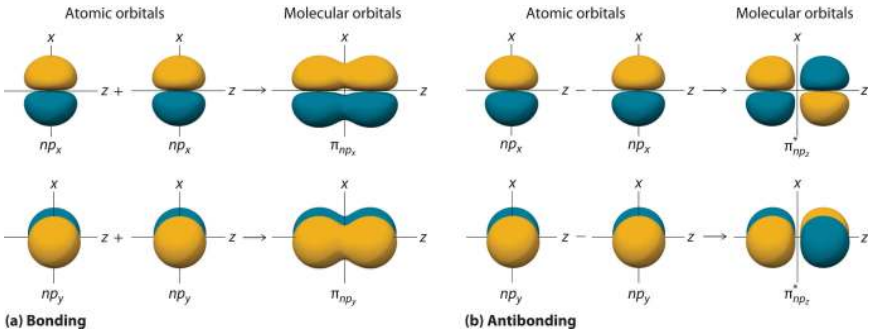


Figure 9.3.4: LCAO-MO approach to combining ψ_{p_x} or ψ_{p_y} AO wavefunctions parallel to the internuclear axis (z) to form pi and π^* bonds. Note the axis is in a nodal plane and there is no electron density along the axis, but the antibonding orbitals have a second nodal plane perpendicular to the axis (xy plane of drawing).

Summary

To distinguish these type of orbitals we need some convention rules:

- **σ or (π) refer to bonding orbitals**
- **σ^* or (π^*) refer to anti-bonding orbitals**

An antibonding orbital reduces electron density between the nuclei and causes them to repel each other (it actually creates a node). These are a consequence of the wave-particle duality of the electron.

Note:

In valence bond theory a σ or π bond results from the overlap of two atomic orbital probability density functions of two different bonding atoms ψ^2 and thus there is no concept such as antibonding orbitals. In Molecular orbital theory σ and π bonds are the actual orbital, and one way of identifying MOs is through the LCAO-MO approach, where you combine the actual wavefunctions of the AO (ψ, and thus you can have cancellation of the wavefunction and antibonding orbitals. There are other approaches in quantum mechanics but the LCAO-MO is probably the easiest to visualize.

It should also be noted that the LCAO-MO approach to MO is not the same as hybridization. In hybridization you are combining different ψ^2 of the same atom, in LCAO-MO you are combining ψ of different atoms. These are completely different approaches.

Bond Order

In section 8.3.3 we introduced the concept of Bond Order and how molecules with resonance structures could have fractional bond orders. MO theory gives an alternative method to approach bond order, which is simply the number of occupied bonding orbitals minus the number of antibonding orbitals. In the next section we will look at MO electron configurations of various diatomic molecules and we can use those to determine the bond order of the bond between the two atoms of the diatomic.

Note, a bond order of zero means there is no bond.

MO Electron Configurations

Calculating the electron configuration of a Molecular Orbital (MO) is similar to the process we used in section 7.2 to calculate the electron configuration of an atomic orbital. Summarizing the rules:

1. Count the total number of electrons contributed by each atom
2. Aufbau Principle - fill up the lowest energy orbitals first.
3. Hund Rule of Maximum Multiplicity (give all electrons in degenerate orbitals the same spin)
4. Pauli Exclusion (a MO can only have two electrons, which must be of opposite spin).

The first step is determine the ranking of the orbitals, noting that the number of MOs equals the number of AOs combined to form them, and that the sum of the energies of the bonding and antibonding MOs equals the energy of the AOs that form them. So the the σ_{1s} is lower than the 1s by the same amount of energy that the σ^*_{1s} is higher

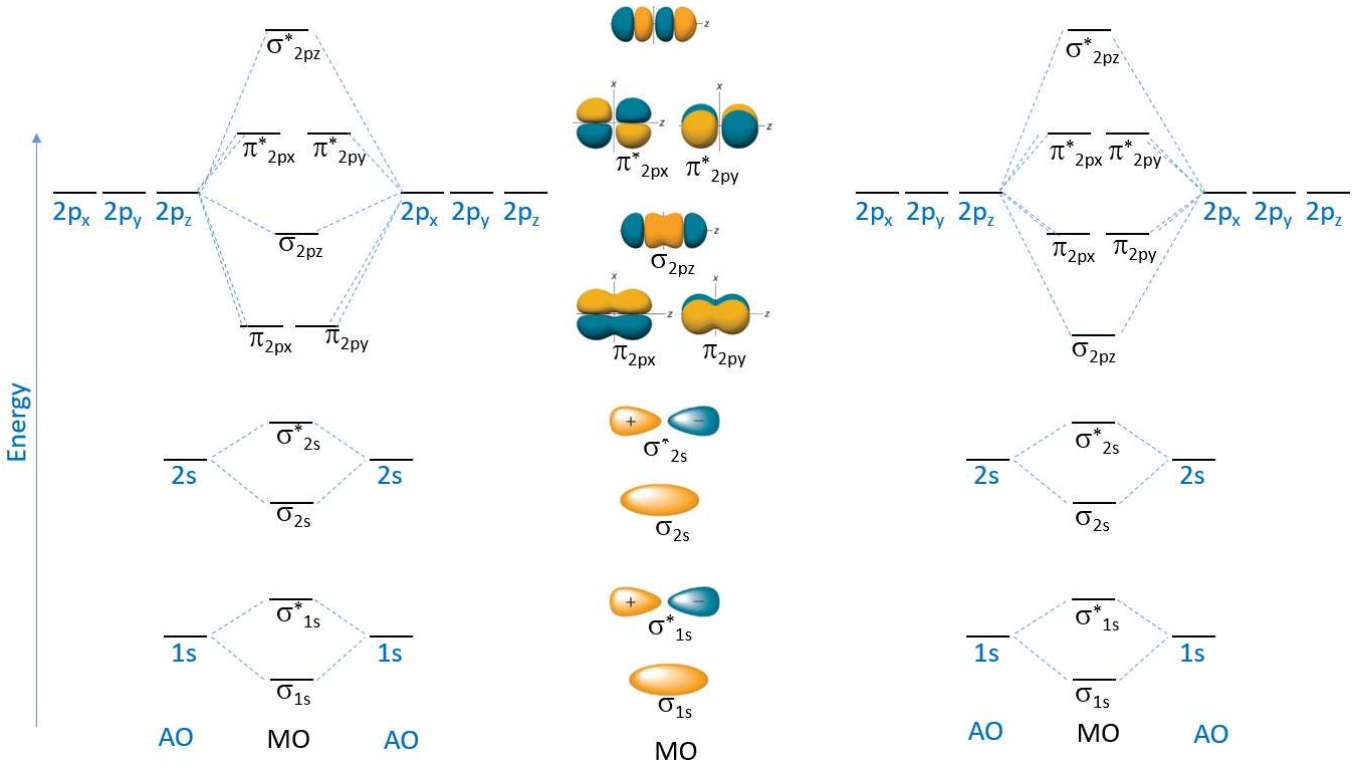


Figure 9.3.5: Relative Energy ranking of different MOs and AOs. On the left and right are the ways the AOs form MOs, and in the middle is a visualization of the MO wavefunctions. Note, there are two different configurations for the MOs formed from the mixing of the 2p AOs.

In calculating the energies of the MOs the electron-electron interactions have an effect. One would expect the σ_{2p_z} to have a greater lowering of energy than the π_{2p}, but what you notice in the MO configuration is that there are 2 σ orbitals in the second period, those formed from 2s and 2p interactions along the internuclear axis. Since these are in the same region of space, the filled σ_{2s} orbitals interact with the σ_{2p} more than the π_{2p} and raise its energy, and the left hand ranking of energies is used while filling the bonding orbitals of the second period. Once all the bonding orbitals are filled, there is no lowering of energy, and the right hand part is used. See below.

First Period

The first period only has s orbitals and Figure 9.3.6 shows the electron configuration for diatomic hydrogen and helium.

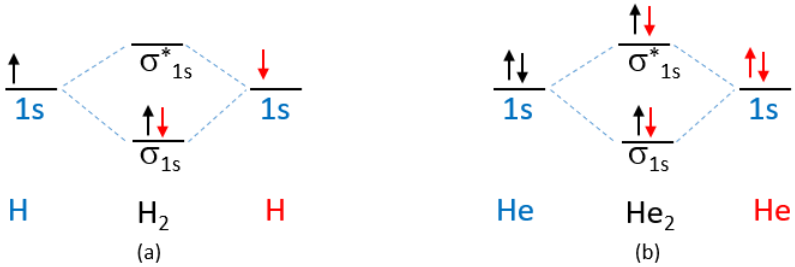


Figure 9.3.6: MO electron configurations of H_2 and He_2.

The electrons on the AOs of Figure 9.3.6 are color coded to help students keep track of what is going on. In (a) each hydrogen donated one electron, while in (b) each helium donates two electrons.

Exercise 9.3.7

Based on MO theory, answer the following questions

a. What is the bond order of hydrogen?

b. What is the bond order of helium?
c. Does MO theory predict H2 to be stable, and if so, how?
d. Does MO theory predict He_2 to be stable, and if so, how?

Answer a

one

Answer b

zero

Answer c

Yes, the bond order is one and there is a lowering of energy by filling the σ_{1s} orbitals of H_2 as compared to having one electron is the 1s orbital of each hydrogen.

Answer d

No, the bond order is zero and there is not net stabilization of diatomic helium as compared to monatomic. The stabilization gained by the σ_{1s} bonding orbital is offset by the destabilization of the σ^*_{1s} antibonding orbital

Second Period

Because Helium has a bond order of zero we can ignore the effect of the first period on the electron configuration of the second period. Lithium and beryllium have MO electron configurations analogous to hydrogen and helium except that it is the σ_{2s} and σ^*_{2s} MO that is being filled. In this section we will focus on the filling of the p orbitals. In Figure 9.3.5 we showed two orbital filling diagrams for the p-orbitals, and the general trend for energies is shown in Figure 9.3.7, note diatomics formed from atoms with more than 3 electrons in the p orbital have the σ_{2p_z} lower than the $\pi_{2p_{xy}}$ (oxygen and fluorine, which are [He]$2s^2 2p^4$ [He]$2s^2 2p^5$ and respectively).

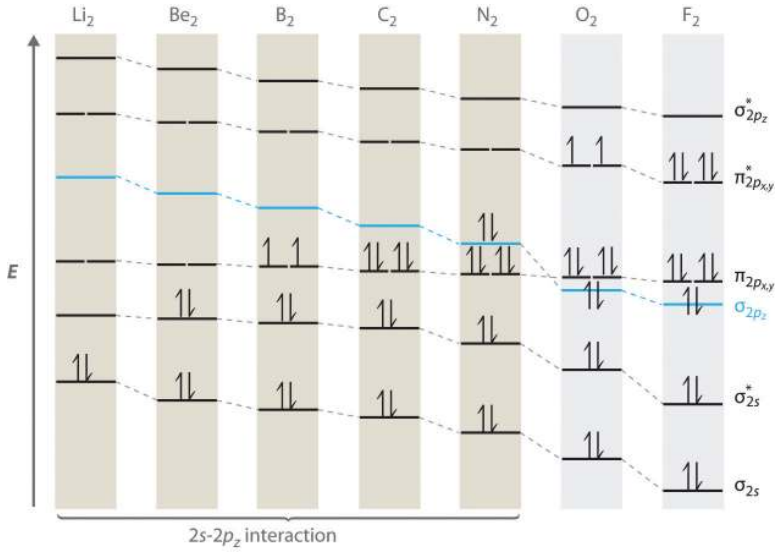


Figure 9.3.7: MO electron configuration of second period homonuclear diatomics.

Note

When we studied the electron configuration of the atoms (section 7.3.1) we noted some interesting behaviors like chromium having an electron configuration of [Ar]:$4s^1 3d^5$ in contrast to the trend of [Ar]:$4s^2 3d^4$, and this was due to the fact that the Coulombic energy of orbitals are influenced by both positive (nuclear) and negative (electron) interactions, and as electrons fill orbitals those interactions can change. The fact that both the σ_{2s} and σ_{2p} have electron density along the internuclear axis means interactions between these orbitals is significant, with the net result that these orbitals "perturb" (mix with) each other in a manner that the σ_{2p} undergoes an increase in energy while the σ_{2s} has a lowering in energy, as shown in Figure 9.3.8. For

this mixing to occur the unperturbed orbitals need to be of similar energy. As you go across the periodic table you are increasing the effective nuclear charge and so both the σ_{2s} and σ_{ps} are lowered, but the σ_{2s} has a greater effect (is lowered more) and thus the energy separation between them increases, reducing the ability to mix. This effect becomes negligible after nitrogen, and so for oxygen and fluorine the σ_{2s} is lower in energy thant the π_{2p} the.

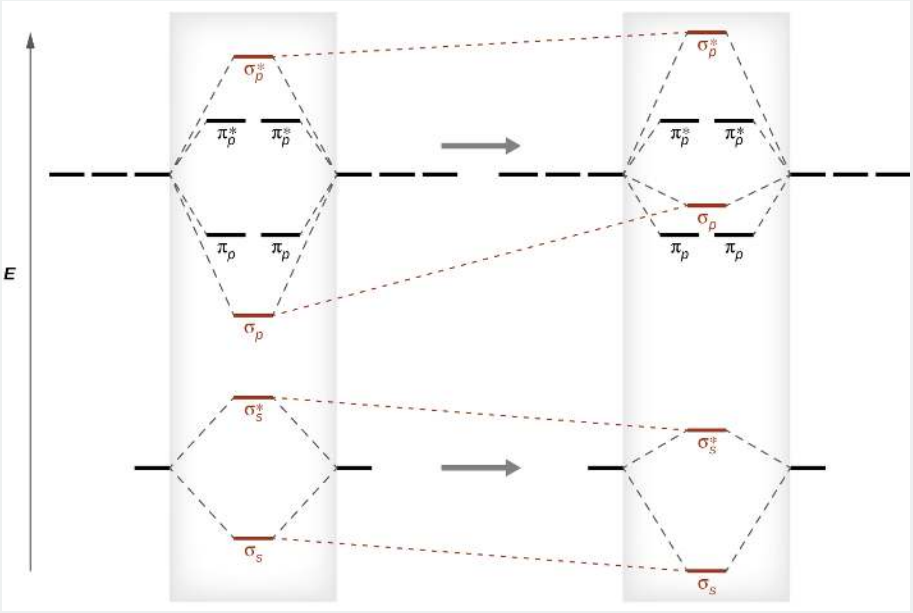


Figure 9.3.8: On the left is the "expected" ordering of energies based on a σ bond having electron density along the internuclear axis and thus resulting in a lower energy than a π bond, which does not have electron density in this region. This trend is only seen in oxygen and fluorine. On the right is the actual ordering of energies until all the bonding orbitals have been filled (Li_2-N_2). (image credit: OpenStax)

A rigorous discussion of this effect is beyond the scope of this text, but students are required to know that the empty $\sigma_{2s}$and σ_{2p} orbitals in a manner that causes the trend in Figures 9.3.7 and 9.3.8.

Writing MO electron configurations.

Atomic electron configurations are written in terms of atomic orbitals and molecular electron configurations are written in terms of molecular orbitals.

Table 9.3.1: *Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements*

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2$	0
B_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^2$	1
C_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4$	2
N_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$	3
O_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\pi^*_{2pz})^2$	2
F_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^4$	1
Ne_2 (unstable)	$(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\pi^*_{2pz})^4(\sigma^*_{2px})^2$	0

Magnetism

Another success of MO theory is its ability to predict the magnetic properties of diatomics like oxygen, as demonstrated in the following video from BerkeleyChemDemos. Oxygen's MO electron configuration has two unpaired electrons, which makes it a paramagnetic molecule that interact with a magnetic field. On the other hand nitrogen, has no unpaired electrons and is classified as a diamagnetic compound which does not interact with a magnetic field.



Video 9.3.1: 1'19" YouTube from BerkeleyChemDemos showing interactions of liquid nitrogen and oxygen with a magnet. (https://youtu.be/QN391RkUHnQ)

- **Paramagnetic Substance** - molecules that have unpaired electrons with aligned spins that interact with external magnetic fields.
- **Diamagnetic Substance** - molecule that do not interact with magnetic fields. All the electrons are spin coupled in electron pairs, thus cancelling their net magnetic moment.
- **Ferromagnetic Substance** - this is the iron based classical magnet and is a result of electron orientations in a metallic bond.

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CHAPTER OVERVIEW

10: Gases

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Topic hierarchy

10.1: Gas Properties
10.2: Gas Laws
10.3: Gas Phase Reactions
10.4: Gas Mixtures
10.5: Kinetic Molecular Theory of Gases
10.6: Diffusion and Effusion
10.7: Nonideal Gases

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10.1: Gas Properties

Introduction

In section 1.3 we introduced the phases of matter and in section 5.3 we covered phase transitions from a thermodynamic perspective. In this Chapter we will take a deeper look into the gas phase. We will start with covering basic gas properties and then learn several "equations of state", which are mathematical equations that relate measurable values like the volume, pressure and temperature of a gas to the quantity of particles (n) in the gas. We will apply these to gas phase stoichiometry, describe multi-component gases as homogenous mixtures (solutions), cover the kinetic molecular theory, which describes an ideal gas, and how real gases can deviate from it. We will also look at gases as dispersed particulate systems and cover properties like effusion and diffusion.

Characteristics of Gases

1. **Fluid** - A gas is a fluid and will take the shape of a container it fills. There is zero viscosity (resistance to flow) and it fills the entire container.
2. **Compressible** - The density of a gas changes as its volume changes. Thus, unlike incompressible solids or liquids, density alone can not be used to help identify a gas. That is, liquid water has a density of 1g/ml at normal temperature and pressure, and so that can be used to help identify a substance as water. But gaseous water (water vapor) fills a container, its density depends on the size of the container.
3. **Gases Form Solutions** - Gas forms homogenous mixtures. Note, for liquid phase solutions we often identify a solvent and a solute, where the solute is dissolved in the solvent to form a solution. We usually consider the solvent to be the substance in greatest quantity, and an aqueous solution is one where water is the solvent. This is because the "space" of matter is being occupied by the liquid particles (which is why they are incompressible). In the gas phase, most of the "space" of matter is the "void" (which is why gasses are compressible), and so it is not normal to consider gas phase solutions to have a solute and solvent. Instead we use the concept of mole fraction to identify the relative proportions of different species in a gas mixture.

Measuring Gases: State Variables

State Variables - an **equation of state** relates measurable state variables to the number of gas particles. The **Ideal Gas Law** (**PV=nRT**) is an equation of state that relates the measurable state variables of **Pressure**, **Temperature** and **Volume** to the number of particles. There are other equations of state and we will discuss some at the end of the Chapter, but this course will expect a mastery of the ideal gas equation of state.

PV=nRT
P=Pressure, V=Volume, n=moles, T=Temperature (Kelvin)
R=0.08206(l-atm/mol-K) = 8.314J/(mol-K)

Pressure

Pressure is defined as force per unit area,

$$P = \frac{F}{A} \tag{10.1.1}$$

and the SI unit is the Pascal.

$$Pa = \frac{1N}{m^2} = \frac{1kg}{m \cdot s^2} \tag{10.1.2}$$

Note, the above definition if founded on the SI base units (kg, s and m) and since May of 2019 these have been defined by the 7 defined constants of nature (section 1B.3.1.2), with the relevant units being the Cs hyperfine transition frequency (atomic clock), speed of light in a vacuum and Boltzmann's constant. Of course we will use more practical definitions here, and the important thing to note is any measurable quantity can be traced back to the 7 SI Base units

This pressure of a gas can be understood by visualizing gas particles in constant motion, as exemplified in Figure 10.1.1.

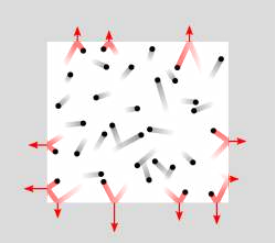


Figure 10.1.1: *Gas particles in a sealed container. As the gas particles move they eventually hit the surface and impart a force on the surface as they change their direction of motion (red particles). The pressure is this force per unit area due to these collisions, which in SI units is the Pa ($1N/m^2$).*

It is more common to see pressure described in atm or torr (mm Hg), which are the units we will predominantly use in this class, and have macroscopic definitions that are more easily measured. Table 10.1.1 shows the common units of pressure, and their conversion factors.

Table 10.1.1: Common units of pressure and conversion factors. UALR students are required to memorize the conversion factors in red

1 atm =	**760 torr**
1 atm =	**760 mm Hg**
1 atm =	14.7 lb/in^2
1 atm =	101,325 Pa

Note, because all values in table 10.1.1 are set to one atmosphere, you can go directly between the other units (14.7 lb/in^2 = $1.01x10^5$ Pa = 760 torr...)

Atmosphere (unit)

One atmosphere of pressure is roughly the pressure felt at sea level by earth's atmosphere, as is shown in Figure 10.1.1. Note, this is not an easily reproducible value because the force felt on the earth changes over both your location and time. This YouTube from the National Naval Aviation Museum does a good job of showing how the air pressure changes as a function of altitude. That is, at the top of Mt Everest (about 5.5 miles high) there is a smaller column of air above you and so the pressure is less than at sea level, while in the Salton Sea CA (-228 ft) the pressure is higher than at sea level.

But also, because the atmosphere of the earth is really a mixture of gasses (mostly nitrogen and oxygen), with many species like water vapor, carbon dioxide, and air pollutants varying over time, so the mass of the column changes over time. So although the concept of an atmosphere of pressure is easy to understand, and it is important because reactions that occur on the surface of the earth occur at around one atmosphere of pressure, its variance over time and location makes it impractical to develop a scale on.

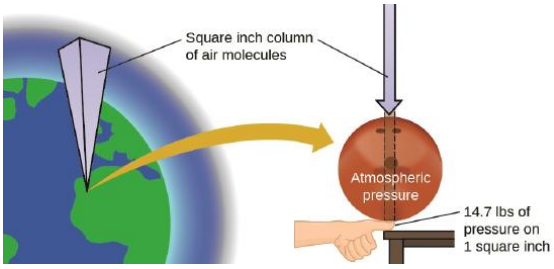


Figure 10.1.2: *This image illustrates the concept of an atmosphere of pressure, which is the pressure felt at sea level due to the column of earth's atmosphere.*



Video 10.1.1: YouTube from State Climate Office of NC demonstrating how the force of atmospheric pressure can collapse an empty can.https://youtu.be/QVayky_b-6U

In the above video, water vapor displaced the air when the water was boiled on the hotplate. It was then inverted and placed in an ice bath such that the opening was under the water surface, this caused the water vapor to condense and a vacuum was formed since there was no way for air to enter, and so the pressure on the inside became less than on the outside, and at some point it became great enough to collapse the can.

Torr (unit)

The torr or mm Hg is a reproducible definition of pressure based on the height of a column of mercury, and can be used to make an instrument to measure atmospheric pressure, the barometer. Using the conversion factor of 1 atm = 760 mm Hg, we could calibrate the barometer in units of atm. This is illustrated in Figure 10.1.3, where the height of the mercury column is dependent on the atmospheric pressure. If the atmospheric pressure is one atm the column is exactly at 760 mm Hg (760 torr). On a humid day the pressure outside goes up and the system is no longer at equilibrium, which forces the mercury up the tube (greater than 760 torr) until they balance out. On an arid day it lowers until they balance out.

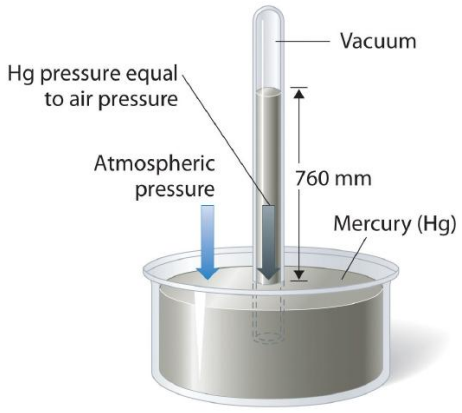


Figure 10.1.3: When at equilibrium the pressure due to the height of the column of mercury must equal the pressure due to the column of air.

Figure 10.1.3 gives a feel for how pressure can be measured. If the atmospheric pressure is higher than that due to the column of mercury it will push the column up until they are equal, if it is less, the column of mercury will go down until they are equal. For this to work, the mercury must be an incompressible fluid so that the mass of mercury in the column is proportional to the height of the column.

The following video from the North Carolina School of Science and Mathematics (NCSSM) shows how to make a mercury barometer.



Video 10.1.1 1'35" YouTube from NCSSM on how to make a barometer.

Exercise 10.1.1

Why do you think the column of mercury is 744 mm Hg in the above youtube from NCSSM?

Answer

Obviously NCSSM is above sea level, but on closer look, it is in Durham NC, which is only 400 feet above sea level, and so it was also probably an arid day.

How could you measure the pressure of a gas in a sealed container?

A manometer is similar to a barometer, but allows you to measure the pressure of a gas in a sealed container.

Manometer

The manometer is the device that can measure the pressure of a gas in a closed container. There are two types of manometers, open ended and closed ended. Figure 10.1.4 shows the two basic types of manometers. The principle is that if the gas pressure on the left and right side of the manometer are not equal, the system will adjust until they are equal.

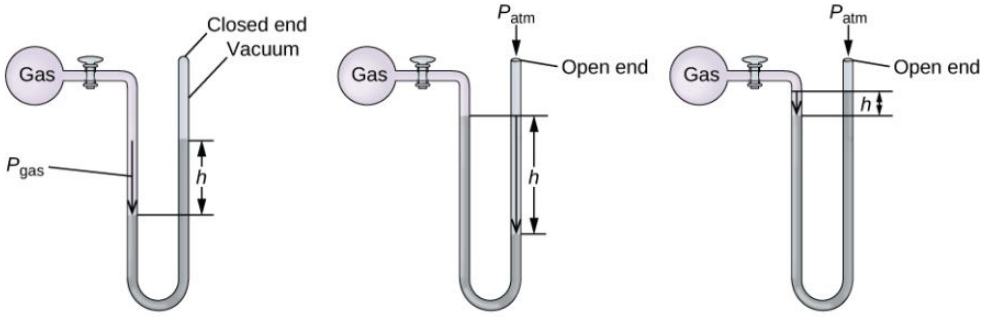


Figure 10.1.4: *Closed (left) and open (middle and right) manometers. If the fluid is mercury, it reads directly in mmHg (or Torr).*

Closed Barometer: In the closed barometer you are pushing the gas against a column of mercury where the opposite end is in a vacuum, and so the column of of fluid goes up until the pressure due to the column equals the pressure of the gas, and if the fluid is mercury, this is the pressure in mm Hg (torr).

Open Barometer: For the open barometer there are three options. The gas is less than, equal to, or greater than the atmosphere. If the gas pressure equals atmospheric pressure there is no difference in the heights of the columns.

- **Gas Pressure < Atmospheric Pressure**

$$P_{gas} + h = P_{atm} \tag{10.1.3}$$

The middle manometer in Figure 10.1.4 shows this case and since the atm pressure is greater it moves the mercury in towards the gas container until the forces cancel out.

- **Gas Pressure > Atmospheric Pressure**

$$P_{gas} = P_{atm} + h \tag{10.1.4}$$

The right manometer in Figure 10.1.4shows the case where the gas pressure is greater, and so it pushes the mercury back against to atmosphere until the forces balance out.

Mercury is a common fluid because it is dense and so the height of the column is managable and can be described in units of mm (mm Hg to be exact), which is one definition of a unit of pressure. The same principle works for any incompressible fluid, where the pressure in Pascal is given by ρgh, where ρ is the density, g is the gravitational constant (9.81 m/s^2) and h is the height of the column.

Exercise 10.1.2

Show that 760.0 mm Hg is approximately 101,325 Pa, given the density of mercury is 13.6g/ml and g= 9.81m/s^2

Answer

Solution: For mercury, ρ = 13.6g/cm^3 and P=ρgh. Pleae note, physics is not a prerequisite for this course and we have not gone over gravitational forces, but you should be able to do this problem based on two things. First you were given the equation and so should be able to substitute in the values, and second, you know the Pa is the SI unit, and can be expressed in terms of the 7 SI base units, which for this problem were the kg (mass), m (length) and time (s). So all you have to do is convert the units to the SI base units, and you have the value in Pa.

$$P = \rho gh = 13.6\frac{g}{cm^3}\left(9.81\frac{m}{s^2}\right)760mm\left(\frac{kg}{1000g}\right)\left(\frac{100cm}{m}\right)^3\left(\frac{1m}{1000mm}\right) = 101,396\frac{kg}{m\cdot s^2} = 101,000Pa \quad (10.1.5)$$

Note g only had three significant digits.

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10.2: Gas Laws

Gas Phase Chemistry

Gasses are compressible fluids which form homogenous solutions. An ideal gas is a gas where there are no attractive (or repulsive) forces between the particles and their kinetic energy (the energy of motion) is linearly proportional to the absolute temperature (K). This relationship is expressed by the Ideal Gas Law as presented in the last section.

$$PV = nRT \tag{10.2.1}$$
$$variables = P, V, n, T$$
$$constant = R = 0.082057 \left(\frac{L \cdot atm}{mol \cdot K} \right)$$

The value of the Ideal Gas constant R depends on the units. The bottom left unit of table $10.2.1$(R=8.314 $\left(\frac{J}{mol \cdot K}\right)$) is of special significance and will be used extensively in the second semester of this class (when you will need to memorize that value), as it relates the energy (Joules) of a gas to the absolute Temperature (K) and number of gas particles in the gas (n). In this class you only need to memorize the first value to four significant digits, (R=0.08206 $\left(\frac{L \cdot atm}{mol \cdot K}\right)$. And hopefully you have realized by now that all these constants can be converted to SI base units (bottom right value of table, which is expressed in units of kg, m, mol and second).

Table 10.2.1: Select Values of R.

R=0.082057 $\left(\frac{L \cdot atm}{mol \cdot K}\right)$	R=62.36367 $\left(\frac{L \cdot torr}{mol \cdot K}\right)$
R=8.3144598 $\left(\frac{J}{mol \cdot K}\right)$	R=8.3144598 $\left(\frac{kg(m^2)}{(s^2)mol \cdot K}\right)$

In the next section we will develop the empirical gas laws. What is important is that you be able to derive these from the ideal gas law.

Empirical Gas Laws

Empirical data is experimental data, and an experiment typically involves two variables, the independent variable, which we change, and the dependent variable, whose value changes as the independent variable is changed. We generically define these variables as (X,Y) where X is the independent and Y is the dependent variable, and then set up an equation where Y is a function of X, or Y =fct(X). A common function is the linear function as expressed in fig. 10.2.1

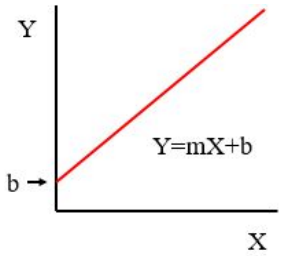


Figure 10.2.1: Linear function where the value of Y (dependent variable) depends on the value of X (independent variable).

If we take a closer look at the ideal gas law, we see there are four variables, (P, T, V and n) and 1 constant (R). To make a plot of n variables you need n-dimensions. So two variables gives a line, three gives a surface (x,y,x axes), and there is no way we can draw 4 variables. What the early scientists could do is hold 2 of the 4 variables constant, and make 2D plots, and the empirical gas laws are the plots that result in linear equations. These were historically determined, and then later the Ideal gas law was developed. But we can use each of the empirical gas laws as a special case of the ideal gas law, defined by which variables are constant, and which are measured. So the idea is simple, you hold two variables constant, change the third (independent variable) and observe how the fourth adjusts (dependent variable).

The Ideal Gas Law can be written as

$$\frac{PV}{nT} = R \tag{10.2.2}$$

Each of the Empirical Gas laws is an expression of the above equation where two of the four variables are held constant, and thus each of the empirical gas constants is related to the Ideal Gas constant through the values of the variables that were held constant.

Boyle's Law (constant n,T)

PV=Constant

This describes the relationship between the pressure and volume of a gas with a constant number of particles at constant temperature.

From the Ideal Gas Law we would predict:

$$PV = nRT \Rightarrow V = (nRT)\,\frac{1}{P} \tag{10.2.3}$$

since n, R and T are all constants, we have

$$PV = k \tag{10.2.4}$$

$$PV = k \;\; where, k = (nRT) \tag{10.2.5}$$

Note, there are two possible graphs that come out of this relationship,

1. P vs. 1/V
2. V vs. 1/P

These graphs of of the form Y=function of X, where Y is the dependent variable and x is the independent variable. That is, if you change X, how does Y change? So if I have a sealed cylinder and I double the volume the pressure will change and so one would plot pressure as a function of volume. But if you had a frictionless piston in a cylinder and then changed the pressure in the cylinder, the piston would move until a new equilibrium was achieved, and we would say the volume is a function of pressure.

Part (a) of Figure 10.2.2 shows that P and V are not linear, but as predicted above and shown in part (b), V is linear to the reciprocal of P.

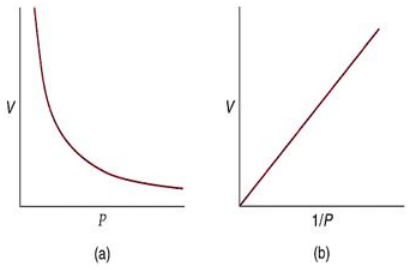


Figure 10.2.2: *Plot (a) shows a non linear relationship of V as a function of P, while (b) shows V and P are inversely related.*

What the data says is that as P goes down, 1/P goes up, and V goes up proportional to 1/P.

Note

This might be easier to understand if we switched the axes and look at how the pressure is dependent on the volume.

$$P = k'\frac{1}{V} \text{ where, k=}\frac{1}{k'} \tag{10.2.6}$$

The pressure is the force per unit area, and the pressure is due to the collision of gas particles against the surface of the container. The greater the collision frequency of particles with the wall, the greater the pressure. If you have a gas in a rigid container and reduce its volume, 1/V goes up, and the pressure goes up because there is a shorter path distance between the walls (increasing the collision frequency).

> We will revisit this after we cover the Kinetic Molecular Theory of gases, where you will find a better explanation (section 10.5.4).

Gay-Lussac's Law (constant n,V)

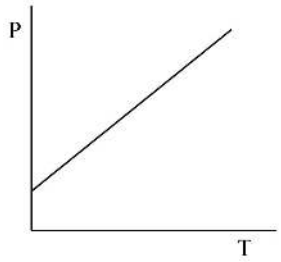
$\frac{P}{T} = Constant$

This describes the relationship between the pressure and temperature of a gas with a constant number of particles at constant temperature. From the Ideal Gas Law we would predict:

PV=nRT $\Rightarrow P = \left(\frac{nR}{V}\right) T$

since n,V & R are constants

P=kT where, k=$\left(\frac{nR}{V}\right)$



This describes a rigid closed container containing a fixed number of gas particles. As the temperature goes up the particles move faster, hit the wall more frequently at higher velocities and so the pressure goes up (remember P=$\frac{F}{A}$. As the temperature rises the pressure continues to rise and at some point the material of the rigid container will rupture and an explosion will occur as the gas escapes.

Likewise, as the temperature goes down the molecules slow down, hit the wall less frequently at lower velocities and so the pressure drops. Note, there is a lower limit to this equations, which is defined as the boiling point, and at temperatures below that Temperature the particle condenses out as a liquid (it is no longer a gas), and the Ideal gas law does not describe the system.

Charles's Law (Constant n,P)

This describes the relationship between the volume and the temperature of a gas with a constant number of particles at constant pressure. This relationship is demonstrated in the following YouTube where a balloon full of air is dropped into liquid nitrogen, and then returned to room temperature.



Video 10.2.1: 2'39" YouTube by Jefferson Lab showing the temperature effect on a balloon full of air (https://youtu.be/ZgTTUuJZAFs).

Mathematically, Charles's Law can be derived from the ideal gas equation at constant pressure and number of particles and would be modeled by an ideal balloon (closed system) that had no resistance to expansion or contraction (constant pressure).

$$PV = nRT \Rightarrow V = \left(\frac{nR}{P}\right) T \Rightarrow V = kT \; where, k = \left(\frac{nR}{P}\right) \; or \; T = k'V \; where, k = \frac{1}{k'} \tag{10.2.7}$$

Note, just as for Gay-Lussac's Law there is a lower limit for the temperature, being the "boiling point", at which temperature the gas converts to a liquid and no longer follows the gas laws. Figure $10.2.4$ shows experimental (empirical) data for the volume of a gas as a function of temperature.

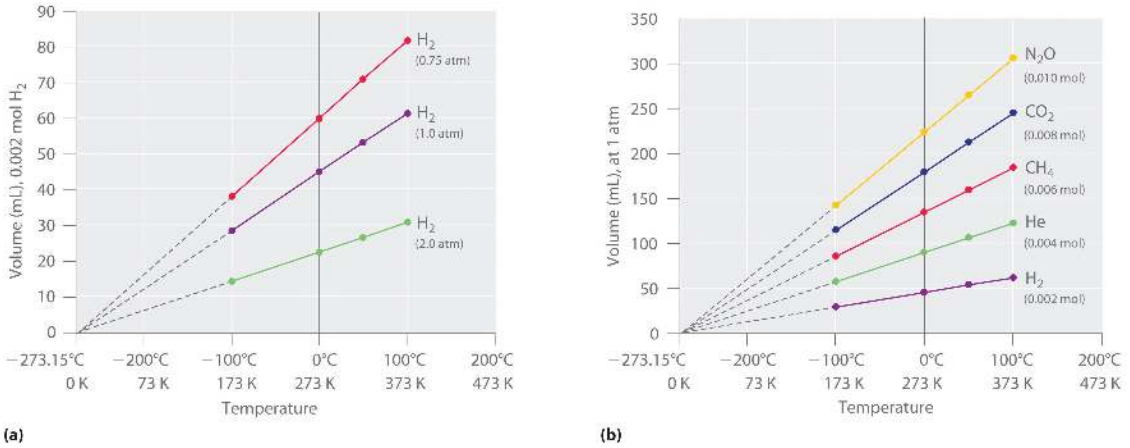


Figure 10.2.4: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at $V = 0$ (−273.15°C = 0 K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of $V = 0$ at −273.15°C, regardless of the identity or the amount of the gas (CC BY-SA-NC; anonymous by request).

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that −273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

Avogadro's Law (Constant P,T)

This describes the relationship between the volume and the number of particles in a gas at constant pressure and temperature. We can derive Avogadro's Law from the ideal gas law using these constants:

$$PV = nRT, \qquad \text{at constant P,T} \tag{10.2.8}$$

$$V = \left(\frac{RT}{P}\right) n, \qquad where\ k = \left(\frac{RT}{P}\right)$$

$$V = kn$$

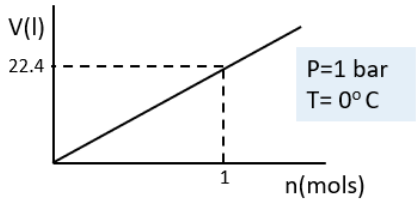


Figure 10.2.5: Avogadro's Law states that at constant P and T the volume is proportional to the number of gas particles.

An important facet of Avodadro's Law is that this relationship does not depend on the identity of the molecule (we will learn later that there are deviations), but the value of the constant does depend on the value of P and T held constant

Historically, around 1811 Avogadro postulated his hypothesis, which was that equal volumes of gasses contain equal numbers of particles, and Avogadro's Law derives from that relationship. It is common to use STP (standard temperature and pressure) as the value for the constants (T and P) in Avagadro's Law

STP (Standard Temperature and Pressure)

STP is the standard temperature and pressure that many gas values are tabulated at. You may notice different values in different textbooks because in 1982 the definiton of the standard pressure changed from 1 atm to 1 bar.

- Until 1982, STP was defined as a T= 0 °C and P = 1 atm (101.325 kPa).
- Since 1982, STP is defined as a T= 0 °C and P = 1 bar (100kPa)

Molar Volume at STP

Avogadro's hypothesis states that the volume of a mole should be the same for any substance, and as can be seen from Table 10.2.1.

Table 10.2.1: Molar Volumes of Several Gases at STP

Substance	Formula	Molar Volume/liter mol^{-1}
Hydrogen	$H_2(g)$	22.43
Neon	$Ne(g)$	22.44
Oxygen	$O_2(g)$	22.39
Nitrogen	$N_2(g)$	22.40
Carbon dioxide	$CO_2(g)$	22.26
Ammonia	$NH_3(g)$	22.09

The data in Table 10.2.1, then, indicate that for a variety of gases, 6.022×10^{23} molecules occupy almost exactly the same volume (the ***molar volume***) if the temperature and pressure are held constant, and the molar volume for an ideal gas is 22.4 l/mol. So if you can measure the volume of a gas at STP, you can calculate the number of moles.

Ideal Gas Law Calculations

There are three basic types of calculations involving the ideal gas law

1. PV=nRT calculations.
2. Calculations involving Density and formula weights.

3. Two State Problems

PV=nRT

These are simple algebraic problems where you are given 3 of the 4 variables. The trick is to keep your units in your equations and be sure the units of the answer make sense. If you think about it, the numerical value of R depends on the units of R (see table 10.2.1), and your variables must have the units of R or they will not cancel. This is especially important for temperature, which must be in units of Kelvin.

Exercise 10.2.1

The following problems represent various solutions to the ideal gas equation

a. A sample of gaseous Cl_2 has a volume of 12.4 L at 500.0 K and 0.521 atm. How many moles are present?
b. What is the mass of chlorine gas in a 12.4L container at 500.0K and 0.521 atm?
c. What volume is occupied by 1.06 mol of CO_2 gas at 299 K and a pressure of 0.89 atm?
d. What is the temperature of 1.41 mol of methane gas in a 5.0 L container at 1.00 atm?
e. What is the pressure exerted by a 1.75 mol sample of water at 7.0L and 20°C?

Answer a

$$n = \frac{PV}{RT} = \frac{0.521atm\,(12.4L)}{0.08206\,\frac{L{\cdot}atm}{mol{\cdot}K}(500K)} = 0.157mol$$

Answer b

$$n = \frac{PV}{RT} = \frac{0.521atm\,(12.4L)}{0.08206\,\frac{L{\cdot}atm}{mol{\cdot}K}(500K)} = 0.157mol$$

$$0.157mol\,Cl_2\left(\frac{70.90g\,Cl_2}{mol}\right) = 11.1g \tag{10.2.9}$$

Answer c

$$V = \frac{nRT}{P} = \frac{1.06mol\left(0.08206\,\frac{L{\cdot}atm}{mol{\cdot}K}\right)299K}{0.89atm} = 29L$$

Answer d

$$T = \frac{PV}{nR} = \frac{1.00atm\,(5.0L)}{1.41mol\left(0.08206\,\frac{L{\cdot}atm}{mol{\cdot}K}\right)} = 43K$$

Answer e

$$P = \frac{nRT}{V} = \frac{1.75mol\left(0.08206\,\frac{L{\cdot}atm}{mol{\cdot}K}\right)293.15K}{7.0L} = 6.0atm$$

Density and formula weight.

The formula weight of a compound can be expressed in terms of the number of moles, where

$$fw(\frac{g}{mol}) = \frac{m(g)}{n(mol)} \tag{10.2.10}$$

solving for n:

$$n = \frac{m}{fw} \tag{10.2.11}$$

Substituting for n in the ideal gas law (PV=nRT) gives:

$$PV = \left(\frac{m}{fw}\right) RT \tag{10.2.12}$$

This allows us to solve for both density and the formula weight

1. Density

Rearranging eq. 10.2.9 to $d = \frac{m}{V}$ gives

$$d = \frac{m}{V} = \frac{P(fw)}{RT} \tag{10.2.13}$$

2. Formula Weight

Solving Equation 10.2.9 directly for formula weight gives

$$fw = \frac{mRT}{PV} = \left(\frac{m}{V}\right)\frac{RT}{P} = \frac{dRT}{P} \tag{10.2.14}$$

note how the above eq. can be expressed in terms of density, or mass and volume.

Example 10.2.1: Calculating the formula weight from density, pressure and temperature.

What is the formula weight of an unknown gas if it has a density of 4.08g/l at 88 °C and 1.4 atm?

Solution

NOTE: There are many ways you can solve this problem, and in video we note that we are looking for the formula weight, and so we start with an equation that has the formula weight, and solve it for the formula weight by identifying what variables we do not have, and substituting for them.



If you know the identity of a gas, you know its formula weight. The following problem calculates the density of a gas if we know what it is. In solving this it is good to reflect on the fact that a gas is compressible, that is, it expands or contracts to a change in volume. So you can not use the simple $d = \frac{m}{v}$ that you could use for an incompressible substance like a liquid or a solid.

Example 10.2.2: Calculating the density of a known gas at a given temperature and pressure

What is the density of sulfur dioxide gas at 88 deg C and 1.4 atm?

Solution

Note, since we know what the gas is, we know its formula weight. Since we are solving for density, we start with the density equation.



Example 10.2.3: Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (Figure 10.2.1)

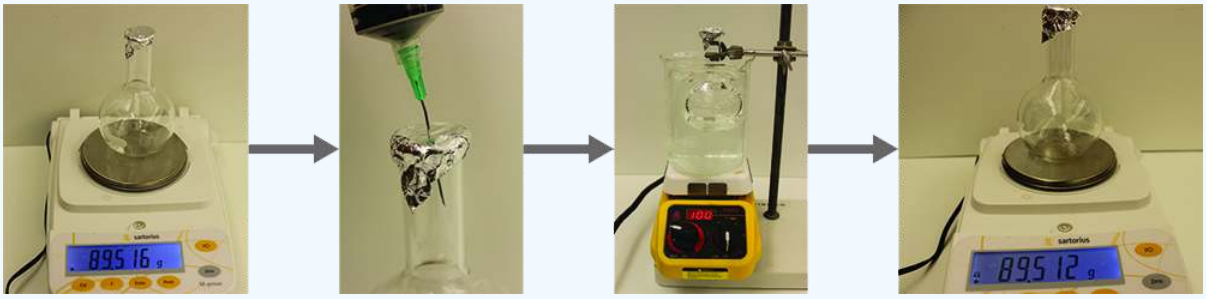


Figure 10.2.1: When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $t_{l \longrightarrow g}$, *the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)*

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm^3 at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since

$$fw = \frac{m}{n} \tag{10.2.15}$$

and

$$n = \frac{PV}{RT} \tag{10.2.16}$$

substituting and rearranging gives

$$fw = \frac{mRT}{PV} \tag{10.2.17}$$

then

$$fw = \frac{mRT}{PV} = \frac{(0.494\ \text{g}) \times 0.08206\ \text{L} \cdot \text{atm/mol K} \times 372.8\ \text{K}}{0.976\ \text{atm} \times 0.129\ \text{L}} = 120\ \text{g/mol} \tag{10.2.18}$$

Two State Approach

If you have a gaseous system and then perturb it by changing one of more variables the other variables adjust to that change. The two state approach is a quick way to solve these problems. The idea is simple, you have a relationship PV=nRT, so at one state, $P_1V_1 = n_1RT_1$ and $P_2V_2 = n_2RT_2$, so we can set up the equivalence:

$$\frac{P_1V_1}{P_2V_2} = \frac{n_1RT_1}{n_2RT_2} = \frac{n_1T_1}{n_2T_2} \tag{10.2.19}$$

so

$$\frac{P_1V_1}{P_2V_2} = \frac{n_1T_1}{n_2T_2} \tag{10.2.20}$$

(note: the constant (R) cancels out)

Warning: T must be in Kelvin, as the equation PV=nRT requires T to be in Kelvin, and even though R cancels in the two state approach, T still needs to be in Kelvin.

When solving these problems it is wise to make a table and write down what you are given. If something is held constant, it cancels out of the equation.

State 1	State 2
T_1=	T_2=
P_1=	P_2=
V_1=	V_2=
n_1=	n_2=

Example 10.2.3

What is the volume of a perfectly elastic balloon if it rises to an altitude where the pressure drops to 0.100 atm and the temperature drops to 173 K if it had a volume of 5.00 liters at sea level where the pressure was 1.00 atm and the temperature was 273K?

Solution

(a) Set up two state equation and solve for V_1 or V_2 (which either is easier, as we have not assigned the data to the states

$$\frac{P_1V_1}{P_2V_2} = \frac{n_1T_1}{n_2T_2} \tag{10.2.21}$$

$$becomes$$

$$V_1 = V_2\left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right)\left(\frac{P_2}{P_1}\right)$$

(b) Fill our the data table so we properly identify the data with the state.

TIP, Since we want the volume in the upper atmosphere we will call that state 1, but we could have called sea level state one, in which case we would solve for V_2.

State 1	State 2
T_1= 173K	T_2= 273K
P_1= 0.100 atm	P_2= 1.00 atm

State 1	State 2
V_1= ?	V_2= 5.00 L
n_1=	n_2=

NOTE: This is a closed system and no gas entered or escaped from the balloon and so n_1=n2 and they cancel.

$$V_1 = 5.00L \cancel{\left(\frac{n_1}{n_2}\right)} \underbrace{\left(\frac{173K}{273K}\right)}_{\substack{T \text{ must be} \\ \text{in Kelvin}}} \left(\frac{1atm}{0.100atm}\right) \tag{10.2.22}$$

The solution to this problem is demonstrated in video 10.2.4



Video 10.2.4: 5'10" YouTube solving this problem (https://youtu.be/BCYEZv9IQFA)

Note

Many textbooks cover the "combined gas law":

$$\frac{P_1V_2}{T_1} = \frac{P_2V_2}{T_2} \tag{10.2.23}$$

On closer inspection the combined gas law is applying the two-state approach to the ideal gas law where n, the number of molecules is constant, and that was the case we just solved (example 10.3.2). The advantage of the two state approach is that it not only allows us to handle changes in the number of particles, but it is a technique that can be applied to many equations, not just the ideal gas equation.

If you have a relationship y=mx, you can always say that $\frac{y_1}{y_2} = \frac{x_2}{x_2}$, and during the second semester this technique will be applied to power functions ($Y=AX^m$) and exponential functions $Y=Ae^{xm}$. It is worth mastering the two state approach now.

Exercise 10.2.2

Solve the following problems using the two state approach.

a. What pressure would 6.1 moles of a gas in a rigid container have at 20.0 ^oC have if it had a pressure of 0.45 atm at -45.0 ^oC?
b. A pressure tank containing chlorine gas at a pressure of 2.00 atm and a temperature of 40^oC is set with a pressure relief valve set to open at a pressure of 10.0 atm. At what temperature will the relief valve open?
c. A gas is in a sealed cylinder at 25^oC with a piston which can expand or contract to change the volume. The initial volume and pressure are 75.0 L and 980.0 torr. A force is applied to the piston and the volume adjusts to a final pressure and temperature of 5.00 atm at 188^oC. What is the final volume?

Answer a

$$P_1 = P_2 \frac{T_1}{T_2} = (0.45atm)\left(\frac{293.15K}{228.15K}\right) = 0.58atm \tag{10.2.24}$$

Answer b

$$T_2 = T_1 \frac{P_2}{P_1} = (313.15K)\left(\frac{10.0atm}{2.00atm}\right) = 1570K \tag{10.2.25}$$

Answer c

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right) = 75.0L\left(\frac{980torr\left(\frac{1atm}{760torr}\right)}{5.00atm}\right)\left(\frac{461.15K}{298K}\right) = 29.9L \tag{10.2.26}$$

Contributors and Attributions

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10.3: Gas Phase Reactions

Introduction

Now that we have covered the ideal gas law we can revisit the stoichiometric equations of Chapter 4 and account for gas phase reactants and products in a more meaningful manner. While going over this material you may wish to review the following sections.

- 3.2: Types of Chemical Reactions (combustion and many types of single displacement involve gasses)
- 3.5.4: Acid Reactions Evolving Gases (Strong acid reactions with salts of oxyanions [acid anhydrides])
- 4.1: Stoichiometry
- 4.2: Limiting & Excess Reagents

In the previous sections we would report gasses in terms of their moles, or even their mass. Lets take a second look at Exercise 4.2.1, where we calculated the mass of carbon dioxide formed upon the combustion of 25.00g glucose with 40.0 g of oxygen. Sure we could solve the problem, but at standard conditions oxygen or carbon dioxide are gasses not solids, and so you would not be able to directly measure their mass, and a more realistic problem would be to define them in terms of measurable quantities like pressure, temperature and volume.

Overview of Stoichiometry:

In stoichiometric calculations you typically have three steps.

1. Convert measured quantities to moles (assuming you don't start with moles, but something measurable)
2. Use balanced equations to relate moles of starting material to moles of desired substance sought.
3. Convert moles of desired substance to measurable quantities (assuming you don't want moles, but something measurable)

mass	solute in solution	
n=$\frac{m}{fw}$	n=MV	n=$\frac{PV}{RT}$
m=mass fw=formula weight	M=Molarity=$\frac{mol_{solute}}{liter_{solution}}$ V=Volume in liters	P=Pressure V=Volume R=Ideal Gas Constant T=Temperature in Kelvin

As in Chapter 4, it is a good idea to write out and balance the equation, write under it what is given, and then solve the problem. The following problems involves calculations involving all three phases.

Example 10.3.1

What volume of gas would be produced at 760.0 torr and 298 K if 1.00 g of magnesium metal is dropped into 50.0 ml of 1.00 M Hydrochloric Acid?

Solution
(See Video 10.3.1 for solution)

Step 1: Write out and balance equation and write underneath it what is given:

$$\underset{\substack{m=1.00g\\ fw=24.3\frac{g}{mol}}}{Mg(s)} + \underset{\substack{0.0500L\\ 1.00M}}{2HCl(aq)} \rightarrow Mg(Cl)_2(aq) + \underset{\substack{P=760.0atm\\ T=298K\\ n=?\\ V=??}}{H_2(g)} \quad (10.3.1)$$

NOTE: We want V_{H_2}, but have two unknowns (V and n), so we need to calculate n

Step 2: Calculate theoretical yield of n (based on complete consumption of limiting reagent)

$$1.00g\ Mg\left(\frac{mol\ Mg}{24.3g}\right)\left(\frac{1}{1mol\ Mg}\right)=0.0411 \tag{10.3.2}$$

$$0.0500L\left(\frac{1.00mol\ HCl}{L}\right)\left(\frac{1}{2mol\ HCl}\right)=.025$$

$$HCl=limiting\ reagent$$

$$n_{H_2}=0.025\left(1mol\ H_2(g)\right)=0.025mol\ H_2(g)$$

Step 3: Now that we have n_{H_2}, use ideal gas law to solve for V at the conditions of the problem.

$$V=\frac{nRT}{P}=\frac{0.02500mol\left(0.08206\left(\frac{l\cdot atm}{mol\cdot K}\right)\right)298K}{760\ torr\left(\frac{1atm}{760\ torr}\right)}=.6113L=611mL \tag{10.3.3}$$



Video 10.3.1: 5'35" YouTube showing solution for problem above

Exercise 10.3.2

Solve the following problems

a. 5.00 g of Mg is added to 50.0 mL of 0.800M HCl. A single displacement reaction occurs in a sealed container at 25.0°C. What is the pressure of the hydrogen gas generated if the volume above the solution is 100.0 ml, and we ignore any pressure due to the evaporated water?

b. Nitrogen dioxide is formed in a closed container at 90°C and 1.00 atm when 1.50 g NO and 2.00 mole of O_2 are mixed. After the reaction is finished the pressure changes to 3.90 atm. What is the final temperature?

Answer a

$$P_{H_2}=\frac{n_{H_2}RT}{V}=\frac{0.0200mol\ H_2\left(0.08206\frac{L\cdot atm}{mol\cdot K}\right)298K}{0.100L}=4.89atm \tag{10.3.4}$$

Answer b

$$T_2=T_1\left(\frac{n_1}{n_2}\right)\left(\frac{P_2}{P_1}\right)=363.15K\left(\frac{2.05mol}{2.025mol}\right)\left(\frac{3.90atm}{1.00atm}\right)=1433.77K=1400K \tag{10.3.5}$$

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10.4: Gas Mixtures

Introduction

Gasses disperse throughout a container and form homogenous mixtures or solutions. Unlike liquid solutions where it is common to have a solvent that the solute actually interacts with and dissolves in, the component of a gaseous mixture are so dispersed that they essentially behave as free particles, and so there is no concept of a solute of solvent. The air that you are breathing is a mixture of gasses with 99.96% of dry air consisting of three substances; nitrogen, oxygen and argon.

Table 10.4.1: Composition of air near the surface of the earth, percent values are based on moles . Note many of these gasses will vary based on anthropomorphic and geologic activities.

N_2	78.08%		H_2O	0-4%		He	5 ppm		H_2	0.5 ppm
O_2	20.95%		CO_2	325 ppm		CH_4	2 ppm		N_2O	0.3 ppm
Ar	0.93%		Ne	18 ppm		Kr	1 ppm		CO	0.05-0.2 ppm

As each gas interacts independently of the other gasses, each gas exerts its own pressure when its particles collide with a surface, which would be known as the partial pressure of that gas.

Partial Pressure

Consider a mixture of two gasses A & B (right side of Figure 10.4.1, which being in the same container have the same volume and pressure. If n_A is the mole of gas A and n_B is the moles of gas B, we could define a partial pressure of each gas (noting that V and T are constant).

$$P_A = n_A\left(\frac{RT}{V}\right) \quad and \quad P_B = n_B\left(\frac{RT}{V}\right) \tag{10.4.1}$$

where P_A= partial pressure of gas A and p_B = partial pressure of gas B.

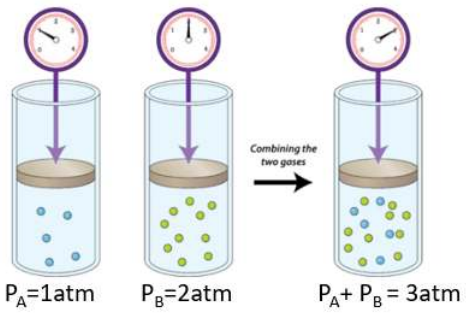


Figure 10.4.1: In a mixture each gas has its own partial pressure, which is the pressure that gas would exert if it was alone. Note, these cylinders are at the same volumn and temperature

If there were three gasses, the total pressure would be the sum of all three gases, and this leads to Dalton's Law of Partial Pressures.

Dalton's Law of Partial Pressure

Dalton's Law of Partial Pressures states the total pressure of a gas mixture is the sum of the partial pressures of the individual gasses

$$P_{total} = P_1 + P_2 + P_3 \ldots = \sum_i P_i \tag{10.4.2}$$

The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50×10^{-3} mol of H_2, 1.00×10^{-3} mol of He, and 3.00×10^{-4} mol of Ne at 35 °C.

a. What are the partial pressures of each of the gases?
b. What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$P_{H_2} = \frac{(2.50 \times 10^{-3}\ \text{mol})(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(308\ \text{K})}{10.0\ \text{L}} = 6.32 \times 10^{-3}\ \text{atm} \tag{10.4.3}$$

$$P_{He} = \frac{(1.00 \times 10^{-3}\ \text{mol})(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(308\ \text{K})}{10.0\ \text{L}} = 2.53 \times 10^{-3}\ \text{atm} \tag{10.4.4}$$

$$P_{Ne} = \frac{(3.00 \times 10^{-4}\ \text{mol})(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(308\ \text{K})}{10.0\ \text{L}} = 7.58 \times 10^{-4}\ \text{atm} \tag{10.4.5}$$

The total pressure is given by the sum of the partial pressures:

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076)\ \text{atm} = 9.61 \times 10^{-3}\ \text{atm} \tag{10.4.6}$$

Exercise 10.4.1

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Answer

1.137 atm

Mole Fractions and Gas Mixtures

The mole fraction of a gas in a mixture of gasses is defined as the moles of that gas divided by moles of all gasses, for gas "A" given the symbol X_A.

$$X_A = \frac{n_A}{n_T} \quad where \quad n_T = \sum_{i=A}^{all\ i} n_i \tag{10.4.7}$$

Exercise 10.4.2

Using the data from table 10.4.2, determine the mole fraction of nitrogen, oxygen and argon for earth's lower atmosphere.

Answer

Nitrogen = 0.7908, Oxygen = 0.2095 and Argon = 0.0093

The mole fraction can also be expressed in terms of pressure

$$X_A = \frac{P_A}{P_T} \tag{10.4.8}$$

which is derived in the third step of the following derivation.

Prove: $P_A = X_A P_T$

Solution

$$P_A = \left(\frac{n_A RT}{V}\right) \quad and \quad P_T = \left(\frac{n_T RT}{V}\right) \tag{10.4.9}$$

so

$$n_A = P_A\left(\frac{V}{RT}\right) \quad and \quad n_T = P_T\left(\frac{V}{RT}\right) \tag{10.4.10}$$

substituting n_A and n_T into

$$x_A = \frac{n_A}{n_T} = \frac{P_A \cancel{\left(\frac{V}{RT}\right)}}{P_T \cancel{\left(\frac{V}{RT}\right)}} = \frac{P_A}{P_T} \tag{10.4.11}$$

rearranging gives:

$$P_A = X_A P_T \tag{10.4.12}$$

The following video shows how $P_A = X_A P_T$ for a system of three gasses.



Video 10.4.1: 4'15" YouTube video showing how the partial pressure of a gas is the mole fraction of that gas times the total pressure (https://youtu.be/MD16T5yXvPE). [Video Corregendum: about 2:04 in the video it states "3 moles" N_2, when it is really 7 (and 7 is written)]

Example 10.4.1

Calculate the Partial pressure if 78 g nitrogen and 42 g helium are in a pressure tank at 3.75 atm and 50.0 deg. C

Solution



Video 10.4.2: Solution to example 10.4.2 (https://youtu.be/V9JMfV4cV8Y).

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10.5: Kinetic Molecular Theory of Gases

Introduction

The **Kinetic Molecular Theory** (KMT) describes an Ideal Gas, PV=nRT. Understanding Kinetic Molecular Theory can help us identify when a gas will behave like an ideal gas, and when it will deviate and not behave like an ideal gas.

There are five postulates to the Kinetic Molecular Theory, and gases will deviate from the ideal gas law when these postulates break down.

Five Postulates of KMT.

1. Gas particles travel in straight lines unless they collide with other particles or the walls of the container.
2. Gas particles have negligible volume compared to the free space between them..
3. Molecular collisions are perfectly elastic and kinetic energy is conserved.
4. Gas particles experience negligible intermolecular forces, there are no attractive or repulsive forces between particles.
5. The average kinetic energy of the particles in a sample of gas is proportional to the absolute temperature.

The fifth postulate is very important to note as it relates kinetic energy to temperature. For a gaseous particle most of the kinetic energy is in translation.

$$E_K = \frac{1}{2}mv^2 \tag{10.5.1}$$

But a gas is not a particle, but an ensemble of particles, all moving with different velocities in different directions. So the challenge is to describe bulk measurable properties based on the behavior of particles.

Particulate to Macroscopic Transformations

The postulates of KMT define the behavior of the particles of the gas, but the gas laws are empirical laws, in that they are derived from experimental measurements, which are not at the particulate (molecular) level. This means they are based on macroscopic observations of many molecules and not the behavior of one. A liter of oxygen is an easily measurable quantity, but how many molecules would be in a liter at STP?... and would you expect them all to have the same energy?

Exercise 10.5.1

How many particles of Xenon are in 1.00 liter at STP?

Answer

STP is 1 bar (0.98592 atm) at 273.15K, which is the freezing point of water, and we know that the molar volume of any ideal gas is 22.4L. So:

$$1.00L(\frac{1molXe}{22.4L})\frac{6.022x10^{23}atoms}{mol} = 2.69x10^{22}atoms\ Xe \tag{10.5.2}$$

Yes, that was 2.693x10^{22} atoms in one liter! So when we describe a gas we are not describing a molecule, but an ensemble of molecules, a group of particles that is observed as the whole, not at the level of the individual molecule. This means there is a distribution of characteristics of the individual gas particle, like velocity. At any point in time some molecules are moving real fast, others slow, and some may in fact be in the middle of a collision at are not moving at all, but changing the direction that they are moving in.

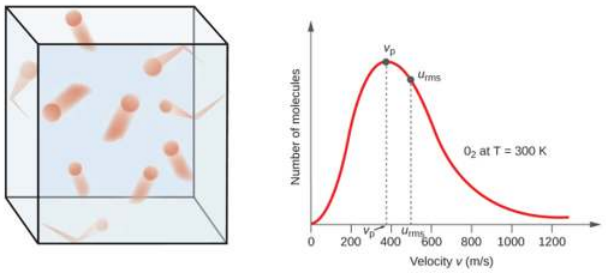


Figure 10.5.1: On the left is an illustration of gas particles in a container and on the right is the velocity profile for a gaseous system The discrete particles that form the gas have a range of velocities, and their distribution over the range is expressed by the area under the curve.

Typically a curve like the one in Figure 10.5.1 represents a macroscopically observable system in the order of a mole of particles. At any given time there is a distribution of velocities as described by the curve, and the measured values of macroscopic observables like pressure and temperature are all related to the shape of this curve, and likewise, if those values change, the shape of the curve changes.

Exercise 10.5.2

What is wrong with the label of the x-axis of the velocity distribution curve in Figure 10.5.1?

Answer

Velocity is a vector and has direction, which means that the distribution of speeds is mapped out in 3D space (left side of Figure 10.5.1, and so although some gasses may be moving at 400 m/s in one direction, other molecules will be moving the same speed in the opposite direction with a cancelling out effect. Speed is the magnitude of velocity, and the x-axis really represents the distribution of the speed of the particles in the ensemble.

Although the kinetic energy of each particle in a stationary gas is 1/2mv^2, we can not use the average velocity of the particles because it vectoraly adds to zero. Instead we relate its kinetic energy to the room mean square velocity, μ_{rms}.

μ_{rms}

For a gaseous system the average kinetic energy is

$$E_{K_{ave}} = \frac{1}{2} m \mu_{rms}^2 \tag{10.5.3}$$

Average root mean square speed for a system of n particles with individual velocities v_i:

$$\mu_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + \dots}{n}} \tag{10.5.4}$$

Exercise 10.5.3

Why do we use root mean square speed and not the arithmetic average velocity

Answer

Remember velocity is a vector, and something can be moving along either the [+] or [-] directions of an axis, and for a large system of particles in random motion the number moving in the [+] or [-] is directions are roughly the same. The sum of a symmetric distribution of speeds and directions would be zero. By squaring each individual velocity all values become [+], allowing summation without cancelation, and then dividing by the total number of particles gives the average velocity square. The square root is taken to remove the effect of squaring. The resulting value is a speed (scalar) as it has a magnitude, but no direction (vector).

The important take-home message of Figure 10.5.1 is that a gas is a system of particles, each particle of which has a unique location, velocity and kinetic energy, and that we use μ_{rms}^2 to calculate the average kinetic energy of the gas (even though most of the particles actually have a different energy).

$$E_{Kave} = \frac{1}{2} m u_{\text{rms}}^2 \tag{10.5.5}$$

It can be shown that $E_{K_{ave}}$ of a collection of gas molecules is directly proportional to the temperature of the gas and may be described by the equation:

$$E_{K_{ave}} = \frac{3}{2} RT \tag{10.5.6}$$

where *R* is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J $mol^{-1}K^{-1}$ (8.314 kg $m^2s^{-2}mol^{-1}K^{-1}$). These two separate equations for $E_{K_{ave}}$ may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2} m u_{\text{rms}}^2 = \frac{3}{2} RT \tag{10.5.7}$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}} \tag{10.5.8}$$

Calculation of u_{rms}

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30^\circ C + 273 = 303\ K \tag{10.5.9}$$

Determine the mass of a nitrogen molecule in the SI base unit of kilograms (because Joules can be expressed in the SI base units):

$$\frac{28.0\ \cancel{\text{g}}}{1\ \text{mol}} \times \frac{1\ \text{kg}}{1000\ \cancel{\text{g}}} = 0.028\ \text{kg/mol} \tag{10.5.10}$$

Replace the variables and constants in the root-mean-square velocity formula (Equation 10.5.8), replacing Joules with the equivalent kg m^2s^{-2}:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}} \tag{10.5.11}$$

$$u_{\text{rms}} = \sqrt{\frac{3(8.314\ J/mol\ K)(303\ K)}{(0.028\ kg/mol)}} \tag{10.5.12}$$

$$= \sqrt{2.70 \times 10^5\ m^2 s^{-2}} \tag{10.5.13}$$

$$= 519\ m/s \tag{10.5.14}$$

Exercise 10.5.4

Calculate the root-mean-square velocity for an oxygen molecule at –23 °C.

Answer

440 m/sec

Boyle's Law & KMT (const. n,T)

At constant n and T, the velocity profile on part (b) of Figure 10.5.1 stays the same. Here we are looking at closed (constant n) isothermal (constant T) elastic system that has no resistance or heat loss to expansion or contraction.

a. Effect of ΔV on P:

Reducing the volume of the cube in part (a) of Figure 10.5.1 increases the pressure because it increases the collision frequency of the particles with the wall. This is because they are maintaining the same velocity but have less distance to travel as they traverse the cube. Likewise, Increasing Volume decreases pressure beacuse it takes longer to traverse the expanded cube, resulting in a reduction in the collision frequency. Remember Pressure is force per unit area, and the force is the consequence of the change in momentum of the gas particle as it undergoes an elastic collision with the wall of the container (this is called an impulse in physics).

b. Effect of ΔP on V:

Figure 10.5.2 shows this effect. Here we have a cylinder type system with a gas in a closed system. If the internal pressure is not equal to the external, the system will adjust until the are equal. Consider a system starting at state (b) where the internal volume is 3 dm^3 and the pressure is 1.97 atm. If you then reduced the external pressure to 0.987 atm, the force/unit ares inside is greater than outside and the system expands until they balance and equilibrium is re-established (a). Note, in this case we cut the pressure in half, and so the volume doubled.

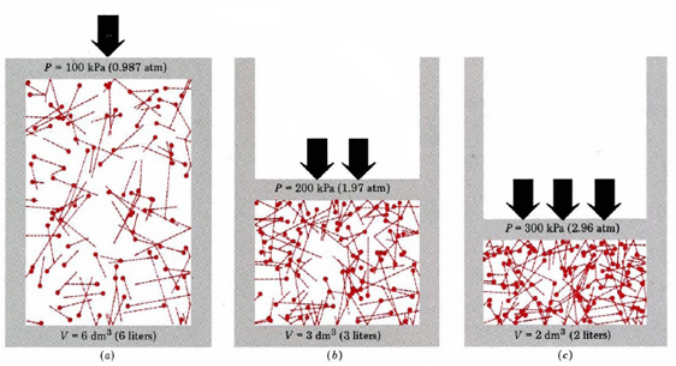


Figure 10.5.2: Relationship between P and V, note, these conditions are equilibrium conditions.

On the other hand, we could have increased the pressure of the system at (b) to 2.96 atm and now the external pressure is greater and so the system contracts until a new equilibrium is acheived (c). KMT accounts for these effects because the particles are seen to travel in straight lines until they collide with the walls of the container. Since T and n are constant, the relationship is defined by the length of the path the particles travel as they traverse the container. A larger free path (bigger V) means they collide less with the wall and so P goes down. A smaller free path means the collide with the wall more frequently, and so P goes up.

Charles Law (constant n,P)

This describes a closed elastic isobaric system that can freely expand and contract. Figure 10.5.3 shows how heating a system affects the velocity profile. Note, since n (number of molecules) is constant the area under each curve is the same. At higher temperatures the curves flatten out and move to the right, increasing u_{rms} and thus the average kinetic energy. This has two effects, first, collision frequency goes up because the the faster moving particles traverse the container quicker, and second, each collision has more energy because the particle is moving faster ($E_K=1/2mv^2$). Since the pressure (force per unit area) is being maintained constant, the area must go up to offset the increased force, and so the container expands as T goes up.

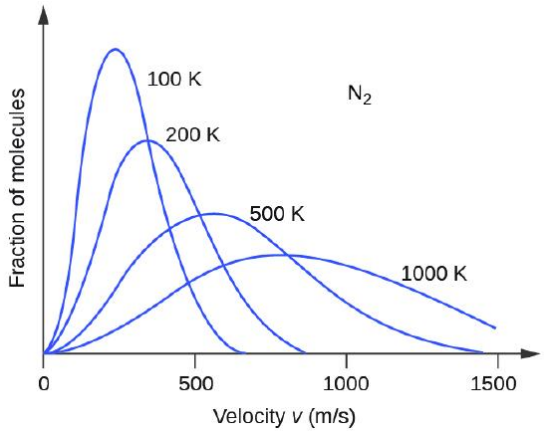


Figure 10.5.3 Velocity profiles of Nitrogen at different temperatures. Note that even at high temperatures some of the molecules have low velocities, but as T goes up, u_{rms} goes up.

Can you cool the curve to absolute zero?

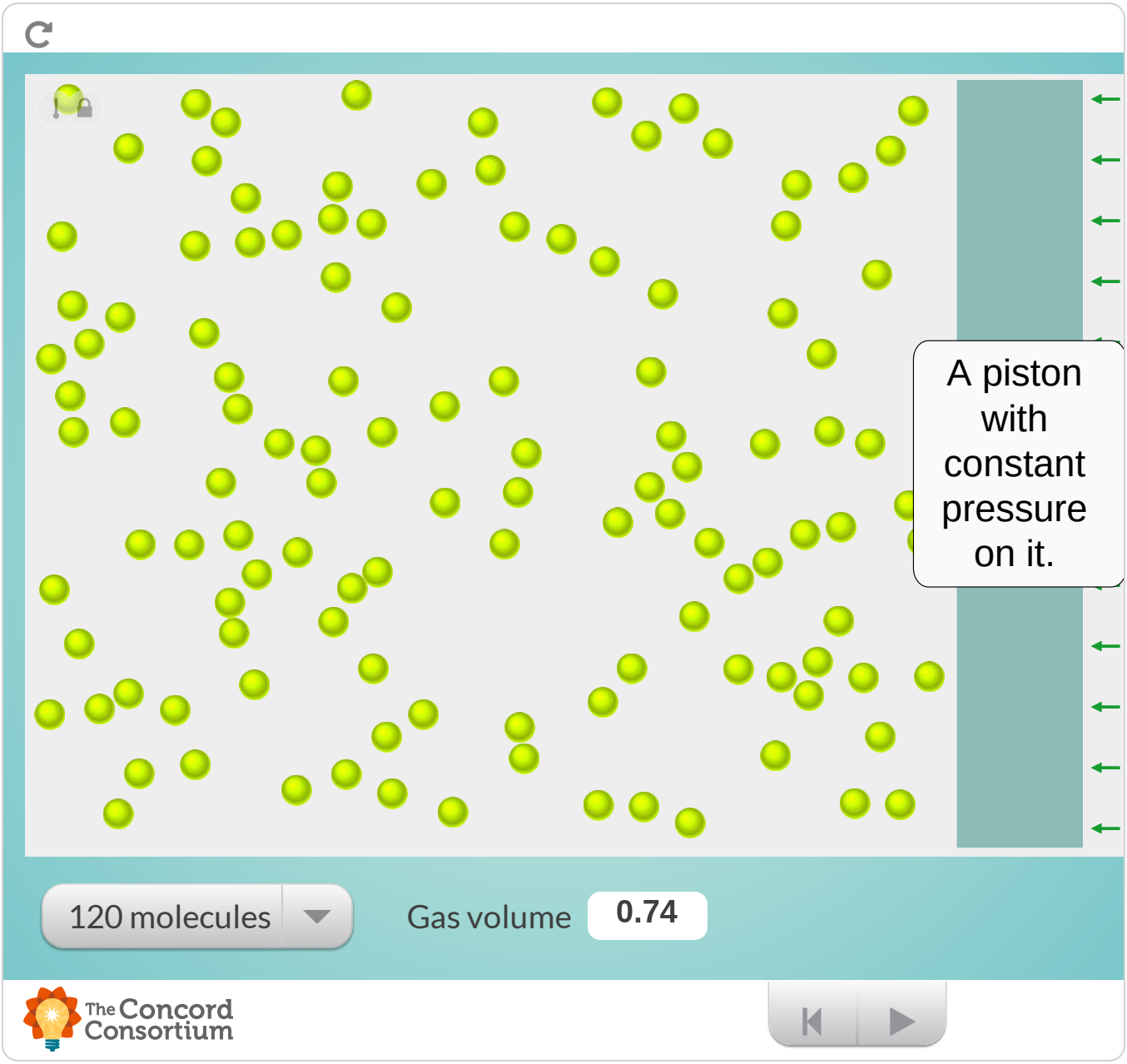
No, at some point you reach the boiling point and cooling below that causes the system to convert to a liquid, and you no longer have a gas.

Gay-Lussac's Law (constant n,V)

This is similar to Charles Law, except now instead of having a perfectly elastic container (that has no resistance to expansion or contraction) you have a rigid container of constant size. As T goes up the root mean velocity goes up and so the average kinetic energy goes up and thus the force imparted by collisions with the container are greater. Also, since the molecules tend to be moving faster (remember, there is a velocity profile), the collision frequency is greater.

Avogadro's Law (const P,T)

This describes an elastic container at isobaric and isothermal conditions. According to KMT increasing the number of particles increases the collision frequency on the surface which effectively increases the force. Since pressure (force per unit area) is constant, the system must expand (increase surface area) to accommodate the increased number of collisions.



Animation 10.5.1: Change the number of molecules and click the start button. Note how adding molecules increases the collision frequency. Since pressure is being kept equal, the system adjusts its volume so the collision frequency returns to the original value.

KMT and Ideal Gas Law

Qualitatively,KMT predicts:

1. More particles means more collisions with the wall (P $\propto n$)
2. Smaller volume means more frequent collisions with the wall ($P \propto \frac{1}{V}$)
3. (P $\propto T$)... the higher the temperature the faster the particles move, which increases both the collision frequency and the impact of each collision.

Putting all of these together yields

$$P \propto \frac{nT}{V} = k\frac{nT}{V} \tag{10.5.15}$$

which can be rewritten as the familiar Ideal gas equation:

$$PV = nRT \tag{10.5.16}$$

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10.6: Diffusion and Effusion

Diffusion

Diffusion is how a gas disperses through space and is the result of the random motion as illustrated in Figure 10.6.1. The gas follows the postulates of the Kinetic Molecular Theory, moving like a classical particle and changing directions every time there is a collision. Note a typical gas molecule has in the order of 10^{10} collisions per second and the distance between collisions is the mean free path.

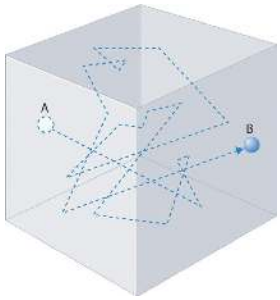


Figure 10.6.1: Random path a particle takes as it traverses a container.

The following YouTube gives a good demonstration of diffusion and effusion.



Video 10.6.1: (4:00 YouTube). Note, at 1:22 they show the diffusion of gas into a vacuum, while at 1:51 the same gas diffuses into a container with air. At 2:36 there is a good example involving HCl and NH_3 demonstrating Grahm's Law of Effusion.

Effusion

Effusion is related to diffusion and is how a gas escapes through a hole in one container into another (evacuated) container.

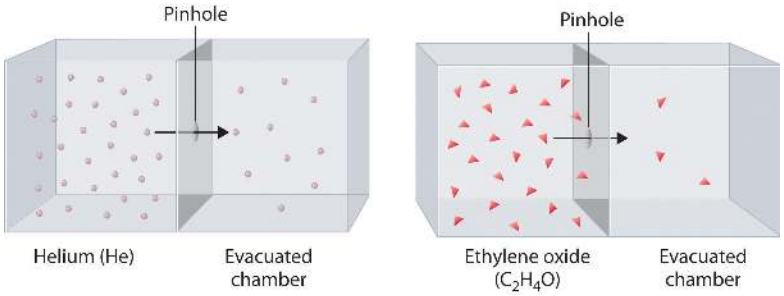


Figure 10.6.2: demonstrating effusion, note the lighter helium effuses fastere than the heavier ethylene oxide.

The Scottish chemist Thomas Graham measured the effusion rates of gases at constant temperature and discovered that they were inversely proportional to the square root of the molar mass.

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\mathfrak{M}}},\ \mathfrak{M} = Molar\ Mass \tag{10.6.1}$$

This results in the common relationship known as Graham's Law

$$\frac{Rate\ of\ effusion\ of\ A}{Rate\ of\ effusion\ of\ B} = \frac{(u_{rms})_A}{(u_{rms})_B} = \frac{\sqrt{\mathfrak{M}_B}}{\sqrt{\mathfrak{M}_A}} \tag{10.6.2}$$

Which can be derived from KMT and ideal gases (last section of 10.5)

$$u_{rms} = \sqrt{\frac{3RT}{\mathfrak{M}}} \tag{10.6.3}$$

Where,

$$\frac{Rate\ of\ effusion\ of\ A}{Rate\ of\ effusion\ of\ B} = \frac{(u_{rms})_A}{(u_{rms})_B} = \frac{\sqrt{3RT\mathfrak{M}_A}}{\sqrt{3RT/\mathfrak{M}_B}} = \frac{\sqrt{\mathfrak{M}_B}}{\sqrt{\mathfrak{M}_A}} \tag{10.6.4}$$

A simple way to remember this is to remember postulate 5 of KMT, which states that the kinetic energy of a gas is proportional to the absolute temperature and then equate the average kinetic energy of two gases

$$e_K = \frac{1}{2}mu_{rms}^2 \tag{10.6.5}$$

so,

$$e_K = (\frac{1}{2}mu_{rms}^2)_A = (\frac{1}{2}mu_{rms}^2)_B \tag{10.6.6}$$

which rearranges to the above relationship

$$\frac{(u_{rms})_A}{(u_{rms})_B} = \frac{\sqrt{\mathfrak{M}_B}}{\sqrt{\mathfrak{M}_A}} \quad or \quad \frac{(u_{rms})_A^2}{(u_{rms})_B^2} = \frac{\mathfrak{M}_B}{\mathfrak{M}_A} \tag{10.6.7}$$

Trick:

If a gas were a particle, you could say the kinetic energy of the particle of gas is $\frac{1}{2}mv^2$ and you could equate to kinetic energies of two gas particles as

$$\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2 \tag{10.6.8}$$

Now the above equation does NOT represent a gas, which has many particles possessing a range of velocities, like those in Figure 10.6.3, but it has the same form as equation 10.6.6. The difference is if the particles represent different chemicals, the mass is the molar mass, and you use the root mean square velocity for a gas, instead of the velocity of a single particle. So this may help you remember the equation.

Since gasses at the same temperature have the same kinetic energy the energy profile plots skew to the right for small molecules (that have small m and large v), while heavy molecules (larger m) have smaller velocities.

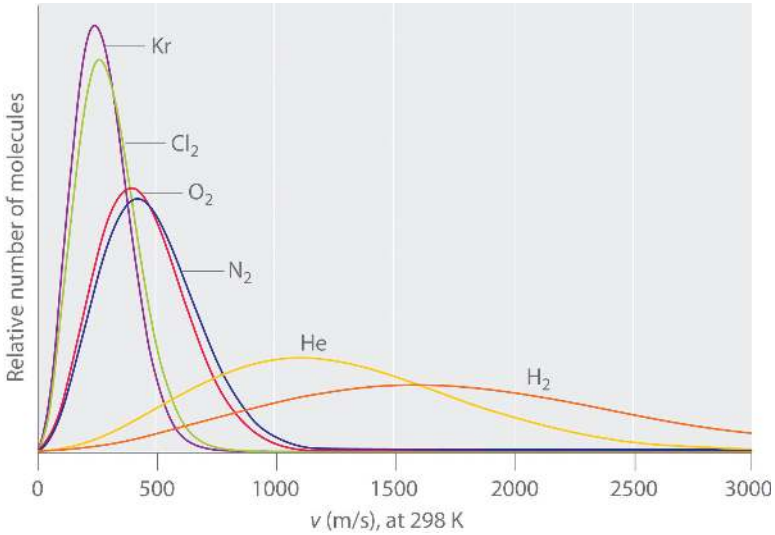


Figure 10.6.3: Velocity profiles for different gasses at the same temperature. note the average kinetic energy is the same, and so the lighter molecules tend to travel faster.

Example 10.6.1: Graham's Law Problem

Ammonia and nitric acid are swabbed onto cotton and placed at the ends of a 1 meter evacuated tube, like is done at 2:36 in the above youTube (video 10.6.1). How far from the ammonia side does the ammonium nitrate form?



Video 10.6.2

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10.7: Nonideal Gases

Skills to Develop

- To recognize the differences between the behavior of an ideal gas and a real gas.
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases do have volume and occupy space. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressure, where particles are forced close to each other and so the gas deviates from the Kinetic Molecular Theory's postulate stating that the volume of the gas particle is negligible. Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (part (b) in Figure 10.7.1).

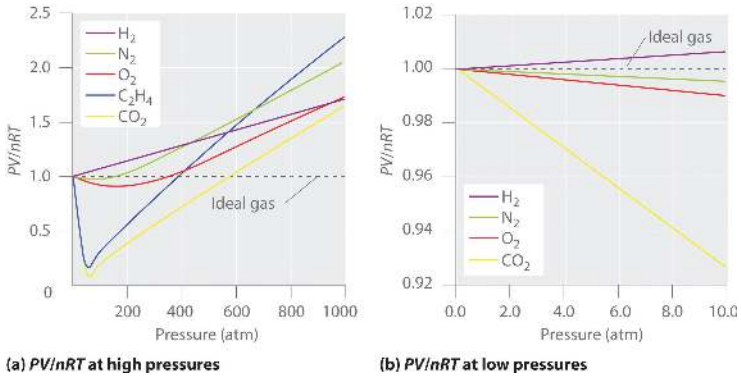


Figure 10.7.1: *Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of PV/nRT versus P at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.*

Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure 10.7.2 for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

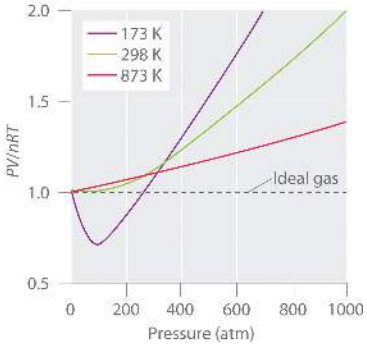


Figure 10.7.2: *The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.*

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure 10.7.3). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of *PV*/*nRT* is greater than the value predicted by the ideal gas law.



Figure 10.7.3: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected. Thus as shown in Figure 10.7.2 , at low temperatures, the ratio of \(PV/nRT\) is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

> **Note**
>
> Nonzero molecular volume makes the actual volume *greater* than predicted at high pressures; intermolecular attractions make the pressure *less* than predicted.

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called *van der Waals* equation,

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT \tag{10.7.1}$$

a and *b* are empirical constants that are different for each gas. The values of a and b are listed in Table 10.7.1 for several common gases.

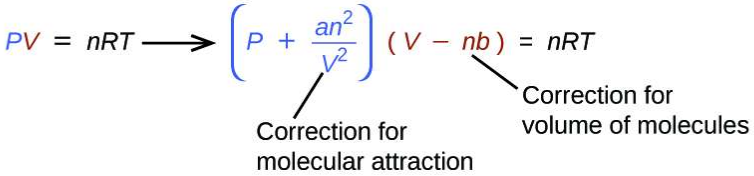


Figure 10.7.4: Van der Waals Equation

Table $PageIndex1$: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	a ($L^2 \cdot atm/mol^2$)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in the van der Waals equation ($P + (an^2/V^2)$) corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure $PageIndex4$. The volume term $V - nb$ corrects for the volume occupied by the gaseous molecules.

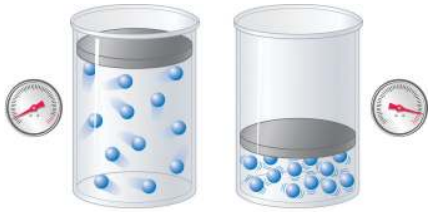


Figure $PageIndex4$: *The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.*

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on V and P, respectively. Because nonzero molecular volumes produce a measured volume that is larger than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is less than that expected based on the ideal gas law, so the an2/V2 term must be added to the measured pressure to correct for these effects.

Example 10.7.1:

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table 6.9.1. Use the van der Waals equation to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} = \frac{500\ \text{g}}{70.906\ \text{g/mol}} = 7.052\ \text{mol} \tag{10.7.2}$$

Nothing

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} = \frac{7.052\ \text{mol} \times 0.08206 \dfrac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} = 43.1\ \text{atm} \tag{10.7.3}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table 6.9.1. Solving for *P* gives

$$\begin{aligned} P &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\ &= \frac{7.052\ \text{mol} \times 0.08206 \dfrac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \dfrac{\text{L}}{\text{mol}}} - \frac{6.260 \dfrac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \\ &= 28.2\ \text{atm} \end{aligned}$$

Nothing

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise 10.7.1

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant Figures at 27°C using the

1. ideal gas law.
2. van der Waals equation.

Answer a

77 atm

Answer b

67 atm

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CHAPTER OVERVIEW

11: Intermolecular Forces and Liquids

Topic hierarchy

11.1: States of Matter and Intermolecular Forces
11.2: Ion-Dipole Forces
11.3: Dipole-Dipole Forces
11.4: NonPolar Molecules and IMF
11.5: Hydrogen Bonds

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11.1: States of Matter and Intermolecular Forces

Learning Goals

- Identify States of Matter
- Introduce concept of IMF (InterMolecular Forces) or van der Waals forces
- Introduce properties of matter that can depend on IMFs

We have learned how chemistry is the study of matter and how matter transforms from one type of "stuff" into another. We have been introduced to 4 states of matter and the next two chapters will look at the condensed phases of matter, the solid and liquid states. We are going to start with a quick review, and then move into the cohesive forces that hold matter together.

States of Matter:

1. Gas State (Chapter 10)
    - Compressible, variable density
    - Fluid with negligible resistance to flow
    - Dispersed state where matter fills entire volume of container
    - negligible IMFs (InterMolecular Forces)
2. Liquid State (Chapter 11)
    - Incompressible, essentially constant density
    - Fluid of measurable viscosity (resistance to flow)
    - essentially constant density (varies slightly with temperatue)
    - cohesive IMFs hold it together
3. Solid State (Chapter 12)
    - Incompressible, essentially constant density
    - Non-Fluid, maintains own shape
4. Plasma State (Chapter 1A.3.2.4, not thoroughly covered in this class)
    - High Energy State (stellar matter)
    - Has free electrons and charged particles

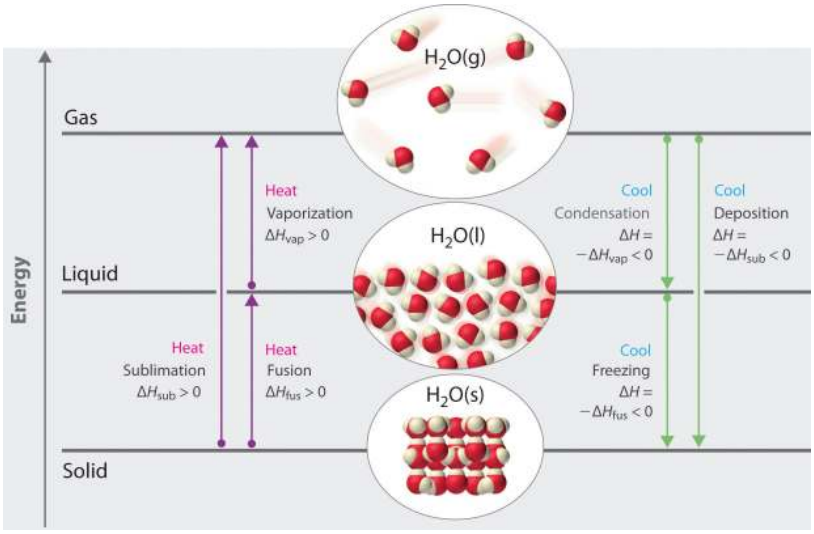


Fig. 11.1a: Energy diagram showing states of water and the phase transitions between these states.

You should already be familiar with the 6 phase transitions described in figure 11.1a

- Melting: The transition from the solid to the liquid phase
- Freezing: The transition from the liquid phase to the solid phase
- Evaporating: The transition from the liquid phase to the gas phase
- Condensing:The transition from the gas phase to the liquid phase

- Sublimation: The transition from the solid phase to the gas phase
- Deposition: The transition from the gas phase to the solid phase

It should be mentioned that the majority of matter in the universe is in a fourth state, the plasma state, which we will not be considering in this chapter. A plasma is a high energy gas with free moving positive ions and electrons flowing around. Stars are in the plasma state and it is actually the most common state in the universe. Figure 11.1b shows the transitions between all 4 states of matter.

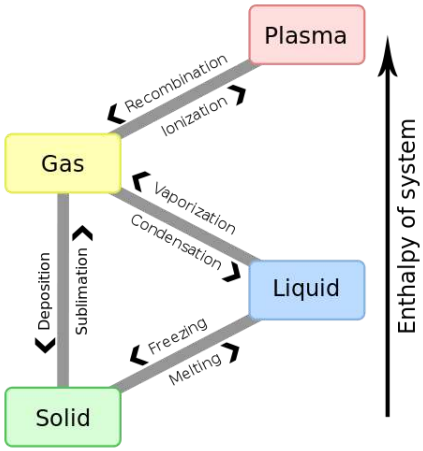


Fig. 11.1b: Four states of matter with transitions between them.

Intermolecular Forces (IMF)

The the term InterMolecular Force (IMF) literally means the forces between molecules, and as such, is often a misnomer, as simply speaking, not all matter is composed of molecules. Yet this term is used pervasively, and so we will use it, but first lets compare it to the so called "intramolecular forces", the forces within the proverbial "molecule." We typically consider two types of bonds, ionic (which are not molecular) and covalent (which are molecular). So if I have liquid water, where the discrete entity of matter is the H_2O molecule, there are two type of bonds, those between H and O of a water molecule (covalent intramolecular) and those between the H of one molecule and the O of another (intermolecular).

Shortcomings of the term Intermolecular

1. We classify bonds between an ion and polar molecule as intermolecular, when in reality, the ion need not be a molecule (polyatomic ions are molecules, monatomic ions are not).
2. Not all covalently bonded compounds are molecules with discrete formula, like diamond, which is a covalent network, and so even though it is a covalently bonded entity, it does not fit the paradigm of a molecule with a unique molecular formula.

With these shortcomings in mind we are going to look at the following types of Intermolecular Forces. It should also be noted that the later types of forces are also called van der Waals forces, which are the short range forces of attraction between atoms or molecules that do not fit into the model of a covalent or ionic bond.

Types of Intermolecular Forces

1. Ion-Dipole Forces (these may not be true IMF, but we will call them IMFs)
   - Solutions
2. Dipole-Dipole Forces (between two polar molecules)
   - Pure substance or solutions
3. Hydrogen Bonding (special type of dipole-dipole)
   - Pure substance or solutions
4. Dipole-Induced Dipole (between polar and nonpolar molecules)
   - Solutions
5. Instantaneous Dipole-Induced Dipole (between two nonpolar molecules, often called London Dispersion Forces)

- Solutions or Pure Substances

Please note that in recognizing what type of intermolecular forces are involved we need to know if a molecule is polar or non-polar. This requires a review of Lewis Dot Structures, VSEPR Theory, Electronegativity, and Bond Polarity.

Properties of Matter that Depend on IMFs

- boiling point, melting point, stable phases
- enthalpies of phase transitions
- vapor pressure
- solubility and miscibility of different substances
- viscosity

There are many physical properties of matter that are strongly influenced by IMFs, and over the next few chapters we will look at many of these. Lets ask a simple question;

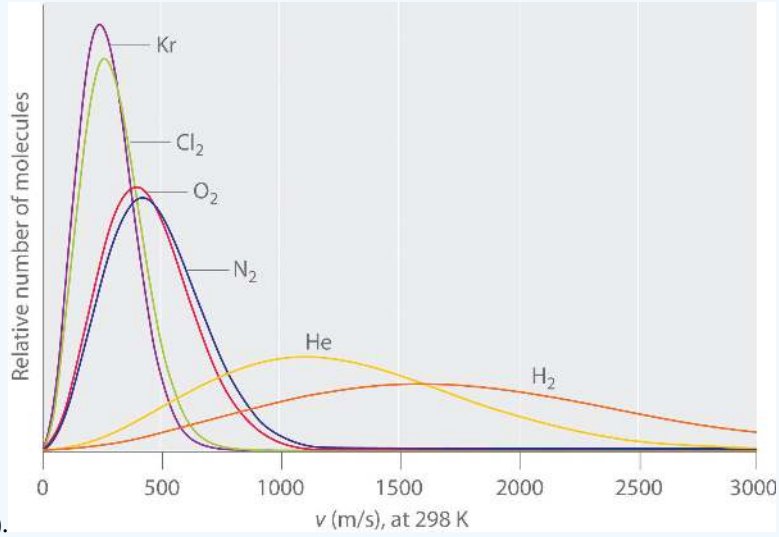
Exercise 11.1.1

At a given temperature, would it be easier to vaporize a light molecule or a heavy molecule?

Answer

You need more information. From our study of gases and the Kinetic Molecular Theory we learned that the average kinetic energy of a molecular system is proportional to the absolute temperature, and both molecules have the same average kinetic energy, and so at first thought, we would predict that the lighter molecule would tend to have the higher velocity (review Graham's Law of Effusion) and be easier to vaporize (see image below).

The problem is we need to identify the intermolecular forces that attract the molecules to each other, and if the lighter molecule had stronger intermolecular forces, this would be wrong. Look at the case of carbon dioxide and water (the next question deals with this).



Note: This image is for the velocity distribution of a gas at a given temperature, and not a liquid, but the concept is valid, in that if all other things are equal, lighter molecules tend to move faster, and gas phase systems move faster than liquid. The problem is, there are often other factors, as indicated in the next question, on why is carbon dioxide a gas at ambient questions while water is a liquid?

Exercise 11.1.2

So why at ambient conditions is Carbon Dioxide (the heavier molecule at 44 amu) a gas, but water (the lighter molecule at 18 amu) is a liquid?

Answer

That is, shouldn't it be easier to vaporize the lighter molecule than the heavier one? The answer lies within the Intermolecular Forces, and if you review molecular shapes and polarity you will see that water is a polar molecule while carbon dioxide is non-polar, and this leads to different physical properties like the boiling and melting points. That is, in this chapter you will learn that water has stronger intermolecular forces than carbon dioxide, and that is why it is a liquid, while carbon dioxide is a gas. But to answer that question you first had to determine the Lewis Dot Structure, then determine the geometry, and then determine the polarity of the molecule, and so you should have a basic understanding of that pre-requisite material before proceeding.

Another interesting things to note about molecular properties that result from IMFs is that they are not really properties of a single molecule, but the result of an ensemble or large system of many molecules, which must be viewed as a whole, and not as individual molecules. Simple speaking, an individual molecule can not have a boiling point, which is really a function of the interaction between a large number of molecules. So the boiling point of water is not a property of a water molecule, but a bunch of water molecules. So, if you have a liquid at a given temperature there is a distribution of velocities, some of the molecules have enough kinetic energy to escape the attractive cohesive forces on the surface and enter the vapor phase, while others do not. So the vapor pressure above a liquid is also influenced by intermolecular forces. The point is some properties of a substance, like it's atomic mass or its polarity, are the property of a single molecule, while others, like the melting point or vapor pressure, are the properties of a huge number (ensemble) of molecules

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11.2: Ion-Dipole Forces

Ion-Dipole Interactions

Ion-Dipole Forces are involved in solutions where an ionic compound is dissolved into a polar solvent, like that of a solution of table salt (NaCl) in water. Note, these must be for solutions (and not pure substances) as they involve two different species (an ion and a polar molecule).

$$Na^+ \leftrightarrow (H_2O)_n$$

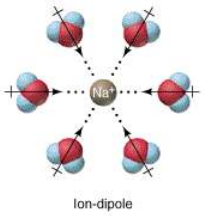


Figure 11.2.1: Ion-Dipole interaction. Note the oxygen end of the dipole is closer to the sodium than the hydrogen end, and so the net interaction is attractive (see figure 11.2.2).

The name "Ion dipole forces" describes what they are, which simply speaking, are the result of the Coulombic electrostatic interactions between an ion and the charged ends of a dipole. Note that here, the term **"Intermolecular Force" is a misnomer**, even though it is commonly used, as these are the forces between ions with molecules possessing a dipole moment, and ions do not have to be molecular. To gain an understanding of the nature of these forces we can start by looking at the Coulombic potential between two ions (Equation 11.2.1) and ask the following question.

Exercise 11.2.1

What is the difference between Coulombic Ion-Ion and Ion-Dipole interactions in terms of the distance between the particles?

Answer

One is an inverse distance relationship, the other is an inverse distance square relationship. The following material explains this.

In the introduction to this chapter we saw that two charged particles q_1 and q_2 had a potential energy related to Equation 11.2.1, and this describes the potential energy interaction between two ions.

$$\underbrace{E = k\frac{q_1 q_2}{r}}_{\text{ion-ion potential}} \tag{11.2.1}$$

For ion-dipole interactions the interaction is between a dipole moment (μ), which is really a vector with a magnitude of $\delta \cdot r$, where δ is the value of the partial charge in the dipole moment (δ^+ or δ^-, noting they are of the same magnitude, just opposite in sign), with an ion of charge q. (We are using δ to indicate the partial charge in the dipole just to prevent it from being confused with q, the charge of the ion).

So there are two ion-dipole interactions, with one being attractive and the other repulsive, as shown in figure 11.2.2

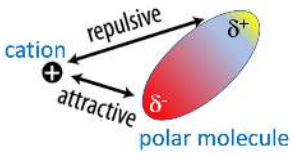


Figure 11.2.2: *Interactions between a positive cation and a polar molecule.*

Now if you think about it, the cation repels the positive end of the dipole and attracts the negative end, so the negative end is closer to the cation than the positive end. This means the attractive energies are greater than the repulsive (as they are closer together, the r of coulombs law is in the denominator of eq. So the net force is attractive since the radius (in the denominator of Coulombs Law, Equation 11.2.1) for the +/- attraction is smaller than the radius for the +/+ repulsion. This difference is greatest when the polar molecule is "touching" the cation, and as they become further separated the relative differences in the radii between the two interactions become less, and at great distances they become equal, making these short range forces. This can be understood by looking at Figure 11.2.3

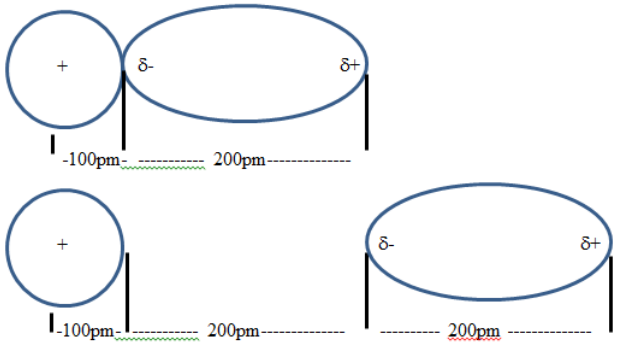


Figure 11.2.3: *Showing how the relative distance between the ion-dipole interaction falls off as they become separated. In the top interaction the +/+ radius is 3 times as far as the +/- (300 pm to 100 pm), but in the bottom it is 5/3rds as far (500 pm to 300 pm) and so the difference between the repulsive and attractive forces is less. That is, at large distances the distances between the ion and the two partial charges narrow with a consequent cancelation of the effect.*

The result in an inverse square of the distance function ($1/r^2$) for the decrease for ion-dipole interactions as compared to a 1/r effect for ion-ion interactions, as shown in Equation 11.2.2.

$$\underbrace{E \propto \frac{-|q_1|\mu_2}{r^2}}_{\text{ion-dipole potential}} \tag{11.2.2}$$

or

$$\underbrace{E = -k\frac{|q_1|\mu_2}{r^2}}_{\text{ion-dipole potential}} \tag{11.2.3}$$

(ion-dipole potential)

- α means "proportional to" (the proportionality constant depends on the medium)
- r is the distance of separation.
- q is the charge of the ion (only the magnitude of the charge is shown here.)
- k is the proportionality constant (Coulomb's constant).
- μ is the permanent dipole moment of the polar molecule (sections 8.7.4.2 and 8.8).
  From section 8.7 and 8.8 we treat define the dipole moment by the following equation

$$\vec{\mu} = q\,\vec{r} \tag{11.2.4}$$

where q is the partial charge of each end of the dipole (δ^+ *or* δ^-) and r is the separation between the charges within the dipole, but these symbols are being used to describe the ion interactions in equations 11.2.1-11.2.3, and so we will rewrite eq. 11.2.4 with δ instead of q representing the magnitude of the partial charge of the dipole (δ^+ *or* δ^-) and $\vec{d}$ representing the distance between the center of positive and negative charge in the polar molecule $\vec{r}$.

$$\vec{\mu} = \delta\,\vec{d} \tag{11.2.5}$$

Realize eq. 11.2.4 is the most common way to describe the dipole moment, but when looking at ion-dipole interactions there are two types of charges (those of the ion, and the partial charge separations of the dipoles), and two types of distance, the distance between the ion and dipole, and the distances between the dipoles. So for this section we will rewrite eq. 11.2.4 in terms of 11.2.5.

> **Note**
>
> Equations 11.2.1 and 11.2.3 are dimensionally equivalent. This is because μ has the units charge times distance (Equation 11.2.4), and if you substitute eq. 11.2.5 into eq. 11.2.3, you will see it is dimensionally equivalent to 11.2.1

Key differences between ion/ion and ion/dipole interactions

1. Ions have integer charges (1,2,3.. for cations and -1,-2,-3... for anions), while dipole's have partial charges ($\delta^{+ \, or \, -}$) and the partial charges can be very small fractions.
2. Ion-ion interactions fall off slower than ion-dipole. Tripling the distance between two ions reduces the energy by 1/3, while tripling the distance between the ion and a dipole reduces it by 1/9. That is, one is inversly proportional to the distance between them (1/r) and one is proportional to the inverse square of the distance ($1/r^2$).

Exercise 11.2.2

Why does the Coulombic ion-dipole equation (11.2.2) have a negative sign and the absolute value on the charge, while the ion-ion equation (11.2.1) does not?

Answer

- The ion dipole interactions are always attractive resulting in a lowering of the potential energy. Since μ is always positive, but q can be positive (cation) or negative (anion), so we use it's absolute value and add the negative sign to ensure there is a lowering of energy. For ion-ion, they can be attractive (+/-) which results in a negative E, or repulsive (+/+ or -/-), both of which result in a positive E.

Exercise 11.2.3

How does the ion-dipole equation show that ion dipole interactions are shorter range than ion-ion interactions?

Answer

- The ion-ion interaction energy is inversely proportional to the distance between the ions (1/r), while the ion-dipole energy is inversely proportional to the square ($1/r^2$). So doubling the distance decreases the first by a factor of 2, and the later by a factor of 4 (and tripling the distance decreases the first by a factor of 3, and the later by a factor of 9). So ion dipole interactions are much shorter ranged.

It also needs to be understood that these equations are based on electrostatic interactions and molecules in a solution are rotating and vibrating and actual systems are quite complicated, with the medium (molecular environment) influencing the actual behavior. Coulombs constant is based on the permittivity of an electric field in a vacuum, and actual chemical systems are not in a vacuum, and so the permittivity will be different. The important thing to realize is that these interactions are Coulombic in nature, and these equations show this in terms of the magnitude of the charges and their distances from each other, which are the two major factors influencing the strength of intermolecular forces. In this class we will not be calculating dipole moments or the magnitudes of them, but understanding how to read the equations, and developing qualitative understandings that allow us to predict trends.

It should also be understood that not all ion-dipole interactions are in solutions. For example, hydrated salts where the water is "captured" in a crystal's interstitial regions (holes in the lattice) are ion-dipole in nature. In fact these can be necessary to form certain crystalline geometries as the polar water molecule can reduce the repulsion of like charges within a lattice. We will look at crystals in the next chapter.

Periodic Trends and Hydration Energy

The enthalpy of hydration is often defined as the energy released when a mole of a gaseous cation is dissolved in water, and is related to ion-dipole forces.

$$M^+_{(g)} + water \rightarrow M^+_{(aq)} \tag{11.2.6}$$

The smaller the cation, the closer the particles, and for a given charge the stronger the ion-dipole forces and the greater the enthalpy of hydration (more exothermic). This is exemplified by the enthalpies of hydration in Table 11.2.1. It needs to be noted that the above definition aligns with thermodynamic principles, where greater means more exothermic (negative). That is, from the first law of thermodynamics a positive energy change occurs when is energy added to the system (endothermic) and a negative energy change occurs when is is released (exothermic). The small Lithium ion has a lower value (-515 kJ/mol) than the larger Cesium (-263 kJ/mol), meaning it is more exothermic, and more energy is released. This may be easier to see by looking at the back reaction, where you need to add energy to remove the hydrated ion and place it in the gas phase, since adding energy is endothermic, the reaction as drawn must be exothermic.

Table **11.2.1***: Enthalpies of hydration for alkali metals show the smaller the radi the larger the energy, and this is related to the ion-dipole forces of the solvated ions.*

Cation	Ionic Radius (pm)	Enthalpy of Hydration (kJ)
Li^+	90	-515
Na^+	116	-405
K^+	152	-312
Rb^+	166	-296
Cs^+	181	-263

From general chemistry 1 students should know the trends in the sizes of ions, and based on these, they should be able to predict the relative rankings of the ions in table 11.2.1. Since lithium is smaller, it would take more energy to remove it, so the formation of the hydrated ion is more exothermic (negative) than the large Cesium. You must always correlate the sign of an energy to its process, and recognize that you can "form" or "break" any bond or intermolecular force. As written, this is the formation, which is the exothermic process. If you had written the reverse reaction, all the values would be positive.

Hydrated Salts: Ion-dipole forces also explain why many salts will trap water when they crystallize and form hydrated salts. This is common for small cations like sodium and lithium, which form hydrates like sodium carbonate decahydrate Na_2CO_3-$10H_2O$, while larger salts like rubidium and cesium do not tend to form hydrates, as they have weaker ion-dipole interactions.

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References

1. Chemical Principles: Atkins and Jones

Contributors and Attributions

- Robert E. Belford (University of Arkansas Little Rock; Department of Chemistry). The breadth, depth and veracity of this work is the responsibility of Robert E. Belford, rebelford@ualr.edu. You should contact him if you have any concerns. This material has both original contributions, and content built upon prior contributions of the LibreTexts Community and other resources, including but not limited to:
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11.3: Dipole-Dipole Forces

Dipole–Dipole Interactions

Dipole-Dipole interactions occur between **polar molecules.** In section 8.8 we learned that polar covalent bonds occur between atoms of different **electronegativity** (section 8.7), where the more electronegative atom attracts the electrons more than the electropositive atom, and based on the geometry, this may or may not result in a polar molecule. If the center of positive charge (defined by the nuclei) does not coincide with the center of negative charge (defined by the electron orbitals), the molecule is polar, which is easiest to visualize for nonsymmetric orientations of bonds between atoms of different electronegativities. That is, a polar molecule with a permanent dipole results if all the bond dipole vectors add to a net dipole. In this case the molecule's center of positive charge (denoted by δ^+) does not coincide with the center of negative charge (denoted by δ^-) and the molecular dipole moment (μ) is this partial charge times the distance between them. Please review sections 8.7 and 8.8 if needed, and remember that if bond dipoles are of symmetric orientation, like in the linear carbon dioxide, they cancel each other and the molecule is non-polar. So polar bonds can result in non-polar molecules! You should also note that the center of positive charge need not be where there is a nucleus. For example, in water, the center of positive charge is half way between the two hydrogens.

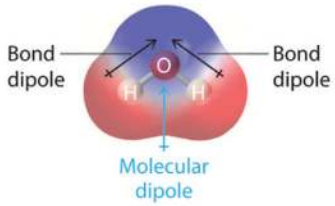


Figure 11.3.1: Water's dipole moment has a positive center between the two nuclei of the hydrogens.

Although molecules in a liquid are in constant motion, they tend to align in the lowest energy orientation, which would be to maximize attractions (parts a & b of fig. 11.3.1) and minimize repulsion (parts c & d of fig. 11.3.1). This follows the same logic we used for ion-dipole interactions, in that the attractive interactions cause dipoles of opposite charge to be closer, resulting in stronger interactions, while dipoles of like charge tend to be farther apart, resulting in reduced interactions. Therefore, unlike ion-ion interactions, but like ion-dipole interactions, dipole-dipole are always attractive.

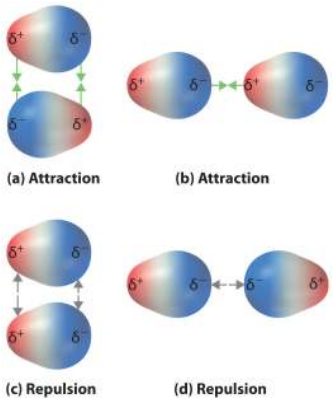


Figure 11.3.2: *Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.*

Exercise **11.3.1**

Why are the attractive forces greater than the repulsive?

Answer

Molecules in a liquid are in constant motion and experience both attractive and repulsive dipole–dipole interactions, as shown in Figure 11.3.2. For reasons similar to those outlined in the section on ion-dipole forces (11.2), the attractive interactions dominate the repulsive because the attraction causes them to be closer together, which increases the Coulombic interactions. Likewise, the repulsions mean they move farther away, which reduces the Coulombic interactions.

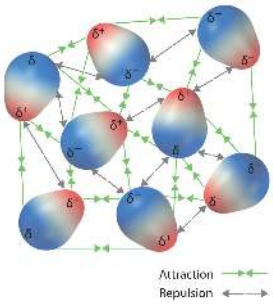


Figure 11.2.2: Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

The equation for dipole-dipole potential energy is

$$E\,\alpha\,\frac{-\mu_1\mu_2}{r^3} \qquad (11.3.1)$$

$$or$$

$$\underbrace{E=-k\frac{\mu_1\mu_2}{r^3}}_{\text{dipole-dipole potential}}$$

This can be compared to eq. 11.2.1 (ion/ion) and 11.2.2 (ion-dipole), and it becomes clear that the dipole-dipole forces are even shorter range. (remember μ =qd, where q is the *|($\delta^{+/-}$)| of the dipole, and d is the distance between δ^+ and δ^-*. This is further weaker because the magnitude in the charge is a partial charge and less than 1, while the charge in an ion is +/- 1, 2,3...(an integer multiple of 1).

Note that R is an inverse cube power, and so doubling the distance reduces the energy by a factor of 8. Also note that this is consistent with eq.'s 11.2.2 and 11.2.4 because the term mu has distance built into it.

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge.

Exercise 11.3.2

Show how $\frac{-\mu_1\mu_2}{r^3}$, $\frac{-|q_1|\mu_2}{r^2}$ and $\frac{q_1q_2}{r}$ are dimensionally equivalent?

Answer

$\frac{-\mu_1\mu_2}{r^3}=\frac{(dq_1)(dq_2)}{r^3}$, which has units of $\frac{charge^2}{length}$

$\frac{-\mu_1|q_2|}{r^2}=\frac{(dq_1)(q_2)}{r^2}$, which has units of $\frac{charge^2}{length)}$

$\frac{q_1q_2}{r}$, has units of $\frac{charge^2}{length)}$

In summary, the above relationships show that the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–dipole interactions, which in turn fall off quicker than ion-ion interactions. Doubling the

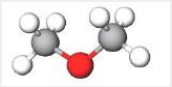
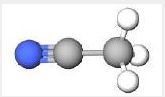
distance ($r \rightarrow 2r$) decreases the attractive energy between ions (which is proportional to 1/r) by one-half, which increases ion-dipole by 1/4, that is ($1/2^2$), while dipole-dipole interactions decrease to 1/8 ($1/2^3$).

Boiling Point Trends

Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about physical properties that depend on intermolecular forces, like the relative boiling points of similar molecules.

Exercise 11.3.3

Given the following information:

Compound	C_3H_6 (cyclopropane)	CH_3OCH_3 (dimethyl ether)	CH_3CN (acetonitrile)
Structure			
Molar Mass (g/mol)	42	46	41

(a) Associate the following Dipole Moments with the above compounds: Zero D, 1.30 D and 3.9 D. (Hint: rank in order of increasing polarity)

Answer

Cyclopropane is nonpolar and is zero, dimethyl either is 1.30 and acetonitrile is 3.9. The cyclopropane was a gift, but differentiating the second two is tougher, as oxygen is more electronegative (χ = 3.5) then nitrogen (χ=3.0), but acetonitrile is linear while dimethyle ether is bent, and part of the two bond dipoles cancel, and the later has a far greater effect (both oxygen and nitrogen are highly electronegative). That is, the dipole for dimethyl ether goes straight up from the oxygen to in between the two carbons, and the horizontal components cancel out. In acetonitrile there is no such cancellation.

(b) Associate the following boiling points with the above compounds: Rank in order of increasing boiling point. 240K, 248K & 355K

Answer

The boiling points follow the trends in the strength of the intermolecular forces, so cyclopropane is 240K, dimethyl ether is 248 and acetonitrile is 355.

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11.4: NonPolar Molecules and IMF

Introduction

Van der Waals interactions are very weak short range interactions involving non-polar molecules and are inversely proportional to the 6th power of the distance of separation. There are two types of IMF involving non-polar molecules.

1. **Dipole-Induced Dipole:** The Intermolecular forces between a polar and non-polar molecule.

$$E = -k\frac{\mu_1^2\alpha_2}{r^6} \tag{11.4.1}$$

2. **Instantaneous Dipole-Induced Dipole**: (London Dispersive Forces) The intermolecular forces between two nonpolar molecules.

$$E = -k\frac{\alpha_1\alpha_2}{r^6} \tag{11.4.2}$$

- k is the proportionality constant (this is not Coulomb's constant, it has different units)
- r is the distance of separation between the molecules.
- α is the polarizability of the non-polar molecule (see below), it has units of C m^2V^{-1}.
- μ is the permanent dipole moment of the polar molecule.

$$\vec{\mu} = q'\,\vec{d} \tag{11.2.3}$$

where q' is the partial charge of each end of the dipole ($\delta^+ or\ \delta^-$) and d is the separation between the charges within the dipole

Polarizability (α)

The ease with which an electron cloud can be distorted by an electric field is its polarizability.

$$\mu_{ind} = \alpha E \tag{11.4.3}$$

Where

- E denotes the strength of the electric field and
- α is the polarizability constant with units of C m^2V^{-1}.

All molecules are polarizable, but this is important in nonpolar symmetric molecules as it relates to how easy an external field can induce a dipole in the otherwise nonpolar molecule, and give it polar character. When an external electric field is applied it can attract electrons towards its positive pole and repulse them from its negative pole, which induces ("brings about or gives rise to") a dipole. The "tighter" the electrons are held by the molecule's nuclei the harder it is to induce a dipole, the "looser" the electrons are held, the easier it is to induce a dipole. The Polarizability (α) of a molecule is a measure of the ease with which a dipole can be induced. Molecules with a large $alpha$ are easy to induce a dipole.

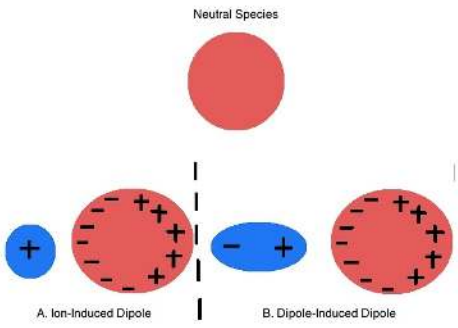


Figure 11.4.1: *A neutral nonpolar species's electron cloud is distorted by (A.) an Ion and (B.) a polar molecule, to induce a dipole moment.*

Note, α has distance square in the denominator

In general, polarizability inversely correlates with the strength of the interaction between electrons and the nucleus. The tighter the valence electrons are held by the nuclei the less polarizable the molecule or atom. Conversely, well shielded valence electrons that are far from the nuclei in diffuse orbitals are highly polarizable, and easily distorted by external electric fields. In figure 11.4.1, the Electric field is coming from the (A.) positive charged ion, and (B.) the positive end of the dipole. Note, if a negative ion (or negative end of a dipole) approached a neutral molecule, the opposite would occur, as it would repel electrons, inducing a positive dipole in the neutral molecule that is near it, and a negative one that is far away.

Factors that Influence Polarizability

The relationship between polarizability and the factors of electron density and atomic radii, and molecular orientation are as follows:

1. The greater the number of electrons, the greater the polarizability.
2. The greater the distance of electrons from nuclear charge, the greater the polarizability of the atom.

Exercise 11.4.1

Rank the noble gasses in order of increasing polarizability (least to most)

Answer

He<Ne<Ar<Kr<Xe<Rn

Dipole-Induced Dipole Forces

These occur between a polar molecule and a nonpolar molecule, and thus must describe solutions. The polar molecule with a permanent dipole induces a dipole moment in the non-polar molecule. The more polarizable the nonpolar molecule, the easier it is to induce a dipole, and so the greater the interaction. .

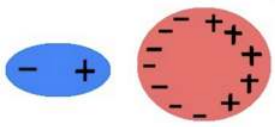


Figure 11.4.d: Dipole (blue) inducing a dipole in an otherwise non-polar (red) molecule

$$E = -k\frac{\mu_1^2\alpha_2}{r^6} \tag{11.4.4}$$

These are the intermolecular forces for the dissolution of many types of gases in a solvent like water. The most common gases in the atmosphere are small nonpolar compounds like nitrogen, oxygen and carbon dioxide. A saturated solution of oxygen is 256 \mu M, or 2.56x10^{-4} moles/l, which is an indication of how weak these intermolecular forces are. Larger and more polarizable nonpolar molecule tend to have higher solubility in polar solvents than smaller molecules of lower polarizability. We need to be careful in extrapolating trends here though, especially if the solute is not a gas, and will take a more detailed look at solutions in chapter 13, where in addition to the solute/solvent interactions described by dipole-induced dipole interactions of polar/nonpolar intermolecular interactions, we will also take into account solute/solute and solvent/solvent interactions.

Instantaneous Dipole-Induced Dipole Forces (London Dispersion Forces)

Instantaneous Dipole: A non-polar molecule like H_2, O_2 ,He or Ne are symmetric with their center of electron density over all time coinciding with their center of positive charge, resulting in a symmetric non-polar molecule. This symmetry is actually the time average of the molecular wavefunction, and at any instant in time the electron distribution may be asymmetric, resulting in short lived transient dipole moment. This is called an instantaneous dipole.

Induced Dipole: Just as ions and polar molecules can induce a dipole moment in an adjacent nonpolar molecule, so can an instantaneous dipole. The polarizability is a measure of how easy it is to induce a dipole. For symmetric nonpolar molecules these

can form waves as successive instantaneously induced dipoles that in turn induce dipoles on their neighbors, and thus are often called dispersion forces.

London Dispersion Forces and Polarizability

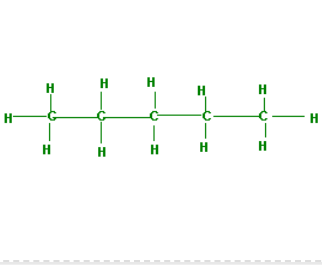
The dispersion force is the weakest intermolecular force. It is an attractive force that arises from an instantaneous dipole inducing a transient dipole in an otherwise non-polar molecule. Surrounding molecules are influenced by these temporary dipole moments and a sort of chain reaction results in which subsequent weak, dipole-induced dipole interactions are created. These cumulative dipole-induced dipole interactions create the attractive dispersion forces. Dispersion forces are the forces that make nonpolar substances condense to liquids and freeze into solids when the temperature is low enough. These occur with polar molecules too, but since they are weaker, they are normally negligible.

Polarizability affects dispersion forces in the following ways:

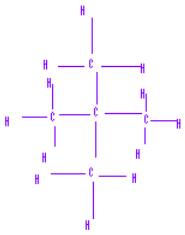
- As polarizability *increases*, the dispersion forces also become *stronger*. Thus, molecules attract one another more *vigorously* and melting and boiling points of covalent substances *increase* with *larger* molecular mass and volume.
- Polarazibility also affects dispersion forces through the molecular shape of the affected molecules. Elongated molecules have electrons that are less tightly held, increasing their polarizability and thus strengthening the dispersion forces.

Exercise 11.4.2

Consider two isomers of C_5H_{10}, n-pentane and neopentane (2,2-dimethylepropane). Note, isomers are different molecules with the same molecular formula (C_5H_{10}, these are called "structural isomers" because the atom connectivity is different).



n-pentane



neopentane (2,2-dimethylepropane)

(a) What are the dominant intermolecular forces for these isomers

Answer

Since these are both nonpolar, they have London Dispersion or Instantaneous-Induced Dipole interactions

(b) Which has the stronger intermolecular forces and why?

Answer

n-pentane is more elongated and so has a larger polarizability, and thus has stronger dispersion forces than the tighter neopentane

(c) n-pentane bp=36°C, while, neopentante bp=10°C, why are they different?

Answer

n-pentane has the stronger dispersion forces, and thus requires more energy to vaporize, with the result of a higher boiling point.

Van der Waals Forces

It should be noted that short range molecular interactions with a $1/r^6$ distance dependency are collectively referred to as Van der Waals interactions, being named of Johannes van der Waals. These include dipole-dipole forces in the gas phase, London

dispersion forces and dipole-induced dipole forces. It should also be noted that London dispersion forces occur all the time, but are often negligible compared to other forces.

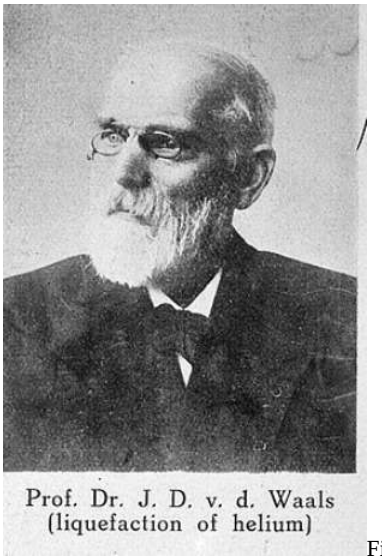


Figure 11.4.5: Johannes Diderik van der Waals (1837-1923), Dutch physicist and thermodynamicist who studied gasses and their condensation to liquids. (CC0: WikiMedia Commons)

In van der Waals thesis he not only postulated the existence of molecules (atoms were actually still being disputed at the time), but was one of the first to postulate intermolecular forces between them, which have often been collectively lumped into "van der Waals forces". The van der Waals equation of state for gases took into account deviations from ideality due to the volume of gases and their intermolecular attractions. The size of molecules are often identified by their van der Waals radii.

Test Yourself

Homework

Sources: Chemical Principles: The Quest for Insight, 4th Ed., Atkins & Jones

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11.5: Hydrogen Bonds

Introduction

Figure 11.5.1: In this rotating model oxygen are red, carbon grey and hydrogen white.

Hydrogen bonds are a strong type of dipole-dipole interaction. As a Rule of Thumb, they are weaker than covalent and ionic ("intramolecular") bonds", but stronger than most dipole-dipole interactions. There are two requirements for hydrogen bonding.

Two Requirements for Hydrogen Bonding:

1. **First molecule has hydrogen attached to a highly electronegative atom (N,O,F).**
   - (hydrogen bond donor)
2. **Second molecule has a lone pair of electrons on a small highly electronegative atom (N,O,F).**
   - (hydrogen bond acceptor)

Highly electronegative atoms like N, O, and F can not completely remove the valence electron from hydrogen and form an ion because there are no core electrons in hydrogen. Removing the hydrogen's 1s electron would produce a subatomic particle, the proton, whose small size results in a high charge density that would pull back the electron. So it will not happen. The result is that hydrogen forms polar covalent bonds when attached to an electronegative atom and does not form ions. The electronegative atoms pull on the valence electron "deshields" the hydrogen's proton resulting in a large $\delta+$ charge over a small area. A highly electronegative atom has a large $\delta-$ charge and if it has a lone pair of electrons, they are strongly attracted to the "deshielded proton" of another hydrogen and create a hydrogen bond. It should also be noted that the small size of the hydrogen allows it to move in real close, resulting is a strong bonding interaction.

? Exercise 11.5.1

How many hydrogens in figure 11.5.1 can form hydrogen bonds?

Answer

Only one, the one at the very top which is attached to the highly electrongative oxygen atom (red), all the others are attached to carbon and can not hydrogen bond.

Does Chlorine form Hydrogen Bonds?

Even though chlorine is highly electronegative, the best answer is no, and in this class we will consider chlorine not to form hydrogen bonds (even though it has the similar electronegativity as oxygen - 3.16 vs. 3.44). This is because chlorine is large and its lone electron is in a diffuse orbital, covering a large area, and thus do not have the high charge density to act as a strong hydrogen bond acceptor. But it does form weak hydrogen bonds in solid crystalline hydrogen chloride at very low temperatures.

H-Bonds and Water

H-bonding occurs in water. In the liquid state they are rapidly being formed and broken as the mobile particles move over each other. Note in figure 11.5.2 that there are two types of O-H bonds, the intramolecular O-H bond within a molecule (bond length = 1.01Å) and the intermolecular bond between atoms (bond length = 1.75Å). The closeness of the bond length indicates that the intramolecular bond is very strong, and of comparable magnitude to the intramolecular one. On a macroscopic scale this is obvious to anyone who falls on ice (frozen water) and quickly realizes how hard it is, and how strong the bonds are that hold the water molecules to each other.

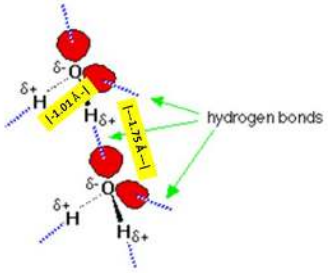


Figure 11.5.2: Hydrogen bonding interactions within water. Note the similarity in length between the intermolecular O---H bond, and the intramolecular O-H bond.

Water also has two lone pairs and two H atoms attached to the highly electronegative oxygen. This means each water molecule can participate in up to 4 bonds (two where it is the h-bond acceptor, and two where it is the h-bond donor). One interesting consequence of this is that water forms a 3D crystalline structure that is sort of based on a distorted tetrahedron. That is, the oxygen is sp^3 hybridized with a tetrahedral electronic geometry, having two bonding orbitals and two lone pairs. All of these are involved with hydrogen bonds. The lone pairs are functioning as H-bond acceptors, and the hydrogen on the bonding orbitals are functioning as h-bond donors. So each oxygen is attached to 4 hydrogens, two are 1.01Å covalent bonds and two are 1.75 Å hydrogen bonds, and this results in a structure like figure 11.5.3, which has lots of void space, and the consequence that ice is less dense than liquid water and floats.

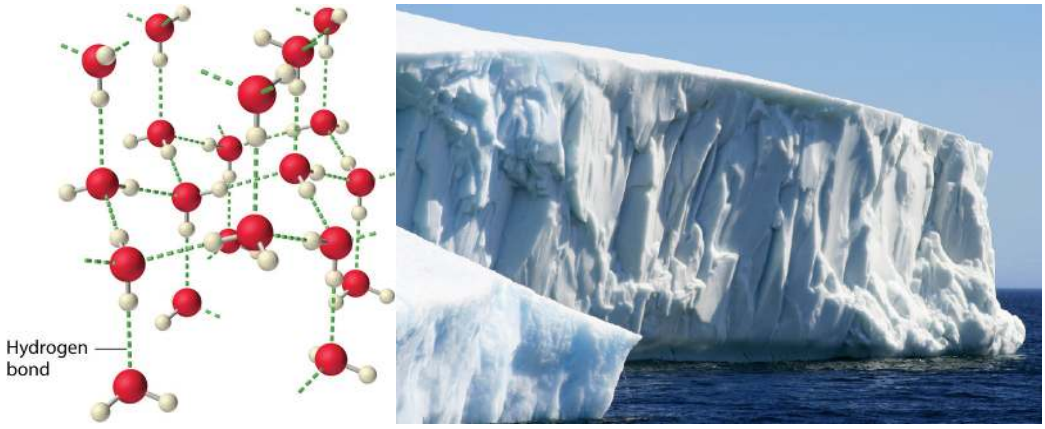


Figure 11.5.3: Hydrogen bonding and the crystal structure of ice (left), which floats on liquid water (cc0.0, negative space)

The fact that ice floats has great ramifications for life. The ice, with it's void space, acts as an insulator. If the ice sunk to the bottom, lakes would completely freeze and aquatic life like fish would not be able to survive the winters.

Hydrogen Bonding and Biology

We have all heard of DNA, which consists of nucleotide strands that join together to form the infamous double helix. DNA helix showing the base pairs adenine/thymine (A-T) an Guanine/Cytosine. (G-C), which form the double helix through the base pair interactions that are made through hydrogen bonding (11.5.4).

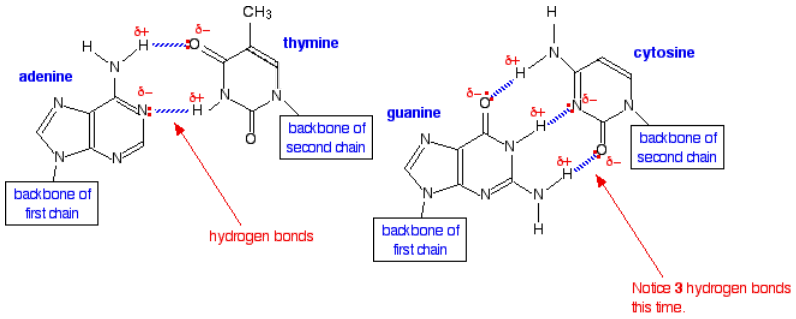


Figure 11.5.5: The adenine-thymine base pair held together by two hydrogen bonds(left) and the guanine-cytosine base pair held together by three hydrogen bonds (right). These are the

Proteins are based on amino acids and have four structural levels (Figure 11.5.5): Primary, Secondary, Tertiary, and Quaternary.

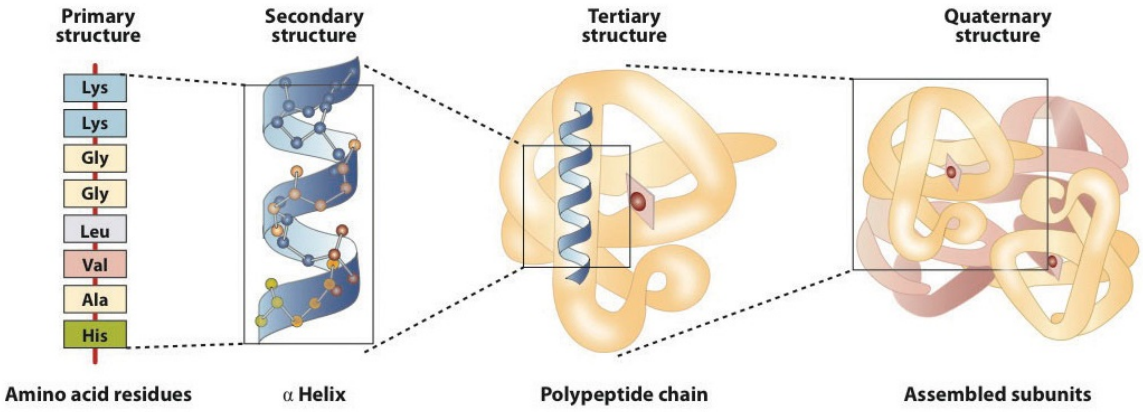


Figure 11.5.6: The 4 structural levels of proteins

The secondary level structure of proteins form alpha helixes and beta-pleated sheets, which are held together by hydrogen bonds.

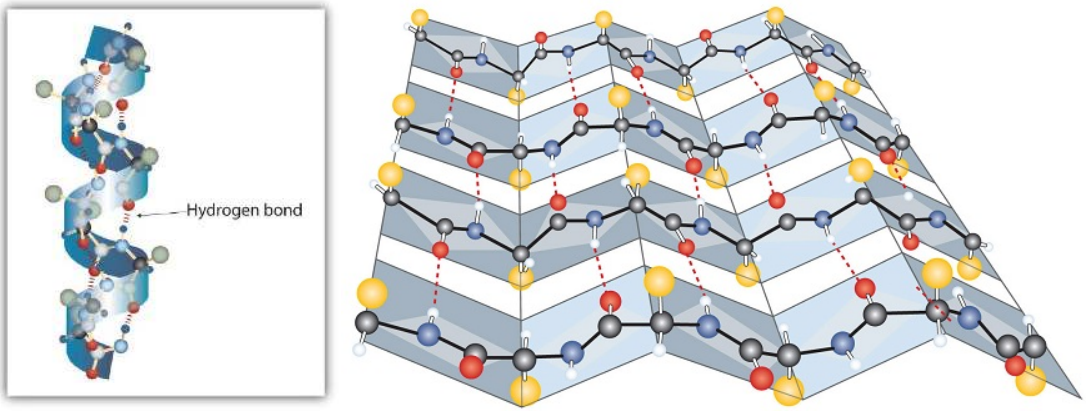


Figure 11.5.7: Protein alpha helixes (left) and beta pleated sheets (right) maintain their secondary structure through hydrogen bonding interactions (dotted red lines in the beta pleated sheet).

Test Yourself

Homework

Contributors and Attributions

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- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Jose Pietri (UCD)
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