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College of Geophysics and Remote Sensing
Department of Geophysics

CHEMISTRY I

For geophysics students / first semester

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1. Basic Concepts

1.1: Introduction to Matter

1.2: Elements and Compounds

Chemistry

"The study of the properties of materials and the changes that materials undergo"

1.1: Introduction to Matter

Matter

"Matter is the physical material of the universe; it is anything that occupies space and has mass"

Matter can exist in three physical states:

1. *Gas* or *vapor*
2. *Liquid*
3. *Solid*

Gas

No fixed volume or shape - it conforms to the volume and shape of its container. Gases can be *compressed* or *expanded* to occupy different volumes.

Liquid

A liquid has a distinct volume, independent of its container, but it has no specific *shape*. It assumes the shape of the container it is in. Liquids cannot be appreciably compressed.

Solid

A solid has a definite shape and volume; it is rigid. Solids cannot be appreciably compressed.

Substances

A pure substance has a fixed composition and distinct properties. Most matter we come in contact with in our daily lives is not a pure substance, but a mixture of substances.

Physical and Chemical Properties

Every pure substance has a unique set of *properties* - characteristics which allow us to distinguish it from other substances. These properties fall into two general categories: *physical* and *chemical*.

Physical properties - properties we can measure without changing the basic identity of the substance.

Chemical properties - describe the way a substance may change or "react" to form other substances.

Physical and Chemical Changes

Substances can undergo various changes in properties, these changes may be classified as either physical or chemical.

Physical changes - a substance changes its physical appearance but not its basic identity. All changes of state (e.g. solid to liquid to gas) are physical changes.

Chemical changes - also known as **chemical reactions**, a substance is transformed into a chemically different substance.

Mixtures

Mixtures refer to combinations of two or more substances in which each substance retains its own chemical identity and hence its own properties.

Heterogeneous mixtures are not uniform throughout the sample, and have regions of different appearance and properties

Homogenous mixtures are uniform throughout the sample, however, the individual substances retain their individual chemical and physical nature. Homogenous mixtures are also called **solutions**, however, the most common type of solution is described by a solid (the **solute**) dissolved in a liquid (the **solvent**).

An important characteristic of mixtures is that the individual components **retain** their physical and chemical properties. Thus, it is possible to **separate** the components based on their different properties. For example, we can separate ethanol from water by making use of their different boiling temperatures, in a process known as distillation.

1.2: Elements and Compounds

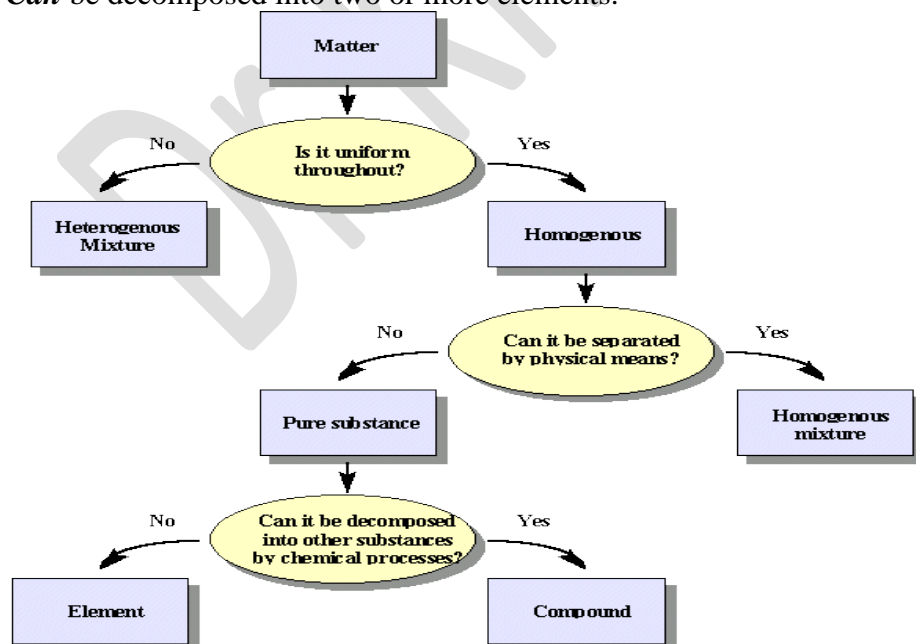
Pure substances have an invariable composition and are composed of either **elements** or **compounds**.

Elements

"Substances which cannot be decomposed into simpler substances by chemical means".

Compounds

Can be decomposed into two or more elements.



Elements

Elements are the basic substances out of which all matter is composed.

- Everything in the world is made up from only **109** different elements.
- 90% of the human body is composed of only three elements: Oxygen, Carbon and Hydrogen

Elements are known by common names as well as by their **abbreviations**. These consisting of one or two letters, with the first one capitalized. These abbreviations are derived from English or foreign words (e.g. Latin, German).

Element	Abbreviation
Carbon	C
Fluorine	F
Hydrogen	H
Iodine	I
Nitrogen	N
Oxygen	O
Phosphorus	P
Sulfur	S
Aluminum	Al
Barium	Ba
Calcium	Ca
Chlorine	Cl
Helium	He
Magnesium	Mg
Platinum	Pt
Silicon	Si
Copper	Cu (from <i>cuprum</i>)
Iron	Fe (from <i>ferrum</i>)
Lead	Pb (from <i>plumbum</i>)
Mercury	Hg (from <i>hydrargyrum</i>)
Potassium	K (from <i>kalium</i>)
Silver	Ag (from <i>argentum</i>)
Sodium	Na (from <i>natrium</i>)
Tin	Sn (from <i>stannum</i>)

2. Atoms, Molecules and Ions

2.1: The Atomic Theory of Matter

2.2: The Discovery of Atomic Structure

2.3: Modern View of Atomic Structure

2.4: The Periodic Table

2.5: Molecules and Ions

2.6: Naming of Inorganic Compounds

2.1: The Atomic Theory of Matter

Dalton's atomic theory of 1803:

1. Each element is composed of extremely small particles called atoms
2. All atoms of a given element are identical; the atoms of different elements are different and have different properties (including different masses)
3. Atoms of an element are not changed into different types of atoms by chemical reactions; atoms are neither created nor destroyed in chemical reactions
4. Compounds are formed when atoms of more than one element combine; a given compound always has the same relative number and kind of atoms.

Atoms are the *basic building blocks of matter*; they are the smallest units of an element:

- An *element* is composed of only one kind of atom
- In *compounds* the atoms of two or more elements combine in definite arrangements
- *Mixtures* do not involve the specific interactions between elements found in compounds, and the elements which comprise the mixture can be of varying ratios

Atoms are the smallest particle of an element which retains the chemical properties of that element

2.2: The Discovery of Atomic Structure

The Modern View of Atomic Structure

Physicists have identified a long list of particles which make up the atomic nucleus. Chemists, however, are primarily concerned with the following sub-atomic particles:

- electron
- proton
- neutron

Electron

The electron is **negatively** charged, with a charge of -1.602×10^{-19} Coulombs (C). For convenience, the charge of atomic and sub-atomic particles are usually described as a **multiple of**

this value (also known as the **electronic charge**). Thus, the charge of the electron is usually simply referred to as **-1**.

Proton

The proton has a charge of **+1 electron charge** (or, $+1.602 \times 10^{-19}$ C)

Neutrons

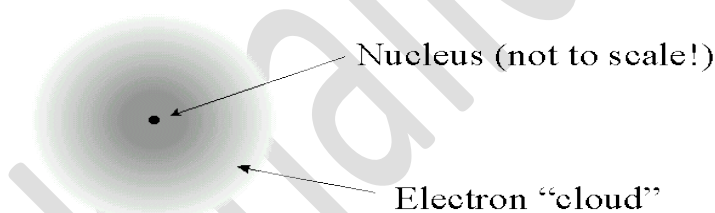
Neutrons have no charge, they are electrically **neutral**.

Note: Because atoms have an equal number of electrons and protons, they have no net electrical charge

Protons and neutrons are located in the nucleus (center) of the atom. The nucleus is small compared to the overall size of the atom. The majority of the space of an atom is the space in which the electrons move around.

Electrons are attracted to the protons in the nucleus by the force of attraction between particles of opposite charge.

Note: The strength of attraction between electrons and protons in the nuclei for different atoms is the basis of many of the unique properties of different atoms. The electrons play a major role in chemical reactions. In atomic models, the electrons are represented as a diffuse electron cloud



The mass of an atom is extremely small. The units of mass used to describe atomic particles is the **atomic mass unit** (or **amu**).

An atomic mass unit is equal to 1.66054×10^{-24} grams.

How do the different sub-atomic particles compare as far as their mass?

Proton = 1.0073 amu

Neutron = 1.0087 amu

Electron = 5.486×10^{-4} amu

From this comparison we can see that:

- The mass of the proton and neutron are nearly identical
- The nucleus (protons plus neutrons) contains virtually all of the mass of the atom
- The electrons, while equal and opposite in charge to the protons, have only 0.05% the mass

The **size** of an atom is quite small also, the typical range for atomic diameters is between 1×10^{-10} and 5×10^{-10} meters.

*Note: a convenient unit of measurement for atomic distances is the **angstrom** (Å). The angstrom is equal to 1×10^{-10} meters. Thus, **most atoms are between 1 and 5 angstroms in diameter**.*

Pinheads and Bouillon Cubes

Pinheads have a diameter of about 1×10^{-3} meters (a millimeter across). If an atom had a diameter of 2.5×10^{-10} meters, then

$$(1 \text{ atom} / 2.5 \times 10^{-10} \text{ meters}) * (1 \times 10^{-3} \text{ meters}) = 4 \times 10^6 \text{ atoms}$$

i.e. four million of them could line up across the head of a pin.

The diameter of atomic *nuclei* are about 10^{-4} Å. Thus, **the nuclei is about 0.01% the diameter of the atom as a whole**. If the nucleus had a diameter equal to that of a pinhead, then the atom itself would have a diameter of some 10 meters (*about 39 and a half feet*).

The nucleus of an atom is therefore quite dense. Consider a simple case of a nucleus containing 1 neutron and 1 proton:

$$\text{mass of nucleus} = \sim 2.0 \text{ amu} = 2 * (1.66 \times 10^{-24} \text{ grams}) = \mathbf{3.32 \times 10^{-24} \text{ grams}}$$

$$\text{diameter of nucleus} = (\text{approximately}) 1 \times 10^{-4} \text{ Å} = 1 \times 10^{-14} \text{ meters}$$

$$\text{radius of nucleus} = 1 \times 10^{-14} \text{ meters} / 2 = 0.5 \times 10^{-14} \text{ meters}$$

$$\text{volume of nucleus} = (4/3)\pi(\text{radius of nucleus})^3$$

$$\text{volume of nucleus} = 5.24 \times 10^{-43} \text{ meters}^3$$

$$\text{mass/volume} = 3.32 \times 10^{-24} \text{ grams} / 5.24 \times 10^{-43} \text{ meters}^3$$

$$\text{mass/volume} = \mathbf{6.34 \times 10^{18} \text{ grams/meter}^3}$$

a bouillon cube (stuff you can make soup out of if you are really broke) is about one cubic centimeter, or $1 \times 10^{-6} \text{ meters}^3$ and if it were made up of atomic nuclei it would weigh:

$$(1 \times 10^{18} \text{ grams/meter}^3) * (1 \times 10^{-6} \text{ meters}^3) = 6.34 \times 10^{12} \text{ grams}$$

or about six billion kilograms, or about **2.8 billion tons**.

Isotopes, Atomic Numbers and Mass Numbers

What characteristic feature of sub-atomic particles distinguishes one element from another?

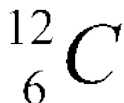
- All atoms of an element have the same number of protons in the nucleus
- Since the net charge on an atom is 0, the atom must have an equal number of electrons.
- What about the neutrons? Although usually equal to the number of protons, the number of neutrons can vary somewhat. Atoms which differ only in the number of neutrons are called isotopes. Since the neutron is about 1.0087 amu (the proton is 1.0073), different isotopes have different masses.

Your friend, Carbon

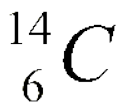
All atoms of the element Carbon (C) have 6 protons and 6 electrons. The number of **protons** in the carbon atom are denoted by a **subscript on the left** of the atomic symbol:



This is called the **atomic number**, and since it is always 6 for carbon, it is somewhat redundant and usually omitted. Another number, the "**Mass Number**" is a **superscript** on the left of the atomic symbol. It denotes the *sum of the number of protons and neutrons* in the particular isotope being described. For example:



refers to an isotope of carbon which has (as expected for the element carbon) six protons, and six neutrons. The following **isotope** of carbon:



has 6 protons (atomic number) and **8 neutrons** ($8=14-6$). This isotope is also known simply as "carbon 14". Carbon 12 is the most common form of carbon (~99% of all carbon). An atom of a specific isotope is called a **nuclide**.

Since all atoms are composed of protons, electrons and neutrons, all chemical and physical differences between elements are due to the differences in the number of these sub-atomic particles. Therefore, an atom is the smallest sample of an element, because dividing an atom further (into sub-atomic particles) destroys the element's unique identity.

2.3: The Periodic Table

As more and more elements were discovered and characterized, efforts were made to see whether they could be **grouped**, or classified, according to their chemical behavior. This effort resulted, in 1869, in the development of the **Periodic Table**.

Certain elements show similar characteristics:

- Lithium (Li), Sodium (Na) and Potassium (K) are all soft, very reactive metals
- Helium (He), Neon (Ne) and Argon (Ar) are very non-reactive gasses

If the elements are arranged in order of increasing atomic number, their chemical and physical properties are found to show a repeating, or periodic pattern.

Note: This table lists the atomic number (number of protons) in the upper left corner of each box. The atomic number is formally placed as a subscript preceding the atom name.

Periodic Table
1998 Dr. Michael Blaber

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012																
11 Na 22.99	12 Mg 24.30	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95										
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	
87 Fr 223.0	88 Ra 226.0	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 241.1	96 Cm 244.1	97 Bk 249.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 258.1	102 No 259.1	103 Lr 262.1	

← s → ← d → ← p → ← f →

Lanthanides

Actinides

As an example of the periodic nature of the atoms (when arranged by atomic number), each of the soft reactive metals comes immediately after one of the nonreactive gasses.

The elements in a column of the periodic table are known as a **family** or **group**. The labeling of the families are somewhat arbitrary, but are usually divided into the general groups of:

- Metals (everything on the left and middle region)
- Non-metals (upper diagonal on the right hand side - green, salmon and red)
- Metalloids (atoms in the boundary between the metals and metalloids: Boron(B), Silicon(Si), Germanium(Ge), Arsenic(As), Antimony(Sb), Tellurium(Te), Astatine(At)). These are some of the more useful materials for semi-conductors.

or, another convention is the 'A' and 'B' designators with column number labels (either in Roman or Arabic numerals). These columns have different types of classifications:

Group	Name	Elements
1A	Alkali metals	Li, Na, K, Rb, Cs, Fr
2A	Alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra
6A	Chalcogens ("chalk formers")	O, S, Se, Te, Po
7A	Halogens ("salt formers")	F, Cl, Br, I, At
8A	Noble gases (or inert, or rare gases)	He, Ne, Ar, Kr, Xe, Rn

The elements in a family of the periodic table have similar properties because they have the same type of **arrangement of electrons** at the **periphery** of their atoms.

The majority of elements are metals:

- high luster
- high electrical conductivity
- high heat conductivity
- solid at room temperature (except Mercury [Hg])

Note: hydrogen is a non-metal (at left hand side of the periodic table)

Non-metals

- solid, liquid or gas at room temp

2.4: Molecules and Ions

Although atoms are the smallest unique unit of a particular element, in nature only the noble gases can be found as isolated atoms. Most matter is in the form of **ions**, or **compounds**.

Molecules and chemical formulas

A **molecule** is comprised of two or more **chemically bonded** atoms. The atoms may be of the same type of element, or they may be different.

Many elements are found in nature in **molecular form** - two or more atoms (of the same type of element) are bonded together. Oxygen, for example, is most commonly found in its molecular form "**O₂**" (two oxygen atoms chemically bonded together).

Oxygen can also exist in another molecular form where three atoms are chemically bonded. O₃ is also known as ozone. Although O₂ and O₃ are both compounds of oxygen, they are **quite different** in their chemical and physical properties. There are seven elements which commonly occur as **diatomic** molecules. These include H, N, O, F, Cl, Br, I.

An example of a commonly occurring compound that is composed of two different types of atoms is pure water, or "H₂O". The **chemical formula** for water illustrates the method of describing such compounds in atomic terms: there are two atoms of hydrogen and one atom of oxygen (**the "1" subscript is omitted**) in the compound known as "water". There is another compound of Hydrogen and Oxygen with the chemical formula H₂O₂, also known as hydrogen peroxide. Again, although both compounds are composed of the same types of atoms, they are chemically quite different: hydrogen peroxide is quite reactive and has been used as a rocket fuel (it powered Evil Kenievelpart way over the Snake River canyon).

Most molecular compounds (i.e. involving chemical bonds) contain only non-metallic elements.

Molecular, Empirical, and Structural Formulas

Empirical vs. Molecular formulas

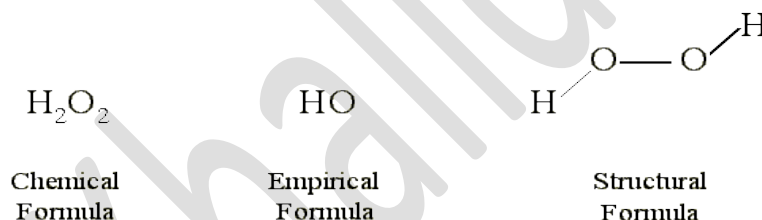
- Molecular formulas refer to the **actual** number of the different atoms which comprise a single molecule of a compound.
- Empirical formulas refer to the **smallest whole number ratios** of atoms in a particular compound.

Compound	Molecular Formula	Empirical Formula
Water	H ₂ O	H ₂ O
Hydrogen Peroxide	H ₂ O ₂	HO
Ethylene	C ₂ H ₄	CH ₂
Ethane	C ₂ H ₆	CH ₃

Molecular formulas provide more information, however, sometimes a substance is actually a **collection of molecules** with different sizes but the same empirical formula. For example, carbon is commonly found as a collection of three dimensional structures (carbon chemically bonded to carbon). In this form, it is most easily represented simply by the empirical formula "C" (the elemental name).

Structural formulas

Sometimes the molecular formulas are drawn out as **structural formulas** to give some idea of the actual chemical bonds which unite the atoms.

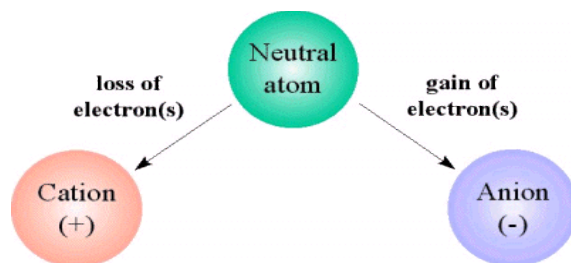


Structural formulas give an idea about the connections between atoms, but they don't necessarily give information about the **actual geometry** of such bonds.

Ions

The nucleus of an atom (containing protons and neutrons) remains unchanged after ordinary chemical reactions, *but atoms can readily gain or lose **electrons***.

If electrons are lost or gained by a neutral atom, then the result is that a *charged particle* is formed - called an **ion**.



For example, Sodium (Na) has 11 protons and 11 electrons. However, it can easily lose 1 electron. The resulting **cation** has 11 protons and 10 electrons, for an overall **net charge of 1+** (the units are electron charge). The ionic state of an atom or compound is represented by a superscript to the right of the chemical formula: Na^+ , Mg^{2+} (note the in the case of 1+, or 1-, the '1' is omitted). In contrast to the Na atom, the Chlorine atom (Cl) easily gains 1 electron to yield the chloride ion Cl^- (i.e. 17 protons and 18 electrons).

In general, metal atoms tend to lose electrons, and nonmetal atoms tend to gain electrons.

Na^+ and Cl^- are *simple ions*, in contrast to *polyatomic ions* such as NO_3^- (nitrate ion) and SO_4^{2-} (sulfate ion). These are compounds made up of chemically bonded atoms, but have a net positive or negative charge.

The chemical properties of an ion are greatly different from those of the atom from which it was derived.

Predicting ionic charges

Many atoms gain or lose electrons such that they end up with the same number of electrons as the noble gas closest to them in the periodic table.

The noble gasses are generally chemically non-reactive, they would appear to have a stable arrangement of electrons.

Other elements must gain or lose electrons, to end up with the same arrangement of electrons as the noble gases, in order to achieve the same kind of electron stability.

Example: Nitrogen

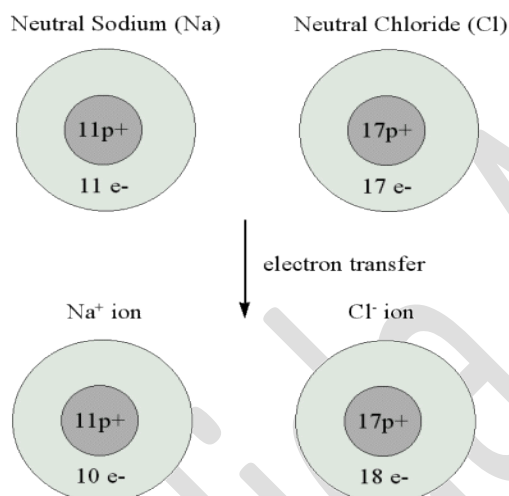
Nitrogen has an atomic number of 7; the neutral Nitrogen atom has 7 protons and 7 electrons. If Nitrogen gained three electrons it would have 10 electrons, like the Noble gas Neon (10 protons, 10 electrons). However, unlike Neon, the resulting Nitrogen **ion** would have a net charge of N^{3-} (7 protons, 10 electrons).

The location of the elements on the Periodic table can help in predicting the expected charge of ionic forms of the elements.

This is mainly true for the elements on either side of the chart.

Ionic compounds

Ions form when one or more electrons transfer from one neutral atom to another. For example, when elemental sodium is allowed to react with elemental chlorine an electron transfers from a neutral sodium to a neutral chlorine. The result is a sodium ion (Na^+) and a chlorine ion, chloride (Cl^-):



The oppositely charged ions attract one another and bind together to form NaCl (sodium chloride) an **ionic compound**.

An ionic compound contains positively and negatively charged ions

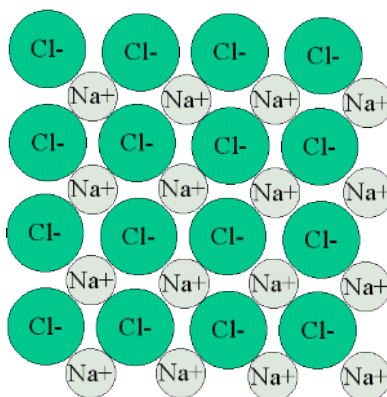
It should be pointed out that the Na^+ and Cl^- ions are **not chemically bonded** together. Whereas atoms in molecular compounds, such as H_2O , are chemically bonded.

Ionic compounds are generally combinations of metals and non-metals.

Molecular compounds are general combinations of non-metals only.

Pure ionic compounds typically have their atoms in an organized three dimensional arrangement (a crystal). Therefore, we cannot describe them using **molecular formulas**. We can describe them using **empirical formulas**.

Slice through a NaCl crystal



If we know the charges of the ions comprising an ionic compound, then we can determine the empirical formula. The key is knowing that ionic compounds are always **electrically neutral** overall.

Therefore, the concentration of ions in an ionic compound are such that the overall charge is neutral.

In the NaCl example, there will be one positively charged Na^+ ion for each negatively charged Cl^- ion.

What about the ionic compound involving Barium ion (Ba^{2+}) and the Chlorine ion (Cl^-)?

$$1 (\text{Ba}^{2+}) + 2 (\text{Cl}^-) = \text{neutral charge}$$

Resulting empirical formula: BaCl_2

2.5: Naming Inorganic Compounds

With over 10 million known chemicals, and potentially dangerous results if chemicals are combined in an incorrect manner, imagine the problem if you are in the lab and say "mix 10 grams of that stuff in with this stuff". We need to be very clear on identification of chemicals.

Two early classifications of chemical compounds:

1. **Organic compounds.** These contain the element Carbon (C). "Life on earth is carbon based"
2. **Inorganic compounds.** All other compounds

Organic compounds were associated with living organisms, however, a large number of organic compounds have been synthesized which do not occur in nature, so this distinction is no longer valid.

Ionic compounds: (an association of a cation and an anion)

The positive ion (cation) is always named first and listed first in writing the formula for the compound.

The vast majority of monatomic (composed of a single atom) cations are formed from metallic elements:

- Na^+ Sodium ion
- Zn^{2+} Zinc ion
- Al^{3+} Aluminum ion

If an element can form more than one positive ion, the positive charge of the ion is indicated by a Roman numeral in parentheses following the name of the metal:

- Fe^{2+} iron(II) ion
- Fe^{3+} iron(III) ion
- Cu^+ copper(I) ion
- Cu^{2+} copper(II) ion

Iron and copper are examples of **transition metals**. They occur in the block of elements from IIIB to IIB of the periodic table.

The transition metals often form two or more different monoatomic cations.

Periodic Table
1998 Dr. Michael Blaber

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.05	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	
87 Fr 223.0	88 Ra 226.0	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 241.1	96 Cm 244.1	97 Bk 249.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 258.1	102 No 259.1	103 Lr 262.1	

← s d p →

Lanthanides: 57 La, 58 Ce, 59 Pr, 60 Nd, 61 Pm, 62 Sm, 63 Eu, 64 Gd, 65 Tb, 66 Dy, 67 Ho, 68 Er, 69 Tm, 70 Yb, 71 Lu

Actinides: 89 Ac, 90 Th, 91 Pa, 92 U, 93 Np, 94 Pu, 95 Am, 96 Cm, 97 Bk, 98 Cf, 99 Es, 100 Fm, 101 Md, 102 No, 103 Lr

← f →

An older nomenclature for distinguishing between the different ions of a metal is to use the suffixes **-ous** and **-ic**. The suffix **-ic** will indicate the ion of *higher* ionic charge:

- Fe²⁺ ferrous ion
- Fe³⁺ ferric ion
- Cu⁺ cuprous ion
- Cu²⁺ cupric ion

Note that the different ions of the same element often have quite different chemical properties (again, pointing to the importance of *electrons* in determining chemical reactivity).

Ionic compounds: Anions

Monatomic anions are usually formed from non-metallic elements. They are named by dropping the ending of the element name and adding **-ide**:

- Cl⁻ chloride ion
- F⁻ fluoride ion
- S²⁻ sulfide ion
- O²⁻ oxide ion

Some common polyatomic anions include:

- OH⁻ hydroxide ion
- CN⁻ cyanide ion

Many polyatomic anions contain **oxygen**, and are referred to as **oxyanions**. When an element can form two different oxyanions the name of the one that contains more oxygen ends in **-ate**, the one with less ends in **-ite**:

- NO₂⁻ nitrite ion
- NO₃⁻ nitrate ion
- SO₃²⁻ sulfite ion
- SO₄²⁻ sulfate ion

Note that unlike the **-ous** and **-ic** suffix nomenclature to distinguish the different cations of a metal, the **-ite** and **-ate** suffix is used to distinguish the relative amounts of the oxygen atoms in a (polyatomic) oxyanion (in the above examples the ionic charge is the same for the **-ite** and **-ate** ions of a specific oxyanion).

Now to get really perverse....

Some compounds can have multiple oxyanion forms (the oxyanions involving the halogens, for example):

- ClO⁻
- ClO₂⁻
- ClO₃⁻
- ClO₄⁻

Note again, that the number of Oxygens relative to the Chlorine is changing, but that the ionic charge is not.

How do we name these? The **-ite** and **-ate** suffixes are still used, but we have to add an additional modification to allow us to distinguish between the **four** forms:

- ClO⁻ **hypochlorite** ion
- ClO₂⁻ **chlorite** ion
- ClO₃⁻ **chlorate** ion
- ClO₄⁻ **perchlorate** ion

The Naming of Anions and Oxyanions

Simple anion
ide
(chloride, Cl⁻)

If an element forms only two possible oxyanions:

Form with *less* oxygen
ite ion
NO₂⁻ (nitrite ion)

Form with *more* oxygen
ate ion
NO₃⁻ (nitrate ion)

If an element forms three or more possible oxyanions:

hypo...ite
(hypochlorite, ClO⁻)

...ite
(chlorite, ClO₂⁻)

...ate
(chlorate, ClO₃⁻)

per...ate
(perchlorate, ClO₄⁻)

It should be pointed out that some of the naming of ions is historical and is not necessarily systematic. It may be frustrating and confusing, but it's all part of chemistry's rich history.

Many polyatomic anions that have high (negative) charges can add one or more hydrogen cations (H⁺) to form anions of lower effective charge. The naming of these anions reflects whether the H⁺ addition involves one or more hydrogen ions:

- HSO₄⁻ **hydrogen** sulfate ion
- H₂PO₄⁻ **dihydrogen** phosphate ion

Acids

- An acid is a substance whose molecules yield hydrogen (H⁺) ions when dissolved in water.
- The formula of an acid consists of an anionic group whose charge is balanced by one or more H⁺ ions.
- The name of the acid is related to the name of the anion
- Anions whose names end in **-ide** have associated acids that have the **hydro-** prefix and an **-ic** suffix:

Cl ⁻ chloride anion	HCl hydrochloric acid
S ²⁻ sulfide anion	H ₂ S hydrosulfuric acid

Using the **-ic** suffix here may seem a bit inconsistent since it was used in naming **metal cations** to indicate the form which had the higher positive charge. However, when you think about it, the

acid compound has a *higher net positive charge* than the anion from which it is derived (the anion is negatively charged and the associated acid is neutral).

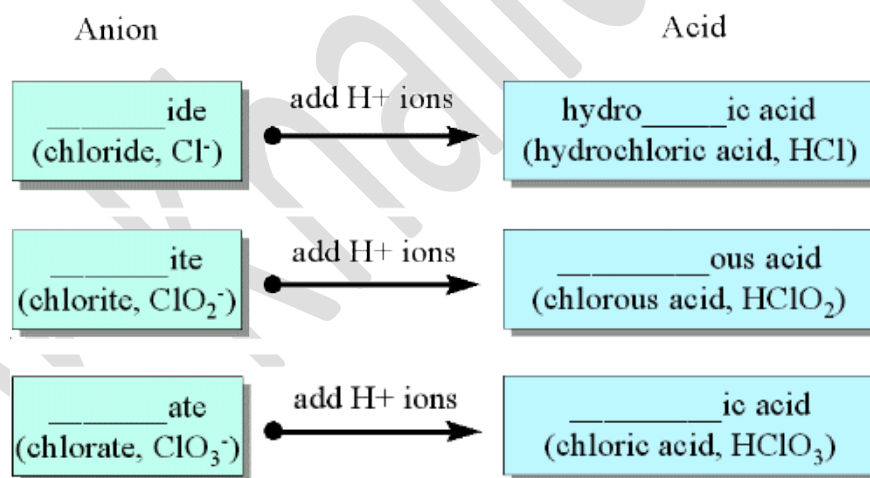
Again, things get complicated when we consider the acids of oxyanions:

- If the anion has an **-ate** ending, the corresponding acid is given an **-ic** ending
- If the anion has an **-ite** ending, the corresponding acid has an **-ous** ending.
- Prefixes in the name of the anion are kept in naming the acid

ClO^- hypochlorite ion	HClO hypochlorous acid
ClO_2^- chlorite ion	HClO_2 chlorous acid
ClO_3^- chlorate ion	HClO_3 chloric acid
ClO_4^- perchlorate ion	HClO_4 perchloric acid

This is confusing: we previously had used the **-ous** and **-ic** suffixes to indicate the ionic charge differences in metal *cations* (**-ic** had a higher positive charge). Although in comparison to the ionic form, the **-ic** and **-ous** acid forms have a higher net positive charge, the **-ic** suffix would indicate forms with a higher oxygen content, and not an apparent *charge* difference.

Relationship between anion names and corresponding acids



Molecular compounds

Although they may not be ionic compounds, chemically bonded compounds of two different elements can be thought of as being made up of an element with a more positive chemical nature, and one that has a more negative nature in comparison. Elements on the left hand side of the periodic table prefer to donate electrons (thus taking on a more positive chemical nature), and elements on the right hand side prefer to accept electrons (thus taking on a more negative chemical nature). *The element with the more positive nature in a compound is named first. The second element is named with an **-ide** ending.*

Often a pair of elements can form several different molecular compounds. For example, Carbon and Oxygen can form CO and CO₂. Prefixes are used to identify the relative number of atoms in such compounds:

- CO carbon **mon**oxide (carbon **mono** oxide)
- CO₂ carbon **di**oxide

Such prefixes can extend for quite a way for some organic and polymeric compounds (a common detergent in shampoos is sodium dodecylsulfate, or "SDS", also known as Sodium Laurel Sulfate because it sounds more benign and holistic). The list of such prefixes includes:

Prefix	Meaning
Mono-	1
Di-	2
Tri-	3
Tetra-	4
Penta-	5
Hexa-	6
Hepta-	7
Octa-	8
Nona-	9
Deca-	10
Undeca-	11
Dodeca-	12

3.Stoichiometry: Chemical Formulas and Equations

- 3.1: Chemical Equations
 - 3.2: Patterns of Chemical Reactivity
 - 3.3: Atomic and Molecular Weights
 - 3.4: The Mole
 - 3.5: Empirical Formulas from Analyses
 - 3.6: Quantitative Information from Balanced Equations
 - 3.7: Limiting Reactants
-

3. Stoichiometry: Chemical Formulas and Equations

What happens to matter when it undergoes chemical changes?

The law of **conservation of mass**:

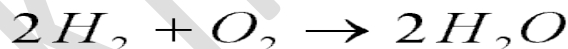
Atoms are neither created, nor destroyed, during any chemical reaction

Thus, the same collection of atoms is present after a reaction as before the reaction. The changes that occur during a reaction just involve the *rearrangement* of atoms.

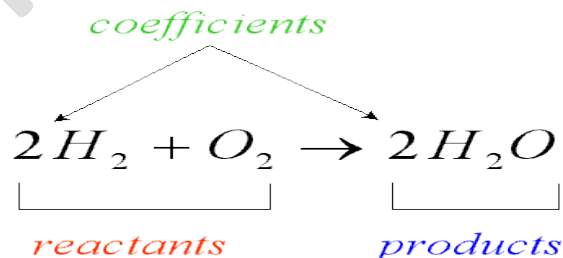
In this section we will discuss *stoichiometry* (the "measurement of elements").

3.1:Chemical equations

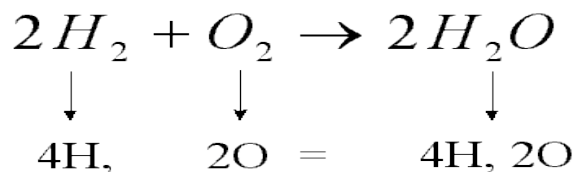
Chemical reactions are represented on paper by **chemical equations**. For example, hydrogen gas (H_2) can react (burn) with oxygen gas (O_2) to form water (H_2O). The *chemical equation* for this *reaction* is written as:



The '+' is read as 'reacts with' and the arrow " \rightarrow " means 'produces'. The chemical formulas on the **left** represent the starting substances, called **reactants**. The substances produced by the reaction are shown on the **right**, and are called **products**. The numbers in front of the formulas are called **coefficients** (the number '1' is usually omitted).



Because atoms are neither created nor destroyed in a reaction, **a chemical equation must have an equal number of atoms of each element on each side of the arrow** (i.e. the equation is said to be 'balanced').



Steps involved in writing a 'balanced' equation for a chemical reaction:

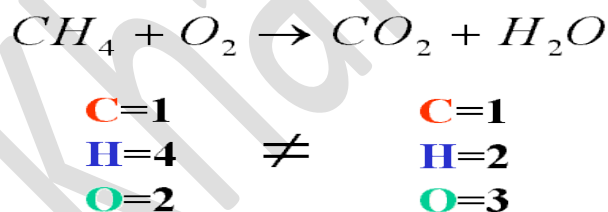
1. Experimentally determine reactants and products
2. Write 'un-balanced' equation using formulas of reactants and products
3. Write 'balanced' equation by determining coefficients that provide equal numbers of each type of atom on each side of the equation (generally, whole number values)

Note! Subscripts should never be changed when trying to balance a chemical equation. Changing a subscript changes the actual identity of a product or reactant. Balancing a chemical equation only involves changing the relative amounts of each product or reactant.

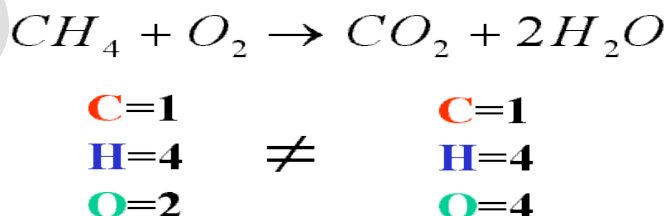
Consider the reaction of burning the gas methane (CH₄) in air. We know experimentally that this reaction consumes oxygen (O₂) and produces water (H₂O) and carbon dioxide (CO₂). Thus, we have accomplished step #1 above. We now write the *unbalanced* chemical equation (step #2):



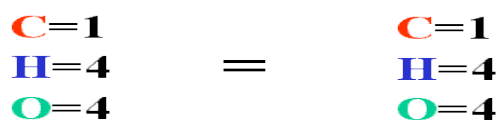
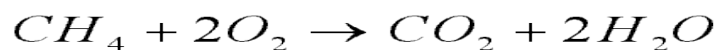
Now let's count up the atoms in the reactants and products:



We seem to be o.k. with our number of carbon atoms in both the reactants and products, but we have only half the hydrogens in our products as in our reactants. We can fix this by doubling the relative number of water molecules in the list of products:

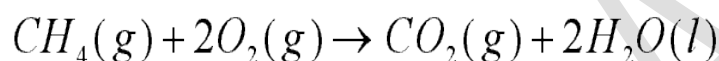


Note that while this has balanced our carbon and hydrogen atoms, we now have 4 oxygen atoms in our products, and only have 2 in our reactants. We can balance our oxygen atoms by doubling the number of oxygen atoms in our reactants:



We now have fulfilled step #3, we have a *balance chemical equation* for the reaction of methane with oxygen. Thus, *one molecule of methane reacts with two molecules of oxygen to produce one molecule of carbon dioxide and two molecules of water.*

The physical state of each chemical can be indicated by using the symbols (g), (l), and (s) (for *gas*, *liquid* and *solid*, respectively):



2.2: Patterns of Chemical Reactivity

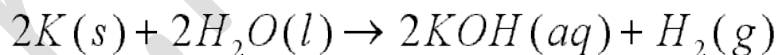
Using the periodic table

We can often predict a reaction if we have seen a similar reaction before. For example, sodium (Na) reacts with water (H₂O) to form sodium hydroxide (NaOH) and H₂ gas:



note: (aq) indicates aqueous liquid

Potassium (K) is in the same family (column) of elements in the periodic table. Therefore, one might *predict* that the reaction of K with H₂O would be similar to that of Na:



In fact, *all alkali metals react with water to form their hydroxide compounds and hydrogen.*

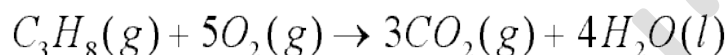
Combustion in air

Combustion reactions are rapid reactions that produce a flame. Most common combustion reactions involve oxygen (O₂) from the air as a *reactant*. A common class of compounds which can participate in combustion reactions are *hydrocarbons* (compounds that contain only carbon and hydrogen).

Examples of common hydrocarbons:	
Name	Molecular formula

Methane	CH ₄
Propane	C ₃ H ₈
Butane	C ₄ H ₁₀
Octane	C ₈ H ₁₈

When hydrocarbons are combusted they react with oxygen (O₂) to form carbon dioxide (CO₂) and water (H₂O). For example, when propane is burned the reaction is:



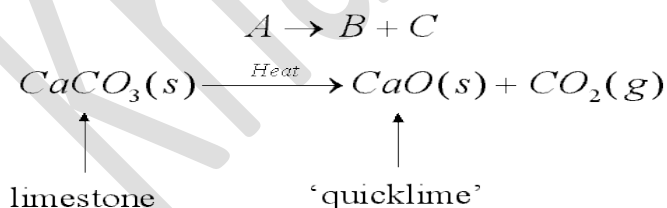
Other compounds which contain carbon, hydrogen and oxygen (e.g. the alcohol *methanol* CH₃OH, and the sugar *glucose* C₆H₁₂O₆) also combust in the presence of oxygen (O₂) to produce CO₂ and H₂O.

Combination and decomposition reactions

In **combination reactions** two or more compounds react to form *one* product:



In **decomposition reactions** one substance undergoes a reaction to form two or more products. For example, many metal carbonates undergo a heat dependent decomposition to the corresponding oxide plus CO₂:

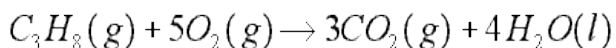


3.3: Atomic and Molecular Weights

The subscripts in chemical formulas, and the coefficients in chemical equations represent *exact* quantities.

H₂O, for example, indicates that a water molecule comprises exactly **two** atoms of hydrogen and **one** atom of oxygen.

The following equation:



not only tells us that propane reacts with oxygen to produce carbon dioxide and water, but that **1** molecule of propane reacts with **5** molecules of oxygen to produce **3** molecules of carbon dioxide and **4** molecules of water.

Since counting individual atoms or molecules is a little difficult, quantitative aspects of chemistry rely on knowing the *masses* of the compounds involved.

The atomic mass scale

Atoms of different elements have different masses. Early work on the separation of water into its constituent elements (hydrogen and oxygen) indicated that 100 grams of water contained 11.1 grams of hydrogen and 88.9 grams of oxygen:

100 grams Water → 11.1 grams Hydrogen + 88.9 grams Oxygen

Later, scientists discovered that water was composed of **two atoms** of hydrogen **for each atom** of oxygen. Therefore, in the above analysis, *in the 11.1 grams of hydrogen there were twice as many atoms as in the 88.9 grams of oxygen.* Therefore, an oxygen atom must weigh about 16 times as much as a hydrogen atom:

$$\left(\frac{\left(\frac{88.9 \text{ g Oxygen}}{1 \text{ atom}} \right)}{\left(\frac{11.1 \text{ g Hydrogen}}{2 \text{ atoms}} \right)} \right) = 16$$

Hydrogen, the lightest element, was assigned a relative mass of '1', and the other elements were assigned 'atomic masses' relative to this value for hydrogen. Thus, oxygen was assigned an atomic mass of 16.

We now know that a **hydrogen** atom has a mass of **1.6735 x 10⁻²⁴** grams, and that the **oxygen** atom has a mass of **2.6561 X 10⁻²³** grams. As we saw earlier, it is convenient to use a reference unit when dealing with such small numbers: the **atomic mass unit**. The atomic mass unit (**amu**) was not standardized against hydrogen, but rather, against the ¹²C isotope of **carbon** (**amu = 12**).

Thus, the mass of the **hydrogen atom** (¹H) is 1.0080 *amu*, and the mass of **an oxygen atom** (¹⁶O) is 15.995 *amu*. Once the masses of atoms were determined, the **amu** could be assigned an actual value:

$$\begin{aligned} 1 \text{ amu} &= 1.66054 \times 10^{-24} \text{ grams} \\ \text{conversely:} \\ 1 \text{ gram} &= 6.02214 \times 10^{23} \text{ amu} \\ &\text{Average atomic mass} \end{aligned}$$

Most elements occur in nature as a mixture of *isotopes* (i.e. populations of atoms with different numbers of neutrons, and therefore, mass). We can calculate the average atomic mass of an element by knowing the relative abundance of each isotope, as well as the mass of each isotope.

Example: Naturally occurring carbon is 98.892% ^{12}C and 1.108% ^{13}C . The mass of ^{12}C is 12 amu, and that of ^{13}C is 13.00335 amu. Therefore, the *average atomic mass of carbon* is:

$$(0.98892) \times (12 \text{ amu}) + (0.01108) \times (13.00335 \text{ amu}) = 12.011 \text{ amu}$$

The average atomic mass of each element (in amu) is also referred to as its **atomic weight**. Values for the atomic weights of each of the elements are commonly listed in periodic tables.

Formula and Molecular Weights

The **formula weight** of a substance is the sum of the atomic weights of each atom in its chemical formula.

For example, water (H_2O) has a formula weight of:

$$2 \times (1.0079 \text{ amu}) + 1 \times (15.9994 \text{ amu}) = 18.01528 \text{ amu}$$

If a substance exists as discrete molecules (as with atoms that are *chemically bonded* together) then the *chemical formula* is the *molecular formula*, and the *formula weight* is the *molecular weight*. For example, carbon, hydrogen and oxygen can chemically bond to form a molecule of the sugar **glucose** with the chemical and molecular formula of $\text{C}_6\text{H}_{12}\text{O}_6$. The formula weight and the molecular weight of glucose is thus:

$$6 \times (12 \text{ amu}) + 12 \times (1.00794 \text{ amu}) + 6 \times (15.9994 \text{ amu}) \\ = 180.0 \text{ amu}$$

Ionic substances are not chemically bonded and do not exist as discrete molecules. However, they do associate in discrete ratios of ions. Thus, we can describe their formula weights, but not their *molecular weights*. Table salt (NaCl), for example, has a formula weight of:

$$23.0 \text{ amu} + 35.5 \text{ amu} \\ = 58.5 \text{ amu}$$

Percentage composition from formulas

In some types of analyses of it is important to know the **percentage by mass** of each type of element in a compound. Take for example methane:

$$\begin{aligned} & \text{CH}_4 \\ \text{Formula and molecular weight: } & 1 \times (12.011 \text{ amu}) + 4 \times (1.008) = 16.043 \text{ amu} \\ \% \text{C} = & 1 \times (12.011 \text{ amu}) / 16.043 \text{ amu} = 0.749 = 74.9\% \\ \% \text{H} = & 4 \times (1.008 \text{ amu}) / 16.043 \text{ amu} = 0.251 = 25.1\% \end{aligned}$$

3.4: The Mole

Even tiny samples of chemicals contain huge numbers of atoms, ions or molecules. For convenience sake, some kind of reference for a collection of a large number of these objects would be very useful (e.g. a "dozen" is a reference to a collection of 12 objects). In chemistry we use a unit called a *mole* (abbreviated *mol*).

A mole is defined as the amount of matter that contains as many objects as the number of atoms in exactly 12 grams of ^{12}C .

Various experiments have determined that this number is...

$$6.0221367 \times 10^{23}$$

This is usually abbreviated to simply 6.02×10^{23} , and is known as *Avogadro's number*.

One mole of atoms, volkswagens, people, etc. contains 6.02×10^{23} of these objects. Just how big is this number? One mole of marbles spread over the earth would result in a layer *three miles* thick.

Molar Mass

A single ^{12}C atom has a mass of 12 *amu*. A single ^{24}Mg atom has a mass of 24 *amu*, or twice the mass of a ^{12}C atom. Thus, one mole of ^{24}Mg atoms should have twice the mass as one mole of ^{12}C atoms. Since one mole of ^{12}C atoms weighs 12 grams (by definition), one mole of ^{24}Mg atoms must weigh 24 grams.

Note that the mass of one atom in atomic mass units (amu) is numerically equal to the mass of one mole of the same atoms in grams (g).

The mass in grams of 1 mole (mol) of a substance is called its *molar mass*.

The molar mass (in grams) of any substance is always numerically equal to its formula weight (in amu).

One H_2O molecule weighs 18.0 amu; 1 mol of H_2O weighs 18.0 grams

One NaCl ion pair weighs 58.5 amu; 1 mol of NaCl weighs 58.5 grams

Interconverting masses, moles, and numbers of particles

Keeping track of units in calculations is necessary when interconverting masses and moles. This is formally known as **dimensional analysis**.

"Igor! bring me 1.5 moles of calcium chloride"

Chemical formula of calcium chloride = CaCl_2

Molecular mass of Ca = 40.078 amu

Molecular mass of Cl = 35.453 amu

Therefore, the *formula weight* of $\text{CaCl}_2 = (40.078) + 2(35.453) = 110.984 \text{ amu}$ (remember, this compound is ionic, so there is no "molecular" weight).

Therefore, one mole of CaCl_2 would have a mass of 110.984 grams.

so, 1.5 moles of CaCl_2 would be:

$$(1.5 \text{ mole})(110.984 \text{ grams/mole}) = 166.476 \text{ grams}$$

"Igor! I have 2.8 grams of gold, how many atoms do I have?"

Molecular formula of gold is: Au

Molecular weight of Au = 196.9665 amu

Therefore, 1 mole of gold weighs 196.9665 grams. So, in 2.8 grams of gold we would have:

$$(2.8 \text{ gram})(1 \text{ mole}/196.9665 \text{ gram}) = 0.0142 \text{ mole}$$

From Avogadro's number, we know that there are approximately 6.02×10^{23} atoms/mole. Therefore, in 0.0142 moles we would have:

$$(0.0142 \text{ mole})(6.02 \times 10^{23} \text{ atoms/mole}) = 8.56 \times 10^{21} \text{ atoms}$$

3.5: Empirical Formulas from Analyses

An empirical formula tells us the relative ratios of different atoms in a compound. The ratios hold true on the *molar* level as well. Thus, H_2O is composed of two atoms of hydrogen and 1 atom of oxygen. Likewise, **1.0 mole of H_2O is composed of 2.0 moles of hydrogen and 1.0 mole of oxygen.**

We can also work backwards from molar ratios:

if we know the molar amounts of each element in a compound we can determine the empirical formula.

Mercury forms a compound with chlorine that is 73.9% mercury and 26.1% chlorine by mass. What is the empirical formula?

Let's say we had a 100 gram sample of this compound. The sample would therefore contain 73.9 grams of mercury and 26.1 grams of chlorine. How many moles of each atom do the individual masses represent?

For Mercury:

$$(73.9 \text{ g}) \cdot (1 \text{ mol} / 200.59 \text{ g}) = 0.368 \text{ moles}$$

For Chlorine:

$$(26.1 \text{ g}) \cdot (1 \text{ mol} / 35.45 \text{ g}) = 0.736 \text{ mol}$$

What is the molar ratio between the two elements?

$$(0.736 \text{ mol Cl} / 0.368 \text{ mol Hg}) = 2.0$$

Thus, we have twice as many moles (i.e. atoms) of Cl as Hg. The empirical formula would thus be (remember to list cation first, anion last):



Molecular formula from empirical formula

The chemical formula for a compound obtained by composition analysis is always the empirical formula. We can obtain the chemical formula from the empirical formula if we know the molecular weight of the compound.

The chemical formula will always be some *integer multiple* of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula).

Vitamin C (ascorbic acid) contains 40.92 % C, 4.58 % H, and 54.50 % O, by mass. The experimentally determined molecular mass is 176 *amu*. What is the empirical and chemical formula for ascorbic acid?

In 100 grams of ascorbic acid we would have:

40.92 grams C

4.58 grams H

54.50 grams O

This would give us how many moles of each element?

$$(40.92 \text{ grams}(C)) * \left(\frac{1 \text{ mole}}{12.011 \text{ grams}} \right) = 3.407 \text{ moles}(C)$$

$$(4.58 \text{ grams}(H)) * \left(\frac{1 \text{ mole}}{1.008 \text{ grams}} \right) = 4.544 \text{ moles}(H)$$

$$(54.50 \text{ grams}(O)) * \left(\frac{1 \text{ mole}}{15.999 \text{ grams}} \right) = 3.406 \text{ moles}(O)$$

Determine the simplest whole number ratio by dividing by the smallest molar amount (3.406 moles in this case - see Oxygen):

$$C = \frac{3.407 \text{ moles}}{3.406 \text{ moles}} = 1.0$$

$$H = \frac{4.544 \text{ moles}}{3.406 \text{ moles}} = 1.333$$

$$O = \frac{3.406 \text{ moles}}{3.406 \text{ moles}} = 1.0$$

The relative molar amounts of carbon and oxygen appear to be equal, but the relative molar amount of hydrogen is higher. Since we cannot have "fractional" atoms in a compound, we need to normalize the relative amount of hydrogen to be equal to an integer. 1.333 would appear to be 1 and 1/3, so if we multiply the relative amounts of each atom by '3', we should be able to get integer values for each atom.

$$C = (1.0) * 3 = 3$$

$$H = (1.333) * 3 = 4$$

$$O = (1.0) * 3 = 3$$

or, **C₃H₄O₃**

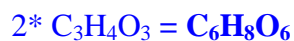
This is our **empirical formula** for ascorbic acid. What about the chemical formula? We are told that the experimentally determined molecular mass is **176 amu**. What is the molecular mass of our empirical formula?

$$(3 * 12.011) + (4 * 1.008) + (3 * 15.999) = 88.062 \text{ amu}$$

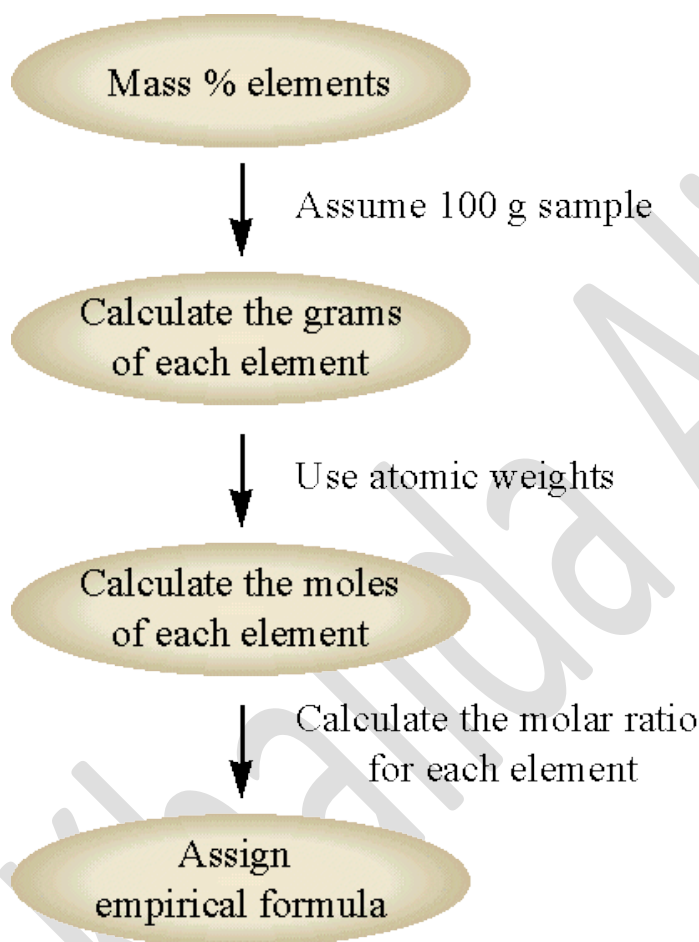
The molecular mass from our empirical formula is significantly lower than the experimentally determined value. What is the ratio between the two values?

$$(176 \text{ amu} / 88.062 \text{ amu}) = 2.0$$

Thus, it would appear that our empirical formula is essentially one half the mass of the actual molecular mass. If we multiplied our empirical formula by '2', then the molecular mass would be correct. Thus, the actual molecular formula is:

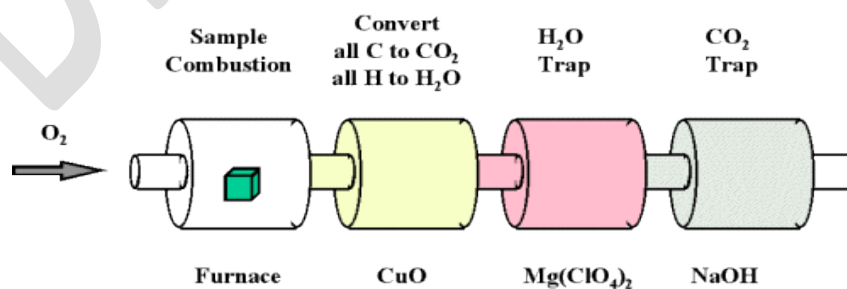


The general flow chart for solving empirical formulas from known mass percentages is:



Combustion analysis

When a compound containing carbon and hydrogen is subject to combustion with oxygen in a special combustion apparatus all the carbon is converted to CO_2 and the hydrogen to H_2O .



The amount of carbon produced can be determined by measuring the amount of CO_2 produced. This is trapped by the sodium hydroxide, and thus we can monitor the mass of CO_2 produced by

determining the increase in mass of the CO₂ trap. Likewise, we can determine the amount of H produced by the amount of H₂O trapped by the magnesium perchlorate.

Consider the combustion of isopropyl alcohol. The sample is known to contain only C, H and O. Combustion of 0.255 grams of isopropyl alcohol produces 0.561 grams of CO₂ and 0.306 grams of H₂O. From this information we can quantitate the amount of C and H in the sample:

$$(0.561\text{grams}(\text{CO}_2)) * \left(\frac{1.0\text{mole}(\text{CO}_2)}{44.0\text{grams}} \right) = 0.0128\text{moles}(\text{CO}_2)$$

Since one mole of CO₂ is made up of one mole of C and two moles of O, if we have 0.0128 moles of CO₂ in our sample, then we know we have 0.0128 moles of C in the sample. How many grams of C is this?

$$(0.0128\text{moles}(\text{C})) * \left(\frac{12.011\text{grams}}{\text{mole}(\text{C})} \right) = 0.154\text{grams}(\text{C})$$

How about the hydrogen?

$$(0.306\text{grams}(\text{H}_2\text{O})) * \left(\frac{1.0\text{mole}(\text{H}_2\text{O})}{18.0\text{grams}} \right) = 0.017\text{moles}(\text{H}_2\text{O})$$

Since one mole of H₂O is made up of one mole of oxygen and *two* moles of hydrogen, if we have 0.017 moles of H₂O, then we have 2*(0.017) = 0.034 moles of hydrogen. Since hydrogen is about 1 gram/mole, we must have **0.034 grams of hydrogen** in our original sample.

When we add our carbon and hydrogen together we get:

$$0.154\text{ grams (C)} + 0.034\text{ grams (H)} = \mathbf{0.188\text{ grams}}$$

But we know we combusted 0.255 grams of isopropyl alcohol. The 'missing' mass must be from the oxygen atoms in the isopropyl alcohol:

$$0.255\text{ grams} - 0.188\text{ grams} = 0.067\text{ grams oxygen}$$

This much oxygen is how many moles?

$$(0.067\text{grams}(\text{O})) * \left(\frac{1.0\text{mole}(\text{O})}{15.994\text{grams}} \right) = 0.0042\text{moles}(\text{O})$$

Overall therefore, we have:

0.0128 moles Carbon

0.0340 moles Hydrogen

0.0042 moles Oxygen

Divide by the smallest molar amount to normalize:

C = 3.05 atoms

H = 8.1 atoms

O = 1 atom

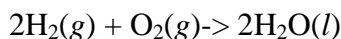
Within experimental error, the most likely empirical formula for propanol would be:



3.6: Quantitative Information from Balanced Equations

The coefficients in a balanced chemical equation can be interpreted both as the relative numbers of *molecules* involved in the reaction and as the relative number of *moles*.

For example, in the *balanced* equation:



the production of two moles of water would require the consumption of 2 moles of H_2 and one mole of O_2 . Therefore, when considering *this* particular reaction

2 moles of H_2
1 mole of O_2
and
2 moles of H_2O

would be considered to be *stoichiometrically equivalent quantities*. Represented as:



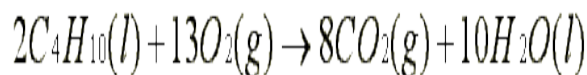
Where ' $\stackrel{\text{---}}{\sim}$ ' means "stoichiometrically equivalent to".

These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H_2O would be produced from 1.57 moles of O_2 (assuming the hydrogen gas is not a limiting reactant)?

$$(1.57 \text{ mol O}_2) * \left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} \right) = 3.14 \text{ mol H}_2\text{O}$$

The ratio $\left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol O}_2} \right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

For the combustion of butane (C_4H_{10}) the balanced equation is:



Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10} .

First of all we need to calculate how many moles of butane we have in a 100 gram sample:

$$(1.0 \text{ grams } C_4H_{10}) * \left(\frac{1 \text{ mol } C_4H_{10}}{58.0 \text{ grams } C_4H_{10}} \right) = 1.72 \times 10^{-2} \text{ mol } C_4H_{10}$$

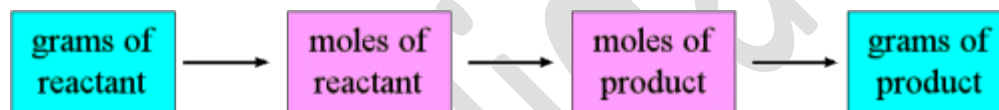
now, the stoichiometric relationship between C_4H_{10} and CO_2 is: $\left(\frac{8 \text{ moles } CO_2}{2 \text{ moles } C_4H_{10}} \right)$,
therefore:

$$\left(\frac{8 \text{ moles } CO_2}{2 \text{ moles } C_4H_{10}} \right) * 1.72 \times 10^{-2} \text{ mol } C_4H_{10} = 6.88 \times 10^{-2} \text{ mol } CO_2$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$(6.88 \times 10^{-2} \text{ mol } CO_2) * \left(\frac{44.0 \text{ grams } CO_2}{1 \text{ mol } CO_2} \right) = 3.03 \text{ grams } CO_2$$

Thus, the overall sequence of steps to solve this problem were:

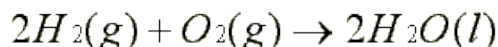


In a similar way we could determine the mass of water produced, or oxygen consumed, etc.

3.7: Limiting Reactants

Suppose you are a chef preparing a breakfast for a group of people, and are planning to cook French toast. You make French toast the way you have always made it: one egg for every three slices of toast. You never waiver from this recipe, because the French toast will turn out to be either too soggy or too dry (arguably, you are anal retentive). There are 8 eggs and 30 slices of bread in the pantry. Thus, you conclude that you will be able to make 24 slices of French toast and not one slice more.

This is a similar situation with chemical reactions in which one of the reactants is used up before the others - the reaction stops as soon as one of the reactants is consumed. For example, in the production of water from hydrogen and oxygen gas suppose we have 10 moles of H_2 and 7 moles of O_2 .



Because the **stoichiometry** of the reaction is such that 1 mol of O_2 $\xrightarrow{\quad}$ 2 moles of H_2 , the number of moles of O_2 needed to react with all of the H_2 is:

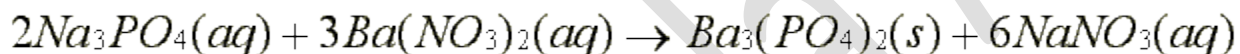
$$\left(\frac{1 \text{ mole } O_2}{2 \text{ moles } H_2} \right) * 10 \text{ moles } H_2 = 5 \text{ moles } O_2$$

Thus, after all the hydrogen reactant has been consumed, there will be 2 moles of O₂ reactant left.

The reactant that is completely consumed in a chemical reaction is called **the limiting reactant** (or **limiting reagent**) because it determines (or limits) the amount of product formed. In the example above, the H₂ is the limiting reactant, and because the stoichiometry is $2\text{H}_2 \xrightarrow{\quad} 2\text{H}_2\text{O}$ (i.e. $\text{H}_2 \xrightarrow{\quad} \text{H}_2\text{O}$), it limits the amount of product formed (H₂O) to 10 moles. We actually have enough oxygen (O₂) to form 14 moles of H₂O ($1\text{O}_2 \xrightarrow{\quad} 2\text{H}_2\text{O}$).

One approach to solving the question of which reactant is the limiting reactant (given an initial amount for each reactant) is to calculate the amount of product that could be formed from each amount of reactant, assuming all other reactants are available in unlimited quantities. In this case, the limiting reactant will be the one that produces the **least** amount of potential product.

Consider the following reaction:



Suppose that a solution containing 3.50 grams of Na₃PO₄ is mixed with a solution containing 6.40 grams of Ba(NO₃)₂. How many grams of Ba₃(PO₄)₂ can be formed?

1. First we need to convert the grams of reactants into **moles**:

$$(3.50 \text{ grams Na}_3\text{PO}_4) * \left(\frac{1 \text{ mole}}{163.94 \text{ grams}} \right) = 0.0213 \text{ moles Na}_3\text{PO}_4$$

$$(6.40 \text{ grams Ba}(\text{NO}_3)_2) * \left(\frac{1 \text{ mole}}{261.34 \text{ grams}} \right) = 0.0245 \text{ moles Ba}(\text{NO}_3)_2$$

2. Now we need to define the stoichiometric ratios between the reactants and the product of interest (Ba₃(PO₄)₂):



3. We can now determine the moles of product that would be formed if reactant were to be consumed in its entirety during the course of the reaction:

$$(0.0213 \text{ moles Na}_3\text{PO}_4) * \left(\frac{\text{Ba}_3(\text{PO}_4)_2}{2 \text{ Na}_3\text{PO}_4} \right) = 0.0107 \text{ moles Ba}_3(\text{PO}_4)_2$$

$$(0.0245 \text{ moles Ba}(\text{NO}_3)_2) * \left(\frac{\text{Ba}_3(\text{PO}_4)_2}{3 \text{ Ba}(\text{NO}_3)_2} \right) = 0.0082 \text{ moles Ba}_3(\text{PO}_4)_2$$

4. The limiting reactant is the $\text{Ba}(\text{NO}_3)_2$ and we could thus make at most 0.0082 moles of the $\text{Ba}_3(\text{PO}_4)_2$ product.

5. 0.0082 moles of the $\text{Ba}_3(\text{PO}_4)_2$ product would be equal to:

$$(0.0082 \text{ moles Ba}_3(\text{PO}_4)_2) * \left(\frac{601.93 \text{ grams}}{1 \text{ mole Ba}_3(\text{PO}_4)_2} \right) = 4.94 \text{ grams}$$

Theoretical yields

The quantity of product that is calculated to form when all of the limiting reactant is consumed in a reaction is called the **theoretical yield**.

The amount of product actually obtained is called the **actual yield**.

Actual yield < Theoretical yield

for the following reasons:

- for some reason not all the reactants may react
- there may be some significant *side reactions*
- physical recovery of 100% of the sample may be impossible (like getting all the peanut butter out of the jar)

The **percent yield** of a reaction relates the actual yield to the theoretical yield:

$$\text{Percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100$$

For example, in the previous exercise we calculated that 4.94 grams of $\text{Ba}_3(\text{PO}_4)_2$ product should be formed. This is the theoretical yield. If the actual yield were 4.02 grams the percent yield would be:

$$\left(\frac{4.02 \text{ grams}}{4.94 \text{ grams}} \right) \times 100 = 81\%$$

4.Aqueous Reactions and Solution Stoichiometry

Water possesses many unusual properties. One of the most important properties of water is its ability to dissolve a wide variety of substances. It may sound strange, but absolutely pure water can be considered corrosive due to its capacity to absorb other compounds and ions.

Solutions in which water is the dissolving medium are called **aqueous solutions**.

Limestone caves, for example, are formed by the dissolving action of water, and dissolved CO₂, on solid Calcium Carbonate. The dissolved mineral is then deposited as stalagmites and stalagmites as the water evaporates:



Many **physiological** chemical reactions occur in aqueous solutions.

How do we express solution composition?

What are the chemical forms in which substances occur in aqueous solutions?

4.1: Solution Composition

A **solution** is a homogenous mixture of two or more substances, consisting of

1. The **solvent** - usually the substance in greater concentration
2. The other component(s) is (are) called the solute(s) - they are said to be **dissolved** in the solvent

When a small amount of NaCl is dissolved in a large quantity of water, we refer to the water as the **solvent** and the NaCl as the **solute**.

Molarity

The term **concentration** is used to indicate the amount of solute dissolved in a given quantity of solvent or solution.

The most widely used way of quantifying concentration in chemistry is **molarity**.

The **molarity** (symbol M) of a solution is defined as the number of **moles** of **solute** in a **liter volume** of **solution**:

$$\text{Molarity} = \frac{\text{moles solute}}{\text{volume solution(liters)}}$$

For example, a 1.0 molar solution (1.0 M) contains 1.00 mol of solute in every liter of solution.

What is the molarity of a solution made by dissolving 20 grams of NaCl in 100 mls of water?

$$20\text{gramsNaCl} * \left(\frac{1\text{mol}}{58.5\text{grams}} \right) = 0.34\text{molesNaCl}$$

$$\left(\frac{0.34\text{molesNaCl}}{0.1\text{liter}} \right) = 3.4\text{moles / liter} = 3.4$$

M solution

If we know the molarity of a solution we can calculate the number of moles of solute in a given volume. Thus, molarity is a conversion factor between volume of solution and moles of solute:

Calculate the number of moles of CaCl₂ in 0.78 liters of a 3.5 M solution:

$$\left(\frac{3.5\text{molesCaCl}_2}{1\text{liter}} \right) * 0.78\text{liters} = 2.73\text{moles}$$

CaCl₂

How many liters of a 2.0 M solution of HNO₃ do we need to have 5 moles of HNO₃?

$$\left(\frac{1\text{liter}}{2\text{moles}} \right) * 5\text{moles} = 2.5\text{liters}$$

Note: we had to invert the stock solution (i.e. convert to liters per mole) to be able to calculate the needed volume (i.e. to keep the dimensional analysis correct)

Dilution

For convenience, solutions are either purchased or prepared in concentrated **stock** solutions which must be **diluted** prior to use.

When we take a sample of a stock solution we have a certain number of **moles** of molecules in that sample. Dilution alters the **molarity** (i.e. *concentration*) of the solution but *not the total number of moles of molecules in the solution* (in other words, dilution does not create or destroy molecules).

One of the standard equations for determining the effects of dilution upon a sample is to set up an equation comparing (*concentration*)*(*volume*) before and after dilution. Since (*concentration*)*(*volume*) gives us the *total number of moles in the sample*, and since this *does not change*, this value before and after dilution are equal:

$$(\text{concentration}) * (\text{volume}) = (\text{concentration}) * (\text{volume})$$

$$(\text{moles/liter}) * (\text{liter}) = (\text{moles/liter}) * (\text{liter})$$

$$\text{moles} = \text{moles}$$

How much of a 5 M stock solution of NaCl will you need to make up 250 mls of a 1.5 M solution?

$$\left(\frac{5\text{moles}}{\text{liter}}\right) * (X \text{ liters}) = \left(\frac{1.5\text{moles}}{\text{liter}}\right) * (0.25 \text{ liters})$$

$$X \text{ liters} = \left(\frac{1.5\text{moles}}{\text{liter}}\right) * (0.25 \text{ liters}) * \left(\frac{\text{liter}}{5\text{moles}}\right)$$

$$X \text{ liters} = \mathbf{0.075 \text{ liters}} \text{ (or 75 mls)}$$

Thus, we would need 0.075 liters of our 5M NaCl stock solution. The rest of the 0.25 liter volume is made up by the addition of water:

$$0.25 \text{ liters} - 0.075 \text{ liters} = 0.175 \text{ liters}$$

So we would take 0.075 liters of stock 5M NaCl solution and add to that 0.175 liters of water for a final volume of 0.25 liters with a final concentration of 1.5 moles/liter (i.e. 1.5 M)

What is the concentration of water?

Molecular weight of H₂O = 18.0g/mole

Density of H₂O = 1g/ml or 1000g/L

$$\left(\frac{1\text{mole}}{18.0\text{g}}\right) * \left(\frac{1000\text{g}}{\text{L}}\right) = 55.6M$$

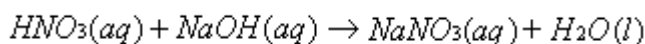
Pure water is 55.6M H₂O

4.2: Solution Stoichiometry

For balanced chemical equations involving solutions we calculate the number of moles by knowing the concentration (moles/liter, or **Molarity**) and volume (in **liters**).

How many moles of water form when 25.0 mls of 0.100 M HNO₃ (nitric acid) solution is completely neutralized by NaOH (a base)?

1. Let's begin by writing the balanced equation for the reaction:



2. The stoichiometric relationship between HNO_3 and H_2O is $\text{HNO}_3 \rightarrow \text{H}_2\text{O}$, therefore, for one mole of HNO_3 that is completely consumed (i.e. neutralized) in the reaction, one mole of H_2O is produced.

3. How many moles of HNO_3 are we starting with?

$$(.025\text{liters}) * \left(\frac{0.100\text{moles}}{\text{liter}} \right) = 0.0025\text{moles} \quad \text{HNO}_3$$

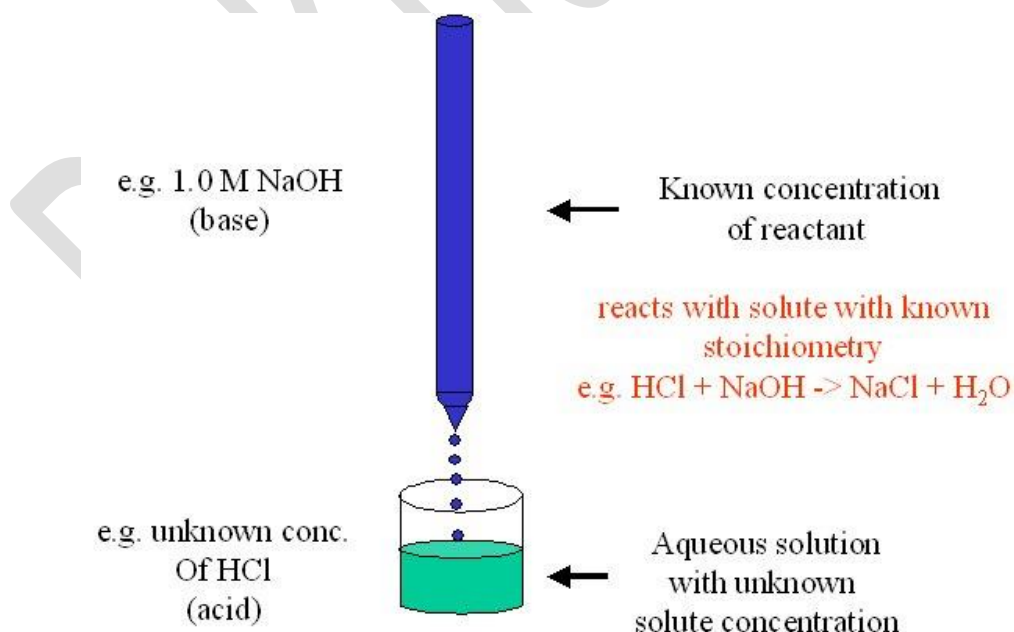
4. Therefore, we should have **0.0025 moles of H_2O** produced

Titration

How can we know the concentration of some solution of interest? One answer to this problem lies in the method of **titration**. In titration we will make use of a **second solution** known as a **standard solution** which has the following characteristics:

1. The second solution contains a chemical which reacts in a defined way, with **known stoichiometry**, with the solute of the first solution
2. The **concentration** of the solute in this second solution is **known**.

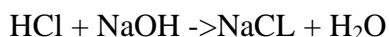
Classic titrations include so-called **acid-base** titrations. In these experiments a solution of an acid with an unknown concentration is titrated with a solution of known concentration of base (or *vice versa*). For example, we may have a solution of hydrochloric acid (HCl) of unknown concentration and a standard solution of NaOH . To a fixed amount of the HCl solution is added incremental amounts of the NaOH solution until the acid is completely neutralized - i.e. a stoichiometrically equivalent quantity of HCl and NaOH have been combined. This is known as the **equivalence point** in the titration. By knowing the concentration of the standard solution, and the amount added to achieve stoichiometric equivalency, we can determine the amount of moles of HCl in the original sample volume.



How do we know when we have reached the equivalence point in such a titration experiment? In this type of acid-base titration, so called **indicator-dyes** are used. For example **phenolphthalein** is **colorless in acidic solutions** and turns **red in basic solutions**. Thus, in the above experiment we will add a small amount of this indicator-dye and add base until we barely begin to see a color change to red.

25 ml of a solution of HCl with an unknown concentration is titrated with a standard solution of 0.5 M NaOH. The phenolphthalein indicator dye begins to turn color after the addition of 2.8 ml of standard solution. What is the concentration of the HCl?

Balanced equation for the reaction:



$$(0.0028 \text{ liters}) * \left(\frac{0.5 \text{ moles}}{\text{liter}} \right) = 0.0014 \text{ moles}$$

of NaOH was added

Since the stoichiometry of the NaOH and HCl is 1:1, the sample of HCl must have contained 0.0014 moles of HCl. The concentration of the HCl solution is therefore:

$$\left(\frac{0.0014 \text{ moles HCl}}{0.025 \text{ liters}} \right) = 0.056 \text{ moles/liter}$$

, or 0.056 M

5. Energy Relations in Chemistry: Thermochemistry

5.1: The Nature of Energy

5.2: Heat and Enthalpy Changes

5.3: Calorimetry

5.4: Hess's Law

5.5: Enthalpies of Formation

5.6: Foods and Fuels

5. Energy Relations in Chemistry: Thermochemistry

Sugar you eat is "combusted" by your body to produce CO₂ and H₂O. During this process *energy is also released*.

This energy is used (among other things) to:

- Operate your muscles
- Maintain your body temperature

Chemical reactions involve changes in energy:

- Some reactions produce energy
- Some reactions require energy

Our society as an "organism" requires energy: 90% of our energy comes from chemical reactions involving the combustion of petroleum products.

The study of energy and its transformations is known as *thermodynamics*

This area of study began when steam engines were developed during the industrial revolution and the relationships between *heat*, *work* and *energy* for different fuels was being studied.

The relationship between chemical reactions and energy changes is known as *thermochemistry*

5.1: The Nature of Energy

A *Force* is any kind of push or pull exerted on an object.

- *Gravity* is a force which keeps us stuck to the earth.
- The *Electrostatic force* attracts electrons to protons in an atom.

If you *move* an object against some *force*, *work* is being done.

The amount of work (*w*) being done is relative to the *distance* (*d*) the object is moved and the strength of the *force* (*F*) against the object:

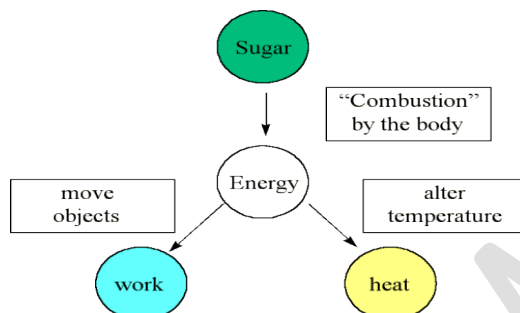
$$w = F * d$$

Energy, in the form of work, must be used to move an object against a force.

When we do work, our body temperature increases (and we sweat to cool us down). Our bodies are generating *Heat* energy.

Heat is an energy which is transferred from one object to another depending on the relative temperature:

- Heat energy flows from an object towards other objects of lower temperature



Energy is the capacity to do work or to transfer heat

Objects can possess energy due to their ***motions*** and ***positions***, as ***kinetic energy*** and ***potential energy***.

Kinetic and Potential Energy

Kinetic energy is the energy of ***motion***. The magnitude of the kinetic energy (E_k) of an object depends upon its mass (m) and velocity (v):

$$E_k = \frac{1}{2}mv^2$$

In other words, both the mass and the speed of an object determines how much energy it has, and thus, how much work it can accomplish.

An object can also possess energy based upon its position relative to other objects - a type of stored up energy, or "***potential energy***"

Potential energy is the result of the attractions and repulsion between objects. An electron has potential energy when located near a proton due to the attractive electrostatic force between them.

Chemical and ***thermal*** energy are terms which relate to potential and kinetic energy at the atomic level

- Chemical energy is the potential energy stored in the arrangement of electrons and protons
- Thermal energy reflects the kinetic energy of the molecules of a substance.

Energy Units

The SI unit for energy is the ***joule*** ("J"). In honor of James Prescott Joule (1818-1889) a British Scientist who investigated work and heat. (Note: SI is short for the French term *Systeme International d'Unites*. Which defines metric standards). Kinetic energy for example is defined as:

$$E_k = \frac{1}{2}mv^2$$

Thus, the joule must have units of:

$$kg \cdot (meters/second)^2$$

and, in fact, 1 joule is defined as:

$$1 \text{ Joule} = \frac{1 kg \cdot m^2}{s^2}$$

Traditionally, energy changes accompanying chemical reactions have been expressed in *calories*, which is a non-SI unit (though still widely used).

$$1 \text{ calorie} = 4.184 \text{ J}$$

Systems and surrounding

When we focus on a study of energy changes we look at a small, well defined and isolated part of the universe - the flask or container the reactants are in. This is called the *system*.

Everything else is called the *surroundings*.

Usually the system is isolated from its surroundings such that there will be an exchange of energy between system and surroundings, but not matter.

Thus, the system will contain the same *mass* after an experiment, but the system can lose or gain *energy* (in the form of *heat*, *work*, or *both*).

Lowering the energy of the system

Systems tend to attain as low an energy as possible

Systems with a high potential energy are less stable and more likely to undergo change than systems with a low potential energy.

Like a shopping cart at the top of a hill, *chemical reactants move spontaneously toward a lower potential energy when possible*.

5.2: Heat and Enthalpy Changes

When a chemical reaction occurs in an *open* container most of the energy gained or lost is in the form of *heat*. Almost no *work* is done (i.e. nothing is being moved).

Heat flows between the system and surroundings until the two are at the same temperature.

- When a chemical reaction occurs in which the system absorbs heat, the process is *endothermic* (it feels cold)
- When a chemical reaction occurs in which the system produces heat it is *exothermic* (it feels hot)

Enthalpy

Under conditions of *constant pressure* (e.g. most biological processes under constant atmospheric pressure) the heat absorbed or released is termed **enthalpy** (or "heat content").

We do not measure enthalpy *directly*, rather we are concerned about **the heat added or lost** by the system, which is the *change* in enthalpy (or ΔH).

In formal terms: *The change in enthalpy, ΔH , equals the heat, q_p , added to or lost by the system when the process occurs under constant pressure:*

$$\Delta H = q_p$$

ΔH represents the difference between the enthalpy of the system at the beginning of the reaction compared to what it is at the end of the reaction:

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

We are considering the enthalpic state of the **system**. Thus:

- if the **system** has higher enthalpy at the end of the reaction, then it **absorbed** heat from the surroundings (**endothermic** reaction)
- if the system has a lower enthalpy at the end of the reaction, then it **gave off heat** during the reaction (**exothermic** reaction)

Therefore:

- For **endothermic** reactions $H_{\text{final}} > H_{\text{initial}}$ and ΔH is **positive** ($+\Delta H$)
- For **exothermic** reactions $H_{\text{final}} < H_{\text{initial}}$ and ΔH is **negative** ($-\Delta H$)

Enthalpies of Reaction

Because the enthalpy change for a reaction is described by the final and initial enthalpies:

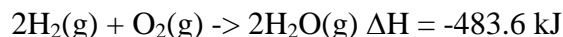
$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

we can also describe ΔH for a reaction by comparing the enthalpies of the products and the reactants:

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

The enthalpy change that accompanies a reaction is called **the enthalpy of reaction** (ΔH_{rxn}).

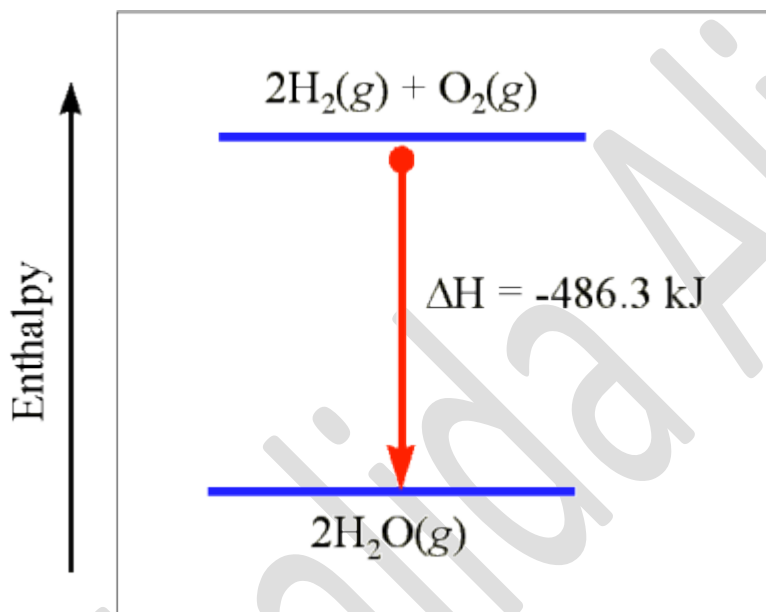
It is sometimes convenient to provide the value for ΔH_{rxn} along with the balanced chemical equation for a reaction (also known as a **thermochemical equation**):



Note the following:

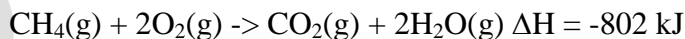
- ΔH is negative, indicating that this reaction results in the release of heat (exothermic)
- The reaction gives of 483.6 **kilo Joules** of energy when **2 moles** of H_2 combine with **1 mole** of O_2 to produce **2 moles** of H_2O .

The relative enthalpies of the reactants and products can also be shown on an **energy diagram**:



Properties of enthalpy:

1. Enthalpy is an **extensive** property. The magnitude of ΔH is dependent upon the amounts of reactants consumed. Doubling the reactants, doubles the amount of enthalpy.
2. Reversing a chemical reaction results in the same magnitude of enthalpy but of the **opposite sign**. For example, splitting two moles of water to produce 2 moles of H_2 and 1 mole of O_2 gas requires the **input** of +483.6 kJ of energy.
3. The enthalpy change for a reaction depends upon the state of the reactants and products. The states (i.e. *g*, *l*, *s* or *aq*) must be specified.



Given the above thermochemical equation for the combustion of methane, how much heat energy is released when 4.5 grams of methane is burned (in a constant pressure system)?

$$(4.5gCH_4) * \left(\frac{1\text{mole}}{16.003g} \right) = 0.281\text{moles}$$

$$(0.281 \text{ moles } CH_4) * \left(\frac{-802 \text{ kJ}}{1 \text{ mole } CH_4} \right) = -225.5 \text{ kJ}$$

The negative sign (exothermic) indicates that 225.5 kJ of energy are given off by the system into the surroundings.

5.3: Calorimetry

Experimentally, we can determine the heat flow (ΔH_{rxn}) associated with a chemical reaction by *measuring the temperature change it produces*.

- The measurement of heat flow is called **calorimetry**
- An apparatus that measures heat flow is called a **calorimeter**

Heat capacity and specific heat

The temperature change experienced by an object when it absorbs a certain amount of energy is determined by its **heat capacity**.

- The **heat capacity** of an object is defined as ***the amount of heat energy required to raise its temperature by 1 K (or °C)***
- The greater the heat capacity of an object, the more heat energy is required to raise the temperature of the object

For pure substances the heat capacity is usually given for a specified amount of the substance

- The heat capacity of 1 mol of a substance is called its **molar heat capacity**
- The heat capacity of 1 gram of a substance is called its **specific heat**

The specific heat of a substance can be determined experimentally by measuring the temperature change (ΔT) that a known mass (m) of the substance undergoes when it gains or loses a specific quantity of heat (q):

$$\text{Specific heat} = \frac{q}{m * \Delta T}$$

209 J of energy are required to increase the temperature of 50.0 g of water by 1.00 K. What is the specific heat of water?

$$\text{Specific heat} = \frac{209 \text{ J}}{(50 \text{ g}) * (1.00 ^\circ \text{K})}$$

$$\text{Specific heat} = 4.18 \text{ J g}^{-1} \text{ } ^\circ \text{K}^{-1}$$

Specific heat values of some substances ($\text{J g}^{-1}\text{K}^{-1}$)

Al (s)	0.90	CaCO_3 (s)	0.85
C (s)	0.71	CCl_4 (l)	0.86
Fe (s)	0.45	H_2O (l)	4.18
Hg (l)	0.14		

We can calculate the quantity of heat that a substance has gained or lost by using its specific heat together with its measured mass and temperature change:

$$\text{Specific heat} = \frac{\text{quantity of heat transferred}}{(\text{grams of substance}) * (\text{temperature change})}$$

rearrange:

$$\text{quantity of heat transferred} = (\text{Specific heat}) * (\text{grams}) * (\Delta T)$$

How much heat is required to raise the temperature of 250g of water from 22°C to 98°C ? (specific heat of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$).

$$q = (4.18 \text{ J g}^{-1} \text{ K}^{-1}) * (250\text{g}) * (371 - 295 \text{ K})$$

$$q = \mathbf{79,420 \text{ J}} \text{ (79.420 kJ, or } 7.942 \times 10^4 \text{ J)}$$

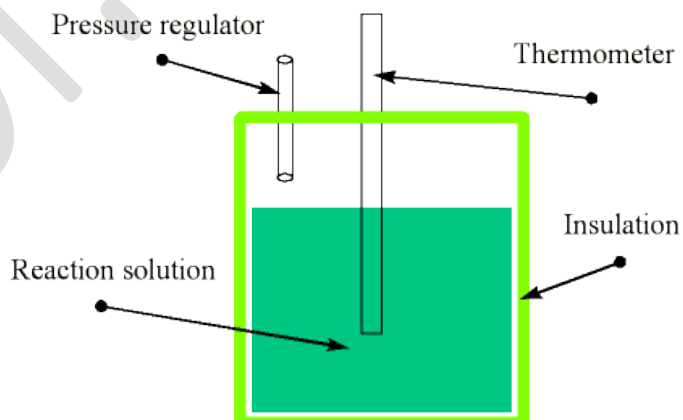
What is the molar heat capacity of water?

$$\begin{aligned} \text{Molar heat capacity} &= 4.18 \text{ J g}^{-1} \text{ K}^{-1} * (18 \text{ grams}/1.0 \text{ mole}) \\ &= 75.2 \text{ J mole}^{-1} \text{ K}^{-1} \end{aligned}$$

Constant-Pressure Calorimetry

Recall that ΔH is defined as the quantity of heat transferred under constant pressure ($\Delta H = q_p$).

A calorimeter for such measurements would have the following general construction:



Note that the pressure regulator could be just a vent to allow the pressure to be maintained at atmospheric pressure

- For reactions which involve dilute aqueous solutions, the specific heat of the solution will be approximately that of water ($4.18 \text{ J g}^{-1} \text{ K}^{-1}$)
- The heat absorbed by an aqueous solvent is equal to the heat given off by the reaction of the solutes:

$$q_{\text{aq solvent}} = -q_{\text{rxn}}$$

Remember: If a reaction gives off heat, it is *exothermic* and ΔH is *negative*. The enthalpy of the products is less than the enthalpy of the reactants

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

In our calorimeter with an aqueous solution, if the reaction of the solutes is exothermic, the solution will absorb this heat and *increase* in temperature.

Thus, for an exothermic reaction:

- The solutes have a lower final enthalpy after the reaction (ΔH negative)
- The solution has a higher final enthalpy after the reaction (ΔH positive)

So, to determine the actual ΔH_{rxn} we would *invert the sign* of the ΔH_{soln} (the actual value we will measure)

50 ml of 1.0 M HCl and 50 ml of NaOH are combined in a constant pressure calorimeter. The temperature of the *solution* is observed to rise from 21.0°C to 27.5°C . Calculate the enthalpy change for the *reaction* (assume density is 1.0 gram/ml, and that the specific heat of the solution is that of water).

$$\Delta T_{\text{solution}} = 27.5 - 21.0^\circ\text{C} = 6.5^\circ\text{C} (\text{K})$$

$$\text{specific heat} = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\text{mass} = (100 \text{ ml}) \cdot (1 \text{ gram/ml}) = 100 \text{ grams}$$

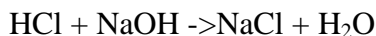
$$\Delta H_{\text{solution}} = q_p = (4.18 \text{ J g}^{-1} \text{ K}^{-1}) \cdot (100 \text{ g}) \cdot (6.5 \text{ K}) = 2,717 \text{ J}$$

We know that $\Delta H_{\text{rxn}} = -\Delta H_{\text{solution}}$ therefore,

$$\Delta H_{\text{rxn}} = -2,717 \text{ J}$$

Note: exothermic reactions have *negative* values for ΔH_{rxn} thus, if the reaction gave off heat (i.e. raised the temperature of the solution) you know that the sign for ΔH_{rxn} **must be negative**.

What is the enthalpy change on a molar basis?



This is the balanced equation, and we combined:

$$(0.05 \text{ liters HCl}) \cdot (1.0 \text{ mol/liter}) = 0.05 \text{ moles HCl}$$

and

$$(0.050 \text{ liters NaOH}) \cdot (1.0 \text{ mol/liter}) = 0.05 \text{ moles NaOH}$$

The stoichiometry for HCl and NaOH in this reaction is 1:1, so they are combining in stoichiometrically equivalent amounts and will produce 0.05 moles of NaCl (and H₂O).

So, the enthalpy change for the production of 0.05 moles of NaCl in the above reaction would be:

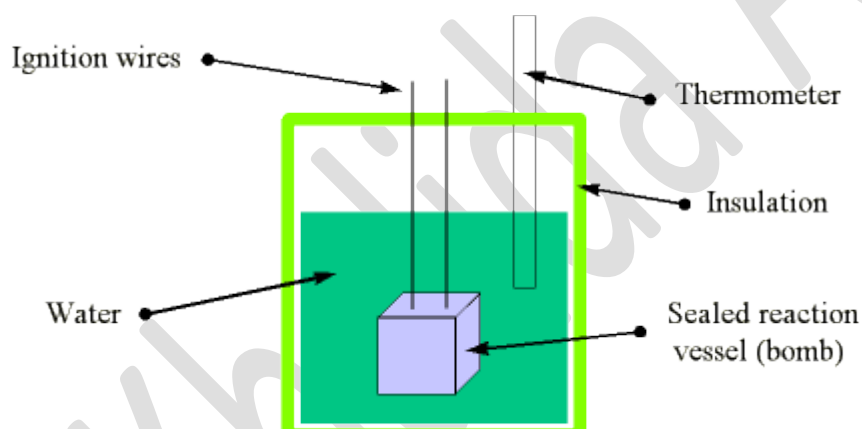
$$\begin{aligned} & -2717 \text{ J for each 0.05 moles NaCl, or} \\ & -2717 \text{ J}/0.05 \text{ moles} = 54,340 \text{ J/mole} = 54.34 \text{ kJ/mole} \end{aligned}$$

Bomb Calorimetry (constant-volume calorimetry)

Since combustion reactions involve dramatic increases in pressure, they are typically studied under conditions of **constant volume** in a device known as a **bomb calorimeter**.

The bomb calorimeter is essentially a **sealed** insulated instrument with no pressure regulation.

The sealed reaction chamber is surrounded by water, and the energy released, or absorbed, by the sample is measured indirectly by monitoring the temperature change of the water.



Analyses under constant volume allow determination of ΔE (energy change at constant volume), not ΔH (energy change at constant pressure).

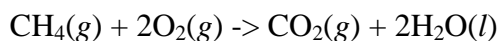
5.4: Hess's Law

It is often possible to **calculate** ΔH for a reaction from listed ΔH values of **other reactions** (i.e. you can avoid having to do an experiment)

Enthalpy is a **state function**

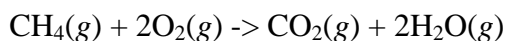
- It depends only upon the **initial and final state** of the reactants/products and **not on the specific pathway** taken to get from the reactants to the products
- Whether one can arrive at the products via either a single step or multi-step mechanism is unimportant as far as the enthalpy of reaction is concerned - they should be equal

Consider the combustion reaction of methane to form CO₂ and **liquid** H₂O

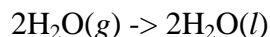


This reaction can be thought of as occurring in two steps:

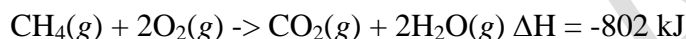
- In the first step methane is combusted to produce water vapor:



- In the second step water vapor condenses from the gas phase to the liquid phase:



Each of these reactions is associated with a specific enthalpy change:



(Note: under conditions of standard temperature and pressure the liquid state of water is the normal state. Thus, the gas would be expected to condense. This is an exothermic process under these conditions. In a related process, it should get warmer when it rains)

Combining these equations yields the following:



$$\Delta H = (-802) \text{ kJ} + (-88) \text{ kJ} = -890 \text{ kJ}$$

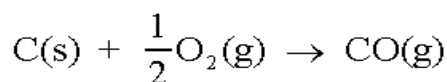
Hess's Law

if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps

*the overall enthalpy change for the process is **independent** of the **number of steps** or the particular nature of the **path** by which the reaction is carried out.*

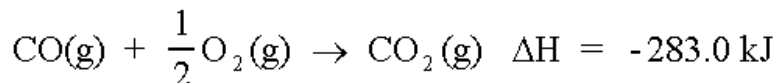
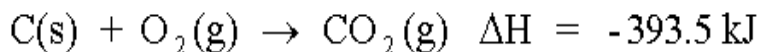
Thus we can use information tabulated for a relatively small number of reactions to calculate ΔH for a large number of different reactions

Determining ΔH for the reaction

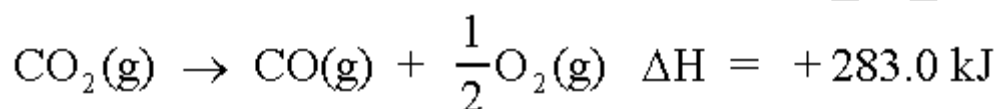


is difficult because some CO_2 is also typically produced.

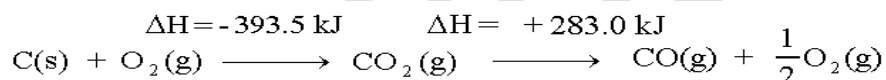
However, complete oxidation of either C or CO to yield CO₂ is experimentally pretty easy to do:



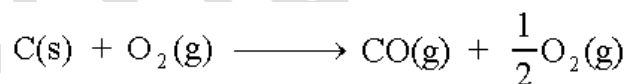
We can invert reaction number 2 (making it *endothermic*) and have CO(g) as a **product**. (This describes the decomposition of CO₂ to produce CO and O₂)



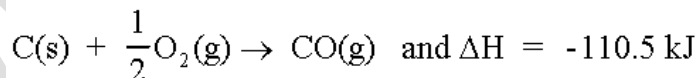
Thus, we now have two equations with known enthalpies of reaction: the first describes the combustion of carbon and oxygen to produce CO₂ and the second describes how CO₂ can be decomposed to produce carbon monoxide (and oxygen). We can combine these together to describe the production of carbon monoxide from the combustion of carbon and oxygen:



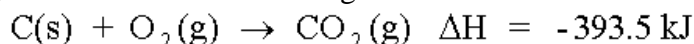
The overall reaction, going from left-hand side reactant(s) to the right-hand side product(s) would be:



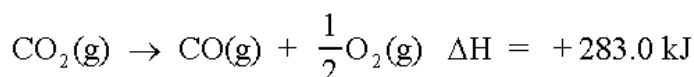
We can algebraically subtract the one-half O₂ from both sides to yield the following equation with the associated overall enthalpy:



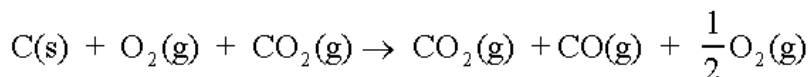
Another way to look at the method of combining reactions would be as follows:



plus

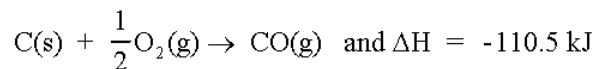


gives:

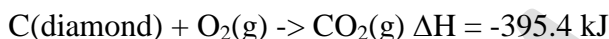
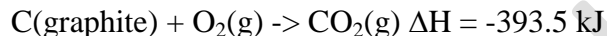


$$\Delta H = (-393.5 \text{ kJ}) + (283.0 \text{ kJ}) = -110.5 \text{ kJ}$$

canceling out identical compounds from the left and right hand sides of this reaction gives

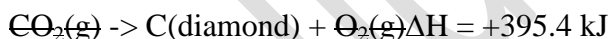
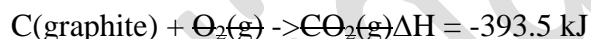
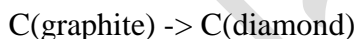


Carbon occurs in two forms: graphite and diamond. The enthalpy of combustion of graphite is -393.5 kJ, and that of diamond is -395.4 kJ



Calculate ΔH for the conversion of graphite to diamond

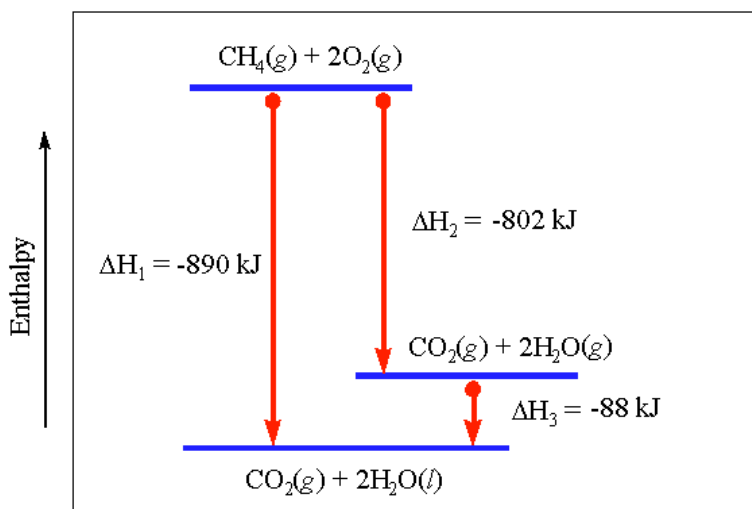
What we want is ΔH for the reaction:



We can never expect to obtain more or less energy from a chemical reaction by changing the method of carrying out the reaction ("conservation of energy").

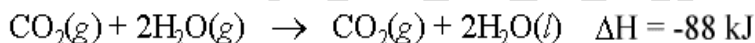
Another way of saying this is that the particular pathway chosen to arrive at the same reactants yields the same ΔH for the overall reaction.

Consider the previous example of the combustion of methane to produce gaseous H_2O and then the condensation of the gaseous H_2O to the liquid state. How is this represented in an **Enthalpy Diagram**?

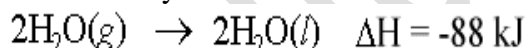


The key features are the following:

1. Each line represents a set of reactants or products for a **balanced** chemical reaction. When going from one line to another, the atoms must balance. For example, if we were to ask what is the enthalpy associated with the condensation of water we would have (from the above data):



The $\text{CO}_2(\text{g})$ on both sides will cancel to yield:



2. The relative distance of each line must reflect the relative enthalpy difference (ΔH) between the reactants/products. If the enthalpy change in going from reactants to products is negative, then the line for the products must be below the reactants. Furthermore, the length of the distance must be proportional. For example, the distance reflecting the enthalpy associated with the condensation of water ($\Delta H = -88 \text{ kJ}$) is only about 10% as long as the distance between the reactants and products for the combustion of methane to CO_2 and liquid water ($\Delta H = -890 \text{ kJ}$)

5.5: Enthalpies of Formation

Using Hess's Law we can calculate reaction enthalpies for a variety of reactions using tables of known enthalpies

Many experimentally determined enthalpies are listed by *the type of process*

- ΔH for converting various *liquids to the gas phase* are listed in tables of *enthalpies of vaporization*
- ΔH for *melting solids to liquids* are listed in tables of *enthalpies of fusion*
- ΔH for *combusting a substance in oxygen* are listed in tables of *enthalpies of combustion*

The enthalpy change associated with the formation of a compound from its constituent elements is called the **enthalpy of formation** (ΔH_f)

Conditions which influence enthalpy changes include:

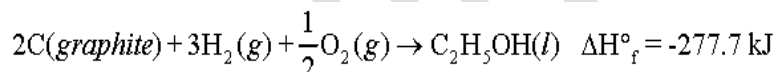
- temperature
- pressure
- state of reactants and products (*s, g, l, aq*)

The **standard state** of a substance is the form most stable at 298 °K (25 °C, or standard "room temperature") and 1 atmosphere (1 atm) of pressure

When a reaction occurs with all reactants and products in their standard states, the enthalpy change is **the standard enthalpy of reaction** (ΔH°)

Thus, **the standard enthalpy of formation** (ΔH_f°) of a compound is the change in enthalpy that accompanies the **formation of 1 mole** of that substance from its elements, with all substances in their **standard states**

The standard enthalpy of formation for ethanol (C₂H₅OH) is the enthalpy change for the following reaction



Notes:

- Elemental source of oxygen is O₂ and not O because O₂ is the stable form of oxygen at 25 °C and 1 atm, likewise with H₂
- Elemental source of carbon is specified as *graphite* (and not, for example, diamond) because graphite is the lowest energy form of carbon at room temp and 1 atm
- Why is the O₂ stoichiometry left at "1/2"? The stoichiometry of formation reactions *always indicates the formation of 1 mol of product*. Thus, ΔH_f° values are reported as kJ / mole of the substance produced

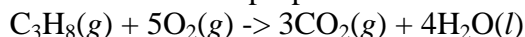
If C(*graphite*) is the lowest energy form of carbon under standard conditions, then what is the ΔH_f° for C(*graphite*)?

- By definition, *the standard enthalpy of formation of the most stable form of any element is zero* because there is no formation reaction needed when the element is *already* in its standard state
- ΔH_f° for C(*graphite*), H₂(g) and O₂(g) = 0

Using enthalpies of formation (ΔH_f°) to calculate enthalpies of reaction under standard conditions ($\Delta H_{\text{rxn}}^\circ$)

We can determine the standard enthalpy change for any reaction (ΔH°_{rxn}) by using standard enthalpies of formation (ΔH°_f) and Hess's Law

Consider the following combustion reaction of propane:

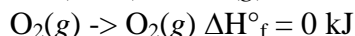


The reactants:

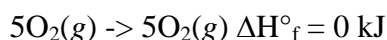
- The standard heat of formation (ΔH°_f) of propane gas from its elemental constituents in the standard state is 103.85 kJ/mole



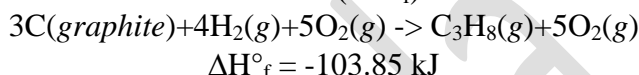
- The standard heat of formation (ΔH°_f) for $\text{O}_2(g)$ is zero



and so...



Overall, therefore, the standard heat of formation (ΔH°_f) for the reactants is:



The products:

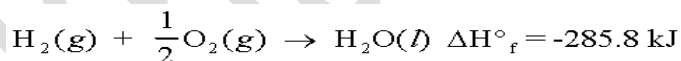
- The standard heat of formation (ΔH°_f) of $\text{CO}_2(g)$ from its elemental constituents in the standard state is 393.5 kJ/mole



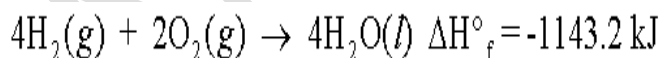
so, for 3 moles of CO_2 molecules the standard heat of formation would be:



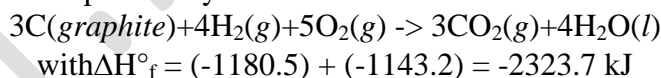
- The standard heat of formation (ΔH°_f) of $\text{H}_2\text{O}(l)$ from its elemental constituents in the standard state is 285.8 kJ/mole



and so the ΔH°_f for 4 waters would be:

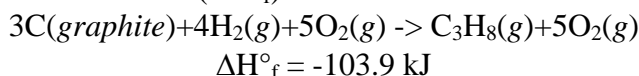


combining the ΔH°_f for both products yields:

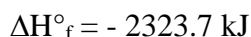
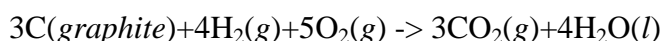


Let's summarize what we have determined so far:

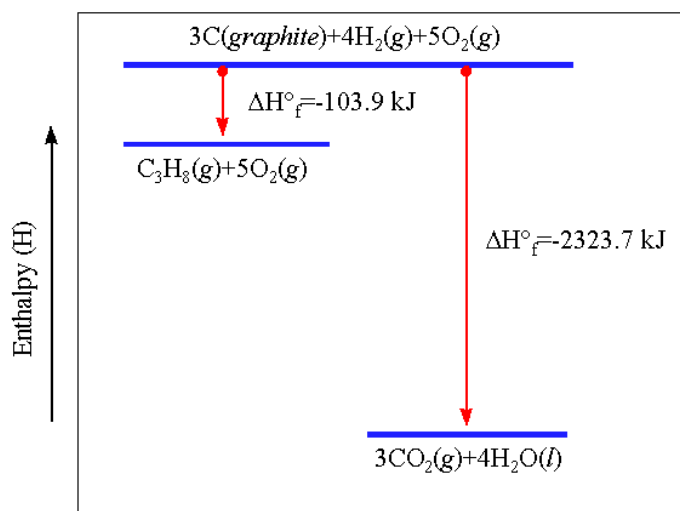
Overall the standard heat of formation (ΔH°_f) for **the reactants** is:



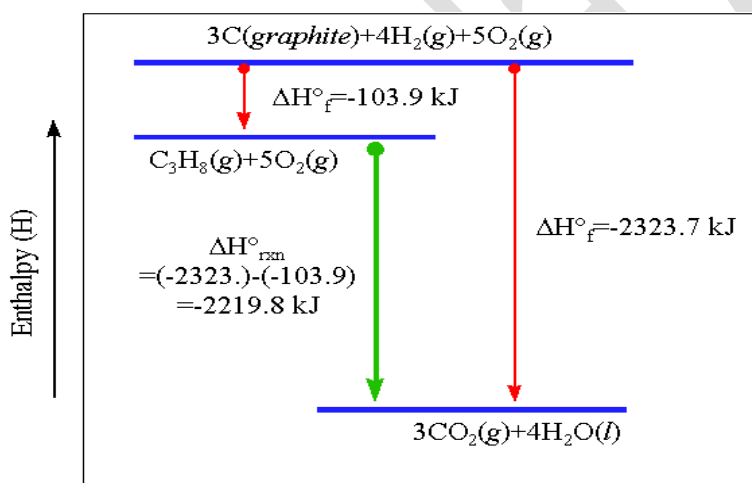
Overall the standard heat of formation (ΔH°_f) for **the products** is:



Lets plot these on a relative scale of enthalpy:

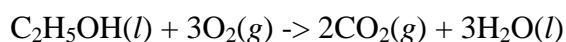


This information can be used to determine the relative enthalpy difference under standard conditions (ΔH°) between the reactants and products:

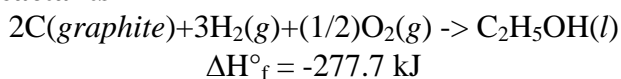


This enthalpy difference (-2219.8 kJ) is the enthalpy of the reaction for the combustion of propane under standard conditions ($\Delta H^\circ_{\text{rxn}}$)

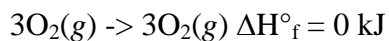
Calculate the enthalpy change ($\Delta H^\circ_{\text{rxn}}$) for the combustion of 1 mol of ethanol



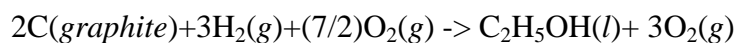
heat of formation for reactants



plus



gives:

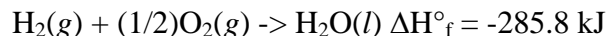
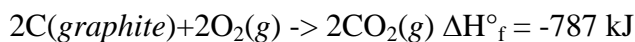


$$\Delta H^{\circ}_f = -277.7 \text{ kJ}$$

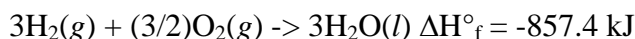
heat of formation for products



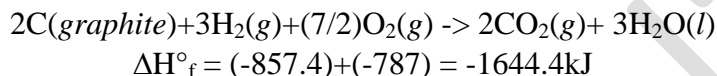
therefore



therefore



combining gives:



$\Delta H^{\circ}_{\text{rxn}}$

$$\Delta H^{\circ}_{\text{rxn}} = \Delta H^{\circ}_f (\text{products}) - \Delta H^{\circ}_f (\text{reactants})$$

$$(-1644.4) - (-277.7) = \mathbf{-1366.7 \text{ kJ}}$$

5.6: Foods and Fuels

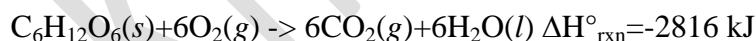
The energy released when 1 gram of material is combusted is called its *fuel value*

Note: since all heats of combustion are exothermic it is customary to leave off the negative sign when reporting fuel values.

Foods

Most of the energy our body needs comes from fats and carbohydrates.

Carbohydrates are broken down in the intestines to glucose. Glucose is transported in the blood to cells where it is oxidized to produce CO_2 , H_2O and energy:



The breakdown of *fats* also produces CO_2 and H_2O

Any excess energy in the body is *stored as fats*

- Insoluble in water so they can be separated and stored in the body
- They produce more energy per gram than carbohydrates or proteins

Compound	Fuel Value (kJ/gram)
Fats	38
Carbohydrates	17
Proteins	17

About 100 kJ per kilogram of body weight per day is required to keep the body functioning at a minimum level

Exercise

- Light exercise burns up about 800 kJ/hour of energy
- Heavy exercise burns up about 2000 kJ/hour

Fuels

Different types of fuels contain varying amounts of carbon, hydrogen and oxygen.

The greater the percentage of carbon and hydrogen in the fuel the higher the fuel value

Fuel	C (%)	H (%)	O (%)	Fuel Value (kJ/g)
Wood	50	6	44	18
Bituminous Coal	77	5	7	32
Gasoline	85	15	0	48
Hydrogen	0	100	0	142

The average daily consumption of energy per person in the U.S. is about 8.8×10^5 kJ, or about 100 times greater than our food energy requirements

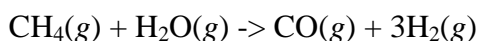
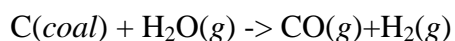
Our energy comes primarily from the combustion of **fossil fuels** (hydrocarbons derived from ancient plants and animals)

Coal represents 90% of the fossil fuels on earth. However, it typically contains sulfur, which when combusted can lead to environmental pollution (acid rain)

Solar energy: on a clear day the sun's energy which strikes the earth equals 1kJ per square meter per second.

If we could utilize the solar energy which strikes 0.1% of the U.S. land mass we would have enough power to run the country

Hydrogen: clean burning (produces only water) and high fuel value. Hydrogen can be made from coal as well as methane



6. Electronic Structure of Atoms**6.1: The Wave Nature of Light****6.2: Quantum Effects and Photons****6.3: Bohr's Model of the Hydrogen Atom****6.4: The Dual Nature of the Electron****6.5: Quantum Mechanics and Atomic Orbitals****6.6: Representations of Orbitals****6.7: Orbitals in Many-electron Atoms****6.8: Electron Configurations****6.9: Electron Configurations and the Periodic Table**

6. Electronic Structure of Atoms

Electrons hold the key to understanding why substances behave as they do. *When atoms react it is their outer parts, their electrons, that interact.*

We refer to the arrangements of electrons in atoms as *their electronic structure*.

- Number of electrons
- Where they can be found
- The energies they possess

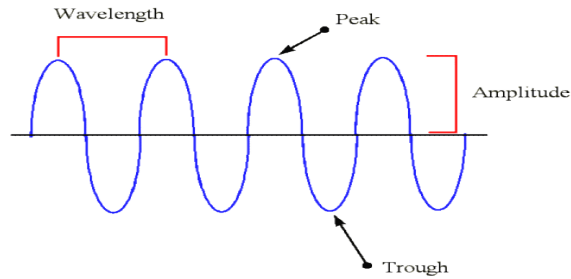
Be warned!: *electrons do not behave like anything we are familiar with in the macroscopic world*

6.1: The Wave Nature of Light

Much of our present understanding of the electronic structure of atoms has come from *analysis of the light emitted or absorbed* by substances

Electromagnetic radiation

- Carries energy through space (also known as radiant energy)
- Includes visible light, dental x-rays, radio waves, heat radiation from a fireplace
- Share certain fundamental characteristics
- All move through a vacuum at 3.00×10^8 m/s ("speed of light")
- Have "wave-like" characteristics



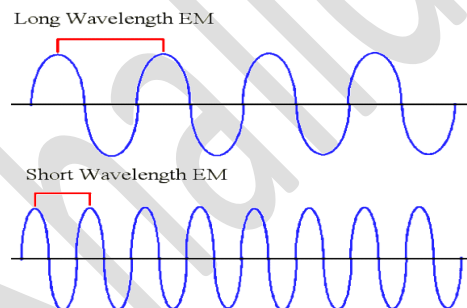
- The number of complete wavelengths, or *cycles*, that pass a given point in 1 second is the **frequency** of the wave

(frequency=cycles/second)

Electromagnetic radiation has both *electric* and *magnetic* properties. The wave-like property of electromagnetic radiation is due to the periodic oscillations of these components.

We can assign a *frequency* and a *wavelength* to electromagnetic radiation

Because all electromagnetic radiation moves at the same speed (speed of light) *wavelength and frequency are related*



- If the *wavelength is long*, there will be fewer cycles passing a given point per second, thus *the frequency will be low*
- If the *wavelength is short*, there will be more cycles passing a given point per second, and the *frequency will be high*
- Thus, there is an *inverse relationship between wavelength and frequency*

$$\text{frequency} = \left(\frac{1}{\text{wavelength}} \right) * \text{speed of light}$$

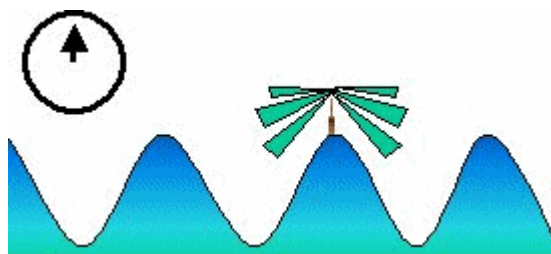
$$\nu = \left(\frac{1}{\lambda} \right) * c$$

$$\nu \lambda = c$$

- (frequency [nu] * wavelength[lambda]) is a constant (c)

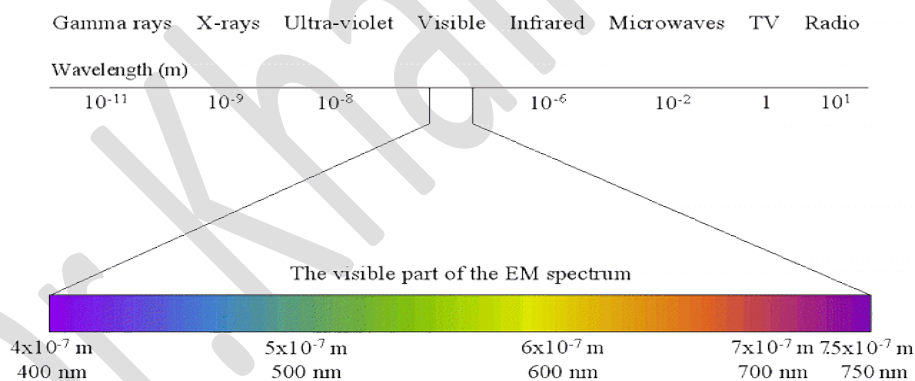
What is the speed of a wave?

Imagine you are on the beach watching the ocean waves go by, and you want to know the speed of the waves. There is an island offshore with a palm tree that will serve as a convenient frame of reference. You count the number of waves that pass by the tree in one minute:



In this case, two peaks (two wavelengths) pass by the tree in one minute. Thus, the frequency is 2 wavelengths/minute. If we measure the distance between the peaks (i.e. the wavelength) we can determine the speed of the wave:

$$\begin{aligned}\text{Speed of the wave} &= (\text{distance between peaks}) * (\text{frequency}) \\ &= (\text{wavelength}) * (\text{frequency})\end{aligned}$$



The unit of length chosen to describe a particular wavelength is typically dependent on the type of electromagnetic radiation

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X-ray
Nanometer	Nm	10^{-9}	UV, visible
Micrometer	M	10^{-6}	Infrared
Millimeter	Mm	10^{-3}	Infrared
Centimeter	Cm	10^{-2}	Microwave
Meter	M	1	TV, radio

The range of EM wavelengths is dramatic

- The wavelengths of *gamma-rays* ($<0.1 \text{ \AA}$) are similar to the diameter of *atomic nuclei*
- The wavelengths of some *radio waves* can be larger than a *football field*

Frequency

- Frequency is expressed in *cycles per second*, also known as **hertz (Hz)**
- Usually the dimension 'cycles' is omitted and *frequencies thus have the dimension of s^{-1}*

Sodium vapor lamps are sometimes used for public lighting. They give off a yellowish light with a wavelength of 589 nm. What is the frequency of this radiation?

$$\begin{aligned}\text{frequency} \times \text{wavelength} &= \text{speed of light} \\ \text{frequency} &= \text{speed of light} / \text{wavelength} \\ &= (3.00 \times 10^8 \text{ m/s}) / (589 \times 10^{-9} \text{ m}) \\ &= 5.09 \times 10^{14} \text{ s}^{-1} \\ &= 5.09 \times 10^{14} \text{ cycles per second or } \mathbf{5.09 \times 10^{14} \text{ hertz}}\end{aligned}$$

6.1: Quantum Effects and Photons

What's the difference between a "red hot" poker and a "white hot" poker?

- The pokers are different temperatures ("white hot" poker has a higher temperature)
- The pokers emit different intensities and wavelengths of electromagnetic radiation (especially in the visible spectrum)

Max Planck (1900)

Energy can be released (or absorbed) by atoms *only* in "packets" of some minimum size

- This minimum energy packet is called a **quantum**
- The energy (E) of a quantum is related to its frequency (ν) by some constant (h):
-

$$\mathbf{E = h \nu}$$

- h is known as "**Planck's constant**", and has a value of **6.63×10^{-34} Joule seconds (Js)**
- *Electromagnetic energy is always emitted or absorbed in whole number multiples of ($h \times \nu$)*

Calculate the smallest amount of energy (i.e. one quantum) that an object can absorb from yellow light with a wavelength of 589 nm

$$\text{Energy quantum} = h\nu$$

so we need to know the frequency ν

$$\begin{aligned}\nu \lambda &= c \\ \nu &= c / \lambda \\ \nu &= (3.00 \times 10^8 \text{ m/s}) / (589 \times 10^{-9} \text{ m}) \\ \nu &= 5.09 \times 10^{14} \text{ s}^{-1}\end{aligned}$$

plugging into Planck's equation:

$$E = (6.63 \times 10^{-34} \text{ Js}) * (5.09 \times 10^{14} \text{ s}^{-1})$$
$$E (1 \text{ quanta}) = 3.37 \times 10^{-19} \text{ J}$$

Note that a quanta is quite small. When we receive infrared radiation from a fireplace we absorb it in quanta according to Planck's Law. However, we can't detect that the energy absorption is incremental.

On the atomic scale, however, the quantum effects have a profound influence

The Photoelectric Effect

Light shining on a metallic surface can cause the surface to *emit* electrons

- For each metal there is *a minimum frequency of light below which no electrons are emitted*, regardless of the **intensity** of the light
- The higher the light's frequency above this minimum value, the greater the kinetic energy of the released electron(s)

Using Planck's results Einstein (1905) was able to deduce the basis of the photoelectric effect

- Einstein assumed that the light was a stream of tiny energy packets called **Photons**
- Each photon has an energy proportional to its frequency ($E=h\nu$)
- When a photon strikes the metal its energy is transferred to an electron
- A certain amount of energy is needed to overcome the attractive force between the electron and the protons in the atom

Thus, if the quanta of light energy absorbed by the electron is insufficient for the electron to overcome the attractive forces in the atom, the electron will not be ejected - regardless of the intensity of the light.

If the quanta of light energy absorbed is greater than the energy needed for the electron to overcome the attractive forces of the atom, then the excess energy becomes kinetic energy of the released electron.

Since different metals have different atomic structure (number of protons, different electronic structure) the quanta of light needed to overcome the attractive forces within the atom differs for each element

The Photoelectric effect as a carnival game:

A popular carnival game is where you are given a giant mallet and have to hit a pad on the ground. This sends a small metal slug shooting up a vertical track and, if you hit it hard enough, it will hit a bell at the top. This is like the photoelectric effect - if the electron will be released from the atom if it absorbs a photon with enough energy. Imagine that you have a 10 year old child and Arnold Schwarzenegger. The child is too weak to hit the pad hard enough to ring the bell. It doesn't matter if you have an army of 10 year olds lined up to take their turn - none of

them will ever hit it hard enough to ring the bell. However, Arnold (being Arnold) will have no problem ringing the bell.

Thus, if the light shining on a metal does not have photons with the necessary energy to cause an electron to be ejected, then it does not matter how bright the light is. The key thing is to increase the energy of the individual photons, and this is achieved by increasing the frequency (i.e. decreasing the wavelength)

High energy photons, from x-rays for example, can cause electrons from many atoms to be ejected and with high kinetic energy as well. The release of such high energy electrons can cause tissue damage (cancer).

Radio waves have such a low quanta of energy that even though we are bombarded by them, they do not cause the release of electrons.

Einstein's interpretation of the photoelectric effect suggests that light has characteristics of particles. Is light a wave or does it consist of particles?

In 1913 Niels Bohr developed a theoretical explanation for a phenomenon known as *line spectra*.

6.3: Bohr's Model of the Hydrogen Atom

Line Spectra

Lasers emit radiation which is composed of a *single wavelength*. However, most common sources of emitted radiation (i.e. the sun, a lightbulb) produce radiation containing *many different wavelengths*.

When the different wavelengths of radiation are separated from such a source a *spectrum* is produced.

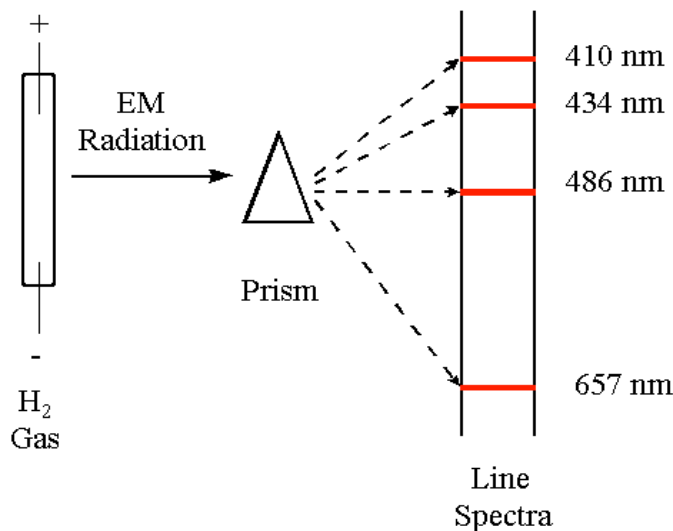
A *rainbow* represents the spectrum of wavelengths of light contained in the light emitted by the sun

- Sun light passing through a *prism* (or raindrops) is separated into its component wavelengths
- Sunlight is made up of a *continuous spectrum* of wavelengths (from red to violet) - there are no gaps

Not all radiation sources emit a continuous spectrum of wavelengths of light

- When high voltage is applied to a glass tube containing various gasses under low pressure different colored light is emitted
 - Neon gas produces a red-orange glow
 - Sodium gas produces a yellow glow
- When such light is passed through a prism only a *few wavelengths* are present in the resulting spectra
 - These appear as lines separated by dark areas, and thus are called *line spectra*

When the spectrum emitted by *hydrogen gas* was passed through a prism and separated into its constituent wavelengths *four lines* appeared at characteristic wavelengths



In 1885 a Swiss school teacher figured out that the *frequencies* of the light corresponding to these wavelengths fit a relatively simple mathematical formula:

$$\nu = C * \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{ where } n = 3, 4, 5, 6$$

where $C = 3.29 \times 10^{15} \text{ s}^{-1}$ (*not the 'c' used for the speed of light*)

However, the physical basis for this relationship was unknown.

Bohr's Model

- Bohr began with the assumption that electrons were orbiting the nucleus, much like the earth orbits the sun.
- From classical physics, a charge traveling in a circular path should lose energy by emitting electromagnetic radiation
- If the "orbiting" electron loses energy, it should end up spiraling into the nucleus (which it does not). *Therefore, classical physical laws either don't apply or are inadequate to explain the inner workings of the atom*
- Bohr borrowed the idea of quantized energy from Planck
 - He proposed that only orbits of certain radii, corresponding to defined energies, are "permitted"
 - An electron orbiting in one of these "allowed" orbits:
 - Has a defined energy state
 - Will not radiate energy
 - Will not spiral into the nucleus

If the orbits of the electron are restricted, the energies that the electron can possess are likewise restricted and are defined by the equation:

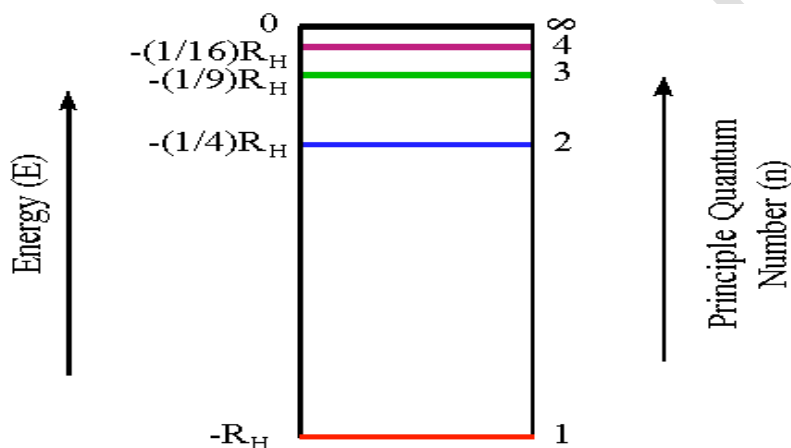
$$E_n = (-R_H) \left(\frac{1}{n^2} \right)$$

Where R_H is a constant called the **Rydberg constant** and has the value

$$2.18 \times 10^{-18} \text{ J}$$

' n ' is an **integer**, called the **principle quantum number** and corresponds to the different allowed orbits for the electron. Thus, an electron in the first allowed orbit (closest to the nucleus) has $n=1$, an electron in the next allowed orbit further from the nuclei has $n=2$, and so on.

Thus, the relative energies of these allowed orbits for the electrons can be diagrammed as follows:



All the relative energies are **negative**

- The lower the energy, the more stable the atom
- The lowest energy state ($n=1$) is called the **ground state** of the atom
- When an electron is in a higher (less negative) energy orbit (i.e. $n=2$ or higher) the atom is said to be in an **excited state**
- As n becomes larger, we reach a point at which the electron is completely separated from the nucleus
 - $E = (-2.18 \times 10^{-18} \text{ J})(1/\text{infinity}) = 0$
 - Thus, the state in which the electron is separated from the nucleus is the reference or zero energy state (actually **higher** in energy than other states)

Bohr also assumed that the electron can change from one allowed orbit to another

- Energy must be absorbed for an electron to move to a higher state (one with a higher n value)
- Energy is emitted when the electron moves to an orbit of lower energy (one with a lower n value)
- The overall change in energy associated with "orbit jumping" is the difference in energy levels between the ending (final) and initial orbits:

$$\Delta E = E_f - E_i$$

Substituting in for the previously defined energy equation:

$$\Delta E = \left(\frac{-R_H}{n_f^2} \right) - \left(\frac{-R_H}{n_i^2} \right) = (-R_H) * \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_H * \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

When an electron "falls" from a higher orbit to a lower one the energy difference is a defined amount and results in emitted electromagnetic radiation of a defined energy (ΔE)

- Planck had deduced that the energy of the photons comprising EM radiation is a function of its frequency ($E = h\nu$)
- Therefore, if the emitted radiation from a falling electron had a defined energy, then it must have a correspondingly defined frequency

$$\Delta E = R_H * \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = h\nu$$

Note:

- **ΔE is positive** when n_f is greater than n_i , this occurs when energy is absorbed and an electron moves up to a higher energy level (i.e. orbit).
- When **ΔE is negative**, radiant **energy is emitted** and an electron has **fallen** down to a lower energy state

Revisiting Balmer's equation:

In 1885 a Swiss school teacher figured out that the **frequencies** of the light corresponding to these wavelengths fit a relatively simple mathematical formula:

$$\nu = C * \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{ where } n = 3, 4, 5, 6$$

where $C = 3.29 \times 10^{15} \text{ s}^{-1}$ (**not the 'c' used for the speed of light**)

Since energy lost by the electrons is energy "gained" by the emitted EM energy, the EM energy from Bohr's equation would be:

$$h\nu = R_H * \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Thus, Balmer's constant 'C' = (R_H/h) (Rydberg constant divided by Planck's constant), and $n_f = 2$. Thus, the only emitted energies which fall in the visible spectrum are from those electrons which fell down to the **second** quantum orbital. Those which fell down to the first orbital have a higher energy (frequency) than can be seen in the visible spectrum.

Calculate the **wavelength** of light that corresponds to the transition of the electron from the $n=4$ to the $n=2$ state of the hydrogen atom. Is the light absorbed or emitted by the atom?

Since the electron is "falling" from level 4 down to level 2, energy will be given up and manifested as emitted electromagnetic radiation:

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = h\nu$$

$$\Delta E = (2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{16} - \frac{1}{4} \right) = -4.09 \times 10^{-19} \text{ J (light is emitted)}$$

$$4.09 \times 10^{-19} \text{ J} = (6.63 \times 10^{-34} \text{ Js}) * (\nu)$$

$$6.17 \times 10^{14} \text{ s}^{-1} = \nu$$

$$\lambda = (3.00 \times 10^8 \text{ m s}^{-1}) / (6.17 \times 10^{14} \text{ s}^{-1}) = 4.87 \times 10^{-7} \text{ m} = 487 \text{ nm}$$

Bohr's model of the atom was important because it introduced quantized energy states for the electrons. However, as a model it was only useful for predicting the behavior of atoms with a single electron (H, He^+ , and Li^{2+} ions). Thus, a different model of the atom eventually replaced Bohr's model. However, we will retain the concept of quantized energy states

6.4: The Dual Nature of the Electron

Depending on the experimental circumstances, EM radiation appears to have either a *wavelike* or a *particlelike (photon) character*.

Louis de Broglie (1892-1987) who was working on his Ph.D. degree at the time, made a daring hypothesis:

if radiant energy could, under appropriate circumstances behave as though it were a stream of particles, then could matter, under appropriate circumstances, exhibit wave-like properties?

For example, **the electron in orbit around a nucleus**. DeBroglie suggested that the electron could be thought of *as a wave with a characteristic wavelength*.

He proposed that the wavelength of the electron was a function of its mass (m) and its velocity (ν):

$$\lambda = \frac{h}{m * \nu}$$

i.e. the wavelength for "matter waves", where h is Planck's constant and is ν velocity (not, the frequency). The quantity $m\nu$ for any object is its **momentum** (mass * velocity).

What is the characteristic wavelength of an electron with a velocity of $5.97 \times 10^6 \text{ m/s}$? (the mass of the electron is $9.11 \times 10^{-28} \text{ g}$)

$$\lambda = \frac{h}{m * v}$$

Planck's constant (h) is 6.63×10^{-34} J s (also, recall that $1\text{J} = 1 \text{ kg m}^2/\text{s}^2$)

$$\lambda = \frac{6.63 \times 10^{-34} \text{ J s}}{(9.11 \times 10^{-28} \text{ g}) * (5.97 \times 10^6 \text{ m s}^{-1})}$$

$$\lambda = 1.219 \times 10^{-13} \text{ J s}^2 \text{ m}^{-1} \text{ g}^{-1}$$

converting g to kg:

$$\lambda = 1.219 \times 10^{-13} \text{ J s}^2 \text{ m}^{-1} \text{ g}^{-1} * \left(\frac{1000\text{g}}{1\text{Kg}} \right) = 1.219 \times 10^{-10} \text{ J s}^2 \text{ m}^{-1} \text{ Kg}^{-1}$$

Converting from $\text{kg m}^2/\text{s}^2$ to Joules:

$$\lambda = 1.219 \times 10^{-10} \text{ J s}^2 \text{ m}^{-1} \text{ Kg}^{-1} * \left(\frac{1 \text{ Kg m}^2 / \text{s}^2}{1 \text{ J}} \right) = 1.219 \times 10^{-10} \text{ m}$$

or 0.122 nm

- The relationship between energy (E) and frequency (ν) for electromagnetic radiation (Planck's quantum of energy)

$$E = h * \nu$$

- The relationship between wavelength (λ) and frequency (ν) for electromagnetic radiation

$$\lambda * \nu = c$$

From these relationships, we can determine the relationship between energy and wavelength:

$$E = h * \frac{c}{\lambda}$$

or, rearranging:

$$\lambda = h * \frac{c}{E}$$

- The relationship between wavelength (λ) and momentum (m*v) for DeBroglie's "particle wave"

$$\lambda = \frac{h}{m * v}$$

From the above relationships, we can calculate the relationship between energy (E) and momentum ($m \cdot v$)

$$\frac{h}{m \cdot v} = h \cdot \frac{c}{E}$$

Simplify, and solve for E :

$$E = m \cdot v \cdot c$$

The highest velocity (v) attainable by matter is the speed of light (c), therefore, the maximum energy would seem to be:

$$E = m \cdot c \cdot c$$

or

$$E = m \cdot c^2$$

Why do nuclear bombs make such a loud "pop"?

- The Fuel value of hydrogen is $142 \times 10^3 \text{ J g}^{-1}$
- If all matter were converted into energy

$$E = 1 \times 10^{-3} \text{ kg} \cdot (3 \times 10^8 \text{ m/s})^2$$

$$E = 9 \times 10^{13} \text{ kg m}^2 \text{ s}^{-2}$$

$$E = 9 \times 10^{13} \text{ J}$$

In other words, we can get out about 9 orders of magnitude greater energy if the hydrogen is converted directly into energy, rather than combusting it.

Nuclear fission and fusion reactions convert a fraction of their matter into energy. The bomb that was dropped on Hiroshima contained about 15 kg of the ^{235}U isotope, a fissionable material. The actual amount of mass that was converted into energy is estimated at about 1 kg (releasing around $1 \times 10^{17} \text{ J}$ of energy in a split second). The estimated temperature at the moment of detonation is estimated to have been around 5 million degrees. In addition to the sun-like heat, much of the damage was due to the pressure wave that was produced.

The Uncertainty Principle

For a relatively large solid object, like a bowling ball, we can determine its position and velocity at any given moment with a high degree of accuracy.

However, if an object (like an electron) has wave-like properties then how can we accurately define its' position?

Werner Heisenberg (1901-1976) concluded that due to the dual nature of matter (both particle and wavelike properties) it is impossible to simultaneously know both the position and momentum of an object as small as an electron.

Thus, it is not appropriate to imagine the electrons as moving in well-defined circular orbits about the nucleus.

6.5: Quantum Mechanics and Atomic Orbitals

1926 Erwin Schrödinger

Schrödinger's wave equation incorporates both wave- and particle-like behaviors for the electron.

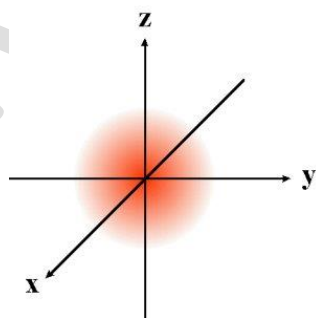
Opened a new way of thinking about sub-atomic particles, leading the area of study known as *wave mechanics*, or *quantum mechanics*.

Schrödinger's equation results in a series of so called wave functions, represented by the letter ψ (*psi*). Although has no actual physical meaning, the value of ψ^2 describes the **probability distribution of an electron**.

From Heisenberg's uncertainty principle, we cannot know both the location and velocity of an electron. Thus, Schrödinger's equation does not tell us the exact location of the electron, rather it describes the **probability** that an electron will be at a certain location in the atom.

Departure from the Bohr model of the atom

In the Bohr model, the electron is in a **defined orbit**, in the Schrödinger model we can speak only of probability distributions for a given energy level of the electron. For example, an electron in the ground state in a Hydrogen atom would have a probability distribution which looks something like this (a more intense color indicates a greater value for ψ^2 , a higher probability of finding the electron in this region, and consequently, greater electron density):



Orbitals and quantum numbers

Solving Schrödinger's equation for the hydrogen atom results in a series of wave functions (electron probability distributions) and associated energy levels. These wave functions are called **orbitals** and have a characteristic energy and shape (distribution).

The lowest energy orbital of the hydrogen atom has an energy of -2.18×10^{18} J and the shape in the above figure. Note that in the **Bohr model** we had the same energy for the electron in the ground state, but that it was described as being in a defined **orbit**.

The Bohr model used a single quantum number (n) to describe an **orbit**, the Schrödinger model uses **three** quantum numbers: n , l and m_l to describe an **orbital**.

The principle quantum number 'n'

- Has integral values of 1, 2, 3, etc.
- As n increases the electron density is further away from the nucleus
- As n increases the electron has a higher energy and is less tightly bound to the nucleus

The azimuthal (second) quantum number 'l'

- Has integral values from 0 to ($n-1$) for each value of n
- Instead of being listed as a numerical value, typically 'l' is referred to by a letter ('s'=0, 'p'=1, 'd'=2, 'f'=3)
- Defines the **shape** of the orbital

The magnetic (third) quantum number 'm_l'

- Has integral values between 'l' and '-l', including 0
- Describes the orientation of the orbital in space

For example, the electron orbitals with a principle quantum number of 3 (i.e. $n=3$) would have the following available values of 'l' and 'm_l':

N (principle quantum number)	l (azimuthal) (defines shape)	Subshell Designation	m_l (magnetic) (defines orientation)	Number of Orbitals in Subshell
3	0	3s	0	1
	1	3p	-1,0,1	3
	2	3d	-2,-1,0,1,2	5

- A collection of orbitals with the same value of 'n' is called **an electron shell**
- A collection of orbitals with the same value of 'n' and 'l' belong to the same **subshell**

Thus:

- the **third electron shell** (i.e. 'n'=3) consists of the **3s**, **3p** and **3d subshells** (each with a different shape)

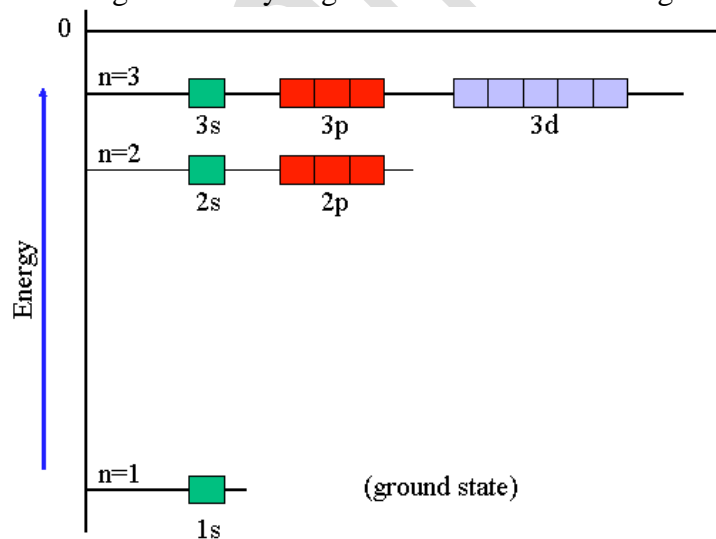
- The **3s subshell** contains **1 orbital**, the **3p subshell** contains **3 orbitals** and the **3d subshell** contains **5 orbitals**. (within each subshell, the different orbitals have different orientations in space)
- Thus, the **third electron shell** is comprised of **nine distinctly different orbitals**, although each orbital has the **same energy** (that associated with the third electron shell) *Note: remember, this is for hydrogen only.*

Restrictions on the possible values for the different quantum numbers (n , l and m_l) gives rise to the following patterns for the different shells:

- Each shell is divided into a number of *subshells equal to the principle quantum number* (e.g. the fourth shell is divided into four subshells: **s**, **p**, **d**, and **f**; whereas the first shell has a single subshell: **s**)
- Each subshell is divided into orbitals (*increasing by odd numbers*):

Subshell	Number of orbitals
S	1
P	3
D	5
F	7

The number and relative energies of all hydrogen electron orbitals through $n=3$ are shown below:



- At ordinary temperatures essentially all hydrogen atoms are in their ground states
- The electron may be promoted to an excited state by the absorption of a photon with appropriate quantum of energy

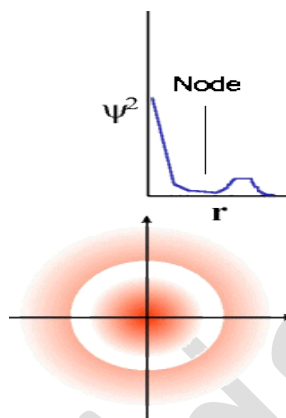
6.6: Representations of Orbitals

The s Orbitals

The $1s$ orbital is spherically symmetrical

This indicates that in the ground state the electrostatic attraction of the electron for the proton in the nucleus is such that the electron is unlikely to be found far from the nucleus.

The higher energy s orbitals are also spherically symmetrical, however, they exhibit distinct nodes in the distribution probability:



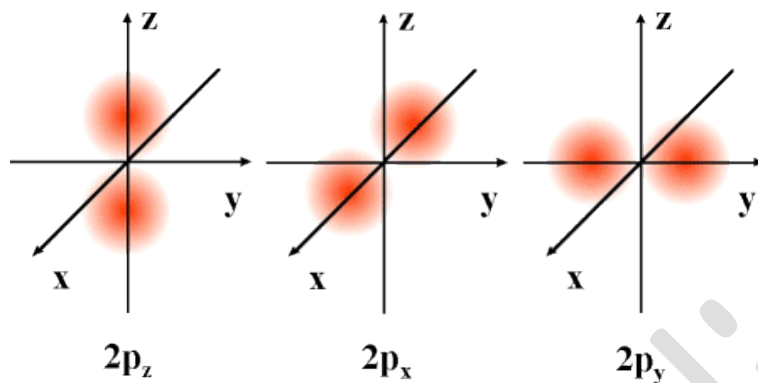
- In the higher s orbitals there exists **node** regions where the electron density approaches zero (2s has 1 node, 3s has 2 nodes, etc)
- The higher s orbitals (excited states) have electron density distributions which indicate that there is a higher probability of finding the electron further away from the nucleus

The size of the orbital increases as n increases

The most widely used representation of the Schrödinger orbits is to draw a boundary which represents 90% of the total electron density distribution. *For the s orbitals this would be a **sphere** representation.*

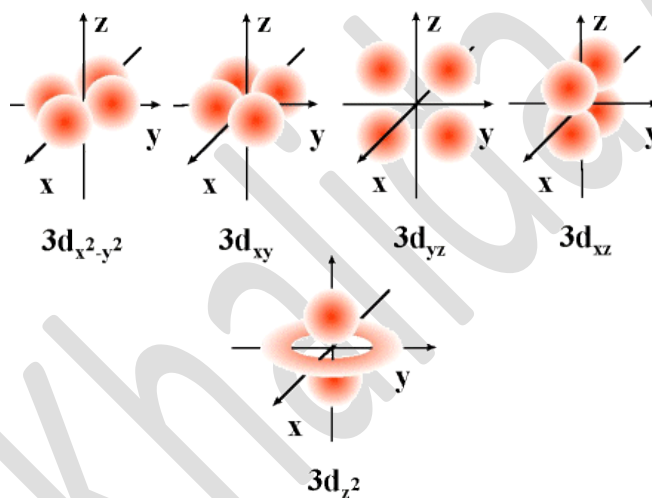
p Orbitals

- The **p** orbitals are 'dumbbell' shaped orbitals of electron density, with a node at the nucleus.
- There are three distinct p orbitals, they differ in their orientations
- There is no fixed correlation between the three orientations and the three magnetic quantum numbers (m_l)



The d and f orbitals

In the third shell and beyond there are five d orbitals, each has a different orientation in space:



Although the $3d_{z^2}$ orbital looks different, it has the same energy as the other *d* orbitals.

There are 7 equivalent *f* orbitals (for each value of *n* 4 or greater). They are pretty difficult to represent on a 3-d contour diagram.

Understanding orbital shapes is key to understanding the molecules formed by combining atoms

6.7: Orbitals in many-electron atoms

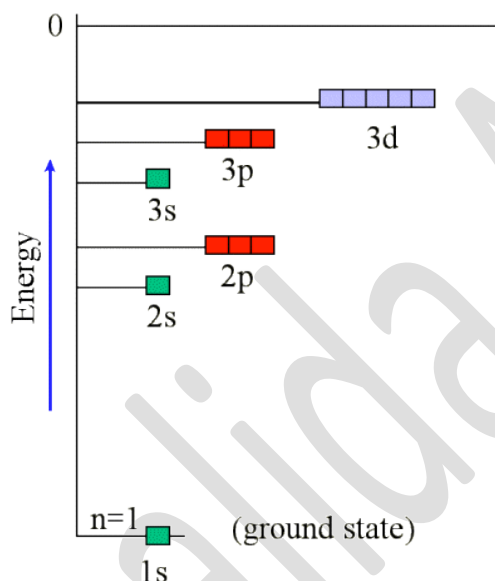
The hydrogen atom is a simple system having only *one electron*.

The quantum mechanical description of the hydrogen atoms places all subshells (i.e. *l* quantum number, or the *s*, *p*, *d* and *f* subshells) with the same principle quantum number (*n*) on the same energetic level.

An atom with more than 1 electron is called a **many-electron** atom.

Although the **shape** of electronic orbitals for many-electron atoms are the **same** as those for the hydrogen atom, *the presence of more than 1 electron influences the energy levels of the orbitals (due to electron-electron repulsion).*

For example, the 2s orbital is a lower energy state than the 2p orbital in a many-electron atom: (note: this is a qualitative representation for an "average" many-electron atom)



Effective Nuclear Charge

In a many-electron atom, each electron is simultaneously:

- **attracted** to the protons in the nucleus
- **repelled** by other electrons (like-charge repulsion)

What is the **average environment**, created by the nucleus and all the other electrons in the atom, which is "felt" by a particular electron in the atom?

The net positive charge attracting the electron is called **the effective nuclear charge**

- Any electron density between the nucleus and the electron of interest will reduce the nuclear charge acting on that electron
- The effective nuclear charge (Z_{eff}) equals the number of protons in the nucleus (Z), minus the average number of electrons (S) that are between the electron in question and the nucleus

$$Z_{\text{eff}} = Z - S$$

- The positive charge "felt" by the outer electrons is ***always less than the full nuclear charge*** (inner electrons "screen" the nuclear charge).

Energies of orbitals

The extent to which an electron will be screened by the other electrons depends on the shape of the electron distribution as we move out from the nucleus

- Probability of being closer to the nucleus (based on orbital shapes) is as follows:

$$\begin{array}{ccccc} (n)s < (n)p < (n)d < (n)f \\ \text{closer} & & & & \text{further away} \end{array}$$

- For the 3rd principle quantum number, for example, the 3s electrons experience the ***least shielding*** and the 3d electrons ***the most***
- Conversely, the 3s electrons experience a ***greater Z_{eff}*** and the 3d electrons ***the least***

In a many-electron atom, for a given principle quantum number ('n'), Z_{eff} decreases with increasing 'l'

The energy of an electron depends on Z_{eff}

- Because Z_{eff} is larger for 3s electrons (in the above n=3 example) they have a ***lower energy*** than 3p electrons (which in turn have ***lower energy*** than 3d electrons)

In a many-electron atom, for a given principle quantum number ('n'), the energy level of an orbital increases with increasing 'l'

Note: all the orbitals of a give sub-shell still have the same energy level (e.g. all the 3d orbitals (with different m_l quantum values))

The sodium atom has 11 electrons, two in a 1s orbital, two in a 2s orbital, six in 2p orbitals and one in a 3s orbital. As far as the electrons in s type subshells, which experiences the ***smallest*** effective nuclear charge (Z_{eff})?

Answer: the ***outermost*** electron, or the one in the 3s orbital

Electron spin and the Pauli exclusion principle

- What determines the orbitals in which the electrons reside?
- How do the electrons populate the available orbitals?

Line spectra revisited...

- Lines which were thought to be single lines actually were composed of *two very closely spaced* lines
- Thus, there were *twice* as many energy levels as there were "supposed" to be

It was proposed (Uhlenbeck and Goudsmit, 1925) that electrons have yet another quantum property called **electron spin**:

- A new quantum number for the electron called **the electron spin quantum number**, or m_s
- m_s has a value of $+1/2$ or $-1/2$
- The electron spin quantum number characterized the "direction of spin" of the electron
 - A spinning charge **produces a magnetic field**
 - The opposite spins produce **opposite magnetic fields** which results in the splitting of the line spectrum into two closely spaced lines

Electron spin is crucial for understanding the electron structures of atoms:

- The **Pauli exclusion principle** (Wolfgang Pauli, 1925) states that **no two electrons in an atom can have the same set of four quantum numbers** (n , l , m_l and m_s)
- For a given orbital (e.g. $2p_z$) the values of n , l and m_l are **fixed**. Thus, if we want to put more than one electron into an orbital we must assign unique values to the magnetic spin (m_s quantum number)
- the m_s quantum number can only have two values ($+1/2$, and $-1/2$) therefore, **only two electrons at most can occupy the same orbital, and they have opposite values for magnetic spin**

What are the consequences of magnetic spin quantum number and the Pauli exclusion principle?

- If we know the number of electrons in an atom we can assign probable quantum numbers and know something about their orbital shapes
- Provides an understanding for the periodic nature of the elements

Orbitals in many-electron atoms

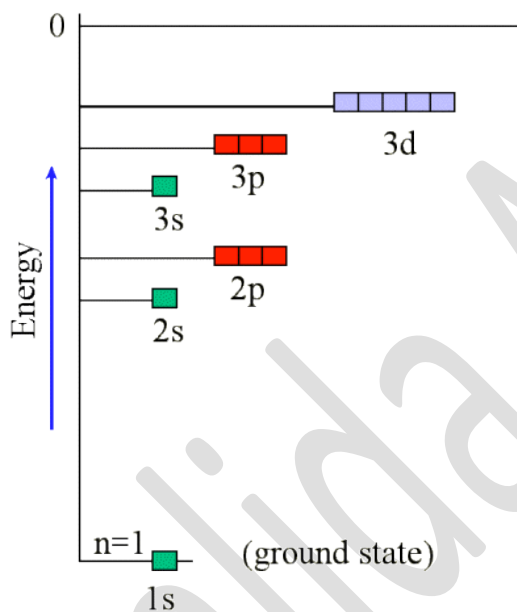
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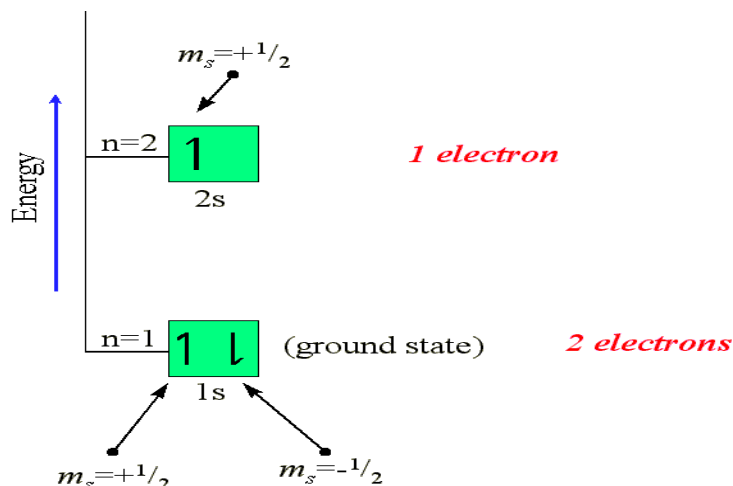
- If we know the number of electrons in an atom we can assign probable quantum numbers and know something about their orbital shapes
- Provides an understanding for the periodic nature of the elements

6.8: Electron Configurations

The way in which electrons are distributed among the various orbitals is called the **electron configuration**

Orbitals are filled in order of increasing energy, with no more than two electrons per orbital

Lithium
This element has 3 electrons. We would thus begin by placing two electrons in the $1s$ ground state, or lowest energy, orbital. These two electrons would have opposite magnetic spin quantum numbers. We would then place the third electron in the next highest energy level orbital - the $2s$ orbital:



- The arrows indicate the value of the magnetic spin (m_s) quantum number (up for $+1/2$ and down for $-1/2$)
- The description of the occupation of the orbitals would be described in the following way:

$1s^2 2s^1$
or, "1s two, 2s one".

- Electrons having opposite spins are said to be "paired" electrons, as with the electrons occupying the Li 1s orbital
- Likewise, the single electron in the 2s orbital (for Li) is said to be "unpaired"

Writing electronic configurations

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1s	2s	2p	3s	
H	1	↑				$1s^1$
He	2	↑↓				$1s^2$
Li	3	↑↓	↑			$1s^2 2s^1$
Be	4	↑↓	↑↓			$1s^2 2s^2$
B	5	↑↓	↑↓	↑		$1s^2 2s^2 2p^1$

- The two electrons in He represent the complete filling of the first electronic shell. Thus, the electrons in He are in a very stable configuration
- For Boron (5 electrons) the 5th electron must be placed in a 2p orbital because the 2s orbital is filled. Because the 2p orbitals are equal energy, it doesn't matter which 2p orbital is filled

What do we do now with the next element, Carbon (6 electrons)? Do we pair it with the single 2p electron (but with opposite spin)? Or, do we place it in another 2p orbital?

Element	Total Electrons	Orbital Diagram					Electron Configuration	
		1s	2s	2p				3s
C	6	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑</div></div>	<div><div>↑</div></div>	<div></div>	<div></div>	$1s^2 2s^2 2p^2$
N	7	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑</div></div>	<div><div>↑</div></div>	<div><div>↑</div></div>	<div></div>	$1s^2 2s^2 2p^3$
Ne	10	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div></div>	$1s^2 2s^2 2p^6$
Na	11	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑↓</div></div>	<div><div>↑</div></div>	$1s^2 2s^2 2p^6 3s^1$

The second 2p electron in Carbon is placed in another 2p orbital, but with the same spin as the first 2p electron:

Hund's rule: for degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized

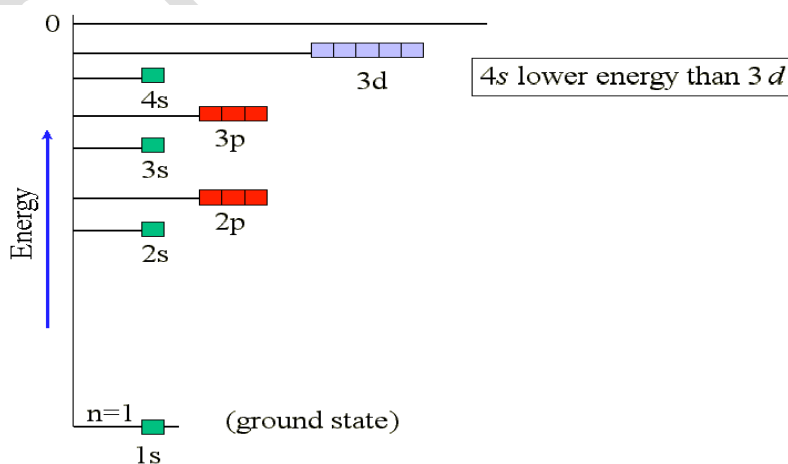
Electrons repel each other, by occupying different orbitals the electrons remain as far as possible from one another

- A carbon atom in its lowest energy (ground state) **has two unpaired electrons**
- Ne has *filled up the n=2 shell*, and has a *stable electronic configuration*

Electronic configurations can also be written in a short hand which references the *last completed orbital shell* (i.e. all orbitals with the same principle quantum number 'n' have been filled)

- The electronic configuration of Na can be written as $[\text{Ne}]3s^1$
- The electronic configuration of Li can be written as $[\text{He}]2s^1$

The electrons in the stable (Noble gas) configuration are termed **the core electrons**



The 4s orbital would be filled when we have an element with 20 electrons (Calcium).

Then we go back and fill up the 3d orbitals, which can hold a maximum of 10 electrons

Thus, the 4th row of the periodic table is 10 elements wider than the previous row - we have available five 'd' orbitals we can fill (with 10 electrons). These 10 elements are the **Transition Elements, or Transition Metals**.

With Cerium (element 58) the 'f' orbitals enter the picture. These orbitals can hold 14 electrons.

- The first 'f' orbitals are the 4f orbitals (n=4; l=0(s), 1(p), 2(d), 3(f))
- These additional elements are represented by the 14 lanthanide (4f orbital filling) and actinide (5f orbitals) series of elements
- The energy of the 5d and 4f orbitals are very close

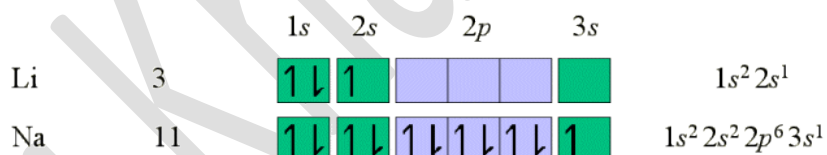
Something curious

The noble gas Argon (18 electrons) marks the end of the row started by Sodium

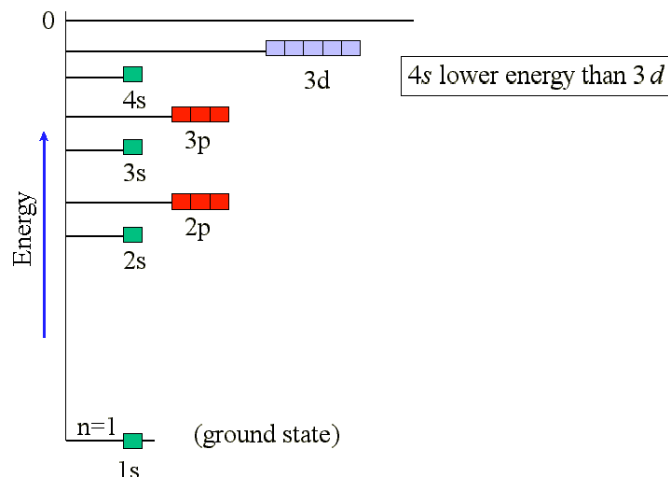


Will the next element (K with 19 electrons) put the next electron one of the 3d orbitals?

- Chemically, we know **Potassium** is a lot like **Lithium** and **Sodium**



- What these elements (the alkali metals) have in common is *an unpaired valence electron in an s orbital*
- If Potassium has an unpaired electron in an s orbital it would mean that it is in the 4s orbital
- Thus, the 4s orbital would appear to be of **lower energy** than the 3d orbital(s)



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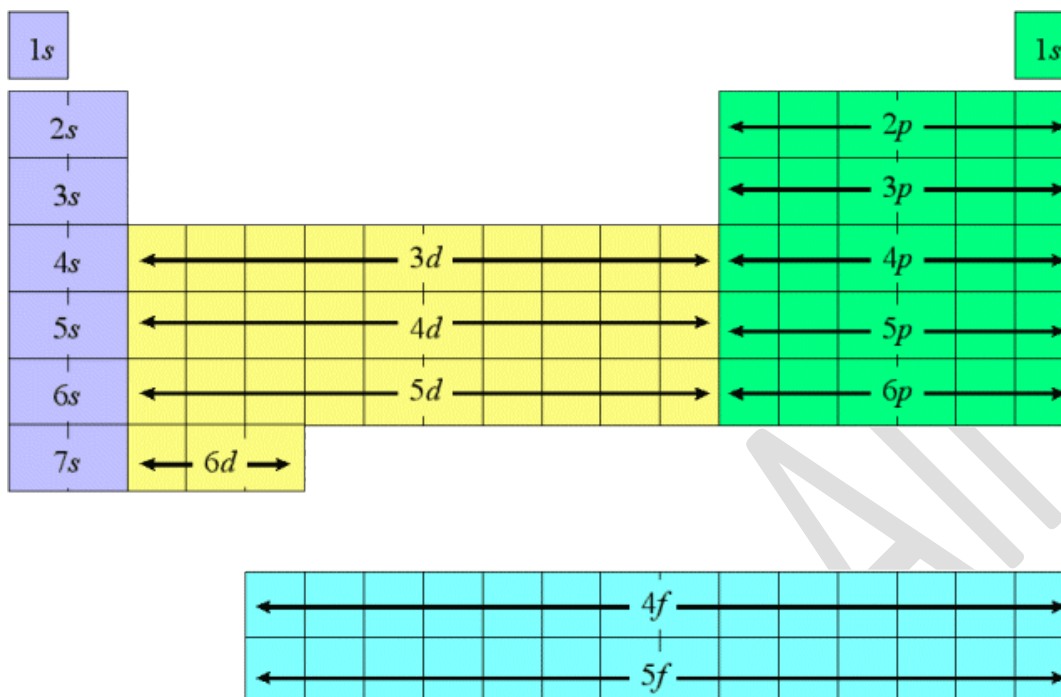
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6.9: Electron Configurations and the Periodic Table

The periodic table is structured so that elements with the same type of valence electron configuration are arranged in columns.



- The left-most columns include the alkali metals and the alkaline earth metals. ***In these elements the valence s orbitals are being filled***
- On the right hand side, the right-most block of six elements are those in which ***the valence p orbitals are being filled***

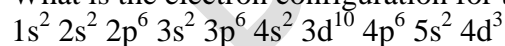
These two groups comprise the main-group elements

- In the middle is a block of ten columns that contain ***transition metals***. ***These are elements in which d orbitals are being filled***
- Below this group are two rows with 14 columns. These are commonly referred to the ***f-block metals***. In these columns ***the f orbitals are being filled***

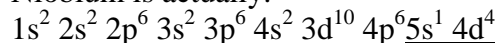
Important facts to remember:

1. 2, 6, 10 and 14 are the number of electrons that can fill the ***s, p, d*** and ***f*** subshells (the $l=0,1,2,3$ azimuthal quantum number)
2. The 1s subshell is the first ***s*** subshell, the 2p is the first ***p*** subshell ($n=2, l=1$), 3d is the first ***d*** subshell, and the 4f is the first ***f*** subshell

What is the electron configuration for the element Niobium? (41)

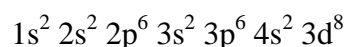


Niobium is actually:



The reason is that the 5s and 4d energy levels are quite close and certain electronic arrangements can result in the levels being slightly different than expected.

What is the electron configuration of the element Nickel? (28)



What is the electron configuration for Nickel in terms of the nearest noble gas?

$[\text{Ar}] 4s^2 3d^8$

How would the last valence orbital be filled?

$3d$

1↓	1↓	1↓	1	1
----	----	----	---	---