Kotz and Treichel
Chapter 2

Atoms, Molecules, and Ions

Milestones in the Development of Chemistry and the Modern View of Atoms and Molecules

Milestones in the Development of Chemistry and the Modern View of Atoms and Molecules

Pages 335-343 in edition 8 of the textbook

The Early History of Chemistry
(Just an introduction - not in the text)

Elements

The ancient Greeks believed there were four – Earth, Fire, Water, Air.

Atoms

Democritus and Leucippos (~400 BC) proposed the concept.

Alchemy

Attempts to transmute "base" metals (the cheap ones) in to gold. This went on for about 2000 years, but lead to the discovery of many elements and important chemicals like mineral acids.

Extraction of Metals

Georges Bauer (German 1494 – 1555) was one of the big names.

Medicinal Use of Minerals

Philippus Theophrastus Bombastus von Hohenheim a.k.a. Paracelsus (Swiss, 1493 – 1541) also did a lot of synthetic chemistry.

Early History of Chemistry

Study of Gases

Robert Boyle (English, 1627 – 1691) was one of the first to measure things. He did not believe in the Greek four-element idea, but he did introduce the idea that a substance which could not be further broken down was an element. He did not believe the metals were elements, which lead him to dabble in alchemy.

Phlogiston

Another major scientific dead-end. When substances burned, they lost phlogiston. Since metal oxides are *heavier* than the metal from which they come, phlogiston was presumed to have a *negative* mass!

Joseph Priestly (English, 1733 – 1804) discovered oxygen.

Antoine Lavoisier (French, 1743 – 1794) was an important contributor to disproving the phlogiston theory.

The Early History of Chemistry

Dalton's Atomic Theory

- Each element is made up of tiny particles called atoms.
- The atoms of a given element are identical: the atoms of different elements differ in some fundamental way or ways.
- Chemical compounds are formed when atoms combine with each other. A given compound always has the same relative numbers and types of atoms.
- Chemical reactions involve reorganization of the atoms - changes in the way they are combined. The atoms themselves are not changed in a chemical reaction.

Dalton made up a list of atomic masses (atomic weights) but he made the mistake of assuming that the formula of water was HO (it is H_2O of course), so he introduced many errors where he was out by a factor of 2.

The Theory of Atomic Structure

Static Electricity

Known for a long time but recognized by Benjamin Franklin (US, 1706 – 1790) as positive (+) and negative (-).

When you shuffle you feet on a dry carpet, for example, charge is separated, leaving one kind on the carpet and the other kind on you. In fact the amount of charge generated is equal on the carpet and on you, but opposite in sign.

Like charges repel each other and opposite charges attract.

The Theory of Atomic Structure

Radioactivity

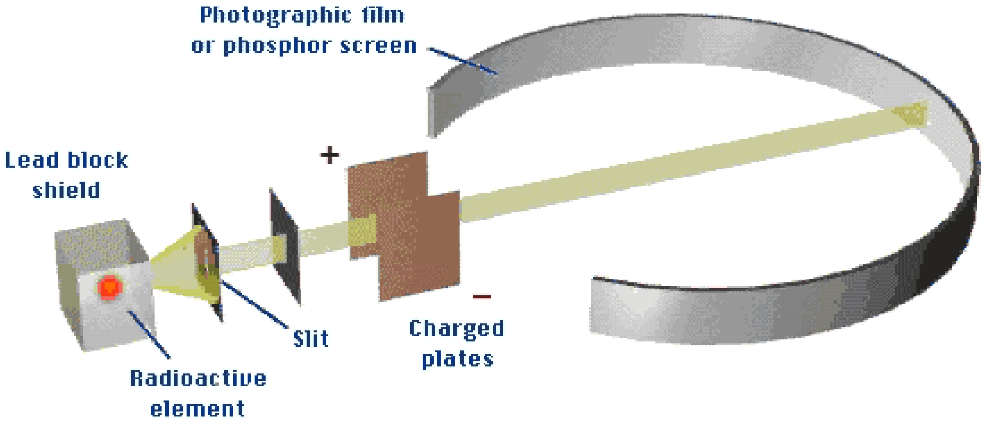
Henri Becquerel (French, 1852 – 1908) discovered that uranium gave off invisible radiation that could fog a piece of photographic film through black paper.

Radium and polonium first isolated by Marie Curie et al. in 1898 have the same property. She suggested they were emitting this radiation as the elements decayed to form other elements.

This discovery was important because it showed that Dalton's atomic theory was not quite correct: atoms of elements can be broken into smaller pieces.

The Theory of Atomic Structure

Radioactivity (continued)



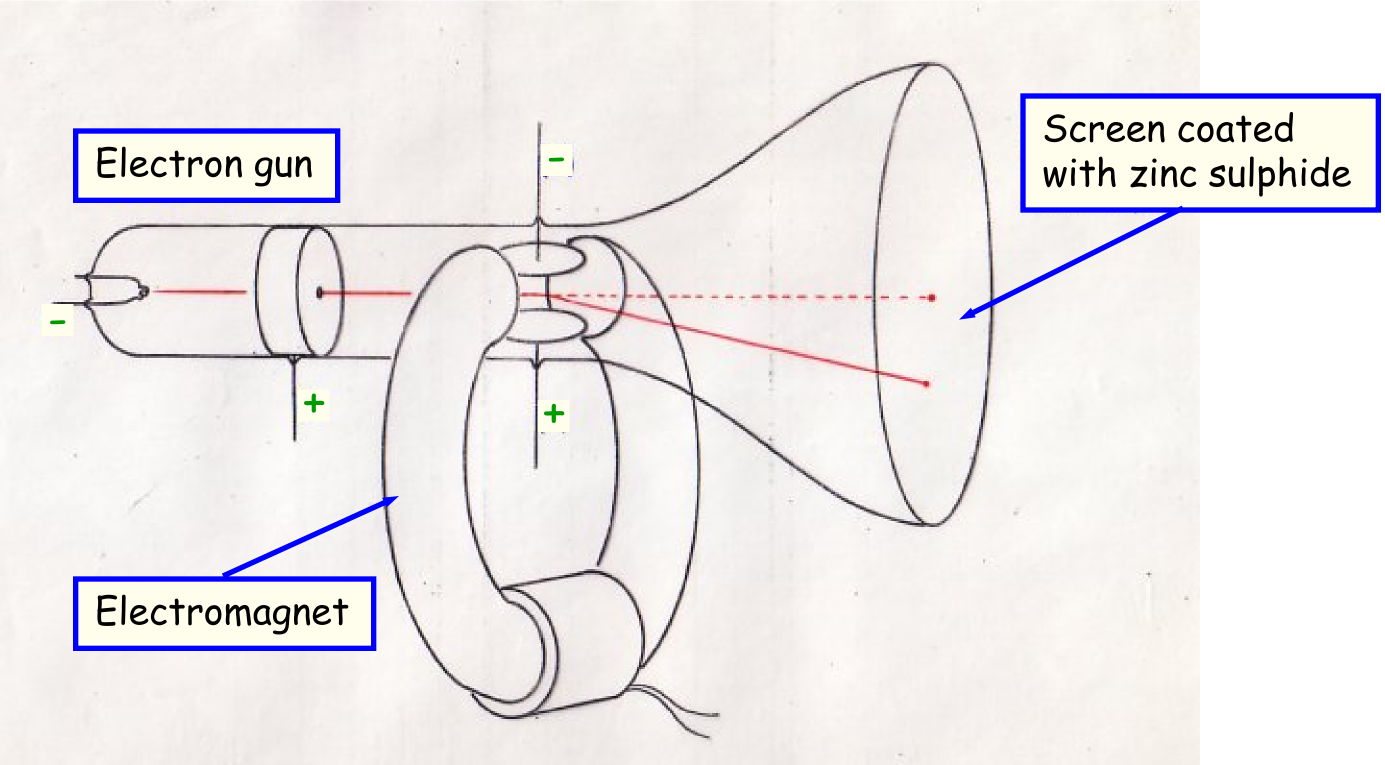
The radiation can be analysed and shown to contain three components:

- Alpha (α, He^{2+}) particles
- Beta (β, e^-) particles
- gamma (γ) rays.

The Theory of Atomic Structure

Electrons

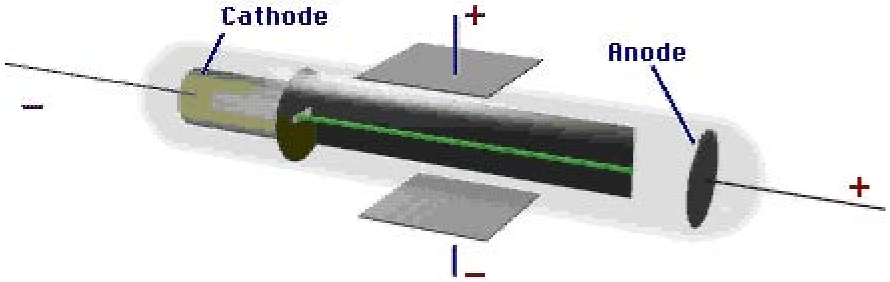
The properties of electrons were established by two main experiments. The first was an investigation of cathode rays by J.J. Thomson (English, 1856 – 1940):



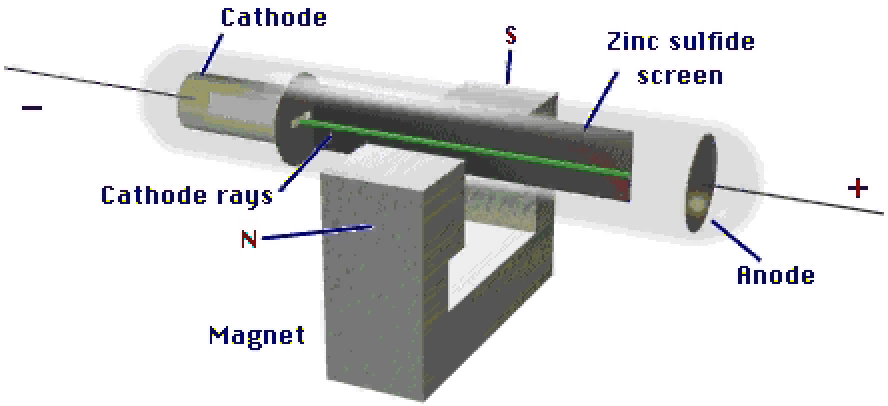
The Theory of Atomic Structure

Electrons

Thomson Experiment – Effect of the Charged Plates



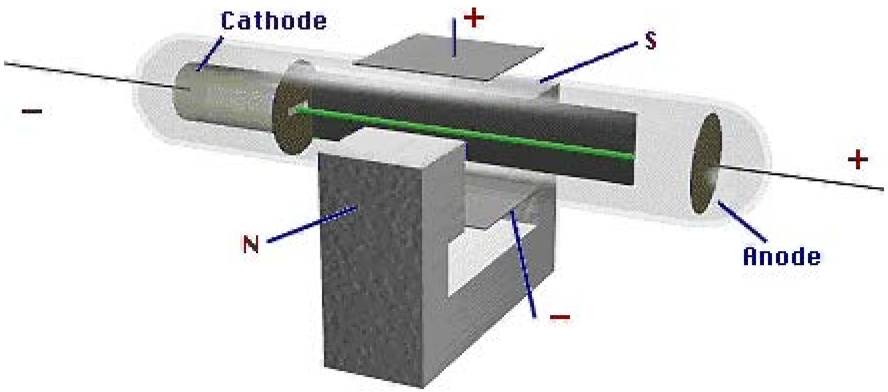
Thomson Experiment - Effect of the Magnetic Field



The Theory of Atomic Structure

Electrons

The Thomson Experiment – What he did



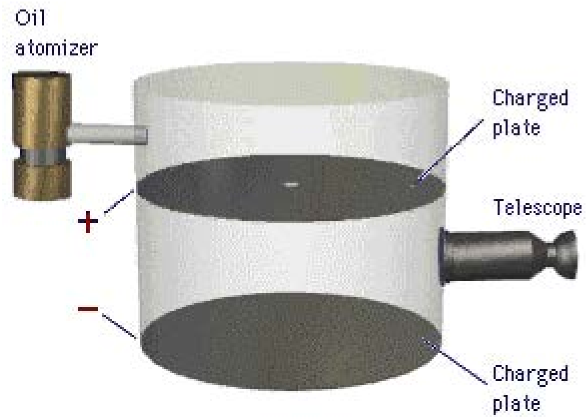
The charge on the plates and the magnetic field strength were adjusted so that the electron beam did not deviate from a straight line. Some relatively simple calculations enabled Thomson to calculate the ratio of the charge to the mass of the electron:

$$\frac{e}{m} = -1.76 \times 10^{8}\ C/g$$

The Theory of Atomic Structure

Electrons

The charge and mass of the electron were established separately by Robert Millikan (US, 1868 – 1953) who measured the charge.



Millikan measured the charge on a number of oil drops and took the smallest difference as the charge on the electron.

$$e = -1.60 \times 10^{-19}\ C$$

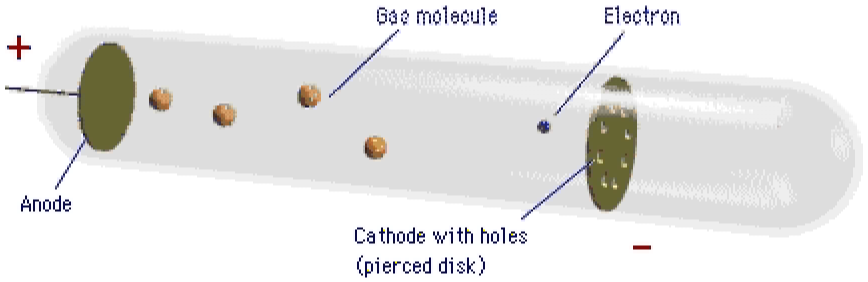
The mass of the electron, using Thomson's value for e/m works out to:

$$m = 9.11 \times 10^{-28}\ g$$

The Theory of Atomic Structure

Canal Rays - Protons

The first experiments which detected positively charged particles called canal rays used a specially constructed cathode ray tube.



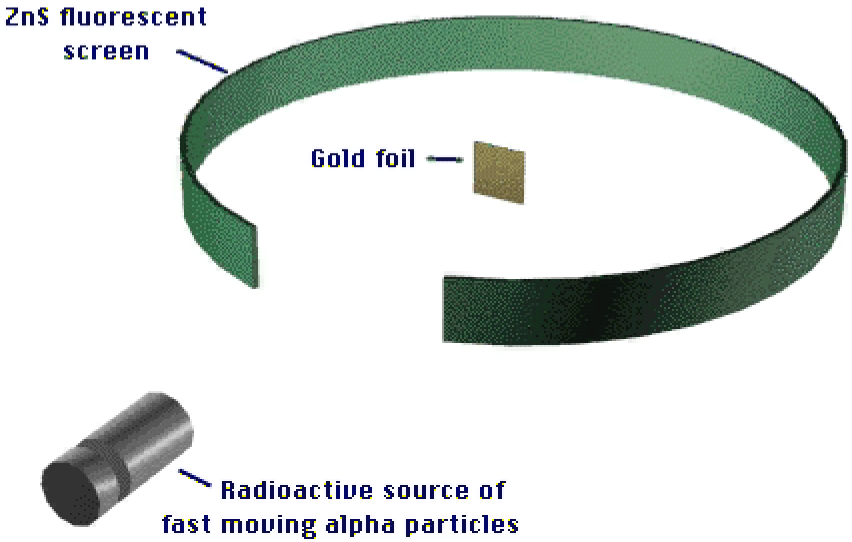
Later, an adaptation of this equipment called a mass-spectrometer has been used to determine the mass of the particles. The lightest detected was named the proton.

Mass: 1.67×10^{-24} g   Charge: $+1.60 \times 10^{-19}$ C

The Theory of Atomic Structure

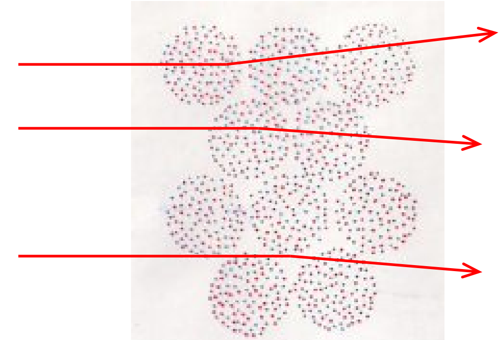
The Nuclear Atom

Ernest Rutherford (New Zealand, 1871 – 1937) designed an experiment to probe the interior of an atom. A beam of a particles was directed at a thin gold foil to investigate how it would be scattered.

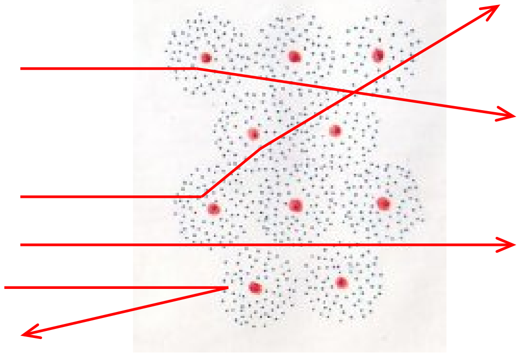


The Theory of Atomic Structure

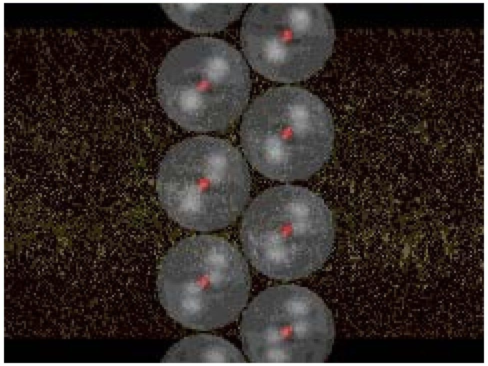
The Rutherford Experiment (cont.)



Even distribution of protons and electrons: The "plum pudding model"



The nuclear model: almost all the mass and positive charge is is in the centre.



The Theory of Atomic Structure

Neutrons

The nuclear mass, as calculated by Rutherford, did not correspond, to the appropriate charge and mass of the protons. It was too great.

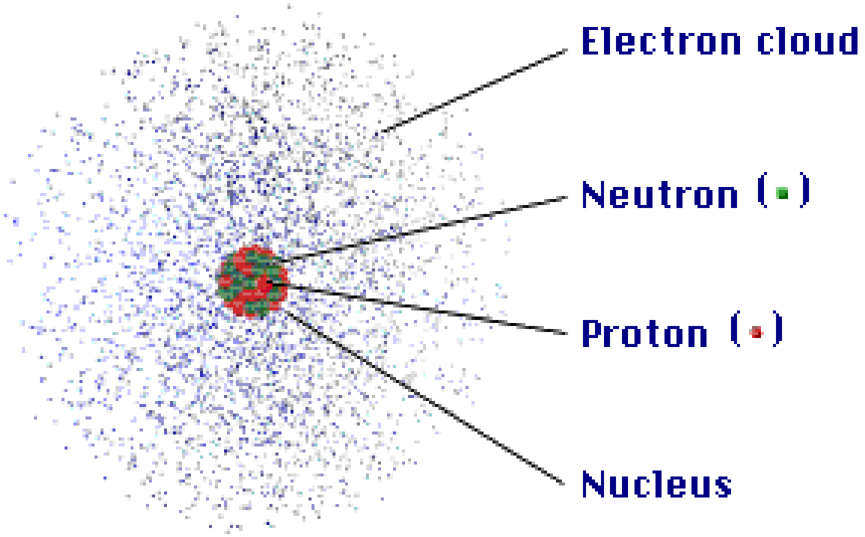
The missing mass was discovered by James Chadwick (English, 1891 – 1974) while he was investigating the radioactivity of polonium.

Highly penetrating radiation from polonium, when directed onto a beryllium target, generated a new kind of radiation. When this new radiation hit a paraffin wax target, it generated protons.

The best explanation was that the new radiation consisted of uncharged particles which he called neutrons.

Mass: 1.67×10^{-24} g   Charge: 0

The Theory of Atomic Structure – Summary



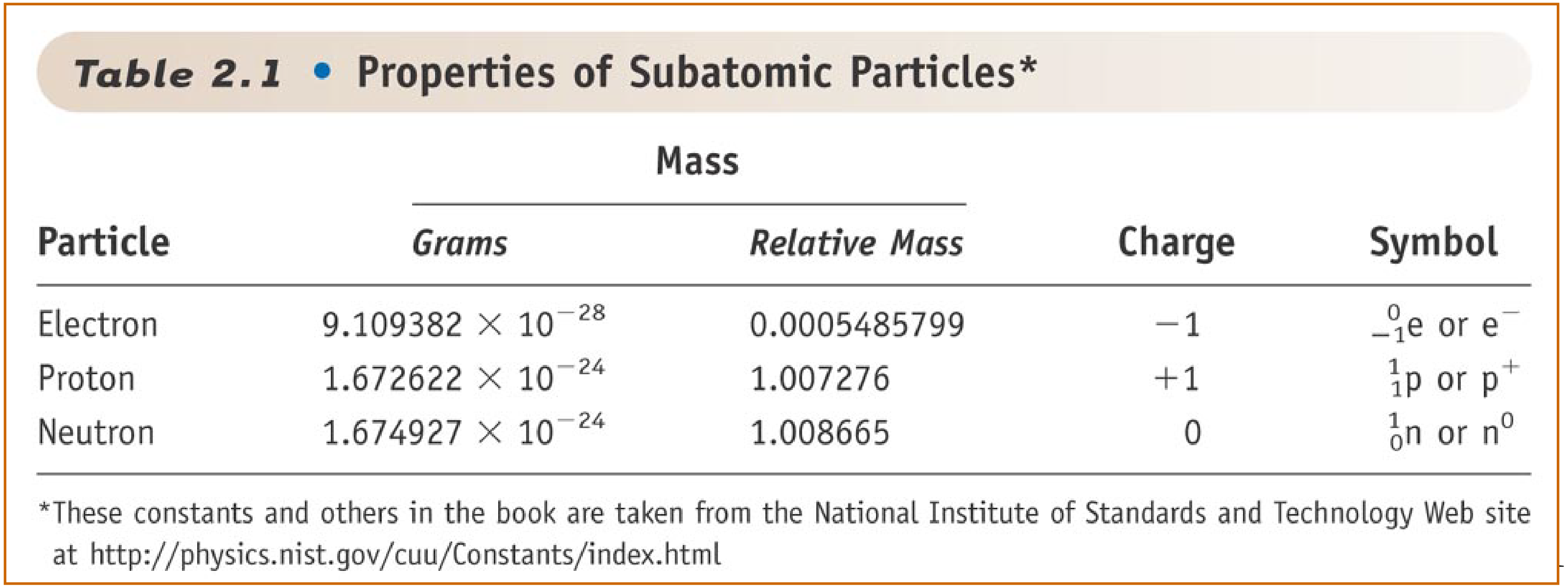


Table 2.1 • Properties of Subatomic Particles*

Particle	Mass		Charge	Symbol
	Grams	*Relative Mass*		
Electron	9.109382×10^{-28}	0.0005485799	-1	${}_{-1}^{0}e$ or e^{-}
Proton	1.672622×10^{-24}	1.007276	$+1$	${}_{1}^{1}p$ or p^{+}
Neutron	1.674927×10^{-24}	1.008665	0	${}_{0}^{1}n$ or n^{0}

*These constants and others in the book are taken from the National Institute of Standards and Technology Web site at http://physics.nist.gov/cuu/Constants/index.html

The size of the nucleus

- diameter of a hydrogen nucleus = 1.0×10^{-3} pm
- diameter of a hydrogen atom = 1.0×10^{2} pm
- Diameter atom / diameter nucleus = 1.0×10^{5}
- If diameter nucleus = 10 cm = 1.0×10^{-1} m (a grapefruit)

  diameter atom = 1.0×10^{4} m = 10 km

Consequences:

- Most of the volume of the atom is nearly weightless
- The density of the nucleus is enormous: you calculate it!

Now, starting at the beginning of chapter 2

in edition 9 of the textbook

Atomic Number, Mass Number, Charge

Atomic Number

All atoms of the same element have the same number of protons in their nuclei. The number of protons is called the **atomic number** of the element. Since atoms are neutral, the number of electrons is equal to the number of protons.

Mass Number

The **mass number** of an atom is the sum of the number of protons and neutrons.

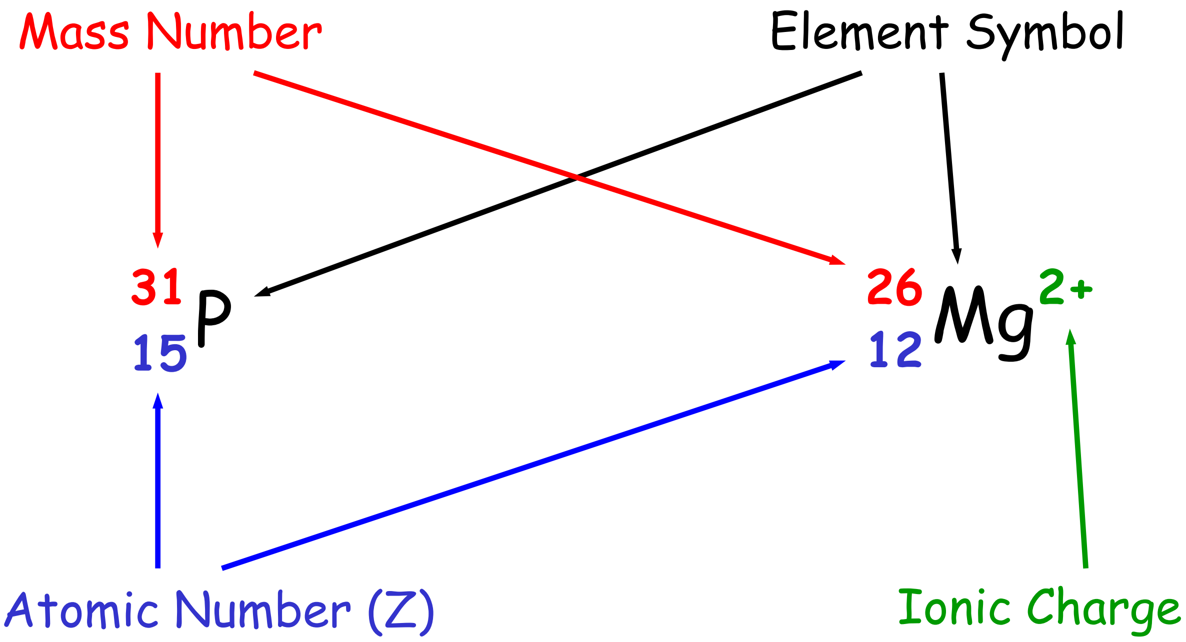
Ionic Charge

In compounds, atoms, or groups of atoms have sometimes lost or gained electrons. The resulting species are called ***ions***.

If an atom loses an electron or electrons, it becomes a *positively* charged *cation*. Examples: Na^+ , NH_4^+

If it gains an electron or electrons, it become a *negatively* charged *anion*. Examples: Cl^- , OH^-

Atomic or Ionic Symbols



Mass Number

Element Symbol

${}^{31}_{15}\mathrm{P}$

${}^{26}_{12}\mathrm{Mg}^{2+}$

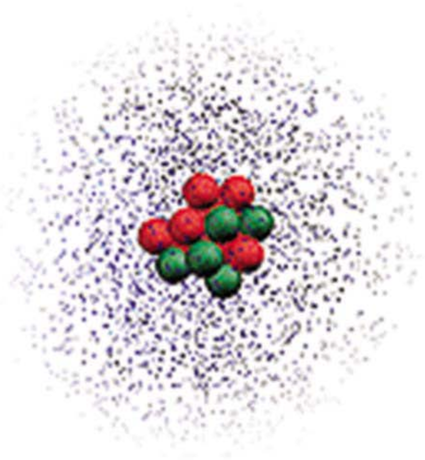
Atomic Number (Z)

Ionic Charge

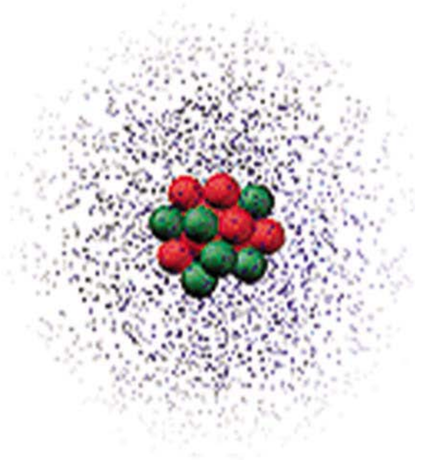
Note that the atomic number is actually redundant because it is implicit in the element symbol. Most commonly we write only the element symbol and sometimes the charge, if any.

Not all atoms of the same element have the same number of neutrons, and therefore the same mass number. We refer to a particular ***isotope*** by its mass number e.g. “phosphorus-31”.

Isotopes



Boron–10, ^{10}B
5 protons and
5 neutrons



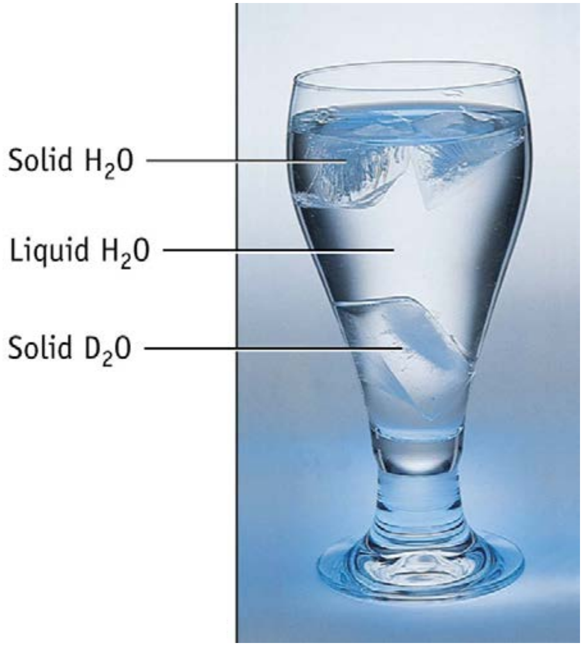
Boron–11, ^{11}B
5 protons and
6 neutrons

There are three isotopes of hydrogen which have special names:

Hydrogen: ^{1}H

Deuterium: ^{2}H or $^{(2)}D$

Tritium: ^{3}H or $^{(3)}T$



Isotope Abundance and Atomic Mass

The Atomic Mass Unit

By convention, we specify isotope masses, atomic masses and molecular masses by comparison with the standard of the isotope of carbon ^{12}C with 6 protons and 6 neutrons which is assigned the mass 12 **amu** = 12 **u** (newest IUPAC symbol)

Atomic Mass

Naturally occuring elements are often a mixture of isotopes and, in calculations, we use a weighted average of the individual isotopic masses. "Atomic weight" is the old name for "**atomic mass**."

Example:

Naturally occurring chlorine is 75.77% ^{35}Cl with a mass of 34.96885 u and 24.23% ^{37}Cl with a mass of 36.96699 u.

Therefore the "atomic weight" we find tabulated is:

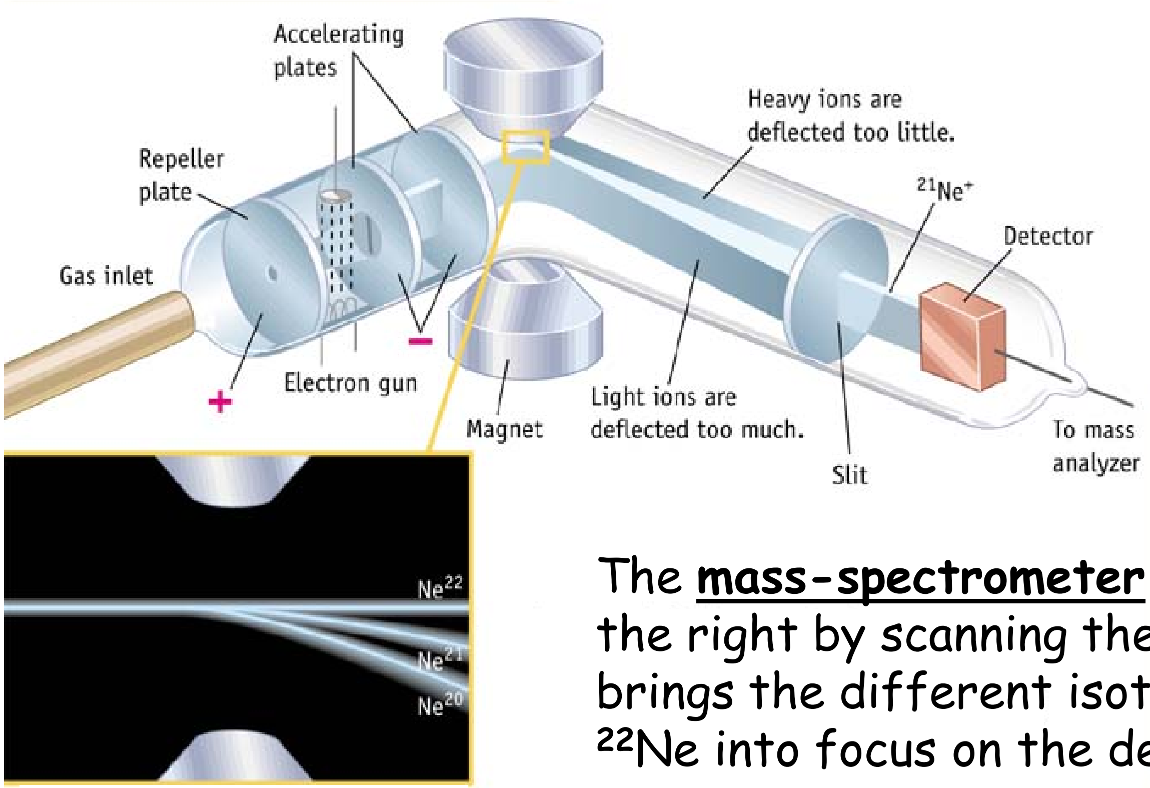
$$34.96885 \times 0.7577 + 36.96699 \times 0.2423 = 35.45 \text{ u}$$

Percent abundance

$$\text{Percent abundance} = \frac{\text{Number of atoms of a given isotope}}{\text{Total number of atoms of all isotopes of that element}} \times 100$$

Isotope Abundance and Atomic Mass

Determination of Relative Masses and Abundances



The **mass-spectrometer** produces the graph on the right by scanning the magnetic field. This brings the different isotopes; ^{20}Ne, ^{21}Ne and ^{22}Ne into focus on the detector one by one.

The peak heights give the abundances, and the exact positions on the m/e axis give the exact masses, *which are not exactly 20, 21 and 22.*

Calculating Isotopic Abundances

Problem: Antimony, Sb, has two isotopes, ^{121}Sb, 120.904 u, and ^{123}Sb, 122.904 u. What are the relative abundances of these two isotopes?

Solution: From the periodic table, we know that the average atomic mass of antimony is 121.760 u.

Let's call f_1 the fractional abundance of ^{121}Sb

f_2 the fractional abundance of ^{123}Sb

Average atomic mass of Sb = $(120.904 \times f_1) + (122.904 \times f_2) = 121.760$ u

In addition $f_1 + f_2 = 1$ since Sb has only two stable isotopes => $f_2 = 1 – f_1$

$120.904\, f_1 + 122.904\,(1- f_1) = 121.760$ => $f_1 = 0.5720$

$f_1 = 0.5720$ => 57.20 % of ^{121}Sb

$f_2 = 1 – 0.5720 = 0.4280$ => 42.80 % of ^{123}Sb

Atomic Mass and the Mass Defect

Things don't quite add up!

The exact masses of the elements cannot be determined from the exact masses of the particles which make them up.

The masses of the proton, 1.007276 amu, and the neutron, 1.008665 amu, add to 2.015941 amu.

The mass of a deuterium nucleus is actually 2.01355 amu, so:

$$2.015941 - 2.01355 = 0.00239 \text{ amu}$$

Have disappeared!

The missing mass is called the *binding energy:*

It can be calculated using Einstein's formula: $E = m \times c^2$ to be 2.1×10^8 kJ for every 2.01355 g of deuterium.

The Periodic Table

Group 1A
Lithium — Li (top)
Potassium — K (bottom)

Group 2A
Magnesium — Mg

Transition Metals
Titanium — Ti, Vanadium — V, Chromium — Cr, Manganese — Mn, Iron — Fe, Cobalt — Co, Nickel — Ni, Copper — Cu

Group 2B
Zinc — Zn (top)
Mercury — Hg (bottom)

Group 8A, Noble Gases
Neon — Ne

Group 3A
Boron — B (top)
Aluminum — Al (bottom)

Group 4A
Carbon — C (top)
Lead — Pb (left)
Silicon — Si (right)
Tin — Sn (bottom)

Group 5A
Nitrogen — N_2 (top)
Phosphorus — P (bottom)

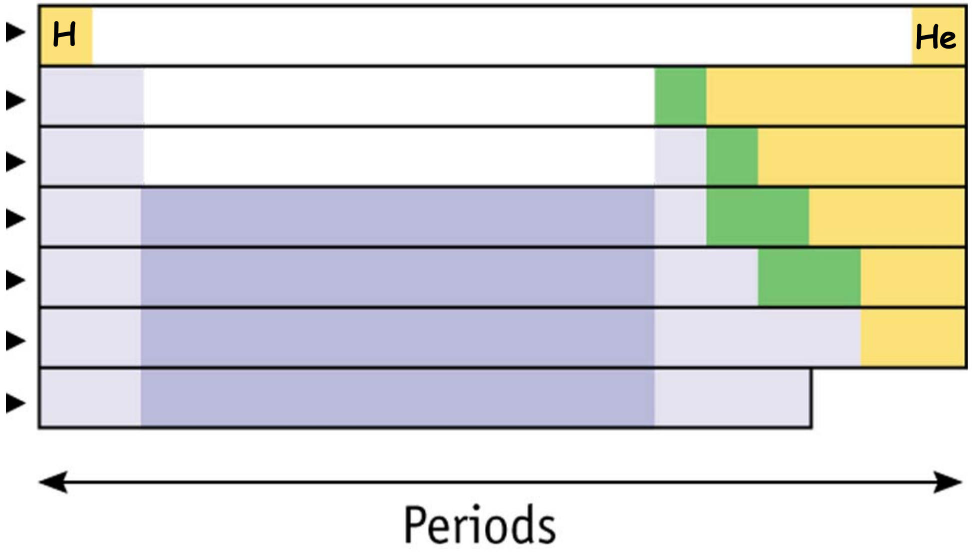
Group 6A
Sulfur — S (top)
Selenium — Se (bottom)

Group 7A
Bromine — Br

The Periodic Table

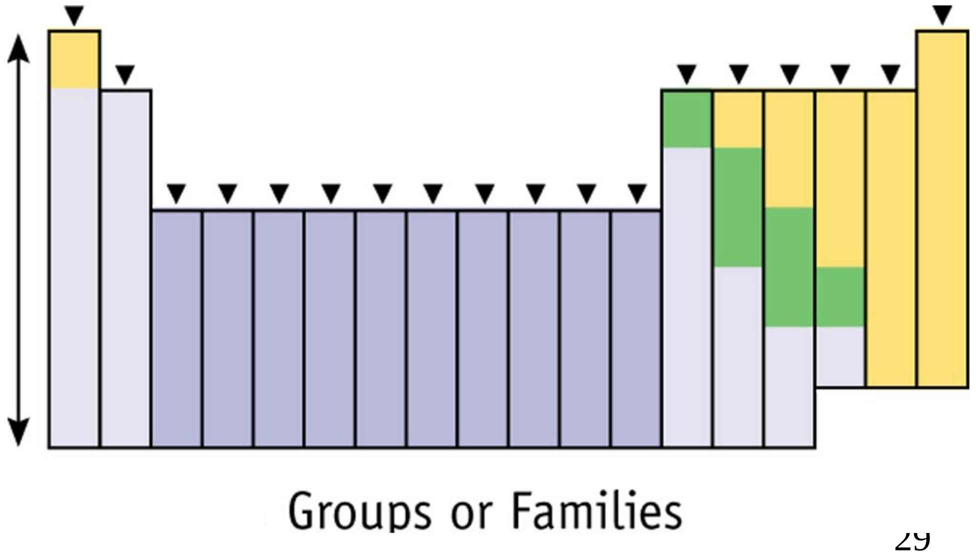
Periods

The horizontal rows are called **periods**, beginning at the top with period 1 for the one containing only H and He.

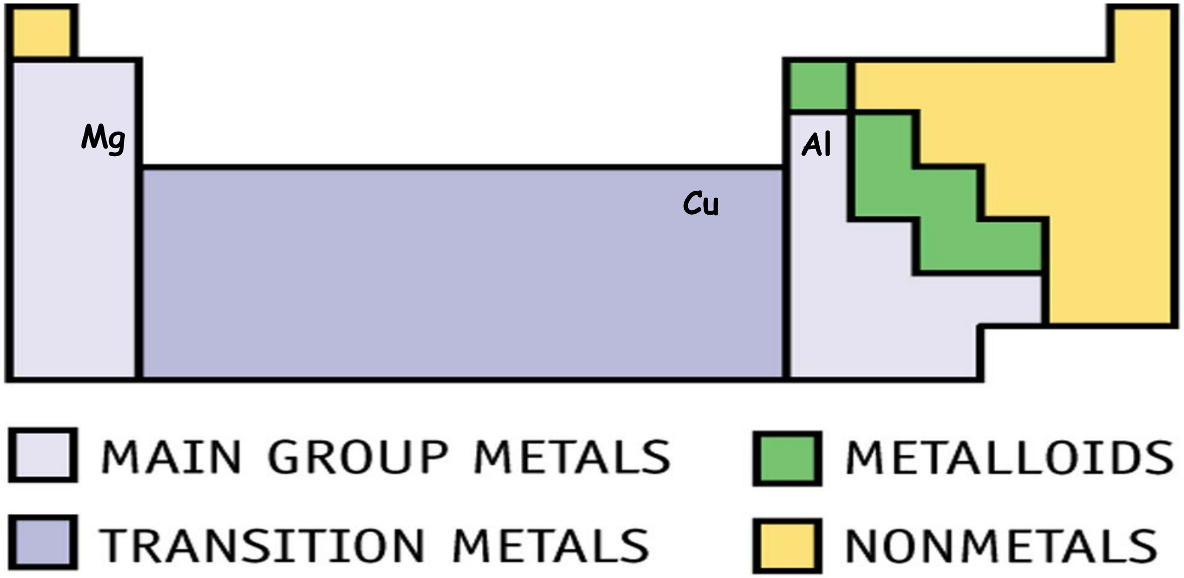


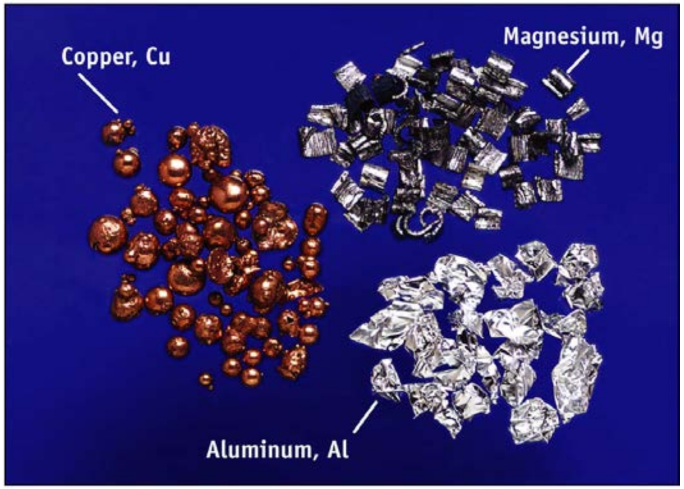
Groups

The vertical columns are called **groups** and are numbered **1 to 18** in modern tables, but still **1A, 2A**, etc., especially in American texts.



The Periodic Table





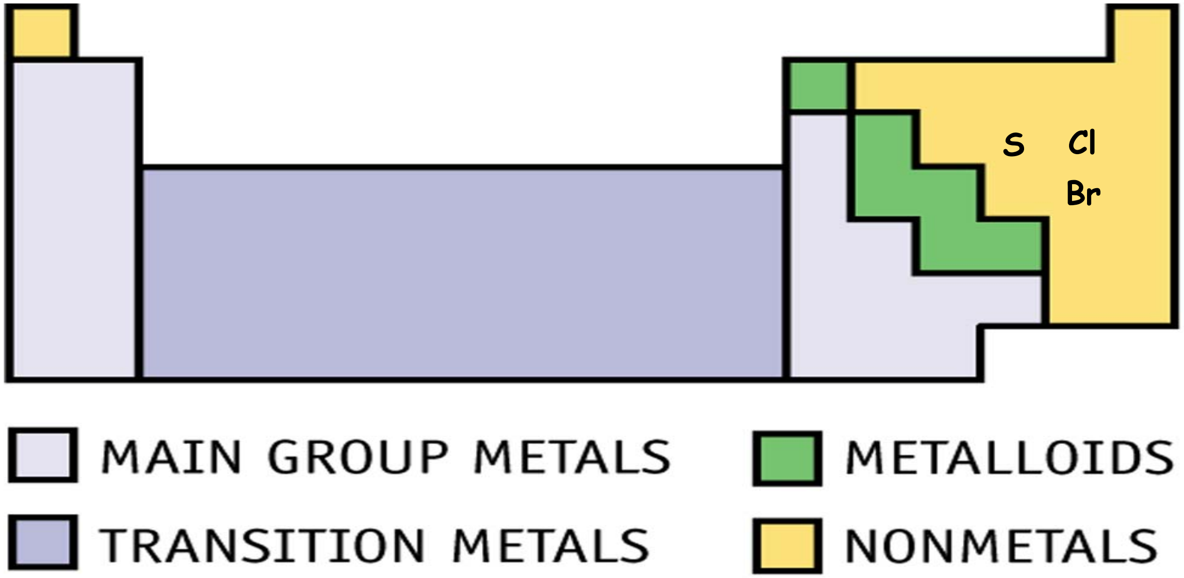
(a) Metals

Metals

All are solids, except Hg, and on warm days, Ga. They conduct electricity well. They are usually ductile and maleable, and often have a shiny metallic appearance.

The main group metals are quite soft and reactive; the transition metals less so.

The Periodic Table

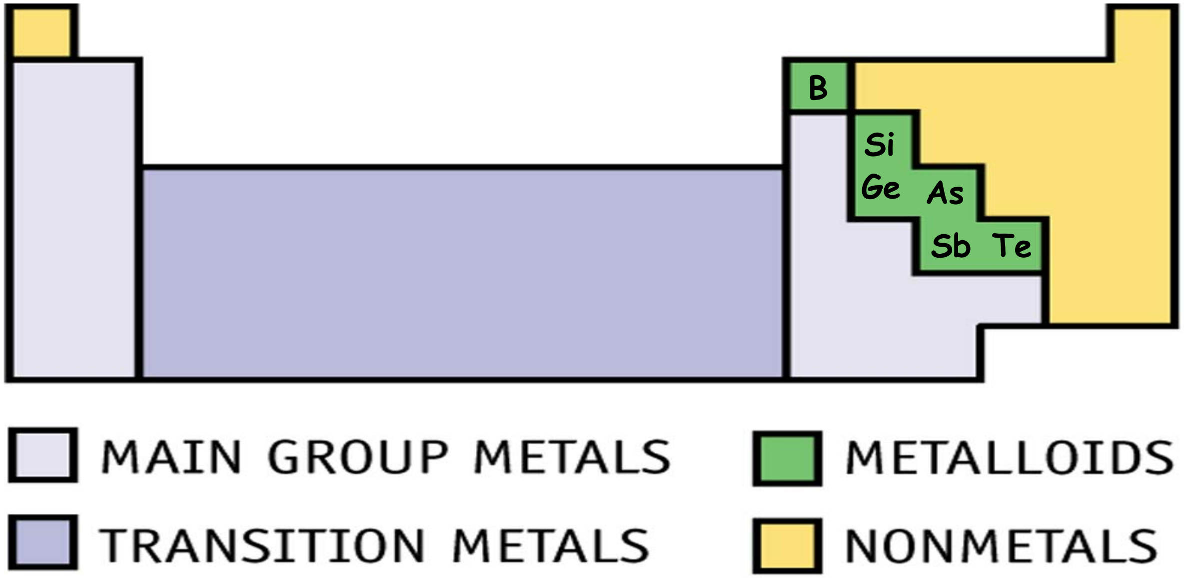


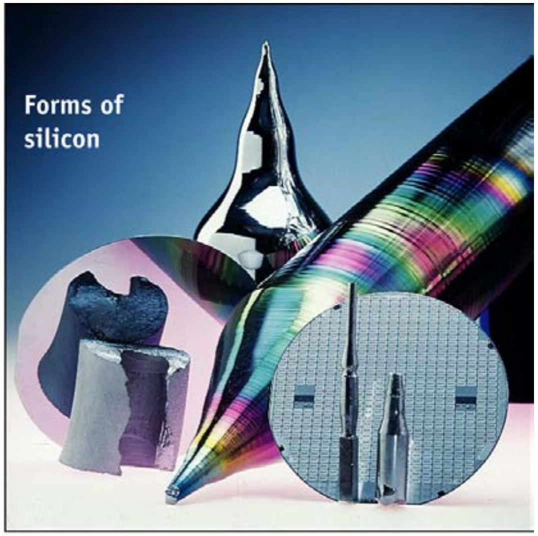
(b) Nonmetals

Non-metals

Can be solids, liquids (Br_2) or gases (N_2, O_2 F_2 and Cl_2). They do not conduct electricity (insulators), except carbon in the form of graphite. The ones towards the right tend to be most reactive as elements.

The Periodic Table





(c) Metalloids

Metalloids

Sometimes called **semi-metals**, they have physical properties that resemble those of the metals, and chemical properties that resemble non-metals.

It is not obvious which ones to include in the list: the text includes B, Si, Ge, As, Sb and Te in this category.

The Periodic Table

The Development of the Periodic Table

The forerunner of the modern periodic table was proposed by Dimitri Ivanovich Mendeleev (Russian, 1834 – 1907)

He arranged the elements in order of increasing atomic mass, and began a new row when the next element was similar in properties to a previous one.

For example:

Li	Be	B	C	N	O	F	
Na	Mg	Al	Si	P	S	Cl	
K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni
Cu	Zn	Ga	Ge	As	Se	Br	

The noble gases He, Ne, Ar etc. were still to be discovered.

He left gaps for elements he thought were still to be discovered, for example , what he called ekasilicon, and identified elements whose atomic mass he believed were in error. The missing element, germanium was later discovered.

The Periodic Table

Atomic Number

Even after the careful re-measurement of the atomic masses which Mendeleev believed to be in error, some elements still seemed out of order, Co (58.9332) and Ni (58.6934), for example.

H. G. J. Moseley (English, 1887 – 1915) studied the wave length of the X-rays which were emitted when the elements were bombarded with electrons. He arranged the elements in order of increasing X-ray energy and found that this correlated with atomic number.

It was recognized that the Mendeleev order was by atomic number and not by atomic mass.

Group 1 (1A) – Li, Na, K, Rb, Cs, Fr

The Alkali Metals

These metals are very reactive and only found in nature combined with other elements, e.g. NaCl – rock salt, K_2CO_3 – potash.

They are all silvery in colour and soft enough to cut with a knife.

They react with air to form oxides and are stored under oil.

The metals all react with water, more and more violently going down the group. The product is an alkaline solution of the hydroxide, MOH:

$$2\ M(s) + 2\ H_2O(l) \longrightarrow 2\ M^+(aq) + 2\ OH^-(aq) + H_2(g)$$

Li

Na

K

For more check out: http://www.youtube.com/watch?v=cqeVEFFzz7E

Group 2 (2A) – Be, Mg, Ca, Sr, Ba, Ra

The Alkaline Earth Metals

Like the alkali metals, they are also silvery relatively soft metals.They all react with water, except Be which is only reactive with steam.

$$M(s) + 2H_2O \longrightarrow M^{2+}(aq) + 2OH^{-}(aq) + H_2(g)$$

Except Beryllium and Magnesium, they are slowly oxidized in air.

Magnesium is one of the more common elements in the earth's crust (7th). It important in biologically in molecules such as Chlorophyll. It is used in fireworks, and in light weight alloys.

Calcium is also a common element (5th) and occurs in teeth, bones, sea shells. It occurs naturally as limestone, $CaCO_3$.

Radium, like francium in group 1, is radioactive.

Group 13 (3A) – B, Al, Ga, In, Tl

This group has no special name - we call it “The Boron Group”.

Boron, a metalloid occurs in borax, $Na_2B_4O_5(OH)_4.8H_2O$, mined in Death Valley California in the town of the same name. It is used to make borosilicate glass – e.g. pyrex.

Aluminum is the most abundant metal in the earth’s crust, and turns up in all sorts of clays and minerals. It would be quite easily oxidized by the air except that it forms a thin protective oxide film. Ruby is aluminium oxide, Al_2O_3, doped with a small quantity of Cr. In sapphire, the dopant is iron, Fe, or titanium, Ti.

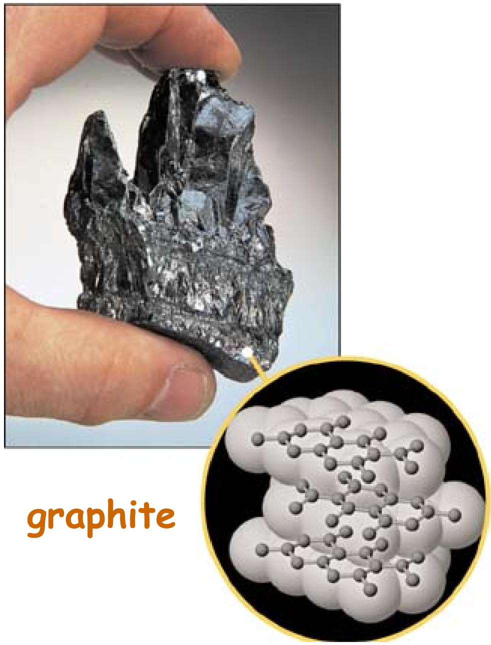
The other elements in the group all metals. Gallium has some importance in the semiconductor, gallium arsenide.

Group 14 (4A) – C, Si, Ge, Sn, Pb

No special name again – we call it “The Carbon Group”.

This is one of the more interesting groups. Carbon is a non-metal, Silicon and Germanium are metalloids, both important in the semiconductor industry, and tin and lead are metals.

Carbon has at least three *allotropic forms* – different structures of the same element: graphite, diamond and various recently-discovered “buckminsterfullerenes”.



graphite

diamond

bucky-ball

Group 14 (4A) – C, Si, Ge, Sn, Pb

Silicon is found widely in silicate rocks. It is used to make artificial oils and rubbery materials which have a variety of uses due to their chemical inertness and heat resistance.

Tin, Sn, and lead, Pb, were among the first metals isolated from their ores, because it is quite easy to do so.

Tin mixed with copper forms the alloy bronze. Because it is relatively more resistant to corrosion than iron, it is used to coat tin cans.

Lead in small quantities alloyed with tin is the alloy pewter. It was also extensively used in water pipes: although it is dangerously toxic, it becomes covered with an insoluble film of carbonate and sulphate.

Group 15 (5A) – N, P, As, Sb, Bi

This group has newly invented name – The Pnictogens

Nitrogen is a gas, N_2. Phosphorus comes in several solid allotropic forms, the most common of which are the relatively safe "red" phosphorus,and the highly in flammable "white" phosphorus, P_4. Arsenic and Antimony (Sb) are metalloids, and bismuth is a metal.

Nitrogen forms about 75% of the atmosphere. It is converted by bacteria living on the roots of certain plants to some of its compounds, notably nitrate, NO_3^- and ammonia, NH_3. It turns up all over the place in biologically important molecules.

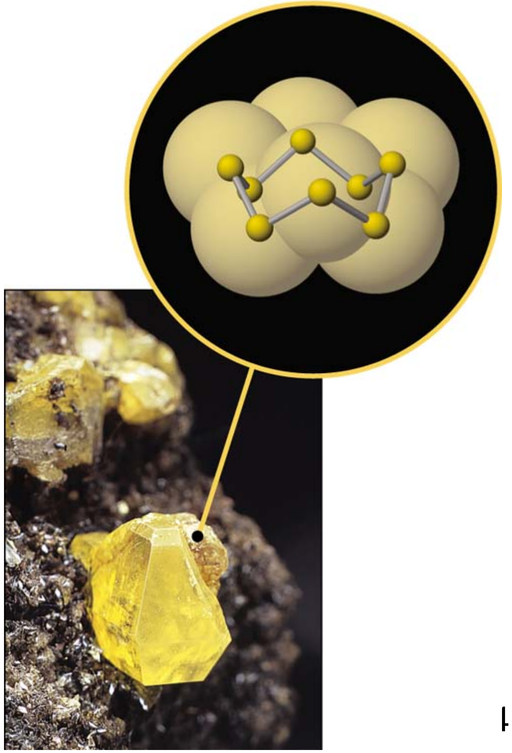
Phosphorus is also essential to life, mostly in the form of phosphates. Red phosphorus is a constituent of match heads. Phosphoric acid, H_3PO_4, is an important industrial chemical.

Group 16 (6A) – O, S, Se, Te, Po

The Chalcogens

Oxygen is normally a gas, O_2. Sulphur is a solid element with several allotropic forms, S_8 (monoclinic, rhombic), S_n "plastic sulphur", and S_6. Selenium also has allotropic forms. Tellurium, Te, is a metalloid, and Polonium is a radioactive metal, and dangerously poisonous.

Oxygen, O_2 make up approximately 20% of our atmosphere and is a major element in many many minerals. Another form of oxygen is ozone, O_3.



Sulphur is found in underground deposits. In the form of sulphuric acid, H_2SO_4, it is one of the most important industrial chemicals. In the form of sulphur dioxide, SO_2 and hydrogen sulphide, H_2S, it is also a major pollutant.

Group 17 (7A) – F, Cl , Br, I, At

The Halogens

These elements all exist as diatomic molecules. Chlorine and fluorine are yellow and green gases, respectively. Bromine is a brown volatile liquid. Iodine is a black volatile solid with purple vapour. Astatine is radioactive.

These elements are all very reactive, for example they react with many metals to form chlorides, particularly violently with the alkali metals:

$$X_{2(g)} + 2M(s) \longrightarrow 2M^{+}X^{-}(s)$$

Fluorine, F_2 is very corrosive and will attack glass and fingers!

Group 18 (8A) He, Ne, Ar, Kr, Xe, Rn

The Noble Gases

These elements are also known as the “rare gases”, although argon is not particularly rare!, and the “inert gases” because for many years they were not believed to form any compounds.

After hydrogen, helium is the most abundant element in the universe. It is found on earth with reserves of natural gas and comes form radioactive decay of heavy elements producing α particles.

Neon is used in lighting, and argon is used as an inert atmosphere for manipulating chemicals which react with nitrogen. Both are chemically inert.

Krypton and xenon both form a few compounds, and some xenon compounds are strong oxidizing agents used in synthetic chemistry.

Radon, produced by radioactive decay of transuranium elements and has been a cause for concern in peoples basements if badly ventilated.

Groups 3 to 12 (1B to 8B)

The Transition Elements

These are all metals. (Note that the US group numbers are not in order: 1B and 2B come after 3B to 8B.

Unlike the alkali and alkaline earth metals, these elements are all quite hard and relatively unreactive. Only gold, silver and platinum can be found as the pure element in nature. The rest are found in compounds, often as oxides or sulfides. Most find commercial uses. One, technetium, Tc, is radioactive and artificially produced: it is used in nuclear medicine.

The Lanthanides or Rare Earth Elements

Are a set of 14 metals following lanthanum, La, in the periodic table. They are characterized by having very similar physical and chemical properties which make them difficult to separate.
They are used in phosphors for TV screens.

Actinides

The 14 elements following actinium. All are radioactive, some with very short half-lives, so that only miniscule quantities can be made.

Interesting Statistics

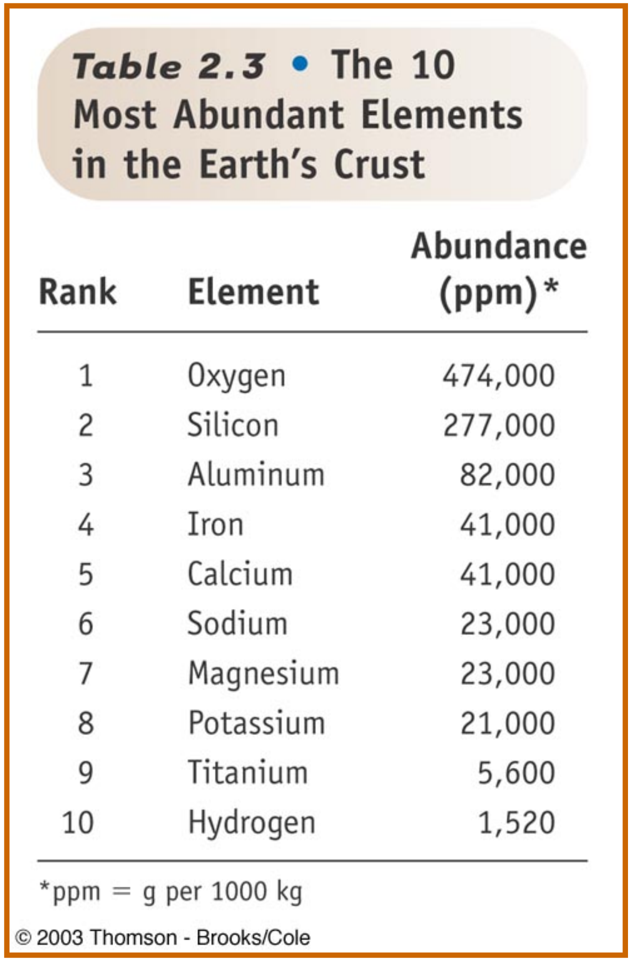


Table 2.3 • The 10 Most Abundant Elements in the Earth's Crust

Rank	Element	Abundance (ppm)*
1	Oxygen	474,000
2	Silicon	277,000
3	Aluminum	82,000
4	Iron	41,000
5	Calcium	41,000
6	Sodium	23,000
7	Magnesium	23,000
8	Potassium	21,000
9	Titanium	5,600
10	Hydrogen	1,520

*ppm = g per 1000 kg

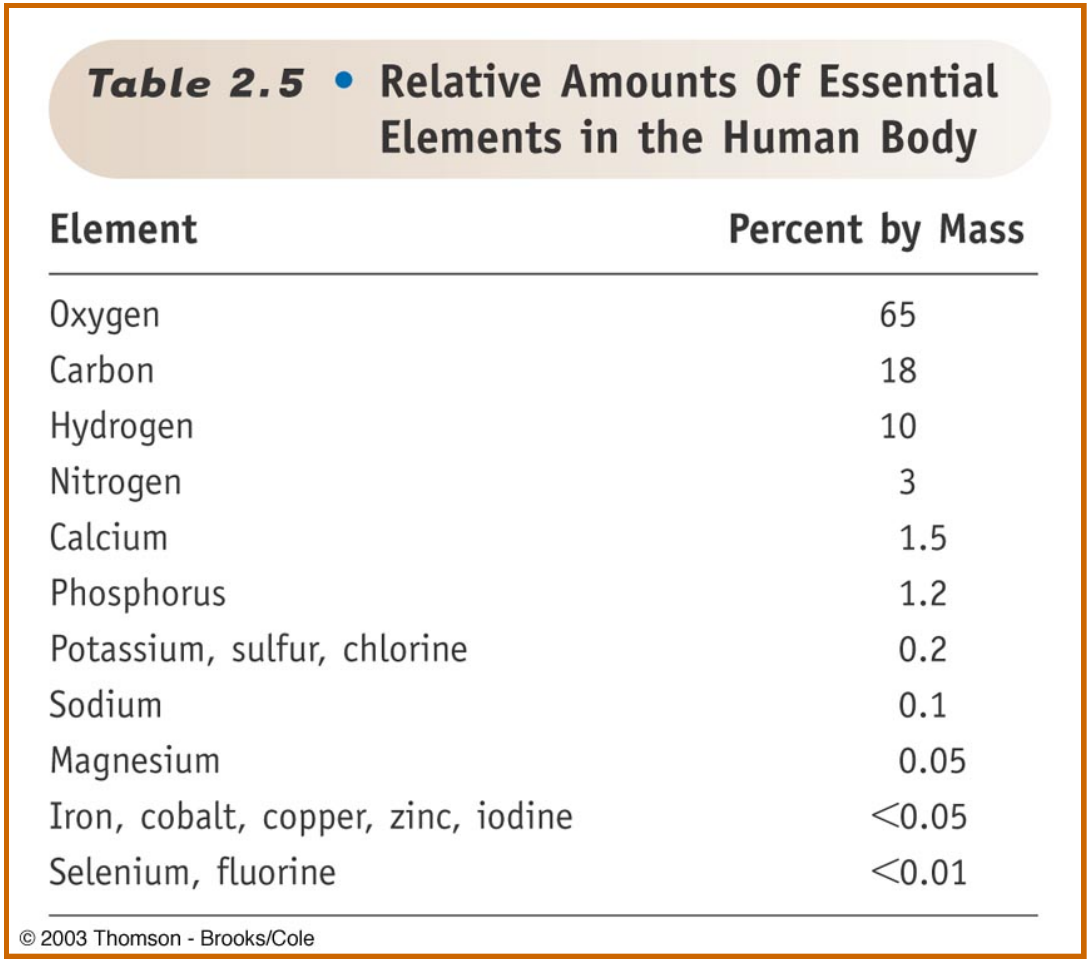


Table 2.5 • Relative Amounts Of Essential Elements in the Human Body

Element	Percent by Mass
Oxygen	65
Carbon	18
Hydrogen	10
Nitrogen	3
Calcium	1.5
Phosphorus	1.2
Potassium, sulfur, chlorine	0.2
Sodium	0.1
Magnesium	0.05
Iron, cobalt, copper, zinc, iodine	<0.05
Selenium, fluorine	<0.01

Molecules: Compounds, Formulas, Equations

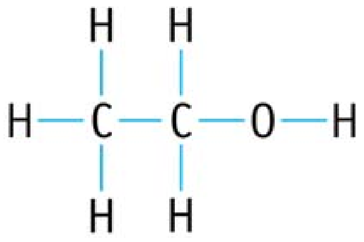
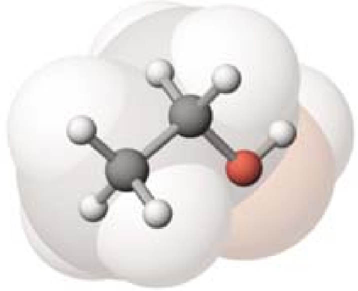
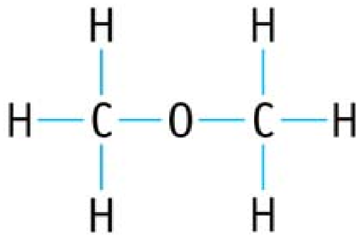
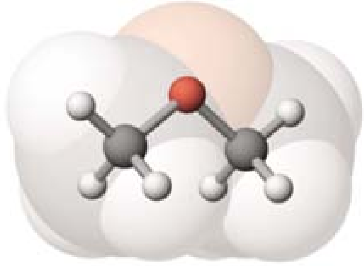
$2Al(s) + 3Br_2(l) \longrightarrow Al_2Br_6(s)$

aluminum bromine aluminum bromide

$Zn(s) + S(s) \longrightarrow ZnS(s)$

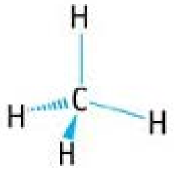
zinc sulfur zinc sulfide

Molecules: Compounds, Formulas

NAME	MOLECULAR FORMULA	CONDENSED FORMULA	STRUCTURAL FORMULA	MOLECULAR MODEL
Ethanol	C_2H_6O	CH_3CH_2OH		
Dimethyl ether	C_2H_6O	CH_3OCH_3		

Compounds are pure substances made of more than a single element.

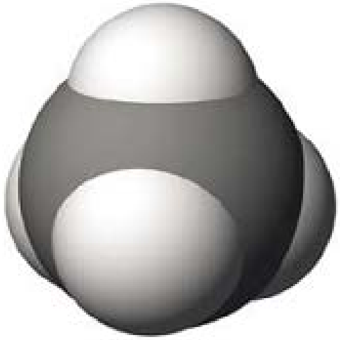
Molecular Models



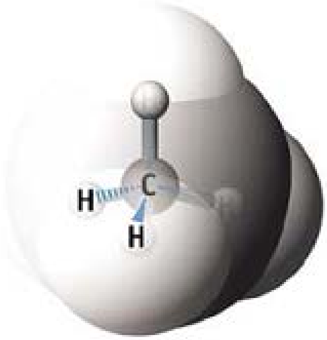
Simple perspective drawing

Plastic model

Ball-and-stick model



Space-filling model



All visualizing techniques represent the same molecule.

Simple Perspective Drawing – This is what we use to communicate, e.g. exams

Plastic Model – available from the bookstore. Useful when studying various aspects of molecular structures (especially left/right handedness)

Ball and stick, Space Filling – Computer generated. The ball and stick diagram is used the same way as a plastic model. The space-filling diagram is used to represent the outer surface of a molecule more realistically, usually to understand how molecules can interact with each other.

(There are lots of these on the disk which comes with the text.)

Quick overview of “Electronegativity”

Definition

“**Electronegativity**” is the ability of an atom in a molecule or in a polyatomic ion to attract shared electrons to itself.

Trends within the periodic table **(will be justified later):**

- Metals have a low electronegativity, non-metals have a high electronegativity, noble gases have zero (or nearly zero) electronegativity
- it decreases down a group: EN(H)>EN(Li)
- it increases from left to right: EN(Li)<EN(Be)
- it is about constant along a diagonal from top left to bottom right: EN(Li) ≈ EN(Mg) => **Diagonal relationship**
- Trends work well for main groups elements, not much applicable to transition elements, lanthanides and actinides

Bonding types

There are 3 types of bonding (real bonding is often intermediate between two of these, or even between the three in some cases):

- **ionic bonding**: between metals and non-metals (large difference of electronegativity): **ions** are formed, **cations** (Na^+) (metal atoms lose electrons) and **anions** (Cl^-) (non-metal atoms gain electrons), and **electrostatic attraction between cations and anions** form the ionic bonding; only in the solid state or liquid state;

- **covalent bonding** or **valence bonding**: between two non-metals (difference of electronegativity is not large enough to form ions) (examples: H_2, HCl, H_2O). **Sharing of electrons between atoms** for the covalent bond

- **metallic bond**: between metal atoms, only in the solid state or liquid state. Metal atoms lose **electrons, which are delocalized** over the whole sample and highly mobile, making metals excellent electrical conductors and heat conductors [Not studied in this course]

Types of compounds

Molecular compounds: Formed of **discrete** molecules (discrete = that can be identified and separated without braking the compound).

Bonding is covalent. Examples: H_2O, HCl, O_2

Polymeric compounds: No discrete molecules can be identified. They contain covalent bonding that extend to billions of atoms.

Example: plastics

Metals and ionic compounds: No discrete molecules can be identified. They contain metallic or ionic bonding that extend to billions of ions.

Example: in solid NaCl: each Na^+ binds to six Cl^- ion, and each Cl^- ion binds to six Na^+ ion.

In contrast, NaCl gas is molecular with one Na atom bonded to one Cl atom => Na-Cl in the gas phase, **never** in the liquid or the solid

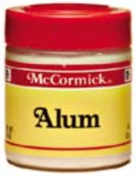
Ionic Compounds: Formulas Names, and Properties

The previous slides showed compounds that were **molecular** and the atoms are held together by what we call **covalent bonds** (the sticks).

Salt, sodium chloride, NaCl
contains Na^+ cations, Cl^- anions

Sodium fluoride, NaF
contains Na^+ cations, F^- anions

Copper sulfate, $CuSO_4$
contains Cu^{2+} cations, SO_4^{2-} anions

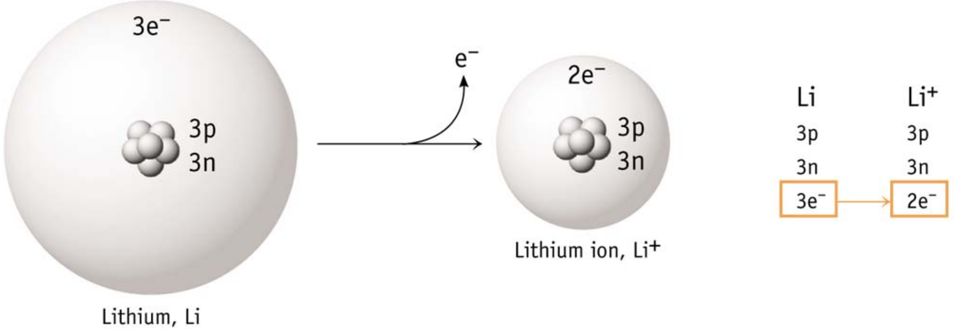


Alum, $KAl(SO_4)_2 \cdot 12\ H_2O$
contains K^+ cations, Al^{3+} cations, SO_4^{2-} anions, and H_2O molecules

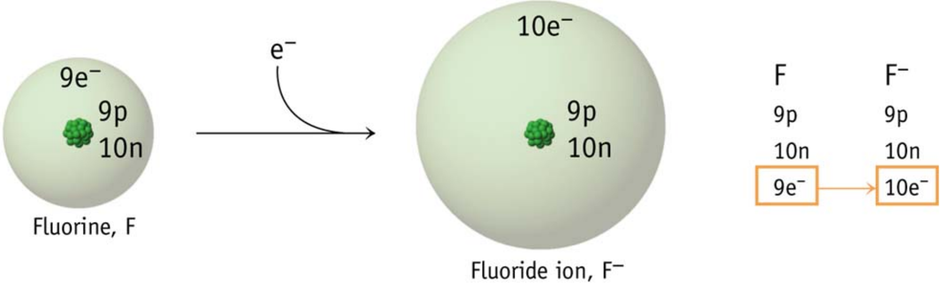
There is another class of compounds that are composed of ions:

- Elements, usually metals, which have lost electrons – **cations**, e.g. Mg^{2+}.
- Elements, usually non-metals, which have gained electrons – **anions**, e.g. S^{2-}.
- **Molecular ions = Polyatomic ions** – species with more than one atom, bonded covalently, but having an overall charge, e.g. ammonium ion, NH_4^+.

Monatomic Cations and Anions

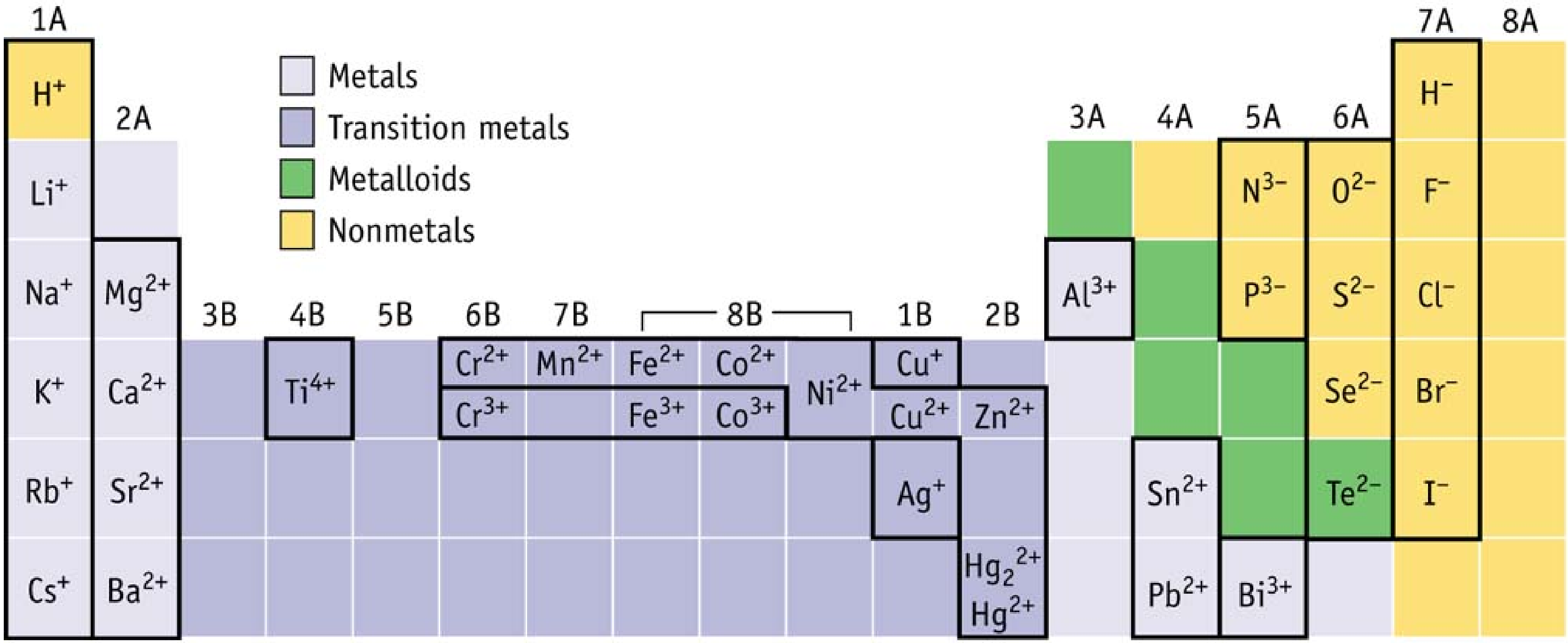


Cations are always smaller than the atom from which they are derived.



Anions are always larger than the atom from which they are derived.

Monatomic Cations and Anions



The charges are easily predictable for groups 1 (1A), 2 (2A) and 13 (3A)
- It is the same as the group number.

The charges are easily predictable for groups 15 (5A), 16 (6A) and 17 (A)
- It is the group number – 18 (or minus 8 if you use the US numbering)

For tin and lead the normal ions have a 2+ charge; for bismuth, 3+.

The transition metals often have several possible charges which are difficult to predict. You have to learn them.

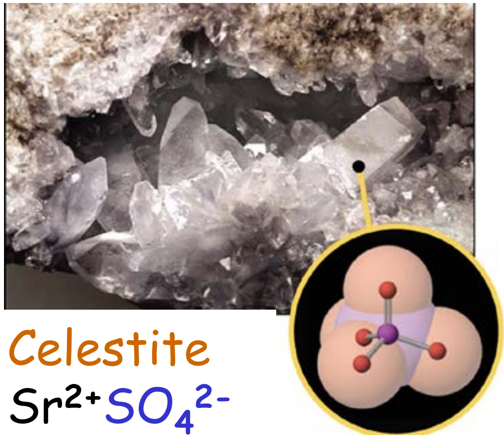
Polyatomic Ions

There are many, many polyatomic ions, both anionic and cationic.

Calcite

$Ca^{2+}CO_3^{2-}$

$(CaCO_3)$



Celestite

$Sr^{2+}SO_4^{2-}$

$(SrSO_4)$

Fluorapatite

$Ca^{2+}_5(PO_4^{3-})_3F^-$

$(Ca_5(PO_4)_3F)$

Bonding type when polyatomic ions are present

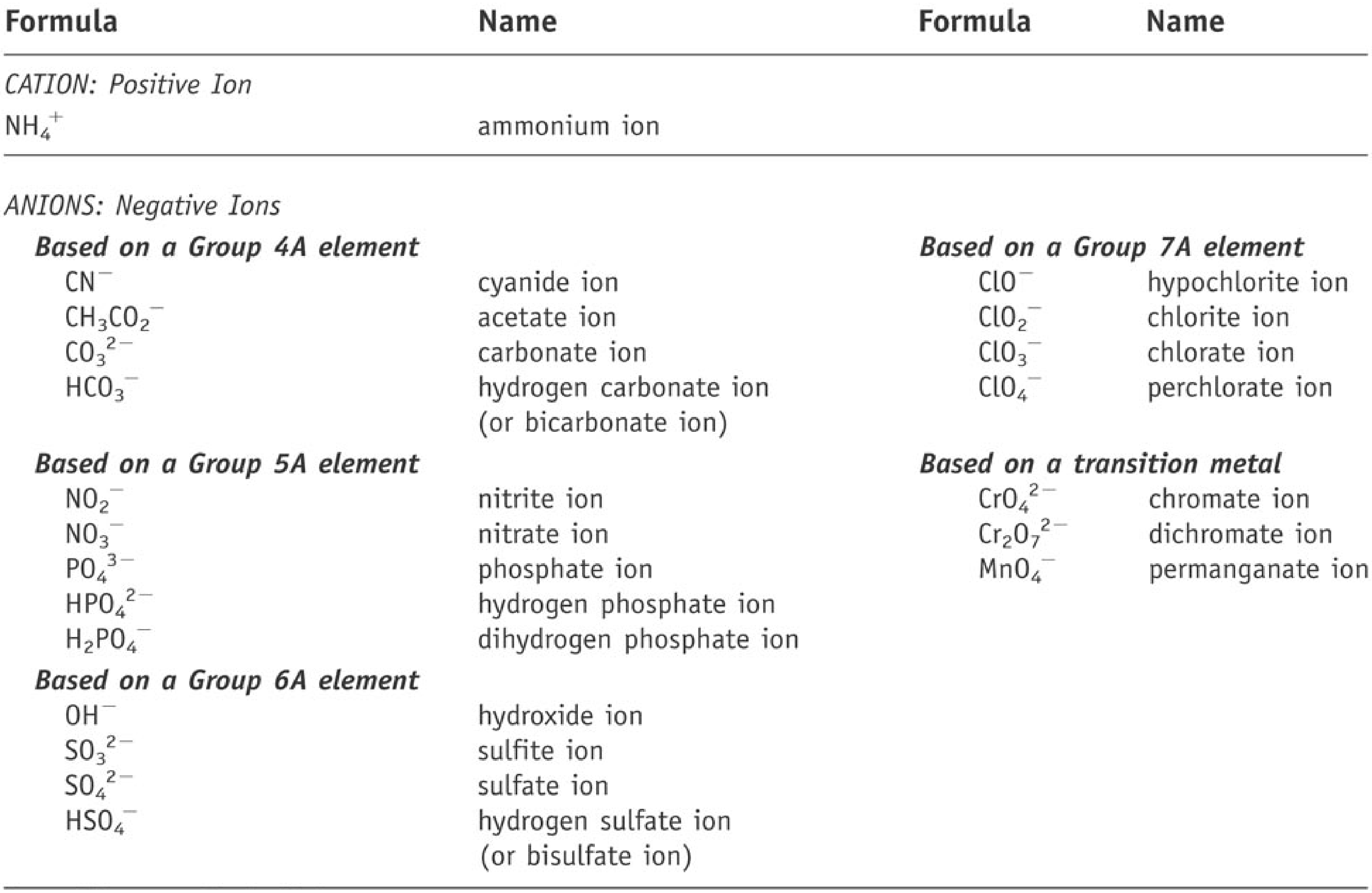
There are covalent bonding within the polyatomic ions, and ionic bonding between the ions

Example: KNO_3 potassium nitrate

- ions K^+ (monoatomic) and $[NO_3]^-$ (polyatomic)
- three N-O covalent bonds within the nitrate ion
- ionic bonding between the potassium ions and the nitrate ions

Polyatomic Ions

(Kotz, Table 3.1)



Formula	Name	Formula	Name
CATION: Positive Ion			
NH_4^+	ammonium ion		
ANIONS: Negative Ions			
Based on a Group 4A element		***Based on a Group 7A element***	
CN^-	cyanide ion	ClO^-	hypochlorite ion
$CH_3CO_2^-$	acetate ion	ClO_2^-	chlorite ion
CO_3^{2-}	carbonate ion	ClO_3^-	chlorate ion
HCO_3^-	hydrogen carbonate ion (or bicarbonate ion)	ClO_4^-	perchlorate ion
Based on a Group 5A element		***Based on a transition metal***	
NO_2^-	nitrite ion	CrO_4^{2-}	chromate ion
NO_3^-	nitrate ion	$Cr_2O_7^{2-}$	dichromate ion
PO_4^{3-}	phosphate ion	MnO_4^-	permanganate ion
HPO_4^{2-}	hydrogen phosphate ion		
$H_2PO_4^-$	dihydrogen phosphate ion		
Based on a Group 6A element			
OH^-	hydroxide ion		
SO_3^{2-}	sulfite ion		
SO_4^{2-}	sulfate ion		
HSO_4^-	hydrogen sulfate ion (or bisulfate ion)		

Formula of Ionic Compounds

Since there is no molecule as such, the formulae given are always "simplest" or **empirical formula (= unit formula)**, which just specify the ions and their proportions in the compound.

By contrast, we write usually the formulae of molecular compounds to indicate, at the very least, the structural unit.

For example, glucose $C_6H_{12}O_6$ and acetic acid $C_2H_4O_2$ both have the same empirical formula (CH_2O), but are completely different molecules.

An ionic *compound* is electrically neutral, so the charges on the individual ions *must* sum to zero.

For example, fluorapatite is $Ca^{2+}{}_5(PO_4{}^{3-})_3F^-$:

$$\text{The total charge} = 5 \times (+2) + 3 \times (-3) + (-1) = 0$$

Oxidation state = Oxidation number

Definition: **it is a way for accounting for electron distribution. Charges are real only for monoatomic ions**

- For **monoatomic ions**, the oxidation state is equal to the charge of the ion: + 1 for Na^+ , +2 for Ca^{2+} , -1 for Cl^- , -2 for O^{2-}.

- For **atoms that form covalent bonds,** the oxidation number of each atom is equal to the charge that would the atom have if bonding were ionic. Example: H_2O Covalent bonding: H-O-H

  EN(H) < EN(O) => ON(H) > 0 and ON(O) < 0 => for the purpose of calculating oxidation numbers, treat it like if it were ionic:

  H^+ => ON = +1 O^{2-} = -2

Metals: One oxidation state only, or several oxidation states?

Oxidation number = oxidation state

- **Oxidation state = 0 for elements:** e.g. He, H_2, C (diamond or graphite), Al metal

- **One** oxidation state: groups 1-3, 12, Al, Ag, all lanthanides except Ce and Eu

  Example: in Ca^{2+}, Ca has the +2 oxidation state

  In Cl^-, Cl has the -1 oxidation state

- **Several** oxidation states: all other main group metals + transition metals of groups 4-11, Ce and Eu (lanthanides) + all actinides

Oxidation Number vs. bonding type

Ionic bonding: oxidation number = number of electrons lost (ON>0) for least electronegative element, and = number of electrons gained (ON<0) for most electronegative element

Example: in CaF_2: Ca^{2+} (ON = +2) and F^- (ON = -1)

Covalent bonding: oxidation numbers are calculated like if bonding were ionic.

Example: in H_2O : H is the least electronegative (ON = +1)
O is the most electronegative (ON = -2)

The sum of the oxidation number of all atoms = charge of the species (= 0 for molecules, = charge of the polyatomic ion)

Examples: H_2O : 2xON(H) + ON(O) = 2x(+1) -2 = 0
$[NH_4]^+$: ON(N) + 4xON(H) = -3 + 4x(+1) = +1

Oxidation Numbers vs. position in the periodic table

Main group elements: Oxidation number are predictable

Group 1: +1 (in addition, H is -1 if bonded to a metal)
Group 2: +2
Group 13: +3 (all) and +1 (Ga, In, Tl)
Group 14: C: +4 or +2 (can also be <0 if bonded to metals)
Si: +4 only
Ge, Sn, Pb: +4 and +2
Group 15: -3, +1, +3, +5
Group 16: O: -2, unless bonded to F or to another O
S, Se, Te: -2, +2, +4, +6
Group 17: F: -1
Cl, Br, I: -1, +1, +3, +5, +7
Group 18: He, Ne, Ar: always 0 (form no compound)
Kr: +2
Xe: +2, +4, +6, +8

Full oxidation state = maximum positive: +6 for Te

Suboxidations states = positive lower that the maximum : +2 and +4 for Te

Difference of 2 between the different oxidation numbers of a given **main group element**.

Oxidation Numbers vs. position in the periodic table (Continued)

Transition elements: **Much less predictable**

Groups 3–7: maximum oxidation number = group number

Home exercise : Check whether this is true in $[CrO_4]^{2-}$ and $[MnO_4]^-$

Group 3: +3 only

Groups 7-10 and Cu(in group 11): +2 is the most common

Group 11: +1 (less stable for Cu) and Au, most stable for Ag

Group 12: +2 only, except for Hg if bonded to another Hg

Groups 4-11: other oxidation numbers exist

The difference between two oxidations numbers of the same transition element can be only 1 (in contrast with main group elements)

Lanthanides: all are +3 (Ce can also be +4 and Eu can be +2)

Actinides: Several oxidation numbers possible (difference of 1 common)

Using oxidation numbers to understand the formula of compounds and polyatomic ions

Ionic compounds: Use the ionic charges to get neutral compounds.

Is magnesium sulfide MgS_2, or MgS_3, or MgS, or Mg_2S, or…?

What is the formula of chromium(III) oxide?

Covalent compounds and polyatomic ions:

Is ClF_3 a possible compound?

F is most electronegative: ON(F) = -1

Cl is least electronegative => ON(Cl)>0 => +1, +3, +5 and +7 allowed => ON(Cl) + 3xON(F) = 0=> ON(Cl) – 3 = 0

=> ON(Cl) = +3 => allowed.

Try ClF_5, ClO_2, $[BF_4]^-$, $[ClO_4]^-$, As_2O_3, and others

Mixed oxidation state compounds

Case of non-integer oxidation states:

Magnetite Fe_3O_4 is a naturally occurring magnet. What is the oxidation state of iron?

3xON(Fe) + 4xON(O) = 0 => 3xON(Fe) – 8 = 0 => ON(Fe) = +8/3

Oxidation numbers of monoatomic ions must be integer since electrons are transferred as wholes

Solution: Fe_3O_4 is $Fe(III)_2Fe(II)O_4$ => Fe_3O_4 is a **mixed oxidation state compound**, i.e. it contains **the same element in more than one oxidation states**.

Try some others: PbO, PbO_2, Pb_2O_3, Pb_3O_4, InO

Note: When bonding is covalent, non-integer oxidation states are possible.

Mixed oxidation state compounds

Case of forbidden integer oxidation states:

A compound of SnF_3 empirical formula exists. What is the oxidation state of tin?

ON(Sn) + 3xON(F) = 0 => ON(Sn) – 3 = 0 => ON(Sn) = +3

It is integer, however, it is not expected since only +2 and +4 are allowed for Sn (group 14)

Solution: the molecular formula of SnF_3 is Sn_2F_6: it contains one Sn(II) and one Sn(IV) => $Sn(II)Sn(IV)F_6$. It is a mixed oxidation state compound

Unexpected oxidation states

Case of bonding between two atoms of the same element:

H_2O_2 hydrogen peroxide H-O-O-H

What is the oxidation state of oxygen?

Oxygen is the most electronegative => ON(O) = -2 is usual

However, with O-O bond, the usual -2 cannot be expected.

H is the least electronegative => ON(H) = +1

2xON(H) + 2xON(O) = 0 => 2 + 2xON(O) = 0 => ON(O) = -1

An unusual oxidation number is obtained.

Determine the oxidation number of nitrogen in ammonia NH_3 (3 N-H bonds) and in hydrazine N_2H_4 (one N-N bond and two N-H bonds to each N).

Naming Simple (Binary) Ionic Compounds

First type – when the metal has only one **oxidation state** (charge):

1. Name the cation first, the anion second.
2. For the metal, use the same name as the element.

   The species Na^+ is called sodium ion, but in naming the compound, only the word sodium is used.
3. Name the anion with the stem of the element name + "ide".

   For example Cl^-: chlorine gives chlor + ide = chloride.

Examples:

$MgBr_2$ is ionic and made up of magnesium ion (Mg^{2+}), and the ion derived from bromine, bromide (Br^-), so the compound is called magnesium bromide.

Na_2O is made up of sodium ion (Na^+), and the ion derived from oxygen, oxide (O^{2-}), so the compound is called sodium oxide.

Naming Simple (Binary) Ionic Compounds

Second type – when the metal has two or more **oxidation states**:

1. Name the cation first, the anion second.
2. Cation

   (a) **Systematic method**: Use the same name as the metal, and add the charge in parentheses as a roman numeral:

   For example: Fe^{2+} is called iron(II), Fe^{3+} is called iron(III).

   (b) **Older method**: use the stem of the old element name, plus "ous" for the lower oxidation state, or "ic" for the higher.

   For example: iron was called ferrum, hence ferrous and ferric for Fe^{2+} and Fe^{3+}, respectively.
3. Name the anion as before

Example:

FeO is made of Fe^{2+} and O^{2-} and would be called iron(II) oxide (spoken - iron-two oxide), or ferrous oxide.
Fe_2O_3 is made of Fe^{3+} and O^{2-} and would be called iron(III) oxide, or ferric oxide.

Naming Compounds with Polyatomic Anions

1. Name the cation first, then the anion.
2. The rules for the metal cation naming are the same.
3. The names of the most common anions must be memorized – See table 3.1. Nevertheless, there is a little regularity in the naming of **oxoanions**:

				ClO_4^-	perchlorate
SO_4^{2-}	sulphate	NO_3^-	nitrate	ClO_3^-	chlorate
SO_3^{2-}	sulphite	NO_2^-	nitrite	ClO_2^-	chlorite
				ClO^-	hypochlorite

(They have suffixes, and sometimes prefixes, depending on how may oxygens there are.)

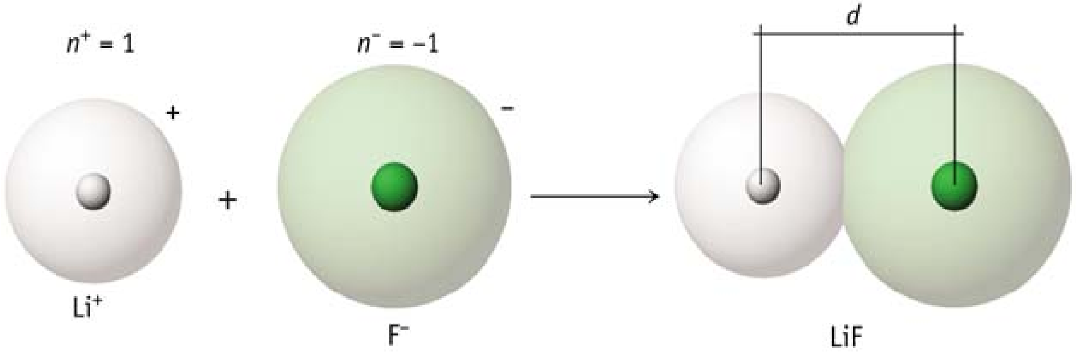
And the hydrogen containing oxoanions:

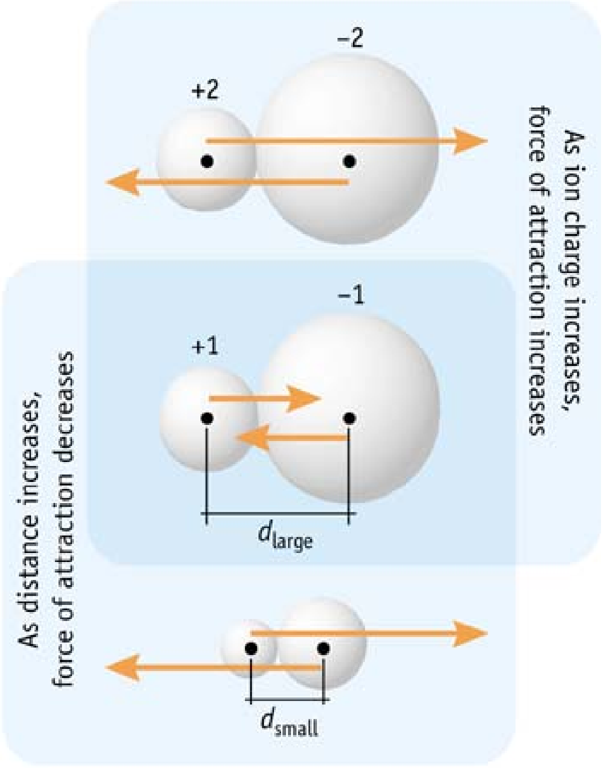
HPO_4^{2-}	hydrogen phosphate	
$H_2PO_4^-$	dihydrogen phosphate	
HCO_3^-	hydrogen carbonate	(bicarbonate)
HSO_4^-	hydrogen sulphate	(bisulphate)
HSO_3^-	hydrogen sulphite	(bisulphite)

The Properties of Ionic Compounds

Ionic compounds are held together by the electrostatic forces between the charged ions. For just a pair of ions:

$$\text{Force of attraction} = k\,\frac{(n^{+}e)(n^{-}e)}{d^2}$$





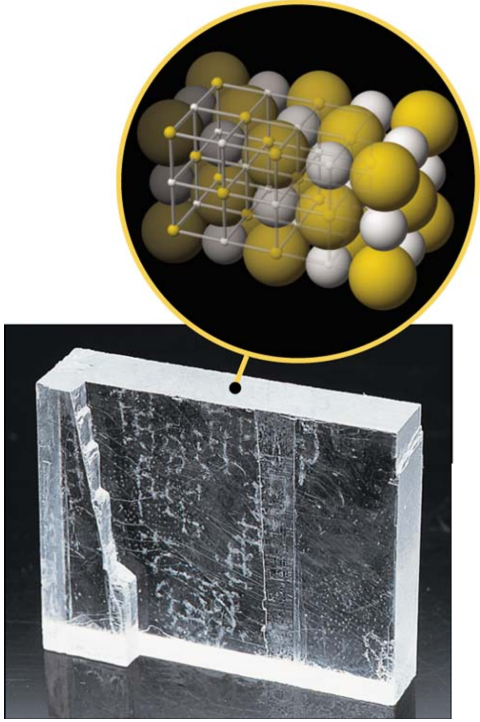
In a three dimensional **crystal lattice**, we have to consider all the attractions and repulsions in the entire crystal.

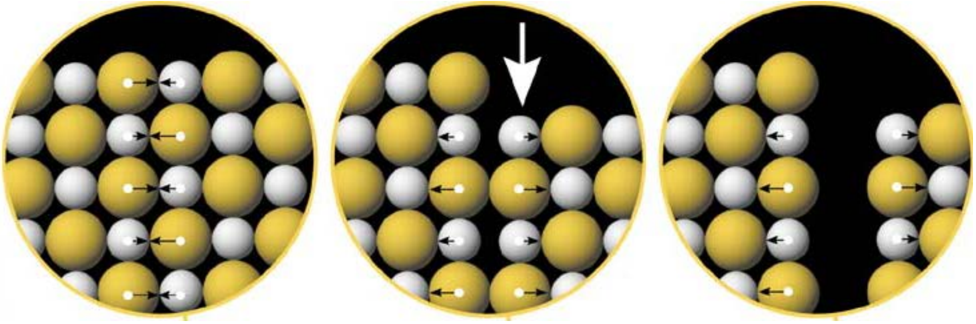
The Properties of Ionic Compounds

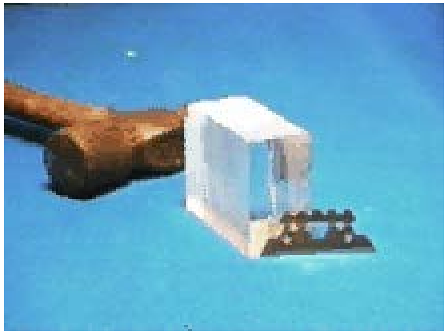
Many ionic compounds are quite hard solids with relatively high melting points due to the strong forces between the ions.

Compounds with highly charged or small ions tend to be hardest, and the most difficult to melt. Compare NaCl, m.p. 801 °C, and Al_2O_3, m.p. 2072 °C.

The internal structure of ionic solids is often evident from their crystal habits and the way they cleave.







Molecular Compounds: Formulae and Names

Many compounds made exclusively of nonmetals are not ionic; they are molecular. They can be very complicated, and very complicated to name! In this section we deal only with simple binary compounds.

Hydrogen compounds

Hydrogen forms molecular compounds with most non-metals except the noble gases. Such compounds, in groups 17 (7A) and 16 (6A) are named with the word hydrogen first, and then the other element designated as if it were an anion:

	16 (6A)		17 (7A)
H_2S	hydrogen sulphide	HF	hydrogen fluoride

In the other groups they have special names:

	14 (4A)		15 (5A)
CH_4	methane	PH_3	phosphine
SiH_4	silane	AsH_3	arsine
GeH_4	germane	SbH_3	stibine (from stibium)

Molecular Compounds: Formulae and Names

Other Binary Molecular Compounds

1. In the formula, the elements are often, but not always, written in the order of **electronegativity**.
2. The first element is given its normal name.
3. The second element is named as if it were an anion.
4. Prefixes are used to designate the number of atoms.

   If the atom or anion name begins with a vowel, the final "o"or "a" of the prefix is dropped.

   The prefix "mono" is never used before the first element named.

Examples:

Cl_2O	dichlorine mon~~o~~oxide	dichlorine monoxide
ClO_2	~~mono~~chlorine dioxide	chlorine dioxide
Cl_2O_7	dichlorine hept~~a~~oxide	dichlorine heptoxide

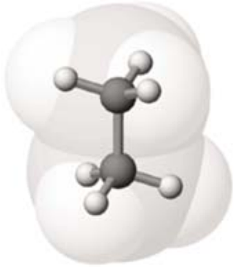
Molecular Compounds: Formulae and Names

More Common ("trivial") Names

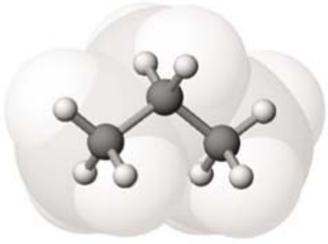
NH_3	ammonia
N_2H_4	hydrazine
NO	nitric oxide
N_2O	nitrous oxide
H_2O	Water

These "**organic**" molecules all belong to a class of hydrocarbons called **alkanes**.

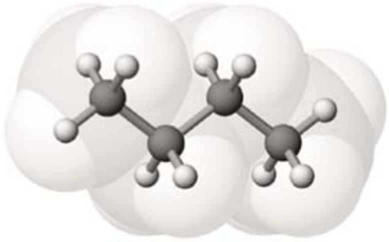
methane, CH_4



ethane, C_2H_6



propane, C_3H_8



butane, C_4H_{10}

The Mole Concept

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No! Not this guy!

A **mole** is the amount of substance that contains as many elementary entities (atoms, molecules, ions, etc.) as there are atoms in 12 g of ^{12}C.

The number is $6.02214199 \times 10^{23}$ and it is called **Avogadro's number**

This is an enormous number: a mole of marbles would cover the entire Earth to a depth of 50 miles

The Mole Concept

The Molar Mass

The molar mass of one mole of an element is the mass of $6.022 X 10^{23}$ atoms of that element. It's units are g mol^{-1}.

For elements, the molar mass in grams is numerically equal to the atomic mass in amu.

Examples:

1.008 g of hydrogen atoms
35.45 g of Cl atoms
12.02 g of C atoms

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The Mole Concept

Sample Calculation:

How many moles and atoms are there in a 200.0 mg of phosphorus?

Convert to grams: $200.0 \text{ (mg of P)} \times \frac{1 \text{ (g)}}{1000 \text{ (mg)}} = 0.20000 \text{ (g of P)}$

Calculate the number of moles: $0.20000 \text{ (g)} \times \frac{1}{30.97 \text{ (g mol}^{-1}\text{)}}$

$= 6.458 \times 10^{-3}$ mol of P (6.45786 × 10^{-3} mol)

Calculate number of atoms:

$6.45786 \times 10^{-3} \text{ (mol)} \times 6.022 \times 10^{23} \text{ (atoms mol}^{-1}\text{)}$

$= 3.889 \times 10^{21}$ atoms of P

Molar Mass (old name: Molecular Weight)

The **molar mass** is the mass obtained by summing all the atomic masses of the atoms represented by the formula of a substance.

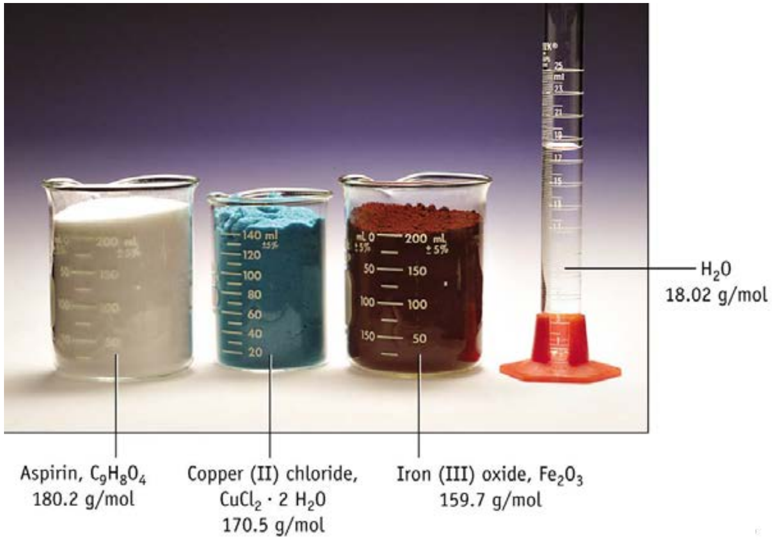
Example: The molar mass of ethanol (ordinary alcohol) represented by the molecular formula C_2H_6O is calculated as follows:

Mass of 2 moles of C = 2 x 12.01 g (2 x 6.022 x 10^{23} atoms of C)

Mass of 6 moles of H = 6 x 1.008 g (6 x 6.022 x 10^{23} atoms of H)

Mass of one mole of O = 16.00 g (6.022 x 10^{23} atoms of O)

Total = 46.07 g (6.022 x 10^{23} molecules of ethanol)



(We sometimes use the term molar mass loosely when we should strictly be referring to formula mass for any formula that does not correspond to a molecular compound e.g. NaCl.)

Molar Mass or Molecular Weight

Example: A standard 12 oz bottle contains 340. g of beer which is 5.50% ethanol by weight. How many moles of ethanol does the bottle contain, how many molecules, and how many atoms of hydrogen (in the ethanol)?

Mass of ethanol:

$$340 \text{ (g beer)} \times \frac{5.50 \text{ (g ethanol)}}{(100 \text{ g beer})} = 18.7 \text{ g ethanol}$$

Number of moles of ethanol:

$$18.7 \text{ (g ethanol)} \times \frac{1 \text{ (mol)}}{46.07 \text{ (g)}} = 0.406 \text{ mol}$$

Number of Molecules of ethanol:

$$0.40590 \text{ (mol)} \times 6.022 \times 10^{23} \text{ (molecules mol}^{-1}\text{)}$$

$$= 2.44 \times 10^{23} \text{ molecules}$$

Number of atoms of hydrogen:

$$2.4443 \times 10^{23} \text{ (molecules)} \times 6 \text{ (atoms molecule}^{-1}\text{)}$$

$$= 1.47 \times 10^{24} \text{ atoms}$$

Empirical and Molecular Formulae

One of the primary jobs to do when isolating a new compound, or even confirming the isolation of a previously known one, is the determination of its molecular formula.

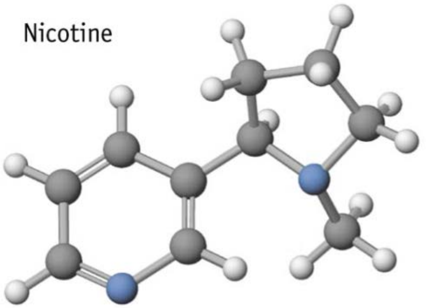
There are two steps:

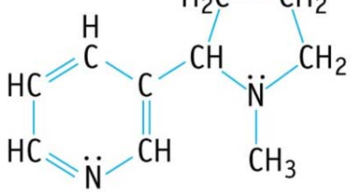
1. An **elemental analysis** can yield data about elements present, and the **percentage composition**. The percentage composition leads to the **empirical formula** (simplest formula).
2. Various methods of molar mass determination (if the compound is molecular or contains molecular ions) gives the molecular formula.

There remains the problem of working out the details of the **molecular structure**, but that is a more advanced topic.

$$? \xrightarrow[\text{Analysis}]{} C_5H_7N \xrightarrow[\text{molar mass determination}]{} C_{10}H_{14}N_2 \xrightarrow[\text{structure determination}]{}$$

Nicotine





Empirical Formulae

From Elemental Analysis

In the case of a simple organic molecule, we are usually interested in carbon, hydrogen, oxygen, and perhaps nitrogen or some other ***heteroatoms***.

In the simplest case we analyze for carbon and hydrogen, and get oxygen by difference.

A weighed sample of the compound is burned in air, and we obtain the mass of water and carbon dioxide produced. The H_2O gives us original the hydrogen content, and the CO_2 gives us the original carbon content.

Empirical Formulae

Example: 0.1156 g of an unknown compound gives 0.1638 g of CO_2 and 0.1676 g of H_2O on combustion. The only other element present is known to be nitrogen. What is the empirical formula of the unknown?

1. Calculate the mass of C and H that were present in the original:

$$\text{Mass C} = \text{mass } CO_2 \times \frac{\text{molar mass C}}{\text{molar mass } CO_2} = 0.1638 \times \frac{12.01}{44.01} = 0.04470 \text{ g}$$

$$\text{Mass H} = \text{mass } H_2O \times \frac{\text{molar mass H} \times 2}{\text{molar mass } H_2O} = 0.0.1676 \times \frac{1.008 \times 2}{18.016} = 0.01875 \text{ g}$$

2. The remaining mass in the original was nitrogen:

$$\text{Mass N} = 0.1156 - 0.04470 - 0.01875 = 0.05215 \text{ g}$$

Continues on the next slide…

Empirical Formulae

Example: 0.1156 g of an unknown compound gives 0.1638 g of CO_2 and 0.1676 g of H_2O on combustion. The only other element present is known to be nitrogen. What is the empirical formula of the unknown?

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$$\text{Mass H} = \text{mass } H_2O \times \frac{\text{molar mass H} \times 2}{\text{molar mass } H_2O} = 0.0.1676 \times \frac{1.008 \times 2}{18.016} = 0.01875\ \text{g}$$

2. The remaining mass in the original was nitrogen:

$$\text{Mass N} = 0.1156 - 0.04470 - 0.01875 = 0.05215\ \text{g}$$

Continues on the next slide…

Empirical Formulae

4. Work out the number of moles of each element that were present in the sample which was burned:

$$\text{Moles of C} = \frac{\text{mass of C}}{\text{molar mass of C}} = \frac{0.04470}{12.01} = 0.003722 \text{ mol}$$

$$\text{Moles of H} = \frac{\text{mass of H}}{\text{molar mass of H}} = \frac{0.01875}{1.008} = 0.01860 \text{ mol}$$

$$\text{Moles of N} = \frac{\text{mass of N}}{\text{molar mass of N}} = \frac{0.05215}{14.01} = 0.003723 \text{ mol}$$

5. Divide each of the numbers of moles by the smallest. This gives the molar ratio of each the other elements to the smallest:

$$C : H : N = 0.003722 : 0.01860 : 0.003723 = 1 : 4.997 : 1.0003$$

6. Hopefully the numbers obtained will be close enough to whole numbers to give the empirical formula:

In this case it looks like the formula is CH_5N

Empirical Formulae

On the previous slide, you have the following instruction regarding the number of moles of each atom in the compound:

5. Divide each of the numbers of moles by the smallest. This gives the molar ratio of each the other elements to the smallest:

C : H : N = 0.003722 : 0.01860 : 0.003723 = 1 : 4.997 : 1.0003

This means doing the following:

C/C = 0.003722/003722 = 1
H/C = 0.01860/003722 = 4.997 ≈ 5 => there are 5 H for each C
N/C = 0.003723/0.003722 = 1.0003 ≈ 1 => there is 1 H for each C

=> The empirical formula is CH_5N

Empirical Formulae

From Percent Composition

Most commonly, we obtain the percent composition from analytical data, but here the percent composition of dimethyl ether is calculated knowing its molecular formula is CH_3OCH_3.

1. Work out the mass of each element in 1 mole of the compound, and the molar mass of the compound:

   Mass of C = 2 mol x 12.01 g mol^{-1} = 24.02 g
   Mass of H = 6 mol x 1.008 g mol^{-1} = 6.049 g
   Mass of O = 1 mol x 16.00 g mol^{-1} = 16.00 g
   Molar mass (the total) = 46.07 g

2. Work out the percentage by mass (w/w) of each element:

   Percent C = 24.02/46.07 x 100 = 52.14 %
   Percent H = 6.049/46.07 x 100 = 13.13 %
   Percent O = 16.00/46.07 x 100 = 34.73 %

3. Check the total adds to 100 %!

Empirical Formulae

Empirical Formula from Percent Composition

Usually, a chemical analysis is done by a specialized lab, often a private company. They would not work out the formula for you, but would simply report the percentage composition of the sample.

In the previous example they would report:

Carbon: 38.67 % Hydrogen: 16.22 % Nitrogen: 45.11%

(Work them out for yourselves!)

The calculation is identical to the one before except you pretend the mass of the sample burned was 100 g and contained masses of C, H and N numerically equal to the percentages.

$$\text{Moles of C} = \frac{\text{mass of C}}{\text{molar mass of C}} = \frac{38.67}{12.01} = 3.220\ \text{mol}$$

$$\text{Moles of H} = \frac{\text{mass of H}}{\text{molar mass of H}} = \frac{16.22}{1.008} = 16.08\ \text{mol}$$

$$\text{Moles of N} = \frac{\text{mass of N}}{\text{molar mass of N}} = \frac{45.11}{14.01} = 3.219\ \text{mol}$$

$\text{C} : \text{H} : \text{N} = 3.220 : 16.08 : 3.219 \approx 1 : 5 : 1$ (as before)

Empirical Formulae

Empirical Formula from Combining Masses

Example: In a (violent) reaction between Al and S, it was found that 4.15 g of Al reacts with 7.40 g S to form a relatively pure sulfide. What is its formula?

1. Convert the masses of Al and S to moles:

$$\text{Moles of Al} = \frac{\text{mass of Al}}{\text{molar mass of Al}} = \frac{4.15}{26.98} = 0.1538\ \text{mol}$$

$$\text{Moles of S} = \frac{\text{mass of S}}{\text{molar mass of S}} = \frac{7.40}{32.07} = 0.2308\ \text{mol}$$

2. Find the empirical formula by dividing by the smallest number of moles to get the molar ratio of Al to S.

$$\text{Al} : \text{S} = 0.1535 : 0.2308 = 1 : 1.50 \approx 2 : 3$$

It is pretty obvious here that the formula is simply Al_2S_3. The compound is ionic, so there is no molecule or molecular formula to find.

Empirical Formulae

Complications!

Sometimes division by the smallest number of moles does not produce whole numbers. For example, consider an unknown compound which is 48.60 % carbon, 8.160% hydrogen and 43.25 % oxygen.

$$\text{Moles of } C = \frac{\text{mass of } C}{\text{molar mass of } C} = \frac{48.60}{12.01} = 4.046 \text{ mol}$$

$$\text{Moles of } H = \frac{\text{mass of } H}{\text{molar mass of } H} = \frac{8.160}{1.008} = 8.095 \text{ mol}$$

$$\text{Moles of } O = \frac{\text{mass of } O}{\text{molar mass of } O} = \frac{43.25}{14.01} = 2.703 \text{ mol}$$

$C : H : O = 4.046 : 8.095 : 2.703 = 1.497 : 2.995 : 1.000$

This is close enough to $C : H : O = 1.5 : 3 : 1$

Multiply by 2 to clear the fraction: $C : H : O = 3 : 6 : 2$
So the empirical formula is $C_3H_6O_2$.

Molecular Formulae

Empirical Formula to Molecular Formula

In order to determine the molecular formula, we need to know the molecular mass, at least approximately.

In the example on the previous slide we find the empirical formula to be $C_3H_6O_2$ which has a formula mass of 74.08 amu.

If, in a separate experiment, we find the molar mass is in the range 140 – 150 amu, we can conclude that the true molecular formula must be $C_6H_{12}O_4$ which has a molecular mass of 148.2 amu.

There are a number of techniques that give approximate molar masses:

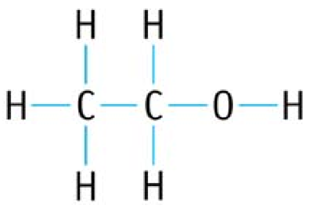
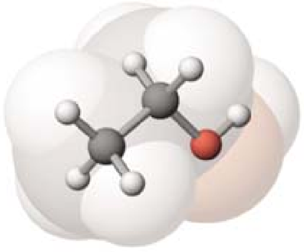
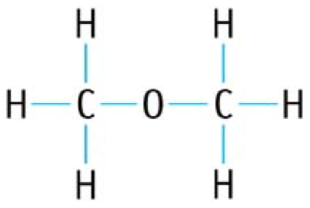
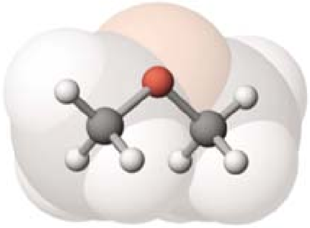
- Freezing point depression
- Boiling point elevation
- Osmotic pressure

Expect to learn about these in Gen. Chem. II.

Structural Formulae

Once the molecular formula is established, we still need to find the structural formula because a particular molecular formula can correspond to more than one **geometrical isomer**.

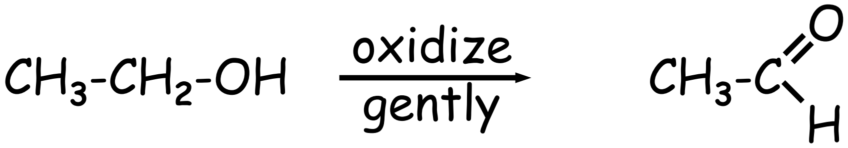
An example of this is C_2H_6O which could be one of two compounds:

NAME	MOLECULAR FORMULA	CONDENSED FORMULA	STRUCTURAL FORMULA	MOLECULAR MODEL
Ethanol	C_2H_6O	CH_3CH_2OH		
Dimethyl ether	C_2H_6O	CH_3OCH_3		

Structural Formulae

Chemical Methods of Structure Determination

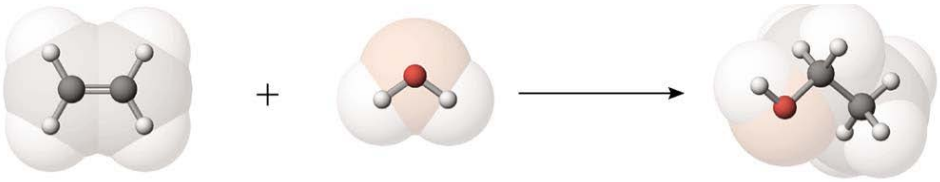
Often chemists figure out what an unknown compound might be by breaking it down chemically stepwise. By studying the fragments, it is often possible to infer what the original compound was.



$$CH_3\text{-}CH_2\text{-}OH \xrightarrow[\text{gently}]{\text{oxidize}} CH_3\text{-}C{\overset{\displaystyle O}{\underset{\displaystyle H}{\lessgtr}}}$$

(There is still a C-C bond)

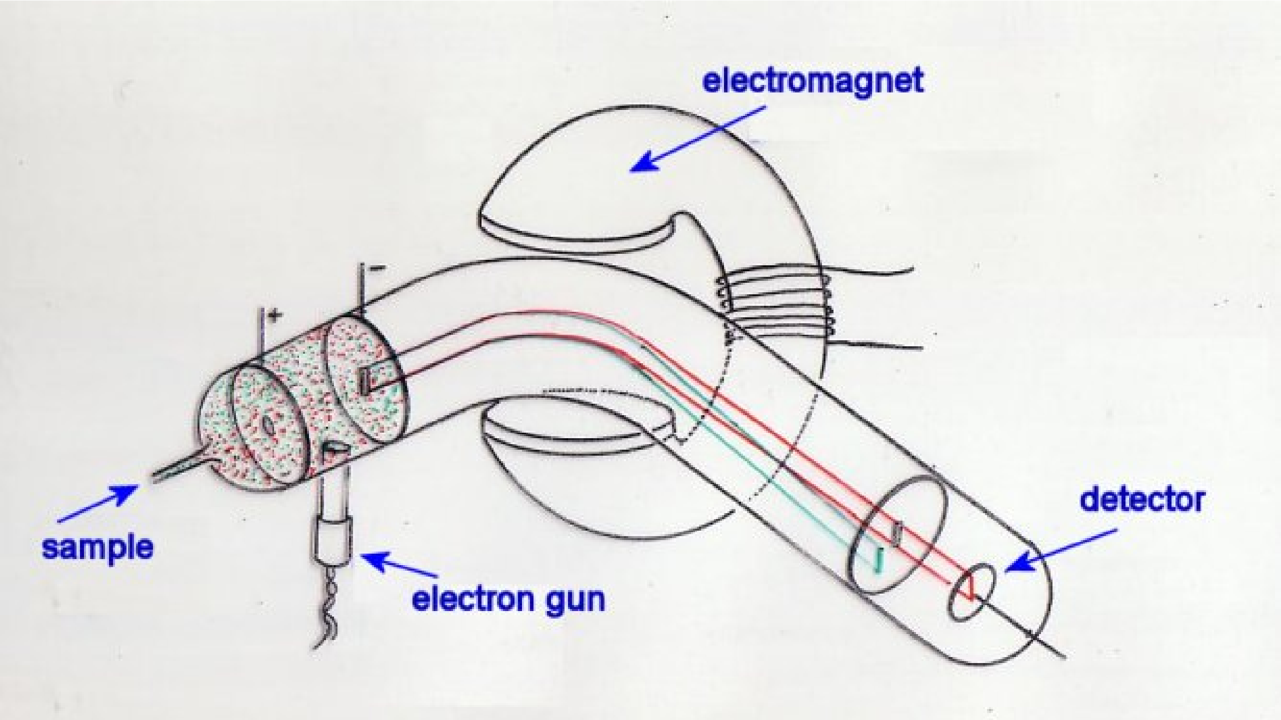
Conversely, the structure of a compound can be confirmed by synthesizing it from smaller pieces to produce a molecule identical to the unknown one.



Physical Methods of Structure Determination

Most are beyond the scope of this course.

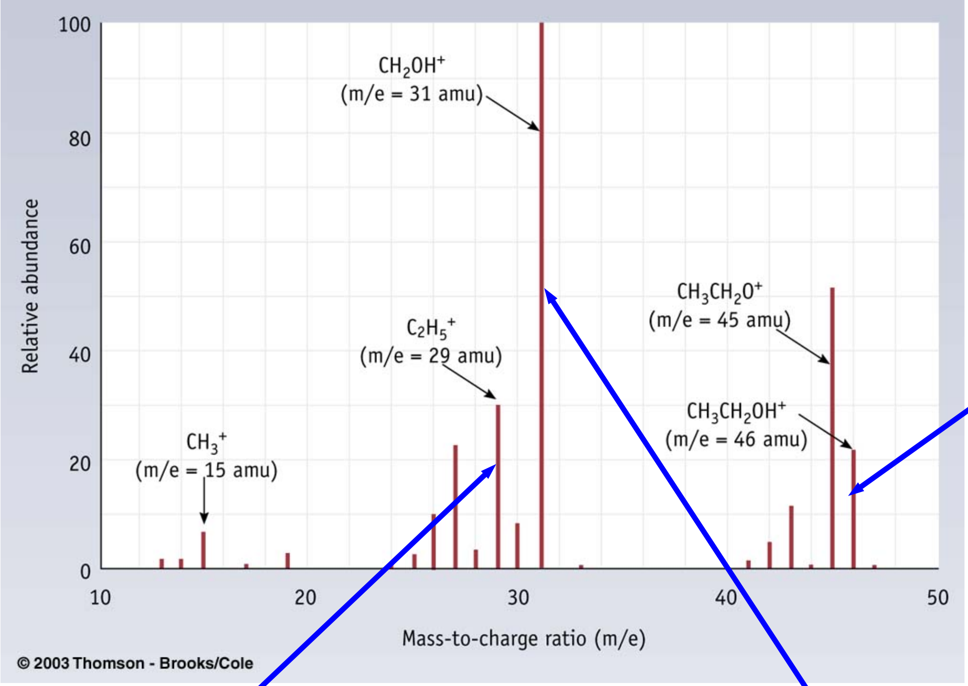
Molecular and Structural Formulae from Mass Spectrometry



A **mass spectrometer** can provide exact information about the molar mass, and often hints about the molecular structure too.

Mass Spectra

Example: Ethanol, C_2H_6O



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"Parent"
ion

Fragment that has lost
an OH group.
This piece would not show if
the molecule had been CH_3OCH_3

Fragment that has lost
a CH_3 group

Hydrated compounds

Compounds in which molecules of water are associated with the compound are called “**hydrated compounds**.”

Do not confuse “hydrated” with “wet.”

Hydrated compounds have a fixed water composition, while wet compounds contain variable amounts of water.

Examples: $CaSO_4.2H_2O$ (Gypsum, used for plaster boards) is a dihydrate

$CaSO_4$ is anhydrous

An anhydrous compound and its hydrates are different compounds.

A wet compound is not a different compound: it is a mixture of the anhydrous compound and water.

Wet compounds dry (lose their water) spontaneously in air

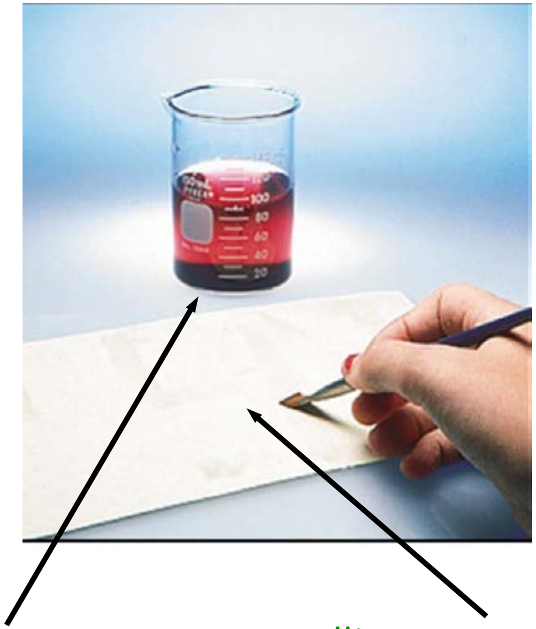
=> attraction of water to rest of compound is weak.

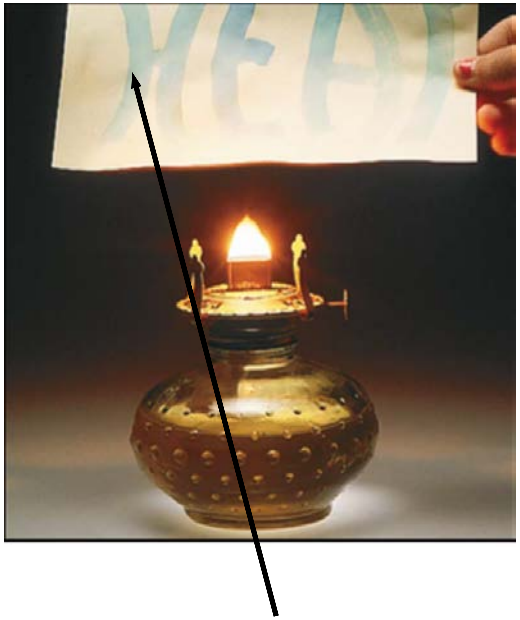
Hydrated compounds do not lose their water spontaneously in air => water forms bonds to the other atoms/ions in the compound.

Hydrated Compounds

These are compounds which contain water molecules – ***water of crystallization*** - which often happens when they are crystallized form aqueous solutions.

Example: “Invisible ink”





$$Co^{2+}(aq) + 2Cl^{-}(aq) \xrightarrow{\text{crystallize}} CoCl_2.6H_2O(s) \xrightarrow{\text{heat}} CoCl_2(s) + 6\ H_2O(g)$$

Hexahydrate

Anhydrous