# Atoms, Elements, and the Nucleus

# **Basic atomics - Getting Started**

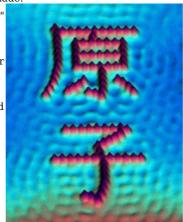
The idea of the atom — at one time a theory, but now directly observable — is the basic concept that unites all aspects of Chemistry, so this is where we begin. This lesson introduces you to these building-blocks of matter, and explains how they are characterized.

Scientists at the IBM Almaden laboratory in California teamed up with artists to create these

striking images. See the <u>IBM site</u> to learn how these were made.



← "Carbon monoxide man" was made by selectively removing CO molecules from a platinum surface. → The Kanji characters for "atom" consist of iron atoms deposited on a copper surface. Atom imaging is discussed farther on; preview <u>here</u>.



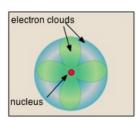
# 1 The idea of the atom

### Atoms and elements: what's the difference?

The parallel concepts of the *element* and the *atom* constitute the very foundations of chemical science.



Sulfur the *element* 



Sulfur the atom

An *element* is an *actual physical substance* that cannot be broken down into a simpler form capable of an independent existence as observable matter. As such, the concept of the element is a *macroscopic* one that relates to the world that we can observe with our senses.

The **atom** is the *microscopic* realization of this concept; that is, it is the *actual* **physical particle** that is unique to each chemical element. Their very small size has long prevented atoms from being observable by direct means, so their existence was not universally accepted until the late 19th Century. The fact that we still hear mention of the "*atomic* **theory** of matter" should not imply that there is now any doubt about the existence of atoms; f ew theories in the history of science have been as thoroughly validated and are as well understood.

Although the word *atom* usually refers to a specific *kind* of particle (an "atom of magnesium", for example), our everyday use of *"element*" tends to be more general, referring not only to a substance composed of a particular type of atom ("bromine is one of the few *elements* that are liquids at room temperature"), but also to atoms in a collective sense ("magnesium is one of the *elements* having two electrons in its outer shell").

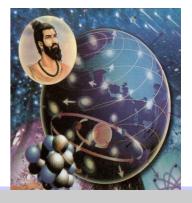
### Atoms are not new!

The underlying concept of atoms as the basic building blocks of matter has been around for a long time.

As early as 600 BCE, the Gujarati (Indian) philosopher <u>Acharya</u> <u>Kanad</u> wrote that "*Every object of creation is made of atoms which in turn connect with each other to form molecules*".

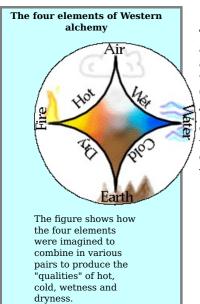
A couple of centuries later in 460 BCE, the Greek philosopher

<u>Democritus</u> reasoned that if you keep breaking a piece of matter into smaller and smaller fragments, there will be some point at which the pieces cannot be made any smaller. He called these "basic matter particles"— in other words, atoms. But this was just *philosophy*; it would not become *science* until 1800 when John Dalton showed how the atomic concept followed naturally from the results of quantitative experiments based on weight measurements.



# **2** The Chemical elements

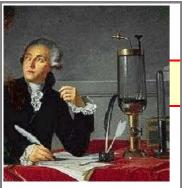
# The philosophers' elements



The concept of the element is an ancient one which developed in <u>many different civilizations</u> in an attempt to rationalize the variety of the world and to understand the nature of change, such as that which occurs when a piece of wood rots, or is burnt to produce charcoal or ash. Most well known to us are the <u>four elements</u> "earth, air, fire and water" that were popularized by Greek philosophers (principally Empedocoles and Aristotle) in the period 500-400 BCE.

To these, <u>Vedic</u> (Hindu) philosophers of India added *space*, while the ancient Chinese concept of <u>Wu Xing</u> regarded earth, metal, wood, fire and water as fundamental. These basic elements were not generally considered to exist as the actual materials we know as "earth", "water", etc., but rather represented the "principles" or *essences* that these elements contributed to the various kinds of matter we encounter in the world.

# The chemists' elements



Antoine Lavoisier (1743-1794)

Eventually, practical experience (largely connected with the extraction of metals from ores) and the beginnings of scientific experimentation in the 18th Century led to our modern concept of the chemical element.

An element is a *substance*: the simplest form to which any other chemical substance can be reduced through appropriate thermal or chemical treatment.

"Simplest", in the context of experimentation at the time, was defined in terms of weight; cinnabar (mercuric sulfide) can be broken down into two substances, mercury and sulfur, which themselves cannot be reduced to any lighter forms.

The first textbook of Chemistry, Traitè <u>Èlèmentaire de Chemie</u>, published by Antoine Lavoisier ("the father of Chemistry") in 1789, contained the table of elements shown here.

Although old Antoine got many of these right, he did manage to include a few things that don't quite fit into our modern idea of what constitutes a chemical element. There are two such mistakes in the top section of the table that you should be able to identify even if your French is less than tip-top— can you find them?

Lav's other mis-assignment of the elements in the bottom section was not really his fault. Chalk, magnesia, barytes, alumina and silica are highly stable oxygencontaining compounds; the high temperatures required to break them down could not be achieved in Lavoisier's time. (<u>Magnesia</u>, after all, is what fire brick is made of!) The proper classification of these substances was delayed until further experimentation revealed their true nature.

Ten of the chemical elements have been known since ancient times. Five more were discovered through the 17th Century.

Lumière Calorique					
Calorique					
Azote					
Hydrogène					
itydrogene					
Soufre					
Phosphore					
Carbone					
Radical muriatique					
Radical Fluorique					
Radical boracique					
Antimoine					
Argent					
Arsenic					
Bismuth					
Cobalt					
Cuivre Etain					
Manganèse					
Mercure					
Molvbdène					
Nickel					
Or					
Platine					
Plomb					
Tungstène					
Zinc					
ZINC					
Chaux					
Magnésie					
Baryte					
Alumine					
Silice					

# Some frequently-asked questions about elements

### How many elements are there?

Ninety-two elements have been found in nature. Around 25 more have been made artificially, but all of these decay into lighter elements, with some of them disappearing in minutes or even seconds.

### Where do the elements come from?

The processes by which elements (or more properly, their nuclei) are formed is known as <u>nucleosynthesis</u>. The very first nuclei of the lightest elements (hydrogen and helium) formed about 20 minutes after the "big bang" 13.8 billion years ago.

The next 23 elements (up through iron) are continuouly being formed mostly by nuclear fusion processes within stars, in which lighter nuclei combine into successively heavier elements. Elements heavier than iron cannot be formed in this way, and are produced only during the catastrophic collapse of massive stars (supernovae explosions).

### How do the elements vary in abundance?

Quite markedly, and very differently in different bodies in the cosmos. Most of the atoms in the universe still consist of hydrogen, with helium being a distant second. On Earth, oxygen, silicon, and aluminum are most abundant. These profiles serve as useful guides for constructing models for the formation of the earth and other planetary bodies.

10<sup>2</sup>%

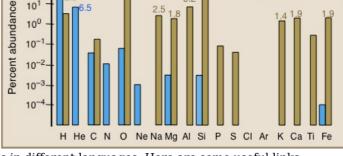
# Elemental abundances in the lithosphere (Earth's crust) and in the universe $\rightarrow$

Note that the vertical axis is logarithmic, which has the effect of greatly reducing the visual impression of the differences between the various elements.

### How did the elements get their names?



This is too big a subject to cover here in detail, especially since most



Universe

Earth

- elements have different names in different languages. Here are some useful links:
- ← By far the most interesting resource is the <u>Elementymology Multidictionary</u> which covers the history, discovery and naming of each element and a list of the names of each element in 97 languages.
- Wikipedia has a comprehensive list of English <u>element name etymologies</u> and also a <u>Timeline of</u> <u>chemical element discoveries</u>.
- The naming of some of the more recently-discovered (artificially-created) elements has been a matter of

some controversy.

• An interesting description of how elements are named in Asian languages.

### How did the element symbols originate?

In 1814, the Swedish chemist <u>Jöns Jacob Berzelius</u> devised the one- and two-letter symbols for the elements known at that time. Prior to that time, <u>graphic alchemical symbols</u> were used, which were later modified and popularized by John Dalton (<u>See here</u>). Fortunately for English speakers, the symbols of most of the elements serve as mnemonics for their names, but this is not true for the <u>seven metals known from antiquity</u>, whose symbols Berzelius based on their Latin names. The other exception is *tungsten* (a name derived from Swedish), whose symbol W reflects the German name which is more widely used.

### How are the elements organized?

Two general organizing principles developed in the 19th Century: one was based on the increasing relative weights (atomic weights) of the elements, yielding a list that begins this way:

The other principle took note of the similarities of the properties of the elements, organizing them into groups with similar properties (<u>Döbereiner's "triads</u>", 1829). It was later noted that *groups of elements* (Chancourtois' "telluric helix", <u>Newlands "octaves"</u>, 1864 and <u>Meyer</u>, 1869) having changing properties tended to repeat themselves within the atomic weight sequence, giving rise to the idea of "periodic" sequences of properties. These concepts were finally integrated into the *periodic table* published by <u>Mendeleev</u> in 1869, which evolved into the various forms of the periodic table in use today.

	IA 1	[	alkali	metal	s		-							no	ble ga	ases	1	VIIA 18		
Γ	н	IA 2		alkal	ine ea	orths		post-t	ransiti	ion me	etals		IIIA 13	IVA 14	VA 15	VIA 16	VIIA	Не		
	LÍ	Be	/	atkat	_		ion me	etals					в	С	N	0	F	Ne		
	Na	Mg	IIIB 3	IVB 4	VB 5	VIB 6	VIIB	VIII 8	VIII 9	VIII 10	11	IIB 12	AI	Si	P	s	СІ	Ar		
	к	Ca	Sc	ті	۷	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
	Rb	Sr	Υ	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	1	Хе		
	Cs	Ва	La	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg	ті	Pb	Bi	Ро	At	Rn		
	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds			semi	metal	s (me	talloid	ls)			
									_				·	_	_	(	halog	ens		
	Ce Pr Nd Pm Sm Eu Gd Th									Tb Dy Ho Er Tr					Tm Yb Lu lanthanides					
	Th	Pa	a U	Np	P	J An	n Cr	n Bl	C C	f E	s Fr	n M	d No	b L	r a	ctinide	_			
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# **3** Atoms become real

Throughout most of history the idea that matter is composed of minute particles had languished as a philosophical abstraction known as <u>atomism</u>, and no clear relation between these "atoms" and the chemical "elements" had been established. This began to change in the early 1800's when the development of balances that permitted reasonably precise measurements of the weight changes associated with chemical reactions ushered in a new and fruitful era of experimental chemistry. This resulted in the recognition of several *laws of chemical change* that laid the groundwork for the atomic theory of matter: *conservation of mass, definite proportions*, and *multiple proportions*.

# Laws of chemical change

Recall that a "law", in the context of science, is just a relationship, discovered through experimentation, that is sufficiently well established to be regarded as beyond question for most practical purposes. Because it is the nature of scientists to question the "unquestionable", it occasionally happens that exceptions do arise, in which case the law must undergo appropriate modification.

### Conservation of mass-energy in chemistry

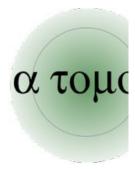
Mass conservation is usually considered the most fundamental of law of nature. It is also a good example of a law that had to be modified; it was known simply as *Conservation of Mass* until Einstein showed that energy and mass are interchangeable. However, the older term is perfectly acceptable within the field of ordinary chemistry in which energy changes are too small to have a measurable effect on mass relations.

Within the context of chemistry, conservation of mass can be thought of as "conservation of atoms". Chemical change just shuffles them around into new arrangements.

Mass conservation had special significance in understanding chemical changes involving gases, which were for some time not always regarded as real matter at all. (Owing to their very small densities, carrying out actual weight measurements on gases is quite difficult to do, and was far beyond the capabilities of the early experimenters.) Thus when magnesium metal is burned in air, the weight of the solid product always exceeds that of the original metal, implying that the process is one in which the metal combines with what might have been thought to be a "weightless" component of the air, which we now know to be oxygen.

> magnesium + oxygen → magnesium oxide 1.00 g 1.66 g

More importantly, as we will see later, this experimental result tells us something very important about the mass of the oxygen atom relative to that of the magnesium atom.



The word "atom" comes from the Greek *a-tomos*, meaning "un-cut-able"

### Law of definite proportions

This law is also known as the *law of constant composition*. It states that the proportion by weight of the element present in any pure substance is always the same. This enables us to generalize the relationship we illustrated above.

Problem Example 1 How many kilograms of metallic magnesium could theoretically be obtained by decomposing 0.400 kg of magnesium oxide into its elements? *Solution:* The mass ratio of Mg to O in this compound is 1/1.66 = 0.602, so 0.400 kg of the oxide contains (0.400 kg) x 0.602 = **0.241 kg of Mg**.

The fact that we are concerned with the *reverse* of the reaction cited above is irrelevant.

The laws of definite and of multiple proportions, along with conservation of mass, are known collectively as the *laws of chemical composition*.

#### Law of multiple proportions

Many combinations of elements can react to form more than one compound. In such cases, this law states that the weights of one element that combine with a fixed weight of another of these elements are integer multiples of one another. It's easy to say this, but please take the time to make sure that you understand how it works!

Consider, for example, the five compounds of nitrogen and oxygen depicted in the chart shown here.

- Line 1 shows the ratio of the relative weights of the two elements in each compound. These ratios were calculated by simply taking the molar mass of each element, and multiplying by the number of atoms of that element per mole of the compound. Thus for NO<sub>2</sub>, we have (1 × 14) : (2 × 16) = 14:32. (These numbers were not known in the early days of Chemistry because atomic weights (i.e., molar masses) of most elements were not reliably known.)
- The numbers in Line 2 are just the mass ratios of O:N, found by dividing the corresponding ratios in line 1. But someone who depends solely on experiment would work these out by finding the mass of O that combines with unit mass (1 g) of nitrogen.
- Line Line (3) is obtained by dividing the figures the previous line by the smallest O:N ratio in the line above, which is the one for N<sub>2</sub>O. Note that just as the law of multiple proportions says, the weight of oxygen that combines with unit weight of nitrogen work out to small integers.
- Of course we just as easily could have illustrated the law by considering the mass of nitrogen that combines with one gram of oxygen; it works both ways!

#### Problem Example 2

Nitrogen and hydrogen form many compounds, some of which involve other elements as well. The mass of hydrogen that combines with 1.00 g of nitrogen to form three of these compounds are: urea, 0.1428 g; ammonia, 0.0714 g; ammonium chloride, 0.2857 g. Show that this data is consistent with the Law of Multiple Proportions.

**Solution:** The "fixed weight" we are considering here is the nitrogen. Inspection of the numbers above shows that the ammonia contains the smallest weight ratio H:N = 0.0714, while the weight ratio of H:N in urea is twice this number, and that in ammonium chloride is four times 0.0714. Thus the H:N ratios are themselves stand in the ratio of 2:1:4, respectively, and the Law is confirmed.

In order to make sure you understand this problem, note carefully that:

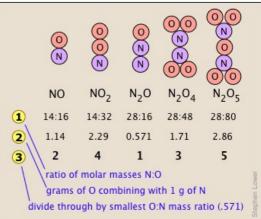
- The masses of hydrogen that react with 1.00 g of nitrogen to form the three compounds .1428 g., .0714 g, and .2857 g are sometimes referred to as *Combining weights*.
- These combining weights would be different if the mass of nitrogen that was used had a value different from 1.00 g.
- In an actual experiment, the mass of nitrogen would almost certainly be different from 1.00 g, but the combining weights would differ in exact proportion. This means that if *n* grams of nitrogen were used, the mass of hydrogen that reacts to form urea, for example, would be .1428 × *n*.

The most systematic way of solving this problem is to construct a table whose three leftmost columns summarize the information given in the problem:

Compound	Formula	Weight ratio H:N	Ratio to 0.0714
urea	CO(NH <sub>2</sub> ) <sub>2</sub>	.1248	2
ammonia	NH <sub>3</sub>	.0714	1
ammonium chloride	NH <sub>4</sub> Cl	.2857	4

Next, identify the smallest weight ratio (.0714 here), and, in the rightmost column, divide each of the values in column 3 by this smallest ratio. What you get are the "small whole numbers" that illustrate the law of simple multiple proportions.

Note that, in some cases, the values in column 4 will not all initially work out to integer numbers. Suppose, for example, that the bottom row refers to some compound other than ammonium chloride, and that the numbers in column 4 (reading from top to bottom), work out to  $\{2 - 1 - 1.33\}$ . If you recognize that the last number corresponds to 4/3, then multiplying each value by 3 yields the whole numbers  $\{6 \ 3 \ 4\}$  — not quite as "small", but at least"whole" as the law requires.



The idea that matter is composed of tiny "atoms" of some kind had been around for at least 2000 years. Dalton's accomplishment was to identify atoms with actual chemical elements.



If Nobel prizes had existed in the early 1800's, the English

schoolteacher/meteorologist/chemist John Dalton (1766-1844) would certainly have won one for showing how the experimental information available at that time, as embodied in the laws of chemical change that we have just described, are fully consistent with the hypothesis that atoms are the smallest units of chemical identity.

These points of Dalton's atomic theory provided satisfactory explanations of all the laws of chemical change noted above:

#### Explanation of the law of conservation of mass

This is really a consequence of "conservation of atoms" which are presumed to be indestructible by chemical means. In chemical reactions, the atoms are simply rearranged, but

never destroyed.

### Explanation of the law of constant composition

If compounds are made up of definite numbers of atoms, each of which has its own characteristic mass, then the relative mass of each element in a compound must always be the same. Thus the elements must always be present in a pure sample of a compound in the same proportions by mass.

### Explanation of the law of multiple proportions

A given set of elements can usually form two or more compounds in which the numbers of atoms of some of the elements are different. Because these numbers must be integers (you can't have "half" an atom!), the mass of one element combined with a fixed mass of any other elements in any two such compounds can differ only by integer numbers. Thus, for the series of nitrogen-hydrogen compounds cited in the Problem Example above, we have the following relations:

Compound	Formula	weight ratio H:N	ratio to 0.0714
urea	CO(NH <sub>2</sub> ) <sub>2</sub>	0.1428	2
ammonia	NH <sub>3</sub>	0.0714	1
ammonium chloride	NH <sub>4</sub> Cl	0.2857	4

### "Seeing" is believing: the atomic force microscope

### Ymm (5½ min, TEDed)

Although Dalton's atomic theory was immediately found to be a useful tool for organizing chemical knowledge, it was some time before it became accepted as a true representation of the world. Thus, as late as 1887, one commentator observed that

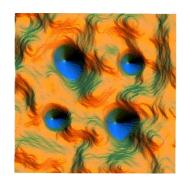
"Atoms are round bits of wood invented by Mr. Dalton."

These wooden balls have evolved into computer-generated images derived from the *atomic force microscope* (AFM), an exquisitely sensitive electromechanical device in which the distance between the tip of a submicroscopic wire probe and the surface directly below it is recorded as the probe moves along a surface to which atoms are adsorbed.

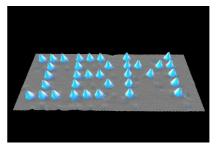
Easy-to-use, compact AFM's that can sit on a desktop are now widely available.

No, atoms don't really come in designer colors; these are created by the computer software in order to provide better contrast.

(Color has no meaning for objects smaller than the wavelength of visible light.)



Atoms of cobalt on a copper surface.



These xenon atoms on a nickel surface make up the world's smallest corporate logo. "Pictures" such as these are created by selectively removing individual atoms or molecules from the surface.

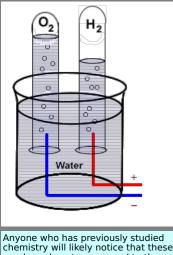
# 4 Combining weights" and relative atomic masses

Dalton's atomic theory immediately led to the realization that although atoms are far too small to be studied directly, their *relative masses* can be estimated by observing the weights of elements that combine to form similar compounds. These weights are sometimes referred to as *combining weights*.

There is one difficulty, however: we need to know the *formulas* of the compounds we are considering in order to make valid comparisons. For example, we can find the relative masses of two atoms X and Y that combine with oxygen only if we assume that the values of n in the two formulas  $xo_n$  and  $yo_n$  are the same. But the very relative masses we are trying to find must be known in order to determine these formulas.

The way to work around this was to focus on *binary* (two-element) compounds that were assumed to have mostly simple atom ratios such as 1:1, 1:2, etc., and to hope that enough 1:1 compounds would be found to provide a starting point for comparing the various pairs of combining weights. Compounds of oxygen, known as *oxides*, played an especially important role here, partly because almost all of the chemical elements form compounds with oxygen, and most of them do have very simple formulas.

### Discovering the formula of water



Anyone who has previously studied chemistry will likely notice that these numbers do not correspond to the atomic weights we presently know. There is good reason for this; laboratory balances sufficiently accurate for weighing small quantities of solids, and especially gases, did not become available until the latter part of the 19th Century.

<

Of these oxygen compounds, the one with hydrogen— ordinary *water*— had been extensively studied. The first proof that water is composed of hydrogen and oxygen was the discovery, in 1800, that an electric current could decompose water into these elements. Notice the 2:1 volumes of the two gases displacing the water at the tops of the tubes. Although the significance of this volume ratio was not recognized at the time, it would later prove the formula we now know for water.

Earlier experiments had given the composition of water as 87.4 percent oxygen and 12.6 percent hydrogen by weight. This means that if the formula of water is assumed to be HO (as it was at the time — incorrectly), then the mass ratio of the two kinds of atoms must be O:H = 87.4/12.6 = 6.9. Later work corrected this figure to 8, but the wrong assumption about the formula of water would remain to plague chemistry for almost fifty years until studies on gas volumes (<u>Avogadro's law</u>) proved that water is H<sub>2</sub>O.

### Dalton's table of relative atomic masses

Dalton fully acknowledged the tentative nature of weight ratios based on assumed simple formulas such as HO for water, but was nevertheless able to compile in 1810 a list of the relative weights of the atoms of some of the elements he investigated by observing weight changes in chemical reactions.

hydrogen	carbon	oxygen	phosphorus	iron	zinc	copper	lead
1	5	5.4	7	9	13	50	56

Because hydrogen is the lightest element, it was assigned a relative weight of unity.

By assigning definite relative masses to atoms of the different elements, Dalton had given reality to the concept of the atom and established the link between atom and element.

Once the correct chemical formulas of more compounds became known, more precise combining-weight studies eventually led to the relative masses of the atoms we know today as the *atomic weights*, which we discuss farther on.

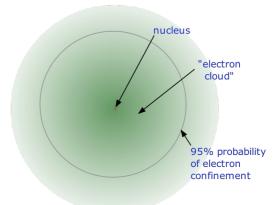
# 5 The nuclear atom

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

• Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense) *nucleus* which carries a positive electric charge whose value identifies each element and is known as the *atomic number* of the element.

• Almost all of the *volume* of an atom consists of empty space in which electrons, the fundamental carriers of negative electric charge, reside.

The extremely small mass of the electron (1/1840 the mass of the hydrogen nucleus) causes it to behave as a *quantum particle*, which means that its location at any moment cannot be specified; the best we can do is describe its behavior in terms of the probability of its manifesting itself at any point in space. It is common (but somewhat misleading) to describe the volume of space in which the electrons of an atom have a significant probability of being found as the *electron cloud*. The latter has no definite outer boundary, so neither does the atom. The radius of an atom must be defined arbitrarily,



such as the boundary in which the electron can be found with 95% probability. Atomic radii are typically 30-300 pm.

## The nucleus is composed of protons and neutrons

The nucleus is itself composed of two kinds of particles. **Protons** are the carriers of positive electric charge in the nucleus; the proton charge is exactly the same as the electron charge, but of opposite sign. This means that in any [electrically neutral] atom, the number of protons in the nucleus (often referred to as the *nuclear charge*) is balanced by the same number of electrons outside the nucleus.

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

The other nuclear particle is the *neutron*. As its name implies, this particle carries no electrical charge. Its mass is almost the same as that of the proton. Most nuclei contain roughly equal numbers of neutrons and protons, so we can say that these two particles together account for almost all the mass of the atom.

# The atomic number is the nuclear charge, and thus the number of electrons in the neutral atom

What single parameter uniquely characterizes the atom of a given element? It is not the atom's relative mass, as we will see in the section on isotopes below. It is, rather, the number of protons in the nucleus, which we call the **atomic number** and denote by the symbol Z. Each proton carries an electric charge of +1, so the atomic number also specifies the electric charge of the nucleus. In the neutral atom, the Z protons within the nucleus are balanced by Z electrons outside it.

Moseley searched for a measurable property of each element that increases linearly with atomic number. He found this in a class of Xrays emitted by an element when it is bombarded with electrons. The frequencies of these X-rays are unique to each element, and they increase uniformly in successive elements. Mosely found that the square roots of these frequencies give a straight line when plotted against Z; this enabled him to sort the elements in order of increasing atomic number. See this <u>example of his experimental plots.</u>

Atomic numbers were first worked out in 1913 by <u>Henry</u> <u>Moseley</u>, a young member of Rutherford's research group in Manchester.

You can think of the atomic number as a kind of serial number of an element, commencing at 1 for hydrogen and increasing by one for each successive element. The chemical name of the element and its symbol are uniquely tied to the atomic number; thus the symbol "Sr" stands for strontium, whose



atoms all have Z = 38.

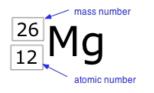
### Mass number

This is just the sum of the numbers of protons and neutrons in the nucleus. It is sometimes represented by the symbol A, so

A = Z + N

in which Z is the atomic number and N is the *neutron number*.

### Nuclides and their symbols



The term **nuclide** simply refers to any particular kind of nucleus. For example, a nucleus of atomic number 7 is a nuclide of nitrogen. Any nuclide is characterized by the pair of numbers (Z, A). The element symbol depends on Z alone, so the symbol <sup>26</sup>Mg is used to specify the mass-26 nuclide of manganese, whose name implies Z=12. A more explicit way of denoting a particular kind of nucleus is to add the atomic number as a subscript. Of course, this is somewhat redundant, since the symbol Mg always implies Z=12.

Because it is not always easy to display a subscript directly beneath a superscript, it is not uncommon to use constructions such as  ${}_{12}Mg^{26}$ , which will often be our practice in this document when it is necessary to show both Z and A explicitly.

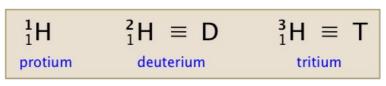
### Isotopes are nuclides having the same atomic number

Two nuclides of the same element (and thus with identical atomic numbers) but different neutron numbers (and therefore different mass numbers) are known as *isotopes*. Most elements occur in nature as mixtures of isotopes, but twenty-three of them (including beryllium and fluorine, shown in the table) are monoisotopic. For example, there are three *natural isotopes* of magnesium:  $^{24}$ Mg (79% of all Mg atoms),  $^{25}$ Mg (10%), and  $^{26}$ Mg (11%); all three are present in all compounds of magnesium in about these same proportions.

	Z	mass numbers
н	1	1 2 3
He	2	3 4
Li	3	6 7
Be	4	9
В	5	10 11
С	6	12 13 14
Ν	7	14 15
0	8	16 17 18
F	9	19
Ne	10	20 21 22

Approximately 290 isotopes occur in nature.

The two heavy isotopes of hydrogen are especially important— so much so that they have names and symbols of their own:



Deuterium accounts for only about 15 out of every one million atoms of hydrogen. Tritium, which is radioactive, is even less abundant. All the tritium on the earth is a by-product of the decay of other radioactive elements.

# 6 Relative atomic masses: the atomic weight scale

For historical reasons, the term *atomic weight* has a special meaning in Chemistry; it does *not* refer to the actual "weight" of an atom, which would be expressed in grams or kg.

Atomic weights, sometimes called relative weights, are more properly known as *relative atomic masses*, and being ratios, are dimensionless.

See this Wikipedia article for a full discussion of these and related terms.

Please note that although the terms *mass* and *weight* have different meanings, the differences between their values are so small as to be insignificant for most practical purposes, so the terms *atomic weight* and *atomic mass* can be used interchangeably. Atoms are of course far too small to be weighed directly; weight measurements can only be made on the massive (but unknown) numbers of atoms that are observed in chemical reactions. The early combining-weight experiments of Dalton and others established that hydrogen is the lightest of the atoms, but the crude nature of the measurements and uncertainties about the formulas of many compounds made it difficult to develop a reliable scale of the relative weights of atoms. Even the most exacting weight measurements we can make today are subject to experimental uncertainties that limit the precision to four significant figures at best.

#### Atomic weights are average relative masses

In the earlier discussion of relative weights of atoms, we explained how Dalton assigned a relative weight of unity to hydrogen, the lightest element, and used combining weights to estimate the relative weights of the others he studied. Later on, when it was recognized that more elements form simple compounds with oxygen, this element was used to define the atomic weight scale. Selecting O = 16 made it possible to retain values very close to those already assigned on the H=1 scale.

Finally, in 1961, carbon became the defining element of the atomic weight scale. But because, by this time, the existence of isotopes was known, it was decided to base the scale on one particular isotope of carbon, C-12, whose relative mass is defined as exactly 12.000. Because

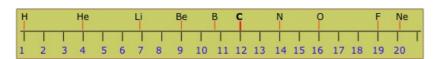
almost 99% of all carbon atoms on the earth consist of  ${}_{6}C^{12}$ , atomic weights of elements on the

current scale are almost identical to those on the older O=16 scale.

Most elements possess more than one stable isotope in proportions that are unique to each particular element. For this reason, atomic weights are really weighted *averages* of the relative masses of each that are found on earth.

Atomic weights are the ratios of the average mass of the atoms of an element to the mass of an identical number of  ${}_{6}C^{12}$  atoms.

You can visualize the atomic weight scale as a long line of numbers that runs from 1 to around 280. The beginning of the scale looks like this:



Atomic weights (relative atomic masses) of the first ten elements

The red vertical lines beneath each element symbol indicate where that element is located on the atomic weight scale.

Of these ten elements, only two, beryllium and fluorine, have a single isotope. The other eight atomic weights are weighted averages of the relative masses of the multiple isotopes that these (and most) elements possess. This is especially noticeable in the case of boron, whose average relative mass falls between 10 and 11. (Historically, observations of cases such as these led to the very concept of isotopes.)

For many elements, one particular isotope so dominates the natural mixture that the others have little effect on the average mass. For example, 99.99 percent of hydrogen atoms consist of  $_{1}H^{1}$ , whereas  $_{1}H^{2}$ , the other stable isotope, amounts to only 0.01 percent. Similarly, oxygen is dominated by

 $_8\mathrm{O}^{16}$  (over 99.7 percent) to the near exclusion of its two other isotopes.

Atomic weights are listed in tables found in every chemistry textbook; you can't do much quantitative chemistry without them! The <u>"standard" values</u> are updated every few years as better data becomes available.

atomic weight atomic weight number number 1.00794 12.0107 C 6 1 He 2 4.00262 N 7 14.0067 8 15,9994 3 6.941 0 9.0121821 Be 4 F 9 18.998403 В 5 10.811 Ne 10 20.1797

You will notice that the precisions of these atomic weights, as indicated by the number of significant figures, vary considerably.

- Atomic weights of the 26 elements having a single stable isotope (*monoisotopic* elements) are the most precisely known. Two of these, boron and fluorine, appear in the above table.
- Owing to geochemical *isotopic fractionation* (discussed farther on), there is always some uncertainty in averaging the atomic weights of elements with two or more stable isotopes.
- Industrial processes associated mainly with nuclear energy and weapons production require the isolation or concentration of particular isotopes. When the by-product elements or compounds from which these isotopes have been depleted eventually get distributed in the environment or sold into the commercial marketplace, their atomic weights can vary from "official" values. This has occurred, for example, with lithium, whose isotope Li-6 has been used to produce hydrogen bombs.
- Naturally-occurring radioactive elements (all elements heavier than  $_{82}$ Pb) all gradually decay into lighter elements, most of which are themselves subject to radioactive decay. These radioactive decay chains eventually terminate in a stable element, the most common of which is one of the three stable isotopes of lead. Subsequent geochemical processes can cause lead ore bodies from such sources to mix with "primeval" Pb (derived from the cosmic dust that formed the solar system), leading to a range of possible average atomic weights. For these reasons, lead, with a listed average atomic weight of 207.2, has the least-certain mass of any stable element.

# Weighing atoms: mass spectrometry

A major breakthrough in Chemistry occurred in 1913 when J.J. Thompson directed a beam of ionized neon atoms through both a magnetic field and an electrostatic field. Using a photographic plate as a detector, he found that the beam split into two parts, and suggested that these showed the existence of two isotopes of neon, now known to be Ne-20 and Ne-22.

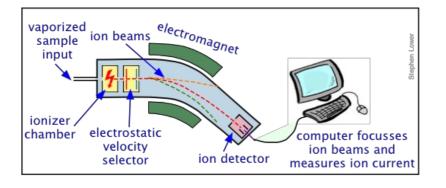
This, combined with the finding made a year earlier by <u>Wilhelm Wien</u> that the degree of deflection of a particle in these fields is proportional to the ratio of its electric charge to its mass, opened the way to characterizing these otherwise invisible particles.

Thompson's student F.W. Aston improved the apparatus, developing the first functional *mass spectrometer*, and he went on to identify 220 of the 287 isotopes found in nature; this won him a Nobel prize in 1921. His work revealed that the mass numbers of all isotopes are nearly integers (that is, integer multiples of the mass number 1 of the protons and neutrons that make up the nucleus.

Neutral atoms, having no charge, cannot be accelerated along a path so as to form a beam, nor can they be deflected. They can, however, be made to *acquire* electric charges by directing an electron beam at them, and this was one of the major innovations by Aston that made mass spectrometry practical.

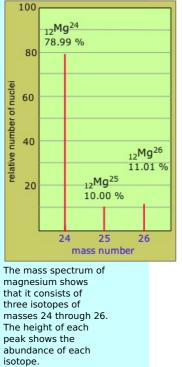
Mass spectrometry begins with the injection of a vaporized sample into an ionization chamber where an electrical discharge causes it to become ionized. An accelerating voltage propels the ions through an electrostatic field that allows only those ions having a fixed velocity (that is, a given charge) to pass between the poles of a magnet. The magnetic field deflects the ions by an amount proportional to the charge-to-mass ratios. The separated ion beams are detected and their relative strengths are analyzed by a computer that displays the resulting mass spectrum. In modern devices, a computer also

controls the accelerating voltage and electromagnet current so as to being successive ion beams into focus on the detector.





The mass spectrometer has become one of the most widely used laboratory instruments. Mass spectrometry is now mostly used to identify molecules. Ionization usually breaks a molecule up into fragments having different charge-to-mass ratios, each molecule resulting in a unique "fingerprint" of particles whose origin can be deduced by a jigsaw puzzle-like reconstruction. For many years, "mass-spec" had been limited to small molecules, but with the development of novel ways of creating ions from molecules, it has now become a major tool for analyzing materials and large biomolecules, including <u>proteins</u>.



### Isotopic mixtures and abundances

Only 26 of the elements that occur on the Earth exist as a single isotope; these are said to be *monoisotopic*. The remaining elements consist of mixtures of between two and ten isotopes. The total number of natural isotopes is 339; of these, 254 are stable, while the remainder are radioactive, meaning that they decay into stable isotopes.

Recalling that a given isotope (also known as a *nuclide*) is composed of protons and neutrons, each having a mass number of unity, it should be apparent that the mass number of a given nuclide will be an integer, as seen in the mass spectrum of magnesium above.

It also follows that the relative atomic masses ("atomic weights") of monoisotopic elements will be very close to integers, while those of other elements, being weighted averages, can have any value.

#### Problem Example 4 Estimate the average atomic weight of magnesium from the isotopic abundance data shown in the above mass spectrometry plot. Solution: We just take the weighted average of the mass numbers:

 $(0.7899 \times 24) + (0.1000 \times 25) + (0.1101 \times 26) = 24.32$ 

*Note:* The measured atomic weight of Mg (24.305) is slightly smaller than this because atomic masses of nuclear components are not strictly additive, as will be explained further below.

When there are only two significantly abundant isotopes, you can estimate the relative abundances from the mass numbers and the average atomic weight.

#### Problem Example 5

The average atomic weight of chlorine is 35.45 and the element has two stable isotopes  ${}_{17}Cl^{35}$  and  ${}_{17}Cl^{37}$ . Estimate the relative abundances of these two isotopes.

**Solution:** Here you finally get to put your high-school algebra to work! If we let *x* represent the fraction of  $Cl^{35}$ , then (1-*x*) gives the fraction of  $Cl^{37}$ . The weighted average atomic weight is then

35x + 37(1-x) = 35.45

Solving for *x* gives 2x = 1.55, x = 0.775, so the abundances are 77.5% Cl<sup>35</sup> and 22.5% Cl<sup>37</sup>.

[Problems of this kind almost always turn up in exams]

#### Problem Example 6

 $Elemental \ chlorine, \ Cl_2, \ is made up \ of the two \ isotopes \ mentioned \ in the \ previous \ example. \ How \ many \ peaks \ would \ you \ expect \ to \ observe \ in \ the \ mass \ spectrum$ 

of Cl<sub>2</sub>?

*Solution:* The mass spectrometer will detect a peak for each possible combination of the two isotopes in dichlorine: <sup>35</sup>Cl-<sup>35</sup>Cl, <sup>35</sup>Cl-<sup>37</sup>Cl, and <sup>37</sup>Cl-<sup>37</sup>Cl.

### Isotope effects: when different isotopes exhibit different chemical behavior

The chemical behavior of an element is governed by the number and arrangement of its electrons in relation to its nuclear charge (atomic number). Because these quantities are identical for all isotopes of a given element, they are generally considered to exhibit identical chemical properties.

However, it turns out that the mass differences between different isotopes can give rise to very slight differences in their physical behavior that can, in turn affect their chemical behavior as well. These *isotope effects* are most evident in the lighter elements, in which small differences in neutron number lead to greater differences in atomic mass.

Thus no element is more subject to isotope effects than hydrogen: an atom of "heavy hydrogen"  $_1H^2$  (also known as *deuterium* and often given the symbol D) has twice the mass

of an atom of  $_1H^2$ . When this isotope is combined with oxygen, the resulting "heavy water"  $D_2O$  exhibits noticeably different physical and chemical properties: it melts at 3.8° C and boils at 101.4° C.  $D_2O$  apparently interferes with cell division in organisms; mammals given only heavy water typically die in about a week.

When two or more elements whose atoms contain multiple isotopes are present in a molecule, numerous isotopic modifications become possible.

For example, the two stable isotopes of hydrogen and of oxygen

 $(O^{16} \text{ and } O^{18})$  give rise to combinations such as  $H_2O^{18}$ ,  $HDO^{16}$ , etc., all of which are readily identifiable in the infrared spectra of water vapor.

The amount of the **rare isotopes of oxygen and hydrogen in water** varies enough from place to place that it is now possible to determine the age and source of a particular water sample with some precision. These differences are reflected in the H and O isotopic profiles of organisms. Thus the <u>isotopic analysis of human hair</u> can be a useful tool for crime investigations and anthropology research. See also this <u>Microbe Forensics page</u>, and <u>this general resource</u> on water isotopes.

### **Isotopic fractionation**

Isotope effects manifest themselves in both physical and chemical changes. In general,

- Chemical bonds involving lighter isotopes tend to be more readily broken, so reactions that depend on the rupture of such bonds will lead to products that are slightly enriched in the lighter isotopes.
- Phase changes such as vaporization similarly favor the lighter isotopes. Thus when water vapor condenses in clouds to form rain, the heavier water isotopes become slightly more concentred in the liquid phase.

These two effects give rise to *isotopic fractionation* as chemical substances move through the environment — or on a much smaller scale, through the various metabolic processes that occur in organisms. Over time, this leads to changes in the isotopic signatures of elements in different realms of the world that can reveal information that would otherwise be hidden.

The extent of isotopic fractionation depends on the temperature. This fact has been put to practical use to estimate the global average temperature in past times by measuring the degree of enrichment of the heavier isotopes of oxygen in glacial ice cores and also in ancient sediments containing the shells of microorganisms.

# Atomic weights, molecular weights and formula weights

Molecules are composed of atoms, so a *molecular weight* is just the sum of the atomic weights of the elements it contains.

Problem Example 7 What is the molecular weight of sulfuric acid,  $H_2SO_4$ ?

**Solution:** The atomic weights of hydrogen and of oxygen are 1.01 and 16.00, respectively (you should have these common values memorized.) From a table, you can find that the atomic weight of sulfur is 32.06. Adding everything up, we have  $(2 \ge 1.01) + 32.06 + (4 \ge 16.00) = 98.08$ 

Because some solids are not made up of discrete molecules (sodium chloride, NaCl, and silica,  $SiO_2$  are common examples), the term *formula weight* is often used in place of molecular weight. In general, the terms molecular weight and formula weight are interchangeable.

# 7 Atomic masses and the atomic mass unit

Here again is the beginning of the atomic weight scale that you saw above:

ť			He			Li		Be		В	ç		N		0			F	Ne
Т											Τ								
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20

You should understand by now that atomic weights are relative weights, based on a scale defined by  ${}_{6}C^{12} = 12$ . But what is the *absolute* weight of an atom, expressed in grams or kilograms? In other words, what actual mass does each unit on the atomic weight scale represent?

The answer is  $1.66053886 \times 10^{-27}$  kg. This quantity (whose value you do *no*t need to memorize) is known as the **unified atomic mass unit**, denoted by the abbreviation *u*. (Some older texts leave off the "unified" part, and call it the amu.

The unified atomic mass unit is defined as 1/12 of the mass of one atom of carbon-12.

Why such a hard-to-remember number? Well, that's just how Nature sometimes does things. Fortunately, you don't need to memorize this value, because you can easily calculate its value from Avogadro's number,  $N_A$ , which you *are* expected to know:

 $1 \text{ u} = 1/N_A \text{ gram} = 1 \div (1000 N_A) \text{ Kg}$ 

... but more about that in the <u>later lesson on moles</u>.

## Masses of the subatomic particles

particle mass, g mass. u charge symbol electron 9.1093897 × 10<sup>-28</sup>  $5.48579903 \times 10^{-4}$ 1 <sub>-1</sub>0e  $1.6726231 \times 10^{-24}$ 1.007276470 1+  $_{1}^{1}H^{+}, _{1}^{1}p$ proton neutron  $1.6749286 \times 10^{-24}$ 1.008664904 0  $0^1 n$ 

Atoms are composed of protons, neutrons, and electrons, whose properties are shown below:

Two very important points you should note from this table:

- The mass of the electron is negligible compared to that of the two nuclear particles;
- The proton and neutron have masses that are almost, but not exactly, identical.

# Nuclear masses and mass defect

As we mentioned in one of the problem examples above, the mass of a nucleus is always slightly different from the masses of the *nucleons* (protons and neutrons) of which it is composed. The difference, known as the *mass defect*, is related to the energy

associated with the formation of the nucleus through Einstein's famous formula  $e = mc^2$ . This is the one instance in chemistry in which conservation of *mass-energy*, rather than of mass alone, must be taken into account. But there is no need for you to be concerned with this in this part of the course.

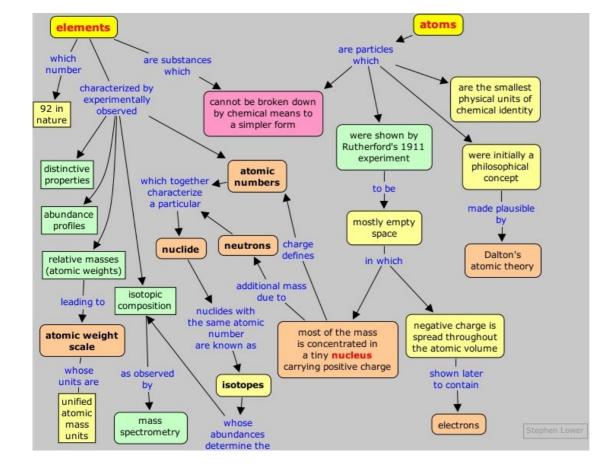
For all practical purposes, until you come to the section of the course on nuclear chemistry, you can consider that the proton and neutron have masses of about 1 u, and that the mass of an atom (in u) is just the sum of the neutron and proton numbers.

# What you should be able to do

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Give a chemical definition of *element*, and comment on the distinction between the terms *atom* and *element*.
- You should know the *names and symbols* of the more common elements, including those whose symbols are derived from their Latin names.
- Describe, in your own words, the Laws of Chemical Change: mass conservation, constant composition, and multiple proportions.
- Explain how these laws follow from *Dalton's atomic theory*.
- Describe <u>Rutherford's alpha-ray scattering experiment</u> and how it led to the present model of the atom.
- Define *atomic number* and *mass number*, and explain the relation between them.
- Define *isotope* and *nuclide*, and write the symbol for a nuclide of a given element with a given number of neutrons.
- Explain the purpose of a *mass spectrometer* and its general principle of operation.
- Describe the *atomic weight scale*.
- Find the *molecular weight* or *formula weight* from a chemical formula.
- Define the *unified atomic mass unit*, and write out the mass numbers of the proton, neutron, and electron.

# **Concept Map**



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