Chapter 2 – Atoms, Molecules, and Ions

2.1 Early Ideas in Atomic Theory

We'll touch on this very briefly, but there are 3 laws of nature that were important to the early development of chemistry and one (#1) that is still important to remember. They are:

1) The law of conservation of mass, which states that the sum of the masses of the reacting species in a chemical reaction equals the sum of the masses of the products. This is also the first law of thermodynamics and can be phrased as matter cannot be created or destroyed.
2) The law of constant composition, which states that, regardless of source, the proportion of each element in a compound is a fixed percentage by mass.
3) The law of multiple proportions, which states that if two elements react to form two different compounds (e.g. water (H_2O) and hydrogen peroxide (H_2O_2)), if the mass of the first element is fixed, then the mass of the other element will occur in a whole number ratio.

Throughout most of history, matter was believed to be infinitely divisible. That is, there was no smallest particle of anything. Although Democritus and Leucippus proposed the atom more than two millennia earlier, it was not until 1803 that John Dalton proposed the modern concept of the atom, which consisted of 5 empirically based postulates:

1) All elements are composed of extremely small particles called atoms.
2) All atoms of a particular element are identical and differ from all atoms of other elements. Atoms of an element have identical properties, which differ from those of other elements.
3) Atoms cannot be created, destroyed, or interconverted [by chemical reactions].
4) Compounds are formed from atoms of different elements in fixed, whole number ratios.
5) Chemical reactions are the rearrangement of atoms in compounds and molecules.

With two minor caveats (bracketed text in #3 and the discovery of isotopes, p. 4), these rules are as valid today as they were more than 200 years ago. The atom represents a dividing line between chemistry and physics. Generally, chemists study atoms and larger species, while physicists study particles smaller than atoms. The Atomic Theory also represents the dividing line between chemistry and alchemy. You know of alchemy as the attempt to turn base (inexpensive) metals into valuable ones (e.g. gold). The Atomic Theory recognized this as impossible. Shortly after publication of the Atomic Theory, alchemy, which was already in decline, disappeared from western science.

2.2 The Observations that Led to the Nuclear Atom Model

While chemists embraced the atom relatively quickly, physicists did so more slowly, and some did not accept atoms until after the turn of the 20th century. Chemists thought of atoms as hard and indivisible, much like billiard balls. Physicists initially thought of atoms as a convenient hypothetical construct, but not real entities because no direct evidence for them existed with the technology of that time.

By the late 1800s, physicists knew that passing an electrical current between two metal plates in an evacuated tube containing a fluorescent screen produced a green trace. It was called a cathode ray because it originated from the negative end of the tube (the cathode). The positive end was called the anode. The cathode ray traveled in a straight line in the absence of electrical or magnetic fields, but curved in their presence. Why was this important?

Remember that at that time atoms were the smallest particles anyone believed to exist. Furthermore, scientists knew that elements did not carry a charge. Thus, what composed the rays? They were originally thought of as energy waves, but magnetic and electrical fields don't affect energy. By altering the fields, physicists determined the rays to be negatively charged.

The implications of this series of experiments were profound.

i) Since "cathode rays" carried a charge, they had to consist of particles (i.e. matter).

ii) Since the particles had charges, they couldn't be atoms.

iii) Since all known matter was composed of atoms and the ray arose from metal plates, cathode rays must be negatively charged particles that were constituents of atoms.

The negatively charged particle was called the electron. (In 1874, G.J. Stoney first proposed the electron and J.J. Thomson discovered it in 1897 in the experiment just described.) In 1909, Robert Milliken confirmed that the electron was indeed smaller than an atom when he determined its mass to be about 1/2000th the mass of a hydrogen atom, the lightest element. This represented strong evidence for the electron as part of the atom.

Before discussing atomic structure further, we need to introduce another topic briefly. Also in the late 1800's, Henri Becquerel and Pierre and Marie Curie were examining a new phenomenon: radioactivity. They found that certain materials spontaneously emitted either particles: helium atoms without electrons (α particles), electrons (β particles), or energy (γ rays). Like cathode rays, the existence of α and β particles provided strong evidence for the existence of atoms.

Physicists reasoned that if the atom had a negative part, it must have a positive part (since the atom has no charge). Initially, they hypothesized that the atom was rather like fruit Jello™, although the analogy in late 19th century England was to "plum pudding." In this model, most of the atom was a positively charged, soft material with negatively charged electrons embedded in it. Applying a large, external positive charge would cause electrons to pull through the soft material and out of the atom. In the early 20th century, Ernest Rutherford tested this idea by taking a source of α particles and putting it in a box with a small hole aimed at a thin gold foil. A photographic plate was placed around the foil. If the positive part of the atom really were a soft material when it hit the foil, it would either be absorbed or go right through. When the experiment was conducted, most of the particles did go through as expected; however, some were deflected through angles of up to 180°.

This was important because a soft, positive ion would not bounce. The only reasonable explanation for this observation was that the positive part of the atom was hard and small.

Rutherford called it the nucleus. The deflections occur when two positively charged particles come near each other but don't touch. Rutherford also predicted the existence of neutrons, particles carrying no charge. (From what you know about the periodic table, can you see the basis of the prediction?) James Chadwick confirmed this in 1935.

2.3 Atomic Structure and Symbolism

Chemists usually use relative charges instead of actual charges. Thus, protons have a +1 charge, neutrons a 0 charge, and electrons a -1 charge. All atoms have equal numbers of protons and electrons and so are always electrically neutral. Protons and neutrons each weigh about 2000 times more than an electron. The nucleus occupies about 1 one-trillionth the total volume (0.01% of diameter) of the atom. If the atom were the size of a football stadium, the nucleus would be the size of a marble. However, atoms are quite small, with an average diameter of *ca.* 10^{-10} m. For reference, the smallest thing you can see with the unaided eye is about 10^{-4} m.

Atoms also have incredibly small masses, weighing roughly 10^{-22} g (there are about 28 g per ounce). This number is much too small to comprehend. To get around this, physicists invented a new unit, the atomic mass unit (amu) or Dalton (Da). A carbon nucleus containing exactly 6 protons and 6 neutrons weighs exactly 12 amu. A proton weighs 1.0073 amu. The neutron weighs just a bit more and the electron much less. We need to say a few more words about atoms before we move on. Earlier, the notes said all atoms of an element were identical. This isn't quite true. All atoms of the same element have the same number of protons. In fact, the number of protons defines the identity of the element. The number of neutrons may vary, though. Atoms of the same element possessing differing numbers of neutrons are called isotopes. With one exception (that we won't worry about in this course), isotopes of an element are chemically identical to each other. Most elements have two or more stable isotopes.

The number of protons in an atom is called its atomic number, Z. Because the mass of protons and neutrons are each nearly exactly 1 amu and the mass of electrons is so small, the mass of an atom (in amu) is approximately the sum of the number of its protons and neutrons. This is called the mass number, A. The following notation is used to describe atoms: ${}^{A}_{Z}X$, where X is the atomic symbol. X is found on the periodic table. Frequently, ${}^{A}_{Z}X$ is shortened to ${}^{A}X$ because the atomic number is always present on the periodic table with the atomic symbol.

Example: There are two naturally occurring isotopes of boron.

B-10 ${}^{10}_{5}B$ or ${}^{10}B$ each is read "boron-10"

Boron-10 contains 5 protons, 5 electrons, and 5 neutrons

B-11 ${}^{11}_{5}B$ or ${}^{11}B$ each is read "boron-11"

Boron-11 contains 5 protons, 5 electrons, and 6 neutrons

As you may have noticed on the periodic table, the atomic masses (or, more commonly, atomic weights) of the elements have different numbers of significant digits. If you haven't, take just a moment and check it out. More important, look at the variation in the number of digits to the right of the decimal point. They range from 1 (for lead) to 7 for (fluorine and aluminum). Why might this be so?

A natural, but incorrect, guess would have to do with error in measuring the mass of the atoms. In fact, the mass of all atoms are measured to the same level of precision. This means that the measured number of digits past the decimal is the same for all atoms. But this creates an apparent contradiction with the previous paragraph.

The thing to remember here is that most elements have isotopes. It turns out that samples located in different parts of the world have different ratios of isotopes and that difference causes a reduction in the number of significant digits reported on the periodic table. (This isn't a problem for elements with only one naturally occurring isotope because they report all digits.) Consider a hypothetical element with two isotopes weighing 9.0000 amu (isotope $\mathcal{A}$) and 10.0000 amu (isotope $\mathcal{B}$). One sample is composed of 50.000% $\mathcal{A}$ and 50.000% isotope $\mathcal{B}$. The apparent atomic mass of the sample would be 9.5000 amu. In contrast, for a sample that was 49.950% $\mathcal{A}$ and 50.050% $\mathcal{B}$ would have an apparent atomic mass of 9.5005 amu. A value of 9.500 amu would be reported on a periodic table because there is a disagreement in fourth decimal place. For this reason, the mass values in a periodic table are average atomic masses. Thus, the numbers on the periodic table tell you something about the similarity of samples of elements from around the world.

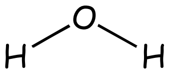
2.4 Chemical Formulas

The composition of a material is frequently expressed as a "formula." There are several different kinds of formulae used by chemists. The most common is the molecular formula, which is the exact composition of a material expressed as atomic symbols followed by a subscript indicating the exact number of atoms of that element in one unit of that material. The subscript is always a whole number. Thus, carbon dioxide is CO_2. Sometimes, the term "molecular" formula is something of a misnomer. It is used on materials that aren't molecules too. For example, Epsom salt, $MgSO_4$, is obviously a salt, not a molecule, but we still refer to the formula as a molecular formula. We'll discuss the difference between salts and molecules later in this chapter.

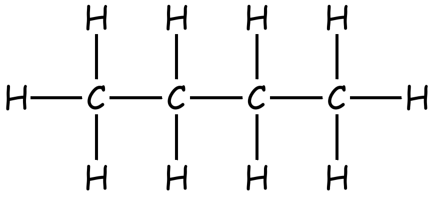
An empirical formula provides the relative number of each kind of atom, thus for ethane, the empirical formula is CH_3, while the molecular formula is C_2H_6. As the name suggests, empirical formulae are experimentally determined. The molecular formula is derived by multiplying the subscript by a number to get whole numbers because you can't have fractional atoms in real materials. In the case of ethane, multiplying each subscript by 2 achieves that goal. In nearly all cases, the smallest multiplier is correct, but there are very important exceptions, particularly in organic chemistry.

A third kind of formula that you will encounter with some frequency is the structural formula, which shows the connectivity of the atoms in a molecule. For example, water consists of two hydrogen atoms each bound to a central oxygen in a chevron shape (see below). Thus, the formula of water is sometimes written as "HOH." This conveys the connectivity. Likewise, butane (the fluid in disposable cigarette lighters) can be written as either C_4H_{10} or $CH_3CH_2CH_2CH_3$. As you can see, the latter formula tells you something about the structure (see picture below).

For water and butane that would be:



water



butane

Note that these structures usually do not show angles within the molecule accurately. The book shows three other ways that chemists use to draw molecules, although ball-and-stick models and space filling models are only used in books and journals.

2.5 The Periodic Table

In order to be successful in chemistry, you'll need to learn to use the periodic table. You are required to know the symbols and names of the first 30 elements. It will help you to memorize the positions of them as well because the book and I will refer to them frequently, but this isn't required. Knowing where they are will save you the trouble of looking them up many times.

From its name, you might guess that there is order to the periodic table. To varying degrees, similarities between elements have been known for hundreds of years. For example, sodium (Na) and potassium (K) were known before the discovery of lithium (Li). Sodium and potassium were first isolated from soda ash and potash, respectively, which are obtained from burning plant materials. Both sodium and potassium are very reactive, soft metals. Both react rapidly with water to produce basic solutions and hydrogen gas (H_2). When lithium was first prepared it was found to be chemically quite similar to sodium and potassium. For this reason, in 1817 J.A. Arfvedson named it after its source: a rock (*Lithos*, from the Greek).

While a rough to nearly correct ordering of the elements was known for quite some time, it wasn't until 1869 that Dmitri Mendeleev (Russia) and Lothar Mayer (Germany) simultaneously and independently proposed modern periodic tables. The columns in the periodic table are called groups or families. Elements in the same group tend to have similar physical and chemical properties. The rows are called periods. Properties change significantly (frequently regularly) across a period. Some of the groups have names, for example: Group 1 (1A) = alkali metals, Group 2 (IIA) = alkaline earth metals, Group 17 (VIIA) = halogens, Group 18 (VIII) = noble gases, and Group 11 (IB) = coinage metals. Less commonly used: Group 16 (VIA) = chalcogens and Group 15 (VA) = pnicogens. Two rows have names. Below the main body of the periodic table is a two row block. The upper row, beginning with cerium (element 58), is called the lanthanides. Below that row are the actinides. You may have heard of the lanthanides because they are elements with low natural abundance, but are very important in the manufacture of electronic devices like your cell phone or computer. The lanthanides are sometimes called rare earth elements.

Please remember that columns are vertical and rows are horizontal. Referring to horizontal columns or vertical rows is confusing and a sure way to get a test question wrong.

You'll also sometimes hear of a few other designations on the periodic table. Collectively the first two columns and the last six are called the representative elements. The 10 column band in the middle contains the transition metals. Finally, elements are broadly divided into three types: metals, nonmetals, and metalloids (or occasionally semimetals). The groups are differentiated by their properties, both physical and chemical. For example:

Metals - These elements comprise over three-quarters of the periodic table, including all transition metals, lanthanides, actinides, and representative elements on the left side of the periodic table and many in the lower right corner beyond the transition metals. In general, they

- have luster (shiny) and are silvery or gray (except copper, gold, and, arguably, cobalt),
- are malleable and ductile,
- are good conductors of heat and electricity, and
- are solids at room temperature (except mercury).

Nonmetals - Occupy the upper right-hand corner of the representative block. In general, they

- are brittle and have low luster when solid,
- are electrical and thermal insulators, and
- tend to have low melting points. (e.g. Several are gases at room temperature.)

Metalloids - have a mix of metal and nonmetal properties (rather than an average). For example, they usually look like metals, but are brittle. They conduct heat and electricity, but poorly.

2.6 Molecular and Ionic Compounds

Recall from Chapter 1 that compounds are pure substances made up of two or more different elements. Broadly speaking, compounds either result from species transferring electrons from one to the other (resulting in ionic compounds) or from the sharing of electrons between two nuclei (usually resulting in molecules).

Compounds are held together by bonds, which are an attractive force between atoms. Ionic bonds result from the attraction between oppositely charged species. Covalent bonds typically occur between two nonmetals and result from the "sharing" of electrons. For now, this is best thought of as the electrons staying in the middle of the two atoms. We will discuss more sophisticated definitions of the types of bonding in Chapter 7, but these definitions will work until then.

Binary ionic compounds are composed of two elements: one a metal and the other a nonmetal. In this kind of compound the atoms are converted to ions, which are charged particles, frequently by one atom transferring one or more electrons to another atom. Earlier you learned that the number of protons in a nucleus determines the element. This is because electrons can be removed from or added to atoms, while protons are never lost or gained. Cations (pronounced cat-ions) are positively charged ions and anions (pronounced an-ions) are negatively charged ions. A cation forms when a species loses electrons. Anions form when species gain electrons. In binary ionic compounds, the metals form cations and the nonmetals anions. Sodium chloride, NaCl, is the prototypical ionic compound. It is composed of a sodium cation (Na^+) and a chloride anion (Cl^-).

Ionic compounds may also contain polyatomic ions. For example, the ammonium ion (NH_4^+) is the most common polyatomic cation. There are many polyatomic anions, some of which are listed in Table 2.5 (pp. 101-102). You should memorize all of these ion names & formulae because you will encounter them throughout the course. The most common ions are hydroxide, acetate, cyanide, carbonate, nitrate, sulfate, phosphate, perchlorate, and permanganate, but the others will appear in the text and problems throughout CHM 211 and 212 (and occasionally on tests).

It is frequently possible to predict the charge that will occur on an ion. The most stable atom in any period is its noble gas. Atoms will usually try to acquire the same number of electrons as the noble gas on the end of the same (anions) or previous (cations) period. Hence, chlorine will add one electron and sodium will lose one (e.g. Na^{1+} has the same number of electrons as Ne). Atoms rarely gain or lose more than 4 electrons. Thus, any element in the Group IA (alkali metals) will lose 1 electron. Any element in Group 2A will lose 2 electrons. Any element in group 5A will tend to gain 3 electrons. And so on . . . Atoms in Group 4 form either +4 cations or -4 anions, when they form ions. Other ions form, but as we will see repeatedly, this tendency is very important in chemistry.

Example: When magnesium reacts with fluorine, magnesium fluoride (MgF_2) forms.

Mg = 12 protons, 12 electrons → Mg^{2+} = 12 protons, 10 electrons

F = 9 protons, 9 electrons → F^- = 9 protons, 10 electrons

Note that both the Mg and F wind up with the same number of electrons, even though one is a cation and the other an anion.

Most species with covalent bonds are called molecules. These are discrete entities with the same number and type of atoms all covalently bonded together. Molecules carry no charge. Water (H_2O) and ammonia (NH_3) are molecules that are compounds. Atmospheric nitrogen (N_2) and oxygen (O_2) are molecules that are elements. The other major type of species possessing only covalent bonds are network covalent solids. These are essentially infinite networks of covalently bound atoms. Glass/quartz (SiO_2) and diamond (C) provide examples.

2.7 Chemical Nomenclature

It will take you some time before you can confidently name all inorganic compounds. We'll go over the rules now. There are a lot of them, so begin practicing now. Reading each compound by its name rather than its formula makes learning names much easier. This is how practicing chemists usually say chemical names. For example, read NaCl as *sodium chloride*, rather than as "en-A-see-ell."

Units of a compound always have the same numbers and types of atoms. Chemists write the composition of a compound using chemical formulas. This is a string of atomic symbols (from the periodic table) followed by a subscript to indicate the number of atoms present. If only one atom is present the subscript one (1) is omitted.

Example: Water has two hydrogen atoms bound to one oxygen atom: H_2O

likewise: ammonia = NH_3 and glucose = $C_6H_{12}O_6$

Ionic Compounds

Metal ions always have the same name as the metal from which it was derived. Thus, Na^+ is the sodium ion. If a metal can form two different ions, then a Roman numeral in parentheses is placed after the metal name to indicate the number of electrons removed (e.g. Fe^{2+} = iron(II) ion, Fe^{3+} = iron(III) ion). Ions from Groups IA and IIA, Al^{3+}, Zn^{2+}, and Cd^{2+} have only one possible charge. Assume all other metals may have 2 or more possible positive charges.

Polyatomic cations that include non-metal atoms end in "-ium." The only two examples of this you will see in this course are ammonium (NH_4^+) and hydronium (H_3O^+). Know Table 2.5, p. 101.

Anions are more complicated. Atomic anions drop their elemental endings and add "-ide." The exact letters dropped depend on the element.

H^- = hydride ion

O^{2-} = oxide ion

F^- = fluoride ion

A few important polyatomic anions also end in -ide.

OH^- = hydroxide ion

CN^- = cyanide ion

O_2^{2-} = peroxide ion

Polyatomic anions tend to end in either "-ite" or "-ate." In almost all cases, a central atom is surrounded by several other atoms, usually oxygen. When two possible numbers of oxygens are possible, the one with the fewer oxygens ends in "ite" and the one with more oxygens ends with "ate."

Example: NO_2^- = nitrite ion

SO_3^{2-} = sulfite ion

PO_3^{3-} = phosphite ion

NO_3^- = nitrate ion

SO_4^{2-} = sulfate ion

PO_4^{3-} = phosphate ion

When such a polyatomic anion has hydrogen atom(s) bound to it, just add the word hydrogen to the front. (e.g. HPO_4^{2-} = hydrogen phosphate, $H_2PO_4^-$ = dihydrogen phosphate).

For ionic compounds, always name the cation first and the anion last.

e.g. NaCl = sodium chloride

NH_4OH = ammonium hydroxide

$Fe_2(SO_4)_3$ = iron(III) sulfate

Some ionic compounds trap water molecules in their solid lattice, some cations covalently bond to water molecules, some do both, others neither. When it does happen, the salt becomes a hydrate. Your book notes that gypsum ($CaSO_4 \cdot 2H_2O$) is a hydrate named calcium sulfate dihydrate. When heated it becomes Plaster of Paris ($CaSO_4 \cdot \frac{1}{2}H_2O$): calcium sulfate hemihydrate. The prefix on "hydrate" follows the Latin numbering nomenclature we use for molecules (vide supra). Hydrates are usually read (e.g. for gypsum: calcium sulfate dot two water).

Binary Molecules

Molecules with exactly two atoms are called diatomic (e.g. O_2), while those with three atoms are triatomic (e.g. H_2O). A few molecules have special names that you will have to memorize:

water = H_2O ammonia = NH_3 ozone = O_3 methane = CH_4

While not listed in your book, many ionic compounds have common names as well. Three you have heard before are lime (CaO), limestone ($CaCO_3$), and plaster of paris ($CaSO_4 \cdot 2H_2O$).

Binary Molecular Compounds

1) The element located furthest left on the periodic table is usually written first.
2) If both elements are in the same group, the lower one comes first.
3) The second element will end in "-ide."
4) The prefixes mono-, di-, tri-, tetra-, penta-, and hexa- are used to indicate the number of each element present. Only when the first element is present as a single atom is the prefix omitted.

Examples: CO = carbon monoxide CO_2 = carbon dioxide

P_2O_5 = diphosphorus pentoxide ClF_3 = chlorine trifluoride

Acids

For acids, use the following rules:

For anions ending in "-ide", add the prefix "hydro-" and replace the "-ide" with "-ic acid." (e.g. CN^- = cyanide becomes HCN = hydrocyanic acid or Br^- = bromide becomes HBr = hydrobromic acid)

For ions ending in "-ite", replace that with "-ous acid." For ions ending in "-ate", replace that with "-ic acid." (e.g. SO_3^{2-} = sulfite becomes H_2SO_3 = sulfurous acid, SO_4^{2-} = sulfate becomes H_2SO_4 = sulfuric acid). CH_3CO_2H (sometimes $HC_2H_3O_2$ or HOAc), acetic acid, is the only organic acid you will encounter in this course.

There is an important distinction here. The physical states of materials are frequently very important. HCl normally exists as a gas and in that form is called hydrogen chloride ($HCl_{(g)}$). When it is dissolved in water, it becomes hydrochloric acid ($HCl_{(aq)}$). We'll return to the subscript method of conveying physical states in Chapter 4. But for now, you should know the difference between a molecule in its molecular form and its acidic form.

Descriptive Structures

Sometimes the way formulas are written out can be used to provide structural information.

When ions form compounds, the total charge on the resulting material will always be zero. Thus, Li^+ and Cl^- will combine to form LiCl, but Li^+ and O^{2-} will combine to form Li_2O. In the latter case, it takes two 1+ charges on the lithium ion to balance the 2- charge on the oxide ion.