Chapter 5 – Early Atomic Theory and Structure

Even if you have never set foot in a chemistry classroom, it is likely that you have a sense for what an atom is. As you also know, millennia ago this wasn't the case. Originally, a Greek philosopher, Empedocles, proposed that all matter was made up of air, earth, fire, & water and that every substance was infinitely divisible (i.e. there was no smallest unit of anything). A few decades later, a second Greek philosopher, Democritus, proposed the existence of atoms, but not in the modern sense. Democritus reasoned that any substance could be broken into pieces, then broken again, and so on, but at some point one would hit the smallest particle of that substance and it couldn't be broken apart. This was an "atom." It is different from the modern atom in that every substance would have its own atom. In contrast, Empedocles did get that all substances were made up of simpler substances, but far fewer than really exist.

It is worth noting that neither Empedocles nor Democritus ever did an experiment and never tested anything to see if their idea was correct. They used the power of argument to convince listeners their idea was correct. In the end, Aristotle picked Empedocles theory and because of the immense authority he carried, made the air/earth/fire/water theory the prevailing scientific belief of matter's composition for centuries. There is a nice description of the history online.

By around 1800, a lot of problems with that theory were being encountered by scientists. In 1803, John Dalton, an English "schoolteacher" first proposed the modern atom. As your book notes, Dalton's original theory had flaws in it, primarily because the data generated in the 1700's came from equipment that wasn't as sophisticated as the equipment we have today. Unlike your book, these notes will present Dalton's theory as it appears in most chemistry textbooks, including the CHM 211 book.

5.1 Dalton's Model of the Atom

After examining a lot of the scientific writings by others before him and in the conducting of his own experiments, Dalton proposed that matter was composed of tiny particles called atoms.

Furthermore, he proposed that there was a limit to the number and kinds of atoms. His observations led to a five component atomic model.

i) All elements are composed of extremely small particles called atoms.
ii) 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.
iii) Atoms cannot be created, destroyed, or interconverted [by chemical reactions].
iv) Compounds are formed from atoms of different elements in fixed, whole number ratios.
v) Chemical reactions are the rearrangement of atoms in compounds and molecules.

Historically, chemistry frequently traces its origin as a discipline to the proposal of this theory. Shortly after this theory was published, alchemy, which was already in decline because it didn't work, disappeared. These five postulates do an excellent job of describing the behavior of chemicals both in reactions and when their physical properties are measured. Interestingly, while chemists embraced this theory quickly, physicists did not for another 75 years or so.

5.2 Electric Charge

While electricity has been known since the first observation of a lightning strike, it wasn't until Benjamin Franklin's famous experiment in 1752 that scientists knew for certain that lightning was form of electricity. By then, scientists knew there was an opposite force to electricity, but didn't know what it was. Franklin assigned the terms "negative and positive charges." In 1874 George Stoney proposed, and in 1897 J.J. Thompson confirmed, the existence of the electron as a negatively charged particle that was a component of atoms.

There are four rules about charge you should remember:

1) There are two charges, positive and negative.
2) Opposite charges (+/–) attract and same charges (+/+ and –/–) repel.
3) Charge may be transferred between objects either by direct contact or through space.
4) Attraction/repulsion increase with increasing charge and decreasing distance of separation

between charged species according to the formula

$$\text{Force of attraction} = \frac{kq_1q_2}{r}$$

Where k = constant, q = charge, and r = distance.

Ions are charged particles, with anions carrying a negative charge and cations carrying a positive charge. Cations and anions never exist in isolation. That is, one can never isolate either cations or anions, they must exist together. It is possible to draw them away from one another, but they can't be isolated. In addition, anions are formed by drawing electrons off a second species leaving a cation. For example, consider the reaction of sodium and chlorine to form table salt:

$$2\ Na_{(s)} + Cl_{2\,(g)} \rightarrow 2\ NaCl_{(s)}$$

When added to water, the sodium chloride separates into Na^+ and Cl^- ions, but the ions still exist in the solid phase with the anions and cations adjacent to each other throughout the solid.

5.3 Subatomic Parts of the Atom

By the mid-to late 1800's chemists and then physicists came to agreement that atoms existed and were the smallest units of elements and combined in fixed ratios to form compounds. Chemists were convinced of their existence because they were the simplest explanation for what chemists observed in the lab. Physicists were convinced of the existence of atoms when particles smaller than atoms that could only come from atoms were discovered.

The first such particle was the electron. The book has a nice picture of a Crooks (cathode ray) tube (CRT), the device used to discover the electron. It is basically a sealed tube that has been evacuated with a metal plate at each end. In it a phosphor screen is placed along the length of the tube and the plates are connected to the outside with wires. When an electric current is passed between the plates, the phosphor glows green indicating that something is passing between the plates (video in the CRT link). What passes is a cathode ray, so called because the ray emanates from the cathode (negative plate). We know the ray is a stream of particles because a special rotating vane only spins when the ray is present. We know the particles are smaller than atoms because the plates *don't change mass over time, so the particles have to be part of the electricity used to generate the cathode ray, not the plate. Thus, we have a ray made of particles smaller than the atoms (electrons) that make up the device, this shows that atoms must have parts and therefore atoms must exist.*

Electrons are tiny, weighing 9.110×10^{-28} g. Remember, a paperclip weighs roughly 1 gram, so this is the smallest of fractions. Fortunately, the absolute weight of subatomic particles isn't typically important to chemists, so remembering this value isn't important. The hydrogen atom contains one electron and that electron represents 1837^{th} of the total mass of the hydrogen atom. To put this in perspective, a typical small box contains 100 paper clips, so the mass of the electron would be similar to one paper clip out of 18 boxes. This raises the question, what is the remaining mass?

The existence of a negative charge on the electron required that there be a positive part of the atom, since nearly all materials don't carry a charge. At the beginning, with no strong evidence either supporting or refuting the model, it was proposed that the atom was a ball of positive charge with electrons imbedded it in. Applying a positive charge outside of the atom, would pull electrons out and applying a negative charge would force electrons in. This would account for ions. (Consider fruit Jello® as a model, although most books use plum pudding as the analogy.)

The result of adding or removing electrons are ions. Note that ions <u>always</u> result from the addition or subtraction of electrons, not the source of positive charge. Again, each electron carries a -1 charge, so making a chloride (Cl^-) ion involves adding one electron to a chlorine atom, while making a sulfide (S^{2-}) ion requires adding two electrons to a sulfur atom. In contrast, a calcium ion (Ca^{2+}) involves the removal of two electrons from a calcium atom.

5.4 <u>The Nuclear Atom</u>

The "plum pudding" model of the atom lasted until 1911, when Ernest Rutherford conducted a famous experiment designed to show that the model was correct. By 1911, it was well known that certain radioactive substances emitted helium ions with a +2 charge (called alpha (α) particles). The prevailing theory predicted that if an α-particle were shot at a sheet of thin metal *foil it would pass through unchanged. Rutherford's lab set up an experiment like the one shown on p. 94 of the textbook. In it, a source of α-particles is aimed at a thin gold foil target and photographic film is put in a circle around it. When an α-particle hits the photographic film, it exposes it just like light would when taking a picture. They expected to see a small, dark patch directly opposite the source and nothing else. What they actually saw was the dark patch, but also a small, but significant number of spots from 180º to nearly 0º. This meant that some of the α-particles were being deflected even to the point of being bounced back to the source. The existing model of the atom just couldn't explain that, so Rutherford proposed a new model.*

In it, all of the positive charge resided in a small particle at the center of the atom, with electrons traveling in circular orbits around the center (called the nucleus). Later, the existence of neutral particles refined this model to have the nucleus filled with positive particles, called protons, and neutral particles called neutrons. The protons carried a +1 charge and equaled the number of electrons in neutral atoms. The rest of the mass of the nucleus was accounted for by neutrons. Protons and neutrons weigh nearly the same amount, although the neutron weighs a very small amount more. This was called the nuclear model of the atom.

The Rutherford experiment was consistent with this model because most of the atom is free space. Another nucleus (the α-particle) would normally just pass through it unchanged, but occasionally when the two positively charged particles got close to one another, the α-particle would deflect to a different course.

A natural question is "how big are the particles relative to the atom as a whole." The book tells you that the atom is about 10,000 times larger than the nucleus. To put this into perspective, a football field is 100 yards or 3600 inches long. Thus, if one took a football stadium and placed a quarter on the 50-yard line, you would have a sense of the size of an atom vs. the nucleus and electrons.

Formally, an element is defined by the number of protons in the nucleus. For example, all hydrogen atoms have exactly 1 proton. All helium atoms have two protons, and lithium atoms have 3 protons. Look at the periodic table and you can see the trend. The atomic number (Z) of an *atom is the number of protons in its nucleus.*

5.5 Isotopes of the Elements

One of Dalton's postulates "All atoms of a particular element are identical" turns out not to be literally true. However, functionally it is nearly always true. Each element is defined by the number of protons in its nucleus and will have an equal number of electrons in neutral atoms. Although not directly, that is what early chemists could measure. Neutrons carry no charge and so varying their number has little effect on an atom. Isotopes are atoms of the same element with different numbers of neutrons.

Under normal circumstances two atoms of the same element with different numbers of neutrons will behave almost identically. With one exception, the only difference in chemistry will be a small difference in the speed of reaction, but the products will be the same. The exception is an isotope of hydrogen, called deuterium, reacts much slower than regular hydrogen. The only other time isotopes will behave differently is in nuclear reactions, but that is physics, not chemistry. (When Dalton published his postulates, radioactivity was still almost 90 years from being discovered.)

Elements are sometimes expressed in written form using the following shorthand notation:

$${}^{A}_{Z}\mathrm{E}$$

Where "E" is the atomic symbol (e.g. H or Ca), "Z" is the atomic number (i.e. number of protons in the atom), and "A," the mass number (i.e. the sum of the number of protons and neutrons in the atom). Since Z defines the element and E is another way of identifying it, they are synonyms and many times writers will leave off the Z as redundant. Most elements have more than one naturally occurring isotope and every element has at least one artificial isotope (one made through a human induced nuclear reaction).

For example, chlorine has two common isotopes that are relatively abundant: ${}^{35}_{17}\mathrm{Cl}$ *and* ${}^{37}_{17}\mathrm{Cl}$*, with about 75% of all naturally occurring chlorine being the first isotope, "chlorine-35" and about*

25% of the second isotope, "chlorine-37." By looking at the symbol, with some experience, you immediately know the element is chlorine. The subscripted atomic number tells you the element has 17 protons. The superscripted mass number gives a good estimate of the mass/weight of the atom. It also indirectly provides the number of neutrons because one can get it by subtraction:

Number of neutrons = mass number – atomic number

In this example, the first isotope has 18 neutrons (35 – 17) and the second isotope has 20 neutrons (37 – 17).

5.6 Atomic Mass

Not surprisingly, individual atoms don't weigh very much. In fact, their masses are literally unimaginably small. For example, a single hydrogen-1 atom, ${}^{1}_{1}\mathrm{H}$, has a mass of about 1.673 x 10^{-24} g, a number far too small to be genuinely comprehended. For this reason, physicists developed a relative scale that is much easier to use and understand.

In the atomic mass scale used today, the mass of a carbon-12 (${}^{12}_{6}\mathrm{C}$) nucleus is defined as have a mass equal to exactly 12.0 atomic mass units (amu or u). Thus, 1 amu equals one-twelfth the actual mass of a carbon-12 nucleus in grams. This greatly simplifies atomic masses because it replaces the incredibly small numbers associated with grams and replaces them with numbers that are easier to remember and manipulate in your head. For example, the hydrogen atom in the previous paragraph weighs 1.673 x 10^{-24} g or 1.00794 amu. For most purposes, only 3 or 4 significant figures are needed so the mass simplifies to 1.01 or 1.008 amu. As a result, most atoms have atomic masses very close to whole numbers.

Recall that when found in nature, most elements are mixtures of isotopes. This means that the masses reported are actually weighted averages of the component isotopes. Earlier, you saw that chlorine has two common isotopes that are relatively abundant: ${}^{35}_{17}\mathrm{Cl}$ (~75%) and ${}^{37}_{17}\mathrm{Cl}$ (~25%). How does this affect atomic masses? When measuring out a sample of the element, the sample will be a mixture of the isotopes whether the element is pure or in a compound. Any sample of the *element will have nearly the same percentage of isotopes.*

For the chlorine example, all naturally occurring samples of chlorine are composed of chlorine-35 (75.78%) and chlorine-37 (24.22%). The value for the atomic mass reported on the periodic table is the weighted average of these percentages:

Atomic mass (Cl) = (34.9688 amu)(0.7578) + (36.9659 amu)(0.2422) = 35.452 amu

which is the value you see on the periodic table. Expressed in grams, the average atomic mass of chlorine is 5.8872×10^{-23} *g, which is why chemists almost never use grams when working with the masses of individual atoms.*

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