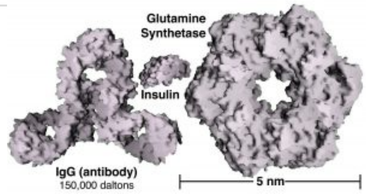
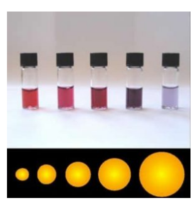
3.1: Elements and Bonding



When atoms interact with one another to form molecules or larger structures, the molecules have different properties than their component atoms; they display what are often referred to as emergent properties, where the whole is more than, or different from the sum of its parts. In a similar way groups of atoms or molecules have different properties from isolated atoms/molecules. For example while groups of atoms/molecules exist in solid, liquid, or gaseous states, and often have distinct colors and other properties, isolated atoms/molecules do not; there are no solid or liquid isolated atoms and they do not have a color or a boiling point. So the obvious question is, how many atoms or molecules need to aggregate before they display these emergent properties, before they have a color, before they have a melting point, boiling point, heat capacity, and other properties that isolated atoms do not? The answer is not completely simple, as you are probably slowly coming to expect. As we add more and more atoms or molecules together their properties change but not all at once. You have probably heard about nanoscience and nanotechnologies, which have been the focus of a great deal of research and economic interest in the past decade or so. Nanoparticles are generally classified as being between 1 and 100 nm in diameter (a nanometer is one billionth of a meter or $1 \times 10^{-9}\ \mathrm{m}$). Such particles often have properties that are different from those of bulk (macroscopic) materials. Nanomaterials can be thought of as a bridge between the atomic-molecular and macroscopic scales.

Assuming that they are pure, macroscopic materials have predictable properties and it doesn't really matter the size of the sample. A macroscopic sample of pure gold behaves the same regardless of its size and if Archimedes (ca. 287–212 bce) were alive today, he could tell you whether it was pure or not based on its properties, for example, its density. But gold nanoparticles have different properties depending upon their exact size. For example, when suspended in water, they produce colors ranging from orange to purple, depending on their diameter (see Figure). Often the differences in the properties displayed are due to differences in the ratio of surface area to volume, which implies that intermolecular forces (forces between molecules) are more important for nanomaterials. As we cluster more and more particles together, the properties of the particles change. Biomolecules generally fall into the size range of nanomaterials, and as we will see their surface properties are very important in determining their behavior.



Unfortunately when we are talking about the properties of atoms and molecules versus substances and compounds, it can be difficult, even for experienced chemists, to keep the differences clear. In addition different representations are often used for different organizational levels; it is an important skill to be able to recognize and translate between levels. We will be using a range of representations to picture atoms and molecules; chemists (and we) typically use various shorthand rules, methods, and chemical equations to represent molecular composition, shape, and behaviors. But just knowing the equations, often the only thing learned in introductory chemistry courses, is not sufficient to understand chemistry and the behavior of atoms and molecules. Much of the information implied by even the simplest chemical equations can easily be missed—or misunderstood—if the reader does not also have a mental picture of what the diagram or equation represents, how a molecule is organized and its shape, and how it is reorganized during a particular reaction. We will be trying to help you get these broader pictures, which should you make sense of the diagrams and equations used here. That said, it is always important to try to explicitly identify what you are assuming when you approach a particular chemical system; that way you can go back and check whether your assumptions are correct.

Where Do Atoms Come From?

> *"We are stardust, we are golden, We are billion-year-old carbon."*
> *– Woodstock, Joni Mitchell*

"Sometimes I've believed as many as six impossible things before breakfast."
– Alice in Wonderland, Lewis Carroll

Did you ever stop to ask yourself where the atoms in your body came from? Common answers might be that the atoms in our bodies come from food, water, or air. But these are not the ultimate answers, because we then need to ask, where did the atoms in food, water, and air come from? Where did the atoms in the Earth come from? There are really two general possibilities: either the atoms that make up the Earth and the rest of the universe are eternal or they were generated/created by some process. How do we decide which is true? What is the evidence favoring one model over the other? The answers come not from chemistry, but from astrophysics.

Given that we are thinking scientifically what kinds of evidence can we look for to decide whether atoms (or the universe) are eternal or recently created? Clearly we must be able to observe the evidence here and now and use it to formulate logical ideas that make clear and unambiguous predictions. As we will see we will be called upon once again to believe many apparently unbelievable things. The current organizing theory in astrophysics and cosmology, known as the Big Bang theory, holds that the universe is $\sim 13,820,000,000 \pm 120,000,000$ years old or 13.82 ± 0.12 billion years – an unimaginable length of time. The Sun and Earth are $\sim 5,000,000,000$ years old, and the universe as a whole is ~ 156 billion light-years in diameter.[1]

The Big Bang theory was put forward in a response to the observation that galaxies in the universe appear to be moving away from one another. Because the galaxies that are further away from us are moving away more rapidly than those that are closer, it appears that space itself is expanding, another seriously weird idea.[2] Based on this observation, we can carry out what scientists call a thought experiment. What happens if we run time backwards, so that the universe is contracting rather than expanding? Taken to its logical conclusion, the universe would shrink until, at some point, all of the universe would be in a single place, at a single point, which would be unimaginably dense. Based on a range of astronomical measurements, this so-called singularity existed $\sim 13.73 \times 10^9$ years ago, which means the universe is about 13.73 billion years old. The Big Bang theory tells us nothing about what happened before 13.73×10^9 years ago, and although there is no shortage of ideas, nothing scientific can be said about it, because it is theoretically unobservable, or at least that is what we have been led to believe by astrophysicists!

Thinking About Atomic Origins

The current model of the universe begins with a period of very rapid expansion, from what was essentially a dimensionless point, a process known as inflation. As you might well imagine there is some debate over exactly what was going on during the first 10^{-43} seconds (known as the Planck time) after the universe's origin. Surprisingly, there is a remarkable level of agreement on what has happened since then.[3] This is because there is lots of observable evidence that makes it relatively easy to compare hypotheses, accepting some and ruling out others. Initially remarkably hot (about 10^{23} K), over time the temperature (local energy levels) of the universe dropped to those that are reachable in modern particle accelerators, so we have actual experimental evidence of how matter behaves under these conditions. At 1 picosecond after the Big Bang, there were no atoms, protons, or neutrons, because the temperature was simply too high. There were only elementary particles such as photons, quarks, and leptons (electrons are leptons) – particles that appear to have no substructure. By the time the universe was ~ 0.000001 seconds old (a microsecond or 1×10^{-6} second), the temperature had dropped sufficiently to allow quarks and gluons to form stable structures, and protons and neutrons appeared. A few minutes later the temperature dropped to about $1,000,000,000$ K(\(1 \times 10^{9} \mathrm{~K}\)), which is low enough for some protons and neutrons to stick together and stay together without flying apart again. That is, the kinetic energy of the particles colliding with them was less than the forces (the weak and strong nuclear forces) holding the protons, neutrons, and nuclei together. At this point the density of particles in the universe was about that of our air.

By the time the universe was a few minutes old it contained mostly hydrogen ($^{1}H^{1} =$ one proton, no neutrons) and deuterium ($^{2}H^{1} =$ one proton and one neutron) nuclei, with some helium ($^{3}He^{2} =$ and $^{4}He^{2} =$ two protons and either one or two neutrons, respectively), and a few lithium ($^{7}Li^{3} = =$ three protons and four neutrons).[4] These nuclei are all formed by nuclear fusion reactions such as

$$^{1}p^{+} + {}^{1}n^{0} \rightarrow {}^{2}H^{+} + \text{gamma radiation and } {}^{2}H^{+} + {}^{2}H^{+} \rightarrow {}^{3}He^{2+} + {}^{1}n^{0}. \tag{3.1.1}$$

These fusion reactions take place in a temperature range where the nuclei have enough kinetic energy to overcome the electrostatic repulsion associated with the positively charged protons but less than that needed to disrupt the nuclei once formed. After a few minutes the temperature of the universe fell below $\sim 10,000,000 (10^{7})$ K At these temperatures, the kinetic energy of protons and nuclei was no longer sufficient to overcome the electrostatic repulsion between their positive charges. The end result was that there was a short window of time following the Big Bang when a certain small set of nuclei (including $^{1}H^{+}$, $^{2}H^{+}$, $^{3}He^{2+}$, $^{4}He^{2+}$, and

$^{7}Li^{3+}$) could be formed. After $\sim 400,000$ years the temperature of the universe had dropped sufficiently for electrons to begin to associate in a stable manner with these nuclei and the first atoms (as opposed to bare nuclei) were formed. This early universe was made up of mostly (> 95) hydrogen atoms with a small percentage each of deuterium, helium, and lithium, which is chemically not very interesting.

The primary evidence upon which these conclusions are based comes in the form of the cosmic microwave background radiation ($CMBR$), which is the faint glow of radiation that permeates the universe. The $CMBR$ is almost perfectly uniform which means that no matter where you look in the sky the intensity of the $CMBR$ is (essentially) the same. To explain the $CMBR$, scientists assume that the unimaginably hot and dense early universe consisted almost entirely of a plasma of hydrogen nuclei that produced vast amounts of electromagnetic radiation, meaning that the early universe glowed. The $CMBR$ is what is left of this radiation, it is a relic of that early universe. As the universe expanded it cooled but those photons continued to whiz around. Now that they have to fill a much larger universe individual photons have less energy, although the total energy remains the same! The current background temperature of the universe is $\sim 2.27\ K$, which corresponds to a radiation wavelength of $\sim 1.9\ mm$ (radiation in the microwave region); hence the name cosmic microwave background radiation.

After a billion years or so things began to heat up again literally (albeit locally). As in any randomly generated object the matter in the universe was not distributed in a perfectly uniform manner and as time passed this unevenness became more pronounced as the atoms began to be gravitationally attracted to each other. The more massive the initial aggregates the more matter was attracted to them. As the clumps of (primarily) hydrogen became denser the atoms banged into each other and these systems, protostars, began to heat up. At the same time the gravitational attraction resulting from the overall mass of the system caused the matter to condense into an even smaller volume and draw in more (mostly) hydrogen. As this matter condensed its temperature increased, as gravitational potential energy was converted into kinetic energy. At a temperature of $\sim 10,000,000 (10^7)\ K$ the atoms (which had lost their electrons again because of the higher temperature) began to undergo nuclear fusion. At this point we would probably call such an aggregate of matter a star. This process of hydrogen fusion produced a range of new types of nuclei. Hydrogen fusion, or hydrogen burning as it is sometimes called, is exemplified by reactions such as the formation of helium nuclei:

$$4^1\backslash(H^+ \rightarrow^4 \backslash(He^{2+} + 2e^+ + \text{energy}. \tag{3.1.2}$$

When four protons are fused together they produce one helium-4 nucleus, containing two protons and two neutrons, plus two positrons (e^+ – the antiparticle of the electron), and a great deal of energy. As the number of particles decreases ($4^1\backslash(H^+$ into 1^4He^{2+}), the volume decreases. Gravity produces an increase in the density of the star (fewer particles in a smaller volume). The star's core, where fusion occurs, gets smaller and smaller. The core does not usually collapse totally into a black hole, because the particles have a huge amount of kinetic energy, which keeps them in motion and moving on average away from one another.[5]

As the star's inner temperature reaches $\sim 108\ K$ there is enough kinetic energy available to drive other fusion reactions. For example three helium nuclei could fuse to form a carbon nuclei:

$$3^4He^{2+} \rightarrow {}^{12}C^{6+} + \text{lots of energy (note again, the result is fewer atoms)}. \tag{3.1.3}$$

If the star is massive enough, a further collapse of its core would increase temperatures so that carbon nuclei could fuse, leading to a wide range of new types of nuclei, including those of elements up to iron ($^{56}Fe^{26+}$) and nickel ($^{58}Ni^{28+}$), as well as many of the most common elements found in living systems, such as nitrogen (Ni^7), oxygen (O^8), sodium (Na^{11}), magnesium (Mg^{12}), phosphorus (P^{15}), sulfur (S^{16}), chlorine (Cl^{17}), potassium (K^{19}), calcium (Ca^{20}), manganese (Mn^{25}), cobalt (Co^{27}), copper (Cu^{29}), and zinc (Zn^{30}).

In some instances these nuclear reactions cause a rapid and catastrophic contraction of the star's core followed by a vast explosion called a supernova. Supernovae can be observed today, often by amateur astronomers, in part because seeing one is a matter of luck. They are characterized by a sudden burst of electromagnetic radiation, as the supernova expels most of its matter into interstellar dust clouds. The huge energies involved in such stellar explosions are required to produce the naturally occurring elements heavier than iron and nickel, up to and including Uranium (Ur^{82+}). The material from a supernova is ejected out into the interstellar regions, only to reform into new stars and planets and so begin the process all over. So the song is correct, many of the atoms in our bodies were produced by nuclear fusion reactions in the cores of stars that, at one point or another, must have blown up; we are literally stardust, except for the hydrogen formed before there were stars!

Looking at Stars

At this point you may still be unclear as to how we know all this. How can we know about processes and events that took place billions of years ago? Part of the answer lies in the fact that all the processes involved in the formation of new elements are still occurring today in the centers of stars. Our own Sun is an example of a fairly typical star; it is composed of ~ 74 (by mass) and ~ 92 (by volume) hydrogen, ~ 24 helium, and trace amounts of heavier elements. There are many other stars (billions) just like it. How do we know? Analysis of the emission spectra of the light emitted by the Sun or the light emitted from any other celestial object enables us to deduce which elements are present.[6] Similarly, we can deduce which elements and molecules are present in the clouds between stars by looking at which wavelengths of light are absorbed! Remember that emission/absorption spectra are a result of the interaction between the atoms of a particular element and electromagnetic radiation (light). They serve as a fingerprint of that element (or molecule). The spectrum of a star reveals which elements are present. No matter where an element is found in the universe it appears to have the same spectroscopic properties.

Astrophysicists have concluded that our Sun (Sol) is a third generation star, which means that the material in it has already been through two cycles of condensation and explosive redistribution. This conclusion is based on the fact that the Sun contains materials (heavy elements) that it could not have formed itself, and so must have been generated previously within larger and/or exploding stars. Various types of data indicate that the Sun and its planetary system were formed by the rapid collapse of a molecular (mostly hydrogen) cloud ~ 4.59 billion years ago. It is possible that this collapse was triggered by a shock wave from a nearby supernova. The gas condensed in response to gravitational attraction and the conservation of angular momentum; most of this gas (> 98) became the Sun, and the rest formed a flattened disc, known as a planetary nebulae. The planets were formed from this disc, with the small rocky/metallic planets closer to the Sun, gas giants further out, and remnants of the dust cloud distributed in the Oort cloud.[7] As we will see, living systems as we know them depend upon elements produced by second and third generation stars. This process of planet formation appears to be relatively common and more and more planetary systems are being discovered every year.[8]

Stars have a life cycle from birth to death; our Sun is currently about half way through this life cycle. There is not enough matter in the Sun for it to become a supernova, so when most of its hydrogen has undergone fusion, ~ 5 billion years from now, the Sun's core will collapse and helium fusion will begin. This will lead to the formation of heavier elements. At this point, scientists predict that the Sun's outer layer will expand and the Sun will be transformed into a red giant. Its radius will grow to be larger than the Earth's current orbit. That will be it for life on Earth, although humans are likely to become extinct much sooner than that. Eventually the Sun will lose its outer layers of gas and they may become a part of other stars elsewhere in the galaxy. The remaining core will shrink, grow hotter and hotter, and eventually form a white dwarf star. Over (a very long) time, the Sun will cool down, stop emitting light, and fade away.

? Questions

Questions to Answer

- How do the properties of isolated atoms or molecules give rise to the world we observe? Why are objects different colors, or have different melting points?
- Do isolated atoms/molecules exist in a state such as solid, liquid, or gas?
- Where do the atoms in your body come from? (Trace their origin back as far as you can.)
- How does the size of the universe influence the density of particles?
- How many protons, neutrons, and electrons does $^{4}\mathrm{He}$ have? How about $^{4}\mathrm{He}^{2+}$?
- Generate a graph that estimates the number of atoms in the universe as a function of time, beginning with the Big Bang and continuing up to the present day.
- Draw another graph to illustrate the number of elements in the universe as a function of time. Explain your reasoning behind both graphs.

Questions to Ponder

- Can an atom of one element change into an atom of another element?
- Is the number of atoms in the universe constant?
- How does the big bang theory constrain the time that life could have first arisen in the universe?