

3.2: Elements and Their Interactions

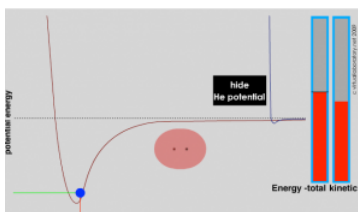
“From the 115 elements you can build a near infinity of molecules, of any type you need, to get all the structural and functional diversity you can ask for. There are at least 100,000 different molecules in the human body. Some 900 volatile aroma components have been found in wine. Chemistry is molecules. We are molecules. Chemistry is a truly anthropic science.”

– Roald Hoffman (1937) quoted by Natalie Angier in *The Canon*

By this point, you probably have some idea or mental image of the basic (low resolution) structure of atoms. We will therefore return to some questions left unanswered at the end of Chapter 1. Why is it that two hydrogen atoms form a strong stable (covalent) bond, a bond that requires temperatures above 5000 K to break, whereas two helium atoms and two hydrogen molecules have only a weak (London dispersion forces) attraction for each other that is broken at very low temperatures (4–20 K)? Because temperature is a measure of the kinetic energy present in the system we have to ask, what gives rise to this huge difference? Is there something fundamentally different going on in these situations? Other potentially troubling questions may also come to mind, in particular, how can pure samples of different elements be so different? Why is carbon either black (graphite) or transparent (diamond)? Why is gold shiny and yellow, while sulfur is dull and yellow? Why are most metals, but not gold or copper, shiny, solid, and colorless, while mercury is shiny, colorless, and liquid? Why are some elements more or less inert (such as gold, which does not tarnish) while others, such as iron (which rusts) and phosphorus (which bursts into flames) are highly reactive? To answer these questions will lead to an understanding of the basics of chemistry or how atoms interact with one another under various conditions. We will approach the answers in a step-by-step manner. In some cases where the answers are very complex (as is the case for why gold is yellow and mercury is a liquid), we will sketch out the answer but probably not provide a satisfying explanation. Luckily, most of the chemistry we need to address is not nearly so arcane!

Before we consider these and other questions, let us recap what we think we know about atoms and electrons. Most of an atom’s mass is localized in a very small region, the nucleus, surrounded by electrons that occupy most of the volume of the atom. Electrons have a number of strange properties because they are quantum mechanical particles. This means that under some conditions their behavior is best described by considering them as negatively charged particles, and under other conditions it is more helpful to consider them as waves; they are really both (and neither). Because of the uncertainty principle when we know the energy of each electron rather accurately we do not (and cannot) know where, exactly, a particular electron is at a particular moment in time. In fact, because all electrons are identical, if we had two electrons and turned away from them we could not tell which was which when we turned back. Within an atom each electron has a discrete energy and is characterized by its set of quantum numbers; no two electrons in an atom have the same set of quantum numbers. Perhaps you will be disappointed (or perhaps pleased) to know that a rigorous quantum mechanical (and relativistic) treatment of atoms and their interactions is beyond the scope of this book.^[9] That said, we can give a reasonable overview of how the behavior of atoms can be explained in terms of atomic and molecular electron orbitals. We will also indicate where our description is an over-simplification.

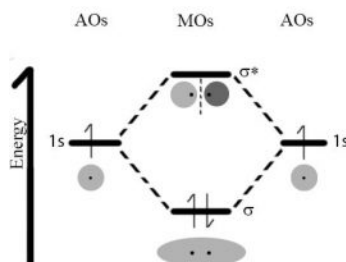
It is worth remembering that there are very few (if any) instances when we come across isolated atoms. Although we often describe matter as being composed of atoms, that is a bit of an abstraction; most atoms are stuck to other atoms by bonds and interactions. As mentioned previously, this leads to emergent properties that are quite distinct from those of the isolated atoms of which they are composed. It is the interactions between atoms and molecules that makes surfaces solid.



If isolated atoms are rare, the obvious question is, why are they rare? What determines when and how atoms interact? The answer is simple really and based on a principle we have already encountered (and that we will return to time and again): systems will adopt the lowest energy state accessible to them. The reason is that at the lowest accessible energy state, the forces of attraction and repulsion are equilibrated. It would take more energy to move the components of the system (that is atoms in molecules, or electrons in atoms) because the forces acting on them would increase. Interactions and bond formation lead to lower potential energy. Whether the bonded system is stable will then depend upon the strength of the interaction/bond and the forces that impact the molecule. For example, surrounding molecules/atoms with a range of kinetic energies may collide with the molecule. If this

kinetic energy of the impacting particle is larger than the interaction/bond energy, the collision can disrupt the interaction or break the bond(s) between them; if not, the interaction/bond will be stable. At the same time, there must be overarching principles governing which interactions occur and which do not; otherwise everything would clump together, which would be messy and not particularly interesting. These principles arise from the way electrons are organized in different types of atoms.

Thinking about the nature of the chemical bond



There is no single explanation that captures all the properties observed when atoms interact to form a bond.^[10] Instead we use a range of models of bonding. Now, what do we mean by model? Models are much more limited than theories, which have global application and can be proven wrong through observation and experimental data. Models are more like strategies that simplify working with and making predictions about complex systems. A model often applies to only very specific situations. For example the Bohr model of the atom applies only to hydrogen and then only under quite specific circumstances. We are going to consider a variety of bonding models, some of which you may already be familiar with, but it is important that you remember that different models are used depending upon which properties you want to predict and explain.

So back to our original dilemma, namely why is it that the interaction between two hydrogen atoms is so much stronger than that between two helium atoms? One useful model of bonding uses the idea that electrons can be described in terms of orbitals.^[11] Each orbital can contain a maximum of two electrons (with opposite spins). Recall that in an isolated atom, the electrons are described by atomic orbitals; therefore when in molecules, they are described by molecular orbitals (MOs). When atoms approach each other, the atomic orbitals containing their outermost electrons, known as the valence electrons, begin to interact. Because of the wavelike nature of the electron, these interactions can be either constructive or destructive. If they interact in a constructive manner, the interaction is stabilizing, which means that potential energy decreases and (if that energy is released into the surrounding system) the two atoms adopt a more stable configuration; they form a bond that holds them together. If the interaction is destructive, there is no stabilizing interaction. In the case of hydrogen each atom has a single (1s) orbital occupied by a single electron. As the atoms approach one another these 1s atomic orbitals interact to form two possible MOs: a lower energy, constructive or bonding MO, and a higher energy, destructive or anti-bonding MO. Notice that the bonding MOs, a so-called σ_{1s} (sigma) orbital, has electron density (that is a high probability that the electrons would be found there if we looked) between the two hydrogen nuclei. In the anti-bonding MO, known as σ^*_{1s} , the electrons are mostly not between the nuclei. One way to think about this is that in the bonding orbital the protons in the hydrogen nuclei are attracting both electrons (one from each atom) and it is this common attractive force between electrons and nuclei that holds the two hydrogen atoms together. In contrast in the anti-bonding orbital there is little electron density between the two nuclei and any electrons in that orbital are actually destabilizing the system by enhancing the repulsive interactions between the nuclei. (Can you provide a short reason why this would be the case?)

Just like an atomic orbital each MO, both bonding and anti-bonding, can hold two electrons. In the case of two approaching hydrogens there are only two electrons present in the system and the lowest energy state would have them both in the bonding orbital. Typically, both electrons in a H–H molecule are found in the lower energy (more stable) σ_{1s} bonding orbital. This arrangement of electrons is referred to as a covalent bond; this is the arrangement that requires temperatures of ~ 5000 K to break, which means it requires a lot of energy to break a covalent bond.

Now let us take a look at what happens when two helium atoms approach. Each He atom has two electrons in its 1s orbital. As the orbitals approach they interact and again produce two MOs, the bonding σ_{1s} orbital and the anti-bonding σ^*_{1s} orbital. The σ^*_{1s} MO has no electron density between the two He nuclei and has considerably higher energy than the atomic orbitals of the isolated atoms. Since there are 4 electrons present in the two He atoms and only two can occupy the σ_{1s} bonding orbital; the other two have to go into the σ^*_{1s} anti-bonding orbital. The end result is that the decrease in potential energy (increased stability) associated with occupying the bonding orbital is more than off-set by the increased energy associated with occupying the σ^*_{1s} anti-bonding orbital. So, the end result is no overall stabilization and no decrease in energy associated with bond formation; no

covalent bond is formed. The only interactions between helium atoms are the van der Waals interactions that occur between the two atoms that depend exclusively on London dispersion forces, as discussed in Chapter 1.

The interaction between two helium atoms is very similar to that between two H_2 molecules. There is no possibility of stabilizing MOs forming and, as in the case of the helium atoms, hydrogen molecules ($H-H$ or H_2) interact exclusively through London dispersion forces (LDFs). The LDFs will be somewhat stronger between hydrogen molecules than between helium atoms, however, because there is a larger surface area over which they can interact.

The idea that—all other things being equal—a system will move to the lowest accessible energy state (losing the excess energy to their surroundings), where the forces of attraction and repulsion are equal, is applicable to a wide range of situations. The potential energy of the system falls as the distance between the atoms decreases until the system reaches a balance between the stabilizing interaction of bond formation and the destabilizing repulsion of the two nuclei. The energy difference between the separated atoms and the minimum energy is called the bond energy and this amount of energy must be supplied to the system to break the two atoms apart again. The distance between the nuclei when the bond energy is at its minimum is the bond length. When a bond is formed between two atoms energy is always released to the surroundings and the new material is always more stable than the two separate atoms. Because energy is conserved a bond cannot form unless this bond energy is transferred from the interacting atoms to the rest of the system (usually by colliding with other atoms and transferring energy). Making bonds is always exothermic (meaning that energy is released not absorbed). This implies that energy (from the surrounding system) is always needed to break a bond. To break a bond energy must be transferred from the surroundings. Bond breaking is endothermic meaning it requires energy from the external world, normally delivered through collisions with other molecules.

When we consider more complex chemical reactions we will find that these generally involve both bond breaking and bond formation; the overall reaction will be exothermic when more energy is released from bond formation than is used for bond breaking. Conversely a reaction is endothermic (that is, uses energy) if more energy is required to break bonds than is released in bond formation. The important point is that we have to consider the system as a whole, including all of the bonds formed and broken. We will come back to this topic (in much greater depth) in Chapters 5 and 7.

Discrete Versus Continuous Molecules

Having considered the bonding situation with hydrogen and helium, the simplest two elements, we can now move on to consider other elements and the types of molecules that they form. In this discussion, we begin with molecules made up of a single type of atom. More complex molecules made of atoms of multiple elements will be considered in the next and subsequent chapters. As the number of protons in the nucleus of an element's atoms increases, from 1 in hydrogen to 10 in neon, we find dramatic changes in physical properties that correlate with whether the elemental form is discrete or continuous. The discrete forms are either monoatomic—meaning that they exist as separate atoms (such as He and Ne) with no covalent bonds between them (although they do interact via van der Waals interactions)—or diatomic molecules (such as H_2 , N_2 , O_2 , and F_2), meaning that they exist as molecules that have only two atoms. The elements that exist as small molecules have very low melting points (the temperatures at which they change from a solid to a liquid) and low boiling points (the temperatures at which they change from a liquid to a gas). But don't confuse these phase transitions with the breaking of a diatomic molecule into separate atoms. Phase transitions, which we will discuss in greater detail later, involve disruption of interactions **between** molecules (intermolecular forces), such as London dispersion forces, rather than interactions **within** molecules, that is, covalent bonds.

Table 3.2.1 The First 10 Elements in Their Naturally Occurring Elemental State

Elemental Form	H_2 molecular	He atomic	Li continuous	Be continuous	B continuous	C continuous	N_2 molecular	O_2 molecular	F_2 molecular	Ne atomic
Melting Point	13.81 K	0.00 K	453.65 K	1560 K	2348 K	3823 K	63.15 K	54.36 K	53.53 K	24.56 K
Boiling Point	20.28 K	4.22 K	1615 K	2744 K	4273 K	4098 K	77.36 K	90.20 K	85.03 K	27.07 K
Bp-Mp (*)	6.47 K	3.27 K	1161 K	1184 K	1925 K	275 K	14.21 K	35.84 K	31.5 K	2.51 K

Elemental Form	H ₂ molecular	He atomic	Li continuous	Be continuous	B continuous	C continuous	N ₂ molecular	O ₂ molecular	F ₂ molecular	Ne atomic
Name	hydrogen	helium	Lithium	beryllium	boron	carbon	nitrogen	oxygen	fluorine	neon

* boiling point (Bp) minus melting point (Mp).

In contrast to the elements that form discrete molecules, the atoms of the other elements we are considering (that is Li, Be, B, C) interact with one another in a continuous manner. Rather than forming discrete molecules, these elements can form ensembles of atoms in which the number of atoms can range from the small (a few billion) to the astronomical (very, very large). Whether the materials are at the nano- or the macroscopic levels, the atoms in these ensembles are held together by bonds that are very difficult to break, like the bond in H – H. That is, a lot of energy must be put into the system to separate the component atoms. However, unlike hydrogen, the atoms that form these structures must form bonds with more than one other atom.

A consequence of this difference in organization is a dramatic increase in both the melting and boiling points compared to atomic (He, Ne) and molecular (H₂, N₂, O₂, and F₂) species (Table 3.2.1). The reason is that when a substance changes from solid to liquid (at the melting point) the component particles have to be able to move relative to one another. When the substance changes from a liquid to a gas (at the boiling point) the particles have to separate entirely. Consequently the magnitude of the melting and boiling points gives us a relative estimate of how strongly the particles are held together in the solid and liquid states. As we have already seen temperature is a measure of the average kinetic energy of the molecules in a system. For elements that exist as discrete atoms or molecules the only forces that are holding these **particles** together are London dispersion forces, which are relatively weak compared to covalent bonds. In contrast, the elements that exist as extensive networks of atoms joined by bonds require much more energy to break as the material goes from solid to liquid to gas.

? Questions

Questions to ponder

- Are all bonds the same?
- What factors might influence bond strength?
- Why are the properties of atoms and molecules different?

Questions to Answer

- Where are the electrons in H₂ when the temperature is greater than 5000 K?
- What would happen if you could form a He – He system with 3 electrons (instead of 4)?
- What would a molecular-level picture of H₂ (g) look like?
- What would a molecular-level picture of H (g) look like?
- Where does the energy to break a bond come from?
- Where does the energy released upon bond formation go?
- The melting point of molecular hydrogen (H₂) is ~ 14 K (–259° C). Draw a molecular level picture of what molecular hydrogen looks like below this temperature (as a solid). Why are the molecules of hydrogen sticking together?
- The boiling point of molecular hydrogen (H₂) is ~ 20 K (–253° C). Draw a molecular level picture of what molecular hydrogen looks like above this temperature (as a gas).
- Molecular hydrogen dissociates at high temperatures (> 6000 K). Draw a picture of what you imagine this might look like. Why do you think it takes such a high temperature to bring about this change?

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