1.7: Interactions Between Atoms and Molecules

At this point we have arrived at a relatively simple model of the atom. Do not to worry, we will move to more complex and realistic models in the next chapter. In this simple model the atom has a very small but heavy nucleus that contains both protons and neutrons. As we talk about biology now and again, take care not to confuse the nucleus of an atom with the nucleus of a cell; they are completely different – besides the fact that they are of very different sizes. For example, there is no barrier round the nucleus of an atom—an atomic nucleus is a clump of protons and neutrons. Surrounding the atomic nucleus are electrons, in the same number as there are protons. The atom has no net electrical charge since the number of electrons is equal to the number of protons.

Where the electrons actually are in an atom, however, is a trickier question to answer, because of quantum mechanical considerations, specifically the Heisenberg uncertainty principle, which we will return to in the next chapter. For now we are going to assume the electrons are outside the nucleus and moving. We can think of them as if they were a cloud of electron density rather than particles whizzing around (don't worry we will provide evidence for this model soon). This simple model captures important features and enables us to begin to consider how atoms interact with one another to form molecules and how those molecules can be rearranged—real chemistry!

There are four fundamental forces that we know about at the moment: gravity, the electromagnetic force, the strong nuclear force, and the weak nuclear force. For now we can largely ignore the strong nuclear force that is involved in holding the nucleus together: .it is an attractive force between neutrons and protons and is the strongest of all known forces in the universe, ~ 137 times stronger than the electromagnetic force. The strong nuclear force, acts at very short ranges, $\sim 10^{-15}$ m, or about the diameter of the nucleus. The other force involved in nuclear behavior, the weak force, plays a role in nuclear stability, specifically the stability of neutrons, but it has an even shorter range of action (10^{-18} m). Because the nucleus is much smaller than the atom itself we can (and will) ignore the weak and strong nuclear forces when we consider chemical interactions. The force we are probably most familiar with is gravity, which is the weakest force, more than 10^{-37} times weaker than the electromagnetic force, and we can ignore it from the perspective of chemistry, although it does have relevance for the biology of dinosaurs, elephants, whales, and astronauts. The electromagnetic force is responsible for almost all the phenomena that we encounter in our everyday lives. While we remain grounded on the Earth because of the gravitational interaction between our body and the Earth, the fact that we don't fall through to the center of the earth is entirely due to electromagnetic interactions. One obvious feature of the world that we experience is that it is full of solid things—things that get in each other's way. If atoms and molecules did not interact with one another, one might expect to be able to walk through walls, given that atoms are mostly empty space, but clearly this is not the case. Similarly, your own body would not hold together if your atoms, and the molecules they form, failed to interact. As we will see, all atoms and molecules attract one another—a fact that follows directly from what we know about the structure of atoms and molecules.

? Questions

Questions to Ponder

- What would a modern diagram of an atom look like and what could it be used to explain?
- Why don't the protons within a nucleus repel one another?
- Why don't the electrons and protons attract each other and end up in the nucleus?
- How the electrons within an atom interact?

Questions for Later

- Can an atom have chemical and/or physical properties; if so, what are they?
- What are chemical and physical properties? Can you give some examples?
- What distinguishes one element from another?

Interactions Between Atoms: A Range of Effects

The attractions and repulsions between charged particles and magnets are both manifestations of the electromagnetic force. Our model of the interactions between atoms will involve only electric forces; that is, interactions between electrically charged particles, electrons and protons. In order to understand this we need to recall from physics that when charged particles come close to each other they interact. You probably recall that "like charges repel and unlike charges attract", and that this interaction, which is known as a Coulombic interaction, depends on the sizes and signs of the charges, and is inversely proportional to the square of the distance between them (this interaction can be modeled by the equation:

$$F=\alpha\frac{(q_1 x q_2)}{r^2}\text{ (Coulomb's Law)}. \tag{1.7.1}$$

where q_1 and q_2 are the charges on the particles and r is the distance between them. That is: there is a force of attraction (or repulsion if the two charges are of the same sign) that operates between any two charged particles. This mathematical description of the electromagnetic interaction is similar to the interaction due to gravity. That is, for a gravitational interaction there must be at least two particles (e.g. you and the Earth) and the force of the attraction depends on both masses, and is inversely proportional to the square of the distance between them:

$$F=\alpha\frac{(m_1 x m_2)}{r^2} \tag{1.7.2}$$

The difference between the two forces are:

a. gravitational interactions are much weaker than electromagnetic interactions and
b. gravity is solely an attractive interaction while electromagnetic interactions can be either attractive or repulsive.

Now, let us consider how atoms interact with one another. Taken as a whole, atoms are electrically neutral, but they are composed of discrete electrically charged particles. Moreover, their electrons behave as moving objects.[19] When averaged over time the probability of finding an electron is spread uniformly around an atom, the atom is neutral. At any one instant, however, there is a non-zero probability that the electrons are more on one side of the atom than the other. This results in momentary fluctuations in the charge density around the atom and leads to a momentary charge build up; for a instant one side of the atom is slightly positive ($delta+$) and the other side is slightly negative ($delta-$). This produces what is known as an instantaneous and transient electrical dipole – that is a charge separation. As one distorted atom nears another atom it affects the second atom's electron density distribution and leads to what is known as an "induced dipole". So, for example, if the slightly positive end of the atom is located next to another atom, it will attract the electron(s) in the other atom. This results in an overall attraction between the atoms that varies as $\frac{1}{r^6}$ – where r is the distance between the atoms. Note that this is different than the attraction between fully charged species, the Coulombic attraction, which varies as $\frac{1}{r^2}$. What does that mean in practical terms? Well, most importantly it means that the effects of the interaction will be felt only when the two atoms are quite close to one another.

As two atoms approach, they will be increasingly attracted to one another. But this attraction has its limit – when the atoms get close enough, the interactions between the negatively charged electrons (and positively charged nuclei) of each atom increase very rapidly, which leads to an overall repulsion,which will stop the two atoms approaching so closely.

A similar effect was in also seen in Rutherford's experiment. Recall that he accelerated positively charged alpha particles toward a sheet of gold atoms. As an alpha particle approaches a gold atom's nucleus, the positively (+2) charged alpha particle and the gold atom's positively (+79) nucleus begin to repel each other. If no other factors were involved, the repulsive force would approach infinity as the distance between the nuclei (r) approached 0. (You should be able to explain why.) But infinite forces are not something that happens in the macroscopic, atomic, or subatomic worlds, if only because the total energy in the universe is not infinite. As the distance between the alpha particle and gold nucleus approaches zero, the repulsive interaction grows strong enough to slow the incoming alpha particle and then push it away from the target particle. If the target particle is heavy compared to the incoming particle, as it was in Rutherford's experiments, the target, composed of gold atoms that weigh about 50 times as much as the alpha particle, will not move much while the incoming alpha particle will be reflected away. But, if the target and incoming particle are of similar mass, then both will be affected by the interaction and both will move. Interestingly, if the incoming particle had enough initial energy to get close enough (within $\sim 10^{-15}$ m) to the target nucleus, then the strong nuclear force of attraction would come into play and start to stabilize the system. The result would be the fusion of the two nuclei and the creation of a different element, a process that occurs only in very high-energy systems such as the center of stars or during a stellar explosion, a supernova. We return to this idea in Chapter 3.

? Questions

Questions to Answer

- How does the discovery that atoms have parts alter Dalton's atomic theory?

- What would the distribution of alpha particles, relative to the incident beam, look like if the positive nucleus took up the whole atom (sort of like the plum pudding)? What if it took up 50% of the atom?
- What does the distribution of alpha particles actually look like (recall that 1 in every 8000 particles were deflected)?

Forces and Energy: an overview.

We would like to take some time to help you think about the interactions (forces) between atoms and molecules, and how these interactions lead to energy changes. These energy changes are responsible for the formation of molecules, their reorganization through chemical reactions, and the macroscopic properties of chemical substances (i.e. everything). While you may have learned about forces and energy in your physics classes, most likely these concepts were not explicitly related to how things behave at the atomic-molecular level. We are going to begin with a discussion of the interactions and energy changes that result from the force of gravity, because these ideas are almost certainly something you are familiar with, certainly more familiar with than electromagnetic interactions – but the purpose of this section is to help you make the connections between what you already know (at the macroscopic level), and how these ideas are transferred to the molecular level, including similarities and differences. For example, Newton's Laws of Motion describe how objects behave when they come into contact, say when a baseball comes in contact with a bat. But often objects interact with one another at a distance. After the ball is hit, its movements are determined primarily by its gravitational interactions with all other objects in the Universe, although because of the nature of the gravitational interaction, by far the most important interaction is between the ball and the Earth (see below).

A force is an interaction between objects that causes a pull (attraction) or a push (repulsion) between those objects. When such an interaction occurs, there is a change in energy of the objects. As noted above, there are four fundamental forces: gravitational, electromagnetic, the strong and the weak nuclear forces. We will have more to say about the electromagnetic force that is relevant for understanding chemical interactions, that is how atoms and molecules behave. Many of the phenomena you are familiar with are based on electromagnetic forces. For example, electromagnetic forces stop the ball from going through the bat – or you from falling down to the center of the Earth.

Now let us consider what happens when you throw a ball straight up into the air. You apply a force to the ball (through the action of your muscles), and once it leaves your hand the only force acting on the ball is gravity (we are, of course, ignoring friction due to interactions with the molecules in the air). The ball, initially at rest, starts moving upward. Over time, you observe the velocity of the ball changes, as the ball slows, stops and falls back to earth. So what forces cause these changes? The answer is the force of gravity, which is a function of the masses of the ball and the Earth, which do not change over time, and the distance (r) between the Earth and the ball, which does. This gravitational force F, can be modeled by an equation that shows it is proportional to the product of the masses of the ball (M_1) and the Earth (M_2) divided by the square of the distance between the objects (r).[20]

In gravitational interactions, the force decreases as the distance between the objects increases (the decrease is proportional to $\frac{1}{r^2}$), which means the further away you get from the Earth the smaller is the attractive force between you and the Earth. If you get far enough away, and you are moving away from the Earth, the interaction will not be enough to keep you attracted to the Earth and you will continue to move away forever.

Of course, **why** objects with mass attract each other is a subject for physics – beyond the scope of this course.[21] What we can say is that the force is mediated by a gravitational field. Any object with mass will interact with other objects with mass through this field. The field can also be said to transfer energy through space between two (or more) objects. That is, the interaction leads to an energy change in the system of interacting objects. In chemistry we are concerned with both the forces that cause interactions and the energy changes that result.

How do forces influence energy?

If we take our macroscopic example of your throwing a ball upwards, we know that you transfer some energy to the ball. Of course this begs the question "what do we mean by energy?" and unfortunately we do not have an easy answer, in fact Richard Feynman once famously said "in physics we have no idea of what energy is". Physicists might say energy is the capacity to do work, and then define work as force times distance, which does not really get us anywhere, especially in chemistry where the notion of work is often not helpful. What we can say is that any changes are accompanied by energy changes, and that we can calculate or measure these energy changes.[22]

You may be familiar with what are often referred to as "forms of energy", such as mechanical, or elastic, or chemical, but at the most basic level all forms of energy we will be concerned with can be described either as kinetic energy, potential energy, or electromagnetic energy (e.g. light). Kinetic energy is often called the energy of motion ($\text{KE} = 1/2mv^2$, where m is the mass and v

the velocity of the object), and potential energy the energy of position, or stored energy (it is calculated in various ways as we will see). Changes between kinetic and potential forms of energy involve forces. The ball that you throw straight up and then comes down has changing amounts of kinetic energy (it changes as the velocity of the ball changes) and potential energy (which changes as the distance between the Earth and the ball changes.) As the ball rises, you can observe that the velocity of the ball decreases, and therefore the KE decreases. At the same time the PE increases since the distance between the Earth and ball is increasing. On the way down the opposite is true, the ball starts moving faster – the KE increases and the PE decreases. Recall the principle of the conservation of energy; after the ball leaves your hand, no energy is added or taken away as the ball is traveling, if one form of energy increases, the other must decrease.

Another important point about energy is that it is a property of a system, rather than of an object. Although it may be tempting to consider that a ball in motion has a certain amount of kinetic energy it is important to remember the frame of reference from which you are considering the ball. Certainly the ball's velocity is related to the KE, but that velocity depends upon where you are viewing the ball from. Usually (almost always) we consider the velocity from the point of view of an observer who is stationary, but if we changed the system we were considering, and viewed the ball while we were also moving, then the velocity of the ball would be different. This may seem quite an abstract point, but it is an important one.

Similarly it is quite tempting to say that the ball has potential energy, but in fact this is also not entirely accurate. It is more accurate – and more useful – to say that the **system of the ball and the Earth** has potential energy – again we are taking a systems perspective here. Unlike kinetic energy, the potential energy in a system also depends on the force that is acting on it, and that force is a function of the position of the objects that are interacting within the gravitational field. For example, a "frictionless" object traveling through a space free of fields (gravitational or otherwise) at a constant velocity has a constant kinetic energy, but no potential energy.

Potential energy (often called stored energy) or the energy of position, raises the question – where is the energy "stored"? A useful way to think about this is that for the example of the ball and the Earth, this energy is stored in the gravitational field. In this way we can accommodate the idea that the PE depends on the distance between the two interacting objects. It will also allow us to generate a more overarching concept of potential energy that will be useful in chemistry, as we extend these ideas to interactions of atoms and molecules. You might ask why then is it OK to say an object has kinetic energy (as long as you specify the frame of reference), and the difference here is that any object in motion can have energy associated with it (for example, you, an atom or a car), but potential energy must be associated with objects that are interacting via a field, be it gravitational or electromagnetic. That said, fields are everywhere – there is no place in the universe where there are no fields (although they can be balanced, leaving the net force zero). What is important here is that

i. you understand that objects interact,
ii. that these interactions cause a change in energy of the system, and
iii. that the interacting forces depend on the distance between the interacting objects (as well as other factors, such as mass, which are constant).

The electromagnetic force:

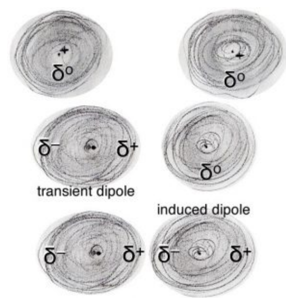
While gravitational interactions are, for all intents and purposes, irrelevant in chemistry (except to hold the beaker down on the lab bench!) they do provide a familiar example of the relationship between the kinetic and potential energies of a system that we can use to explore the electromagnetic interactions that are responsible for the behavior of atoms and molecules. There are some important similarities between gravitational and electromagnetic interactions; both act at a distance, both are mediated by fields, and both display the same relationship between force and distance. There are also important differences. In the context of chemistry, electromagnetic interactions are much stronger and while gravity is always attractive, electromagnetic interactions can be either attractive or repulsive.[23]

All electrically charged objects interact via electromagnetic forces. As we have already seen (and will to return to again) atoms and molecules are made up of charged particles (electrons and protons) and these produce unequal charge distributions that lead to the same kinds of interactions. The strength of these interactions between charged particles can be modeled using an equation, Coulomb's Law. You will note that its form is similar to Newton's Law of Gravitation. Instead of the masses of the two interacting objects, however, the electromagnetic force depends on the charges on the two particles (q_1 and q_2). The electromagnetic force typically acts over much shorter distances than gravitation, but is much stronger. It is the force that affects interactions of atoms and molecules.

As with the gravitational force as the charged particles get closer together, the interaction (whether attractive or repulsive) gets stronger. Just like gravity, the interaction between charged particles is mediated by a field, which transfers energy between interacting objects. We can identify (and calculate) the types of energy changes that are occurring as the particles interact. For example two oppositely charged particles are attracted to each other. As they approach one another, the force of attraction becomes stronger, the particles will move faster – and their kinetic energies increase. Given the fact that energy is conserved, the potential energy of the system of particles must decrease to a similar extent.[24] If, on the other hand the two charges are of the same sign, then the force between them is repulsive. So if two particles of the same charge are moving toward each other, this repulsive force will decrease their velocity (and kinetic energy), and increase their potential energy. As the distance between the particles decreases, the repulsion will eventually lead to the two particles moving away from one another.

Of course you may have noticed that there is a little problem with the equations that describe both gravitation and electromagnetic forces. If the forces change as r decreases, what happens as the distance between the interacting objects approaches zero? If we were to rely on the equations we have used so far, as r approaches 0, the force (whether repulsive or attractive) would approach infinity. Clearly something is wrong here since infinite forces are not possible (do you know why?). The ball is stopped by the surface of the Earth – it does not plummet to the center of the Earth, and charged particles do not merge into each other (or fly away at infinite speed). What is it that we are missing? Well, the problem lies in the idea that these equations are really dealing with idealized situations such as point charges or masses, rather than taking into account the fact that matter is made up of atoms, molecules and ions. When two atoms, or two molecules (or two particles made up of atoms or molecules) approach each other, they will eventually get close enough that the repulsions between like charges will become stronger than the attractive forces between unlike charges. As we will see, when two macroscopic objects appear to touch, they do not really – what stops them is the electron-electron repulsions of the atoms on the surface of the objects.[25] We will revisit all these ideas as we discuss how atoms and molecules interact at the atomic-molecular level, and how electrons behave (quantum mechanically).

Interacting Atoms: Forces, Energy Conservation and Conversion

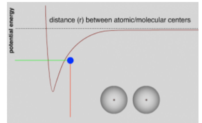


Let us step back, collect our thoughts, and reflect on the physics of the situation. First, remember that the total matter and energy of an isolated system are conserved; that is the first law of thermodynamics. As we mentioned above, while energy and matter can, under special circumstances, be interconverted, typically they remain distinct. That means in most systems the total amount of matter is conserved and the total amount of energy is conserved, and that these are separate.

So let us consider the situation of atoms or molecules in a gas. These atoms and molecules are moving randomly in a container, colliding with one another and the container's walls. We can think of the atoms/molecules as a population. Population thinking is useful for a number of phenomena, ranging from radioactive decay to biological evolution. For the population of atoms/molecules as a whole, there is an average speed and this average speed is a function of the temperature of the system.[26] If we were to look closely at the population of molecules, however, we would find that some molecules are moving very fast and some are moving very slowly; there is a distribution of speeds and velocities (speed + direction).

As two atoms/molecules approach each other they will feel the force of attraction caused by the electron density distortions, these are known as London dispersion forces, which we will abbreviate as LDFs. The effects of these LDFs depend on the strength of the interaction (that is the magnitude of the charges and the distance between them) and on the kinetic energies of the atoms and molecules. LDF are one of a number of intermolecular forces (IMFs), which we will consider later. LDFs are the basis of van der Waals interactions in biological systems.

To simplify things we are going to imagine a very simple system: assume for the moment that there are just two isolated atoms, atom_1 and atom_2. The atoms are at rest with respect to one another, but close enough that the LDF-based attractive interactions between them are significant. For this to occur they have to be quite close, since such attractive interactions decreases rapidly, as $\frac{1}{r^6}$ where r is the distance between the two atoms. At this point, the system, which we will define as the two atoms, has a certain amount of energy. The exact amount does not matter, but as long as these two atoms remain isolated, and do not interact with anything else, the energy will remain constant.



So what does all this have to do with atoms approaching one another? We can use the same kinds of reasoning to understand the changes in energy that occur as the atoms approach each other. Initially, the system will have a certain amount of energy (kinetic + potential). If the atoms are close enough to feel the effects of the attractive LDFs, they begin to move toward each other, think of a ball falling towards the Earth, and some of the potential energy associated with the atoms' initial state is converted into kinetic energy ($\mathrm{E_K} = 1/2mv^2$).

As they approach each other the LDFs grow stronger, the atoms are more strongly attracted to each other; the system's potential energy decreases and is converted into kinetic energy, the atoms move faster.[27] The total energy remains the same as long as there are no other atoms around. This continues until the atoms get close enough that repulsive interactions between the electrons become stronger and as they approach even more closely the repulsive interactions between the positively charged nuclei also come into play, causing the potential energy in the system to rise. As the atoms begin to slow down their kinetic energy is converted back into potential energy. They will eventually stop and then be repelled from one another. At this point potential energy will be converted back into kinetic energy. As they move away, however, repulsion will be replaced by attraction and they will slow; their kinetic energy will be converted back into potential energy.[28] With no other factors acting within the system, the two atoms will oscillate forever. In the graph showing potential energy versus the distance between the atoms, we see that the potential energy of the system reaches a minimum at some distance. Closer than that and the repulsive electromagnetic forces come into play, further away and the attractive electromagnetic forces (LDF's) are dominant. The distance between the two atoms is a function of the relative strengths of the attractive and repulsive interactions. However, even at the minimum, there is some potential energy in the system, stored in the electromagnetic field between the two atoms. At temperatures above absolute zero ($0\mathrm{K}$), the pair of atoms will also have kinetic energy – as they oscillate back and forth.

Here we have a core principle that we will return to time and again: a stabilizing interaction always lowers the potential energy of the system, and conversely a destabilizing interaction always raises the potential energy of the system. In an isolated system with only two atoms, this oscillation would continue forever because there is no way to change the energy of the system. This situation doesn't occur in real life because two-atom systems do not occur. For example, even in a gas, where the atoms are far apart, there are typically large numbers of atoms that have a range of speeds and kinetic energies present in the system. These atoms frequently collide and transfer energy between one another. Therefore, when two atoms collide and start to oscillate, some energy may be transferred to other particles by collisions. If this happens, a stable interaction can form between the two particles; they will "stick" together. If more particles approach, they can also become attracted, and if their extra energy is transferred by collisions, the particles can form a bigger and bigger clump.

As we discussed earlier, LDFs arise due to the fluctuations of electron density around nuclei and are a feature common to all atoms; all atoms/molecules attract one another in this manner. The distance between atoms/molecules where this attraction is greatest is known as the van der Waals radius of the atom/molecule. If atoms/molecules move closer to one another than their van der Waals radii they repel one another. The van der Waals radius of an atom is characteristic for each type of atom/element. As mentioned earlier, it is only under conditions of extreme temperature and pressure that the nuclei of two atoms can fuse together to form a new type of atom; such a nuclear/atomic fusion event results in the interconversion of matter into energy.[29]

? Questions

Questions to Answer

- What is potential energy? Can you provide an example?
- What is kinetic energy? Can you provide an example?
- At the atomic level, what do you think potential energy is?
- At the atomic level, what do you think kinetic energy is?
- Why does raising the temperature affect the speed of a gas molecule?

Questions to Ponder

- What is energy (have your ideas changed from before)?

Questions for Later:

- When we talk about potential energy of a system, what does system mean?
- Helium liquefies at around 4K. What makes the helium atoms stick together? (Why don't they turn into a gas?)
- Consider two atoms separated by 1 spatial unit versus 4 spatial units. How much weaker is the interaction between the more distant atoms? How does that compared to the behavior of simple charges (rather than atoms)?