“From General Chemistry To Organic Chemistry”

A collection of blog posts from MasterOrganicChemistry.com

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Gen Chem and Organic Chem: How Are They Different?

After finishing my freshman year of college, I spent my summer in the university town where I went to school. I had a menial telemarketing job along with some volunteer lab work on the side. Life was pretty easy: many of my friends had also decided to hang around, and there was lots of time for parties, TV, and evenings spent on patios. However, sometime around early July, I started getting this nagging, anxious feeling about the coming semester. I had heard so many second and third-hand stories about the Dreaded Orgo Beast and how it was going to start devouring my life come September. Out of fear, I decided to buy a used textbook off a friend and start going through it at a leisurely pace throughout the following two months.

Many years have passed since then, but fear of the Beast still lives. During the summer, I see these types of questions come up a lot:

1. Is Orgo Hard?
2. How is Organic Chemistry different from Gen Chem?
3. If I want to get ahead in organic chemistry over the summer, what should I do?

Let's focus on the second question for now.

Gen Chem and Organic Chem: How are they different?

As you are probably aware, organic chemistry is the study of carbon-containing compounds, but if you haven't taken the course yet, it won't be a very helpful distinction. Looking at it from a big-picture perspective, I'd say the one tremendous difference you'll find in organic chemistry is that *it is very qualitative*. Whereas gen chem has a large number of formulae and calculations to do, organic chemistry is notable in the *absence* of a lot of calculation work. You could easily write out all the formulae you would ever use in Org1/Org2 on the back of one hand.

Here are some of the types of questions you will typically ***not*** encounter in organic chemistry:

- calculating thermodynamic enthalpies/entropies
- electrochemical calculations
- calculating pH using the Henderson-~~Hasselhoff~~ Hasselbach equation
- Ideal gas law questions
- rate constant calculations
- calculating equilibrium constants.

Before you say, “Hooray!” too loudly, a word of warning: in organic chemistry your professors will assume that you *understand* this stuff, and you can calculate it *if you really have to*. They will expect that you understand these topics on a conceptual level. What does that mean? It means you should be able to intuitively understand things like:

- what happens to an equilibrium if the concentration of the product is changed
- the effect of changing the concentration of a reactant in a second-order reaction on the reaction rate
- how bonding interactions change with electronegativities
- what happens to the Gibbs free energy term of a reaction as the temperature is varied.
- how properties like electronegativity, electron affinity, ionic radius, etc. change as you go across the periodic table.
- And so on.

That’s what I mean by a *qualitative* understanding. Feel comfortable answering those types of questions? If yes, you’re probably set. If not, here’s the plan at “Master Organic Chemistry” for the next few weeks.

“How Gen Chem ties into O-Chem”

There are really six main areas in general chemistry that come back again in organic chemistry. Over the next while I’ll be focusing each of these six topics in turn, and demonstrating how the concepts you learned in Gen Chem will become relevant to what you’re going to learn in Organic Chem come this fall.[*Edit: I’ll be doing a post in this series every Monday for the next 6-8 weeks]*

1. Atomic properties
2. Bonding
3. Thermodynamics.
4. Kinetics.
5. Acids and bases.
6. Equilibria.

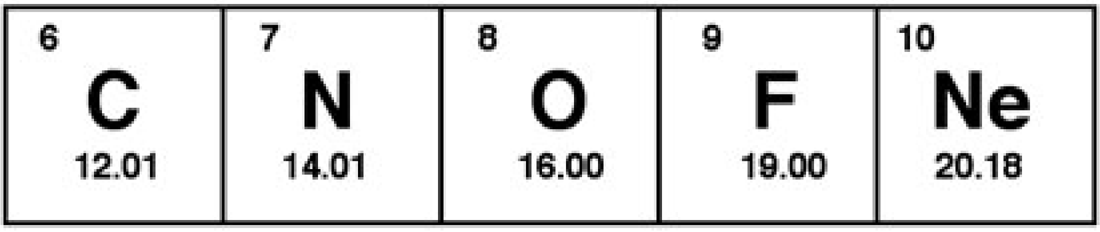
Topics such as electrochemistry, ideal gases, molality, phase diagrams and so forth don’t really make much of an appearance in Org1/Org2. Which isn’t to say they aren’t important to organic chemistry – they can be - they just don’t come up much in the course.

How General Chemistry Relates to Organic Chemistry, Part 1 – The Atom

"If, in some cataclysm, all scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or atomic fact, or whatever you wish to call it) that all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence you will see an enormous amount of information about the world, if just a little imagination and thinking are applied."

-Richard Feynman, *The Feynman Lectures in Physics*

More than Newton's apple, or Einstein's E=mc^2, or even Watson and Crick's double helix, Dimitri Mendeleyev's compilation of the periodic table has my vote as the most thrilling scientific insight of all time. As was wonderfully detailed in the BBC series "Chemistry – a Volatile History", Mendeleyev was the first to make the connection between the masses of the elements and their properties in the periodic, tabular format we are familiar with today. It had its share of omissions – the noble gases, for one – but for the first time, all of the building blocks of the universe were laid out in a fashion that was not only logical but made predictions about the properties of unknown elements.



6	7	8	9	10
C	N	O	F	Ne
12.01	14.01	16.00	19.00	20.18

One of the amazing things about chemistry is how drastic the effect of changing the atomic number can be on the behavior of the elements. Consider:

- Carbon – commonly encountered as soot, or charcoal, which I had to deal with this weekend when I cleaned the barbeque we used for Thursday's Canada Day party.
- Nitrogen – the major component of our atmosphere, litres of which pass every minute through our bodies without leaving a trace.
- Oxygen – the lifeblood of fires and human metabolism, without which our lives would be impossible.
- Fluorine – the Tiger of Chemistry, so incredibly dangerous it mauled a large number of 19th century chemists who first tried to isolate it (and as a gas, is on the shortlist of about six chemicals you need special permission to work with at MIT).

- Neon – the second-lightest of the noble gases. A (small) part of our atmosphere, we have been breathing neon for millenia but discovered it barely a century ago.

The properties of these elements are so different, it is hard to believe that they each represent successive additions of a single proton to the nucleus of an atom. Yet they do.

The components of the atom

- Protons – carry a positive charge.
- Neutrons – the same mass as the proton, but neutral. Do not carry a charge.

Together, protons and neutrons are called nucleons, since they are present in the nucleus of atoms.

Then, on the periphery of the atom – for an atom is mostly empty space, are the electrons. Small particles – 1/1840 of the mass of the nucleons, they carry a negative charge.

Opposite charges attract, like charges repel. So under normal circumstances, an atom is neutral. When an atom carries a charge, it is called an ion. A positively charged ion (protons outnumber electrons) is called a cation, and a negatively charged ion (electrons outnumber protons) is called an anion. It's got an extra "n" in there for negative – that's how I always remembered it.

Everything you need to know about nuclei in organic chemistry

The defining property of an element is the number of protons, or the **atomic number**. Hydrogen has one proton and one electron. If you remove the electron, it's still hydrogen, although this case we call it the hydrogen cation, hydrogen ion, or, more commonly just "proton". Carbon has six protons. Nitrogen seven. The naturally occurirng elements go up to 92, but the elements up to 118 have been made and studied.

- If you keep the number of protons and electrons the same, but change the number of neutrons, you have what we refer to as an **isotope. Isotopes have the same atomic number but different atomic weight.** Deuterium (D) is the isotope of hydrogen with a proton and one neutron, for an atomic mass of 2. Tritium (T) is the isotope of hydrogen with two neutrons, for an atomic mass of 3. Tritium is radioactive – the nucleus is unstable – it slowly decays, with a half-life of about 10 years. Isotopes have (practically) identical chemical properties and for the purposes of sophomore organic chemistry you can treat them as if they behave exactly the same. If you go on in organic chemistry you learn that there are very subtle (and useful!) chemical differences between them, but I wouldn't worry about that at this point. (FYI – this difference in behavior is what helped bust Floyd Landis, to give a prominent example).

- **We define a *mole* as the amount of substance that contains as many "elementary entities" (e.g. atoms, molecules, electrons, ions) as there are atoms in 12 grams of carbon-12.** This is a big number: 6.02 x 10^23 to be exact.
- **The *atomic weight* is the weight of 1 mole of a naturally occuring sample of an element.** For instance since the natural abundance of carbon-13 is about 1.1% relative to carbon-12, when we take 6.02 x 10 ^23 atoms of naturally occuring elemental carbon, we get a weight of 12.011 g.
- **Nuclei have a property called *spin*, which becomes important when they are put in a magnetic field.** This is the basis for a useful spectroscopic technique called *nuclear magnetic resonance* which you will learn about later. The explanation for this phenomena are more in the realm of nuclear physics, so we tend to gloss over them.

In organic chemistry, nuclei are not where the action is. We tend to take the nucleus for granted. It doesn't really change very much. *The real action is in the electrons*.

As we shall see, in chemistry (especially organic chemistry), **the study of chemistry is mostly about the study of how electrons flow between atoms.** If economics is about following the flow of currencies, chemistry is largely about the flow of electrons.

From General Chemistry To Organic Chemistry, Part 2 : Electrons and Orbitals

An atom is (a little bit) like an Indian bus.

This is how they work.

You get in and find an empty seat. The seats fill up.

Then people stand in the aisle. The aisle fills up.

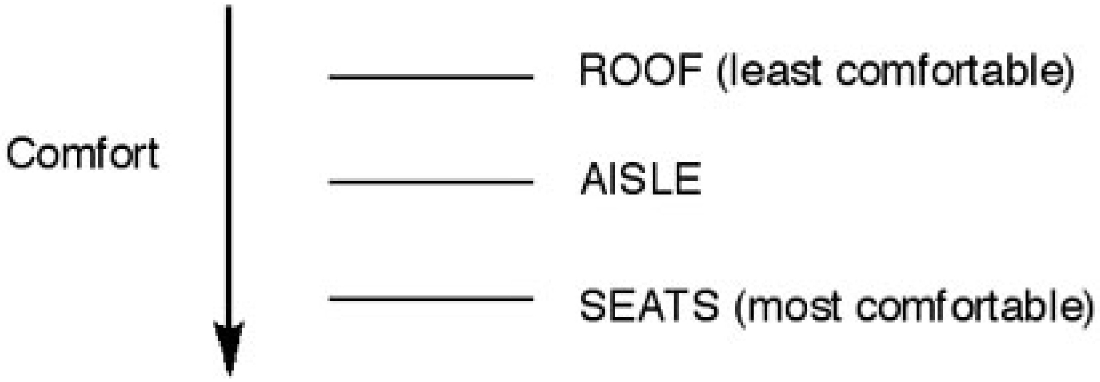
Then people get on the roof. The roof fills up. (Or not).

Then you're ready to go.

The seats are the most comfortable place to ride. That's why they fill up first. Ever been on a bus where everyone is standing in the aisle and nobody is sitting in the seats? Of course not. We're far too lazy to allow that to happen.

Let's say the bus stops at a village and someone leaves their seat to get off. Another person from the aisle will immediately take their place. Then there will be room for someone to go from the roof to the aisle. Then there will be room on the roof for a passenger from the village to get on. [yes, I can understand that maybe the roof could be more comfortable than the aisle in a hot crowded bus. Bear with me.]

Maybe we can draw a comfort diagram here.



If you look around you'll see lots of examples of this behavior. Queues. Seating arrangements in the living room at Super Bowl parties. Open-admission concerts. **Whenever a preferred place vacates, there is a rush to fill it.**

Electrons in an atom are just like passengers in a bus: they each need their **own** seat, and the seats fill up in a very specific order. The "one butt per seat" principle is in effect – just as you can't have 2/3, 0.17 or another fraction of a human, you can't have a fraction of an electron either. This is what we mean by **quantization**. The fact that they fill in a specific order is called the aufbau principle or building-up principle.

The "seats" for the electrons are areas of space we call orbitals. Orbitals are regions of space which represent 3-dimensional graphs of an electron's likely location. Whereas seats correspond to the shape of the human form, the shapes of orbitals are described by an equation developed in the 1920□s by Erwin Schrödinger that we call the Schrödinger wave equation. (Schrödinger figured out that the energies of electrons can be calculated quite effectively by treating them as waves).

If you take upper level chemistry courses, you learn how to play around with the Schrödinger wave equation. If not, here's the boiled down version.

Just as people seek the most comfortable seat on a bus, electrons seek the orbital that is closest to the nucleus – where the force of attraction between the positively charged nucleus and the negatively charged electron is greatest.

- Electrons behave as both particles and waves. Treating electrons as waves, orbitals are shapes that describe areas of space which allow for constructive wave overlap. [note - orbitals are the areas where there's a 95% probability of finding the electron]
- Every electron on an atom has a unique "identification code", or quantum number. [Triva: this property that the quantum numbers not be the same is a general property of a class of particles called fermions, to which electrons belong; these are distinguished from bosons, which can occupy the same quantum states (photons are a prominent example, but you may have heard of the Higgs boson).] The four

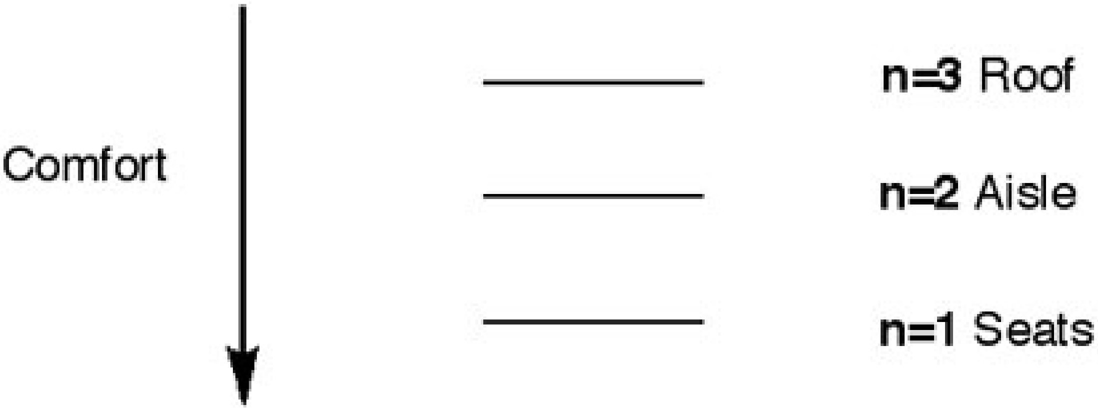
quantum numbers are:

- the principal quantum number n. This defines the energy level of the electron which is ultimately a reflection of how close it is to the nucleus. This also defines the number of “nodes” (areas of zero electron density) in an orbital. If we go back to our bus example, a rough analogy would be n=1 (seats), n=2 (aisle), n=3 (roof). As we increase the number we are decreasing the overall comfort level.
- The azimuthal quantum number *l*. This defines the shape of the orbital, and it ranges from 0 to (n-1).
- The magnetic quantum number *m*. This defines the number of different orientations of a given shape, and is defined by (-l, 0, +l).
- The spin quantum number *s*, which can be either +1/2 or –1/2.

These are the only values that provide solutions for the Schrodinger wave equation.

So for n=1, we get the quantum numbers, n=1, l=0, m = 0, and spin = +1/2 or –1/2 or more succinctly, [1 0 0 +1/2] and [1 0 0 –1/2]

That’s it. Two electrons. If we want to add more electrons we have to increase n. This is like filling up the seats on our bus and then adding the next group of passengers to the aisle.



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The next set of electron “passengers” have to go into the aisle, where n=2.

For n = 2, *l*=0, we get 2 0 0 +1/2 and 2 0 0 –1/2 for a total of two electrons.

When n=2 we can also let *l* = 1. Watch this:

[2 1 1 +1/2]

[2 1 1 – 1/2]

[2 1 0 +1/2]

[2 1 0 –1/2]

[2 1 –1 +1/2]

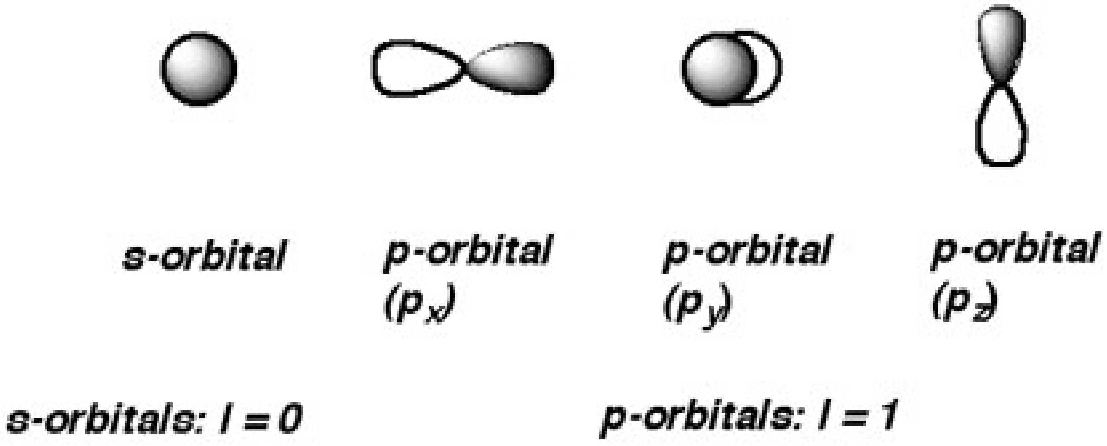
[2 1 –1 –1/2].

So for n=2 we have a total of 8 electrons: 2 for $l=0$, and 6 for $l=1$. If we want to add more electrons, we have to increase n again (to 3) which is like filling the aisle of our bus and sending the next group of passengers up to the roof.

Let's stop here for a second. the different numbers $l=0$ and $l=1$ correspond to different shapes of orbitals. In practice we have names for them. They are the S and the P orbitals.

s orbitals look like spheres. How do we know this? From the wave equation. The fact that m=0 is a clue. It means there is only one orientation possible across all the axes, which can only be possible for a sphere.

p orbitals look like teardrops. Again, we know this from the wave equation. What's interesting here is that we can have 3 different values for m. In practice what this means is that there are 3 different ways to orient the orbitals – along the three different axes x, y, and z.



In Org 1 and Org 2 we will deal exclusively with s and p orbitals. The shapes have tremendous consequences for chemical bonding, as we shall soon see.

What about the higher levels? There are also different shapes of orbitals for $l=3$ and $l=4$. For $l=3$, these are called the d orbitals, found in the transition metal series, and there are 5 different orientations of these orbitals (m=2,1,0,-1,-2). For $l=4$, there are the f orbitals, which are found in the lanthanides and actinides, and there are 7 different orientations of these orbitals.

If you take upper year courses you'll learn more about the d orbital series, since transition metals have many important applications in organic chemsitry. Chemistry of the d orbitals is pretty fascinating. In contrast, the chemistry of atoms involving the f-block tends to be pretty similar, since at this point the electrons are really far apart from the nucleus and thus are far less differentiated. That's why the lanthanides are often found as mixtures – often the trouble is separating their minerals from each other.

The higher orbitals than that (g, h, etc.) dont really appear in chemistry because the very heavy nuclei you'd need (>120) are extremely unstable. Someone has come up with an extended periodic table which incorporates g-block elements. Beautiful! – but more of theoretical rather than practical interest. Compare it to our Indian bus – you could keep adding platforms on top of the bus to fit successive levels of passengers, but there comes a point where the whole thing is just going to collapse under its own weight.

From General Chemistry to Organic Chemistry, Part 3 – Effective Nuclear Charge

If you've taken a physics course, you've probably covered the thrilling (to some) topic of electrostatics. There's a basic formula which allows you to calculate the force between two point charges. We call this relationship Coulomb's Law.

$$F = k_e \frac{q_1 q_2}{r^2}$$

For our purposes we're not really interested in quantifying the magnitude of the forces. This is the point where you can make fun of organic chemists for not liking math. I prefer to think of it as that we're more interested in understanding how different variables are *related* to each other. So let's boil it down a little bit and then go into detail.We'll call the first charge q1 the electron charge. This is always going to be –1. The second component q2 is the **nuclear charge.** This will vary with the number of protons in the nucleus, as we shall see. Finally, we have r, the distance between them. Finally, we'll get rid of the equals sign and the constant to highlight the **proportional** nature of these relationships.

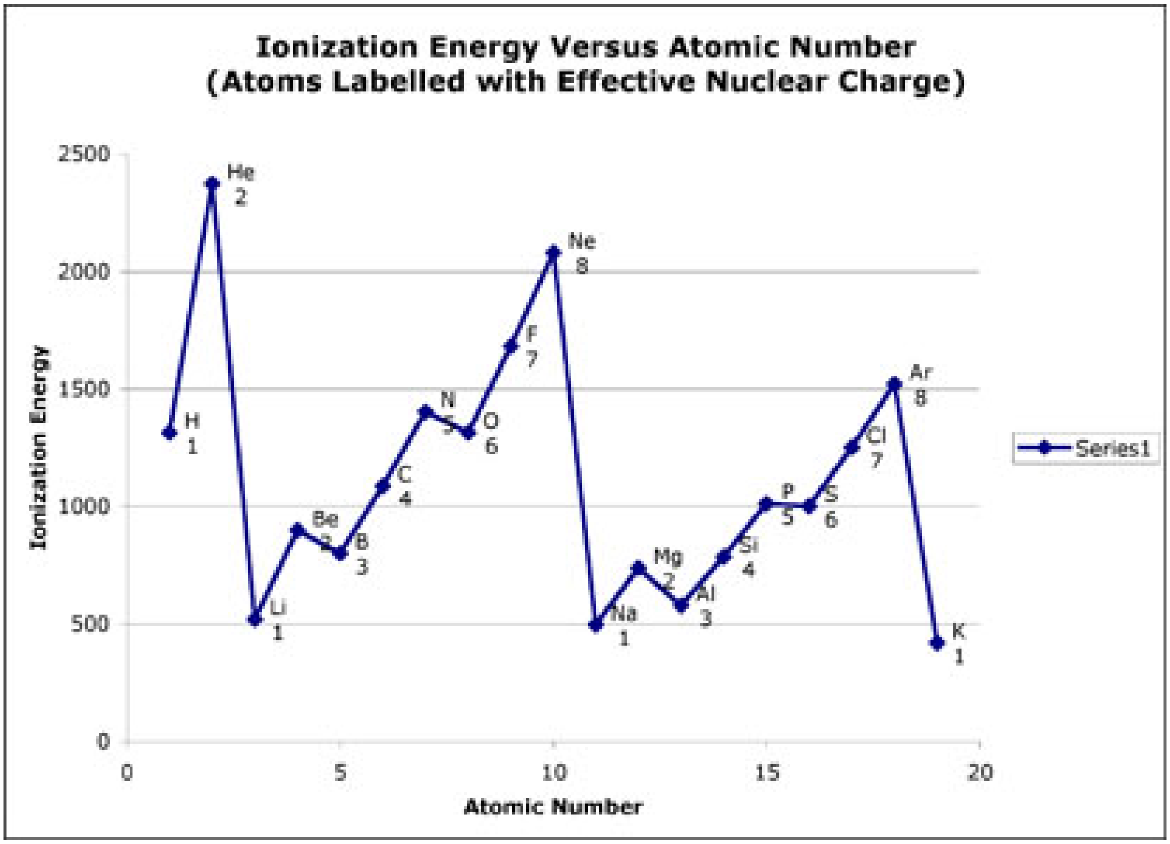
$$\text{Force} \propto \frac{[\text{Charge of electron}]\ [\text{Nuclear Charge}]}{[\text{distance}]^2}$$

One thing to note – *the signs are opposite, so we'll get a negative number, which implies an attractive force*. If the charges were the same, the force would be the same but act in the opposite direction (i.e. repulsion). Secondly, while it's true that the electrons are also going to repel each other, it's relatively small for our purposes and we're going to ignore it.

Two observations:

1) the force falls off in proportion to the square of the distance. So in our example, as the electron moves twice as far away from the nucleus, the force will be 1/4 as great. Remember that electrons can't just go *anywhere* – their positions are determined by the orbitals. So as the orbitals fill up, the interaction between the valence electrons (the highest energy electrons) and the nucleus is going to be less.

2) Since the electronic charge is constant, the magnitude of the interaction is going to be extremely dependent on the nuclear charge. How do we calculate the nuclear charge? Let's look at sodium. The valence electron in sodium is in the 3s orbital. The atomic number of sodium is 11, meaning it has 11 protons in the nucleus. So naïvely we might assign +11 as the nuclear charge. This doesn't make much sense though. If you look at the chart of ionization energies versus atomic number, they have a periodic relationship, so something more complicated is going on.



What's actually going on is that the lower energy electrons in the filled shells are shielding the nuclear charge. So to get a better picture of the true force acting on the electron, we have to account for that. We call this the **effective nuclear charge, or Zeff.**

If we naïvely ignore the repulsive effects of the electrons on each other [and also ignore the howls of outrage from the theoretical chemists as we do so], we can come up with a rough value for the effective nuclear charge as follows:

Z_{eff} = atomic number – atomic number of the preceding noble gas.

Using this, we get Z_{eff} for (Na) = 11 – 10 [Ne] = 1

Using this formula, all the alkali metals have a Z_{eff} of +1, all the alkaline earths have a Z_{eff} of +2, the halogens are +7 and so on.

It is this number, the Z_{eff}, which has the largest impact on the personalities of each of the classes of atoms.

So based on our equation we can confidently make several important predictions

- **Ionization energy (the energy required to take one electron away) is going to <u>decrease</u> as we go <u>down</u> the periodic table, since we are increasing the distance**. This is most vividly demonstrated by the reactions of the <u>different alkali metals with water.</u>
- **Ionization energy is going to <u>increase</u> as we move <u>across</u> the periodic table,** since we're increasing Z_{eff}.
- **Atomic radius will increase as we go <u>down</u> the periodic table**, since the electrons will be less tightly held.
- **Zeff reaches a <u>maximum</u> at the noble gas configuration** ($Z_{eff} = 8$). With this electronic configuration, each electron feels the pull of 8 protons on it.

This is the deep reason for the octet rule. If we tried to add an extra electron to neon (which would have to go into the 3s orbital) the electron would feel a Z_{eff} of 0; we'd be putting it in an orbital where the attraction between the nucleus and the electron would be shielded by the intermediate electrons. Conversely, trying to remove an electron from neon is difficult becuase each electron feels the pull of eight protons on it, which is a very powerful electrostatic interaction.

This equation also goes a long way toward explaining the electronegativity of elements, Why is fluorine the most electronegative element? Because the electrons feel the highest effective nuclear charge (Z=7) and they are the closest to the nucleus (i.e. d is the smallest).

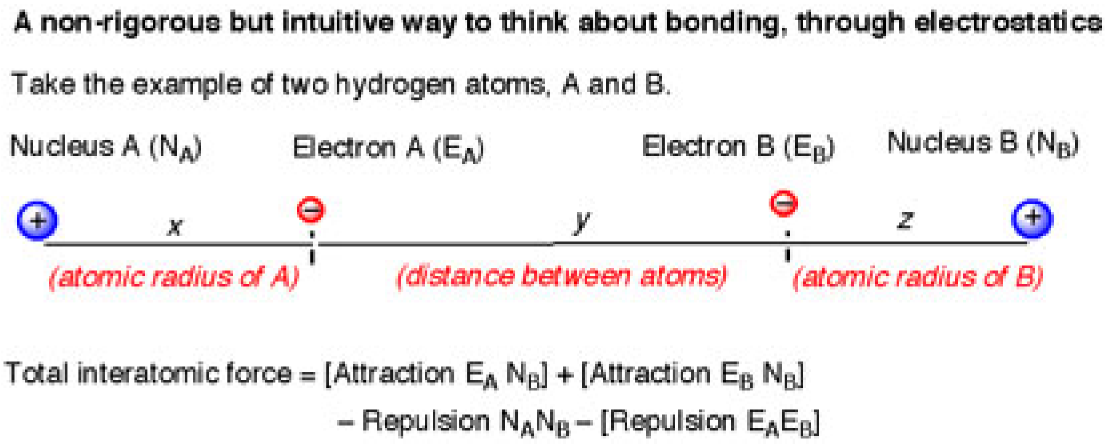
Electronegativity has a **huge** effect in organic chemistry, as we will see. So understanding how it is generated from the formula above will help to give you an intuitive feel for how it works.

From Gen Chem to Organic Chem, Part 4 – Chemical Bonding

Last time in this series we talked about the Coulomb equation and how important it is for understanding the electrostatic interaction between the electron and the nucleus.

Let's ask the next question. *What happens when you bring two atoms close together?*

Here's a diagram showing two hydrogen atoms HA and HB being brought into close proximity.



A non-rigorous but intuitive way to think about bonding, through electrostatics

Take the example of two hydrogen atoms, A and B.

Total interatomic force = [Attraction E_A N_B] + [Attraction E_B N_B]
– Repulsion N_AN_B – [Repulsion E_AE_B]

The opposite charges are going to attract and the like charges are going to repel. We're talking about interactions BETWEEN the two atoms here, so we're putting aside the Nucleus A/Electron A and Nucleus B/Electron B interactions. for a moment. With the Coulomb equation in mind, there's at least 4 things we need to think about:

1. the attraction between electron A and nucleus B
2. the attraction between electron B and nucleus A
3. the repulsion between electrons A and B
4. the repulsion between nuclei A and B.

If you think about it, the first two interactions are actually the same magnitude. So there are *two* attractive forces between the electrons in these positions between the nuclei. Opposing this attractive force is the repulsion between the two electrons. Overall, the attractive force between the electrons and the nuclei dominates the electron repulsion term, leading to the observation that the interaction energy increases as the intermolecular distance decreases.

So in a nutshell, the attractive force is inversely proportional to the distance. The closer they are, the stronger the attraction. The electrons are at the frontier of the atom and therefore they are closer to the other nucleus. Since the distance (x+y) is going to be shorter in the Coulomb equation than the internuclear distance (x+y+z), attraction will dominate at longer distances.

However, there's a catch. **When d gets small enough (i.e. when "y" in our equation**

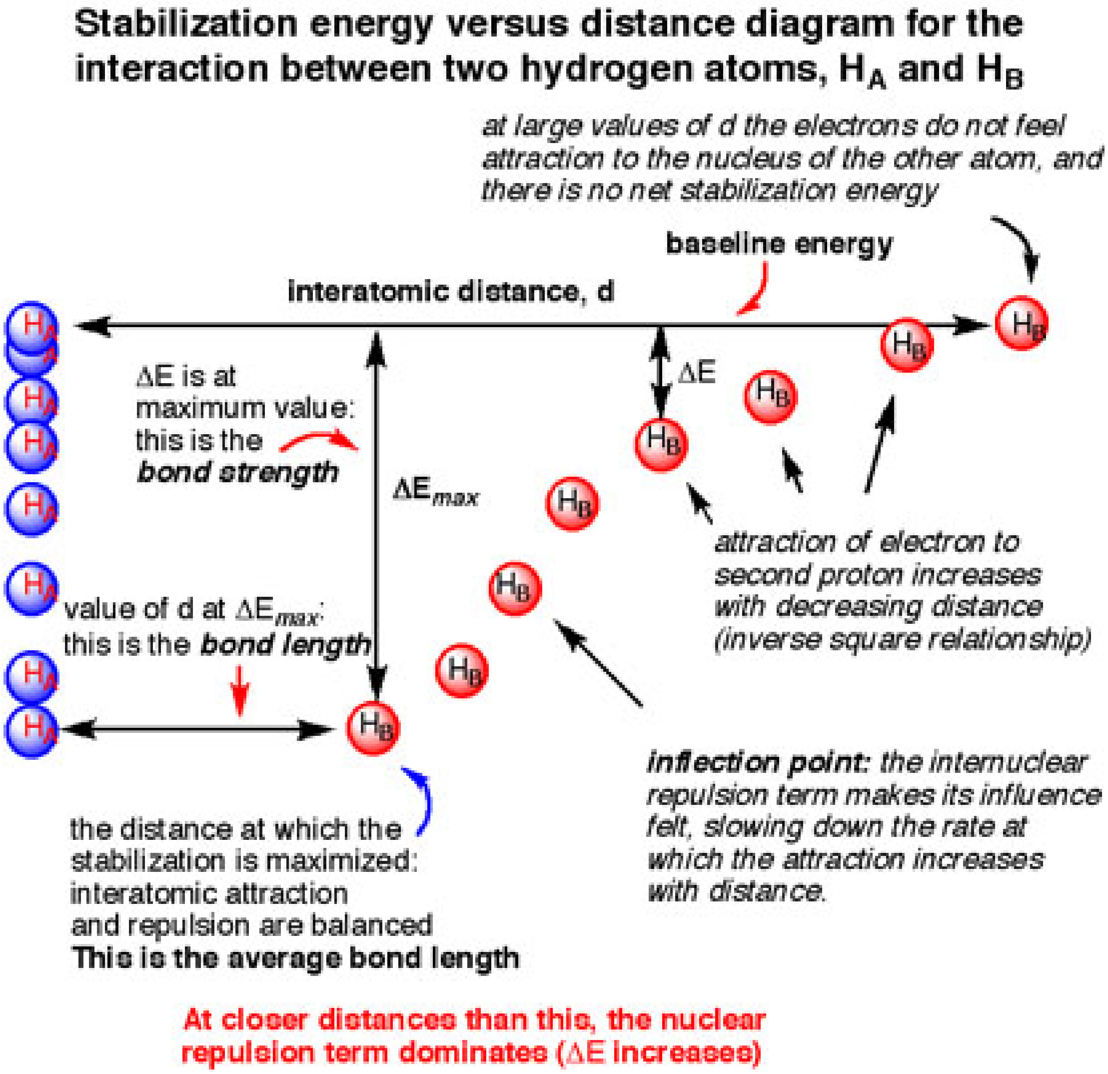
becomes small), the repulsion between the nuclei starts to come into play. See the inflection point in the graph below? As the atoms get closer together, the rate of change in interaction energy with distance begins to decrease, and eventually reaches a minimum. Eventually they meet a "sweet spot" where the two forces are in balance.

The name we give this "sweet spot" is the bond length.

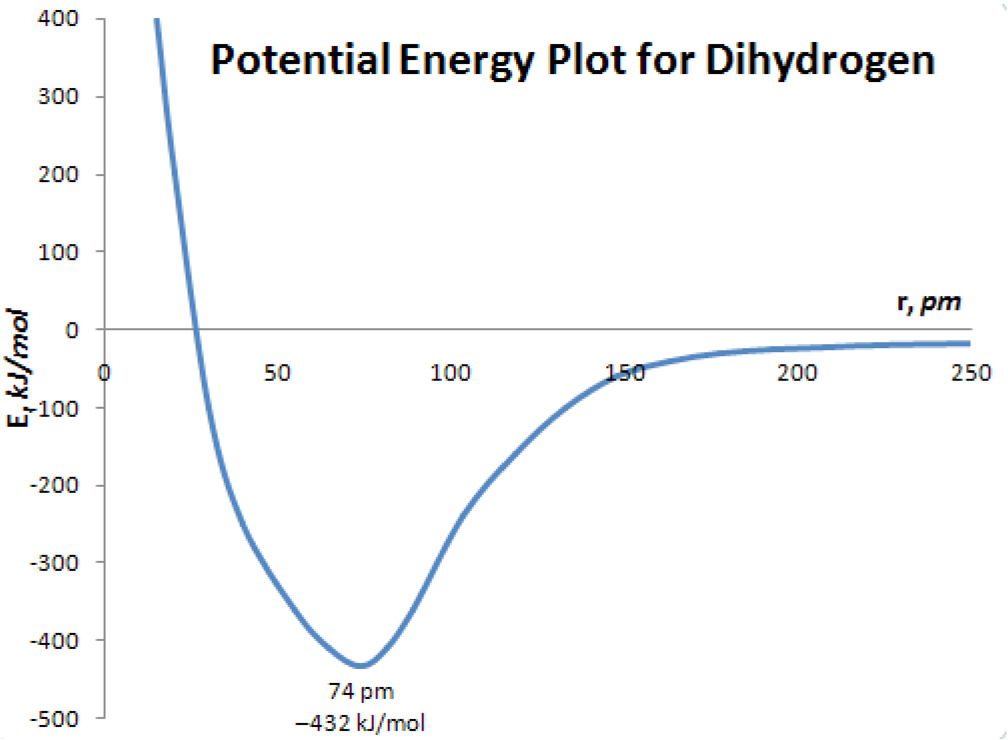
And the stabilization energy at this distance? **It's called the bond dissociation energy** (or sometimes the bond strength).

Another way to think of it is the Goldilocks point. Not too long, not too short – just right, so that the attractive and repulsive forces are balanced.

I made a rough little diagram of the interaction which is depicted here:



A more official looking graph of this interaction comes from LiqC of Carbon Based Curiosities, who gave me permission to reproduce his beautiful looking graph of this interaction energy (taken from this post.)



Note the Goldilocks spot at a bond length of 74 picometers (0.74 Å) and energy of 432 kJ/mol, and how ΔE skyrockets as you decrease the bond length past this point.

There are metaphors for these type of interactions all over the place. Your parents might drive you nuts [far left hand area of graph]. So you decide to go to school somewhere far, far away [far right hand part of graph]. Then you find that, surprise surprise, you miss them. So you move back to the area. But not *too* close!

Note – this discussion doesn't invoke orbitals or quantum mechanics, but in order for the electrons to exist in close proximity in our example, they must have opposite spin. This is due to the Pauli exclusion principle, which states that no two electrons may occupy the same quantum state in an atom or molecule.

From Gen Chem to Organic Chem Part 5 – Understanding Periodic Trends

Let's revisit a few terms that you learned back in Gen chem:

- **ionization energy** – the amount of energy required to remove an electron from an atom
- **electronegativity** - a measure of the ability of an atom to attract electrons toward itself
- **electron affinity** - the energy change when an electron is added to the neutral species to form a negative ion.
- **atomic radius** – a measure of the typical distance of the atom from the nucleus to the boundary of the electron cloud
- **ionic radius** – a measure of the distance across an atom's ion in a crystal lattice.

What do these five properties have in common? **They follow periodic trends.**

What else do they have in common? Well, these trends can all be understood on an intuitive level by grasping the Coulomb equation.

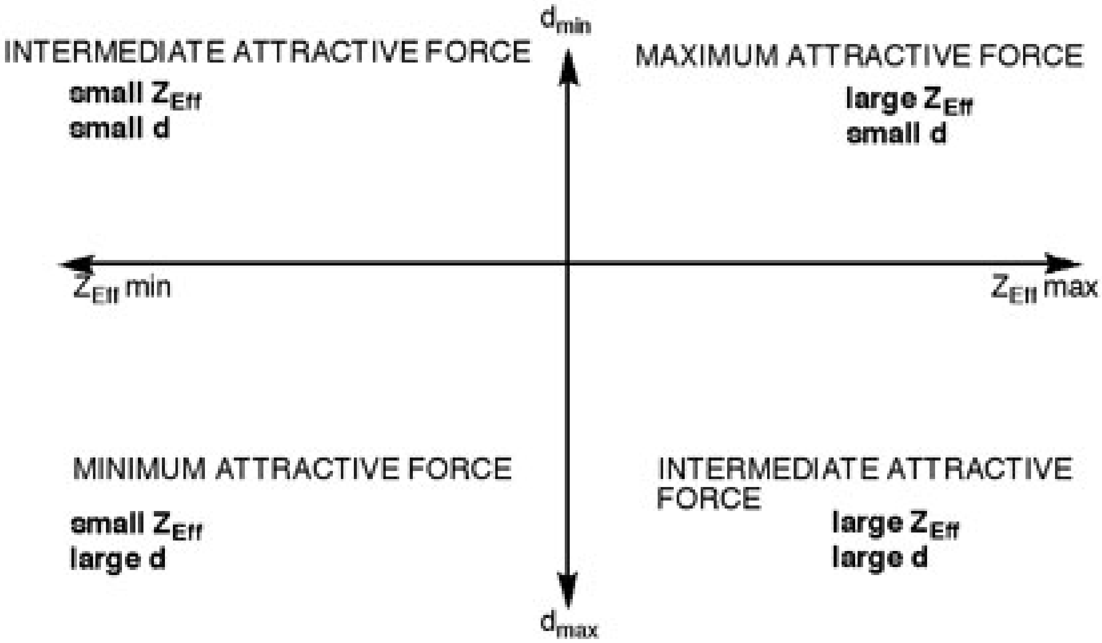
Coulomb's law, as applied to atoms:

$$F = k_e \frac{q_1 q_2}{r^2} \quad \text{or} \quad F \propto \frac{[Z_{Eff}]}{[\text{distance}]^2}$$

As we talked about earlier, the Coulomb equation is the equation that describes the force between two point charges. In the case of chemistry, we can use it to describe the attractive force felt between the positively charged nucleus and the negatively charged valence electrons. The magnitude of the force is determined by two things:

- **Zeff**, the effective nuclear charge (the nuclear charge adjusted for shielding by the electrons between the valence electrons and the nucleus)
- The distance **d** from the valence electrons to the nucleus. Like gravity, the magnitude of the force falls off proportionally to the square of the distance. The distance from the electrons to the nucleus is largely determined by the fact that electrons inhabit a discrete set of energy levels (orbitals) in the atom. Like attendees at an open-air concert, the seats closest to the action are taken first, while the latecomers must settle for a spot further away.

The Coulomb equation is going to be at a maximum when Zeff is big and d is small, and at a minimum when Zeff is small and d is big. Let's make a little graph.



Let's look at the maximum and minimum cases and how they impact the terms mentioned above.

Zeff large, d small:

- The force between the valence electrons and the nucleus is at its maximum.
- electronegativity will be at a maximum
- Electron affinity will be at a maximum (assuming there is room for another electron in the orbital).
- ionization energy will also be at a maximum because the force between the nucleus and the valence electron is at its strongest.
- atomic radius and ionic radius will be at a minimum (since the Zeff is larger, the electrons will be held at a distance closer to the nucleus)

What element best fits this condition? **Fluorine.**

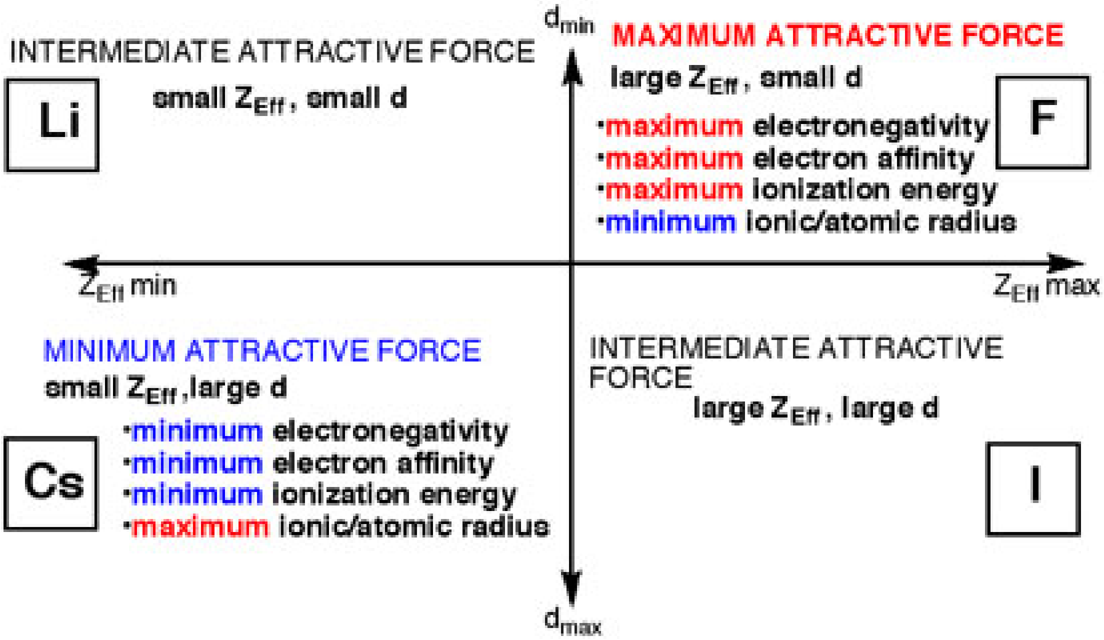
Zeff small, d large:

- The force between the valence electrons and the nucleus is at its minimum.
- Electronegativity will be at a minimum
- Electron affinity will be at a minimum
- Ionization energy will be at a minimum

- Atomic radius and ionic radius will be at a maximum.
- What element best fits this condition? **Cesium.**

There's also the two intermediate cases of low Zeff/small d and high Zeff/large d. These cases are exemplified by **Lithium** and **Iodine** respectively.

Let's make this diagram again.



Cesium and fluorine are truly the two solitudes.

The take home message: periodic trends are extremely important for understanding chemistry, and they can be grasped intuitively as a function of the attraction between the nucleus and the valence electrons.

Note: there's another periodic trend (which I didn't go into here) called polarizability that reflects how tightly the electrons are held by the atom. As you might expect, polarizability increases with size. It helps to explain why, for example, I(–) is a weaker conjugate base than F(–) [and hence more stable]. We'll get to this some other time.

A final note: to get the most out of understanding periodic trends, it's best to compare these properties *either* across a row or across a column – i.e. changing one variable at a time. Changing both variables at once – for instance, trying to rationalize the electronegativity of carbon versus phosphorus – can lead to variable outcomes.

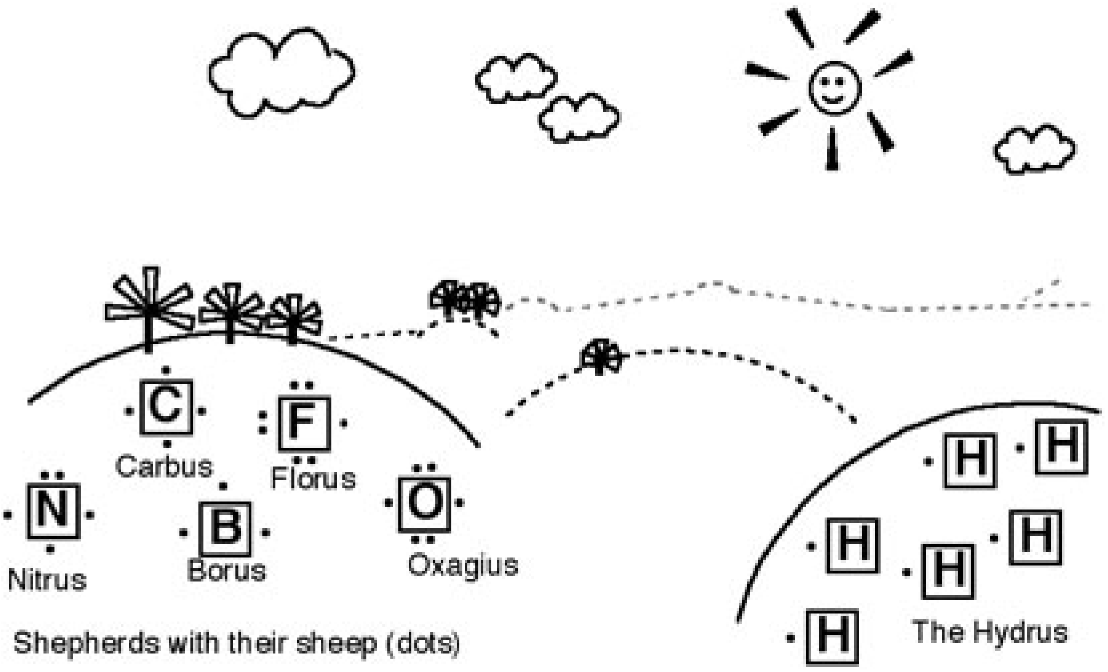
From Gen Chem to Organic Chem Part 6- A Fable

Once upon a time, in a land far, far away, there were six shepherds. They were poor people, but proud and self-reliant, and they each had a small flock of sheep. Borus had five, Carbus six,, Nitrus seven, Oxagus eight, Florus nine, and Neus had ten.

One day the corrupt authorities came to the fields of the shepherds, hoping to shake them down for extra funds to pay for the foreign wars of the Empire. The Emperor, Octavius, was in the throes of madness and had developed a strange fixation around the number eight. He decreed that any shepherd caught with more than eight sheep would have the excess confiscated, and anyone with less than eight sheep would face punishing taxes.

The shepherds huddled together and decided what they would do to outwit the mad Emperor's plans. Neus, being the most dominant shepherd and of a noble lineage, suggested that they each agree to hide away two of their sheep in a secret location. The rest reluctantly agreed, leaving them each with two fewer sheep in the fields than before. Neus was now in the ideal position of having exactly eight sheep and decided to leave the rest of the shepherds to their own affairs, at which he disappears from our story.

At this point the remaining shepherds were at a loss for what to do to avoid the taxes that would surely devastate their families. Just then, over the hills, came a group of boys from the neighbouring Hydrus tribe. Being very young, they only had one sheep each, and they were exempt from the Emperor's tax.

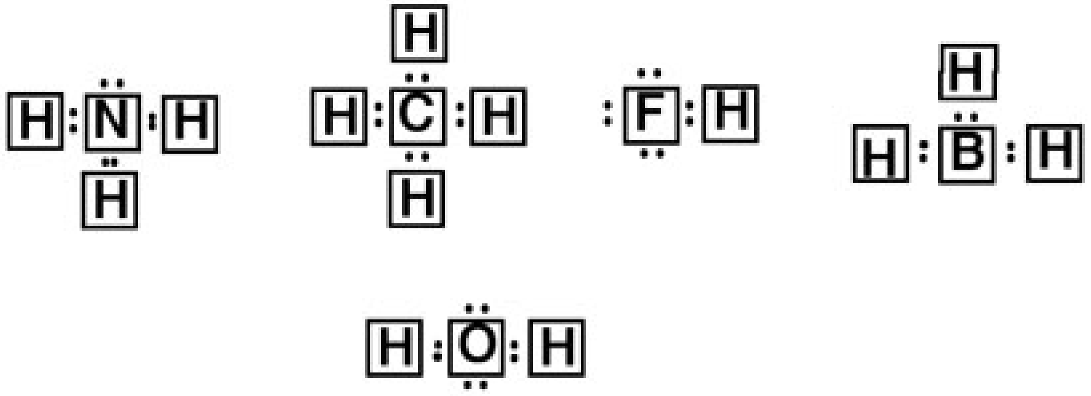


Shepherds with their sheep (dots)

Just then, Carbus excitedly gathered his friends around him. "Countrymen", he said. I have an idea! Let us join together with the Hydrus, and with each other, into a pact of

Joint Ownership". Carbius laid out his scheme. Each of them would keep the sheep they already had, but they could choose to share their sheep jointly with other shepherds such that each of them had eight.

He drew it out on a flat rock on top of the hill they had met on. "Pretend each dot is a sheep, and the letters stand for our names".



How every shepherd (except Borus) can obtain eight sheep - through sharing

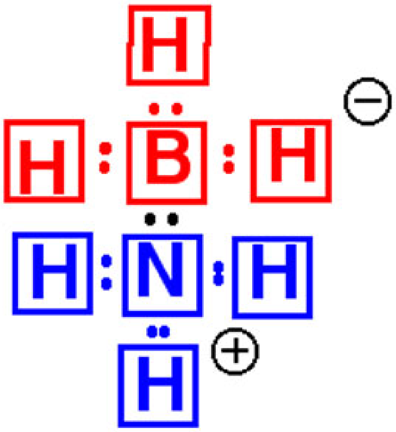
See how each of us, by sharing sheep each according to our need, can obtain eight to our name, and thus avoid the tax. All of them nodded in agreement at the wisdom of the plan, except for one.

"What about me?" said Borus. "I can only look after three sheep by myself, and even when I with the Hydrus I only have six. I'm still screwed!"

"True", said Carbius. "But in order for you to have eight, someone would have to share two sheep with you. It would not be an equal exchange. I have no pair of sheep to give, but maybe someone would like to share their sheep with you?"

At this point Florus, Oxygius, and Nitrus lowered their heads and stared at the ground, trying not to draw attention to themselves. Florus, being the greediest of the shepherds, was least willing to give, followed closely by Oxygius who had a similar miserly temperament. Finally, Nitrus spoke.

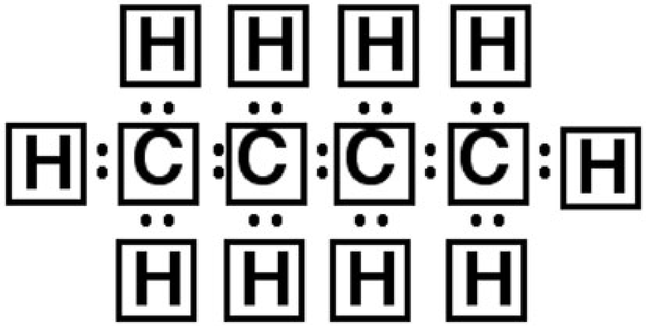
"Very well, in the name of tax evasion, I could choose to do so. However, although it might look to the authorities like we are sharing the sheep equally, I will have you wear a necklace that indicates you are in debt one sheep to me, and I will wear a necklace saying I am owed one. It looked like this.



Borus and Nitrus strike a deal

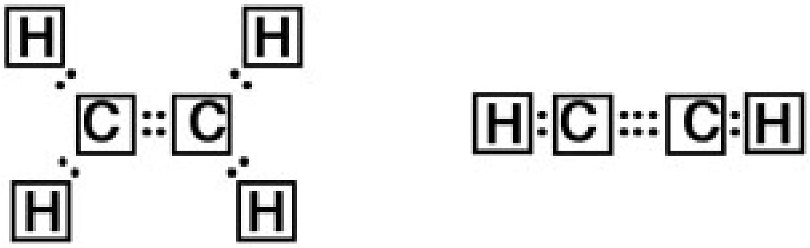
As the scheme took shape over the next few weeks, the shepherds noticed several patterns. First of all, the sheep liked to graze in pairs. Secondly, the pairs of sheep were very territorial, and arranged themselves so that they would have the maximum possible space to graze for themselves. This included both the sheep that belonged exclusively to the shepherds and also to those that they shared with the Hydrus. In the hilly fields, this meant that the shepherds had their sheep both sheep up in the hills, and down in the valleys, because that way they were farthest apart.

In time, the plan grew so successful that Carbus (who was from a large family) invited his many brothers to join. Together with his brothers, Carbus formed many different sheep-leasing partnerships.



"Carbus and his brothers"

They also found that they could share two (or even three) pairs of sheep between them, or with Oxygius or Nitrus. This way, the shepherds could get closer together and it was therefore less work to contain all the sheep, which gave them more time to smoke their water pipes, play backgammon, and complain about their wives.



Sharing of multiple pairs. Each group still seeks to maximize the distance between them

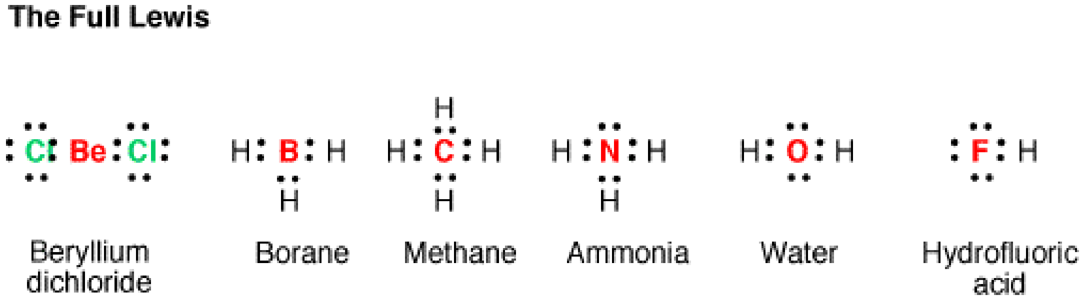
Then, one day, the shepherds were astonished to find two new visitors to their fields. As Phosphus and Sulfus showed off their huge flocks of ten and twelve sheep, respectively, all the other shepherds could do was gape in wonder. But the story of how Phosphus and Sulfus got their Certificates of Exemption from Octavius' Rule is a tale for another day…

From General Chemistry to Organic Chemistry Part 7- Lewis Structures

There are essentially three uses for Lewis structures. They're good at helping you get acquainted with the placement of electrons around atoms, helping to visualize molecular geometry, and finally to remember the location of the lone pairs. As you'll see in Org 1, the geometry of molecules as well as the placement of lone pairs has a huge impact on reactivity, so using Lewis structures to get yourself reacquainted with these principles would be a worthwhile exercise.

What are Lewis structures?

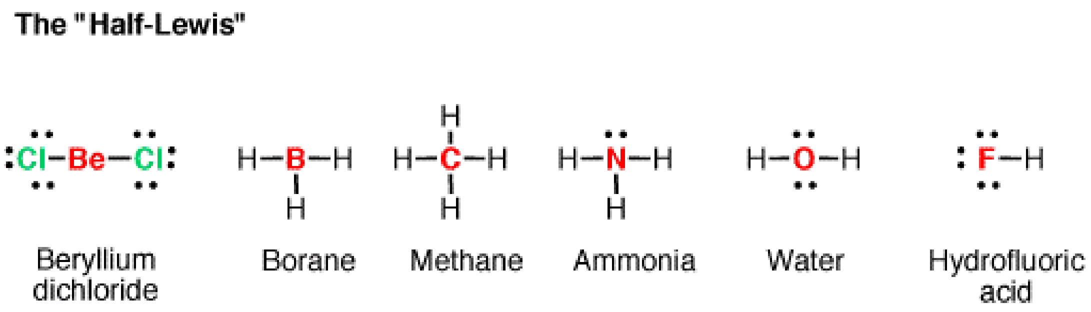
They are a way of drawing molecules that show the placement of electrons between atoms. For instance, here are the lewis dot structures of beryllium difluoride, borane, methane, ammonia, water, and hydrofluoric acid.



The advantage of the full Lewis is that it allows you to see where all the electrons are and to determine if each atom obeys the octet rule. You can see clearly that molecules can have both bonding electrons, which are shared between atoms and non-bonding electrons, otherwise known as lone pairs.

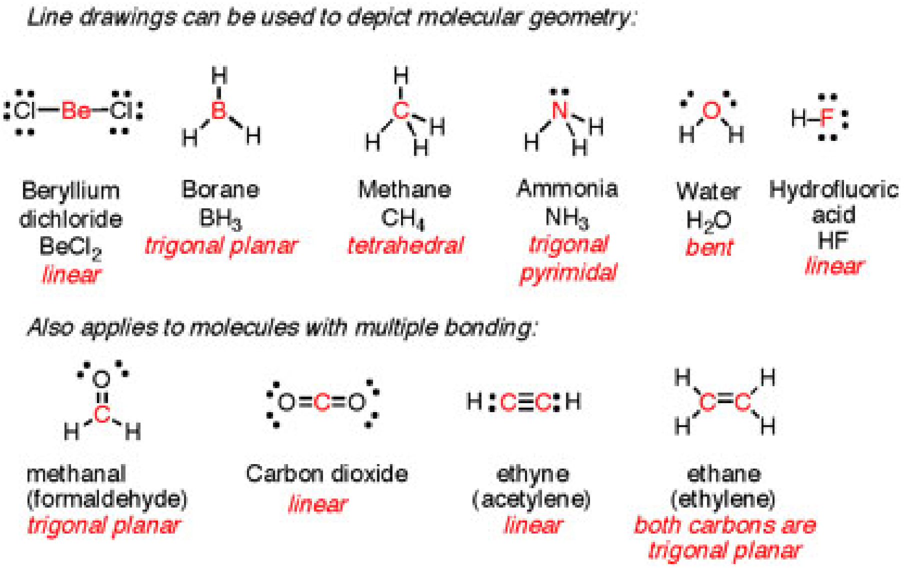
The full Lewis is kind of like training wheels on a bicycle. It's useful when you are just getting started and feeling uneasy about this business of atoms, electrons, and molecules, and want to determine for yourself that the octet rule is indeed a widespread phenomenon that (most) molecules abide by [the exceptions here being beryllium and boron, which are electron-deficient].

However, you will quickly realize that it is actually kind of a pain to draw a full Lewis structure. Once you become familiar with the basics of drawing molecules, you'll find it's much less work to simply draw a line where the bond is, as shown below. This also has the advantage that it is much easier to show geometry using the line bonds, because it's less cluttered.



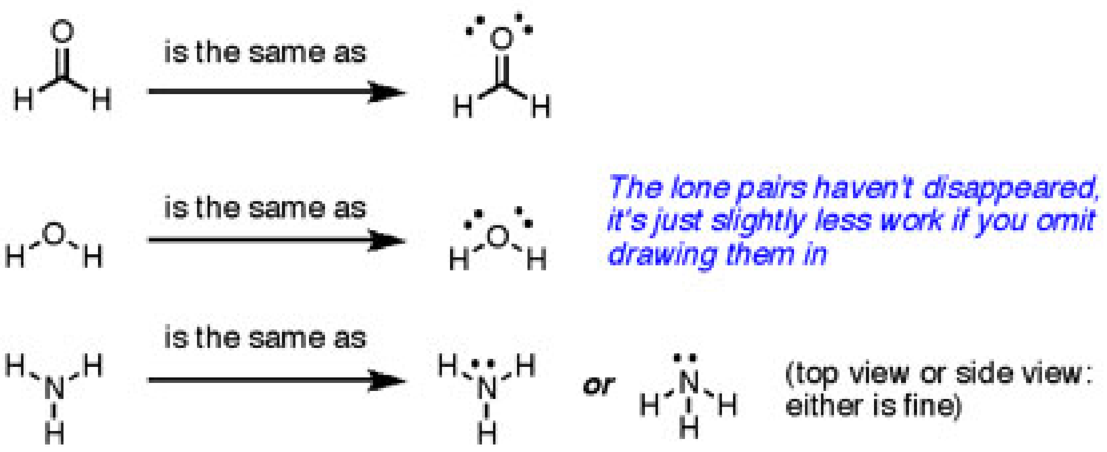
This brings us to our second point. **Electron pairs repel – this applies both to bonding electrons and electrons in lone pairs. So molecules will adopt a geometry which maximizes the distance between them.** This is why methane is tetrahedral, (internal angles 109°) and not square planar (internal angles 90°), and water is bent, not linear. You might recall this is referred to as VSEPR (valence shell electron pair repulsion).

Drawing out molecular geometry using a full Lewis makes for an extremely cluttered drawing. That's why we drop the full Lewis for the half-Lewis, move the lines around, and just leave the electron pairs in.



Now there is even a second tier of laziness. It's less work to just drop drawing the electron pairs altogether. This is by far the most common way molecules are drawn. Let's look at a few examples.

Further examples of laziness (or as we would prefer to put it, ***shorthand***)



The lone pairs haven't disappeared, it's just slightly less work if you omit drawing them in

(top view or side view: either is fine)

You're supposed to know that the lone pairs are still there, even though they're not drawn in. Think of them like chemical stick figures. For instance, xkcd tends not to draw faces, feet, or hands, but that doesn't mean the characters he draws are implied to be faceless amputees. It's just quicker to draw stick figures.**This is important because in organic chemistry, lone pairs often don't just sit around. As you'll see later, lone pairs are nucleophiles – they participate in a host of chemical reactions. So it's crucial to know that they're there, even if they're not drawn in.**

From General Chemistry To Organic Chemistry, Part 8 – Ionic and Covalent Bonding

Previously, I've been talking about how Coulomb's law – the attraction and repulsion between charges – affects the properties of atoms, and is responsible for the phenomenon of chemical bonding. Let's review.

- Atoms share electron pairs between them. These relationships are called chemical bonds.
- Atoms have a property called electronegativity, which is a measure of how much they attract electrons toward themselves.

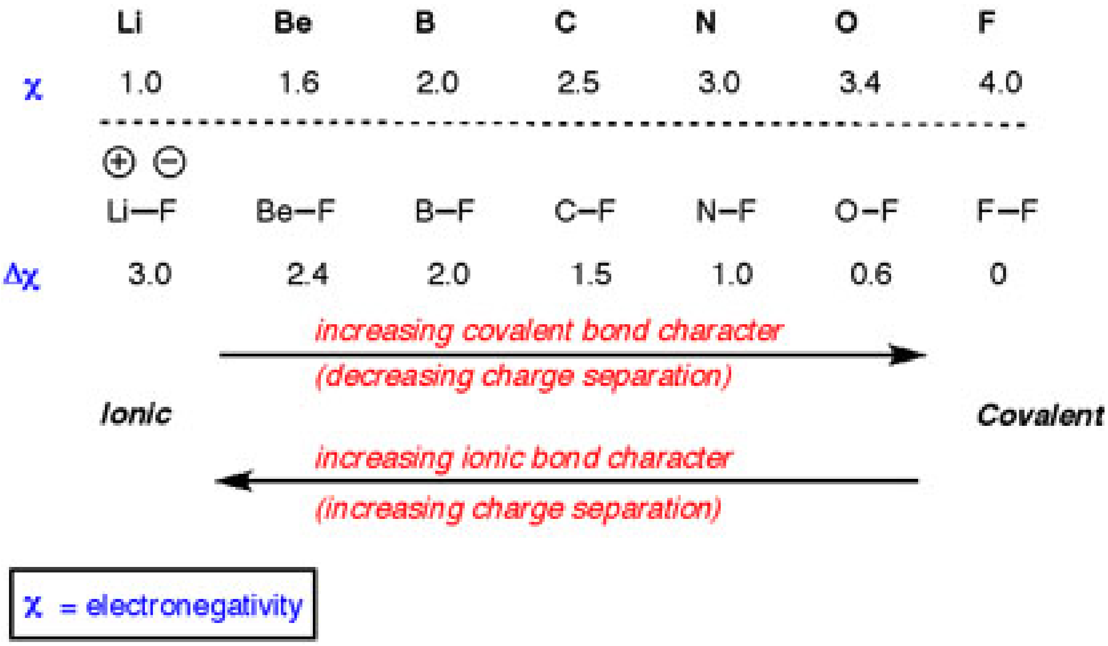
Here's the important consequence of these two facts: when bonds form between atoms of different electronegativity, the electron pair in the bond will not be shared equally. It will be **polarized** toward the atom with the greater electronegativity. What this means is that the more electronegative element will have greater electron density (a net negative charge) and the less electronegative element will have lower electron density (a net positive charge).

The greater the difference in electronegativity, the greater the polarization.

Sometimes the "sharing" of electrons to form a bond is sharing in name only. Let's say the parents of two boys, aged 10 and 8, give them a $20 bill "to share" between them, and walk away. Assuming no further parental interference, what do you think the odds are that the money will get split 50/50 ? Pretty slim (I speak from personal experience). Although the two brothers are *nominally* sharing $20, it's the older brother who has the power to deliver an unbreakable Full Nelson, and thus holds the majority of the purchasing power.

So it is with atoms. At one end of the scale you have the bonds of a highly electronegative element like fluorine with a poorly electronegative element like lithium. In lithium fluoride, the bond is so highly polarized that essentially one can think of lithium's electron as residing exclusively on the fluorine, so that fluorine has a full octet. This type of bonding is referred to as ionic [ions = charged atoms or molecules] , and the bonding behaves essentially like the attraction between two point charges obeying Coulomb's law.

On the other end of the scale, you can have an element like fluorine bound to itself, where there is no dipole (elecronegativity difference being zero) and hence the bonding is not ionic, but what we call covalent – a full and equal partnership.



In between the extremes there are shades of both. Here's an important point. just as one should be hesitant in looking at issues in black and white, chemical bonding is no different. There's a temptation to look at bonds as either covalent OR ionic; instead, it may be more helpful to look at in terms of flavor or character – bonds can have differing amounts of covalent or ionic *character*. So the middle cases have a lot of shades of both.

So what implications does this have for organic chemistry? Too many to talk about in depth! **This is the key phenomenon which underlies a lot of the richness of chemistry.** But here are a few examples.

- **Boiling points/melting points** – *in general*, the more polarized the molecule, the higher the boiling point/melting point. Water is a highly polarized molecule, considering the difference in electronegativity between oxygen (3.4) and hydrogen (2.2) reflected in its extremely high boiling point (relative to its molecular weight) of 100 °C.
- **Solubility** - You've probably come across this as the easy-to-remember slogan "like dissolves like". I*n general*, the more polarized the molecule, the better will be the solubility in a polar solvent (like water, with its polarized O-H bonds).
- **Acidity** – the electronegativity of the atom bound to hydrogen is an important factor (though not the only one!) in determining the acidity of a molecule
- **Reactivity** - for organic chemistry, this is extremely important for the purposes of looking at carbon. Atoms with high electron density will tend to form bonds at carbons with low electron density, and vice versa.

Learning to recognize dipoles at carbon is one of the key skills that will help you determine its reactivity, as you'll see when you learn about electrophlicity (electron-deficiency) and nucleophilicity (electron-richness).

For a useful mnemonic for electronegativity, see here (and the original discussion, here)

Analogies

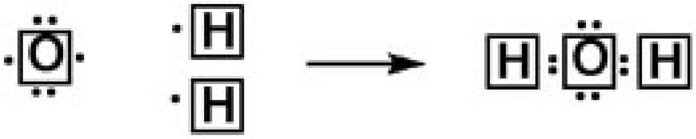
I often think of electronegativity as one of the key factors that give atoms their unique personalities. If we go back to the whimsical analogy of atoms as shepherds and electrons as sheep, you can think of electronegativity as being a lot like greed. The greediest shepherd, Fluorus, will partner with (one) other shepherd so that he can follow Octavius' rule, but the partnerships he enters are usually far from equal (Think of Fluorus as the Gordon Gekko of our little shepherd world). Fluorus hoards the pair of sheep to himself as much as possible, leaving the other shepherd in the bargain somewhat bereft.

This is a brief treatment of one of the most fundamental concepts in chemistry, but we'll be coming back to it again and again. **Take home message**: *Pay close attention to the differences in electronegativity between atoms!*

From General Chemistry to Organic Chemistry, Part 9 – Acids and Bases

First of all, back to the shepherds:

Oxygius, having six sheep to take care of, found he could make a bargain with two of the Hydrus shepherd boys, whom each brought a sheep of their own. In so doing, Oxygius fulfilled his commitments under the law of Emperor Octavius, and each of the Hydrus shared the tending of a pair of sheep with Oxygius.

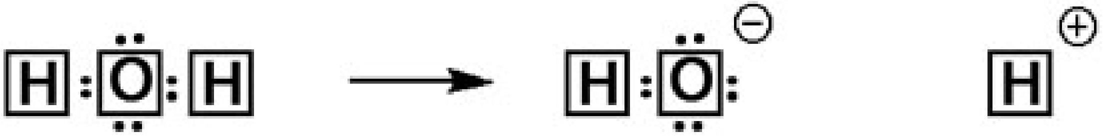


One day one of the Hydrus shepherd boys told Oxygius he wanted to leave the arrangement. He wanted to take his lone sheep and explore some of the lands on distant hillsides, as he used to do before he met Oxygius.

Oxygius was furious. He said a deal was a deal, and the Hydrus couldn't just pack up and leave with his sheep. They had agreed to share the sheep, and the Hydrus must honor the agreement. : "You can't just leave. I forbid it", he said.

It was then that the young Hydrus realized that sometimes it is easier to get into arrangements than get out of them. Although he was nominally sharing his sheep with Oxygius, for all intents and purposes, it was under Oxygius' control. He had entered into an unequal partnership and was not strong enough to win a wrestling match with the more powerful shepherd.

So the Hydrus decided to leave for the distant fields anyway, but had to leave his sheep behind with Oxygius. However, before leaving, Oxygius made a concession. He gave him a necklace with a (+) on it, to signify he was owed a sheep, and Oxygius wore a different necklace with a (-) to signify that he had an extra head in his flock.

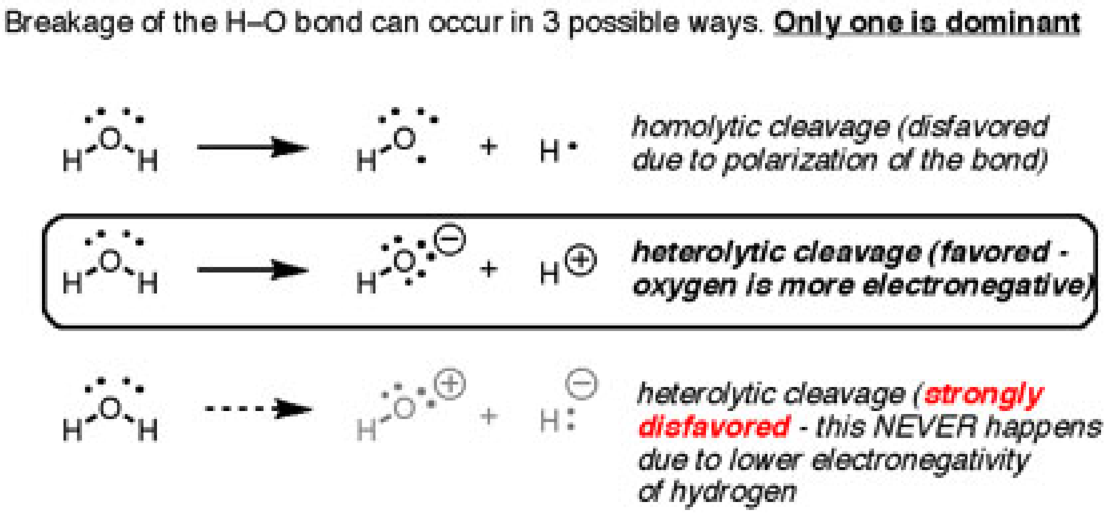


Acids and bases

Today we'll talk about Bronsted-Lowry acidity and basicity and generalize it to Lewis acidity and basicity, concepts you no doubt learned about in Gen Chem but may have forgotten.

Last time we talked about how many bonds are not an equal sharing of electrons, but instead the more electronegative partner tends to take the majority of the electron density from the less electronegative partner. So it is with water, where the oxygen, being more electronegative, contains a partial negative charge and hydrogen, being electron deficient, contains a partial positive charge. [This is the basis for hydrogen bonding, by the way - more about that later].

When the water bond breaks, there are two ways in which it could do so. It could break *homolytically*, whereby each partner obtains one electron. The other way the bond could break is *heterolytically*, where one partner takes both electrons of the bond and the other partner takes none, and is left with a positive charge. There are two ways the bond will break heterolytically. **After heterolytic cleavage, the more electronegative partner will have the negative charge, and the less electronegative partner will have the positive charge.**

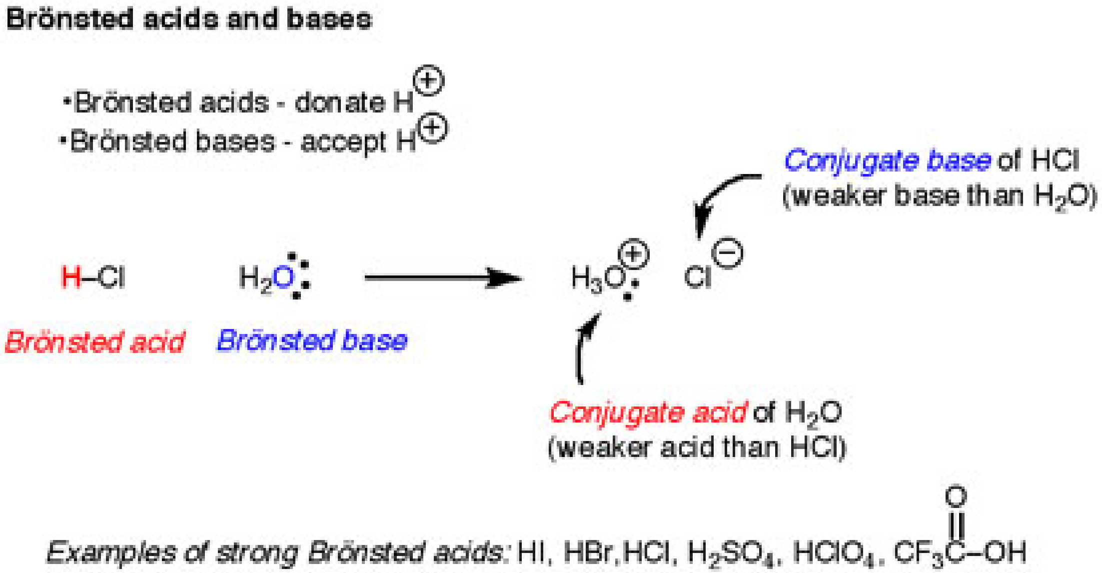


Since the electronegativity of H is 2.2, and most of the other elements are on the right hand side are higher (F,O,N,Cl,Br, C, S, I) hydrogen is often in the position of being partially positive. When bonds containing H break, they tend to break heterolytically, and the H leaves as H+.

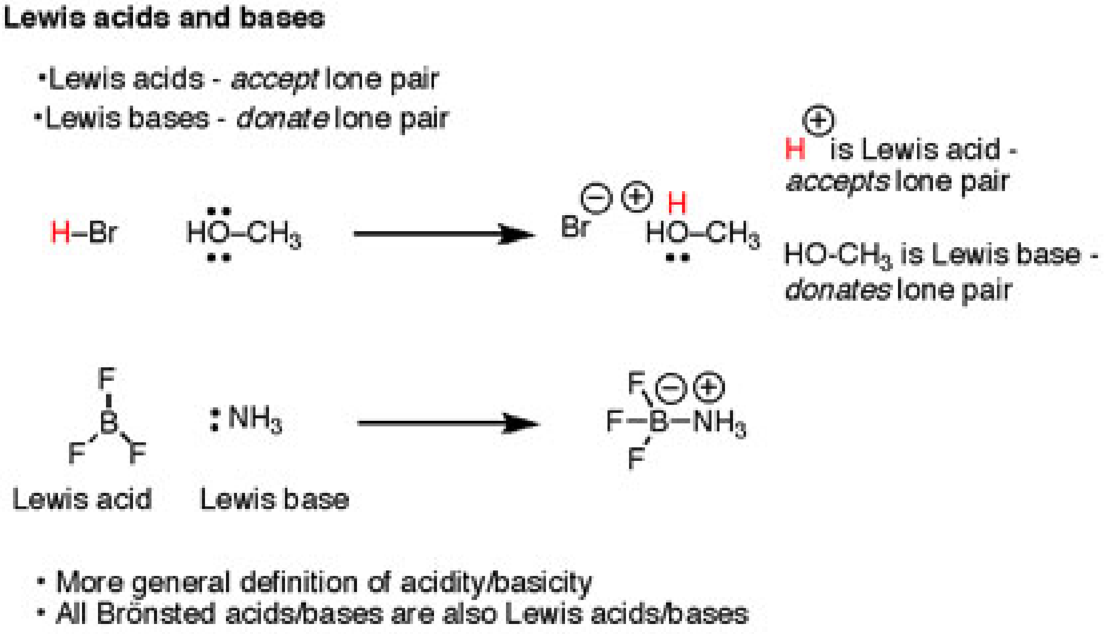
There's a word for this behavior. It's called acidity. Brønsted acidity. in fact.

A Brønsted acid is a chemical species which can donate H+. Conversely, a Brønsted base is any chemical species that can accept H+.

Examples of strong Bronsted acids include HCl, HBr, HI, H_2SO_4, and $HClO_4$. **When an acid loses a proton, it forms what is called the conjugate base.** In general, strong Brønsted acids contain a species that is very stable as an anion. When a Brønsted acid reacts with a Brønsted base to generate a protonated species, the protonated species is called the **conjugate acid**. *In general, acid base reactions proceed such that the acid and base react to give a weaker acid and a weaker base*. The measure of acidity is pKa, which I've alluded to before, but is a measure of how easily a species parts with H+ .

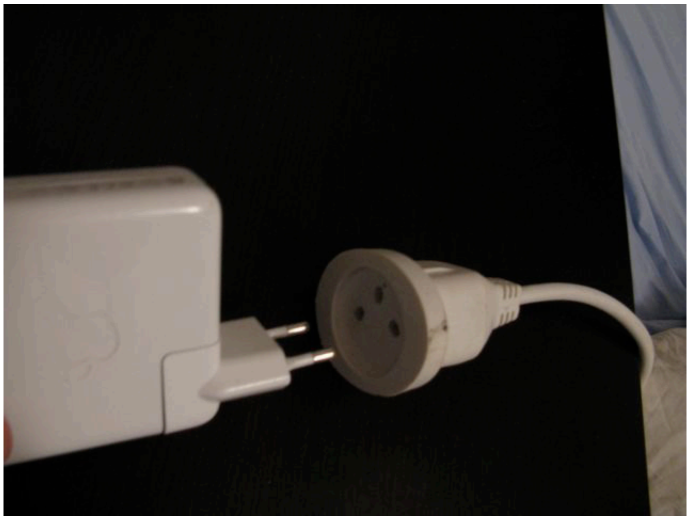


There's another way to look at this reaction. Since you could make the analogy that electron flows are to chemistry what currency flows are to economics, it's helpful to look at this *purely from a basis of examining the flow of electrons*. If you look closely at what's going on in the example above, you'll see that the oxygen of H_2O donates a lone pair to the proton of HCl, and the proton accepts the lone pair from the oxygen. This is a useful way to look at reactions because similar types of reactions (that don't involve H+ *per se*) are extremely common in chemistry, like the reaction of BF_3 with NH_3:



So Gilbert Lewis generalized this concept: in the Lewis definition, **a Lewis acid is a chemical species that accepts a lone pair, and a Lewis base is a species that donates a lone pair.** This is a much broader definition of acidity/basicity and one we will encounter again and again.

Metaphorically, we can even extend it further. What's the Lewis base and the Lewis acid in this picture? (Yes, that's a plug on the left – things are a little different over here).



There's other relationships you could extend the metaphor to as well – hand-glove, sword-scabbard, foot-shoe – the list could go on. As we'll see, the reactions of bases with acids are examples of nucleophiles attacking electrophiles, which is one of the key concepts to master in order to understand the vast array of reactions you'll be presented with in organic chem.

Take home message: *understand the definitions of Brønsted and Lewis acidity, and understand the differences between them.*

From Gen Chem to Organic Chem, Part 10 – Hess' Law

Probably nowhere else does the contrast between the largely quantitative nature of Gen Chem with (relatively) qualitative nature of Org Chem become more apparent than with the topic of thermodynamics. Whereas you probably spent a lot of time in Gen chem figuring out heats of formation, free energy differences, and electrochemical potentials, these types of challenges are largely absent in introductory org chem. However, just because certain types of questions don't come up doesn't mean that the key concepts have gone away. It's still vitally important to understand the meaning of some key thermodynamic equations and to be able to apply them in an intuitive sense to reactions in organic chemistry.

Today we'll talk about Hess' Law and we'll deal with some other key equations over the next few days as we wrap up this series with discussions of chemical kinetics and chemical equilibria.

Hess' Law

Energy in the universe is a constant. It is netiher created nor destroyed, it merely changes form. The enthalpy (**heat**) given off (or absorbed) in a reaction is equal to the enthalpy of formation of the products minus the enthalpy of formation of the reactions. This relationship is referred to as Hess' Law. It's nature's version of the accounting equation: profit(loss) = income – expenses. However, when dealing with enthalpy, the release of heat energy (an exothermic process) is denoted with a negative sign, whereas processes which absorb energy (endothermic processes) maintain the positive sign. By the way, this also applies to the Gibbs free energy, Δ G.

$$\Delta H\text{ (reaction)} = \Delta H\text{(products)} - \Delta H\text{(reactants)}$$

Enthalpy is what is known as a state function, which means the change in enthalpy is independent of the pathway taken. It's intuitive to think of enthalpy as altitude, with each atom/molecule at a fixed "elevation", which represents its standard heat of formation. The distance between my apartment in Jerusalem (2600 feet above sea level) which is where I live, and the Dead Sea about 90 minutes away (1200 feet below sea level) is a constant – 3600 feet. Going from Jerusalem to the Dead Sea, I descend 3600 feet, whether I do it by foot, by helicopter, or via a side trip to Mount Everest. **It's the net result that matters.** You can draw an analogy with currency: bankruptcy courts don't care if you *used* to be a millionaire, they care about how much money you have *now*.

Just as altitude is measured relative to sea level, **enthalpy is not measured directly, but through the measurement of changes.** For instance, you might not think that sodium chloride, NaCl, as very remarkable compound. It might be more exciting if you saw this (the reaction of molten sodium with chlorine gas). There's a lot of energy bound up in your table salt! Alternatively, you could form NaCl any number of other, perhaps less exciting ways – like through the reaction of solid sodium hydroxide with hydrochloric acid. However, no matter which path you take to making NaCl, the compound is identical in every respect. ***The enthalpy of formation of NaCl is independent of how it is made.***

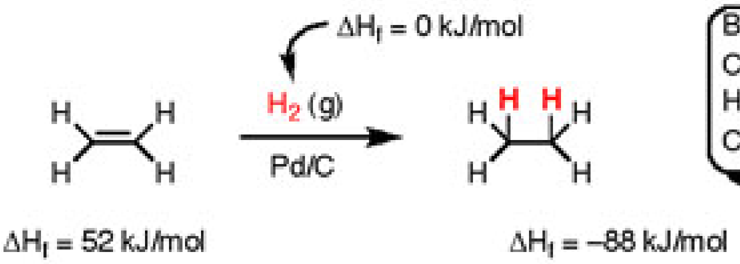
How do we apply these concepts to organic chemistry?

Here's a fairly simple reaction that you'll learn in Org 1, called hydrogenation. In this reaction we treat a very simple olefin (alkene, in this case ethene) with hydrogen gas over a catalyst (typically palladium on charcoal, which we depict as Pd/C)). The result is a saturated hydrocarbon (ethane). The heats of formation of both these compounds have been measured by intrepid scientists before us, so we can just look the values up in a table and use Hess' Law to figure out the ΔH for the reaction as follows:

ΔH(reaction) = ΔHf (product) – ΔHf (reactants).

In the case of the hydrogenation of ethylene this would be –140 kJ/mol.

Two ways to figure out the enthalpy change:



Bond dissociation energies	
C=C (π bond)	264 kJ/mol
H–H	436 kJ/mol
C–H	410 kJ/mol

$$\begin{aligned}\Delta H_{f\ \text{reaction}} &= \Delta H_{f\ \text{products}} - \Delta H_{f\ \text{reactants}}\\ &= (-88\ \text{kJ/mol}) - (52\ \text{kJ/mol} + 0\ \text{kJ/mol})\\ &= -140\ \text{kJ/mol}\end{aligned}$$

OR

$$\begin{aligned}\Delta H_{f\ \text{reaction}} &= \Delta H_{f\ \text{bonds broken}} - \Delta H_{\text{bonds formed}}\\ &= 700\ \text{kJ/mol} - 820\ \text{kJ/mol}\\ &= -120\ \text{kJ/mol}\ \text{(approximate)}\end{aligned}$$

source for bond dissociation energies: Lowry & Richardson "Mechanism and Theory in Organic Chemistry", Harper&Row, 1987

Here's where another facet comes in. A lot of times in organic chemistry we'll be dealing with compounds that we don't happen to know the heats of formation of. But there's a useful way around this dilemma. The enthalpy of the whole molecule can be estimated by examining the enthalpies of the individual bonds. We can break down the thermodynamics of this process even further by applying a table of standard bond dissociation energies. For a pretty thorough table, click here. "Standard" bond dissociation energies refer to an average value of the measured bond energies of the same type of bond in different molecules. **Since we're measuring relative change in energy, we only care about the energies of the bonds that are breaking or forming** (and make the relatively safe assumption that the other bonds don't affect the process very much). For instance, in our case we are breaking a C=C **π** bond (note – only breaking the double bond, not both bonds!) and an H-H single bond. The table tells us the values of these are roughly 264 kJ/mol and 436 kJ/mol respectively. This is what the reaction "costs". What is "gained" is the energy of two C-H bonds (approximately 410 kJ/mol each).

We use the equation ΔH (reaction) = ΔH (bonds broken) – ΔH (bonds formed). We put the bonds broken term first because breaking bonds is an endothermic process – it requires energy. Forming bonds is an exothermic process (it releases energy) and thus has the negative sign in front of it.

When we do the math we have a value of Δ120 kJ/mol, or a release of 120 kJ/mol of heat energy in this process. Within ~15% of the standard value, so not a terrible estimate. The answer isn't exact due to some small cooperative effects, but **this is an excellent first-order way of figuring out if a reaction will be favorable.** [a note of caution - bond dissociation energies generally represent homolytic bond cleavage (i.e. each atom obtains one electron), while many processes in organic chemistry go through heterolytic processes (one atom receives 2 and the other zero) - but the point stands]. If you find yourself breaking a really strong bond – C–F, for instance – something's probably gone wrong.

From General Chemistry to Organic Chemistry, Part 11 – The Second Law

From Wikiquote:

- ***Zeroth law of thermodynamics:*** *you must play the game*
- ***1st law :*** *you can't win*
- ***2nd law:*** *on a very cold day, you can break even*
- ***3rd law:*** *it never gets that cold*

The 2nd Law of Thermodynamics: $\Delta G = \Delta H - T\Delta S$.

(I wrote a really long description of this law and realize that it is probably overkill. But I wrote it, so I'll include it. If you're already somewhat comfortable with thermodynamics, skip to the punchline at the end, "How the second law of thermodynamics applies to organic chemistry").

We've talked about the concept of enthalpy (heat) and how certain reactions are exothermic (produce heat) and endothermic (absorb heat). For instance, one prominent example of an exothermic reaction is the combustion of hydrogen with oxygen to produce water. This gives off 276 kJ/mol.

Back in the earlier days of chemistry and physics, much attetion was given to the development of steam engines, where the combustion of wood or coal (another exothermic reaction) is used to boil water. In a closed system, the resulting high-pressure steam could be used to do work on a paddle wheel or some other contraption and the Industrial Revolution was born. [Recall that a mole of water (18 mL) occupies 22.4 L as a gas at room temperature and even more at 100° C - that's a lot of pressure!] Needless to say, explosions were common in the early days of steam.

Long story short: the work you receive out of these types of processes never equals the energy that goes in (1st law: "you can't win"). It was in the 1870s that Gibbs (among others) determined that one must account for a certain amount of "non-useful" energy which is dissipated during these processes, which was later defined as "entropy". The energy left over – which is available to do work – was termed the 'free energy", or as we call it now, the "Gibbs Energy". Here's the relevant equation:

$$\Delta G = \Delta H - T\Delta S$$

This is the second law of thermodynamics, which has been written in many forms (see above) but in my favorite interpretation, goes: "Energy of all kinds in our material world spontaneously disperses or spreads out if it is not hindered from doing so".

In organic chemistry it's important to have an intuitive grasp of this equation and to understand it implications in certain types of reactions. While the effects of *enthalpy* changes are usually fairly easy to understand, it's easy to get hung up on *entropy* and the Gibbs energy.

Entropy

Remember that all matter is in constant motion, with particles constantly colliding with each other at high speed. *Temperature* is the measurement of how rapidly these molecules are in motion. And at absolute zero, all motion stops. A drop of dye placed in a glass of water will slowly fade to a lighter hue; air in car tires will slowly leak out to the atmosphere; an ice cube taken out of the freezer will slowly melt into a tiny puddle. All of these processes are the result of particles colliding with each other, exchanging energy in the process, and eventually reaching an equilibrium.

One of the interpretations of entropy (in a chemical sense) is the following:

"Entropy change measures the dispersal of energy: how much energy is spread out in a particular process, or how widely spread out it becomes (at a specific temperature)."

If you think about this in terms of forms of matter, it's not hard to grasp intuitively **that the entropy of a given compound will increase as it goes from solid to liquid to gas***:* the particles are spread out over a wider area (at a given temperature, of course).

Similarly, if you take a molecule such as H2 and split it into two molecules of H, the *dispersal* of energy will increase, *since you will have twice as many particles colliding with each other than* you did before. So this also leads to an increase in entropy.

So what the Second Law tells us is that if you account for the enthalpy of a process in addition to the entropy, you can calculate the Gibbs energy, ΔG.

In Gen Chem you learned how to apply this equation to figure out the ΔG of a process if you were given values for H and S. The sign of the ΔG tells you if the process happens spontaneously (if ΔG is negative) or if it requires work in order to occur (when ΔG is positive.)

However, the equation tells you nothing about rates. In chemistry, "spontaneous" means, "someday, but not **necessarily right now"**. The reaction of cellulose (wood) with oxygen to give CO_2 and H_2O (and heat) is highly spontaneous, but our forests survive because the chemical process of burning requires a certain activation energy to get started.

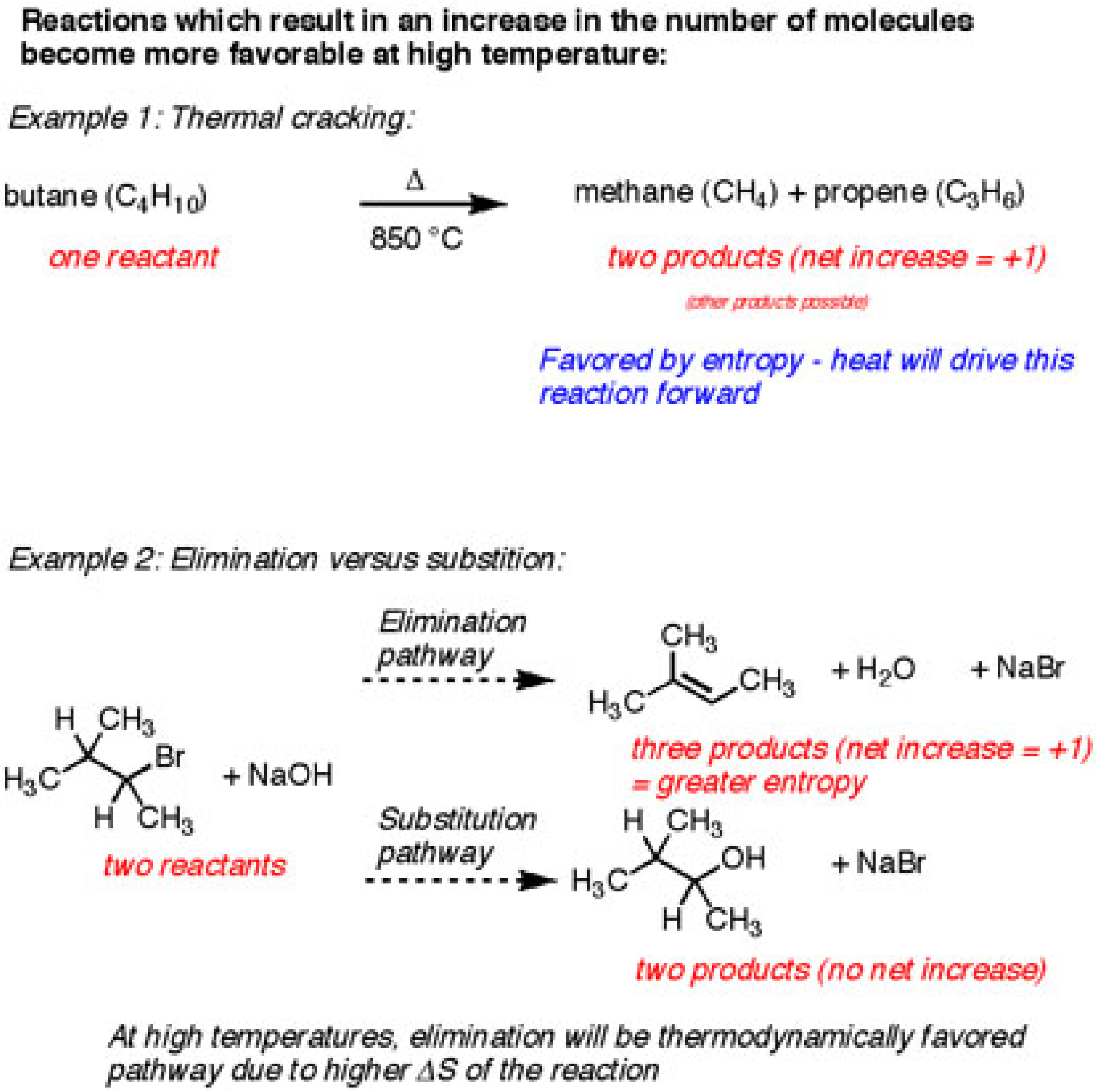
How the Second Law applies to organic chemistry

Here's the key point. For any process that results in an increase in entropy, increasing the temperature will eventually cause it to become (thermodynamically) spontaneous. Because of the $T\Delta S$ term, at high temperatures, any process that increases entropy is eventually going to dominate the Gibbs equation.

There are two types of process in Org1/Org2 where you will see this in action:

1. fragmentation reactions
2. reactions that form gases.

Let’s talk about fragmentation reactions first. Any process that increases the net number of chemical entities (fragmentation reactions, for instance) is going to have a positive ΔS, since the total number of intermolecular collisions (and therefore the entropy) will drastically increase. Fragmentation reactions are one particular example. Thermal cracking is a process used by the petrochemical industry to transform low-value long-chain hydrocarbons into higher value short chain hydrocarbons. It’s typically done at extremely high temperatures. For instance you can heat butane to obtain the smaller molecules methane and propene.



Reactions which result in an increase in the number of molecules become more favorable at high temperature:

Example 1: Thermal cracking:

butane (C_4H_{10}) $\xrightarrow[850\,°C]{\Delta}$ methane (CH_4) + propene (C_3H_6)

one reactant

two products (net increase = +1)

(other products possible)

Favored by entropy - heat will drive this reaction forward

Example 2: Elimination versus substition:

two reactants

three products (net increase = +1) = greater entropy

two products (no net increase)

At high temperatures, elimination will be thermodynamically favored pathway due to higher ΔS of the reaction

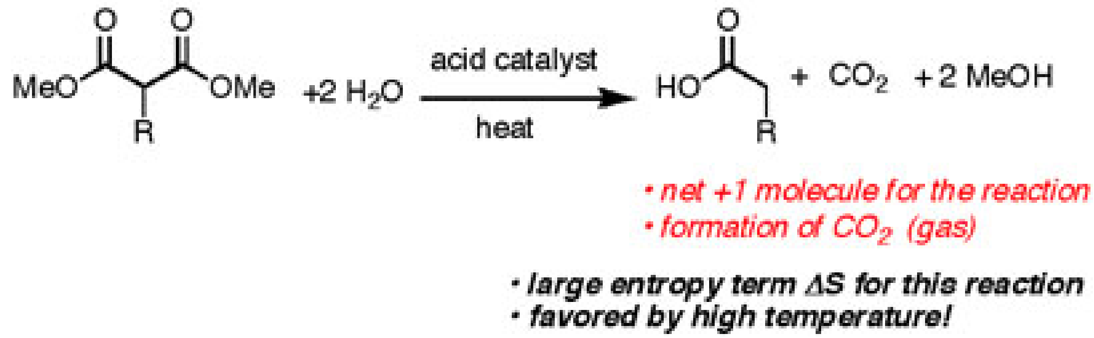
Another example is a reaction you’ll meet in Org 1 called the E2 reaction, which is when a base reacts with an alkyl halide to provide an alkene. *Note that in this process we’ve gone from two entities to three*, which will result in an increase in entropy.

One of the reactions it competes with is the S_N2 reaction (which you’ll also meet later) which forms the other products. How many products are formed here? Two; there is no net change in the number of molecules.

Which of these two processes is going to have a higher entropy? The E2. Therefore, which will be favored at higher temperature? That's right – the E2, since the T ΔS term will start to dominate the equation.

Reactions that form gases are another example. A process which results in the formation of a gas from a liquid or solid will have a positive net entropy, and therefore be favored by high temperature.

Malonic ester synthesis (Org 2)



- *net +1 molecule for the reaction*
- *formation of CO_2 (gas)*

- ***large entropy term ΔS for this reaction***
- ***favored by high temperature!***

One example is a reaction you'll meet in Org 2 called decarboxylation. When you heat molecules like this malonate derivative (shown) to a high enough temperature in the presence of aqueous acid, they'll spontaneously lose carbon dioxide gas to provide you with the carboxylic acid. This particular example is called the malonic ester synthesis. The formation of gas makes for a large value of the entropy term in this reaction. Note that this is also a fragmentation reaction, so it has that going for it as well.

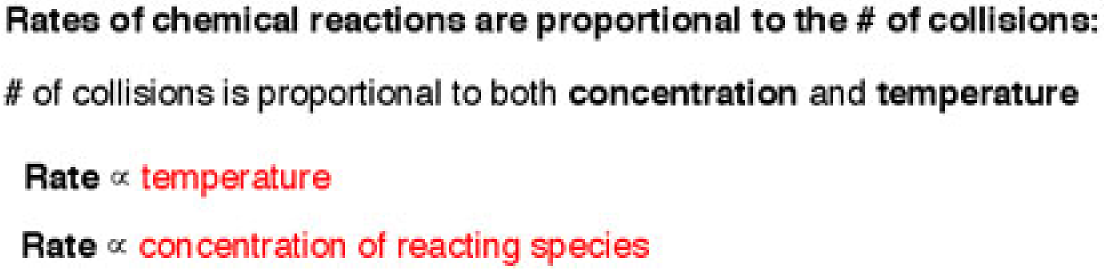
From Gen Chem to Organic Chem, Part 12 – Kinetics

Chemical kinetics is the study of reaction rates. It can be really important in figuring out the mechanisms of chemical reactions. Here are the essentials of what you need to remember about chemical kinetics as you go from Gen chem to organic chemistry.

1. Reaction rates are proportional to concentration and to temperature.

First and foremost, chemical reactions occur when collisions occur between atoms or molecules and there is resulting change in the arrangement of the chemical bonds. Therefore, rate of a reaction is proportional to the number of collisions between molecules. Not every collision will result in a chemical reaction; of the total number of collisions, only a certain percentage will occur at the appropriate energy to allow the processes of chemical bond breaking and forming to occur. Think of a telemarketer selling Ginsu knives – only a small percentage of the calls he makes will result in a sale, but the total sales will be proportional to the number of calls.

In chemical reactions, anything which increases the collision rate will increase the reaction rate. One way to do this is to increase the concentration. Another is to increase the temperature -you might recall that what we call "temperature" can be looked at as a measure of atomic and molecular motion.



Rates of chemical reactions are proportional to the # of collisions:

# of collisions is proportional to both **concentration** and **temperature**

Rate $\propto$ temperature

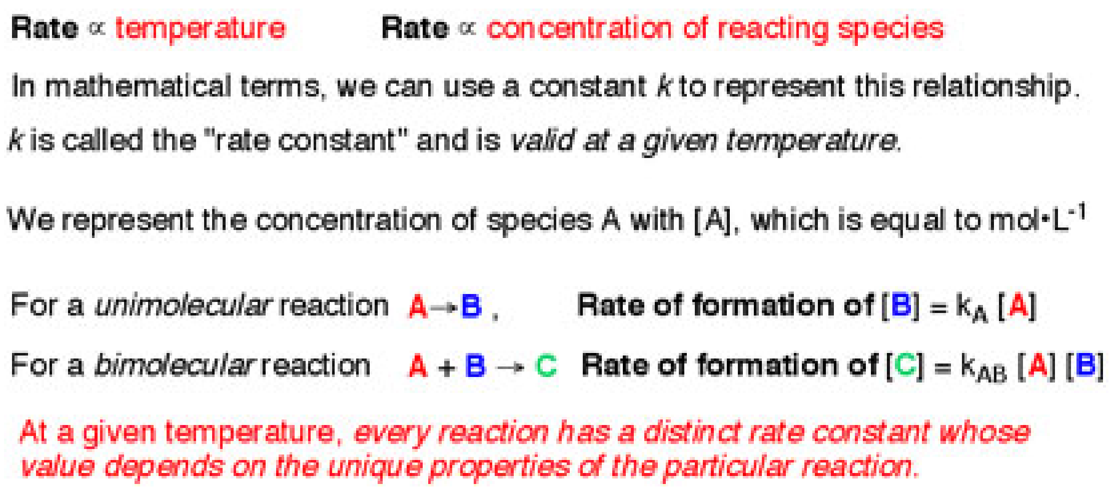
Rate $\propto$ concentration of reacting species

2. First and Second order reactions

Depending on the type of reaction, either one or two chemical species can be involved in the transformation. Reactions involving more than two chemical species are almost never seen due to the improbability of three species all colliding at the same time with the right energy.

The *order* of a reaction is the number of species involved in the reaction.

The *rate* of a reaction is how many molecules of a compound are being made per unit volume per second, as expressed in M/L•s. We can write an equation for this if we take the proportionality relationship, rate [fish] conc, and change into an equation by introducing a constant k called the rate constant. Every reaction has a unique rate constant that *is valid at constant temperature*, which makes sense since increasing the temperature will increase the number of collisions and lead to a different rate.



Rate ∝ temperature **Rate** ∝ concentration of reacting species

In mathematical terms, we can use a constant *k* to represent this relationship.

k is called the "rate constant" and is *valid at a given temperature.*

We represent the concentration of species A with [A], which is equal to $\text{mol}\cdot\text{L}^{-1}$

For a *unimolecular* reaction $A \rightarrow B$, **Rate of formation of** $[B] = k_A [A]$

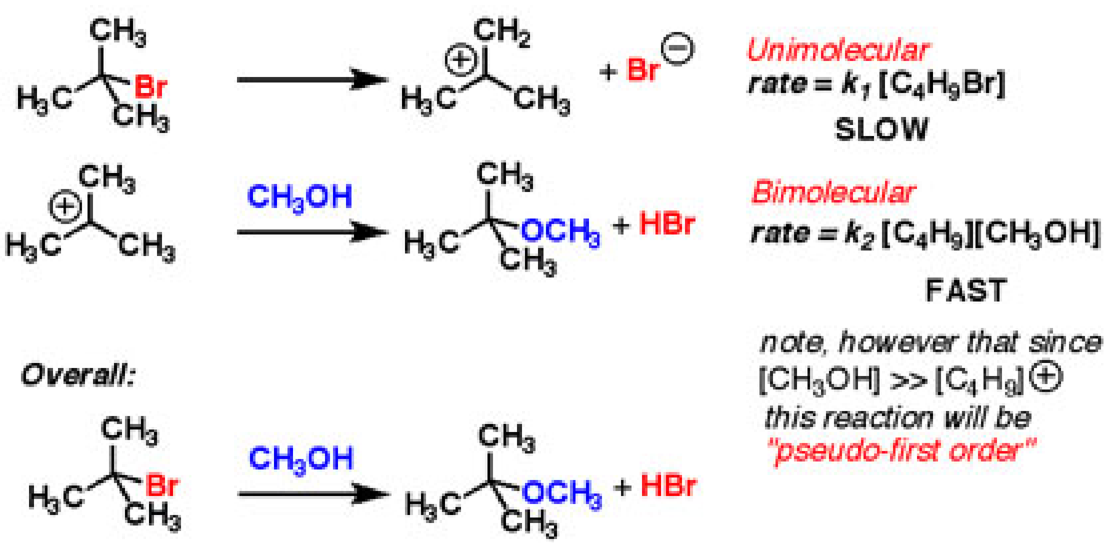
For a *bimolecular* reaction $A + B \rightarrow C$ **Rate of formation of** $[C] = k_{AB} [A] [B]$

At a given temperature, *every reaction has a distinct rate constant whose value depends on the unique properties of the particular reaction.*

For a *unimolecular* reaction involving just one species A, the rate will be equal to k[A] where [A] is the concentration of A in mol/L. For a bimolecular reaction A+B, the rate will be equal to k[A][B] where [A] and [B] are the concentrations of A and B.

For instance in the S_N1 reaction, which you'll learn about in Org 1, the first step is the breaking of a weak bond to provide a halide (bromide in this example) and a carbocation. This is a first order, unimolecular reaction. We can write a rate constant for this reaction as rate = k [A]

Concrete example: The S_N1 reaction:



note, however that since [CH_3OH] >> [C_4H_9]$^{\oplus}$ this reaction will be "pseudo-first order"

The rate law is equal to the rate equation of the ***slowest*** *step in the mechanism:*

rate = k_1 [C_4H_9Br]

Reaction rate is first-order in C_4H_9Br!

The second step involves reaction of the carbocation with a molecule of solvent (methanol for example) to provide an ether. This is a second order reaction. Note here, however, that since the concentration of methanol is extremely high (it is the solvent) its concentration will be unaffected by the small amount of methanol consumed in this reaction. So the reaction rate will really only depend on the concentration of the carbocation, C_4H_9. This is an example of a *pseudo-first order reaction*.

Although there are many examples of reactions that involve just one overall transformation (like HCl + NaOH to give water, for instance), you'll quickly discover in organic chemistry that *reactions like the SN1 that proceed through more than one step are much more common*. The sequence of reactions that lead to a particular product is referred to as the *reaction mechanism*.

3. The rate of a reaction is determined by the slowest step.

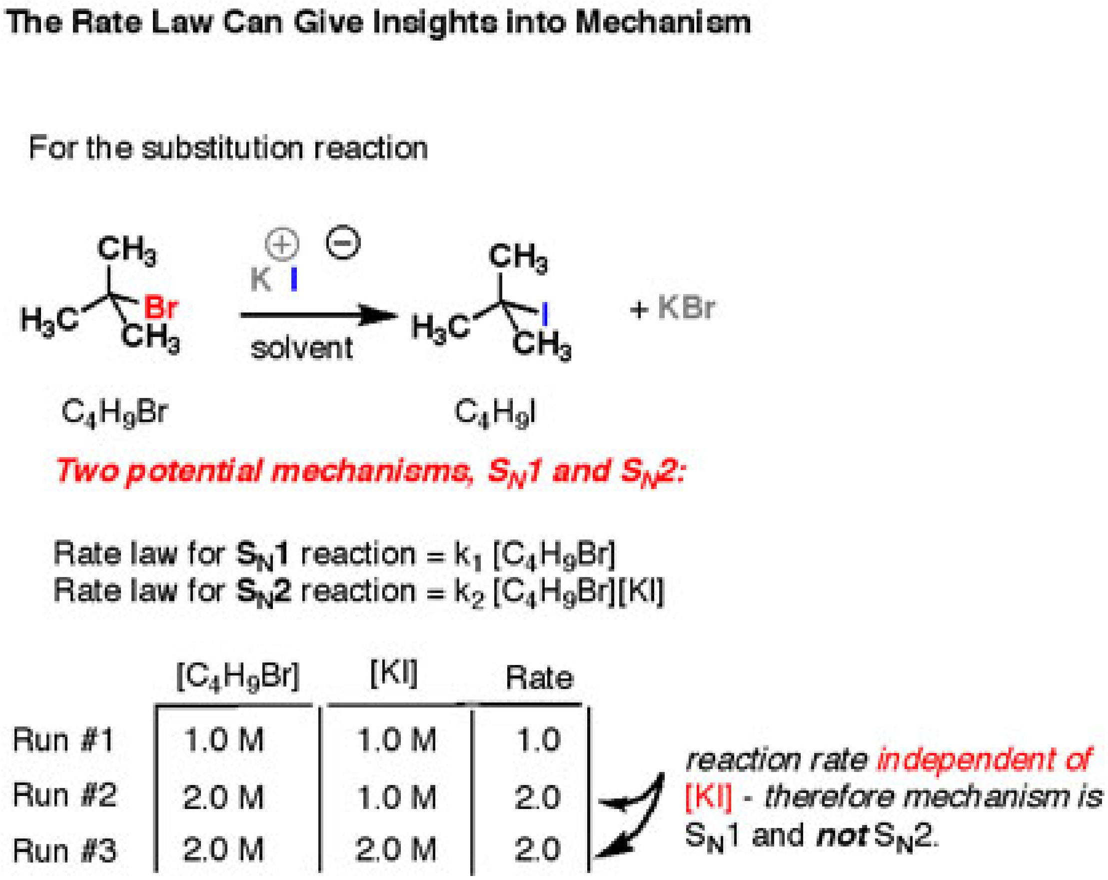
Here's the thing about reaction rates: they're determined by the rate of the slowest step. So in the example of the S_N1 above, since first reaction is the slow step, we can approximate the rate of the reaction by the rate law for this step. So the overall rate law of the S_N1 reaction, above, would be written rate [$C_4H_9OCH_3$] = k [C_4H_9Br]. In other words, the rate of formation of $C_4H_9OCH_3$ at a given temperature is going to be directly proportional to the concentration of C_4H_9Br and won't depend on the concentration of

CH3OH at all.

4. Rate laws can give insight into the mechanism:

Here's a useful tip: *we can actually use rate laws to give us information about mechanisms*. For instance, the SN1 reaction above is part of a general class of reactions called substitution reactions. There's a second type of substitution mechanism called the SN2 reaction. The rate determining step of the SN1 is unimolecular, and the rate determining step of the SN2 is bimolecular.

Let's change our example a bit from MeOH to the nucleophile I (–) (as a dissolved iodide salt like potassium iodide).



The Rate Law Can Give Insights into Mechanism

For the substitution reaction

Two potential mechanisms, S_N1 and S_N2:

Rate law for S_N1 reaction = $k_1 [C_4H_9Br]$
Rate law for S_N2 reaction = $k_2 [C_4H_9Br][KI]$

	$[C_4H_9Br]$	[KI]	Rate
Run #1	1.0 M	1.0 M	1.0
Run #2	2.0 M	1.0 M	2.0
Run #3	2.0 M	2.0 M	2.0

reaction rate independent of [KI] - therefore mechanism is S_N1 and ***not*** S_N2.

Both reactions will give identical product C_4H_9I . How can we tell which mechanism operates?Simple! If the rate changes when we change the concentration of iodide [I(-)] we will know it is the SN2, and if it doesn't change, it will be S_N1.

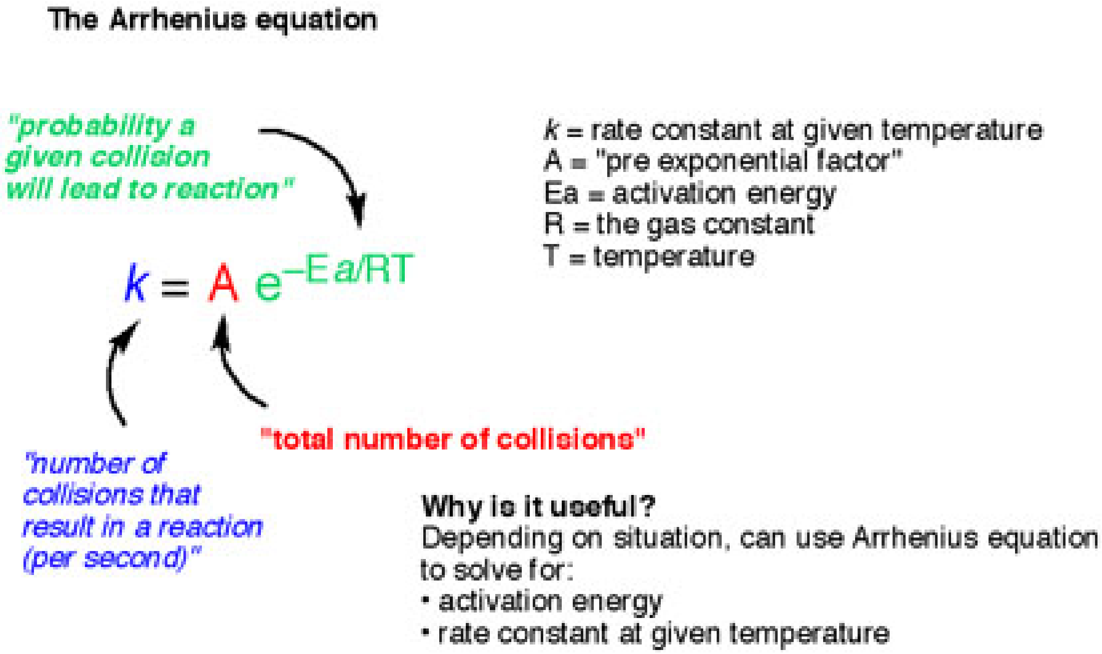
In this example, the lack of change of the rate when we double the concentration of [I (-)] would imply that the mechanism is S_N1 (or to be more precise, it would *disprove* the S_N2, but that's a whole other discussion).

4. The barrier to reaction is called the *activation energy.*

My second-year physical chemistry teacher made the concept of activation energy shockingly clear to us once by telling us that, in thermodynamic terms, the burning of human flesh to CO_2 and water was extremely thermodynamically favorable, but our continued presence in his classroom was a testament to the existence of activation barriers. The point he was trying to make was that the thermodynamics of a process tells you nothing about the rate.

The *rate* of a reaction depends on a value called the *activation energy*, which is essentially the amount of energy required to reach a transition state that will lead to the formation of product.

The relationship between the activation energy, the temperature, and the reaction rate has been worked out in the form of the Arrhenius equation:



The Arrhenius equation

$$k = A\,e^{-Ea/RT}$$

k = rate constant at given temperature
A = "pre exponential factor"
Ea = activation energy
R = the gas constant
T = temperature

Why is it useful?
Depending on situation, can use Arrhenius equation to solve for:
- activation energy
- rate constant at given temperature

In this equation k is the rate constant, T is the temperature, R is the gas constant, Ea is the activation energy, and the mysterious letter A is what's known as the pre-exponential constant.

What it boils down to is that the rate constant *k* is the number of collisions that result in a reaction per second, *A* is the total # of collisions occuring per second, and $e^{-Ea/RT}$ is the probability that any given collision will result in a reaction.

Here's a baseball analogy. Imagine you want to come up with an equation that will give you an estimate of the number of home runs hit in a given ballpark. You could come up with an equation that looked something like this:

# of home runs hit = [total # of balls hit] [probability ball has enough energy for a home run]

The "activation energy" in this case would be the distance from home plate to the outfield fences, which would be part of the "percentage" term (along with the height of the fence, presumably). As the fences get pushed back, the number of home runs will inevitably go down. If you wanted, you could find a way rearrange this equation so that you could figure out the distance to the fence if you knew the # of balls hit and the energy required to clear the fence.

The Arrhenius equation is very powerful and allows you to calculate the value of the activation energy as well as the value of the rate constant at different temperatures. In your course it's doubtful you'll be asked to go too deeply into the Arrhenius equation, but it's still important to appreciate its subtleties.

Final note - **a useful rule of thumb from the Arrhenius equation is that the rate of the reaction doubles for every 10 degree incease in temperature.**

From Gen Chem to Organic Chem, Part 13 – Equilibria

(The last lesson in the series. I wish I had this series done by the time school started for most people, but I initially thought I could cover the basics of Gen Chem in 6 posts and it just kept growing – planning fallacy in action.)

Chemical Equilibria

In chemistry, irreversible reactions get all the press: the familiar fires and explosions that are well represented on YouTube (*gratuitous explosion link: Thermite reaction vs. French automobile*). The thing is, not all reactions go to completion. Sometimes, the products of a reaction can react together and *regenerate* the starting materials, thereby setting up a *reversible* reaction. These are the types of reaction that are in action all around us and are so nondescript we never take notice. In any given moment, a mind-boggling number of protons in my Diet Coke (pH 3.39) are exchanging with water molecules, but since there is no net change, the process is practically invisible.

For the last subject in "From Gen Chem to Org Chem", we're going to talk about chemical equilibrium, which plays a *huge* topic in organic chemistry. A lot of the reactions you will learn about are equilibrium reactions, and this concept extends beyond chemical reactions to a whole number of processes, like how substrates bind to enzymes and even how molecules reversibly change their three-dimensional structure.

So what's chemical equilibrium anyway? Why is it important? What does it mean to say that we have chemical equilibrium?

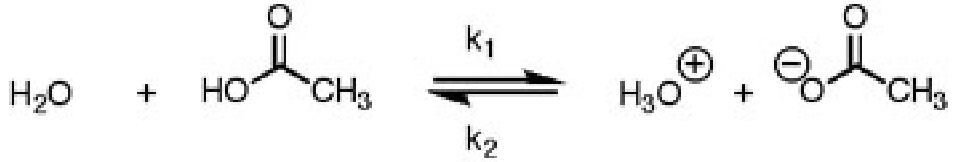
Let's start off with the basics:

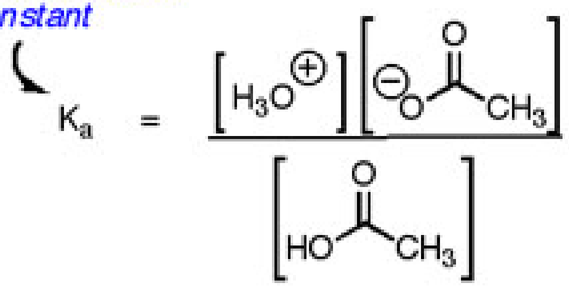
- A chemical equilibrium can only occur in a situation where there is a significant *reverse* reaction.
- When chemical equilibrium is established, there is no change in the concentrations of the reactants and products over time.
- At equilibrium, the delta G of the process is equal to zero. There is no driving force.

Probably the most important way you're introduced to equilibria in Gen Chem is through acid-base reactions. The reaction of the strong acid hydrochloric acid (HCl) with water produces H3O(+), which is essentially an irreversible reaction. In contrast, the weak acid acetic acid (CH3COOH) reacts with H2O to give H3O(+) and CH3COO(–), **but the reverse reaction can happen as well.**

Chemical equilibrium

A reversible reaction where the ratio of starting materials and products remains fixed. At equilibrium, there is no driving force for either reaction Therefore, $\Delta G = 0$





The further the reaction moves to the right, the higher the value of $[H_3O]^{\oplus}$ and the higher the value of K_a

$$pK_a = -\log K_a$$

Strong acids have *low* numbers (due to the negative sign in this equation)

e.g. pK_a of HOAc ---> 4

pK_a of H_2O ---> 15.7

It's important to note that *the relative strengths of acids are gauged by the value of this equilibrium constant*. This provides us with the extremely useful measure called pKa, which is equal to the negative log of the Ka for this reaction. pKa is a great way to compare the relative acidity of different molecules. As the acidity of molecules increase, this equilibrium will proceed further and further to the right. The result is that **strong acids have low pKas** (just as strong acids dissolved in water lead to low pH) and **weak acids have high pKas.]**

You probably don't think about it, but chemical reactions in equlibrium are operating around you all the time in such subtle ways you don't even notice. Inside each of the cans inside the pop machine near you, for instance, equilibria have been established between water and the (pressurized) carbon dioxide dissolved in solution, which forms carbonic acid; at the same time, molecules of carbonic acid are dissociating to provide carbon dioxide and water.

Equilibrium of carbon dioxide in water (i.e. what goes on in a closed can of Coke)

$$\underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2} \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3}$$

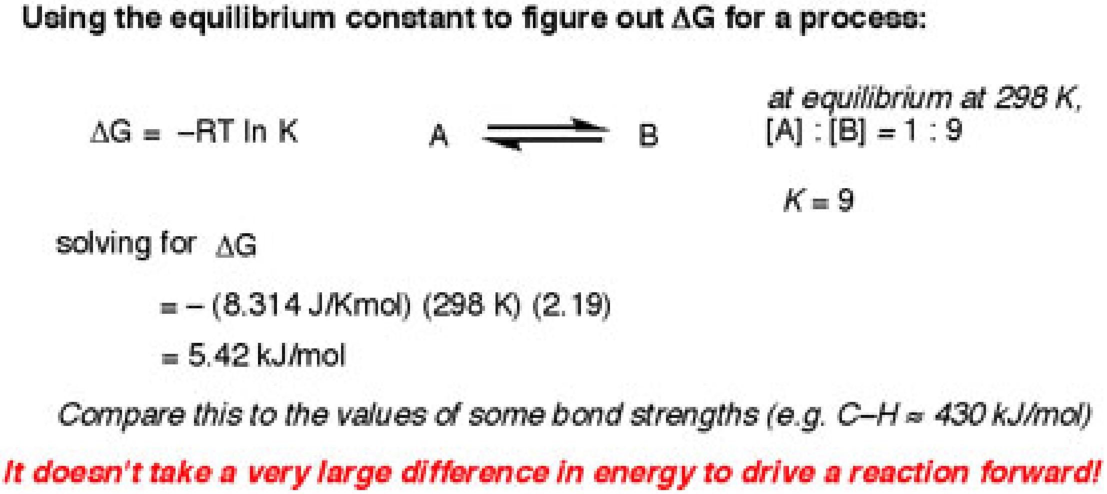
Net change in concentration of carbon dioxide, water, and carbonic acid: zero

The equilibrium constant can be used to determine Δ G.

At equilibrium there is no driving force. The ΔG for the reaction is zero. There is a really useful numerical relationship between the equilibrium constant and ΔG, called the van’t Hoff equation that we can use to solve for ΔG (if we know the equilibrium constant) or the equilibrium constant (if we know ΔG).

The van’t Hoff equation: $\Delta G = -RT \ln K$

In your organic chemistry class you’ll see many examples of reversible reactions that lead to mixtures. [One specific example is in the study of conformations, which are the three dimensional states of molecules formed through the reversible rotation of bonds]. This is how you use the equation to figure out ΔG, if you know K:



Using the equilibrium constant to figure out ΔG for a process:

$\Delta G = -RT \ln K$

$A \rightleftharpoons B$

at equilibrium at 298 K,
[A] : [B] = 1 : 9

K = 9

solving for ΔG

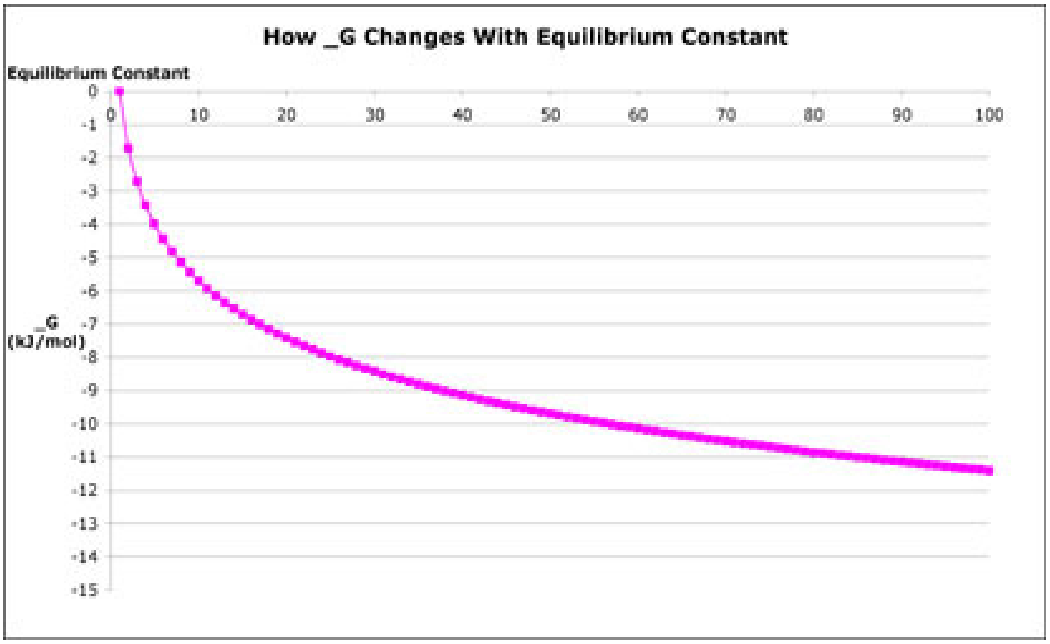
$= -(8.314\ \text{J/Kmol})\ (298\ \text{K})\ (2.19)$

$= 5.42\ \text{kJ/mol}$

Compare this to the values of some bond strengths (e.g. C–H ≈ 430 kJ/mol)

It doesn't take a very large difference in energy to drive a reaction forward!

You can even plug this equation into graphical form to see the relationship (if you can pardon the crappy Excel skills)



Look how steep the beginning part of that curve is! It's pretty amazing how small the energy difference is for a reaction that gives you a 9:1 mixture of products. When you think about it, 5.4 kJ/mol isn't very much – compare it to the strength of the C-H bond, for instance, which is 430 kJ/mol. For a reaction to give you a 99:1 ratio, the difference has to be only 11.4 kJ/mol.

The principle of Lé Châtelier

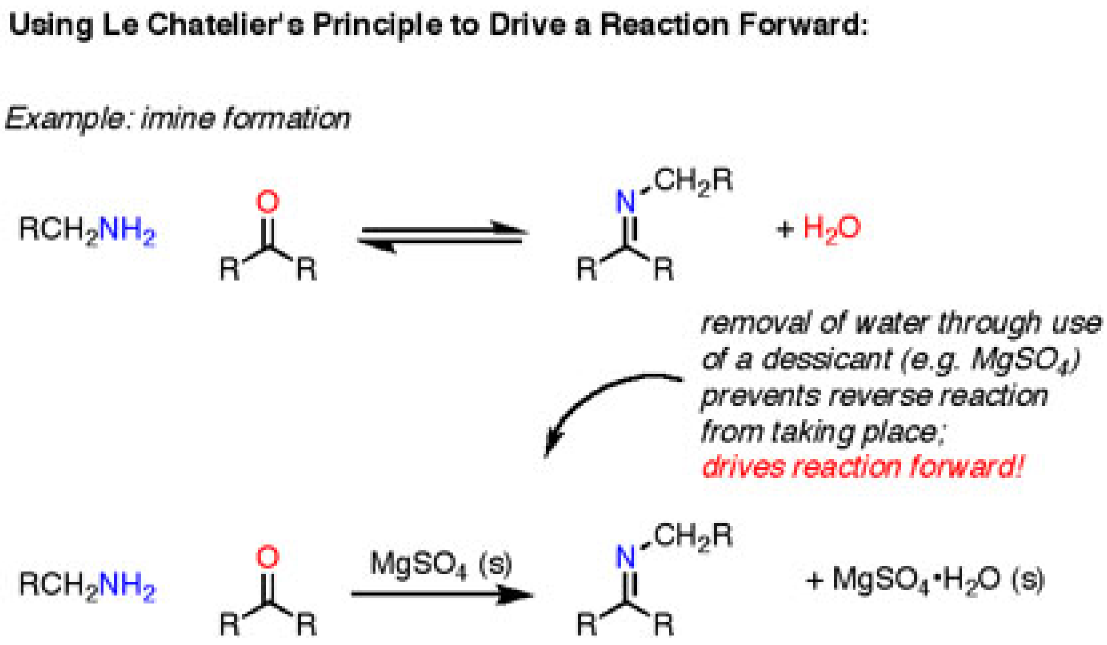
Here's the final key concept about equilibrium. Organic chemistry is a practical science. We're often concerned with transforming one compound into another. **We often want to shut down the reverse reaction to improve our yields of product.**

We can often find a way manipulate the equilibrium to provide us with products that we desire. You'll often hear this described as *driving the reaction forward*. This is done by removing one of the byproducts of the forward reaction, hence preventing the reverse reaction from occurring.

Here's an example. Treating an aldehyde with an amine generates a compound called an *imine* as well as a molecule of water. This reaction is reversible; water can react with the imine to give us back the product.

Here's the key point. If you can find some way to remove the water here, you essentially shut down k2 (the reverse reaction). What's that going to do to the overall reaction? It will *proceed in the forward (rightward) direction until equilibrium is re-established*. Which is never, because we've added the dessicant. Result: one product, instead of a mixture.

Practically, removal of water can be done in several ways, one of them through the addition of a substance (called a *dessicant*) that will react irreversibly with water and therefore remove it from the equation. Magnesium sulfate ($MgSO_4$) is just one example – it forms a hydrate.



The name for this concept should be familiar to you: it's called Le Chatelier's principle.

You'll encounter lots of examples of Le Chatelier's principle in organic chemistry, since you'll encounter a lot of reversible reactions (some in Org 1, but a lot in Org 2).

Bottom line: If you understand a reaction and its products, you can choose conditions that allow for the removal of products that will thereby prevent an equilibrium from establishing itself and drive the reaction toward the products you desire.

This is the last lesson in "From Gen Chem to Organic Chem"! I hope you'll find it a useful resource and guide as you make the transition from the calculation-heavy course that is Gen Chem to the more qualitative realm of organic chemistry. I'll do a wrapup in the next post.

From Gen Chem to Organic Chem, Part 14 – Wrapup

So what are the key concepts from General Chemistry that you need to apply to Organic Chemistry, going in? This past summer, I saw people asking this question on places like Yahoo Answers and SDN all the time. So I decided to do something about it. It was embarrassing how much 1st year chemistry I'd completely forgotten, but putting something like this together was helpful to solidify it again. If you really want to learn something, try teaching it – that goes for anything, by the way.

Anyway, from the perspective of someone going into Organic Chemistry, these are the key lessons I'd take away from General Chemistry:

- atoms are built up from protons, neutrons, and electrons, and the energies of electrons are **quantized** – they ascend not gradually (like a ramp) but in discrete levels (like stairs)
- **electrostatic attraction and repulsion** is the fundamental force that underlies all of chemistry, from the octet rule, the formation of chemical bonds, and even in determining periodic trends in properties like **ionization energies** and **electronegativity**
- there is a driving force for atoms to satisfy the **octet rule**, and **Lewis structures** are the tool we use to visualize the number of electrons surrounding each atom in a molecule.
- **chemical bonding** ranges across a scale from ***ionic*** character (where there is vastly unequal sharing of electrons) to ***covalent*** character (in which electrons are shared equally)
- there are important chemical behaviors called ***acidity*** and ***basicity*** and two important definitions of each – in the **Brønsted definition**, an acid is a species that *donates a proton* (H+) and a base accepts a proton; in the broader **Lewis definition**, an acid *accepts an electron pair* and a base donates an electron pair.
- **thermodynamic*s*** is the study of the exchange of energy between atoms/molecules and their environment; using standard tables, we can use Hess' law to calculate the **enthalpy** (heat) change for a reaction, or if tables are unavailable, approximate it by making calculations based on the energies of the bonds broken and formed. The measure of whether a reaction is favorable is the **Gibbs energy**, ΔG – which takes **entropy** into account – and as temperature is increased, the entropy factor will begin to favor processes that lead to an increase in entropy, like gas formation and fragmentation reactions.
- the **rate** of a chemical reaction depends on 1)*temperature*, and 2) the concentrations of the reactants in the slowest step of the **mechanism** (the *rate-determining step*). By studying reaction rates we can gain insight into reaction mechanisms, as

well as determine the **activation energy** of a process.

- reactions which proceed with no net change in the concentration of reactants or products are in **equilibrium**. We can use the equilibrium constant to figure out the ΔG for a process using the van't Hoff equation. Small differences in ΔG can lead to huge differences in the direction of the equilibria! We can also use Le Chatelier's principle to manipulate chemical equilibria to drive it in the direction we desire.

Here's a list of all the posts:

"General Chemistry and Organic Chemistry: How Are They Different?"

"From Gen Chem to Organic Chem, Part 1: The Atom"

"From Gen Chem to Organic Chem, Part 2: Electrons and Orbitals"

"From Gen Chem to Organic Chem, Part 3: Effective Nuclear Charge"

"From Gen Chem to Organic Chem, Part 4: Chemical Bonding"

"From Gen Chem to Organic Chem, Part 5: Understanding Periodic Trends"

"From Gen Chem to Organic Chem, Part 6: Lewis Structures, A Fable"

"From Gen Chem to Organic Chem, Part 7: Lewis Structures"

"From Gen Chem to Organic Chem, Part 8: Ionic and Covalent Bonding"

"From Gen Chem to Organic Chem, Part 9: Acids and Bases"

"From Gen Chem to Organic Chem, Part 10: Hess' Law

"From Gen Chem to Organic Chem, Part 11: The Second Law of Thermodynamics"

"From Gen Chem to Organic Chem, Part 12: Chemical Kinetics"

"From Gen Chem to Oranic Chem, Part 13: Equilibria"