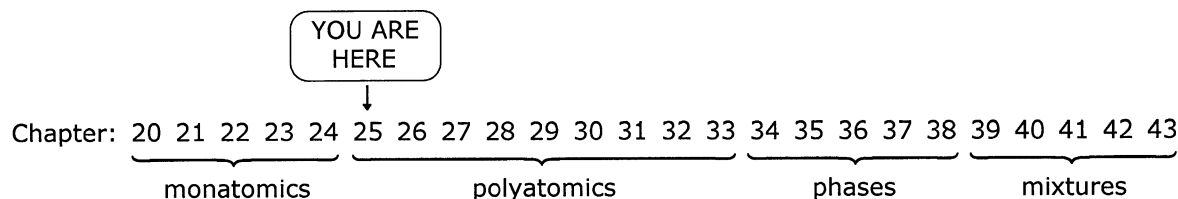


Chapter 25

BONDING RELATIONSHIPS

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Having completed five Chapters of monatomic things, I believe we are ready for the next step. We are going to start bonding.



Bonding gives us compounds. It also gives the elemental forms of most elements. Most elements but not all. Here's how we first started into bonding in Chapter 2.

“ The only neutral substances which are monatomic near normal, Earth-surface conditions are the noble gas elements of Group 18, at least He through Rn. Atoms of these elements don't like to join with other atoms of any kind, including their own kind. Thus, a helium balloon is full of individual helium atoms flying around inside...

All other substances on the planet exist as polyatomic chemical units composed of two or more atoms joined together. Except we don't say joined, we say bonded. We call the connection a "chemical bond". Chemical bonds are due to electrons. (Electrons do chemistry, remember?) There are different kinds of chemical bonds and we will talk a lot more on this in later Chapters. Chemical bonds can hold two or more atoms together in specific chemical units or they can extend over zillions of atoms in one, two or three dimensions to form a bonded "network" of atoms.

I can't tell you how important that last sentence is. Let me say it again.

CHEMICAL BONDS CAN HOLD TWO OR MORE ATOMS TOGETHER IN SPECIFIC CHEMICAL UNITS OR THEY CAN EXTEND OVER ZILLIONS OF ATOMS IN ONE, TWO OR THREE DIMENSIONS TO FORM A BONDED NETWORK OF ATOMS.

This one sentence sets the stage for every compound and every polyatomic elemental form. Don't forget it. ”

I said all of that in Chapter 2. Now, we will see how this works in more detail. We will see bonding in more detail. We will see chemical units in more detail.

From this point, we are embarking on a trail of nine Chapters about bonding and about polyatomic things in general. This is very important stuff and there is much ground to cover. We begin with bonds and the many important aspects of bonds. Then we go into polyatomic units and we see the different roles for electrons in them. We also look at how polyatomics look: in other words, we look at their shape. Then we talk about the kinds of orbitals used for bonds; many of these orbitals are no longer the simple *s*, *p*, *d*, etc. types which are found in monatomic atoms and ions.

As we go, our emphasis will be on covalent bonds and covalent chemical units. We will briefly return to ionic bonding and we will now place it in its correct context relative to covalent bonding. We will also discuss metallic bonding, although we won't get to this until the end of this series in Chapter 33. Of the three bond types, covalent is somewhat central, as we shall see, but all three types are vastly important.

As always, remember: electrons do chemistry. Which electrons? The ones that are the most available: the valence electrons.

Speaking of valence electrons, we need to introduce Lewis. Well, we don't really need Lewis. We need his dots. And some dashes, too.

25.1 -●● --- - ●●●

Dots? Yes, dots. The system is called "dot notation". Lewis dot notation is an extremely useful system for dealing with the distribution of valence electrons within a covalent, polyatomic unit. It actually goes by various names, such as Lewis electron dot system, Lewis structures, electron dot symbols, etc. All of these refer to the same thing. The system portrays each valence electron as a dot or, as we shall see later, it portrays a pair of electrons as a dash. It provides a means of determining how many

electrons are associated with what bonds and with what atoms in the polyatomic unit. It's a nifty system, once you get the hang of it. No, it's not perfect, but it's very good. Not only does it tell us a lot about bonds and things but it's also the starting point for methods which determine shapes and polyatomic orbitals, as we shall see later. There is much to Lewis and this will take a while to cover.

We will start into Lewis at this time as it applies to monatomics. The whole purpose of this is simply an introduction. Lewis really doesn't do much for monatomics and it's fairly boring. We already know about electrons in monatomics from the last five Chapters and the Lewis system does nothing to add to this. The overwhelming value of the Lewis system lies in covalent polyatomics and we will get to these later. I just want to do a simple introduction to Lewis right now, and monatomics are the easiest.

A Lewis structure for a monatomic atom or ion begins with the element's symbol. We then place dots around the symbol, one for each valence electron. For a monatomic, the dots are located in four quadrants: above the symbol, to the right of the symbol, below the symbol and to the left of the symbol. You can use any quadrant in any sequence but you must enter one dot into each of the four quadrants before doubling up. The quadrants connect to the atom having four valence orbitals, namely one *s* and three *p*'s. There is also a connection between doubling up the dots and pairing electrons in orbitals. I point this out FYI but we are not doing orbitals right now. I'm saving them for later.

Let me show an example of Lewis dot notation for a monatomic. Let's do a boron atom. Boron is in Group 13 so it has three valence electrons. We write the symbol, then we place three dots around the symbol in separate quadrants. You can use any three of the quadrants, and this allows four possible answers. All four are correct Lewis structures for a boron atom.



Let's do silicon, Group 14: four valence electrons. You only have one option, as shown $\cdot \overset{\cdot}{\underset{\cdot}{\text{Si}}} \cdot$ at right.

Let's do arsenic from Group 15: five valence electrons. We put these five into the four quadrants. This means we must double up in one quadrant. It doesn't matter which one, so there are four possible answers. I'll do one. You fill in the other possible answers.



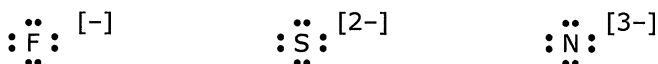
This is really all there is to Lewis structures for monatomics.

We need to go back to noble gas configuration for a moment. Except for He, all noble gases have eight valence electrons. They get eight dots. For example, krypton is shown at left. Notice that the very favorable noble gas configuration is reflected in dot notation as eight electron dots. Eight $\cdot \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Kr}}} \cdot$ represents the optimum usage of valence *s* and *p* orbitals. Even when we get into polyatomics, eight will still represent the optimum usage of valence *s* and *p* orbitals although some electrons are shared. The bottom line is this: the number eight is really important. In fact, this gives rise to the "octet rule". The octet rule says that there is a distinct preference for an atom in a Lewis structure to be associated with eight electron dots. Notice the wording: I said that there is a distinct preference; I didn't say there's an absolute requirement.

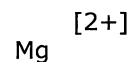
What about He? It only has two electrons and they're both in 1*s*, which is the only valence orbital. Since He only has one valence orbital, it only uses one quadrant in its Lewis structure. Since both electrons are in the single 1*s* orbital, then both dots are in the one quadrant. Although not an octet, this is still optimum usage of helium's valence orbital. $\text{He} \cdot \cdot$

Monatomics are very limited in following the octet rule, since most neutral atoms do not have eight valence electrons. The greatest value for the octet rule will be seen when we do polyatomics, but even then there are exceptions and there are trade-offs. That's later. Monatomics are now.

The above examples are neutral atoms. We can also do dots for monatomic ions; this gets us more octets. The common anions from the *p*-block all have noble gas configurations and they all have octets. For example, take a look at the Lewis structures for fluoride, sulfide and nitride.



On the other hand, cations look different in their Lewis structures. They look different because they lost valence electrons relative to their neutral atoms, which means they lost dots. If the cation has a noble gas configuration, it lost all valence electrons and it has no dots at all in its Lewis structure. Take a look at the Lewis symbol for magnesium ion on the right. No dots. It's still noble gas configuration (which is the important part), but it shows no dots.



OK, this is as far as I want to go with Lewis right now. Again, its real value lies with polyatomic things. We will take care of some other ionic business first and then we will come back to Lewis. I just wanted to introduce this much in order to have it in place when we get to the nit and the grit. We are now ready to proceed into bonding; we will first return to ionic bonding.

25.2 More ionic

Of the various bonding types, ionic bonding is perhaps the easiest to understand. We did the basics for ionic bonding in Chapter 3:

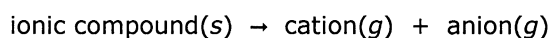
“ Ionic bonding is simply the +/- attraction between cations and anions. Pluses like minuses and vice versa, so cations and anions naturally want to get together. That's ionic bonding. The bonding extends in all three dimensions throughout the sample. Each cation is next to or near anions and each anion is next to or near cations. ”

This stuff from Chapter 3 is still the most important part about ionic bonding. The only things to add at this time are the factors which influence the strength of ionic bonds. When I refer to the strength of ionic bonds, I mean the strength of the attraction between cations and anions in the ionic solid.

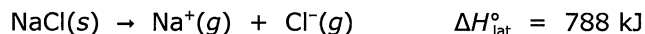
So what makes cations and anions more attracted to each other? It's simple: smaller sizes and higher charges. Before I go into that, we need to bring in some way to compare these things.

Comparisons of ionic bond strengths are not necessarily straightforward because there are a number of complications involved. There are some general indicators which are commonly used for this purpose, although they may not be perfect. One decent indicator is "lattice enthalpy". The word "lattice" refers to the arrangement of the chemical units within a crystal; this meaning is related to the normal dictionary use of "lattice", which refers to a pattern of things. When cations and anions come together to make a crystal, there are different patterns which they can adopt depending on the ratio of cations/anions, their sizes, etc. These patterns are the lattice. (We will see some examples of different lattices later in Chapter 38.) For a specific lattice, there will be some energy associated with that pattern. That energy is the "lattice enthalpy" for that compound in that pattern.

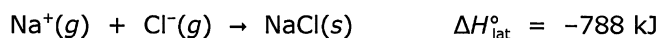
Technically, lattice enthalpy is the enthalpy for the reaction which pulls apart all the ions from the solid and separates them in the gas phase.



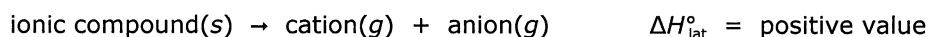
The reason for specifying gas phase is that the gas phase represents a state of no interaction between chemical units. The standard lattice enthalpy is the lattice enthalpy for this process starting at standard conditions and ending at standard conditions, and is symbolized as $\Delta H_{\text{lat}}^{\circ}$. Here is an example using NaCl.



OK, time out. I need to point out that there are a number of inconsistencies in the terminology which is used across the various sources of this information. Firstly, there is a lattice enthalpy and a lattice energy, and they are technically different but the numbers are very close; we are doing lattice enthalpy here. Secondly, some sources define the lattice enthalpy process as the reverse of the above equation, giving

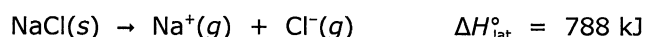


which results in a negative $\Delta H_{\text{lat}}^{\circ}$. Be aware of these inconsistencies if you consult different sources for information. We are exclusively using the positive kJ's format for our lattice enthalpy here.



This ends the time out.

Returning to the first NaCl equation,



you can see that lattice enthalpies can run high, although this value for NaCl is actually quite modest. For other ionic compounds, the lattice enthalpies can easily run into thousands of kJ. These are very expensive processes to do and this is testimony to how strong ionic bonds can be. For stronger ionic bonds, you must pay more kJ's in order to pull everybody apart. Here's the significance for our purposes: HIGHER LATTICE ENTHALPIES indicate STRONGER IONIC BONDS.

Now we will compare the strengths of ionic bonds by using lattice enthalpies. We return to the two factors which I mentioned above for ionic bond strength: ion size and ion charge.

Smaller ions can get closer together and they have a more concentrated charge. This makes everybody happier, since both factors strengthen the attraction between cations and anions. SMALLER IONS can form STRONGER IONIC BONDS which is reflected in HIGHER LATTICE ENTHALPIES. Let's compare some values for some simple ionic compounds, using Group 1 cations and Group 17 anions as

LiF	1,047	examples. On the left, we have the lattice enthalpies	LiF	1,047
NaF	928	(in kJ) for the fluorides of alkali metal cations. As	LiCl	862
KF	827	the cation gets bigger going down Group 1, the	LiBr	818
RbF	793	lattice enthalpy decreases. This is consistent with	LiI	762
CsF	757	weaker ionic bonds. Now consider the list which is		

on the right for lithium halide salts. In this case, it's the anions which are getting bigger as we go down the list: the lattice enthalpies are weaker for bigger ions.

Now consider the effect of charge on the strength of ionic bonds. Ions with higher charges will have greater attraction to their opposites. If you're a cation, then you'll be more attracted to an anion of 2- charge than to an anion of 1- charge. Likewise, if you're an anion, you'll be more attracted to a cation of 2+ charge than to a cation of 1+ charge. HIGHER CHARGES give STRONGER IONIC BONDS as reflected in HIGHER LATTICE ENTHALPIES. I'll do one comparison along this line: we'll compare lattice enthalpies for NaF and CaO. NaF is a 1+/1- combination of ions, while CaO is a 2+/2- combo. (I chose these two compounds since the cation sizes are similar and the anion sizes are similar; this avoids a size effect for purposes of this comparison.) The lattice enthalpy for NaF is 928 kJ, as given above. The lattice enthalpy for CaO is a whopping 3,399 kJ. Needless to say, charge has a humongous effect.

All in all, ionic bonds can be very strong. This accounts for some of the more obvious properties of ionic compounds. For example, they tend to be solids at normal temperatures. What's the significance of this? Keep in mind that these are ionic network compounds and that the ionic bonds extend in three dimensions throughout the solid. You have very strong bonds holding everything in place in three dimensions, and this locks everything in as a solid phase. Yes, you can melt these things, but it takes a lot of thermal J's to do this. Even normal table salt, NaCl, melts at a high temperature of 801 °C. That's 1,470 °F. That's toasty. Real toasty. In fact, you're glowing at that temperature. Compounds with higher charges can melt at extremely high temperatures: for example, CaO melts at 2,580 °C. By the way, melting temperatures are sometimes used as another indicator of ionic bond strength but there are more complications with this than with lattice enthalpies. Nevertheless, the generalities are OK: stronger ionic bonds are often reflected in higher melting temperatures.

Despite the fact that ionic bonds are so very strong and that ionic solids have high melting temperatures, many ionic compounds do crack somewhat easily. You may well know that rock salt shatters and breaks readily. If the bonds are so strong in three dimensions, why do they break so easily? Well, the bonds are so strong as long as you keep the cations and anions in their proper places relative to each other. If you start smacking the solid, you can deform it and this can move cations and anions away from each other and toward their own kind. That's bad news. All of a sudden, you introduce cation-cation repulsions and anion-anion repulsions; the solid can't handle this and cracking can result.

This is as far as we need to go right now with the ionic bond. Don't lose sight of it, since we'll come back to it later in this Chapter. We will be tying together many things which we've touched on so far.

25.3 Covalent bonds

The whole thing about covalent bonding started in Chapter 3.

“ The covalent bond is a chemical bond which involves sharing electrons. Each atom of the bond shares electrons with the other atom of the bond. It is this mutual sharing which holds the atoms together in the bond. ”

At that time in Chapter 3, we used HF as the first example of something with a covalent bond.

“ In our HF molecule, the share involves two electrons but the number of electrons shared in other covalent bonds can vary up to twelve. By far, the most common numbers of shared electrons are two, four and six. Here's another feature: the share can actually occur over three or more atoms. How do you tell how many electrons are shared over how many atoms? Don't worry about that right now. We'll do that later, starting in Chapter 25, when we venture into more details of the covalent bond. ”

Later is now. From here through Chapter 33, we will cover numerous aspects related to covalent bonds. Let me recap some of the points from Chapter 3 and add a bit more that we have picked up since then.

- ▶ The essential feature of the covalent bond is that it involves shared electrons. The electrons which are most available for sharing are the valence electrons.
- ▶ Most commonly, it will be two, four or six electrons that are shared and that's what we'll be covering. Sharing more than six electrons is primarily limited to bonds between transition metal atoms. Those are more limited cases; I mention them but I won't detail them. It is also possible to share an odd number of electrons but those cases are less common.
- ▶ Most cases which we discuss will involve sharing between two atoms but we will also talk about sharing between three or more atoms.
- ▶ How will you know how many electrons are shared and between which atoms? All of that is in the Lewis structure. That's part of what makes those dots so valuable.

Keep these points in mind.

In Chapter 10, we went deeper into the notion about sharing electrons, and we saw that the sharing is usually not even.

“ Yes, a covalent bond involves shared electrons, but the fact is that the sharing is usually not 50-50. In HF, the sharing is very uneven with F taking more of the share; that leaves H short in the share. So it's not 50-50. What is the share? The actual numerical distribution doesn't matter at this point. It only matters that the share is not even. MOST COVALENT BONDS DO NOT INVOLVE AN EVEN SHARE. This has serious consequences.

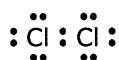
Remember that electrons carry negative charges. If the bond electrons are not evenly distributed over the bond then the charges overall are not evenly distributed either. For hydrogen fluoride, the end of the molecule towards F has more than 50-50 of the bond share. This makes the F end a bit negative overall. The end of the molecule towards H has less than 50-50 of the bond share. This makes the H end a bit positive overall, because now there's not enough electron charge to offset the hydrogen's nuclear charge.

This uneven distribution of charge is called "polarity". The adjective is "polar". These terms can be applied to a covalent bond or, in general, to an entire molecule. We say that HF has a polar covalent bond. The two ends of the bond carry unbalanced charge. The actual value of the charge is not important for our purposes, but typically the charges due to a bond polarity are some fraction of ± 1 . We call these "partial charges" because they are not a full charge. WARNING! Don't confuse these with ion charges: those are completely different. Remember the distinctions. ”

All of that was in Chapter 10. This business about uneven sharing is extremely important, as we shall see. It affects physical properties, such as why some things are solids, liquids or gases. It affects reactivity, since the partial charges of a polar bond can greatly influence how the atoms in the bond react. As we also saw back in Chapter 10, polarity contributed to the weirdness of water itself. I will also mention that some bonds actually do have an even share and we shall see examples of this. You yourself will even be able to determine which bonds share evenly and which do not.

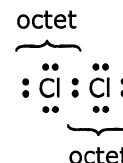
All of these things about sharing will become more evident as we go through this and the next eight Chapters. And, of course, there will be some new stuff, such as orbitals. Not just more atomic orbitals; we will also be doing bond orbitals. These are where the shared electrons reside in the covalent bond. Like atomic orbitals, bond orbitals are field regions but these bond orbitals surround two or more atoms and hold the polyatomic unit together. In addition to bonding orbitals, there are still other kinds of orbitals in polyatomics. We will be tying all these things together. There is much to do and much ground to cover, and much of it is interrelated. We are connecting more portions of the Grand Puzzle.

As we go, the Lewis dot system is an essential tool. I will now take this up one more notch. We will now do a few simple diatomics in order to introduce the basics of Lewis structures for polyatomic things. I will also introduce more aspects of the role of valence electrons in bonding.



The first example is chlorine, in its normal elemental form of diatomic molecule. The Lewis structure for Cl_2 is shown at left. The two dots between the Cl's represent shared electrons. In every Lewis structure, all electron dots between atoms are shared by both atoms. A Cl atom by itself has seven valence electrons. In a Cl_2 molecule, there are fourteen valence electrons in the molecule and there are fourteen dots in the Lewis structure. Two of the fourteen are shared and these make up the covalent bond.

As shown on the right, both Cl atoms in the molecule have an octet. Notice that both atoms are associated with eight dots, although two dots are shared. FOR PURPOSES OF AN OCTET, SHARING DOES NOT MATTER. It only matters that the atom is associated with eight, regardless of how many are shared.

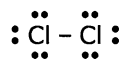


With respect to bonds, we commonly speak in terms of how many electron pairs are shared between the two atoms. (Why pairs? It's got to do with orbitals, which we haven't gotten to yet. For now, I'll just point out that the orbitals in polyatomics can hold at most two electrons, just like any other kind of orbital. Thus, pairs are handy to work with.) We need a new term here: "bond order". Bond order is the number of electron pairs which are shared between two atoms. Both Cl's in this example share one pair, so the bond order is one. We can also say the bond is a single bond.

What about the other electrons in the molecule? There are twelve electrons which are not involved in sharing. These make no significant contribution to bonding and, as such, these are called "nonbonding pairs". A more common term is "lone pairs". Most cases of lone pairs are associated with one (lone) atom; on the other hand, some are associated with more than one atom. I will frequently abbreviate lone pair as LP to make things easier. In our Cl_2 molecule, each Cl atom has three LPs.

In conclusion, here's what the Lewis structure tells us about Cl_2 : the molecule is held together by a single bond and there are three lone pairs on each Cl atom.

There's an alternate representation within the Lewis system which uses dashes for dot pairs. Dashes can be used for bond pairs only or they can also be used for lone pairs. For our purposes here, I will use them only for bond pairs. By this scheme, the Lewis structure for Cl_2 is shown on the left.



There's nothing new to say about it; this is just another way to draw it. Just remember that a dash is a pair.

Let's move on to another example: oxygen. Diatomic O_2 . The Lewis diagram for O_2 is below at the left for the version with dots only and at the right for the version using bond dashes. Notice that four electrons are now shared. (Remember what I said upstairs: all electron dots between atoms are shared by both atoms.) Notice also that each O $\text{:}\ddot{\text{O}} = \ddot{\text{O}}\text{:}$ has an octet although four electrons of the octet are shared. Since four electrons are shared, this means there are two bond pairs. So, the bond order is two; we can also say that the bond is a double bond. There are also lone pairs in the molecule: each O atom has two LPs.

Let me make a minor point here. When we did monatomics, I said the dots are shown in quadrants around the atom's symbol. For polyatomics, this need not be the case. I drew the dots in quadrants for Cl_2 above but not here for O_2 . Lewis structures for polyatomics need not stick to quadrants.

Next example. Diatomic N_2 . The Lewis diagram for N_2 is at the lower left with dots only and on the right using bond dashes. Notice that six electrons are now shared. Once again, both atoms have an octet but now six electrons of the octet are shared. There are three shared pairs and the bond order is three; or, we can say that the bond is a triple bond. In addition, each N has one LP. $\text{:N} \equiv \text{N:}$

These three examples illustrate some very important aspects of Lewis. You might want to read through them again.

Here's another tad bit of terminology: bonds with orders greater than one are collectively called "multiple bonds". Double bonds are multiple bonds. Triple bonds are multiple bonds. Quadruple bonds are multiple bonds. Quintuple bonds are multiple bonds. Sextuple bonds are multiple bonds. Yes, bond orders of four to six apply for eight to twelve shared electrons but, as I mentioned upstairs, we won't go into detail for those.

By the way, I will not continue showing two Lewis versions all the time. We will primarily use the version with dashes for bonds.

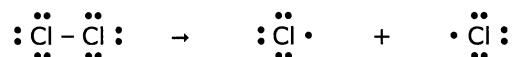
This concludes this level of Lewis for now. We need to discuss a few aspects of covalent bonds, and we have enough of the Lewis system for doing this at this time. We will resume with Lewis in Chapter 26.

25.4 Order! Order!

A bond's order is a very important aspect of that bond. It affects various properties of the bond related to its physical and chemical characteristics (although other factors can also come into play). For now, we look at two bond properties which are affected in part by bond order: bond strength and bond length.

First, bond strength.

The strength of covalent bonds is measured as a "bond energy". Typically, a covalent bond energy is the energy required to break one bond in some polyatomic unit, giving an even split of the shared electrons. For example, the bond energy for the single bond in Cl_2 is the ΔH° for the following process. Notice that each Cl ends with half of the shared electrons.



Since you are pulling bonded atoms apart, this will cost you some amount of energy and all such values of ΔH° are positive. It will cost you more kJ's for stronger bonds and less kJ's for weaker bonds, but it will always cost you. Covalent bond energies are typically in the range of hundreds of kJ's per mole. Below are some representative values, all in kJ per mol.

H-H	436	S-H	339	C-O	352	N-N	161	F-F	153	S-S	213
C-H	413	H-Cl	432	C-F	441	N-F	270.	F-Cl	254	S-Cl	250.
N-H	391	H-Br	366	C-S	259	N-Cl	200.	Si-Si	177	S-Br	212
O-H	463	H-I	299	C-Cl	328	O-O	139	Si-O	369	Cl-Cl	243
H-F	563	C-C	348	C-Br	276	O-F	185	Si-F	541	Br-Br	193
P-H	320.	C-N	292	C-I	240.	O-Cl	203	Si-Cl	359	I-I	151

These are typically averages derived from a number of different compounds which contain that particular bond type. The exact values can vary a bit depending on the specific molecule that the bond is in, but the averages do illustrate how some bonds are weaker or stronger than others. Notice that the numbers jump around a bit. Certain atoms like to bond to certain other atoms and form strong bonds; on the other hand, other combinations are not as strong. For example, Si and F love to bond together and Si-F bonds are very strong. So also is the bond between H and F. In fact, the Si-F and H-F bonds are among the strongest of all single bonds. C-F is not as good but it's still quite strong. O-F is much weaker. F-F is worse than that. How can you tell which atom combinations give strong bonds and which give weak bonds? At this stage, there's no simple way of knowing this. Unlike the case for ionic bonding earlier, size does not help here. If you want some examples, look at the numbers for Si-F, H-F, C-F, O-F and F-F. The bond strengths and the sizes of the bonded atoms just don't follow much of a pattern.

Now, let's bring order into the picture.

Bond order has a very big affect on bond strength. Keep in mind that it is the sharing of electrons which makes up the covalent bond. Shared electrons hold atoms together and the more the better: for the same two atoms bonded together, sharing six electrons is better than sharing four electrons which is better than sharing two electrons. In other words, stronger bonds will result when more electrons are involved in the share. **BONDS ARE STRONGER (BOND ENERGIES ARE HIGHER) when the BOND ORDER IS HIGHER.** Let's bring in some numbers (kJ) here for various bond types.

C-C	348	C=C	418	C≡C	515	N-N	161	N=N	418	N≡N	946
C-O	352	C=O	728	C≡O	1076	O-O	139	O=O	498		
		(CO ₂ ,	797)								

These are typically averages again, so there can be variations depending on what the actual molecules are. In fact, notice that CO₂ gets its own entry. It has two C=O bonds back-to-back and that arrangement changes the energy considerably. Since CO₂ is so common and since its value is so different from the average, it gets its own listing here as 797 kJ for each C=O bond. Nevertheless, the important point to note is that the general bond order relationship holds very nicely overall: higher bond order gives stronger bonds.

Bond energies are extremely important in many ways. Just for one example, most of the energy which you use in your lifetime comes to you in the form of bond energies. We will come back to this in

Chapter 27 when we connect to a bigger picture. Flag the two lists of numbers above: just write "BEs" in the margin.

Now we turn to our second bond parameter, bond length. This is defined as the distance between the nuclei of the two atoms in the bond. That's a nice simple definition but there's more to the picture. The two atoms are held together by shared electrons in bonding orbitals. Just like all other orbitals, these bonding orbitals are field regions and they are not hard objects. In fact, as another Lewis has said, there's a "whole lotta' shakin' going on". The atoms jiggle back and forth while still connected. The specific term for this action is vibration. We can talk about a bond vibration or we can talk about molecular vibration for the polyatomic unit as a whole. All bonds have some vibration but that's not where we need to be right now. Right now, we're just doing bond length. So, despite vibrations, atoms are at some typical separation and this is the bond length.

Here's another point to consider for bond length: if the electrons in the bond are bringing the atoms together, why don't the atoms just keep getting closer until their nuclei bump into each other? Well, if you try to bring two atoms too close to each other, then spin exclusion and electron-electron repulsion increase drastically; nuclear-nuclear charge repulsion can also kick in. The actual bond length lies in the balance of these various interactions.

There are two factors which influence bond length and one of these is bond order. The reason is similar to the reason for bond strength: for the same two atoms bonded together, if there are more shared electrons (higher bond order) which are bringing the atoms together, then the atoms will end up closer and the bond length will be shorter. Let's do the prior comparisons again, now looking at bond lengths (in pm).

C-C	154	C=C	133	C≡C	121	N-N	150.	N=N	124	N≡N	110.
C-O	150.	C=O	129	C≡O	115	O-O	146	O=O	121		

This trend works nicely: in general, a HIGHER BOND ORDER will give a SHORTER BOND. Putting this together with bond energy, we have the essential, overall result for bond order effects:

HIGHER BOND ORDER GIVES STRONGER AND SHORTER BONDS.

Our second factor for bond length is the size of the atoms which are involved. Larger atoms will give longer bond lengths. We saw the Periodic Trend for atomic size in Chapter 23 and numbers for radii were given for Main Group atoms. Now I will tell you that those numbers are representative values derived from single, covalent bonds. Thus, if you want to know a bond length for a single bond combination of those atoms, then you just add up the numbers for those radii. For example, the bond length for N-N is $(75 + 75) \text{ pm} = 150. \text{ pm}$ (above). For N-O, the bond length is $(75 + 73) \text{ pm} = 148 \text{ pm}$ and for N-F it is $(75 + 71) \text{ pm} = 146 \text{ pm}$. These are representative, typical bond lengths; variations can happen.

25.5 Greed

Now we are at the point to address the notion about even and uneven share. This is very important. I'll say this one more time.

“ MOST COVALENT BONDS DO NOT INVOLVE AN EVEN SHARE. This has serious consequences. ”

Although atoms of many different elements can participate in sharing to form a covalent bond, some atoms are more greedy than others for the shared electrons. Let's say you have a covalent bond between atoms of two different elements. The more greedy atom will pull in more than an even share of the bond electrons; the less greedy atom will pull in less than an even share. Thus, bond polarity is a result of the difference in electron greed between two atoms in a bond.

Hopefully, the notion of electron greed seems straightforward, but it is not straightforward to measure this notion quantitatively. The quantitative indicator which is commonly used is called "electronegativity", which is often abbreviated as EN. We use electronegativity as a measure of an atom's ability to pull on shared electrons; it's a measure of an atom's greed for shared electrons.

Why are some atoms greedier than others? Think back to the notions of ionization energy (IE) and of electron affinity (EA): in general, some atoms have a better grip on their own electrons than other atoms do and some atoms have a stronger desire for even more electrons. The reasons were embedded in the electron configurations and a Periodic Trend resulted. We touched on this at the end of Chapter 23; I'm repeating it here, but I'VE CAPITALIZED THE PARTS THAT ARE IMPORTANT FOR NOW.

- “ 1. Elements near the right of the Periodic Table, especially the upper right, want electrons the most. They very much want to keep their own electrons (high IE, strong hold) and they even want another electron (high EA, strong desire). Because of this, these elements
- will not form cations readily at all;
 - will form anions readily; and,
 - WILL TEND TO BE MORE GREEDY FOR SHARED ELECTRONS IN COVALENT BONDS.
2. Elements near the left of the Periodic Table want electrons the least. They do not hold their own very strongly (low IE, weak hold) and they do not want more electrons very much (low EA, weak desire). Because of this, these elements
- will form cations readily;
 - will not form anions readily at all; and,
 - WILL TEND TO BE WEAK FOR SHARED ELECTRONS IN COVALENT BONDS. IN FACT, MANY WILL BECOME CATIONS BECAUSE THEY ARE TOO WEAK TO HOLD ONTO A SHARE WITH ANOTHER ELEMENT. ”

Thus, these various factors are somewhat related and they ultimately relate to configurations. As such, electronegativity gives rise to another Periodic Trend. Although we can relate electronegativity, IE and EA back to configuration effects, there is an important distinction to note. IE and EA are direct energy values for defined experimental processes (as seen in Chapter 23); these have a specific numerical value. On the other hand, electronegativity has various definitions; in fact, over 20 systems of electronegativity have been proposed over the decades. Some of the more common systems are based on bond energies, or on IE and EA, or on effective nuclear charge, or on valence *s* and *p* electron ionization energies, or on whatever. To maintain some comparisons between some systems, they are scaled such that the EN for fluorine is set to approximately 4, and the resulting EN values do not have units. (The scaling to approximately 4 for F was done early on, and numerous later systems stayed with that scale.) A higher number represents a greater electronegativity and a greater pull on shared electrons. Although the various systems were set up differently and they differ in some values, they do agree in general qualitative aspects. It's the trends that are the most important for us.

Of the various systems, I will use the one based on valence *s* and *p* electron ionization energies. In this system, the final values, after scaling, are in the range of 0.66 (for Cs) to 4.79 (for Ne). Here are some numbers.

ELECTRO-NEGATIVITIES

	1	2	13	14	15	16	17	18		
1	H 2.30							He 4.16	HIGHEST EN MOST GREEDY	
2	Li 0.91	Be 1.58	B 2.05	C 2.54	N 3.07	O 3.61	F 4.19	Ne 4.79		
3	Na 0.87	Mg 1.29	Al 1.61	Si 1.92	P 2.25	S 2.59	Cl 2.87	Ar 3.24		
4	K 0.73	Ca 1.03	Ga 1.76	Ge 1.99	As 2.21	Se 2.42	Br 2.68	Kr 2.97		
5	Rb 0.71	Sr 0.96	In 1.66	Sn 1.82	Sb 1.98	Te 2.16	I 2.36	Xe 2.58		
6	Cs 0.66	Ba 0.88	Tl 1.79	Pb 1.85	Bi 2.01	Po 2.19	At 2.39	Rn 2.60		
7	Fr	Ra	Nh	Fl	Mc	Lv	Ts	Og		
	lowest EN least greedy									

As was done in Chapter 23, I am restricting our coverage of Periodic Trends to the Main Groups. Also as in Chapter 23, values for the radioactive elements in the Seventh Period are lacking. On the other hand, note that values for the noble gases are given, although they form relatively few bonds. It was

noted in Chapter 23 that hundreds of xenon compounds are known; there are very few krypton and radon compounds, and there are no neutral compounds of helium, neon and argon at normal conditions.

As in the prior Periodic Trends, electronegativity has a diagonal relationship: the most greedy elements are in the upper right and the least greedy are in the lower left. This follows the aspects from Chapter 23 which were quoted above. The overall diagonal relationship can be broken into two parts: a horizontal part and a vertical part. EN increases to the right in a row. EN increases going up a Group. Yes, there are a few exceptions; notable is the fact the Ne is the most electronegative element, even moreso than He. Despite some exceptions, we emphasize the overall pattern.

Now let's apply electronegativity to evaluate the evenness of the sharing in a covalent bond. The share will be exactly even only between atoms of the same element, since they have the same electronegativity and equal pull on bond electrons. (Technically, the share will be exactly even only between atoms of the same element and in the same bonding arrangement. This doesn't matter for diatomic molecules but, for other polyatomic units, sometimes it will matter. I'm trying to keep things simple, so we will not worry about those other cases.) For cases of bonds between atoms of the same element, the sharing is even and the bond is nonpolar. For example, we had previously discussed the diatomic cases of Cl_2 , of O_2 and of N_2 ; all of those bonds are nonpolar.

On the other hand, for bonds between atoms of different elements, the sharing will not be even. The more electronegative atom will have more than an even share of the bond electrons and the less electronegative atom will have less than an even share. These bonds are polar. By the way, bond order does not matter. The more electronegative atom ends up with more than a fair share of ALL bond pairs between the two atoms.

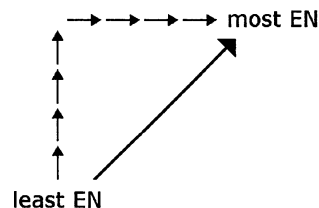
The polar category covers a wide range of covalent bonds and we must also address the question of "how polar" is the bond. Some polar bonds are only slightly polar and some polar bonds are very polar. If the two atoms have only a slight difference in EN, then their share is only slightly uneven and the bond is only slightly polar. If the two atoms have very different ENs, then the bond is very polar. Here's the bottom line: how polar is the bond is a consequence of how different are the ENs.

You can evaluate this with numbers, and I will show one such example. Compare a typical C-Cl bond versus a typical C-F bond: which bond is more polar? The electronegativities are 2.54 for C, 2.87 for Cl and 4.19 for F. For both of the two types of bonds, C is less electronegative so C gets less than an even share in both cases. The bond polarities run as shown on the left. (We'll be using our partial charge notation again, so go back to Chapter 10 and refresh if necessary.) For the question of "Which bond is more polar?", we must find the difference in the ENs for each case. For the C-Cl bond, the ENs differ by 0.33; for the C-F bond, the ENs differ by 1.65. The C-F bond has the greater difference, so this bond is more polar than the C-Cl bond.

It is important to keep in mind that our estimate of relative bond polarity is reflected in the difference in electronegativities of the bonded atoms. Some students get confused and think that greater bond polarity occurs when both atoms have high EN, but that is wrong. It's the difference that counts! For example, an Si-Cl bond has more polarity than an O-F bond. You must look at the difference, not at the separate EN values. (Go ahead compare the numbers for these.)

Like I mentioned a few moments ago, I'd like to put more focus on the general trends. We don't always remember numbers but we do (hopefully) remember trends. Let me restate the Periodic Trend for EN: EN increases going up and EN increases going to the right. This gives an overall diagonal trend as shown at right. Remember these directions. We can use these to compare the ENs of any two elements A and B by their relative positions in the Periodic Table as follows.

- ▶ If B is above A, then B is more electronegative.
- ▶ If B is to the right of A, then B is more electronegative.
- ▶ If B is to the upper right of A, then B is more electronegative.



For any of these cases, the bond polarity would be $\text{A}(\delta^+)-\text{B}(\delta^-)$. Furthermore, if the elements A and B are located in the Periodic Table along any of these trend directions, then we can loosely estimate how close are their ENs by how close A and B are to each other. If A and B are close, then their ENs are likely to be close, and the A-B bond would be slightly polar. If A and B are further apart in the Periodic Table, then their ENs are more different and the A-B bond is more polar.

less and less and less of an even share. The more electronegative atom has more and more and more of the so-called "shared" electrons while the less electronegative atom is losing claim to them. I can represent this in a figurative fashion as follows.

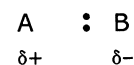
► Consider a separate atom A and a separate atom B which will come together and share two electrons, forming a single bond. (For simplicity, I'm leaving out all lone pair electrons here.)



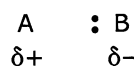
► Suppose atoms A and B are the same element. Under these conditions, the electronegativities are identical. The covalent bond is truly nonpolar and the share is exactly even.



► Now suppose that A and B are different elements, with B slightly more electronegative than A. Under these conditions, the covalent bond is slightly polar and B has slightly more than an even share of both electrons.



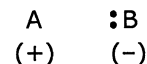
► Now we take B to be considerably more electronegative than A. Under these conditions, the bond is considerably polar and B is assuming a much larger portion of the shared electrons. Atom A is losing out considerably on the share.



These pictures are figurative only but, by scooting the dots over toward B, I hope you get the sense of the uneven share. The real story lies with orbitals. Since we aren't doing orbitals until Chapter 30, let me just point out that shared electrons are really in an orbital and that, as B becomes more and more electronegative than A, then the bond orbital field is becoming more and more concentrated on B. THIS IS THE ACTUAL DESCRIPTION. Moving the dots is useful for figurative purposes, but it's the concentration of the orbital field that matters.

OK, let's extend the gamut to the extreme.

► Now consider B to be far more electronegative than A. Under these conditions, the sense of sharing has lost significance. Atom A has lost out to B and B has assumed almost entire control of the electrons. (More correctly: both electrons are in an orbital which is almost entirely concentrated on B.)



In essence, atom A has lost its original electron and is now a cation. Atom B has its own electron but it has also gained the electron from A; atom B is now an anion. The bond holding A and B is no longer covalent. It is ionic. This is the grand result:

IONIC BONDS ARE ACTUALLY EXTREME CASES OF EXTREMELY UNEVEN SHARING IN A BOND.

Now you have it: covalent bonds and ionic bonds are actually related. This is important. It rounds out the entire range of covalent and ionic bonding types. The range begins at one end with nonpolar covalent bonds, then it goes through polar covalent bonds, and then it ends up at ionic bonds. Throughout this range, our measure of the bond polarity is the difference in EN of the bonded atoms.

equal EN slightly different EN more different EN very different EN

nonpolar covalent slightly polar covalent more polar covalent ionic

The polar covalents are the widest part of this range, followed by the ionic. The nonpolar covalents are small in comparison.

Technically, there's a tad bit of sharing in real ionic bonds. Although it's typically small, we say that there is some "covalent character" in an ionic bond. It's still not the major factor, and the +/- attraction of ion charges remains the dominant factor. This works the other way also. A polar covalent bond has some charge component; this is because the polar covalent bond has the partial charges of $\delta+$ and $\delta-$, and even these are attracted to each other. For this reason, we say there is some "ionic character" in a covalent bond. When significant, ionic character can strengthen a covalent bond and can also shorten bond lengths. Notice that we are now blending bond types. Real bonds are a mix of covalent and ionic character. We label the bond as covalent or as ionic based on the dominant contribution.

Time for another summary. There's a lot of important stuff coming together here. For any bond between atoms A and B:

I. If atoms A and B are of the same element, then the bond is nonpolar covalent. The sharing is even.

II. If atoms A and B are of different elements, then the bond type is related to the difference in ENs of A and B.

- ▶ If the difference in ENs is small to considerable, then the bond is polar covalent.
- ▶ If the difference in ENs is large, then the bond is ionic.

So what's the actual cutoff between the labels polar covalent and ionic? Sorry, there is no simple numerical cutoff. Except for the nonpolar covalents, bond types are not just black and white. Most of this is grey matter. We can estimate and we can do comparisons, but there are no hard cutoffs. We can ask whether AsF bonds are more polar than AsBr bonds. We can ask whether KF bonds are more ionic than NaBr bonds. We can ask whether AlO bonds are more covalent or more ionic than AlCl bonds. But we cannot give an exact cutoff between covalent and ionic bonds based only on the difference in ENs because other factors are also involved. (There are some mathematical approaches which provide better estimates and narrower cutoffs, but there are still grey patches.) Our estimates here provide useful comparisons although there can still be exceptions in that wide, middle ground. The generalities are OK, but the middle ground is muddy.

By the way, these classifications so far have only included covalent and ionic bonds. We haven't done metallic bonding yet. Metallic bonding is another extreme for covalent but in a totally different way. I can't do it now because we need some more background. We will get to it in Chapter 33. There are also electronegativity relationships for metallic bonding, but I won't go into those at all.

25.7 Applying to compounds

So far, we've been talking about bonds being covalent or ionic. Way back in Chapters 3 and 4, we set up compounds as ionic or covalent and this was based on bond types. Now we see that bond types aren't just black and white. Likewise, compound types aren't always black and white. There's a huge grey area again. Let's see how this comes into play with a few examples: consider the binary aluminum halides AlF_3 , AlCl_3 , AlBr_3 and AlI_3 . Of the four, the greatest difference in electronegativity occurs for AlF_3 (Al and F are well separated along the usual trend directions) and the smallest difference occurs for AlI_3 (Al and I are close to counter-diagonal).

AlF_3 forms a lattice of monatomic cations and monatomic anions, held by ionic bonds. The ionic network solid melts at a very hot 1,290 °C. These features are fully consistent with the large difference in electronegativity between Al and F. Overall, we can fully regard AlF_3 as an ionic compound. On the other hand, AlI_3 is a solid composed of individual chemical units of Al_2I_6 ; its melting point is much lower at only 191 °C. These features are typical of a simple molecular compound with covalent bonds and, indeed, these are molecules of Al_2I_6 . AlBr_3 is similar, giving molecules of Al_2Br_6 . AlCl_3 is intermediate: in the solid phase, it has an ionic lattice with fairly ionic bonds but the compound has a low melting point (190 °C) and, when it melts, the liquid is composed of Al_2Cl_6 molecules, typical of covalent bonds. So what are these? Are these ionic compounds or are they covalent compounds?

It depends.

As for bonds themselves, the difference in electronegativity does not provide a rigorous cutoff for compounds. Historically, some compounds were considered representative of ionic compounds (e.g., NaCl) and some were considered representative of covalent compounds (e.g., H_2O), and these were based on physical and chemical characteristics. These characteristics could then be used to classify yet other compounds. Nowadays, electronegativity is yet another characteristic to consider. But then there's always some middle ground where the characteristics overlap. AlCl_3 has some ionic characteristics and some covalent characteristics. Some chemists would consider AlCl_3 ionic and some would consider it covalent, and that is part of the understanding that the borders are not exactly defined.

Although these grey areas exist, I can give some pointers which you can use to help classify bond types and compound types.

1. Except for rare cases, only metal elements can form monatomic cations in a compound. The other elements have too much electronegativity and they won't surrender electrons completely (high IEs), so they won't form cations. On the other hand, some metals can also do covalent bonds, so the presence of a metal doesn't guarantee that the bond is ionic. We can consider two categories for bonds involving a metal element.
 - a. Metal elements of the s-block are very low in electronegativity and virtually all of their compounds are ionic with the metal as the cation. Notice that I say "virtually". Like any generality, there are exceptions. The most frequent exceptions are for beryllium, which has the

highest EN of the bunch. Beryllium is primarily covalent in its compounds; even BeF_2 is covalent. In water, however, some beryllium compounds do behave as ionic, giving Be^{2+} cations.

b. Metal elements of the p -block are low to moderate in electronegativity. These can do ionic or covalent bonds, depending on what they're bonded to.

2. The elements which are not metals will primarily form covalent bonds, although a few of these elements can also form monatomic anions. Only eight elements form monatomic anions to a reasonable extent. These are clustered in the right (and especially the upper-right) region of the Periodic Table: N, O, S, Se, F, Cl, Br and I. A few other elements will do a few compounds as monatomic anions (such as H and C) but these are limited.

3. If a compound contains a polyatomic ion, then the compound is still classified as ionic.

These are pointers. There are still exceptions, but these pointers cover an awful lot of things.

Since we haven't done metallic bonding yet, not everything is yet covered by these categories.

Frankly, I think that's enough for now.

Problems

- True or false.
 - Ions of lower charge give stronger ionic bonds.
 - A double bond involves sharing two electrons.
 - More energy is required to break a $\text{N}\equiv\text{O}$ bond than a $\text{N}-\text{O}$ bond.
 - The bond in Br_2 is nonpolar covalent.
 - A bond between phosphorus and oxygen is polar covalent.
 - A bond between iodine and silicon is ionic.
 - An ionic bond can have some covalent character.
- Which one of the following has the greatest lattice enthalpy?
 KBr KCl NaCl MgS MgO
- Of the following types of bonds, which one is the longest?
 Si-P Si=P Si=S S=O O-F
- Of the following types of bonds, which one is the shortest?
 C-N P=S C-Si N=O C=S
- What is a typical bond length (in pm) for each of the following? (You'll need atomic sizes from Chapter 23.)
 - B-F
 - As-Br
 - P-C
- Which of the following has the most electronegativity?
 Al In Sb P Ge
- Of the following types of bonds, which one is the most polar?
 As-F As-Si P-S P-N Cl-F
- Of the following types of bonds, which one has the least ionic character?
 B-F Te-I Na-Cl Sb-F Ge-O