

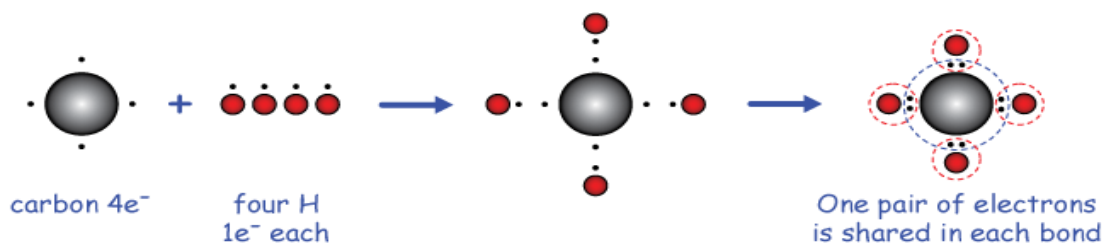
COVALENT BONDS

Ionic compounds form because one or more electrons transfer completely from one atom to another, making a positive-negative ion pair. But the majority of chemical compounds form when two atoms "share" an electron in order to complete a valence shell in each. These are not ionic compounds.

The chemistry of carbon

As an example, let's think about **carbon**, which contains four electrons in its outer shell, two in its 2s subshell and two in its 2p subshell. Carbon needs to gain four electrons to have a full octet. It can do this by bonding with four hydrogen atoms, each of which has one electron, one short of a full 1s shell (remember, H never gets an octet).

The situation is pictured below. When the bonds are formed (right), the carbon atom is effectively surrounded by eight valence electrons, all occupied in the four C-H bonds, and each hydrogen is associated with two electrons, one its own and one from the carbon. The valence shells of each atom are in this way complete and this molecule, methane, is very stable.



Covalent bonds are bonds that complete or partially complete the valence shell (co-valent) of each atom in the bond through the sharing of electrons.

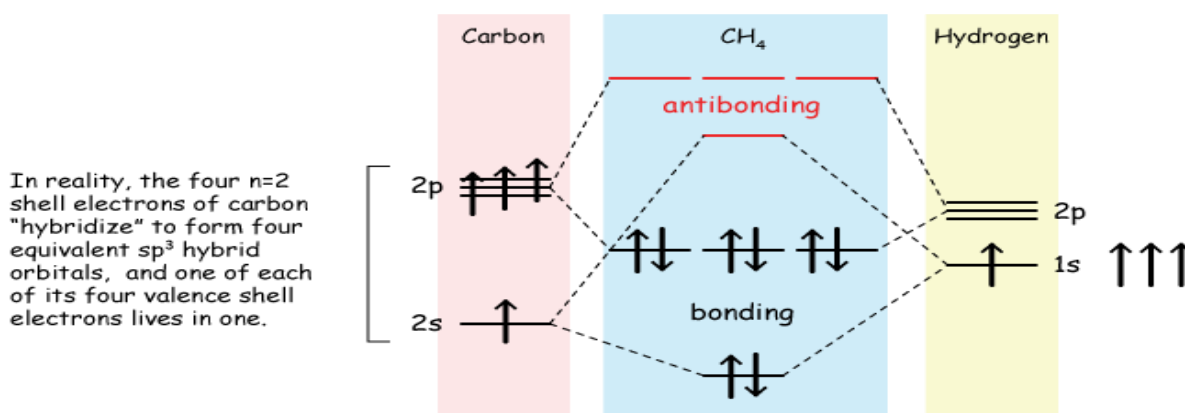
The actual picture is somewhat more complicated.

When atoms that form **covalent bonds** come together, what actually happens to form a covalent bond is that the valence-shell orbitals of each rearrange to produce a different set of orbitals — **molecular orbitals** instead of atomic orbitals. The molecular orbitals have the same capacity to hold electrons as the individual atomic orbitals from which they were formed.

The picture below shows how the s and p-sub orbitals of C and H come together to build two sets of molecular orbitals, which we call the **bonding molecular orbitals (BMO)** and the **anti-bonding molecular orbitals (ABMO)**. You might notice that a hydrogen atom doesn't actually have p-orbitals - why would it with only one electron? But remember that orbitals are formed *by* electrons (and don't exist when they're not there), and when the electrons of four H-atoms and one carbon combine, the need for p orbitals in H is created.

In general, the electrons that form bonds remain in the BMOs because they are of lower energy and therefore more stable.

There is much more to **molecular orbital theory** than I can present here, but I wanted to give you some background about this "sharing" of electrons.



Covalent & ionic bonding: How to tell the difference.

Atoms bond as groups of ions (usually pairs) or they bond covalently by sharing electrons in bonding orbitals. How can we tell how two atoms will bond ahead of time?

One way is to use **electronegativity**, which we discussed in the periodic trends notes. Electro negativities of the elements can be calculated according to a formula developed by Nobel Prize-winning chemist **Linus Pauling** (Pauling was the only person to ever have won two Nobels, one in chemistry, the other the Peace Prize for his work to stop the nuclear arms race).

I won't go into the detail of Pauling's calculation. The Pauling electro negativities of most of the elements are given in red in the periodic table below.

In general, when the difference between electronegativity of two atoms is large, they will tend to bond ionically. When the difference is small, they'll bond covalently.

You've noticed that I haven't said what "large" and "small" actually are. That's because there are always atom pairs that fall somewhere between ionic and covalent bonding. We'll cover those later. Nevertheless, there are a couple of accepted rules.

Δ Electronegativity		
1.2	1.8	
Covalent	(Between)	Ionic

Example: NaCl

Looking at the table below, we see that the electronegativities of sodium (Na) and chlorine (Cl) are 0.93 and 3.16, respectively, for a difference of **2.23**, so we'd expect these atoms to bond ionically, which they do.

Example CH₄

The electronegativities of C and H are 2.25 and 2.20, for a small difference of **0.05**, so we'd expect these atoms to bond covalently, and they do.

It's a little trickier when the electronegativity falls into that in-between area.

Example H₂O

The electronegativities of O and H are 3.44 and 2.20, respectively, for a difference of 1.2. It turns out that the covalent O-H bonds in water have significant ionic character. In water the oxygen atom shares an electron with each hydrogen, but the bonding electron pairs are strongly drawn toward the oxygen, leaving a mostly-bare proton sticking out. That's part of what makes water such an interesting and unique substance. It's why it is polar (has distinct negative and positive "ends") and why it forms hydrogen bonds. See the notes on water for more.

We will look at many more examples of bonding below.

You won't always have to jump to electronegativities to decide whether a bond is covalent or ionic (or some of both). Most of the time the bonding will be clear because of context, and because you'll develop an instinct that comes from memorizing a few important ions and a few structures of some important covalent compounds, like water, methane and ammonia.

Pauling Electronegativities of the Elements
in their most common states

	1A	2A											3A	4A	5A	6A	7A	0	
1	1 H 2.20																	2 He	
2	3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98	10 Ne	
3	11 Na 0.93	12 Mg 1.31	3B	4B	5B	6B	7B	8B				1B	2B	13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16	18 Ar
4	19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96	36 Kr 3.00	
5	37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66	54 Xe 2.60	
6	55 Cs 0.79	56 Ba 0.89	57 La	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Tl 1.62	82 Pb 1.87	83 Bi 2.02	84 Po 2.0	85 At 2.2	86 Rn 2.2	
7	87 Fr 0.7	88 Ra 0.9	89 Ac	104 Rf	105 Ha	106	107	108	109										

Examples of covalent bonding

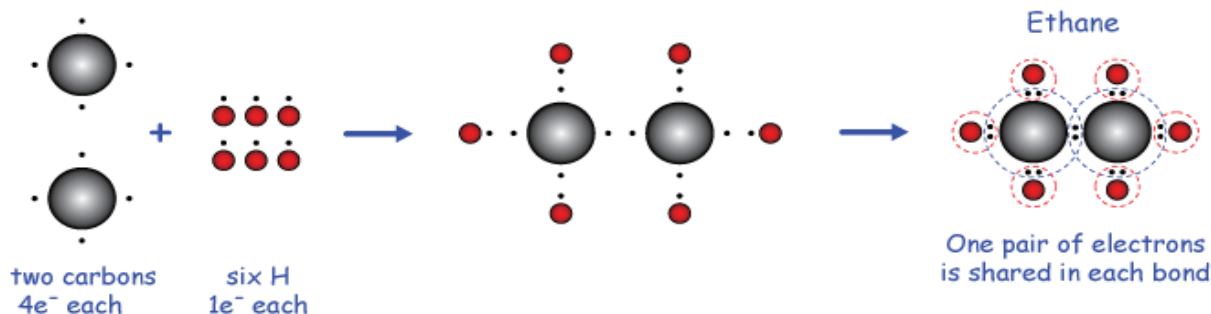
Ethane C₂H₆

Ethane, C₂H₆, is a hydrocarbon molecule, an odorless gas at room temperature. The covalent bonding picture of ethane is very similar to that of methane above. Two carbon atoms, each carrying four valence electrons, come together to share a pair of electrons. We'll start calling that a **single bond** (or sigma bond).

That leaves six unpaired electrons on the C₂ unit. Each of these is paired with the single electron of a hydrogen atom to give each carbon a stable valence octet (dashed circles on the right), and the valence 1s shell of each H-atom is completed by sharing a single electron from a carbon.

A single or sigma bond is formed by the sharing of two electrons between atoms.

Those electrons mostly occupy a space between the two atoms.



Ethylene (or ethene) C₂H₄

Ethylene is a colorless gas at room temperature, and is composed of two carbon atoms and four hydrogens. Ethylene is a precursor in a wide variety of chemical synthesis reactions, including formations of long chains of ethylene molecules called polyethylene — a plastic.

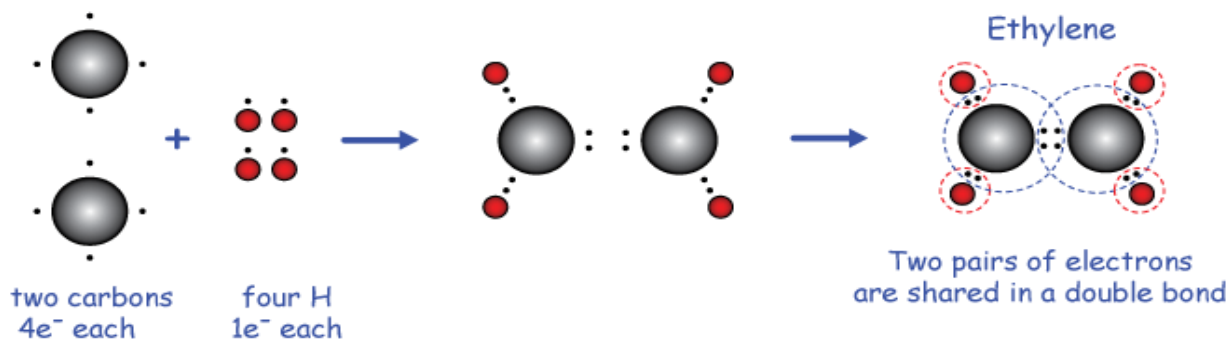
If you review bonding in ethane, the previous example, you'll notice a problem.

How can we expect C₂H₄ to bind together like C₂H₆, when we'd be "missing" two hydrogens? Wouldn't we have two unpaired electrons and some non-octets?

There's a way to do it.

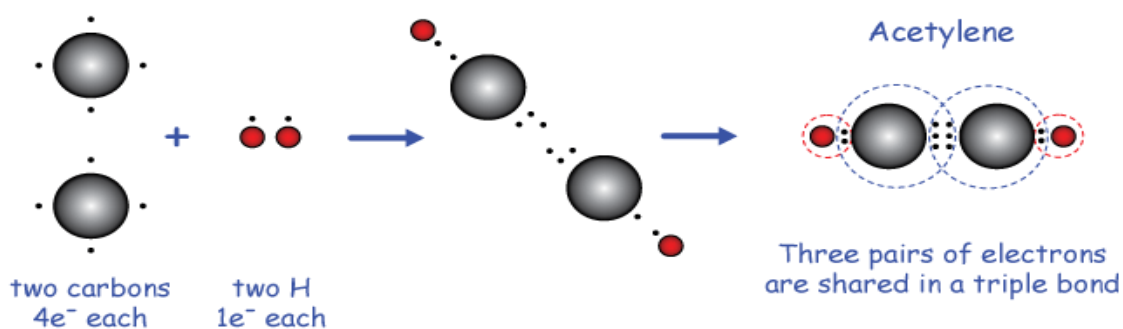
In ethylene, each carbon shares two of its valence electrons with the other carbon, forming a bond that contains four electrons that we call a **double bond** or a **pi bond**.

In this way, each carbon "sees" six electrons just from carbon atoms, four of its own and two from its neighbor. Further pairing of the remaining two unpaired carbon electrons with hydrogens fills up all valence shells nicely.



Acetylene (or ethyne) C_2H_2

Well, why not **triple bonds**? In acetylene, one of the two gases involved in oxyacetylene welding, we only have two hydrogen atoms to bring in extra electrons, so each carbon must share three of its four valence electrons with the other in order to form valence octets. The result is a very strong triple bond. Here's how it looks.



Shorthand drawings

The molecules we just studied as examples can be represented by stick figures like these →.

Each single bond gets a single line. Double bonds get two and triple bonds get three. Each line represents a pair of shared electrons.

Once you've got the hang of this section, you should move on to the notes on Lewis structures, a helpful method for determining what kind of covalent compounds can form from selected atoms.

