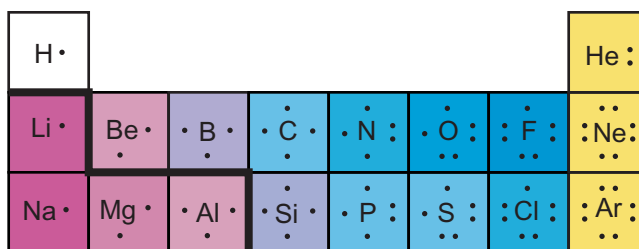


LEWIS DIAGRAMS



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LEWIS DIAGRAMS

CONTENTS

2	Lewis Diagrams For Covalent Bonding
3	Lewis Diagrams For Covalent Bonding
4	Forming Lewis Diagrams
5	Resonance
6	Beyond The Steps
7	Beyond The Steps
7	Orbitals

LEWIS DIAGRAMS

LEWIS DIAGRAMS FOR COVALENT BONDING

In the figure below, the elements of the first three periods are shown with their valence electrons surrounding their symbols. It is only the valence electrons which may become involved in chemical bonding, because the inner electron shells are held too tightly to the atom to be either shared or given up in chemical bonding, although you can blast them off with X-rays.

1 1A	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
H·							He :
Li·	Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
Na·	Mg·	·Al·	·Si·	·P·	·S·	·Cl·	·Ar·

Electronegativity →

If we consider just the nonmetals, as shown below, the electronegativity differences between the elements is fairly small. For this reason a particular kind of bonding, called covalent bonding, occurs between the atoms. Because of the small electronegativity differences, none of the atoms in a covalent molecule pulls any electrons entirely away from any of the other atoms, but rather the atoms share some or all of the valence electrons.

1 1A	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
H·							He :
	Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
			·Si·	·P·	·S·	·Cl·	·Ar·

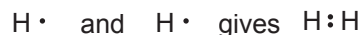
Electronegativity →

There is a particularly simple and convenient way of showing the connections between covalently bound atoms. We do this by forming what are called Lewis diagrams. In Lewis diagrams the atoms are shown by writing the atomic symbol surrounded by one dot for each of the valence electrons. In a covalently bound molecule the dots are arranged in pairs, with the bound pairs placed between the atoms which they connect and the lone pairs at different sides of the atomic symbol.

Later we will give the general rules for forming Lewis diagrams but first we will look at some simple examples beginning with the formation of a hydrogen molecule, H_2 , from two hydrogen atoms, H.

A GOOD DEFINITION OF A MOLECULE IS TWO OR MORE ATOMS COVALENTLY BONDED.

Lets form a covalent bond between two hydrogen atoms:



In covalent bonding electrons are always shared in pairs. In this example the pair of electrons (the two dots) are drawn in between the two H symbols in the H_2 molecule. The molecule H_2 has ONE covalent bond. Each atom in the H_2 molecule has, by sharing, a single pair of electrons. Each H atom now has the electron configuration of a helium atom. It is said to be isoelectronic (having the same number of electrons) with a helium atom. The helium atom electron configuration is very stable because it is a filled energy level. The red circles outline the structures isoelectronic to the helium atom.



In chemistry the covalent bond is often drawn as a single line.



Lets now take an example of an atom with more than one valence electron. The fluorine atom has seven valence electrons (F is in group 7A, 17).



The valence electrons are arranged in pairs around the atomic symbol. The seventh electron is drawn as a single dot and is called an unpaired electron. Two fluorine atoms can share their unpaired electrons and form a covalent bond. We can show this by means of a Lewis diagram as follows:



ATOMS OTHER THAN HYDROGEN SHARE ELECTRONS UNTIL THEY ARE SURROUNDED BY EIGHT VALENCE ELECTRONS. THIS IS CALLED THE OCTET RULE

Draw circles around each fluorine atom to show the octet rule.



What element is isoelectronic with each fluorine atom in the molecule F_2 ?

LEWIS DIAGRAMS

LEWIS DIAGRAMS FOR COVALENT BONDING

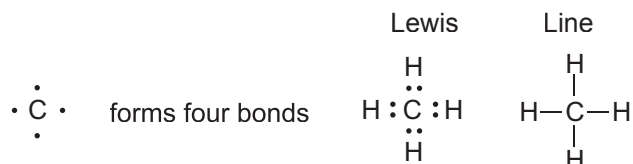
Yes, it is neon, the inert gas to the right of fluorine in the second period.

Note, the F atom is isoelectronic with neon but it is not neon because the F atom has 9 protons in the nucleus and neon has 10 protons in the nucleus.

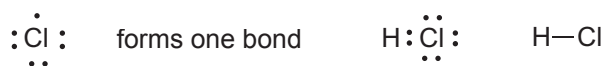
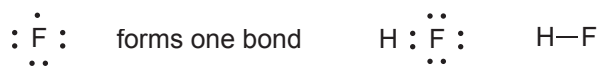
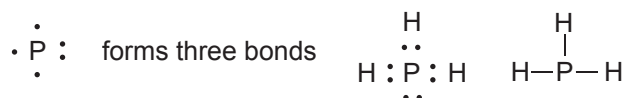
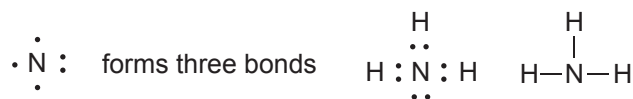
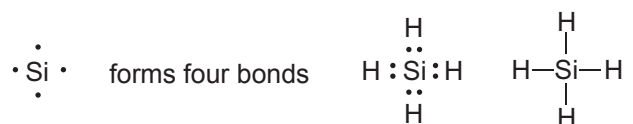
Looking at our section of the periodic table, notice how each element, as we move to the right, adds one more valence electron.

1 1A							18 8A
H·	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	He·
	Be·	B·	C·	N·	O·	F·	Ne·
			Si·	P·	S·	Cl·	Ar·

For example, carbon with four valence electrons (group 4A) can become isoelectronic with Ne (8 valence electrons, group 8A) by sharing 4 electrons from other non-metallic elements.



The octet rule provides a way to find out how many covalent bonds are formed by the representative non-metallic elements.



In the examples, draw circles to illustrate the duplet and octet rules and name to element to which the circled atom is isoelectronic.

So far we have only considered molecules which have single bonds between pairs of atoms. Molecules can have multiple bonds, e.g., double bonds O=O and triple bonds N≡N. Let's see if we can write a Lewis diagram for O₂, dioxygen.



See how in this case each oxygen atom shares two of its electrons with the other oxygen atom. So altogether there are four electrons shared between the two oxygen atoms, forming TWO covalent bonds. This is called a double bond.

Like fluorine in difluorine, each oxygen atom in dioxygen is isoelectronic to neon. Draw circles around each oxygen atom in the dioxygen Lewis diagram above to show the octet rule. The circles do not need to be drawn perfectly circular, but they do need to enclose the correct electrons.

Now you can predict the chemical formula for many molecules formed by combining different non-metallic elements. For example try to predict the formulas for compounds formed by combining:

- a) C and Cl b) F and O
c) N and I (hint: look at the periodic table on page 2).

So far we have introduced Lewis diagrams according to a few simple rules, which are sufficient to write the diagrams of the simple molecules we have been discussing. Lewis diagrams are also useful for more complex molecules. In order to use them for these more complex molecules we will need to use a definite procedure which we give on the next page.

LEWIS DIAGRAMS

FORMING LEWIS DIAGRAMS

We introduce a set of basic rules and procedures by which you can form Lewis structures.

RULE 1. Bonds are pairs of electrons shared between two atoms.

RULE 2. Hydrogen can form only one covalent bond (Duplet Rule).

RULE 3. (Octet Rule) Most covalently bonded atoms (except for hydrogen) have a filled octet of valence electrons.

STEP 1. For a given chemical formula, count the number of valence electrons for each atom (you can use the chart at the top right of the page). Add them up. If the system is charged, add one for each negative charge on the system or subtract one for each positive charge on the system.

STEP 2. Determine the arrangement of the atoms. You may need to obtain this information from another source. However, you can often assume that the least electronegative atom is central and it is always the case that the hydrogen atoms and 7A atoms are on the outside because they only form one bond.

STEP 3. Place single bonds between the atoms as determined in step 2.

STEP 4. Multiply the number of single bonds in step 3 by two and subtract that number from the number determined in step 1. This gives the number of available electrons.

STEP 5. Arrange the available electrons in pairs around the terminal (outside) atoms, except hydrogen, to fulfill the octet rule. Arrange any remaining electrons around the central atom(s) to fulfill the octet rule. If all of the atoms except hydrogen have an octet of electrons then you are finished.

STEP 6. If necessary to complete the central atom octet move electron pairs from the terminal atoms to form multiple bonds with the central atoms.

There are three kinds of exceptions to the above rules.

- A. Free radicals such as NO and NO₂.
- B. Some small atoms: B, Be, and Al which do not have room for a full octet in some molecules.
- C. Some large atoms, such as S and P which will hold more than four pairs of bonding electrons.

1 1A	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
H·							He :
Li·	Be·	·B·	·C·	·N·	·O·	·F·	·Ne·
Na·	Mg·	·Al·	·Si·	·P·	·S·	·Cl·	·Ar·

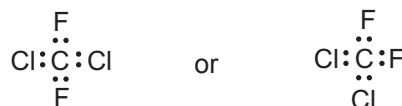
Electronegativity →

EXAMPLE: We will develop the Lewis diagram for Freon-12, CCl₂F₂.

STEP 1: From the periodic table we can find the number of valence electrons: for C it is 4, for each Cl it is 7, for each F it is 7

Number of valence electrons = 4 + (2 x 7) + (2 x 7) = 32

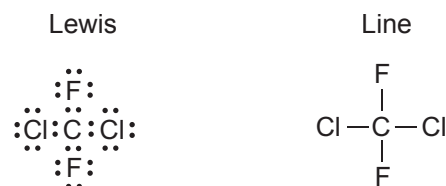
STEP 2 and STEP 3: There is only one carbon atom and two each of chlorine and fluorine, so we will assume that the carbon atom is central. We have already seen that chlorine and fluorine only form one bond each and that carbon forms four bonds so we can see that the arrangement of the atoms is either:



or one of four others, but it does not matter which one we use because these molecules are the same (see later).

STEP 4: There are 4 single bonds in the line diagram, so: Number of available electrons = 32 - (2 x 4) = 24

STEP 5: Arrange the available 24 electrons around the outside atoms in pairs to complete their octets



We have used the 4 x 6 = 24 available electrons to complete the octets of the outside atoms. We do not need step 6 for this molecule.

LEWIS DIAGRAMS

RESONANCE

Sometimes experimental information requires us to use more than one Lewis diagram for a molecule. For example, spectroscopic studies of ozone, O_3 , has identical bonds between oxygen atoms.

Now we will form the Lewis diagram for ozone.

First we determine the arrangement of the atoms.

There are two geometric possibilities.



If you would continue following the steps for constructing Lewis diagrams, you would find that the triangular form for ozone works well but it is excluded by experimental evidence. Therefore we must proceed to work out the linear alternative:



There are a total of $6 \times 3 = 18$ valence electrons, of which 4 are used in the single bonds, leaving 14. By following the steps we arrive at:



Since the central atom does not have a complete octet, we would expect to move a pair of electrons from one of the outside atoms to form another bond with the central atoms, which would complete the Lewis diagram.



However, this would imply that ozone had one single bond and one double bond but experimental evidence shows that both bonds are equal!

In fact ozone lies halfway between the situation shown in the diagram above and the situation shown in the diagram below.



We use the symbol \longleftrightarrow to point to the resonance structures. These structures do not actually exist. The molecule is a hybrid of the two structures. The actual bonds to the central O are 'one and a half' bonds.

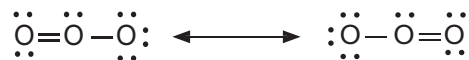
Now we write the final Lewis resonance diagram as:



and the line diagram:

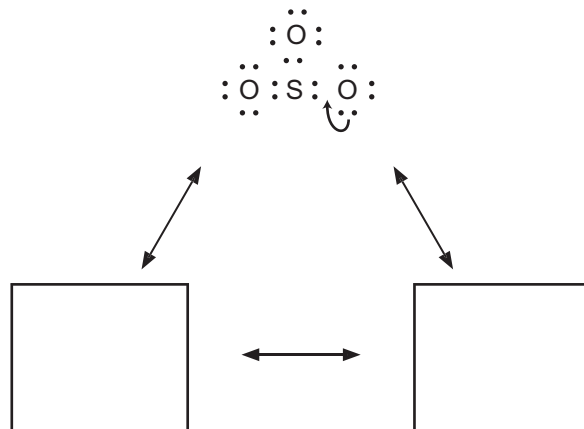


It is often very useful to write a Lewis/line form (especially in organic chemistry). To do this, simply draw in a bond line for every pair of electrons that are between atoms:

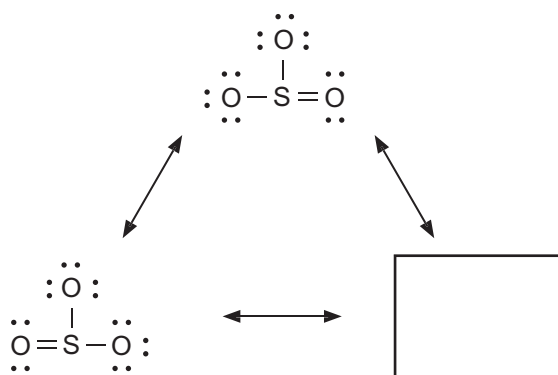


For each of the molecules shown on pages 12-14 draw the Lewis/line diagram.

Another molecule which exhibits resonance is SO_3 . You should be able to fill in the missing diagrams.



And then you write the Lewis/line resonance diagrams as:



Now try to form the Lewis diagram for benzene, C_6H_6 , where the carbon atoms form a ring. Expect resonance.

LEWIS DIAGRAMS

BEYOND THE STEPS

FREE RADICALS

A free radical is an atomic or molecular species with an unpaired electron.

Consider NO₂. There are two possible arrangements.



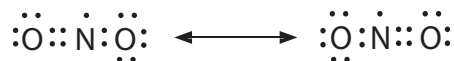
Although neither arrangement will immediately fulfill the conditions that oxygen has two bonds and nitrogen has three bonds, the left hand case is closer, having two bonds for the nitrogen. The total number of valence electrons is $5 + (2 \times 6) = 17$; removing 4 electrons for the single bonds we have 13 remaining electrons to distribute. Following the steps we arrive at:



Here we have two difficulties. The nitrogen atom only has five valence electrons and one of these is unpaired. We leave the unpaired electron but move one pair of electrons from an oxygen into a bond between the oxygen and the nitrogen. Now we have to bring in some more information from experiment. Spectroscopy of NO₂ shows that the oxygen-nitrogen bonds are equivalent, so that this is a case of resonance.



We write the Lewis resonance diagram as:



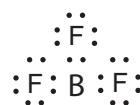
Draw the line and Lewis/line diagrams for NO₂

BERYLLIUM, BORON AND ALUMINUM

Some atoms are simply too small to accommodate a full octet of valence electrons. Let us look at BF₃. Since it only requires sharing a single electron for fluorine to have a filled octet, we write down the arrangement as

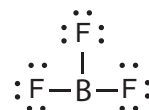


BF₃ has $3 + 3 \times 7 = 24$ valence electrons. Six are used by the single bonds, leaving 18, which we distribute around the outside atoms to fill their octets:

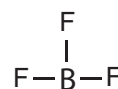


We see that while the fluorine octets are filled, that of boron is not, having only six valence electrons. Do we then move a pair of electrons from one of the fluorine atoms to form another bond with the boron, perhaps forming another resonance structure? In fact we do not because first, the fluorine is more electronegative than the boron, second, that the boron atom is too small to easily accommodate so many electrons.

We also show BF₃ in the Lewis/line form:



and as a line diagram:



LEWIS DIAGRAMS

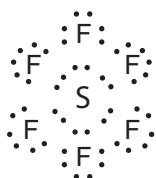
BEYOND THE STEPS

LARGE CENTRAL ATOMS

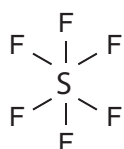
Some central atoms, in particular sulfur and phosphorus from the third period, are so large that it is possible to fit more than eight electrons in their valence shell. Examples are PCl_5 and SF_6 .

If we look at SF_6 we see that the only arrangement which allows each fluorine atom to have only one bond is that in which the sulfur atom is central and connected to each fluorine by a single bond. This is in fact what happens.

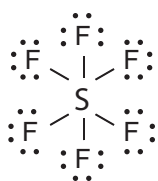
When we distribute the electrons according to our steps we arrive at:



We also have the line drawing:

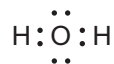


and the hybrid representation:

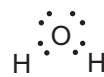


ORBITALS AND SHAPES

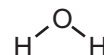
Lewis diagrams are electron dot pictures which give an excellent account of the number of valence electrons in a covalent molecule. The dot diagrams do NOT explain the reasons for covalent bonding - the 'glue' - nor do they explain the shapes of molecules. A good example is water. The Lewis diagram is:



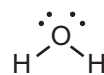
The overwhelming experimental evidence shows that water is a bent polar covalent molecule shaped something like:



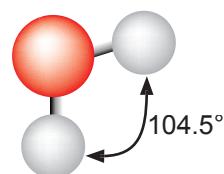
or



or



or



Explanations of shape, etc. require quantum theory and combinations of orbitals.