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Lewis Dot Structures

Gateway to Understanding Molecular Structure

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Molecular Structure & Bonding

A molecular structure, unlike a simple molecular formula, indicates the exact 3-D nature of the molecule. It indicates which atoms are bonded to which atoms, and the 3-D orientation of those atoms relative to each other.

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Molecular Formula vs. Molecular Structure

Molecular formula – H_2O

Molecular structure:

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Molecular Structure

Two issues:

- What is stuck to what?
- How are they oriented?

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What is stuck to what?

The first thing you need to do in drawing a molecular structure is to figure out which atom sticks to which other atoms to generate a skeletal model of the molecule.

The skeletal model is called a Lewis Dot Structure.

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Lewis Dot Structures

The first step towards establishing the full 3-D geometry of a molecule is determining what is stuck to what and how each atom is connected.

Lewis Dot Structures provide this information.

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Two Rules

1. Total # of valence electrons – the total number of valence electrons must be accounted for, no extras, none missing.
2. Octet Rule – every atom should have an octet (8) electrons associated with it. Hydrogen should only have 2 (a duet).

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Total Number of Valence Electrons

The total number of available valence electrons is just the sum of the number of valence electrons that each atom possesses (ignoring d-orbital electrons)

So, for H_2O, the total number of valence electrons = 2 x 1 (each H is $1s^1$) + 6 (O is $2s^2 2p^4$) = 8

CO_2 has a total number of valence electrons = 4 (C is $2s^2 2p^2$) + 2 * 6 (O is $2s^2 2p^4$) = 16

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Determining the number of valence electrons:

Full d-orbitals do not count as valence electrons. They belong to the inner shell.

For example:

As is $[Ar]4s^2 3d^{10} 4p^3$

This is FIVE (5) valence electrons. The 3d is part of the inner shell (n=3) which is full.

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How many valence electrons does Ge have?

A. 12
B. 14
C. 3
D. 4
E. 5

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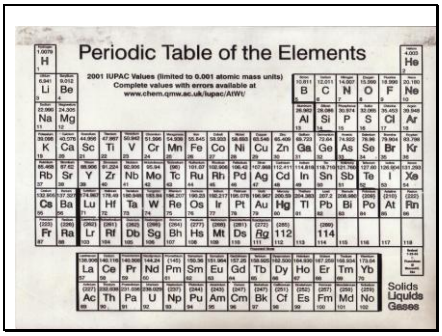

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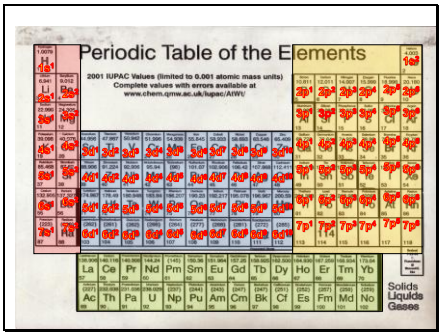

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Take a look at Ge electron structure

$[Ar]4s^2 3d^{10} 4p^2$

Full d-orbitals don't count. So there are 4 valence electrons.

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How many valence electrons does Ti have?

A. 1
B. 2
C. 3
D. 4
E. 5

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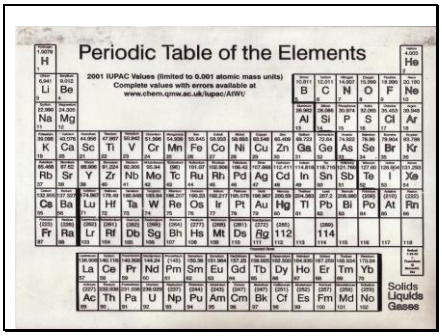

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How many valence electrons does Te have?

A. 15
B. 16
C. 3
D. 5
E. 6

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Central Atom

In a molecule, there are only 2 types of atoms:

1. "central" – bonded to more than one other atom.
2. "terminal" – bonded to only one other atom.

You can have more than one central atom in a molecule.

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Bonds

Bonds are pairs of shared electrons.

Each bond has 2 electrons in it.

You can have multiple bonds between the same 2 atoms. For example:

C-O
C=O
C ≡ O

Each of the lines represents 1 bond with 2 electrons in it.

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Lewis Dot Structure

Each electron is represented by a dot in the structure

That symbol with the dots indicate a chlorine atom with 7 valence electrons.

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Drawing Lewis Dot Structures

1. Determine the total number of valence electrons.
2. Determine which atom is the "central" atom.
3. Stick everything to the central atom using a single bond.

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Dot structure for H_2O

1. Total number of valence electrons:
   $6 + (2 \times 1) = 8$

2. Central Atom – typically, the central atom will be leftmost and/or bottommost in the periodic table. It is the atom that wants more than one thing stuck to it. H is NEVER the central atom.
3. Stick all terminal atoms to the central atom using a single bond.

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Dot structure for H_2O

H – O – H

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Drawing Lewis Dot Structures

1. Determine the total number of valence electrons.
2. Determine which atom is the "central" atom.
3. Stick everything to the central atom using a single bond.
4. Fill the octet of every atom by adding dots.
5. Verify the total number of valence electrons in the structure.

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Dot structure for H_2O

That is a total of 8 valence electrons used: each bond is 2, and there are 2 non-bonding pairs.

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Drawing Lewis Dot Structures

1. Determine the total number of valence electrons.
2. Determine which atom is the "central" atom.
3. Stick everything to the central atom using a single bond.
4. Fill the octet of every atom by adding dots.
5. Verify the total number of valence electrons in the structure.
6. Add or subtract electrons to the structure by making/breaking bonds to get the correct # of valence electrons.
7. Check the "formal charge" of each atom.

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Formal Charge of an atom

"Formal charge" isn't a real charge. It's a pseudo-charge on a single atom.

Formal charge = number of valence electrons – number of bonds – number of non-bonding electrons.

Formal charge (FC) is ideally 0, acceptably +/-1, on occasion +/-2. The more 0s in a structure, the better.

The total of all the formal charges of each atom will always equal the charge on the entire structure (0 for neutral molecules).

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Dot structure for H_2O

FC (H) = 1-1-0 = 0
FC (O) = 6 – 2 – 4 = 0

This is excellent, all the FCs are 0!

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DON'T EVER STOP AND THINK ABOUT WHERE THE ELECTRONS CAME FROM!!!

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Clicker

Choose the best Lewis Dot Structure for: SCl_2

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N_2S

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Another example

Let's try CO_2

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Drawing Lewis Dot Structures

1. Determine the total number of valence electrons.
2. Determine which atom is the "central" atom.
3. Stick everything to the central atom using a single bond.
4. Fill the octet of every atom by adding dots.
5. Verify the total number of valence electrons in the structure.
6. Add or subtract electrons to the structure by making/breaking bonds to get the correct # of valence electrons.
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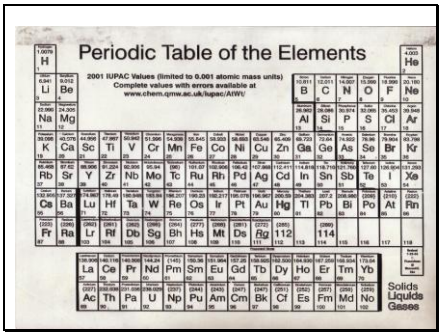

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CO_2

CO_2

Total number of valence electrons = 4 from carbon + 2x6 from oxygen = 16

Central Atom?

Either C or O could be a central atom. C is more likely (to the left, to the left, to the left…)

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CO_2

CO_2

16 total valence electrons

O – C – O

Fill out the octets

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Drawing Lewis Dot Structures

1. Determine the total number of valence electrons.
2. Determine which atom is the "central" atom.
3. Stick everything to the central atom using a single bond.
4. Fill the octet of every atom by adding dots.
5. Verify the total number of valence electrons in the structure.
6. Add or subtract electrons to the structure by making/breaking bonds to get the correct # of valence electrons.
7. Check the "formal charge" of each atom.

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CO_2

16 total valence electrons

:O – C - O:

Structure has 20 electrons in it. Too many!

I need to lose 4 electrons. What's the best way to do that?

Make 2 bonds – each new bond costs 2 electrons

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CO_2

:O = C = O:

Structure has 16 electrons in it. Just right!

Notice, this works because there are 2 ways to count the electrons:

1. When I count the total # of electrons, I count each electron once.
2. When I count the electrons for each atom, I count the bond twice (once for each atom in the bond)

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CO_2

:O = C = O:

Is this the only structure I could have drawn?

I only needed two new bonds, I didn't specify where they needed to go!

:O ≡ C - O:

:O - C ≡ O:

Which is correct?

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Choosing between different structures?

The first test is formal charge:

FC (O) = 6 – 2 – 4 = 0
FC (C) = 4 – 4 – 0 = 0

FC (left O) = 6 – 3 – 2 = 1
FC (C) = 4 – 4 – 0 = 0
FC (right O) = 6 – 1 – 6 = -1
Based on formal charge the upper structure is the better one.

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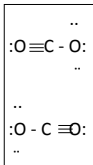
Are these even different?



Depends on what I mean by different!

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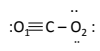
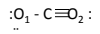
Are they different?





If I label them, I can see a difference. (Isotopic labeling).
If I don't label them, they are interchangeable, just rotate the top one to get the bottom one.

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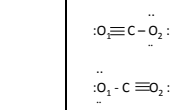
Resonance



Structures that are identical, but differ only in the arrangement of bonds are called resonance structures.

Resonance is always GOOD!

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Resonance

When you have resonance, the real structure is not any one of the individual structures but the combination of all of them.

You can always recognize resonance – there are double or triple bonds involved.

If you take the 3 different CO_2 structures, the "average" is the original one we drew with 2 double bonds.

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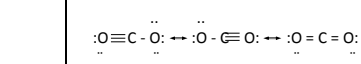
Resonance

Resonance is indicated by drawing all resonance structures, separated by " "



But this is not necessary in this case, as the last structure is also the combination of the 3 structures

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Nitrite ion

Draw the Lewis Dot structure for NO_2^-

How many valence electrons?

N has 5, O has 6, but there's one extra (it's an ion!)

5 + 2 (6) = 17 valence electrons + 1 extra = 18 valence electrons

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Nitrite LDS

What's the central atom?

Nitrogen

O – N – O

:O – N - O:

Total number of electrons?

20 electrons – too many

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Nitrite LDS

:O – N - O:

How do you fix the problem?

Make a bond

:O = N - O:

What do you think?

RESONANCE

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Nitrite LDS

:O = N - O: ↔ :O - N = O:

What's the real structure look like?

It's an average of those 2. Kind of 1-1/2 bonds between each N and O! In fact, if you measure the bond angles in nitrite, you find that they are equal (a double bond would be shorter than a single bond)

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Let's try another…

CO_3^{2-}

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N_2H_2

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Exceptions to the Octet Rule

There are exceptions to the octet rule:

1. Incomplete octets – less than 8 electrons.
2. Expanded octets – more than 8 electrons

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Incomplete Octets

The most common elements that show incomplete octets are B, Be besides H.

So, for example, BCl_3 has the Lewis structure:

Total valence electrons is correct at 24.
FC (B) = 3 - 3 – 0 = 0
FC (Cl) = 7- 1 - 6 = 0

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Expanded Octets

The most common atoms to show expanded octets are P and S. It is also possible for some transition metals.

An example of an expanded octet would be PCl_5:

Total valence e^- = 40

FC(P) = 5 – 5 – 0 =0

FC (Cl) = 7 – 1 – 6 = 0

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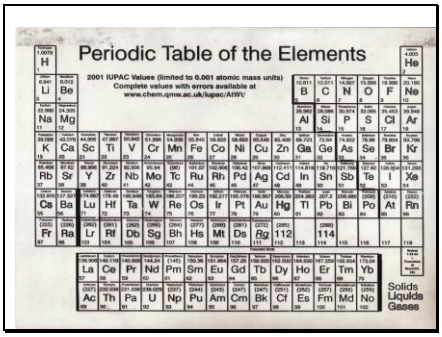

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Let's talk bonds!

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What holds molecules together?

Bonds

Bonds are made up of?

Electrons

How do the electrons hold atoms together?

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Two ways:

- Ionic Bonds – attraction between ions of opposite charges

  $Na^+ Cl^-$

- Covalent Bonds – sharing of electrons between adjacent atoms

  PF_3

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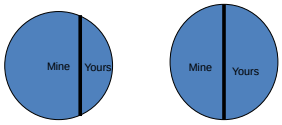
Are they really different?

Let's share a pie!



Which pie are we actually sharing?

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Sharing doesn't have to be equal!

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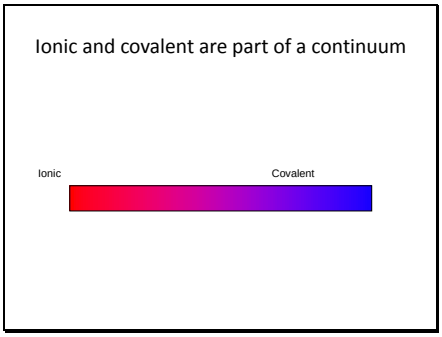

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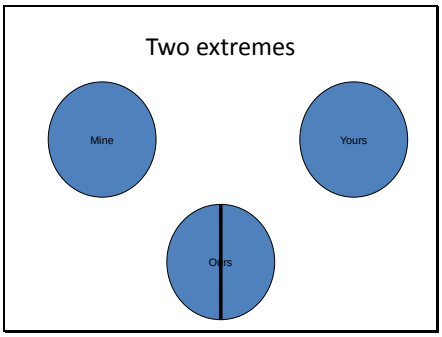

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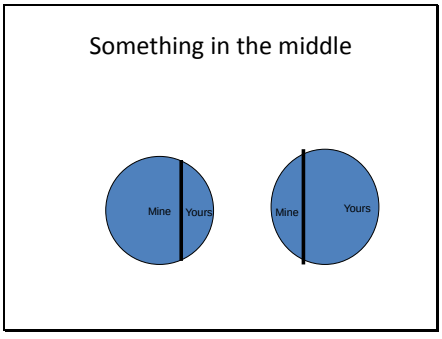

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Ionic and covalent are part of a continuum

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The truth about bonds

Covalent – bonding by sharing of electrons

Ionic – bonding by attraction between oppositely charged ions

Really, they are exactly the same thing!

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So, consider a bond, any bond:

Cl – Cl

Which case is this?

Equal sharing!

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So, consider a bond, any bond:

H-Cl

Which case is this?

Unequal sharing! How do you know?

They are on opposite sides of the Periodic table!

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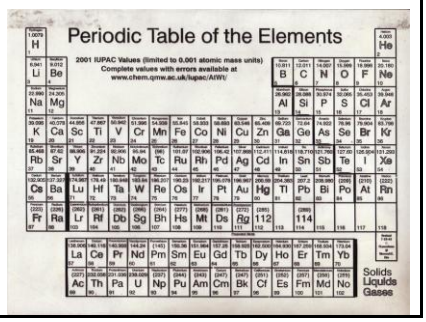

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A metal + a non-metal =

An ionic compound!

Non-metals love electrons, metals don't!

There is a periodic trend for "electron love": electronegativity or electron affinity.

Electronegativity increases to the right and going up (F is most electronegative, Fr is least)

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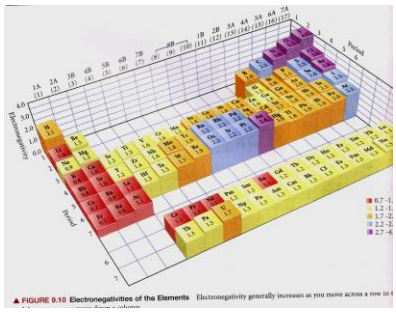

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Electronegativity

Electronegativity is the ability of an atom to attract electrons to itself.

Electronegativity is important in predicting whether a bond is ionic or covalent.

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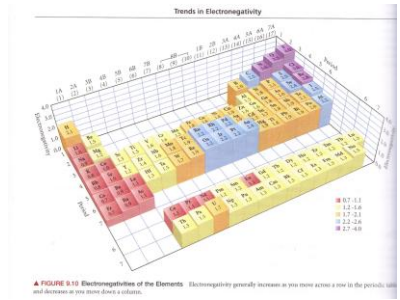

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Loving electrons

I love pie.

I have a pie sitting in front of me.

You sort of like pie (or maybe you're smaller than me!).

You get no pie!

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Loving electrons

I love pie.

I have a pie sitting in front of me.

You really, really, really love pie (or maybe you're bigger than me!).

I get no pie.

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Loving electrons

I like pie.

I have a pie sitting in front of me.

You like pie.

We each get ½ the pie.

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Electrons are like pie!

The “sharing” of electrons is really a sliding scale from completely equal (non-polar bond) to completely unequal (ionic).

The electronegativity helps me decide.

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Suppose I’m oxygen…

…you need me to live!

I’m oxygen. How much do I like pie…er, electrons?

Check my electronegativity…

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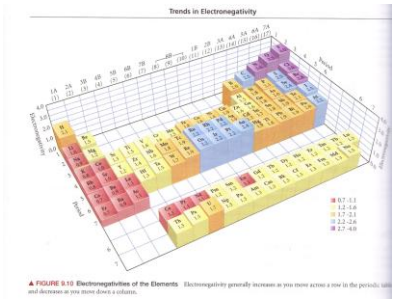

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I'm oxygen, I need a friend…

ONLY O has an electronegativity of 3.5. The only completely equal sharing of electrons is with O.

O_2 – completely equal covalent bond. Non-polar.

Suppose, I make a new friend that is not myself (that would be NICE!) like N.

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O (EN = 3.5)
N (EN = 3.0)

Close, but not the same. The difference is 0.5. What kind of bond is this?

POLAR covalent.

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Arbitrarily:

The polarity of a bond is determined by the difference in electronegativity between the atoms at either end of the bond.

Δ E.N. = Larger E.N. – smaller E.N.

ΔE.N. = 0 to 0.4 - NON-polar covalent bond

ΔE.N. = 0.401 to 1.999 – POLAR covalent bond

ΔE.N. = 2.0+ IONIC bond

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Cl – Cl

Δ E.N. = 3.0 – 3.0 = 0
Non-polar

H-Cl

Δ E.N. = 3.0 – 2.1 = 0.9
Polar

NaCl
Δ E.N. = 3.0 – 0.9 = 2.1
Ionic

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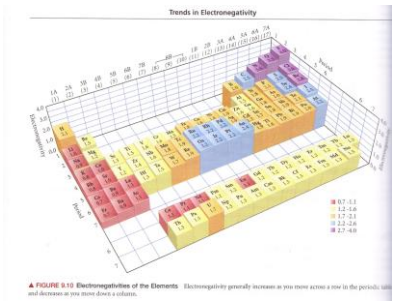

▲ FIGURE 9.10 Electronegativities of the Elements Electronegativity generally increases as you move across a row in the periodic table and decreases as you move down a column.

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Polarity is represented as an arrow…

…pointing toward the more negative atom.

Cl – Cl

H-Cl

NaCl

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Bond polarity is local…

The polarity of a bond refers only to the bond itself: the two atoms that are bonded together.

For molecules as a whole, there is still "polarity" but it is a more complicated thing that depends on 3-D geometry.