Chapter 4: Chemical Bonding and Molecular Geometry

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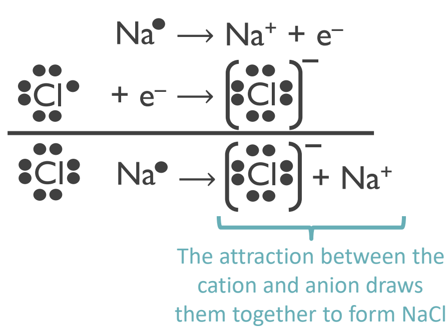
Compounds

A ***compound*** is a substance composed of two or more elements combined in a specific ratio and held together by chemical bonds.

Familiar examples of compounds
water and salt (sodium chloride).

Ionic bonding refers to the electrostatic attraction that holds oppositely charged ions together in an **ionic compound**.



The resulting electrically neutral compound, sodium chloride, is represented with the chemical formula NaCl.

The **chemical formula**, or simply **formula**, of an ionic compound denotes the constituent elements and the ratio in which they combine.

Ionic compounds typically have a metal ion and a non–metal ion to form the compound.

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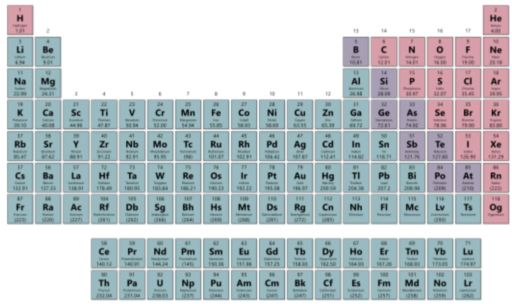
The Periodic Table

Elements can be categorized as **metals**, **nonmetals**, or **metalloids**.

Metals are good conductors of heat and electricity.
solids (except mercury – a liquid)
ductile (can be drawn into wires)
malleable (can be rolled into sheets)



Nonmetals are poor conductors of heat or electricity. (graphite is the one exception)
Occur in all physical states.

Metalloids have intermediate properties.
Boron, silicon, germanium, arsenic, antimony, tellurium, (astatine)
They exhibit metallic and nonmetallic properties:

- Conduct electricity (not as well as metals).
  - Look like metals (shiny).
    - semiconductors.

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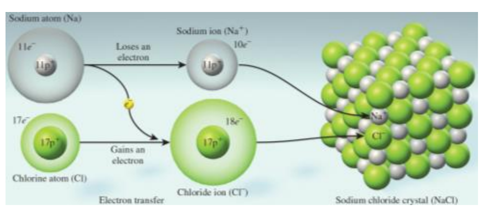
Ionic Compounds and Bonding

A three-dimensional array of oppositely-charged ions is called a **lattice**. **Lattice energy** is the amount of energy required to convert a mole of ionic solid to its constituent ions in the gas phase.

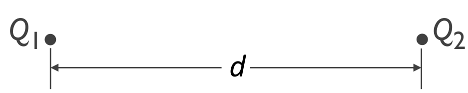


The formation of ionic bonds **releases** a large amount of energy

The magnitude of lattice energy is a measure of an ionic compound's stability. Lattice energy depends on the magnitudes of the charge and on the distance between them.

$$F \propto \frac{Q_1 \cdot Q_2}{d^2}$$

Q = amount of charge
d = distance of separation



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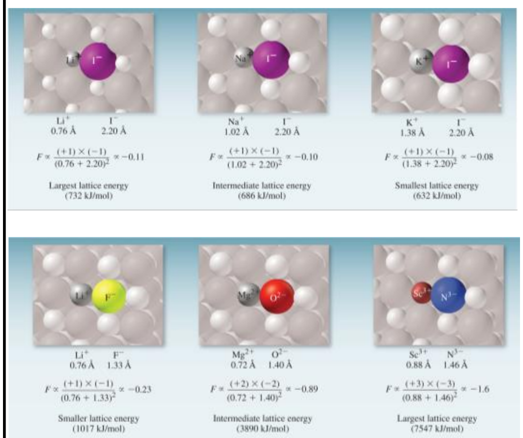
Ionic Compounds and Bonding

The magnitude of lattice energy is a measure of an ionic compound's stability. Lattice energy depends on the magnitudes of the charge and on the distance between them.



Lattice Energies of Selected Ionic Compounds		
Compound	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	860	610
LiBr	787	550
LiI	732	450
NaCl	787	801
KCl	699	772
MgO	3890	2800
ScN	7547	>3000

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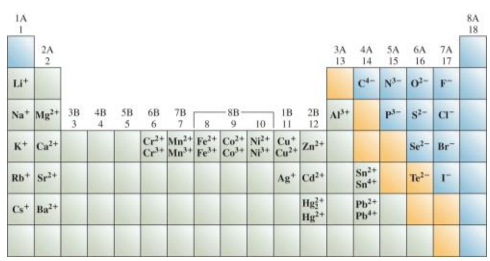
Electron Configurations of Ions

To write the electron configuration of an ion formed by a main group element:

1. Write the configuration for the atom.
2. Add or remove the appropriate number of electrons. Positive ions, remove electrons; negative ions, add electrons

Na: $1s^2 2s^2 2p^6 3s^1 \longrightarrow$ Na^+: $1s^2 2s^2 2p^6$
10 electrons total, **isoelectronic** with Ne

Cl: $1s^2 2s^2 2p^6 3s^2 3p^5 \longrightarrow$ Cl^-: $1s^2 2s^2 2p^6 3s^2 3p^6$
18 electrons total, **isoelectronic** with Ar



Species with identical electron configurations to the noble gas to the right are called **isoelectronic**

Common monatomic ions arranged by their positions in the periodic table

Note that mercury(I) is a **poly**atomic ion (Hg_2^{2+})

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Electronegativity and Polarity

There are two extremes in the spectrum of bonding:

covalent bonds occur between atoms that share electrons

ionic bonds occur between a metal and a nonmetal and involve ions

Bonds that fall between these extremes are **polar**.

In **polar covalent bonds**, electrons are shared but not shared equally. The delta, δ, is used to denote partial charges on the atoms

Pure covalent bond	Polar covalent bond	Ionic bond
Neutral atoms held together by equally shared electrons	Partially charged atoms bonded by unequally shared electrons	Oppositely charged ions held together by electrostatic attraction
M:X	$M^{\delta+}X^{\delta-}$	$M^{+}X^{-}$

H_2 HF NaF

Electron density maps show the distributions of charge. Electrons spend a lot of time in red and very little time in blue.

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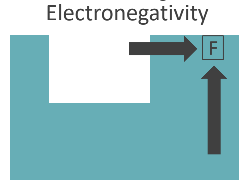
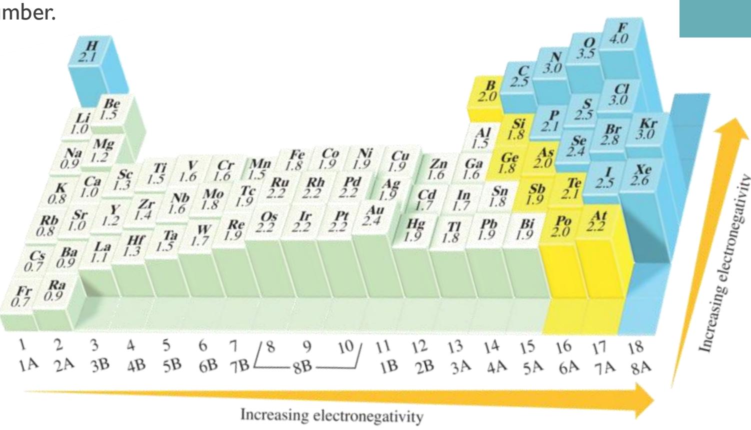
Electronegativity and Polarity

Increasing Electronegativity



Electronegativity is the ability of an atom in a compound to draw electrons to itself. Electronegativity varies with atomic number.



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Electronegativity

There is no sharp distinction between nonpolar covalent and polar covalent or between polar covalent and ionic.

The following rules help distinguish among them:

A bond between atoms whose electronegativites differ by less than 0.5 is general considered purely covalent or **nonpolar**.

A bond between atoms who's electronegativies differ by the range of 0.5 to 2.0 is generally considered **polar covalent**.

A bond between atoms whose electronegativities differ by 2.0 or more is generally considered **ionic**.

Classify the following bonds as nonpolar, polar, or ionic: (a) the bond in ClF, (b) the bond in CsBr, and (c) the carbon-carbon double bond in C_2H_4.

a) The difference in electronegativies: F and Cl is 4.0 – 3.0 = 1.0. The bond in ClF is polar.
b) In CsBr, the difference is 2.8 – 0.7 = 2.1, making the bond ionic.
c) In C_2H_4, the two atoms are identical. The carbon-carbon double bond is C_2H_4 is nonpolar.

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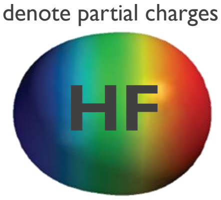
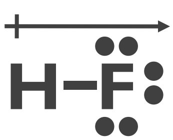
Polar Covalent Bonds

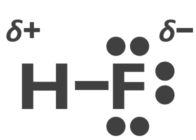
In **polar covalent bonds**, electrons are shared but not shared equally. The delta, δ, is used to denote partial charges on the atoms



Electron density maps show the distributions of charge. Electrons spend a lot of time in red and very little time in blue.



An arrow is used to indicate the direction of electron shift in polar covalent molecules.



The consequent charge separation can be represented as Delta (δ) which denotes a partial positive or negative charge.

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Dipole Moment, Partial Charges, and Percent Ionic Character

A quantitative measure of the polarity of a bond is its **dipole moment (μ)**.

$\mu = Q \times r$

Q is the charge.
r is the distance between the charges.
μ is always positive and expressed in debye units (D).

1 D = 3.336 x10^{-30} C·m. C is Coulomb, and m is meter

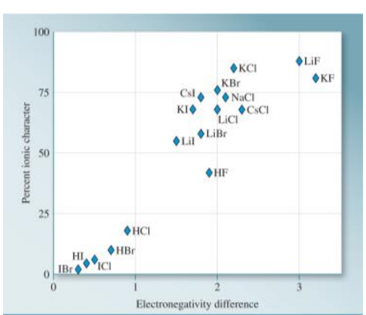
Bond Lengths and Dipole Moments of the Hydrogen–Halides		
Molecule	Bond Length (Å)	Dipole Moment (D)
HF	0.92	1.82
HCl	1.27	1.08
HBr	1.41	0.82
HI	1.61	0.44

Dipole Moment, Partial Charges, and Percent Ionic Character

Although the designations "covalent," "polar covalent," and "ionic" can be useful, sometimes chemists wish to describe and compare chemical bonds with more precision.

Comparing the calculated dipole moment with the measured values gives us a quantitative way to describe the nature of a bond using the term **percent ionic character**.

$$\text{percent ionic character} = \frac{\mu\ (\text{observed})}{\mu\ (\text{calculated assuming discrete charges})} \times 100\%$$



The figure demonstrates the relationship between percent ionic character and the electronegativity difference in a heteronuclear diatomic molecule.

Practice

Determine the partial charges and direction of dipole for the following bonds:

H–Cl	Cl H 3.0 – 2.1 = 0.9	δ^{+} ⟶ δ^{-} H–Cl
C–O	O C 3.5 – 2.5 = 1.0	δ^{+} ⟶ δ^{-} C–O
O–H	O H 3.5 – 2.1 = 1.4	δ^{+} ⟶ δ^{-} H–O
N–F	F N 4.0 – 3.0 = 1.0	δ^{+} ⟶ δ^{-} N–F

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Types of Ionic Compounds

There are two types of ionic compounds:

1. Ionic compounds formed between two elements: a metal and a non-metal
   Example: NaCl, $CaCl_2$
2. Ionic compound formed between a metal and a polyatomic ion (multiple atoms)
   Example: $Ca(BrO_3)_2$

The list of polyatomics is given in your textbook, but in this case, the polyatomic ion is the bromate ion (BrO_3).

The polyatomic ions must be memorized.

Naming ionic compounds composed of only elemental ions requires you to know the names and symbols of the given metal and non-metal ions.

These are given in Table 5.2 of your book. I will also give uploaded notes with them.

To name ionic compounds:

1) Name the cation (omit the word *ion)*

***Use a Roman numeral if the cation can have more than one charge (this happens mostly for transition metals).**

This roman numeral tells the charge on that transition metal.

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2) Name the anion by replacing the ending with -ide (omit the word *ion)*

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Naming Ionic Compounds

		Naming Method	Old System
Examples:	NaBr	sodium bromide	
	$FeCl_2$	iron (II)chloride	ferrous chloride
	$FeCl_3$	iron (III)chloride	ferric chloride

To give ionic compound formula from the name:
When we want to go from the name to the formula there are a few things we need to remember.

Ionic compounds are electronically neutral.

For ionic compounds to be electronically neutral, the sum of the charges in each formula must be zero.

Your task: Find the **smallest coefficients** that will yield a compound with a neutral charge. People accomplish this one of two ways: (1) Sum of Charges or (2) Cross Multiplication

Example: Aluminum oxide: Al^{3+} and $O^{2-} \longrightarrow Al_2O_3$

Sum of charges: $2(+3) + 3(-2) = 0$

Cross Multiplication: Al^{3+} O^{2-}

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Formulas of Ionic Compounds

If you chose to cross multiply, make sure that you are only reporting the empirical formula. What do I mean by that?

Example: What is the formula for Calcium Oxide?

Order to writing the chemical formula:

1. Look for Calcium (Ca) on the periodic table: It is in group 2A (typical ion charge of 2+).
2. Find Oxygen (O) on the periodic table: It is group 6A (typical ion charge of 2–).
3. We write Ca with a +2 charge. We write O with a –2 Charge.
4. We cross multiply
5. We divide to make the simplest coefficients possible.

Step 1 and 2		Step 3		~~~Step 4~~~				Step 5
Ca and O	→	Ca^{2+} O^{-2}	→	Ca^{+2} O^{-2}	→	Ca_2O_2	→	CaO

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Examples

Name the following ionic compounds: (a) CaO, (b) Na_3N, and (c) $CuBr_2$

(a) Calcium oxide **(b) Sodium nitride** **(c) Copper(II) bromide**

Deduce the formulas of the following ionic compounds: (a) Iron(II) chloride, (b) strontium(II) oxide, and (c) potassium bromide.

(a) Fe^{2+} Cl^{-1} ⟶ Fe^{2+} Cl^{-1} ⟶ $FeCl_2$

(b) Sr^{2+} O^{-2} ⟶ Sr^{2+} O^{-2} ⟶ Sr_2O_2 ⟶ SrO

(c) K^+ Br^- ⟶ K^+ Br^- ⟶ KBr

Determine ion charges and make neutral compounds. (a) Mg and P, (b) Rb and F, (c) Na and N, (d) Al and Br, (e) Li and S

(a) Mg_3P_2 **(b) RbF** **(c) Na_3N** **(d) $AlBr_3$** **(e) Li_2S**

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Ionic Compounds formed with polyatomic ions (covalently bonded species)

Polyatomic ions: consist of a combination of two or more atoms. A common list can be found in the textbook in Table 2.5 (Textbook Link: Table 2.5)

Formulas are determined following the same rules as for ionic compounds containing only monatomic ions: ions must combine in a ratio that give a neutral formula overall.

Calcium phosphate: Ca^{2+} and PO_4^{3-}

Sum of charges: $3(+2) + 2(-3) = 0 \longrightarrow Ca_3(PO_4)_2$

Cross Multiply: Ca^{+2} PO_4^{-3} : $Ca_3(PO_4)_2$

Notice that when multiple polyatomic ions are coordinated, there are parenthesis around it. These aren't needed for only one polyatomic ion.

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Polyatomic Ions (Oxoanions)

Oxoanions are polyatomic anions that contain one or more oxygen atoms and one atom (the "central atom") of another element.

Starting with the oxoanions that end in –ate, we can name these ions as follows:

1) The ion with one more O atom than the –ate ion is called the per…ate ion. Thus, ClO_3^- is the chlorate ion, so ClO_4^- is the perchlorate ion.
2) The ion with one less O atom than the –ate ion is called the –ite ion. Thus, ClO_2^- is the chlorite ion.
3) The ion with two fewer O atom than the –ate ion is called the hypo…ite ion. Thus, ClO^- is the hypochlorite ion.

You can apply these guidelines when necessary.

phosphate	PO_4^{3-}	perchlorate	ClO_4^-
phosphite	PO_3^{3-}	chlorate	ClO_3^-
		chlorite	ClO_2^-
sulfate	SO_4^{2-}	hypochlorite	ClO^-
sulfite	SO_3^{2-}		
		nitrate	NO_3^-
		nitrite	NO_2^-

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Examples

Name the following ionic compounds: (a) $Mn_3(PO_4)_2$, (b) $AlCl_3$, and (c) Hg_2O.

(a) Manganese(II) Phosphate **(b) Aluminum chloride** **(c) Mercury(I) oxide**

Write formulas for the following ionic compounds:

(A) Li^+ and N^{3-}, **(A) Li_3N**

(B) (B) Fe^{2+} and Cl^-, **(B) $FeCl_2$**

(C) Mn^{2+} and SO_4^{2-}, **(C) $MnSO_4$**

(D) Co^{2+} and $C_2H_3O_2^-$, **(D) $Co(C_2H_3O_2)_2$**

(E) Mn^{7+} and CO_3^{2-} **(E) $Mn_2(CO_3)_7$**

Name the following compounds: A) $AlCl_3$, B) AgF, C) $CaBr_2$, D) PbO_2

(a) Aluminum(III) chloride **(b) Silver(I) fluoride** **(c) Calcium bromide** **(d) Lead(IV) oxide**

What is the correct, systematic name of Mn_2S_3?

A. Manganese(III) sulfide
B. Dimanganese trisulfide
C. Magnesium(II) sulfite
D. Dimagnesium trisulfide

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Naming Molecular Compounds (New Rules)

Remember that binary molecular compounds are substances that consist of just two different elements. **These are the rules for molecular compounds, not ionic compounds! Use when both elements are nonmetals!**

Nomenclature:
1) Name the first element that appears in the formula.
2) Name the second element that appears in the formula, changing its ending to –ide.
3) Add Greek prefixes to elements (skip the mono- on the first element.)

Greek prefixes are used to denote the number of atoms of each element present.

Prefix	Meaning	Prefix	Meaning
Mono-	1	Hexa-	6
Di-	2	Hepta-	7
Tri-	3	Octa-	8
Tetra-	4	Nona-	9
Penta-	5	Deca-	10

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Naming Molecular Compounds

The prefix mono– is generally omitted for the first element.

For ease of pronunciation, we usually eliminate the last letter of a prefix that ends in "o" or "a" when naming an oxide.

Example: N_2O_5 is dinitrogen pentoxide NOT dinitrogen pent<u>a</u>oxide

Compounds with Greek Prefixes

Compound	Name	Compound	Name
CO	Carbon monoxide	SO_3	Sulfur trioxide
CO_2	Carbon dioxide	NO_2	Nitrogen dioxide
SO_2	Sulfur dioxide	N_2O_5	Dinitrogen pentoxide

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Examples

Name the following binary molecular compounds: (a) PF_3 and (b) N_2O.

a) **Phosphorous trifluoride**
b) **Dinitrogen monoxide**

Write the chemical formulas for the following binary molecular compounds: (a) sulfur tetrafluoride and (b) tetraphosphorus decasulfide.

a) **SF_4**
b) **P_4S_{10}**

Name the following compounds: (a) SO_3, (b) $CuSO_4$, (c) S_2Cl_2, (d) SF_6

a) **Sulfur trioxide**
b) **Copper(II) sulfate**
c) **Disulfur dichloride**
d) **Sulfur hexafluoride**

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Compounds Containing Hydrogen

The names of molecular compounds containing hydrogen usually do not conform to the systematic nomenclature guidelines. Many are common nonsystematic names that do not indicate explicitly the number of H atoms present.

Compound	Name	Compound	Name
B_2H_6	Diborane	SiH_4	Silane
NH_3	Ammonia	PH_3	Phosphine
H_2O	Dihydrogen monoxide/water	H_2S	Hydrogen Sulfide

An **acid** is a substance that produces hydrogen ions (H^+) when dissolved in water (one definition). HCl is an example of a binary compound that is an acid when dissolved in water.

To name these types of acids:

1) remove the **–gen** ending from hydrogen
2) change the **–ide** ending on the second element to **–ic**.

hydro**gen** chlor**ide** → hydrochlor**ic** acid

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Compounds Containing Hydrogen

A compound must contain at least one **ionizable hydrogen atom** to be an acid upon dissolving. An ionizable hydrogen becomes a proton (H^+).

Some Simple Binary Acids

Formula	Binary compound name	Acid Name
HF	Hydrogen fluoride	Hydrofluoric acid
HCl	Hydrogen chloride	Hydrochloric acid
HBr	Hydrogen bromide	Hydrobromic acid
HI	Hydrogen iodide	Hydroiodic acid

Oxoacids, when dissolved in water, produce hydrogen ions and the corresponding oxoanions.
An acid based on an **–ate ion** is called………**ic acid**

$HClO_3$ is chloric acid

An acid based on an **–ite ion** is called………**ous acid**

$HClO_2$ is chlorous acid

Prefixes in oxoanion names **are retained** in naming the oxoacids

$HClO_4$ is perchloric acid

HClO is hypochlorous acid

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Oxoacids

Oxoacids, can be monoprotic (one ionizable hydrogen/one H^+) or polyprotic (more than one ionizable hydrogen/more than one H^+)

The names of the anions indicate the number of the remaining hydrogens

H_3PO_4	Phosphoric acid
$H_2PO_4^-$	Dihydrogen phosphate ion
HPO_4^{2-}	Hydrogen phosphate ion
PO_4^{3-}	Phosphate ion

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Hydrates

A **hydrate** is a compound that has a specific number of water molecules within its solid structure.
For example, in its normal state, copper(II) chloride has two water molecules associated with it (blue compound).

Systematic name: copper(II) chloride dihydrate
Formula: $CuCl_2 \cdot 2H_2O$

When the water molecules are driven off by heating, the resulting compound, is called anhydrous.
Anhydrous: containing no water molecules

Some other hydrates:

$BaCl_2 \cdot 2H_2O$ $MgSO_4 \cdot 7H_2O$
$LiCl \cdot H_2O$ $Sr(NO_3)_2 \cdot 4H_2O$

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Familiar Inorganic Compounds

Common and Systematic Names of Some Familiar Inorganic Compounds

Formula	Common name	Systematic name
H_2O	Water	Dihydrogen monoxide
NH_3	Ammonia	Trihydrogen nitride
CO_2	Dry ice	Solid carbon dioxide
NaCl	Salt	Sodium chloride
N_2O	Nitrous oxide, laughing gas	Dinitrogen monoxide
$CaCO_3$	Marble, chalk, limestone	Calcium carbonate
$NaHCO_3$	Baking soda	Sodium hydrogen carbonate
$MgSO_4 \cdot 7H_2O$	Epsom salt	Magnesium sulfate heptahydrate
$Mg(OH)_2$	Milk of magnesia	Magnesium hydroxide

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The Modern Periodic Table and Lewis Dot Symbols

The outermost electrons of an atom are called the **valence electrons**.
Valence electrons are involved in the formation of chemical bonds.
Similarity of valence electron configurations help predict chemical properties.

All electrons associated with the highest principal quantum number are valence

For Group 1A: [noble gas]ns^1 — [noble gas] = core, ns^1 = valence

For Group 7A: [noble gas]ns^2np^5 — [noble gas] = core, ns^2np^5 = valence

When atoms form compounds, it is their valence electrons that actually interact.

A **Lewis dot symbol** consists of the element's symbol with dots, where each dot represents a valence electron.

Boron: $1s^22s^22p^1$ — $2s^22p^1$: 3 valence electrons → •Ḃ• Lewis dot symbol for boron

other reasonable Lewis dot symbols for boron (do not pair until needed)

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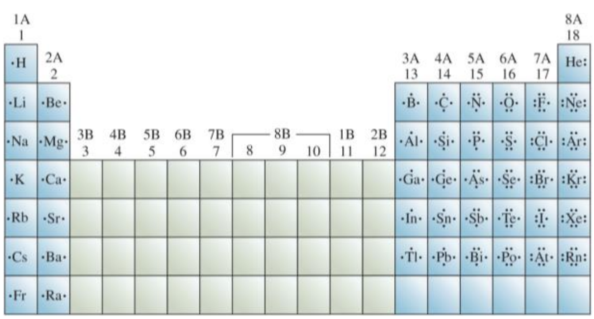
Lewis Dot Symbols



•Ḃ• $1s^22s^22p^1$

•Ċ• $1s^22s^22p^2$

•Ṅ• $1s^22s^22p^3$

5 valence electrons; first pair formed in the Lewis dot symbol

Na• For main group metals such as Na, the number of dots is the number of electrons that are lost.

:Ö: For nonmetals in the second period, the number of unpaired dots is the number of bonds the atom can form.

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Lewis Dot Symbols

Ions may also be represented by Lewis dot symbols.

Na• Na^+ ← Remember the charge

Na: $1s^22s^22p^63s^1$ ⟶ Na^+: $1s^22s^22p^6$

Valence electron lost in the formation of the Na^+ ion.

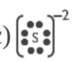
Core electrons not represented in the Lewis dot symbol

O: $1s^22s^22p^4$ ⟶ O^{2-}: $1s^22s^22p^6$

Write Lewis dot symbols for (a) fluoride ion (F^-), (b) potassium ion (K^+), and (c) sulfide ion (S^{2-}).

(a) 

(b) K^+

(c) 

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Practice

What are the valence electrons and Lewis dot diagrams for the following elements?

Mg^{2+} $[Mg]^{2+}$

P 

Se 

Li^+ $[Li]^+$

What are the valence set of electrons for Si?

- A. $3s^23p^2$
- B. $2s^22p^6$
- C. $2s^22p^63s^23p^2$
- D. $3s^23p^1$

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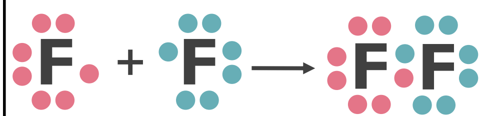
Lewis Dot Symbols

Atoms combine in order to achieve a more stable electron configuration. Maximum stability results when a chemical species is **isoelectronic** with a noble gas.

Na: $1s^22s^22p^63s^1$ ⟶ Na^+: $1s^22s^22p^6$ 10 electrons total, **isoelectronic** with Ne

Cl: $1s^22s^22p^63s^23p^5$ ⟶ Cl^-: $1s^22s^22p^63s^23p^6$ 18 electrons total, **isoelectronic** with Ar

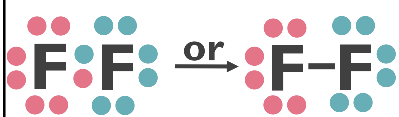
According to the **octet rule**, atoms will lose, gain, or share electrons in order to achieve a noble gas electron configuration. Look at the molecule F_2.



Electron Config. of F: $1s^22s^22p^5$

Only valence electrons contribute to bonding. Only two valence electrons participate in the formation of the F_2 bond.

Each F counts both shared electrons to "feel" as though it has a Ne configuration.



the dash represents two e^-. One e^- from each F.

Pairs of valence electrons not involved in bonding are called **lone pairs**.

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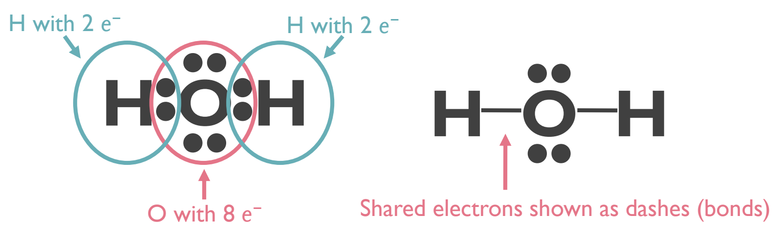
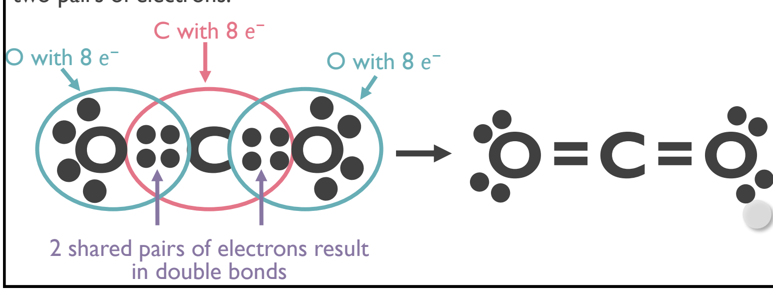
Lewis Structures and Multiple Bonds

A **Lewis structure** is a representation of covalent bonding. **Shared electron pairs** are shown either as dashes or as pairs of dots. **Lone pairs** are shown as pairs of dots on individual atoms.



In a **single bond**, atoms are held together by one electron pair. In a **double bond**, atoms share two pairs of electrons.



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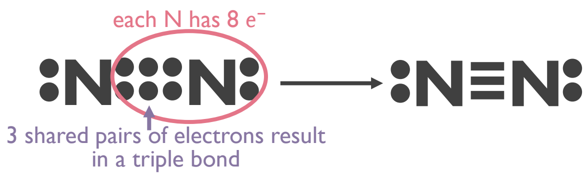
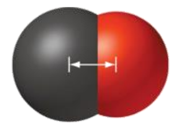
Lewis Structures and Multiple Bonds

A **triple bond** occurs when atoms are held together by three electron pairs.



Average Bond Lengths of Single, Double, and Triple Bonds			
Bond Type	**Bond Length (pm)**	**Bond Type**	**Bond Length (pm)**
C–H	107	C=N	138
O–H	96	C≡N	116
C–O	143	N–N	147
C=O	121	N=N	124
C≡O	113	N≡N	110
C–C	154	N–O	136
C=C	133	N=O	122
C≡C	120	O–O	148
C–N	143	O=O	121


CO

Bond length is defined as the distance between the nuclei of two covalently bonded atoms.

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Multiple Bonds

Multiple bonds are shorter than single bonds.
For a given pair of atoms:
 triple bonds are shorter than double bonds
 double bonds are shorter than single bonds

N≡N <	N=N <	N–N
110 pm	124 pm	147 pm

The shorter multiple bonds are also stronger than single bonds. We quantify bond strength by measuring the quantity of energy required to break it.

$H_2(g) \longrightarrow H(g) + H(g)$ Bond energy = 436.4 kJ mol^{-1}

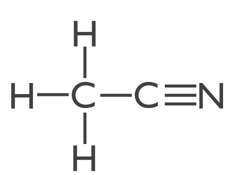
We will examine this in more detail in Chapter 10.

(a) Which would be the strongest bond?

(b) Which would be the longest bond?

C≡N : Strongest Bond

C–C : Weakest and Longest Bond



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Drawing Lewis Structures

Follow these steps when drawing Lewis structure for molecules and polyatomic ions.

1) Count the total number of valence electrons present; add electrons for negative charges and subtract electrons for positive charges

2) Draw the skeletal structure of the compound. The ***least*** electronegative atom is usually the central atom. Draw a single covalent bond between the central atom and each of the surrounding atoms.

3) Use the remaining electrons to complete octets of the terminal atoms by placing pairs of electrons on each atom. Complete the octets of the most electronegative atom first.

4) Place any remaining electrons in pairs on the central atom.

5) If the central atom has fewer than eight electrons, move one or more pairs from the terminal atoms to form multiple bonds between the central atom and terminal atoms.

6)Change Lewis structure to get the best formal charges

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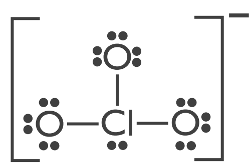
Drawing Lewis Structures

Draw the Lewis Structure for ClO_3^-.

1. Count the total number of valence e⁻ present; add e⁻ for negative charges and subtract electrons for positive charges.

Cl:	1	x	7	=	7	e⁻
O:	3	x	6	=	18	e⁻
Charge:				=	1	e⁻
Total					26	Valence e⁻

2. Draw the skeletal structure of the compound. The **least** electronegative atom is usually the **central atom**. Draw a single covalent bond between the central atom and each of the surrounding atoms. Chlorine's electronegativity = 3.0 and oxygen's electronegativity = 3.5.



3. For each bond in the skeletal structure, subtract two e⁻ from the total valence e⁻. 3 bonds x 2 e⁻ = 6 e⁻ and 26 – 6 = 20 e⁻ left over.

4. Use the remaining e⁻ to complete octets of the terminal atoms by placing pairs of e⁻ on each atom. Complete the octets of the most electronegative atom first.
18 e⁻ placed on the terminal atoms. The structure now has a total of 24 valence e⁻ of the 26.

5. Place any remaining e⁻ on the central atom. Lewis structures for polyatomic ions are enclosed by square brackets and charges.

6. If the central atom has fewer than eight e⁻, move one or more pairs from the terminal atoms to form multiple bonds between the central atom and terminal atoms.

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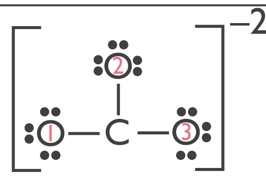
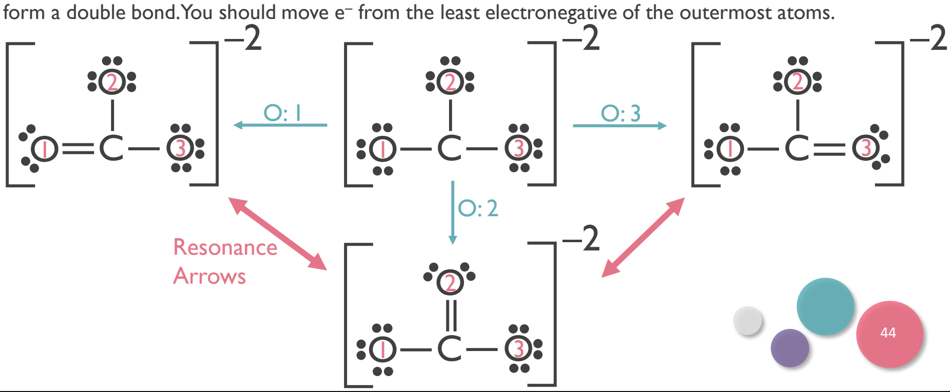
Practice

Draw the Lewis structure for carbonate (CO_3^{2-}).

C:	1	x	4	=	4	e^-	
O:	3	x	6	=	18	e^-	
Charge:				=	2	e^-	
Total					24	Valence e^-	



The center carbon does not have 8 e^- around it. One pair must be moved from the outermost atoms to form a double bond. You should move e^- from the least electronegative of the outermost atoms.



Practice

FNO_2

C_2H_2

ClF_2^+

N_3^-

NH_4^+

HCN

NO^-

$COCl_2$

Formal Charge

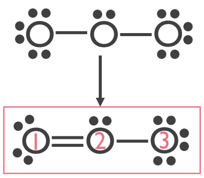
Formal charge can be used to determine the most plausible Lewis Structure when more than one possibility exists for a compound.

Formal Charge = Valence e⁻ – Associated e⁻

To determine associated electrons:

1) All the atom's nonbonding electrons are associated with the atom. (Count each dot as 1)
2) Half the atom's bonding electrons are associated with the atom. (Count each dash as 1)

Determine the formal charges on each oxygen atom in the ozone molecule (O_3).



Oxygen	Dots (e⁻)	Dashes (Bonds)	Associated e⁻
1	4	2	6
2	2	3	5
3	6	1	7

Oxygen	1	2	3
Valence e⁻	6	6	6
Associated e⁻	6	5	7
Formal Charge (Difference)	0	+1	–1

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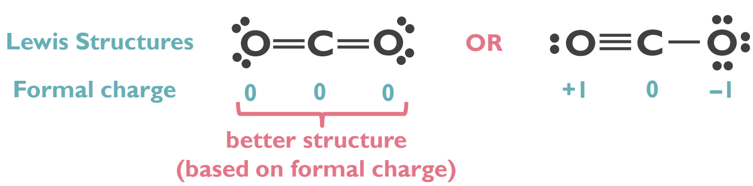
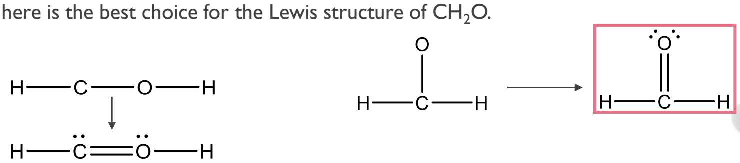
Lewis Structures and Formal Charge

When there is more than one possible structure, the best arrangement is determined by the best formal charge:

1) A Lewis structure in which all formal charges are zero is preferred.
2) Small formal charges are preferred to large formal charges.
3) Formal charges should be consistent with electronegativities.



Formaldehyde (CH_2O), which can be used to preserve biological specimens, is commonly sold as a 37 percent aqueous solution. Use formal charges to determine which skeletal arrangements of atoms shown here is the best choice for the Lewis structure of CH_2O.



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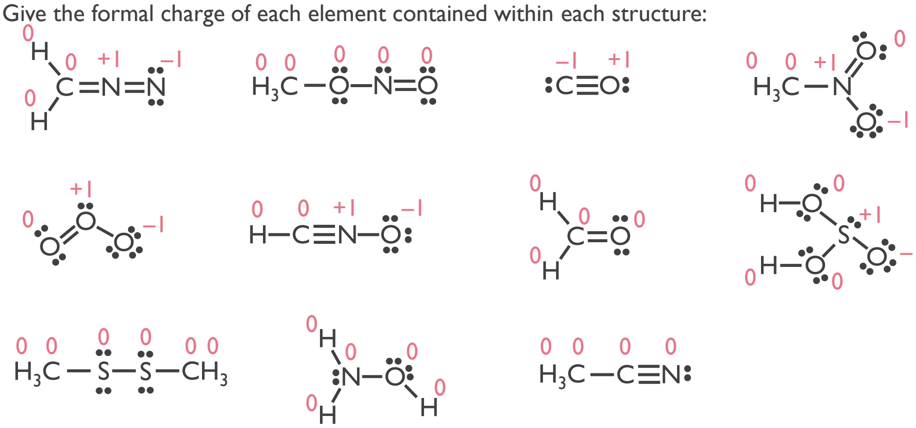
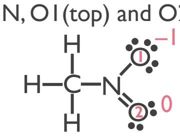
Practice

Give the formal charge of each element contained within each structure:



What is formal charge on N, O1(top) and O2(bottom)?



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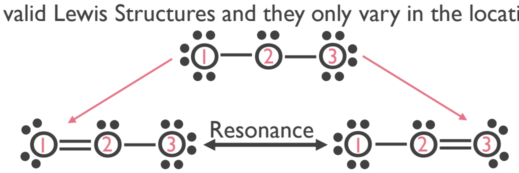
Resonance

A **resonance structure** is one of two or more Lewis structures for a single molecule that cannot by represented accurately by only one Lewis structure. Resonance structures are a human invention. Resonance structures differ only in the positions of their electrons.

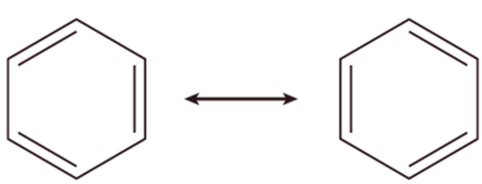
Looking at ozone (O_3): There are two valid Lewis Structures and they only vary in the location of e⁻.

O: 3 x 6 = 18 e⁻

Total: 18 Valence e⁻



The carbonate ion (CO_3^{2-}), another example of resonance, is shown on slide 26. Benzene is another example of resonance.



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Practice

SCN^-

NO_3^-

N_2O

ClO_3^-

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Exceptions to the Octet Rule

Exceptions to the octet rule fall into three categories:

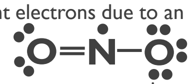
1) The central atom has fewer than eight electrons due to a shortage of electrons.

H—Be—H

only 4 total valence e^- in the system

Elements in group 3A also tend to form compounds surrounded by fewer than eight electrons. Boron, for example, reacts with halogens to form compounds of the general formula BX_3 having six electrons around the boron atom.

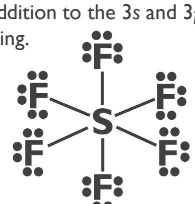
2) The central atom has fewer than eight electrons due to an odd number of electrons.



17 valence e^- in the system

Molecules with an odd number of electrons are sometimes referred to as **free radicals**.

3) The central atom has more than eight electrons. Atoms in and beyond the third period can have more than eight valence electrons. In addition to the 3*s* and 3*p* orbitals, elements in the third period also have 3*d* orbitals that can be used in bonding.



Sulfur has 6 bonds corresponding to 12 e^-

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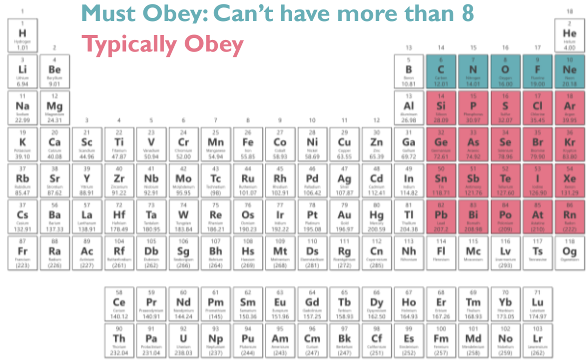
Exceptions to the Octet Rule

What elements must obey the octet rule (i.e. 8 electrons around an atom)?



Draw the Lewis structure of Nitric oxide (NO).

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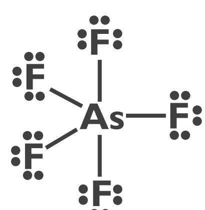
Practice

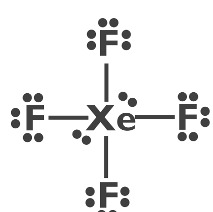
Draw the Lewis structure of arsenic pentafluoride (AsF_5).

As:	1	x	5	=	5	e^-
F:	5	x	7	=	35	e^-
Total					40	Valence e^-



Draw the Lewis structure of xenon tetrafluoride (XeF_4).

Xe:	1	x	8	=	8	e^-
F:	4	x	7	=	28	e^-
Total					36	Valence e^-



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Practice

PCl_5

PO_4^{3-}

SF_6

KrF_2

SeF_6

$SbCl_5$

BrO_3^-

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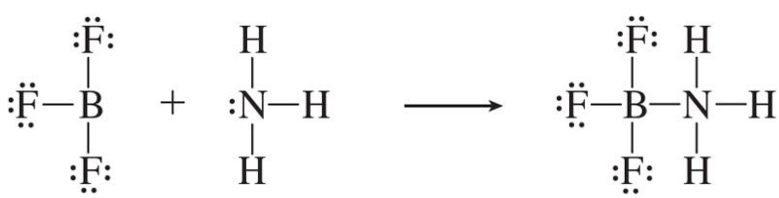
Exceptions to the Octet Rule

The bond between B–N has both the electrons contributed by the N atom.

- This type of bond is a coordinate covalent or dative bond
- This type of bond formation is an example of a Lewis acid–base process



BF_3 is a Lewis acid: it can accept a pair of electrons

NH_3 is a Lewis Base: it donates a pair of electrons

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Molecular Geometry

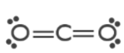
Molecular shape can be predicted by using the **valence-shell electron-pair repulsion (VSEPR)** model.

AB_x A is the central atom surrounded by x B atoms.
x can have integer values of 2 to 6.

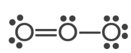
Examples of Ab_x Molecules and Polyatomic Ions	
AB_2	$BeCl_2$, SO_2, H_2O, NO_2^-
AB_3	BF_3, NH_3, ClF_3, SO_3^{2-}
AB_4	CCl_4, NH_4^+, SF_4, XeF_4, ClO_4^-
AB_5	PCl_5, IF_5, SbF_5, BrF_5
AB_6	SF_6, UF_6, $TiCl_6^{3-}$

The basis of the VSEPR model is that e⁻ repel each other, and e⁻ are found in various domains.

Lone pairs Double bonds Single bonds Triple bonds

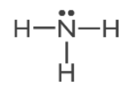


2 double bonds
2 e⁻ domains
(on central atom)



2 single bond (σ)
1 double bond (π)
1 lone pair

3 e⁻ domains
(on central atom)



3 single bonds (σ)
1 lone pair

4 e⁻ domains
(on central atom)

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The VSEPR Model

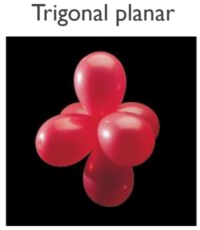
The basis of the VSEPR model is that electrons repel each other. Electrons will arrange themselves to be as far apart as possible. Arrangements minimize repulsive interactions.

2 e⁻ domains
Linear

3 e⁻ domains
Trigonal planar

4 e⁻ domains
Tetrahedral

5 e⁻ domains
Trigonal bipyramidal



6 e⁻ domains
Octahedral

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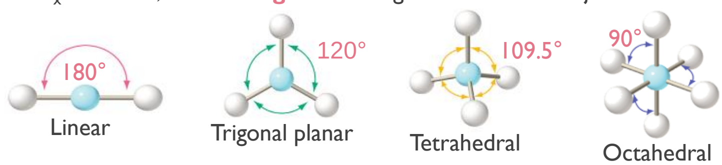
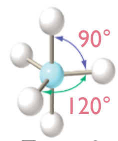
e⁻ Domain Geometry and Molecular Geometry

The **e⁻ domain geometry** is the arrangement of electron domains around the central atom.
The **molecular geometry** is the arrangement of bonded atoms.
In an AB_x molecule, a **bond angle** is the angle between two adjacent A-B bonds.

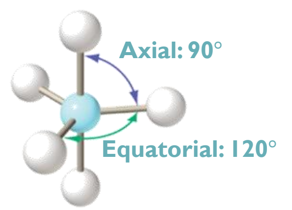




Axial positions; perpendicular to the trigonal plane

Equatorial positions; three bonds arranged in a trigonal plane.

Trigonal bipyramidal



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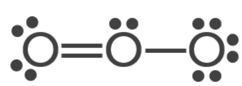
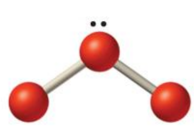
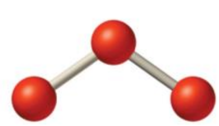
e⁻ Domain Geometry and Molecular Geometry

When the central atom in an AB_x molecule bears one or more lone pairs, the electron–domain geometry and the molecular geometry are no longer the same.





Electron-domain geometry: trigonal planar



Molecular geometry: bent

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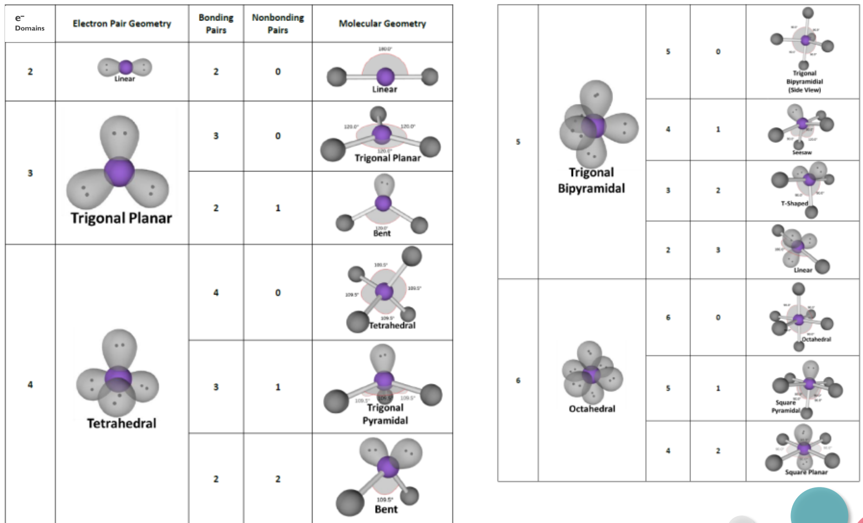
e⁻ Domain Geometry and Molecular Geometry



e⁻ Domains	Electron Pair Geometry	Bonding Pairs	Nonbonding Pairs	Molecular Geometry
2	Linear	2	0	Linear
3	Trigonal Planar	3	0	Trigonal Planar
		2	1	Bent
4	Tetrahedral	4	0	Tetrahedral
		3	1	Trigonal Pyramidal
		2	2	Bent
5	Trigonal Bipyramidal	5	0	Trigonal Bipyramidal (Side View)
		4	1	Seesaw
		3	2	T-Shaped
		2	3	Linear
6	Octahedral	6	0	Octahedral
		5	1	Square Pyramidal
		4	2	Square Planar

https://phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes_en.html

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Electron–Domain Geometry and Molecular Geometry

The steps to determine the electron-domain and molecular geometries are as follows:

Step 1: Draw the Lewis structure of the molecule or polyatomic ion.

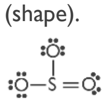
Step 2: Count the number of electron domains on the central atom.

Step 3: Determine the electron-domain geometry by applying the VSEPR model.

Step 4: Determine the molecular geometry by considering the positions of the atoms only.

Use Lewis structures and the VSEPR model to determine first the electron–domain geometry and then the molecular geometry (shape).

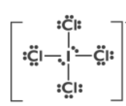
(a) The Lewis structure of SO_3 is:



There are 3 e⁻ domains on the central atom: one double bond and two single bonds.

e⁻ Geometry: Trigonal Planar
Molecular Geometry: Trigonal Planar

(b) The Lewis structure of ICl_4^- is:



There are 6 e⁻ domains on the central atom in ICl_4^-: four single bonds and two lone pairs.

e⁻ geometry: Octahedral
Molecular Geometry: Square Planar

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Electron–Domain Geometry and Molecular Geometry

(a) According to the VSEPR model, three electron domains will be arranged in a trigonal plane. Since there are no lone pairs on the central atom in SO_3, the molecular geometry is the same as the electron-domain geometry. Therefore, the shape of SO_3 is trigonal planar.

Electron-domain geometry: Trigonal Planar → Molecular Geometry: Trigonal Planar

(b) Six electron domains will be arranged in an octahedron. Two lone pairs on an octahedron will be located on opposite sides of the central atom, making the shape of ICl_4^- square planar.

Electron-domain geometry: Octahedral → Molecular Geometry: Square Planar

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Practice

PCl_5 → Trigonal bipyramidal

H_2O → Bent

XeF_2 → Linear

XeF_4 → Square planar

SO_2 → Bent

CO_2 → Linear

SF_4 → Seesaw

BrF_5 → EDG: Octahedral; MG: Square Pyramidal

BrF_3 → EDG: Trigonal Bipyramidal; MG: T-Shaped

SF_6 → EDG: Octahedral; MG: Octahedral

NH_3 → EDG: Tetrahedral; MG: Trigonal Pyramidal

CH_4 → EDG: Tetrahedral; MG: Tetrahedral

BF_3 → EDG: Trigonal Planar; MG: Trigonal Planar

Predict the Electronic Geometry and the Molecular Geometry for IF_4^+

EDG: Trigonal Bipyramidal;
MG: See-Saw

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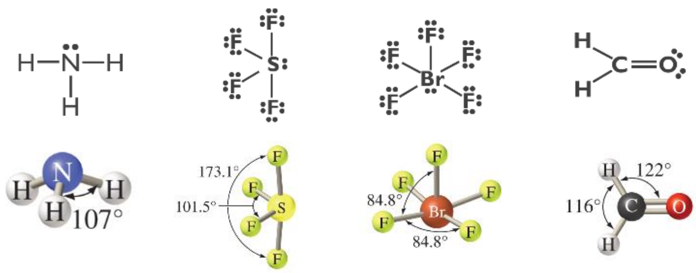
Deviation from Ideal Bond Angles

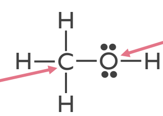
Some electron domains are better than others at repelling neighboring domains.

Lone pairs take up more space than bonded pairs of electrons.

Multiple bonds repel more strongly than single bonds.



The geometry of more complex molecules can be determined by treating them as though they have multiple central atoms.



Central O atom
No. of e⁻ domains: 4
e⁻ geometry: tetrahedral
Molecular geometry: bent

Central C atom
No. of e⁻ domains: 4
e⁻ geometry: tetrahedral
Molecular geometry: tetrahedral

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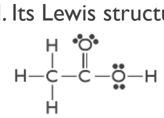
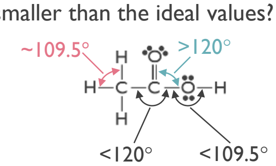
Practice

Acetic acid, the substance that gives vinegar its characteristic smell and sour taste, is sometimes used in combination with corticosteroids to treat certain types of ear infections. It has a molecular formula of CH_3COOH. Its Lewis structure is:



Determine the molecular geometry about each of the central atoms and determine the approximate value of each of the bond angles in the molecule. Which if any of the bond angles would you expect to be smaller than the ideal values?



According to the VSEPR theory, the *actual* O–C–O bond angles in the CO_3^{2-} ion are predicted to be:

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Molecular Geometry and Polarity

Molecular polarity is one of the most important consequences of molecular geometry.
A bond is polar when the electronegativities of the two atoms are different, this is also true for a diatomic molecule (where the molecule only has the one bond.

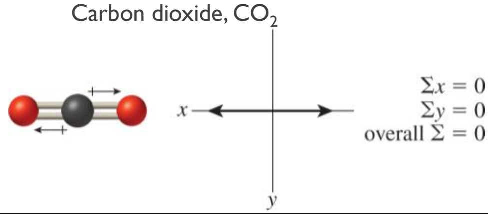
The polarity of a molecule made up of three or more atoms depends on:

(1) the polarity of the individual bonds
(2) the molecular geometry

For a molecule made of three or more atoms, it will be polar if you superimpose vectors over polar bonds (pointing toward the atom of higher electronegativity) do NOT sum to zero.

Carbon dioxide, CO_2

The bonds in CO_2 are polar but the molecule is nonpolar.



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Molecular Geometry and Polarity

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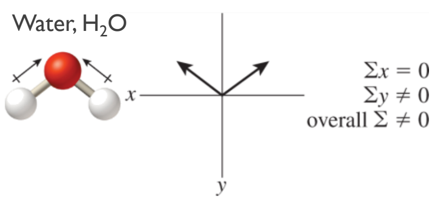
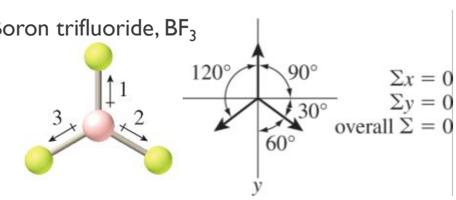
For a molecule made of three or more atoms, it will be polar if you superimpose vectors over polar bonds (pointing toward the atom of higher electronegativity) do NOT sum to zero.

Water, H_2O



The bonds in H_2O are polar and the molecule is polar.

Boron trifluoride, BF_3



The bonds in BF_3 are polar but the molecule is nonpolar.

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Molecular Geometry and Polarity

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(1) the polarity of the individual bonds
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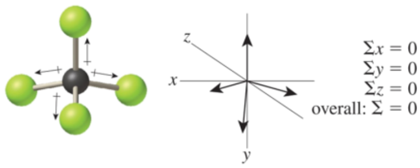
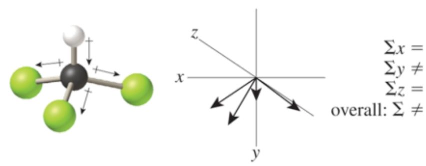
For a molecule made of three or more atoms, it will be polar if you superimpose vectors over polar bonds (pointing toward the atom of higher electronegativity) do NOT sum to zero.



CCl



$CHCl_3$

The bonds in CCl_4 are **polar** but the molecule is **nonpolar**

The bonds in $CHCl_3$ are **polar** and the molecule is **polar**

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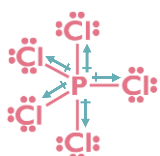
Practice

Determine whether PCl_5 is polar.

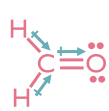


PCl_5 is nonpolar.

First draw the Lewis structure for PCl_5.

With five identical electron domains around the central atom, the electron-domain and molecular geometries are trigonal bipyramidal. The equatorial bond dipoles will cancel one another, just as in the case of BF_3, and the axial bond dipoles will also cancel each other.

Determine whether (b) H_2CO (C double bonded to O) is polar.



H_2CO is polar.

First draw the Lewis structure for H_2CO.

The bond dipoles, although symmetrically distributed around the C atom, are not identical and therefore will not sum to zero.

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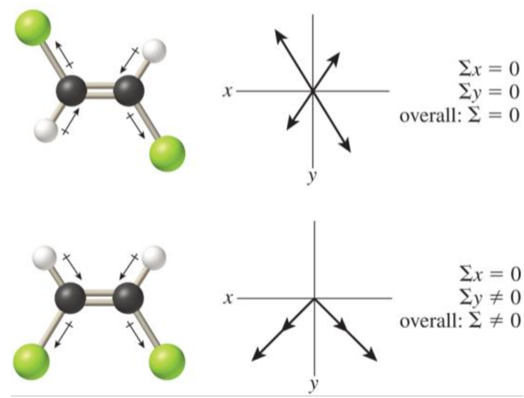
Molecular Geometry and Polarity

Dipole moments can be used to distinguish between **structural isomers**.

trans-dichloroethylene
nonpolar

cis-dichloroethylene
polar



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Practice

Do these molecules have a dipole? (same molecules from slide 50)

- PCl_5 → nonpolar
- H_2O → polar
- XeF_2 → nonpolar
- XeF_4 → nonpolar
- SO_2 → polar
- CO_2 → nonpolar
- SF_4 → polar
- BrF_5 → polar
- BrF_3 → polar
- SF_6 → nonpolar
- NH_3 → polar
- CH_4 → nonpolar
- BF_3 → nonpolar

Explain why CO_2 and CCl_4 are both nonpolar even though they contain polar bonds.

Due to the canceling of all polar bonds

(a) For SCl_2, Does it have polar bonds? (b) Does it have a dipole?

a. Yes b. Yes

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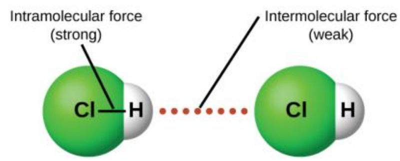
Bonding Forces: 2 Types

1. **Intra**molecular forces

Strong attractive forces between atoms in molecules. Also known as **Covalent bonds**.



2. **Inter**molecular forces (Much weaker than intramolecular forces)

    Dispersion
    Dipole-dipole
        Hydrogen bond (specific dipole-dipole)

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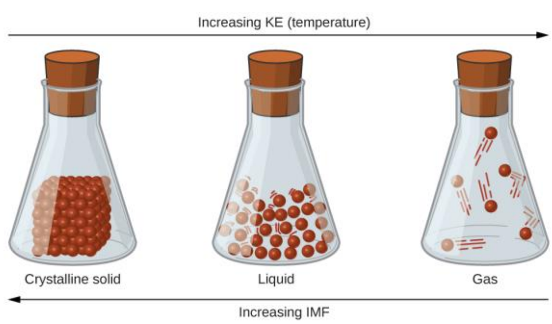
Intermolecular forces (IMFs)

Also known as van der Waals (vdW) forces
Forces **increase** as Kinetic Energy (K.E.) of particles **decreases**



Physical properties depend on the balance between:
- IMFs which pull molecules together
    - (stronger IMFs = stronger interactions between molecules)
- K.E. which separates molecules

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Intermolecular forces (IMFs)

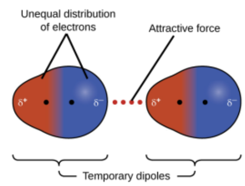
Dispersion

Weakest discussed: Resulting from instantaneous dipoles that arise from random e⁻ motion in a molecule/atom This affects surround atoms/molecules.

Found in all molecules

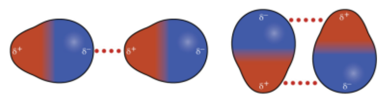
Heavier molecule = more e⁻ = stronger dispersion = Higher M.P./B.P.

Larger surface area = more dispersion = higher M.P./B.P.



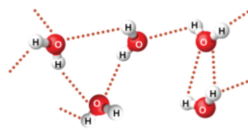
Dipole-dipole

Stronger than dispersion, attractive force between molecules with permanent dipoles (polar covalent molecules)



Hydrogen bond (specific dipole-dipole)

Stronger than other dipoles, occurs between molecules that contain a covalent bond between H and O, N, or F (example H_2O)



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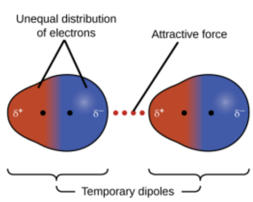
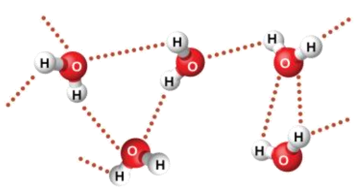
Intermolecular forces (IMFs)

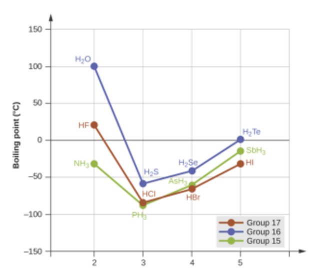
Dispersion



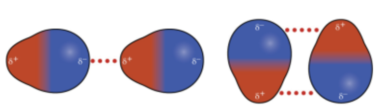
Melting and Boiling Points of the Halogens				
Halogen	Molar Mass	Atomic Radius	Melting Point (K)	Boiling Point (K)
F_2	38 g/mol	72 pm	53	85
Cl_2	71 g/mol	99 pm	172	238
Br_2	160 g/mol	114 pm	266	332
I_2	254 g/mol	133 pm	287	457

Hydrogen bond





Dipole-dipole



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Other Intermolecular forces (IMFs)

Dipole/induced dipole

Occurs between a molecule with a permanent dipole and another molecule without a permanent dipole (non-polar)

Weaker than dipole/dipole; stronger than dispersion   H–Cl·······F–F

Ion/dipole

Occurs between an ion and another molecule with a permanent dipole H_3O^+ ·····H_2O

Ion/ion

Occurs between two ions H_3O^+ ·····OH^- Na^+ ····Cl^-

Ion/induced dipole

Occurs between an ion and another molecule without a permanent dipole Na^+ ····Cl–Cl

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Intermolecular forces

Trends

Stronger intermolecular forces = **Higher** Melting Point/ Boiling Point
Increasing molecular weight = **Higher** Melting Point/ Boiling Point
Increasing surface area = **Higher** Melting Point/ Boiling Point

Overall IMFs Strength:

Ionic > H-bonding > dipole/dipole > dispersion

Predict the relative boiling points (largest to smallest) for the following – water, sodium chloride, chlorine gas

NaCl (Ion/ion) > H_2O (H-bond) > Cl_2 (Dispersion)

Predict the relative boiling points (largest to smallest) for the following non-polar alkanes : C_2H_4, C_4H_{10}, C_8H_{18}

C_8H_{18} > C_4H_{10} > C_2H_4

Dispersion: larger molecules = stronger dispersion

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