CHE 1031: General Chemistry I

7. Chemical bonding

7.1: Ionic bonding [sidebar]

7.2: Covalent bonding

7.3: Lewis symbols & structures

7.4: Formal charges & resonance

7.5: Strengths of ionic & covalent bonds

7.6: Molecular structure & polarity [sidebar]

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7. Chemical bonding

7.1: Ionic bonding

- Explain the formation of cations, anions and ionic compounds
- Predict the charge of common metallic and nonmetallic elements and write their electron configuration

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What are ionic compounds?

Ionic compounds (aka salts)**:** *compounds formed by cations and anions held together by ionic bonds*

Ionic bonds: *electrostatic forces of attraction between oppositely charged ions (cations and anions)*

- Crystalline structure; rigid & brittle; high melting & boiling points
  Ionic bonds are strong but water soluble
- Ionic solutions are good conductors of electricity

sodium (Na)

chlorine (Cl_2)

sodium chloride (NaCl) Chemistry Openstax

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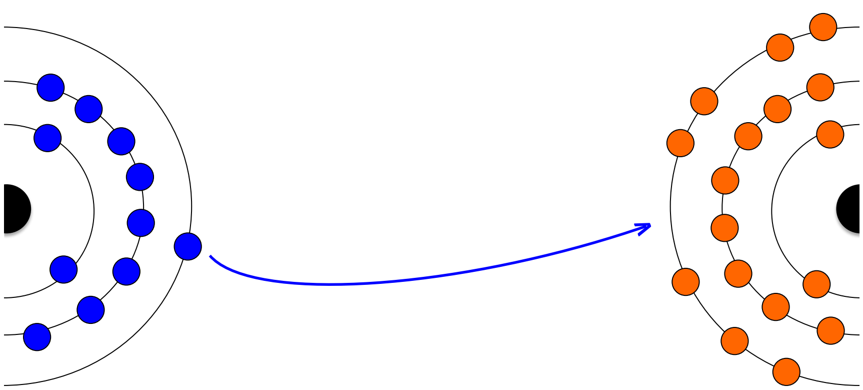
Formation of ionic compounds

Ionic compounds form when atoms **ionize** in order to create **full valence shells.**



Na **Cl**

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Formation of ionic compounds

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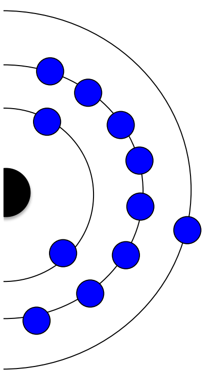
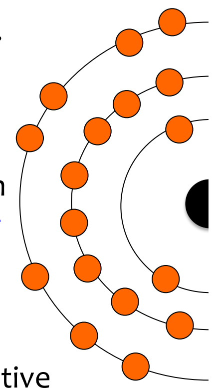


Na

- Simultaneous redox reactions.
- Metals have low-ish ionization energies.
- Non-metals have high electron affinities.
- Ionic compounds have neutral charges: equal number of positive and negative charges.



Cl

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Net zero charge

Ionic compounds must have **overall, or net, zero charges.**

Combine aluminum and oxygen to create an ionic compound.

1

Remember that the formulas of ionic compounds are always **empirical formulas.**

- In reality, the number of ions in a crystal of ionic compound varies, but the **ratio** of cations to anions is **constant** and defined by the salt's formula.

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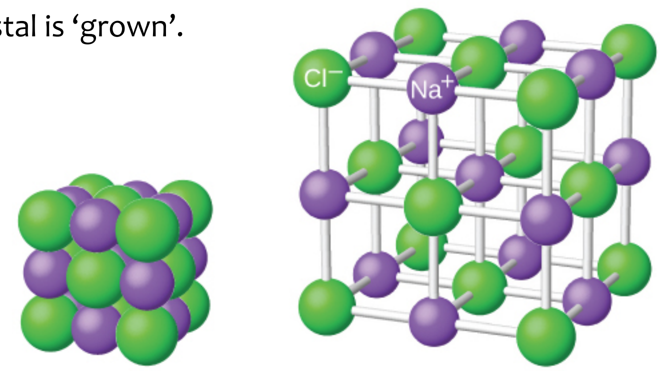
Crystal lattice

Ionic compounds form **crystals (aka crystal lattice)**, as structure in which cations and anions alternate and surround each other.

Ions are held together by **electrostatic force** (opposite charge).

Size of crystals varies with the number of ions in the crystal & conditions under which the crystal is 'grown'.



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Electronic structure of cations

Cations <u>lose electrons</u> to get down to a full valence shell.

- <u>Groups 1A & 2A</u>: (electropositive) lose all valence shell e-
  - Isoelectronic with previous noble gas
  - Charge = group number
- <u>Groups 12A & 17A</u>: lose all valence shell e-
  - Charge = group # - 10
- <u>Transition / inner transition metals</u>: usually +2 or +3 charge from *losing their outermost s electrons first, followed by an electron or two from the next-to-outermost shell*

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Try this:

Write the electron configurations of the Cr^{+3} and Zn^{+2} cations.

2

Write the electron configurations of the K and Mg cations.

3

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Electronic structures of anions

Most monoatomic anions form when atoms fill s & p orbitals and become **isoelectronic with the next noble gas.**

Write the electron configurations of the Se and I anions.

4

Write the electron configurations of the P atom <u>and</u> anion.

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Can you?

(1) Describe ionic compounds and their properties?

(2) Explain how formation of ionic compounds is redox chemistry?

(3) Explain why the formulae of ionic compounds are always empirical formulae?

(4) Write the electron configuration of ions of main group metals, transition metals and main-group nonmetals.

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7. Chemical bonding

7.2: Covalent bonding

- Describe the formation of covalent bonding
- Define electronegativity and assess the polarity of covalent bonds

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What's a covalent bond?

Covalent bond: *a pair of electrons shared between two* atoms.

- Each atom contributes one electron.
- Non-metals bond covalently.
- Covalent bonding gives each atom access to a full valence shell.

Physical properties:

- Lower mp & boiling points.
- Often gases, liquids or 'softer' solids.
- Generally insoluble in water.
- Poor conductors of heat and electricity.

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Formation of covalent bonds

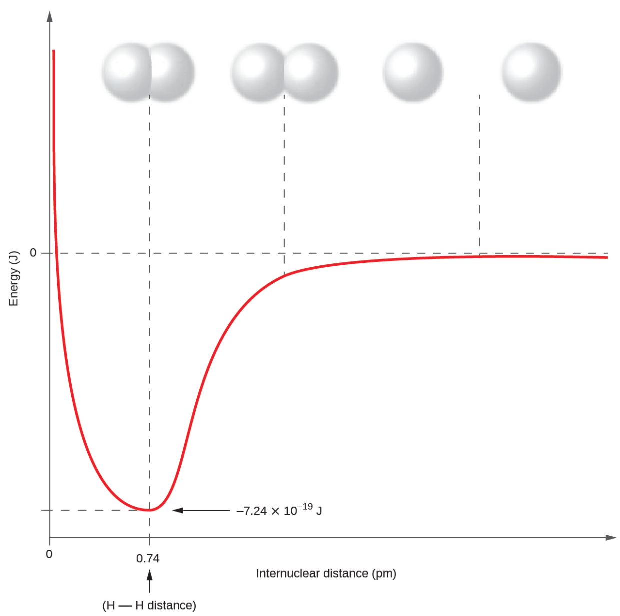
As 2 atoms approach:

(1) No attraction.

(1) ve- shells repel.

(2) Ve- of atom 1 is attracted to nucleus of atom 2 and vv.

(3) Nuclei close enough to repel.



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Covalent bonds lower energy states

When atoms bond covalently (and achieve full valence shells) their **energy state decreases** and becomes more stable.

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = 436 \text{ kJ}$$

$$2H(g) \longrightarrow H_2(g) \qquad \Delta H = -436 \text{ kJ}$$

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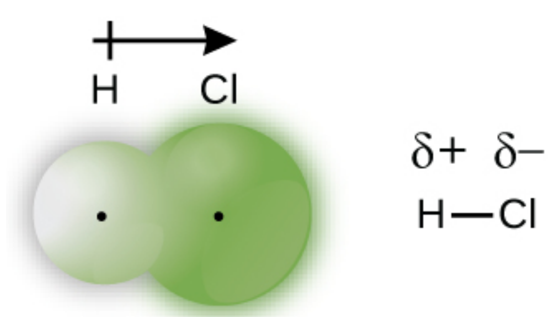
Polar or non-polar?

Covalent bonds are polar or non-polar depending on how evenly the two electrons are shared between bonded atoms.

- **Nonpolar covalent:** *electrons of the bond are shared equally*
- **Polar covalent:** *electrons of the bond are not shared equally*



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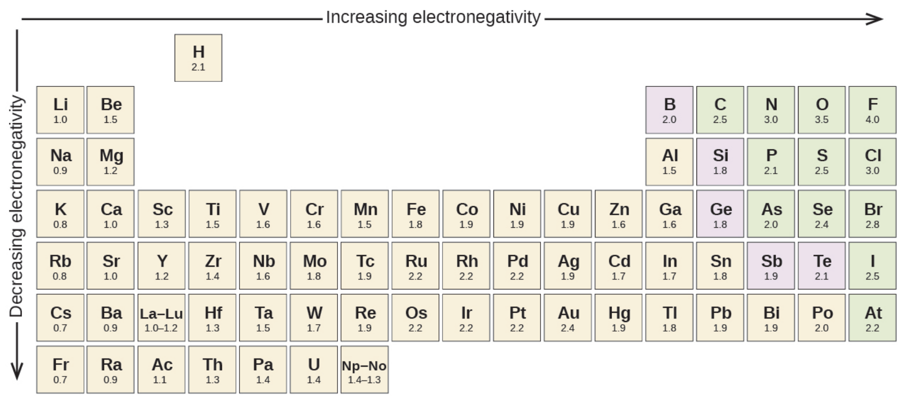
Electronegativity

Electronegativity: *a measure of the ability of an atom to keep its own electrons and to attract other electrons towards it*

- In covalent bonds, electrons are attracted to the more electronegative atom.
- Difference in electronegativity determines bond polarity.



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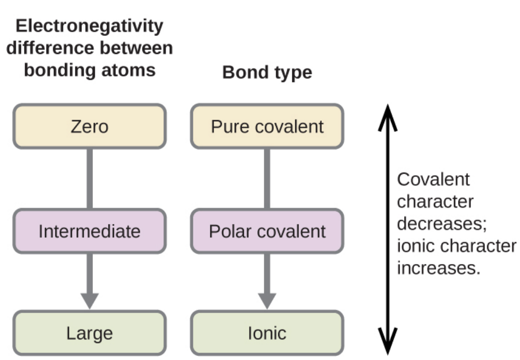
Difference in electronegativity (Δen)

To determine whether bonds are ionic, polar covalent or nonpolar covalent we calculate the difference in electronegativity values of two bonded atoms.

$$\Delta en = |en1 - en2|$$



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

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Difference in electronegativity (Δen)

Covalent bonds are polar or non-polar depending on how evenly the two electrons are shared between bonded atoms.

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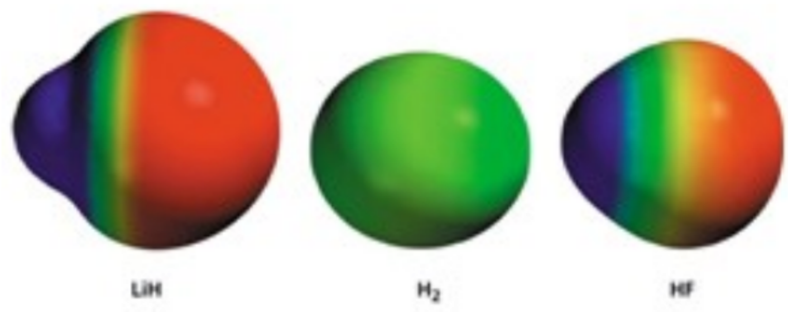

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Try this

Determine the types of bonds between these atoms and label their polarities.

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C – H

S – H

C – N

N – H

C – O

O - H

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Try this

Determine the types of bonds in potassium nitrate and show polarity arrows. $K^{+1} (NO_3)^{-1}$

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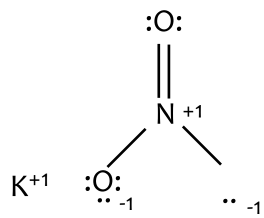

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Can you?

(1) Define the term ‘covalent bond’?

(2) Describe how the properties of covalent compounds differ from those of ionic compounds?

(3) Explain how repulsive and attractive forces, and overall energies, change as atoms approach one another and form covalent bond?

(4) Explain how polar and nonpolar covalent bonds differ and the role of electronegativity in determining bond type.

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7. Chemical bonding

7.3: Lewis symbols & structures

- Write Lewis symbols for neutral atoms & ions
- Draw Lewis structures depicting the bonds in simple molecules.

Lewis symbols

Lewis symbols show the number of **valence electrons** in an atom using a dot for each valence electron.

Calcium is in column 2A, so has 2 valence electrons: .Ca.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na·
magnesium	$[Ne]3s^2$	·Mg·
aluminum	$[Ne]3s^23p^1$	·Ȧl·
silicon	$[Ne]3s^23p^2$	·Si· (one dot above, one below)
phosphorus	$[Ne]3s^23p^3$	·P· (two dots above, one below)
sulfur	$[Ne]3s^23p^4$	:S· (two dots above, one below)
chlorine	$[Ne]3s^23p^5$	:Cl· (two dots above, two below)
argon	$[Ne]3s^23p^6$	:Ar: (two dots above, two below)

Lewis symbols in redox reactions

Lewis symbols show that metals **empty** their valence shell when they become cations, while nonmetals **fill** their shells to become anions.

$$\mathrm{Na.} \longrightarrow \mathrm{Na}^{+1} + e^-$$

$$\mathrm{.Ca.} \longrightarrow \mathrm{Ca}^{+2} + 2e^-$$

$$\mathrm{:\ddot{\underset{..}{Cl}}.} + e^- \longrightarrow \mathrm{:\ddot{\underset{..}{Cl}}:}^{-1}$$

$$\mathrm{.\ddot{\underset{..}{S}}.} + 2e^- \longrightarrow \mathrm{:\ddot{\underset{..}{S}}:}^{-2}$$

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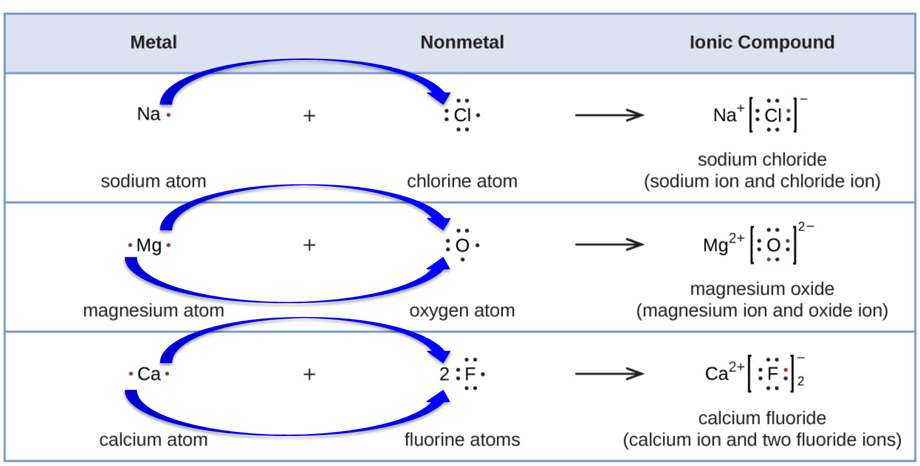
Lewis symbols formation of salts

Lewis symbols show that spontaneous redox (transfer of electrons) occurs when salts form.



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Try this

Use Lewis symbols and arrows to diagram out the formation of aluminum fluoride from aluminum and chlorine atoms. 8

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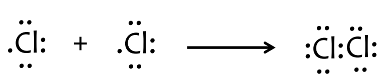
Lewis structures

Lewis structures are used to show the structure and bonding patterns of covalent molecules. 9

- A pair of shared e- = : = ---
- Remember to show the unbonded electron pairs

H. + H. ⟶ H:H



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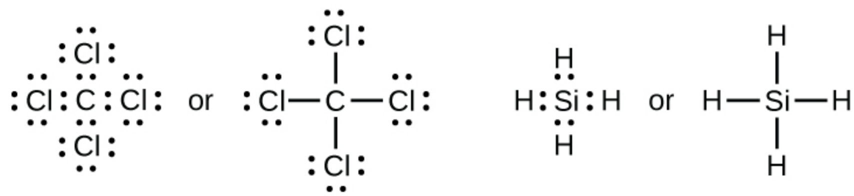
The octet rule

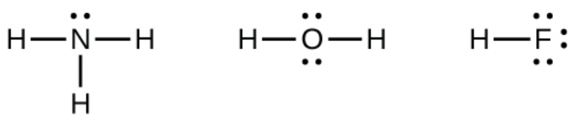
Octet rule: *all atoms ionize of bond to achieve a full valence shell.*

- Most atoms want 8 valence electrons (an octet).
- H & He want only 2 valence electrons (a duet).



carbon tetrachloride

silane



ammonia

Water

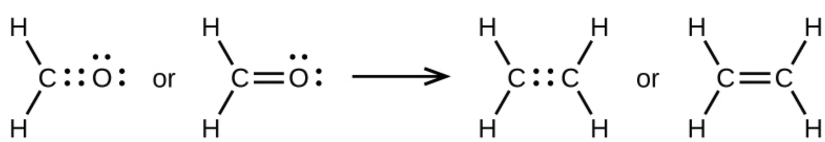
hydrogen fluoride

Count to confirm that each atom has it's octet or duet.

Double & triple bonds

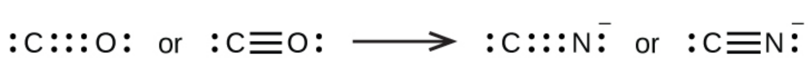
Multiple bonds are used when there is no other way to give 'central atoms' a full valence shell.

- Double bond: 2 shared pairs of valence electrons ::
- Triple bond: 3 shared pairs of valence electrons :::



formaldehyde

ethylene



carbon monoxide

cyanide ion

Writing Lewis structures

Steps:

(1) Count total number of valence electrons (including charge).

(2) Draw symbols for each atom, placing the least electronegative atom (or carbon, or the unique atom) in the center.

(3) Connect each atom with a single bond at a cost of 2 ve- each.

(4) Distribute remaining ve- as lone pairs around the outermost atoms to give each an octet.

(5) Place any remaining ve- on the central atom.

(6) If the central atom doesn't have an octet, create multiple bonds to it using ve- from the outer atoms.

SiH_4

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Try these

Draw Lewis structures for these:

CHO_2^{-1}
NO^{+1}
OF_2

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Try these

NASA's Cassini-Huygens mission detected a cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan's atmosphere also includes ethane (H_3CCH_3), acetylene ($HCCH$) and ammonia (NH_3). Draw their Lewis structures! 11

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One more

Both carbon monoxide and carbon dioxide are produced by combustion of fossil fuels. Draw their Lewis structures. 12

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Exceptions to the octet rule

Chemistry is a field full of exceptions. There are three types of exceptions to the octet rule.

(1) Molecules with an odd number of valence electrons (an unpaired electron).

(2) Molecules whose central atom has <u>less than an octet</u>.

(3) Hypervalent molecules whose central atom <u>has more than an octet</u>.

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(1) Odd-electron molecules

Molecules with an odd number of electrons are **called free radicals.**

<u>Example</u>: nitric oxide (NO)

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(2) e- deficient molecules

Electron deficient molecules generally have central atoms from groups 2A and 12A, outer hydrogen or other atoms that don't form double bonds.

Example: berylium dihydride (BeH_2) 14

Example: boron trifluoride (BF_3) 15

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(3) Hypervalent molecules

Elements below the second row of the periodic table can accommodate more than an octet using d orbitals.

Example: phosphorus pentachloride (PCl_5) 16

Example: sulfur hexafluoride (SF_6) 17

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Try this

Write the Lewis structures for XeF_2, XeF_4, XeF_6 identify any exceptions to the octet rule.

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Can you?

(1) Define the term 'Lewis symbol'.

(2) Use Lewis symbols to diagram out formation of an ionic compound?

(3) List the steps required to draw the Lewis structure of a covalently bonded compound?

(4) Draw Lewis structures for a wide variety of covalently bonded compounds from their molecular formulas?

(5) List and explain the three types of exceptions to the octet rule?

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7. Chemical bonding

7.4: Formal charge & resonance

- Compute formal charge for atoms in any Lewis structure.
- Use formal charge to identify the most reasonable Lewis structures for a given molecule.
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule.

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Try this

Formal charge: *the charge residing on an atom within a Lewis dot structure*

- Calculated for each atom in a structure.

FC = (#ve) – (dots + sticks)

Calculate formal charges in $ICl4^{-1}$. *Where is the -1 charge?* 19

Calculate formal charges in carbon monoxide. 20

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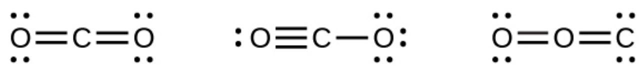
Using formal charge to predict stucture

When there are several Lewis structures for one molecule, which is the best or more appropriate?

- The molecule with **fewest / lowest formal charges** is the best choice because its energy state is lower.

Which is the 'best' structure for carbon dioxide? 21

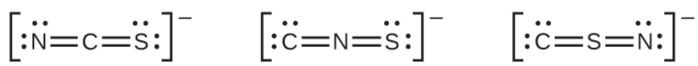


Structure

0 0 0	+1 0 –1	0 +2 –2	Formal charge

Which is the 'best' structure for the thiocyanate ion (-1)? 22

Structure



Formal charge	–1 0 0	–2 +1 0	–2 +2 –1

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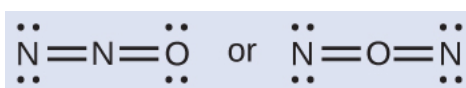
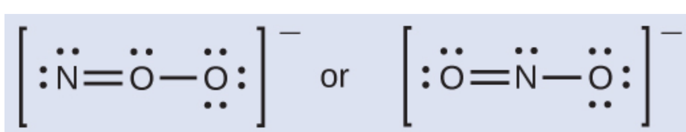
Try this

Nitrous oxide, N_2O, is commonly known as laughing gas. Which is the optimal structure for nitrous oxide? 23



Which is the 'best' structure for the nitrite ion (NO_2^{-1})? 24



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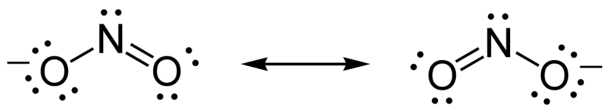
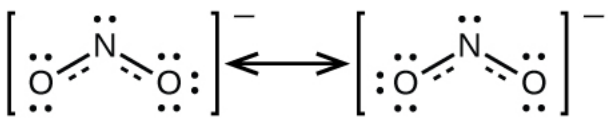
Resonance

Notice that the two possible structures for the nitrite ion (NO_2^{-1}) are **resonance structures:** *identical except for the placement of bonds or electrons.*



From these structures, you might guess that NO_2^{-1} has two different N-O bond lengths since single bonds are longer than double bonds.

- However, experiments show that there is only one N-O bond length and that it's between the lengths of a single and double bond: the **resonance hybrid** or average.



Each N-O bond in the **hybrid** is 1.5 bonds long.

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Try this

(a) Draw one Lewis structure of the carbonate ion, CO_3^{-2}. 25
(b) Draw all other resonance structures.
(c) What determines the number of resonance structures?
(d) Draw the resonance hybrid.

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Can you?

(1) Calculate formal charge for Lewis structures?

(2) Use formal charges to chose the 'best' or lowest energy Lewis structure for a molecule?

(3) Explain what differentiates molecules with resonance from those that lack resonance?

(4) Draw resonance structures and resonance hybrids and explain why hybrids are more relevant?

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7. Chemical bonding

7.5: Strengths of ionic & covalent bonding

- Describe the energetics of covalent & ionic bond formation & breakage.
- Use average covalent bond energies to estimate enthalpies of reaction

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Strength of covalent bonds

An input of energy is needed to break covalent bonds thus this process is said to be **endothermic** (+ ΔH).

$H_2(g) \rightarrow 2H(g)$ ΔH = 436 kJ

$$\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array} (g) \rightarrow C(g) + 4H(g)$$

ΔH = 1660 kJ
ΔH = 1660 kJ/4 mol
= 415 kJ/mol of C – H

<u>Trends in covalent bond strength</u>:
- Increases with increasing number of shared pairs (# of bonds)
- Decreases down columns or groups

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Covalent bonds energies

Examples of bond energies or strengths.

bond	kJ/mol	bond	kJ/mol	bond	kJ/mol
H-H	436	C-S	260	F-Cl	255
H-C	415	C-Cl	330	F-Br	235
H-N	390	C-Br	275	Si-Si	230
H-O	464	C-I	240	Si-P	215
H-F	569	N-N	160	Si-S	225
H-Si	395	N=N	418	Si-Cl	359
H-F	320	N≡N	946	Si-Br	290

What trends do you see here?

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Covalent bonds energies vs. lengths

Bond length is inversely related to bond strength (or energy).

- **Length:** single > double > triple
- **Strength:** triple > double > single

bond	length (Å)	energy (kJ/mol
C-C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C-N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C-O	1.43	350
C=O	1.23	741
C≡O	1.13	1080

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Using bond energies

Bond energies can be used to calculate the overall energy change of chemical reactions: the **enthalpy of reaction (ΔH)**.

$$(\Delta H) = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds made}}$$

where D = bond energies (kJ/mol)

Calculate the enthalpy of the reaction that forms hydrochloric acid: $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

52

Try this

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Calculate the enthalpy change (ΔH) of this reaction:

$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

53

Try this

27

Ethyl alcohol (ethanol) was one of the first chemicals made by man. Calculate the overall enthalpy change for the reaction shown here

$H_2CCH_2 + H_2O \rightarrow CH_3CH_2OH$

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Ionic bond strength & lattice energy

Ionic compounds are held together by electrostatic attraction.
Lattice energy ($\Delta H_{lattice}$): *the energy needed to separate one mole of ionic compound into its components as gaseous ions.*

$MX(s) \rightarrow M^{+n}(g) + X^{-n}(g)$ $\Delta H_{lattice}$ = ________ kJ

$NaCl(s) \rightarrow Na^{+1}(g) + Cl^{-1}(g)$ $\Delta H_{lattice}$ = + 769 kJ

- Lattice energies are **endothermic** (+ΔH) because bonds need to be broken and physical states need to change from solid to gas.

$$\Delta H_{lattice} = \frac{C(Z^+)(Z^-)}{R_o}$$

where C = constant
Z = charge
R_o = sum of ionic radii

- If C and distance are constant increasing charge increases ΔH.
- If C & charge are constant greater ionic size decreases ΔH.

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Comparing lattice energies

Noting that the size of ions is similar, explain why these lattice energies differ:

LiF	1023 kJ/mol
MgO	3900 kJ/mol

Explain why these lattice energies differ: 28

MgF_2	2957 kJ/mol
MgI_2	2327 kJ/mol

Which has higher lattice energy? 29

Al_2O_3
Al_2Se_3

Which has higher lattice energy? 30

ZnO
NaCl

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Can you?

(1) Describe factors contributing to the strength of covalent bonds?

(2) Explain how and why covalent bond strength relates to covalent bond length?

(3) Use bond energies to calculate overall enthalpy (energy change) of chemical reactions.

(4) Define the term 'lattice energy'?

(5) Explain what factors affect lattice energy?

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7. Chemical bonding

7.6: Molecular structure and polarity

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

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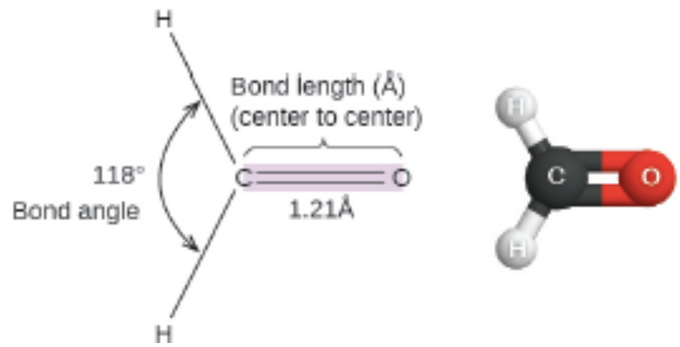
From 2D to 3D structures

Lewis structures provide us with decent 2D molecular structure but don't provide much 3D structure.



To know more, we'd need to know:

- Bond distances; and
- **Bond angles.**

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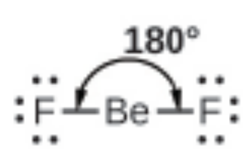
VSEPR theory suggests 3D structure

Valence shell electron pair repulsion (VSEPR) uses the **mutually repulsive behavior of electron pairs** to predict molecular structure.

- When tethered around a central atom electron pairs (either bonds or free pairs) tend to push each other as far away from one another as possible.
  - They maximize their personal spaces.



Here, the central beryllium has only two bonds. These two bonds arrange themselves at 180° to one another to maximize the space between the two bound fluorine atoms and the electrons that bond them to the beryllium.

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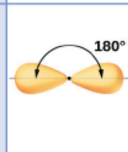
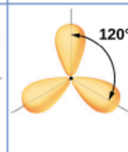
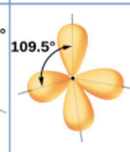
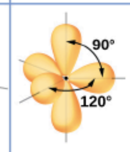
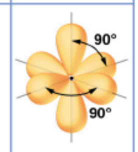
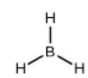
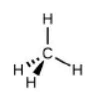
VSEPR geometries

Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	H—Be—H				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

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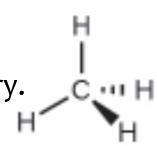
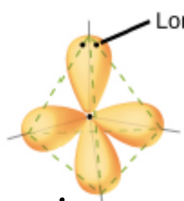
Molecular vs. electron pair geometry

When a molecule like methane has no electron pairs on the central atom, there is **no difference** between its molecular and electron pair geometry.

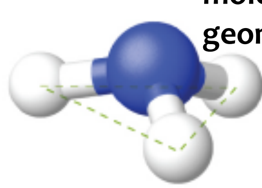


However, molecules like ammonia (NH_3) that have a free electron pair on the central atom have **distinct** molecular and electron pair geometries.

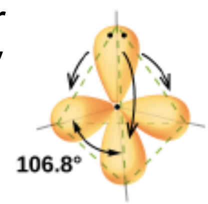
Lone pair



e- pair geometry



molecular geometry



*Note the **distortion** of tetrahedral structure caused by the strong repulsive force of the free e- pair.*

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VSEPR chart

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal planar	<120° Bent or angular			
4	109° Tetrahedral	<109° Trigonal pyramid	<<109° Bent or angular		
5	90° 120° Trigonal bipyramid	<90° <120° Sawhorse or seesaw	<90° T-shape	180° Linear	
6	90° Octahedral	<90° <90° Square pyramid	90° Square planar	<90° T-shape	180° Linear

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Using VSEPR

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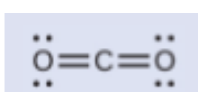
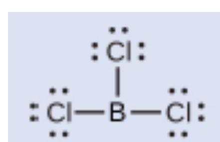
Using the Lewis dot structures for CO2 and BCl3 shown here, use the VSEPR to determine bond angles, electron pair and molecular geometries.





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Try this

Use VSEPR to determine the electron pair and molecular geometries of: 32

(a) H_2O
(b) SF_4

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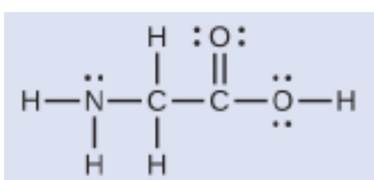
Try this

Use VSEPR to determine the electron pair and molecular geometries of each 'center' of the amino acid glycine. 33



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Module 7: key terms

axial position
bond angle
bond dipole moment
bond distance
bond energy
bond length
covalent bond
dipole moment
double bond
electron-pair geometry
electronegativity
equatorial position
formal charge
free radical
hypervalent molecule
inert pair effect
ionic bond
lattice energy (ΔH lattice)
Lewis structure
Lewis symbol
linear
lone pair
molecular structure
octahedral
octet rule
polar covalent bond
polar molecule
pure covalent bond
resonance
resonance forms
resonance hybrid
single bond
triple bond
valence shell electron-pair repulsion theory (VSEPR)
vector

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Module 7: key equations

- formal charge $= \#$ valence shell electrons (free atom) $- \#$ one pair electrons $- \frac{1}{2} \#$ bonding electrons
- Bond energy for a diatomic molecule: $XY(g) \longrightarrow X(g) + Y(g)$ $\quad D_{X-Y} = \Delta H°$
- Enthalpy change: $\Delta H = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$
- Lattice energy for a solid MX: $MX(s) \longrightarrow M^{n+}(g) + X^{n-}(g)$ $\quad \Delta H_{\text{lattice}}$
- Lattice energy for an ionic crystal: $\Delta H_{\text{lattice}} = \frac{C(Z^+)(Z^-)}{R_o}$

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