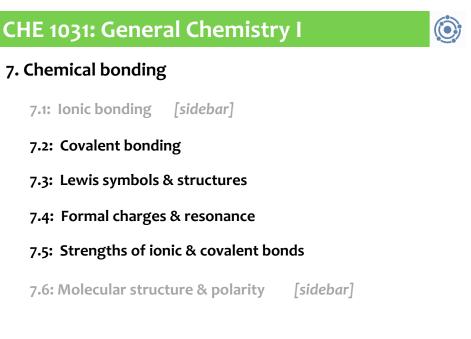
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7. Chemical bonding

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

What are ionic compounds?

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

lonic 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



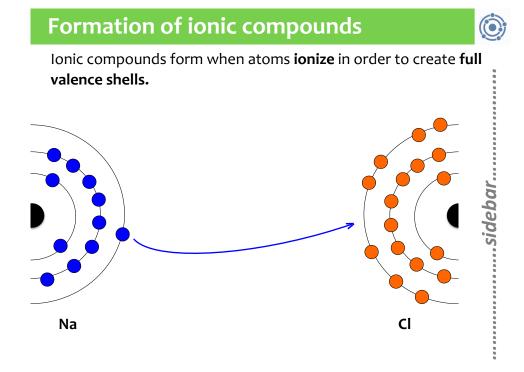
sodium (Na)



chlorine (Cl₂)



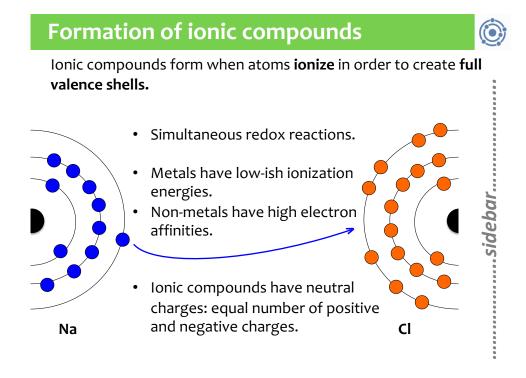
sodium chloride (NaCl) Chemistry Openstax



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Net zero charge

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

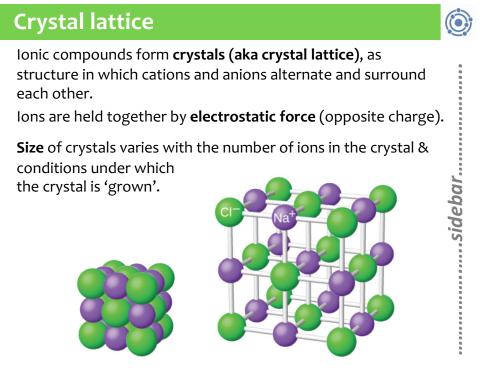
Combine aluminum and oxygen to create an ionic compound.

 $\begin{array}{c|c} AI^{+3} & O^{-2} \\ \hline 2 & 3 \\ \hline +6 & -6 \end{array} \xrightarrow{} Al2O_3$

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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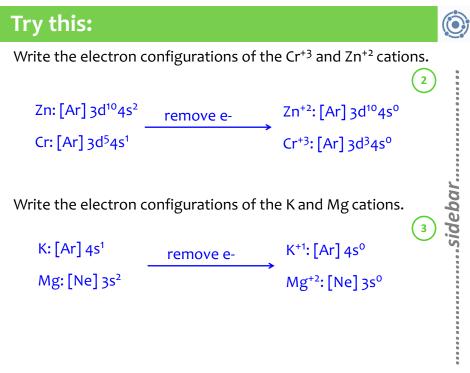


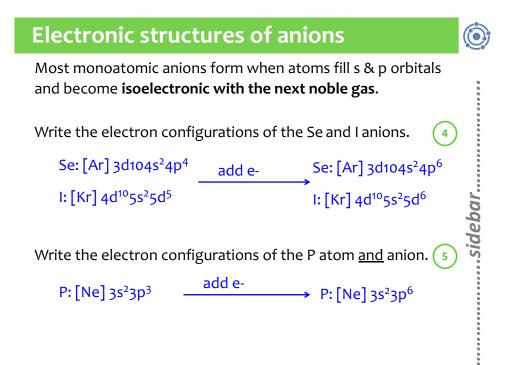
7

Electronic structure of cations

Cations lose electrons to get down to a full valence shell.

- Groups 1A & 2A: (electropositive) lose all valence shell e-
 - Isoelectronic with previous noble gas
 - Charge = group number
- <u>Groups 12A & 17A</u>: lose all valence shell eCharge = 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





(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?



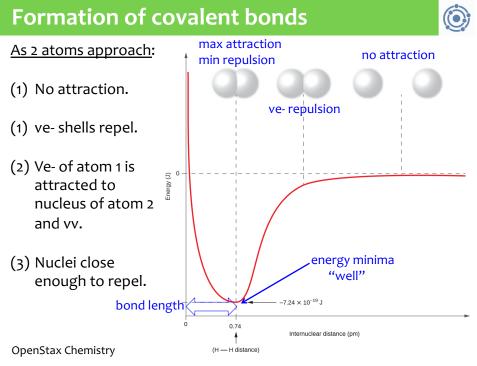
Covalent bond: *a pair of electrons shared between two* atoms.

- 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.





Covalent bonds lower energy states



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

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

An **input of energy is required to break the covalent bond** between the two atoms of hydrogen gas (H₂) and create two hydrogen atoms as shown by the + Δ H value.

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

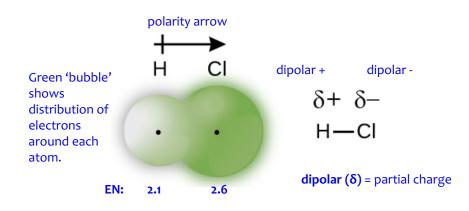
And energy is released when a covalent bond forms between the two hydrogen atoms to form hydrogen gas (H₂) as shown by the - Δ H value.

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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.

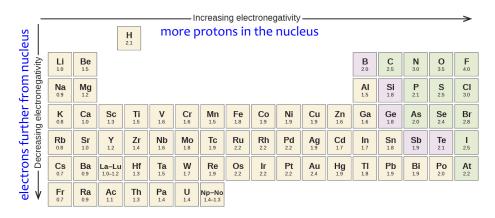
- Nonpolar covalent: electrons of the bond are shared equally
- Polar covalent: electrons of the bond are not shared equally



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.



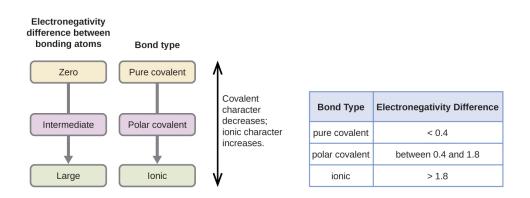
17

Difference in electronegativity (Δen)

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To determine whether bonds are ionic, polar covalent or nonpolar covalent we calculate the difference in electronegativity values of two bonded atoms. $\Delta en = |en1 - en2|$

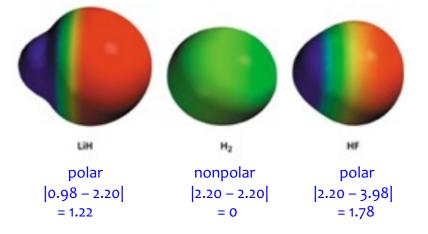


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Difference in electronegativity (Δen)

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

- Nonpolar covalent: electrons of the bond are shared equally
- Polar covalent: electrons of the bond are <u>not</u> shared equally

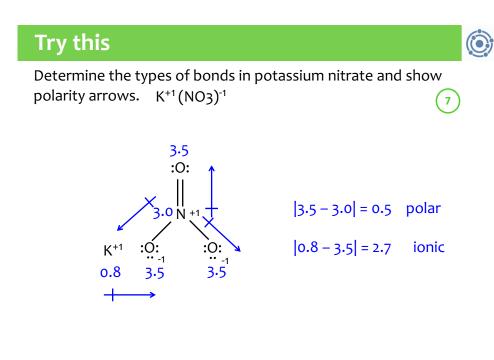


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Try this

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

C – H	2.5 – 2.1 = 0.4	nonpolar	←+
S – H	2.5 - 2.1 = 0.4	nonpolar	←+
C – N	2.5 - 3.0 = 0.5	polar-ish	+>
N – H	3.0 - 2.1 = 0.9	polar	←+
C – O	2.5 - 3.5 = 1.0	polar	$+ \rightarrow$
O - H	3.5 – 2.1 = 1.4	polar	← +



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



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7.3: Lewis symbols & structures

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

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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.

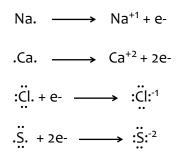
Atoms	Electronic Configuration	Lewis Symbol
sodium	[Ne]3s ¹	Na•
magnesium	[Ne]3s ²	۰Mg・
aluminum	[Ne]3s ² 3p ¹	٠ÅI٠
silicon	[Ne]3s ² 3p ²	۰Si۰
phosphorus	[Ne]3s ² 3p ³	 .P.
sulfur	[Ne]3s ² 3p ⁴	:: ::::
chlorine	[Ne]3s ² 3p ⁵	: CI •
argon	[Ne]3s ² 3p ⁶	: Ăr :

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.

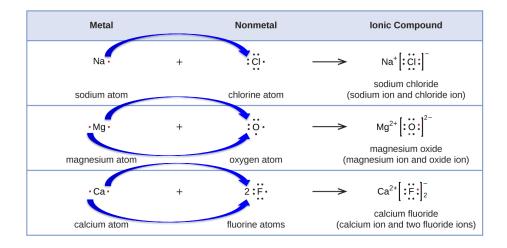


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Lewis symbols formation of salts



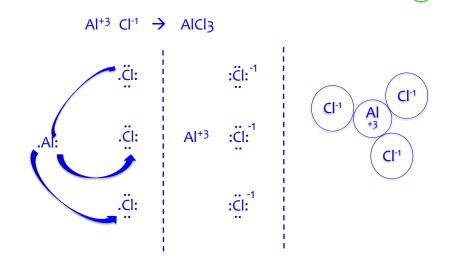
Lewis symbols show that spontaneous redox (transfer of electrons) occurs when salts form.



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Try this

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



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Lewis structures

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

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

$$H. + H. \longrightarrow (H)H H - H$$

$$.\ddot{C}l: + .\ddot{C}l: \longrightarrow (\ddot{C}l)\ddot{C}l: :\dot{C}l - \ddot{C}l:$$

Each H atom has access to the 2 shared ve-; the duet H wants.

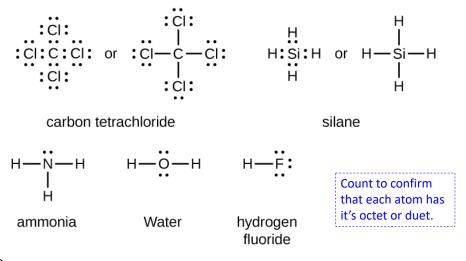
Each Cl atom has access to its 6 ve-& the shared pair; so the octet each wants.

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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).

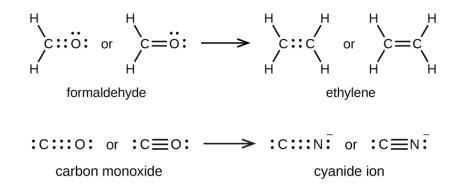


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Double & triple bonds

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

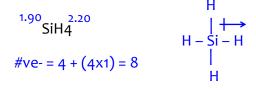
- Double bond: 2 shared pairs of valence electrons ::
- <u>Triple bond</u>: 3 shared pairs of valence electrons :::

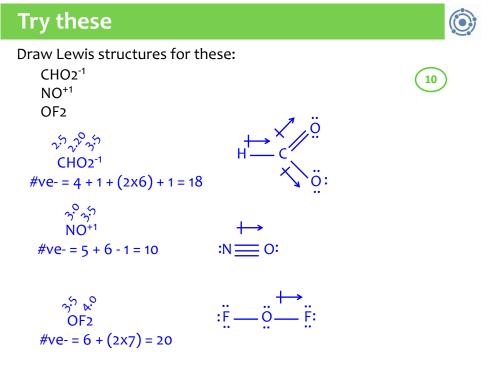


Writing Lewis structures

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.



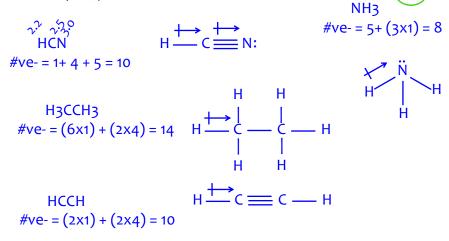


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Try these

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 (H3CCH3), acetylene (HCCH) and ammonia (NH3). 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.

$$\gamma^{\circ} \gamma^{\circ} \gamma^{\circ}$$

$$CO$$

$$\#ve- = 4 + 6 = 10$$

$$:C \stackrel{\leftarrow}{=} \ddot{O}:$$

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

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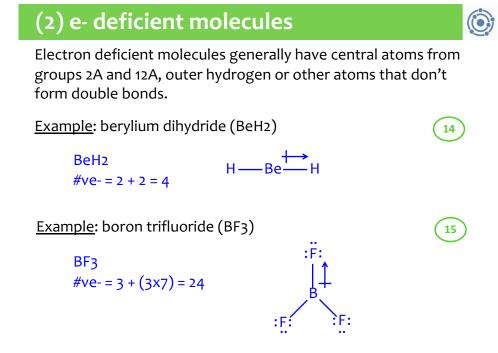
(1) Odd-electron molecules



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

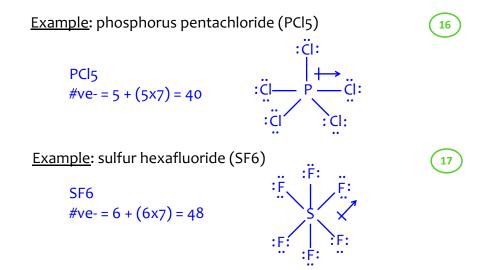
Example: nitric oxide (NO)



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(3) Hypervalent molecules

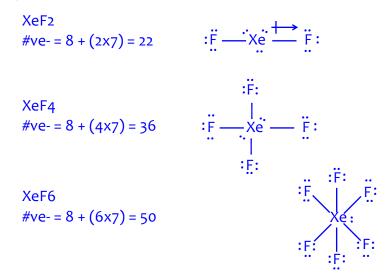
Elements below the second row of the periodic table can accommodate more than an octet using d orbitals.



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Write the Lewis structures for XeF2, XeF4, XeF6 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?

7. Chemical bonding



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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?

$$CI = (7) - (6 + 1) = 0$$

$$I = (7) - (4 + 4) = -1$$

$$:CI = (7) - (4 + 4) = -1$$

$$:CI = (7) - (4 + 4) = -1$$

$$:CI = (7) - (6 + 1) = 0$$

$$:CI = (7) - (6 + 1) = 0$$

$$:CI = (7) - (6 + 1) = 0$$

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$$:CI = (7) - (6 + 1) = 0$$

$$:CI = (7) - (6 + 1) = 0$$

$$:CI = (7) - (7) - (7) = 0$$

$$:CI = (7) =$$

Calculate formal charges in carbon monoxide.

$$C = (4) - (2 + 3) = -1$$

 $O = (6) - (2 + 3) = +1$:C = 0:

Using formal charge to predict stucture

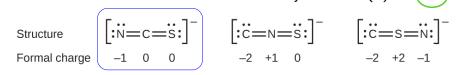
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24

When there are several Lewis structures for one molecule, <u>which</u> 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 'b	21					
ii=c=ii	:o≡c—ö:	ö=o=c	Structure			
0 0 0	+1 0 -1	0 +2 -2	Formal charge			
Which is the 'best' structure for the thiocyanate ion (-1)? (22)						



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Try this

Nitrous oxide, N2O, is commonly known as laughing gas. Which is the optimal structure for nitrous oxide?

$$\underbrace{ \begin{array}{c} N = N = 0 \\ -1 & +1 & 0 \end{array} } or \quad \underbrace{N = 0 = N \\ -1 & +2 & -1 \end{array}$$

Which is the 'best' structure for the nitrite ion (NO2⁻¹)?

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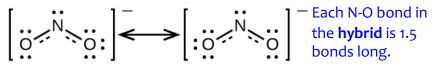
Resonance

Notice that the two possible structures for the nitrite ion (NO2⁻¹) are **resonance structures:** identical except for the placement of bonds or electrons.



From these structures, you might guess that NO2⁻¹ 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.

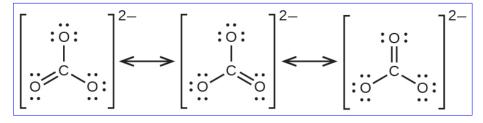


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Try this

(a) Draw one Lewis structure of the carbonate ion, $CO3^{-2}$. (25)

- (b) Draw all other resonance structures.
- (c) What determines the number of resonance structures?
- (d) Draw the resonance hybrid.



(a) & (b) above

(c) The number of identical atoms in the structure.

(d) All C to O bonds are 1.5 bonds (one solid & one dashed).

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Can you?



- (a) Use formed shares to share the (heat' or lowest error
- (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

Strength of covalent bonds

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

H₂(g) → 2H(g)
$$\Delta$$
H = 436 kJ
H
H – C – H (g) → C(g) + 4H(g) Δ H = 1660 kJ
H = 1660 kJ/4 mol
H = 415 kJ/mol of C – H

Trends in covalent bond strength:

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

What trends do you see here?



Covalent bonds energies vs. lengths

Bond length is <u>inversely related</u> 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-0	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** (Δ H).

 $(\Delta H) = \Sigma D$ bonds broken – ΣD bonds made

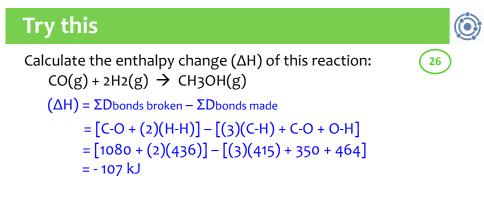
where D = bond energies (kJ/mol)

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

 $(\Delta H) = \Sigma D$ bonds broken – ΣD bonds made

= [H-H + Cl-Cl] – [2x H-Cl] = [436 + 243] – [2(432)] = - 185 kJ

The – indicates that energy is released, so the products are more stable than the reactants.



The – indicates that energy is released, so the products are more stable than the reactants.

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Try this

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

H2CCH2 + H2O → CH3CH2OH

 $(\Delta H) = \Sigma D bonds broken - \Sigma D bonds made$ = [C=C + O-H] - [C-H + C-C + C-O] = [611 + 464] - [415 + 345 + 350] = 1075 - 1110 = - 35 kJ

The – indicates that energy is released, so the products are more stable than the reactants.

Ionic bond strength & lattice energy



Ionic compounds are held together by electrostatic attraction. Lattice energy (Δ Hlattice): the energy needed to separate one mole of ionic compound into its components as gaseous ions. $MX(s) \rightarrow M^{+n}(g) + X^{-n}(g)$ Δ Hlattice = _____ kJ NaCl(s) $\rightarrow Na^{+1}(g) + Cl^{-1}(g)$ Δ Hlattice = + 769 kJ • Lattice energies are endothermic (+ Δ H) because bonds need to be broken and physical states need to change from solid to gas. Δ Hlattice = $\underline{C(Z^+)(Z^-)}$ where C = constant R_0 Z = charge $R_0 = sum of ionic radii$

- 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

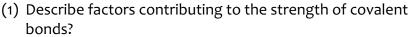
Noting that the size of ions is similar, explain why these lattice energies differ: 1023 kJ/mol 🔶 LiF - +1/-1 MgO 3900 kJ/mol ← +2/-2 sidebar Explain why these lattice energies differ: 28 MgF2 2957 kJ/mol Same charges; I is larger than F. MgI2 2327 kJ/mol 29 Which has higher lattice energy? Charges are the same, but Se is larger than O Al2O3 Al2Se3 so lattice energy of Al2O3 > Al2Se3. Which has higher lattice energy? 30 ZnO +2/-2Higher charges; likely ZnO > NaCl NaCl +1/-1

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Can you?



- (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

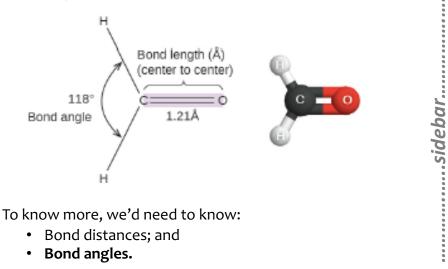
From 2D to 3D structures

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sidebar....

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

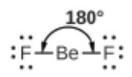


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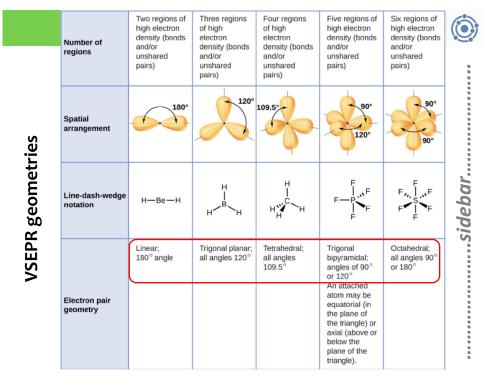
VSEPR theory suggests 3D structure

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.

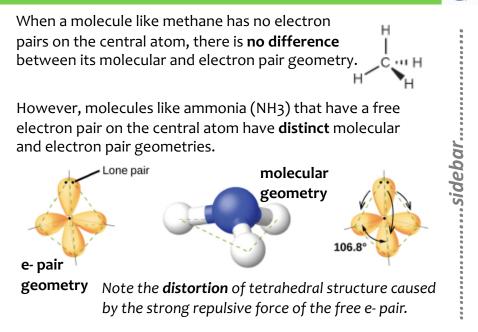


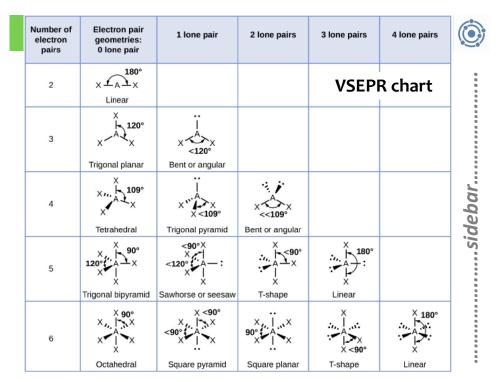
Here, the central beryllium has only two bonds. These two bonds arrange themselves at 180° to one another to maximize the space between the two bound fluorine atoms and the electrons that bond them to the beryllium.



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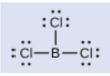
Molecular vs. electron pair geometry





Using VSEPR

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



CO2

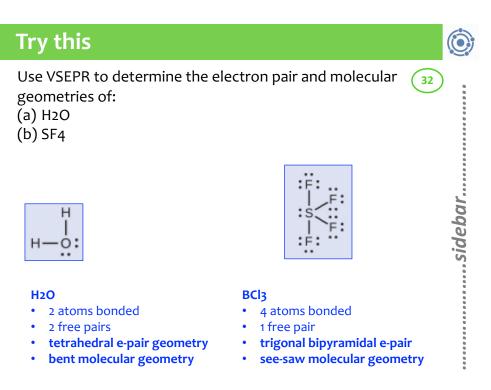
- 2 atoms bonded
- no free pairs
- 180°, linear geometry

BCl3

- 3 atoms bonded
- no free pairs
- 120°, trigonal planar

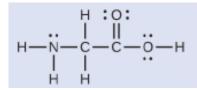
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.....sidebar.....



Try this

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



C1

- 4 atoms bonded
- o free pairs
- tetrahedral e-pair
- tetrahedral mol geometry

0

- 2 atoms bonded
- 2 free pairs
- tetrahedral e-pair
- bent mol geometry

Ν

- 3 atoms bonded
- 1 free pair
- tetrahedral e-pair geometry

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.....sidebar.....

33

pyramidal mol geometry

C2

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- 3 atoms bonded
- o free pairs
- trigonal pyramidal e-pair
- Trigonal pyramidal mol geometry

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 (∆H 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) → X(g) + Y(g) D_{X-Y} = ΔH°
- Enthalpy change: ΔH = ΣD_{bonds broken} ΣD_{bonds formed}
- Lattice energy for a solid MX: $MX(s) \longrightarrow M^{n+}(g) + X^{n-}(g) \qquad \Delta H_{\text{lattice}}$
- Lattice energy for an ionic crystal: $\Delta H_{\text{lattice}} = \frac{C(Z^+)(Z^-)}{R_o}$

