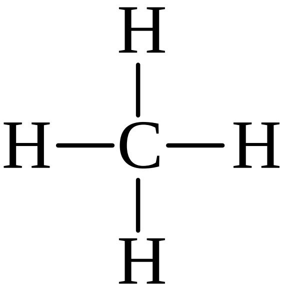
Concept of the Chemical Bond

- The Law of Definite Proportions (Joseph Louis Proust, 1799) and Dalton's development of atomic theory (1803) lead to the recognition that atoms of an element had a characteristic combining ability with other atoms, which came to be called **valence**.

- Existence of atoms suggested that compounds were composed of collections of atoms bound together by **chemical bonds**.

- In 1858 Couper began representing chemical bonds as a line between the symbols of atoms in compounds.

$$\mathrm{H{-}Cl}$$

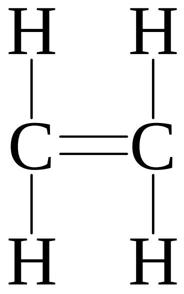


$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

Multiple Bonds

- The idea of fixed atomic valences lead to the postulate of multiple bonds in compounds such as C_2H_4 and C_2H_2.

- These were represented by double and triple lines between the element symbols.



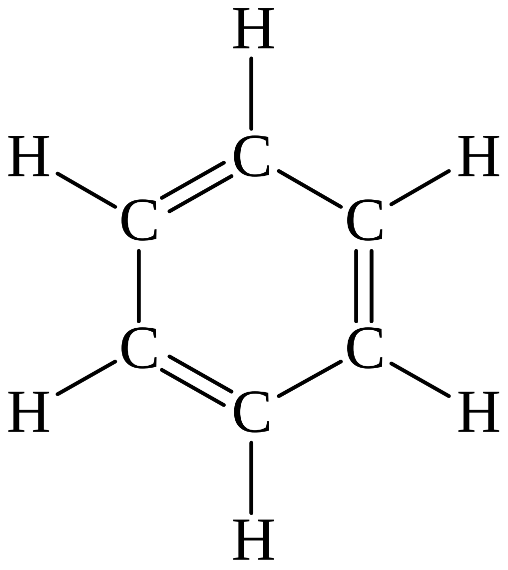
$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

$$H{-}C{\equiv}C{-}H$$

☞ These representations had no association with electrons, whose existence was yet to be realized!

Structural Formula of Benzene

- Using only the ideas of valence and multiple bonding, Butlerov (1864) and Kekulé (1865) were able to deduce one of the first structural formulas, that of benzene.



☞ This structural formula had nothing to do with electrons, which still had not been discovered!

Stereochemistry

- By the second half of the nineteenth century about 10 carbon compounds were know that existed in two forms that rotated plane polarized light in opposite directions.

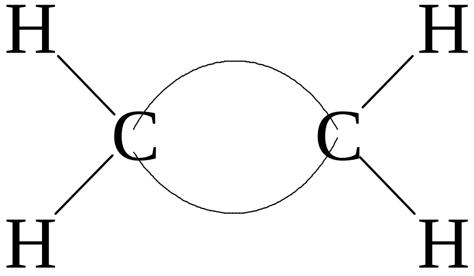
- All these compounds had formulas of the type $CX^1X^2X^3X^4$.

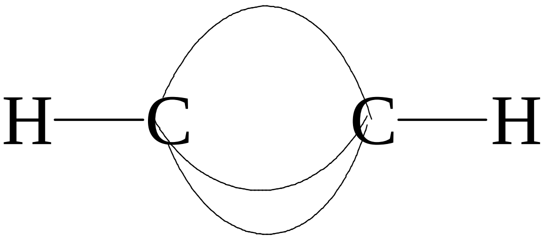
- In 1874 van't Hoff and le Bel independently deduced that this arose from left- and right-handed versions of the same molecule that are non-superimposable mirror images of each other.

- This lead to the postulate of tetrahedral geometry for the four valence positions around carbon.

Bent Bonds

- Double and triple bonds were represented by bent bonds to maintain tetrahedral geometry about carbon.





The Electron and Bonding

- Key developments leading to recognition of the importance of electrons in bonding:

1897	J. J. Thomson characterizes the electron (cathode ray tube experiments).
1906	Robert Mulliken determines electron charge (oil drop experiments).
1910	Ernest Rutherford determines nuclear structure of the atom (gold foil experiments).
1913	Henry G. J. Moseley determines atomic numbers (x-ray frequency experiments)
1913	Niels Bohr’s quantum model of hydrogen atom, consistent with observed line spectra (Lymann, Balmer, Paschen, Brackett, Pfund, etc.).

Shell Model

- In 1916 W. Kossel and G. N. Lewis independently recognized the stability of closed-shell configurations of inert gases (now called noble gases).

- This lead to the **shell model**, in which electrons are arranged in successive spherical shells with fixed capacities:

  K = 2, L = 8, M = 8, N = 18

- Elements in the same group have the same outer shell filling, so similarities in bonding must be related to electronic configuration.

Ionic Model of Bonding

- In 1916 Kossel recognized that common cations (e.g., Na^+, Ca^{2+}) and anions (e.g., Cl^-, O^{2-}) have the same number of electrons as a preceding or following noble gas in the periodic table.

- Kossel reasoned that these cations and anions form because their electronic configurations are stable like noble gases.

- Kossel assumed ionic compounds were held together solely by electrostatic interactions, resulting in a regular three dimensional structure forming a limitless molecule.

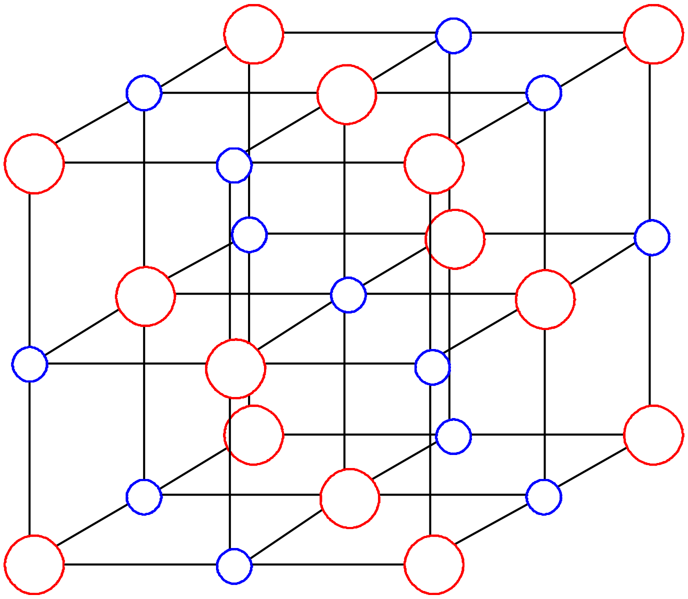
- "Ionic bond" is a hypothetical extreme, assuming no inter-ionic electron sharing.

- Assuming only electrostatic interactions, the lattice energy, U, is seen as the result of an infinite series of attractive and repulsive terms.

- For a mole of NaCl(s) we define

$$\mathrm{NaCl}(s) \rightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \qquad\qquad \Delta H \equiv U$$

Lattice Energy of NaCl



- For an ion pair, the energy of attraction is

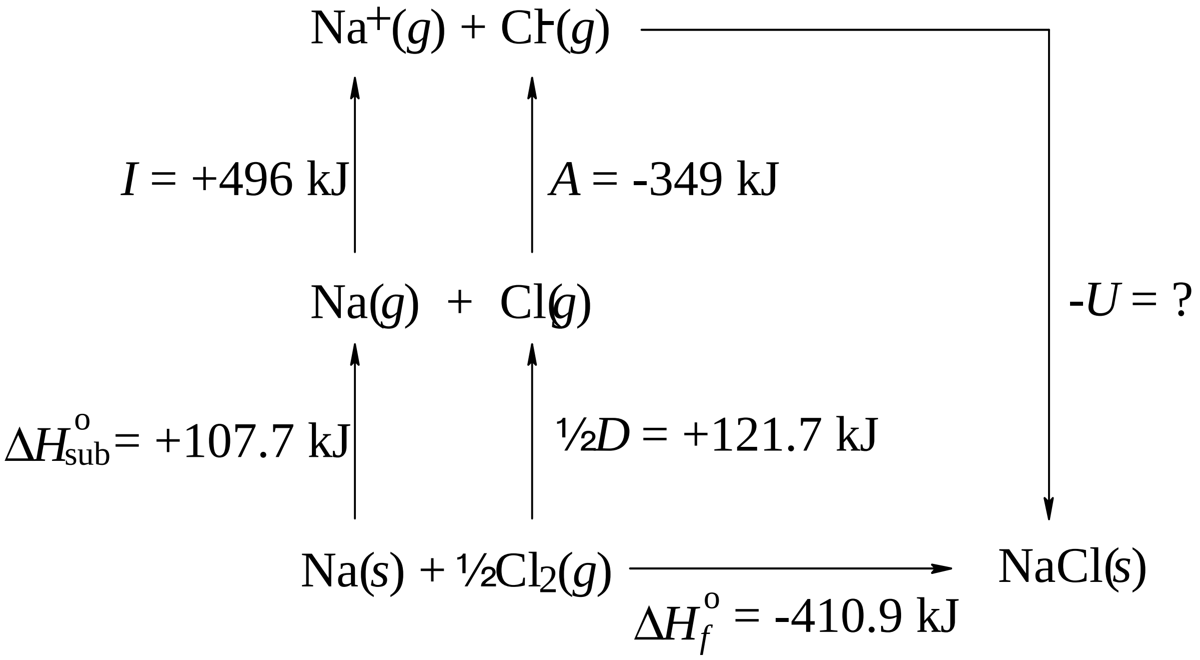
$$E = \frac{-kq^{+}q^{-}}{r}$$

- For the NaCl lattice, interactions of a single ion with its nearest neighbors gives

$$E = \frac{-kq^{2}}{r}\left(\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \ldots\right)$$

- For one mole of NaCl(*s*), $U \propto -NE$

Born-Haber Cycle for NaCl(*s*)



$Na(s) \rightarrow Na(g)$	$\Delta H^{\circ}_{sub} = 107.7$ kJ
$Na(g) \rightarrow Na^{+}(g) + e^{-}$	$I = 496$ kJ
$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	$\frac{1}{2}D = 121.7$ kJ
$Cl(g) + e^{-} \rightarrow Cl^{-}(g)$	$A = -349$ kJ
$Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl(s)$	$-U = ?$
$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$	$\Delta H^{\circ}_{f} = -410.9$ kJ

$$\Rightarrow \quad \Delta H^{\circ}_{f} = \Delta H^{\circ}_{sub} + I + \tfrac{1}{2}D + A - U$$

$$\begin{aligned} \therefore \quad U &= \Delta H^{\circ}_{sub} + I + \tfrac{1}{2}D + A - \Delta H^{\circ}_{f} \\ &= 107.7 \text{ kJ} + 496 \text{ kJ} + 121.7 \text{ kJ} + (-349 \text{ kJ}) - (-410.9 \text{ kJ}) \\ &= 787 \text{ kJ} \end{aligned}$$

Factors Favoring a More Stable Crystal Lattice

Large values of lattice energy, *U*, are favored by

1. Higher ionic charges
2. Smaller ions
3. Shorter distances between ions

Selected Lattice Energies, U° (kJ/mol)
(Born-Haber Cycle Data)

	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1049.0	862.0	818.6	762.7	2830
Na^+	927.7	786.8	751.8	703	2650
K^+	825.9	716.8	688.6	646.9	2250
Rb^+	788.9	687.9	612	625	2170
Cs^+	758.5	668.2	635	602	2090
Mg^{2+}		2522			3795
Ca^{2+}		2253			3414
Sr^{2+}		2127			3217

Covalent Bonds and Lewis Structures

- In 1916 G. N. Lewis proposed a model of bonding to account for non-ionic cases (e.g., Cl_2, CCl_4).

- Noting that most molecules have an even number of electrons, Lewis proposed the shared-electron-pair bond, later renamed the covalent bond by Irving Langmuir (1919).

- Lewis saw achieving a noble-gas configuration (rule of eight) as the impetus for forming covalent bonds.

- Lewis regarded the rule of two, implying pairs of electrons in bonded atoms, as more important than the rule of eight.

- More exceptions to the rule of eight were known (e.g., PCl_5) than to the rule of two (e.g., NO).

- The association between a shared electron pair and a chemical bond became a defining concept of chemistry, and the previous line notation (—) came to symbolize a shared pair.

Steps for Drawing Electron Dot Models

1. Arrange the atoms of the compound or complex ion so as to show how they are linked together by chemical bonds. When in doubt, assume that the *least electronegative* atom is central.

2. Count the valence electrons for each atom. For non-transition elements, the number of valence electrons is the same as the group number of the element. For a complex anion, add electrons equal to the negative charge. For a complex cation, subtract electrons equal to the positive charge. The total is the number of electrons to be used in generating the model.

3. Draw in single bonds (–) between all atoms that are linked together, keeping in mind that each bond represents the use of two electrons from the total established in step 2.

4. With the remaining electrons, first add pairs (:) to all of the outer atoms to make octets (except H), then add any leftover electrons to the central atom. The octet for each atom includes pairs used to make bonds in step 3.

5. Leave no electrons unpaired unless the total number of electrons is odd.

Steps for Drawing Electron Dot Models

6. Count the number of electrons about the central atom to see if an octet has been made there. If not, try moving non-bonding pairs (:) from outer atoms to make double or triple bonds to the central atom. However, note that
   (a) hydrogen and the halogens do not form multiple bonds, and
   (b) elements in the third and higher periods usually do not form effective multiple bonds.

7. If there are too few electrons to give octets to all atoms (except hydrogen), the central atom *might* be electron deficient, particularly if it is Be, B, or Al. Examples: BeH_2, BCl_3, $AlCl_3$. However,
   (a) outer atoms are *never* electron deficient, and
   (b) C, N, O, and F *almost always have an octet*.

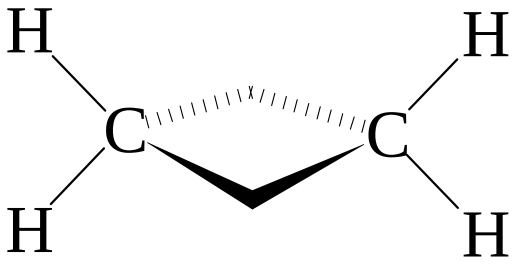
8. Sometimes central atoms from the *third and higher periods* have more than an octet (*hypervalence*), but only when necessary. Examples: PCl_5, XeF_2, XeF_4. However,
   (a) outer atoms are *never hypervalent*, and
   (b) C, N, O, and F are *never hypervalent*.

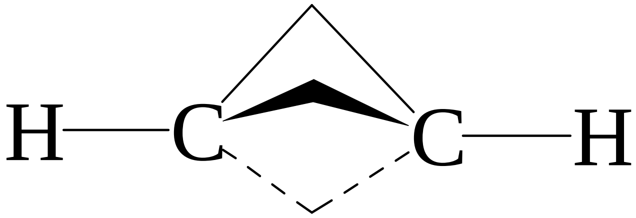
9. The representation of any anion or cation should be surrounded by square brackets ([ ]) with the charge indicated on the outside as a superscript.

10. Count up the number of electrons in the completed model to be sure it is the same as the total established in step 2.

Lewis Models Based on the Tetrahedron

- The prevalence of octets, seen as four electron pairs, suggested a tetrahedral geometry, even for double and triple bond cases.

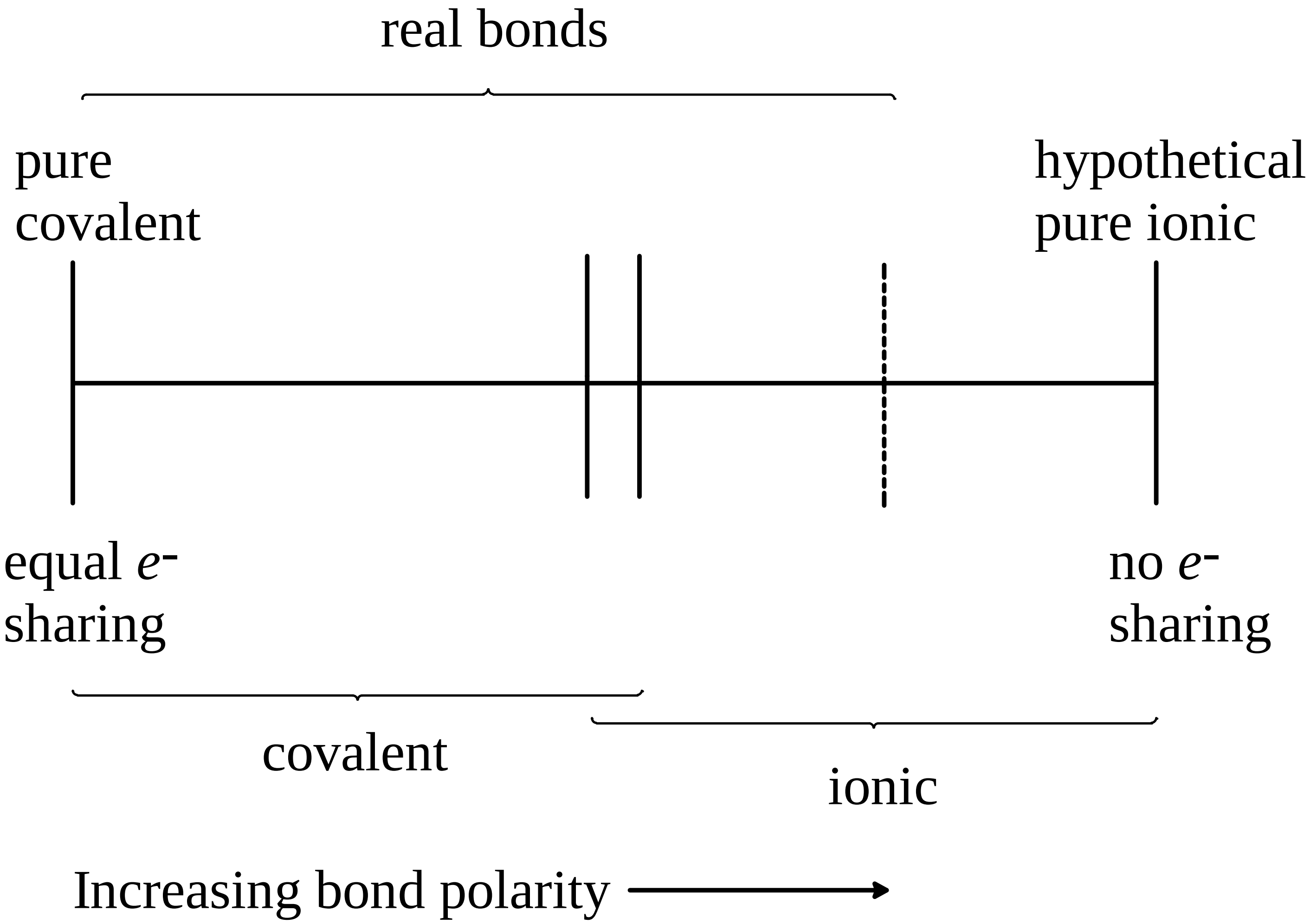




- These structures are similar to the bent bonds postulated from directed valence considerations.

Bond Polarity and Bond Type

- The ionic model of Kossel and the covalent model of Lewis suggested a continuum of bond types, based on the degree of electron sharing.



Electronegativity

- In 1932 Linus Pauling defined the concept of **electronegativity** as the ability of an atom to attract electrons to itself *in a chemical bond*.

- Robert S. Mulliken (1934): Electronegativity calculated as the average of ionization energy and electron affinity.

$$\chi = \frac{I - A}{2}$$

Problems:

☹ Electron affinity data are not reliably known for many elements.

☹ Both A and I refer to gaseous atoms, not atoms in a chemical bond.

Pauling Electronegativities

Linus Pauling - 1930's

☞ Pauling's scale is based on the increase in *bond energy*, *D*, for a heteronuclear bond compared to the average of the homonuclear bond energies of two bonded atoms.

$H_2(g) \rightarrow 2H(g) \qquad \Delta H^\circ = +435 \text{ kJ/mol} \equiv D(H_2)$

$F_2(g) \rightarrow 2F(g) \qquad \Delta H^\circ = +155 \text{ kJ/mol} \equiv D(F_2)$

$HF(g) \rightarrow H(g) + F(g) \qquad \Delta H^\circ = +565 \text{ kJ/mol} \equiv D(HF)$

$$\frac{D(H_2) + D(F_2)}{2} = \frac{435 \text{ kJ} + 155 \text{ kJ}}{2} = 295 \text{ kJ}$$

☞ Pauling attributed the extra bond strength to coulombic attraction between the partial ionic charges on the atoms created by unequal sharing; i.e., *partial ionic character*.

☞ The Pauling scale sets $\chi = 4.0$ as the maximum electronegativity, given to fluorine.

Electronegativities

(Pauling Scale)

	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
1	H 2.1																
2	Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
5	Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
7	Fr 0.7	Ra 0.9	Ac-No 1.1-1.7														

Allred-Rochow Electronegativities

- In 1958, A. L. Allred and E. G. Rochow[1] defined electronegativity as the electrostatic force exerted by the nucleus on the valence electrons.

- Used effective nuclear charges, Z^*, calculated by Slater's rules[2], using the formula

$$\chi_{AR} = (3590\ Z^*/r^2) + 0.744$$

where r is the covalent radius in pm, and the constants fit the values to the Pauling scaling.

- Allred-Rochow values typically add a second decimal place and suggest subtle differences between elements with similar values on the Pauling scale.

Scale	Cl	N
Pauling[3]	3.16	3.04
Allred-Rochow	2.83	3.07

---

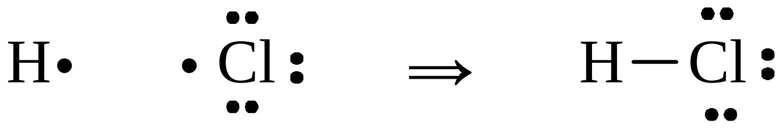
[1] A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, *5*, 264-268 (1958)

[2] J. C. Slater, *Phys. Rev.*, *36*, 57 (1930).

[3] Recalculated by A. L. Allred, *J. Inorg. Nucl. Chem.*, *17*, 215 (1961).

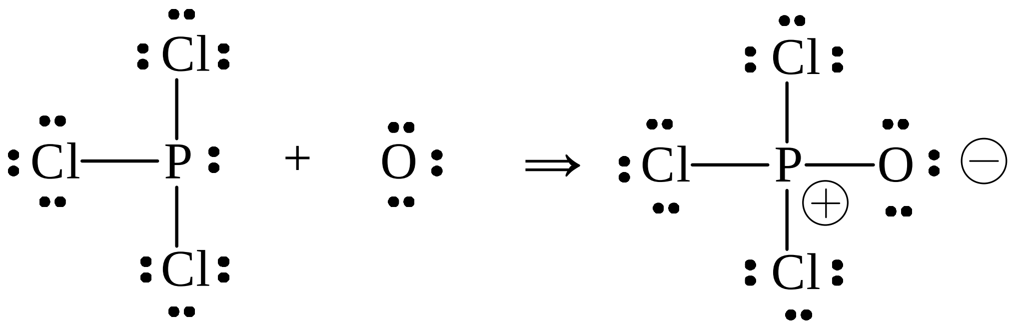
Formal Charge

In terms of "electron bookkeeping" of Lewis models, some bonds are formed by each atom contributing electrons.



no e^- gain or loss

In other cases one atom seems to be donating a pair of electrons to the other.



P “loses” 1e^- by sharing
O “gains” 1e^- by sharing

☞ Formal charges are the *hypothetical* charges atoms would have if all elements had the same electronegativity.

STEPS FOR ASSIGNING FORMAL CHARGES

1. Write the electron dot structure (Lewis dot model) for the compound or complex ion.

2. Count electrons about each atom by the following method:
   non-bonded pair (:) = 2
   bonded pair (–) = 1
   [Note: *This is not the same as the method used to determine octets in constructing Lewis dot models*.]

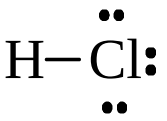
3. Compare the number of electrons counted in this manner with the number of valence electrons the isolated neutral atom would have.

4. If the count is higher than for the neutral atom, assign a negative formal charge equal to the difference. Write the formal charge inside a circle next to the atom (e.g., ⊖).

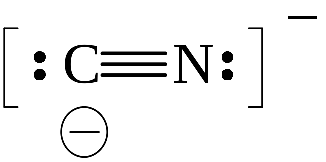
5. If the count is lower than for the neutral atom, assign a positive formal charge equal to the difference. Write the formal charge inside a circle next to the atom (e.g., ⊕).

6. The algebraic sum of all positive and negative formal charges for a neutral molecule should be zero. For a complex ion, it should equal the net charge on the ion.

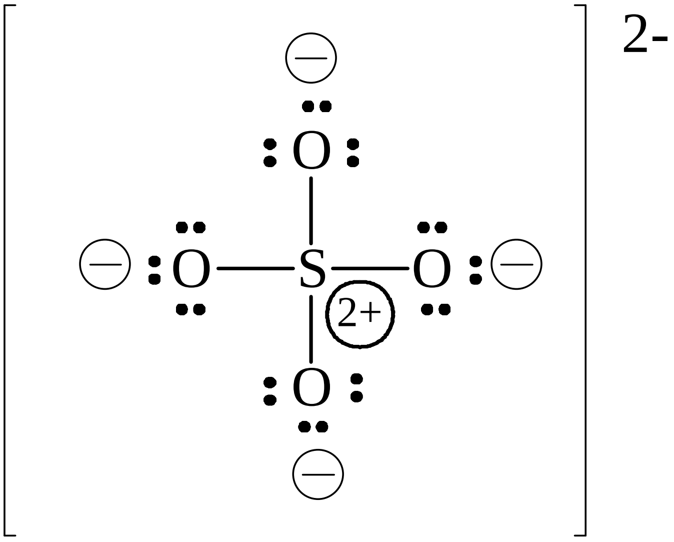
Examples of Formal Charge Assignments



No formal charges



Negative formal charge on carbon

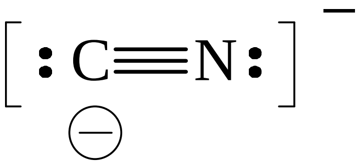


Negative formal charge on O's; 2+ formal charge on S. Charge on the ion is the sum of the formal charges. Negative ion charge resides on oxygen atoms.

Formal Charges for Determining the "Best" Lewis Structure

When trying to decide among possible Lewis structures, those most conforming to the following criteria *probably* are most plausible:

1. All atoms have the smallest formal charges.
2. Negative formal charges are assigned to electronegative elements, and positive charges are assigned to electropositive elements.
3. Adjacent atoms do not have the same formal charge, if a structure that avoids this can be drawn.
4. The preceding guidelines do not apply if there is no other plausible model (e.g., CN^-).



$$\left[\,:\underset{\ominus}{C}\equiv N:\,\right]^{-}$$

(OK to assign ⊖ to carbon, even though nitrogen is more electronegative.)

Exceptions to the Octet Rule

- Sometimes central atoms from the *third and higher periods* have more than an octet (*hypervalence*) in their Lewis structures, but only when necessary. Examples: PCl_5, XeF_2, XeF_4. However,
  - (a) outer atoms are *never hypervalent*, and
  - (b) C, N, O, and F are *never hypervalent* in their common compounds.

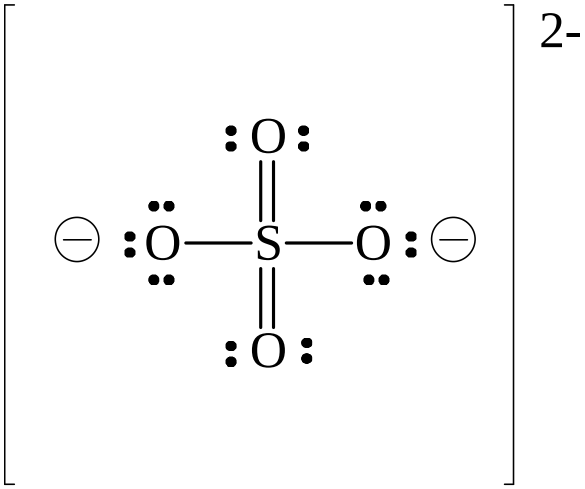
- If there are too few electrons to give octets to all atoms (except hydrogen), the central atom *might* be electron deficient, particularly if it is Be, B, or Al. Examples: BeH_2, BCl_3, $AlCl_3$. However,
  - (a) outer atoms are *never* electron deficient, and
  - (b) C, N, O, and F *almost always have an octet*.

Arbitrary Hypervalence

☞ Do not expand valence in an attempt to minimize formal charges if a structure that obeys the octet rule can be drawn.

- Drawing hypervalent structures in such cases implies use of *d* orbitals by the central atom, which are generally not available for significant participation in bonding with non-transition elements.

Example: The following structure (shown in many books) is *not* reasonable, even though the formal charges have been minimized.



☞ Lewis avoided structures like these! Drawing them is tantamount to taking formal charge too seriously!

Limitations of the Lewis Model

- Wedded to the notion that a bond is defined by a shared pair
- Does not adequately handle bond polarity
- Implies static location of electrons
- Cannot adequately represent differences in electron distribution between atoms in different molecules
- Cannot represent the overall distribution of electrons across molecules
- Must resort to "resonance" to describe cases that do not have simple electron pair bonds
- Cannot represent bonding in cases like boranes (e.g., B_2H_6) that have bridging hydrogens

☞ Nonetheless, Lewis models are the simplest and most direct way of representing qualitatively the linkages and relative bonding strengths in most molecules.