Covalent Compounds

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(Chemistry Notes)

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Covalent Compounds

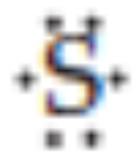
Covalent bonds (result from sharing electrons between atoms, e.g., Cl_2)

Lewis Symbols or Lewis electron-dot symbols

Valence electrons are found in the outermost shell of an atom. They are involved in bonding.

We represent the valence electrons as dots around the symbol for the element. The number of valence electrons available for bonding are indicated by unpaired dots. We generally place the electrons on four sides of a square around the element's symbol.

Sulfur, for example, has the electron configuration [Ne]$3s^2$ $3p^4$



The Octet Rule

Atoms tend to gain, lose or share electrons until they are surrounded by eight valence electrons; this is known as the **octet rule**.

TABLE 8.1 • Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	$[He]2s^1$	Li·	Na	$[Ne]3s^1$	Na·
2A	Be	$[He]2s^2$	·Be·	Mg	$[Ne]3s^2$	·Mg·
3A	B	$[He]2s^22p^1$	·Ḃ·	Al	$[Ne]3s^23p^1$	·Ȧl·
4A	C	$[He]2s^22p^2$	·Ċ̣·	Si	$[Ne]3s^23p^2$	·Ṩi·
5A	N	$[He]2s^22p^3$	·Ṇ̇:	P	$[Ne]3s^23p^3$	·Ṗ̣:
6A	O	$[He]2s^22p^4$	:Ọ̇:	S	$[Ne]3s^23p^4$	:Ṩ:
7A	F	$[He]2s^22p^5$	·F̤̈:	Cl	$[Ne]3s^23p^5$	·C̤̈l:
8A	Ne	$[He]2s^22p^6$	:N̤̈e:	Ar	$[Ne]3s^23p^6$	:Ä̤r:

Covalent Bonding

The majority of chemical substances do not have characteristics of ionic compounds.

A chemical bond formed by sharing a pair of electrons is called a covalent bond.

Both atoms acquire noble-gas electronic configurations.

This is the 'glue' to bind atoms together.

Lewis Structures

Formation of covalent bonds can be represented using Lewis symbols.

The structures are called **Lewis structures**.

We usually show each electron pair shared between atoms as a line and show unshared electrons as dots. Each pair of shared electrons constitutes one chemical bond.

Example: H_2

$$H\cdot + H\cdot \;=\; H\underline{.\;\;\;\;.}H \;=\; H{:}H \;=\; H\text{–}H$$

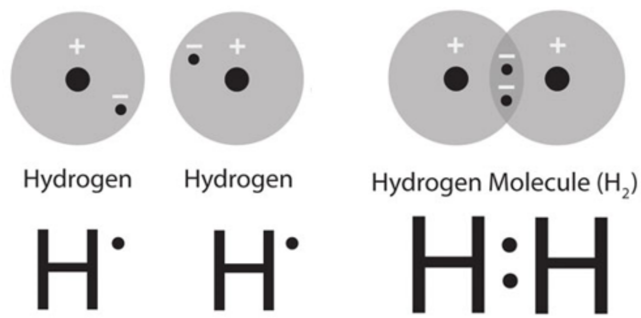
Two electrons are on a line connecting the two H nuclei;

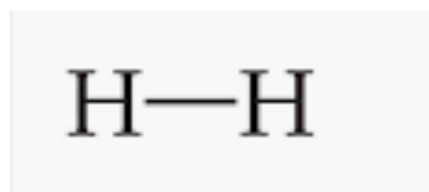
Multiple Bonds

It is possible for more than one pair of electrons to be shared between tow atoms (e.g **multiple bonding**).

Single Bond

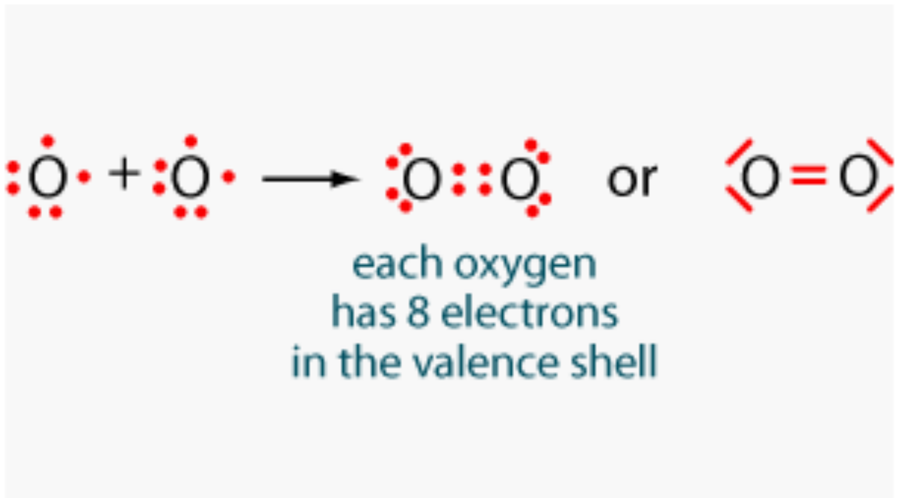
One shared pair of electrons is a **single bond** (e.g., H_2)   H**:**H



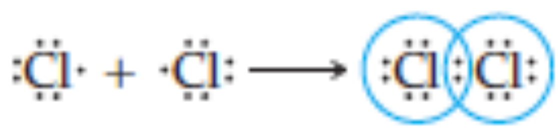


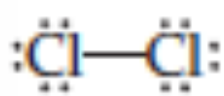
Double Bond

Two shared pairs of electrons is a **double bond** (e.g., O_2)



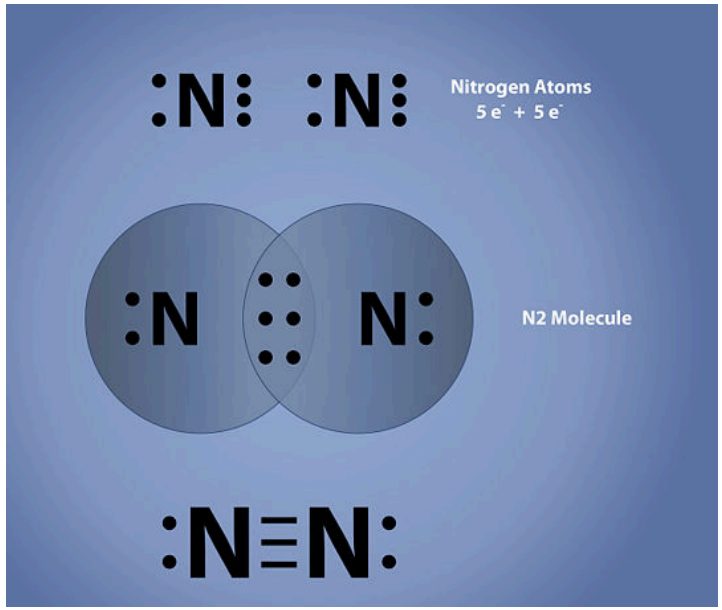
Cl_2





Triple Bond

Three shared pairs of electrons is a **triple bond** (e.g., N_2)



Generally, bond distance decrease as we move from single through double to triple bonds.

$N-N$	$N=N$	$N\equiv N$
1.47 Å	1.24 Å	1.10 Å

Drawing Lewis Structures

Some simple guidelines for drawing Lewis structures:

Add up all of the valence electrons in all atoms. For an anion, add electrons equal to the negative charge. For a cation, subtract electrons equal to the positive charge.

Identify the central atom.

When the central atom has other atoms bound to it, the central atom is usually written first. Example: in CO_2, the central atom is carbon.

Place the central atom in the center of the molecule and add all other atoms around it.

Place one bond (two electrons) between each pair of atoms

Complete the octets for all atoms connected to the central atom (exception: hydrogen can only have two electrons).

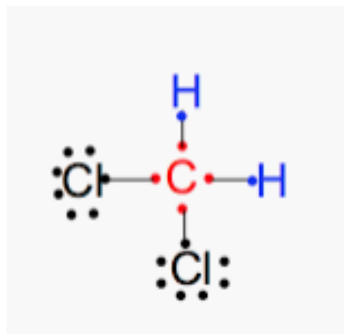
Complete the octet for the central atom; use multiple bonds if necessary.

HONC Rule

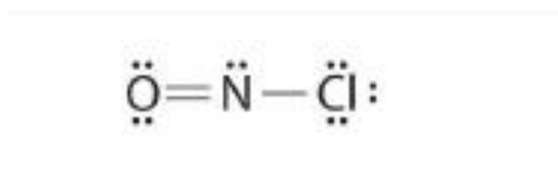
H	O (group 6)	N (group 5)	C (group 4)
1 bond	2 bonds	3 bonds	4 bonds

Examples:

CH_2Cl_2



NOCl



Formal Charges

Sometimes it is possible to draw more than one Lewis structure with the octet rule obeyed for all the atoms. To determine which structure is the most reasonable, we use formal charge.

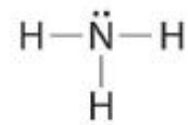
The formal charge on the atoms is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure.

The Lewis structure with the set of formal charges **closest to zero** is usually the most stable

For the most stable Lewis structure, the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion.

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non - bonding\ e^- + \frac{bonding\ e^-}{2}\right)}$$

Example: NH_3

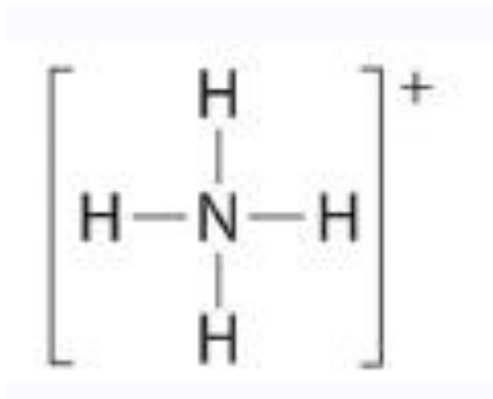


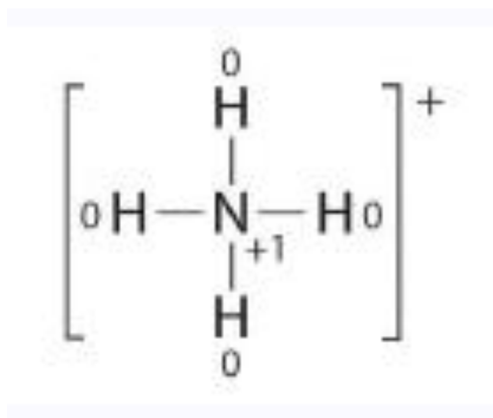
Ammonia

$$formal\ charge\ (N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0$$

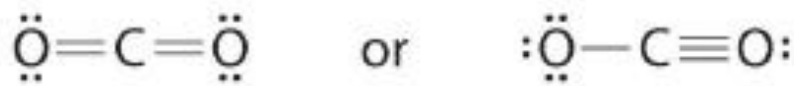
$$formal\ charge\ (H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0$$

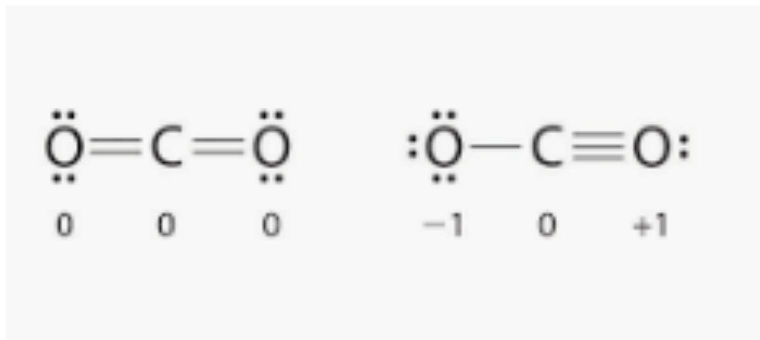
Example: NH_4^+



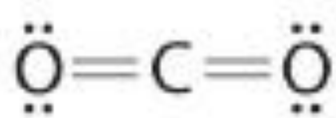


Example: CO_2





So the most stable is



Resonance Structure

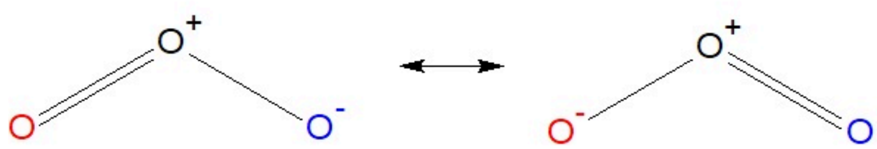
Some structures with multiple bonds can have similar structures with the multiple bonds between different pairs of atoms.

Resonance structures are attempts to represent the real structure that is a mix between several extreme possibilities.

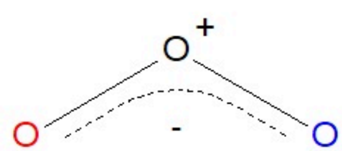
Resonance structures are Lewis structures that differ only with respect to placement of the electrons.

The “true” arrangement is a blend or hybrid of the resonance structures.

Example; in ozone (O_3) the extreme possibilities have one double and one single bond. The resonance structure has two identical bonds of intermediate character. We use a double-headed arrow to indicate resonance.

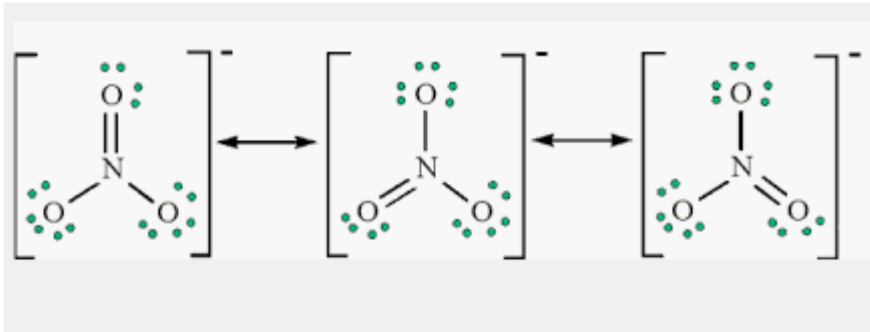


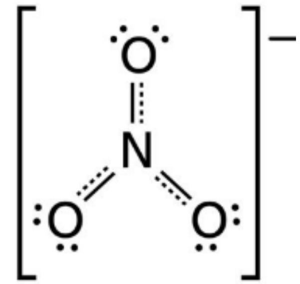
Interconversion is FAST!!!

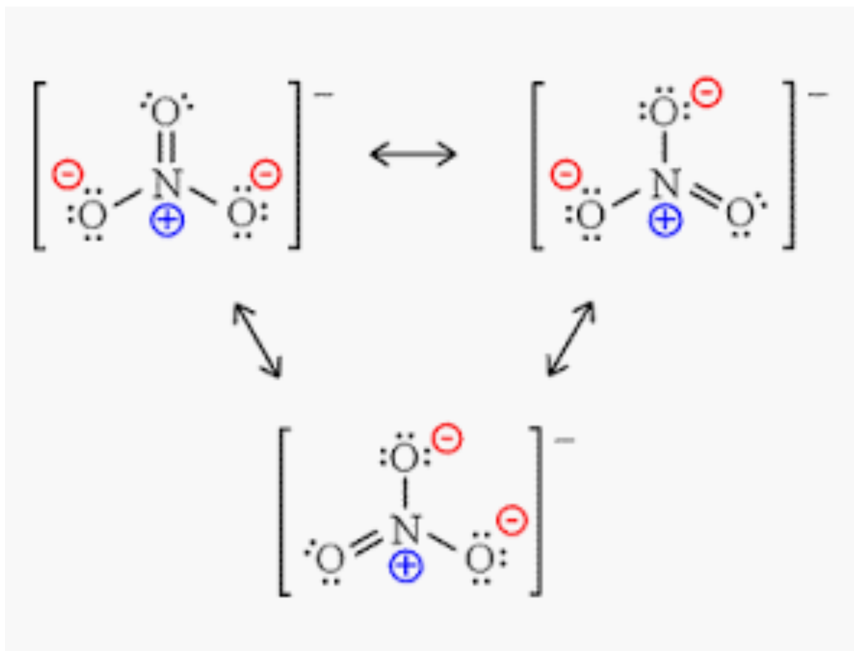


delocalized

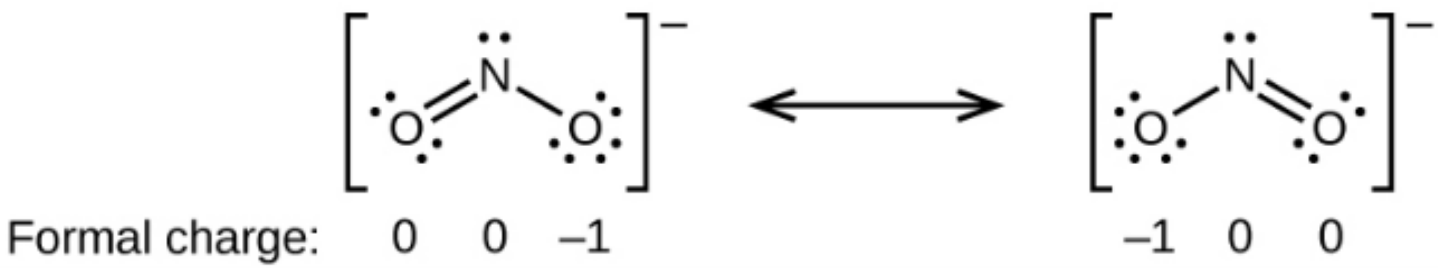
Common example:, NO_3^-, SO_3, NO_2 and benzene.

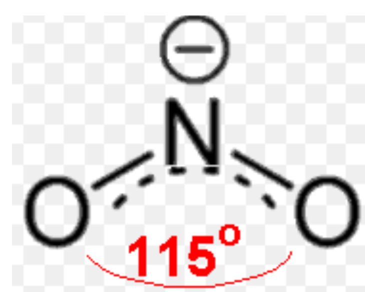






Example: NO_2^-



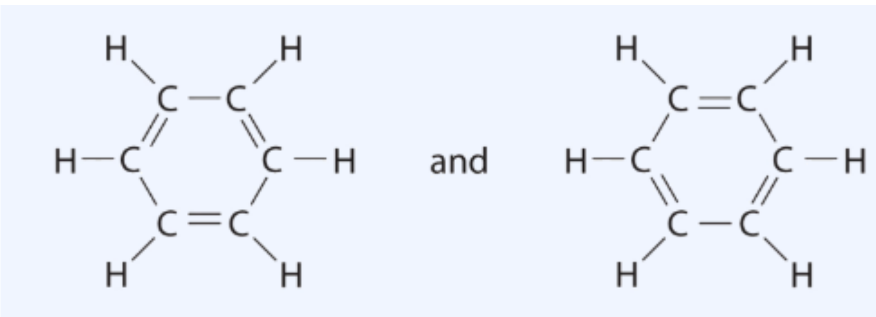


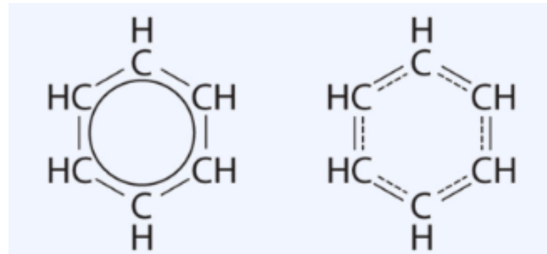
Resonance in Benzene (aromatic compound)

Benzene (C_6H_6) is a cyclic planar structure. There are alternative double and single bonds between the carbon atoms

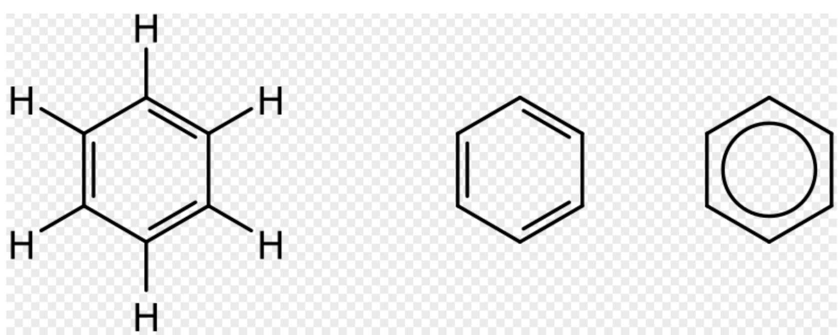
Experimentally, the C C bonds in benzene are all the same length.

Benzene has two resonance Lewis structures. we often represent benzene as a hexagon with a circle in it.





Benzene



Exception to the Octet Rule.

There are three classes of exceptions to the octet rule:

Molecules with an odd number of electrons

Molecules in which one atom has less than an octet.

Molecules in which one atom has more than an octet.

Odd Number of Electrons

Most molecules have an even number of electrons and complete pairing of electrons occurs although some molecules have an odd number of electrons.

Example: ClO_2, NO and NO_2.

Less than an Octet

Molecules with less than an octet are also relatively rare.

Most often encountered in compounds of **boron or beryllium**

A typical example is BF_3.

More than an Octet.

This is the largest class of exceptions.

Atoms from the third period on can accommodate more than an octet.

Example; PCL_5, SF_4, AsF_6^- and ICl_4^-.

Elements from the third period and beyond have unfilled ***d* orbitals** that can be used to accommodate additional electrons.

Size also plays a role.

The larger the central atom, the larger the number of atoms that can surround it.

The size of the surrounding atoms is also important.

Expanded octets occur often when the atoms bound to the central atom are the smallest and most electronegative (e.g., F, Cl, O)

Strengths of Covalent Bonds.

The energy required to break a covalent bond is called the bond **enthalpy,** *D*.

That is for the Cl_2 molecule, $D(ClCl)$ is given by ΔH for the reaction:

$$Cl_2\,(g) \longrightarrow 2\,Cl\,(g)$$

When more than one bond is broken:

$$CH_4\,(g) \longrightarrow C\,(g) + 4\,H\,(g) \qquad \Delta H = 1660\text{ kJ}$$

The bond enthalpy is a fraction of H for the atomization reaction:

$$D(CH) = 1/4\,H = 1/4\,(1660\text{ kJ}) = 415\text{ kJ.}$$

The bond enthalpy is always a positive quantity.

Bond Enthalpies and the Enthalpies of Reactions

We can use bond enthalpies to calculate the enthalpy for a chemical reaction.

We recognize that in any chemical reaction bonds need to be broken and then new bonds form. The enthalpy of the reaction is given by:

The sum of bond enthalpies for bonds broken less the sum of bond enthalpies for bonds formed.

Where ΔH_{rxn} is the enthalpy for a reaction:

$$\Delta H_{rxn} = D(\text{bonds broken}) - D(\text{bonds formed})$$

We illustrate the concept with the reaction between methane, CH_4 and chlorine:

$$CH_4\ (g) + Cl_2\ (g) \longrightarrow CH_3Cl\ (g) + HCl\ (g)$$

In this reaction one CH bond and one ClCl bond are broken while one CCl bond and one HCl bond are formed.

So $\Delta H_{rxn} = [D(\text{CH}) + D(\text{ClCl})] – [D(\text{CCl}) + D(\text{HCl}) = -104$ kJ.

The overall reaction is exothermic which means that the bonds formed are stronger than the bonds broken.The above result is consistent with Hess’s law.

Bond Enthalpy and Bond Length

The distance between the nuclei of the atoms involved in a bond is called **bond length.**

Multiple bonds are shorter than single bonds

We can show that multiple bonds are stronger that single bonds.

As the number of bonds between atoms increases, the atoms are held closer and more tightly together.