Molecules of the Atmosphere

The present atmosphere consists mainly of molecular nitrogen (N_2) and molecular oxygen (O_2) but it has dramatically changed in composition from the beginning of the solar system. The atoms in N_2 and O_2 are held together by strong covalent bond, sigma bonds and pi bonds. Although molecular nitrogen is very unreactive, it is broken apart in lightning structures and reacts with oxygen atom. We can represent the molecules through electron dot structures or Lewis structures.

Outline

Composition of the Atmosphere

The gases in the atmosphere are composed of neutral, uncharged particles. Except for the noble gases, atoms in the gas phase share electrons with other atoms in chemical bonds so that their electron count can approach the more stable filled-shell configuration. The Earth's atmosphere consists of a mixture of noble gas atoms and many kinds of molecules.

Changes in Composition

Earth's primordial atmosphere was probably similar to the gas cloud that created the sun and planets. It consisted of hydrogen and helium, along with methane, ammonia, and water. This was a reducing atmosphere. There was no molecular oxygen or other reactive oxides. Over time, some of this first atmosphere, particularly the lighter gases, outgassed and was lost. More water may have arrived with comets colliding on the surface of the planet. Volcanic activity in the early, Earth created major changes with release of water vapor, carbon dioxide, and ammonia along with small quantities of SO_2, H_2S, HCl, N_2, NO_2, He, Ar, and other noble gases. This produced the second atmosphere.

Comet impacts may have increased the amount of water. Water vapor formed clouds. These produced rain. Over a period of thousands of years, the liquid water accumulated as rivers, lakes, and oceans on the Earth's surface. Bodies of liquid water acted as sinks for carbon dioxide. Chemical and biological processes transformed CO_2 gas to carbonate rocks. The nitrogen and argon accumulated in the atmosphere. They do not react with water or other atmospheric components. Oxygen existed in only trace quantities before life began.

Living things created much of the third atmosphere, the one that now exists on Earth. Cyanobacteria were responsible for the rise in the atmospheric concentration of oxygen beginning 2.3 billion years ago. These bacteria, algae, and other plants produce oxygen by photosynthesis. Although most of this oxygen is used in respiration (biological oxidation) or in the atmospheric oxidation of the carbon-containing products, approximately 0.1 % of the organic matter is sequestered in sediments and that quantity of oxygen is added to the atmosphere. Over time, the excess oxygen has built up so that it is now makes up nearly 20% of the gases close to Earth.

Composition of Earth's Atmosphere	
Nitrogen	78.1%
Oxygen	20.9%
Argon	0.9%
Carbon dioxide, Methane, Rare (inert) gases	0.1%

Molecular nitrogen and molecular oxygen are the most common gases in today's atmosphere. Others are present in small concentrations. The other more common gases are shown in the table below. There is a remarkable difference between the original, reducing atmosphere and the current oxidizing atmosphere.

Formula	Conc. (ppb)	Source
N_2	7.8×10^8	biologic
O_2	2.0×10^8	biologic
H_2O	$10^6 - 10^7$	physical
Ar	9.3×10^6	radiogenic
CO_2	3.5×10^5	biol/industrial
Ne	1.8×10^4	geologic
He	5.2×10^3	radiological
CH_4	1.6×10^3	biological
Kr	1.0×10^3	geologic
H_2	5.0×10^2	biol/photol
N_2O	3.0×10^2	biol/industrial

Formula	Conc. (ppb)	Source
CO	1.0×10^2	photol/indust
SO_2	$< 10^2$	photol/indust
O_3	$< 10^2$	photochemical
Xe	90	geological
NO, NO_2, NO_x	Variable	industrial/bio
CH_3Cl	0.6	biological
CCl_2F_2	0.29	industrial
CCl_3F	0.17	industrial
CCl_4	0.12	industrial
CH_3CCl_3	0.098	industrial
CF_4	0.07	industrial

The concentration of each gas is given in parts per billion ($x/10^9$) of all atoms or molecules present.

- Molecular nitrogen is present as $7.8 \times 10^8/10^9$ or 0.78, 78% of all gas particles.
- Molecular hydrogen is present as $5.0 \times 10^2/10^9$ or only 0.00000050, 0.000050% of all gas particles.

Note that helium in the atmosphere is derived from radioactive decay, loss of an alpha particle from some other nucleus. Many of the molecules are products of living things, oxygen from plants in photosynthesis for example. Chlorofluorocarbons, such as CF_2Cl_2, are made only through industrial processes.

Pressure

A key measure of gas-phase molecules is their **pressure**. For a gas in a container, the pressure of the gas is the force exerted by the gas particles hitting the surface of the container. There isn't really a container for our atmosphere so we need to think of pressure in a slightly different way.

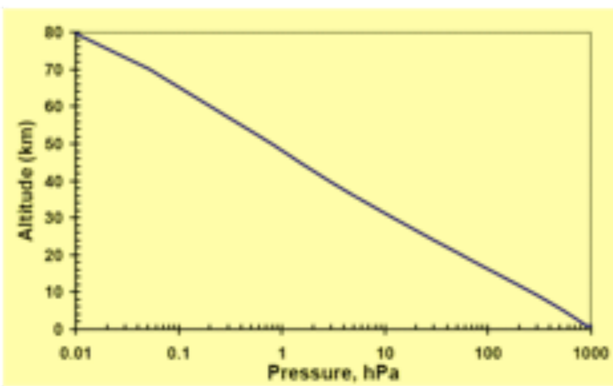
1. All atoms and molecules in the Earth's atmosphere are held by the **gravitational force** of the planet. The force decreases by $1/(\text{distance})^2$ so the particles are held less tightly as the distance between them and the Earth (altitude) increases.

2. The **gas density**, that is the mass of gas particles in every liter of volume, decreases as the altitude increases.

3. The **weight** of a column of gas particles, that is the Earth's gravitational force acting on the mass of the gas particles, above any point must decrease as the altitude increases. This weight is **atmospheric pressure**.

The atmospheric pressure at the Earth's surface is given a unit of 1.0 atmosphere (atm). The SI unit for pressure is the pascal (Pa).

$$\mathbf{1\ atm = 1.013 \times 10^5\ Pa = 1013\ hPa}$$

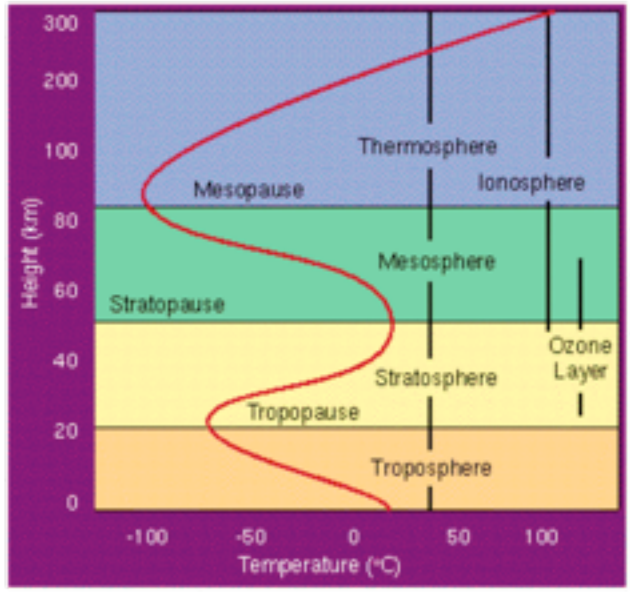


Altitude (km)	Altitude (ft)	Pressure (Pa)	Pressure (atm)
0	0	101325	1
11	36,089	22632	0.2234
20	65,617	5474	0.0540
32	104.987	868	0.00857
47	154,199	110	0.00109
51	167,323	66	0.000651
71	232,940	4	0.0000395

Layers of the Atmosphere

The atmosphere is composed of discrete layers. Atoms and molecules travel rapidly within a layer but only very slowly between layers. The layering results from temperature variations of the gas molecules.

In the **ionosphere**, there is a plasma. High energy solar radiation causes the atoms to ionize, separating free electrons from cations. The average kinetic energy is very high for the particles in the ionosphere but the gas density is very low.



In the **mesophere**, matter exists as atoms. There is sufficient energy in electromagnetic radiation from the sun to break the chemical bonds in molecules. The very highest energy electromagnetic radiation that causes ionization is filtered out by absorbtion in the ionosphere.

The **stratosphere** is home to the ozone layer. In the stratosphere, the chemical bonds between oxygen atoms in molecular oxygen (O_2) break and in ozone (O_3) break when the molecules absorb ultraviolet radiation. Re-forming those bonds releases heat energy so the temperature increases with altitude in this layer.

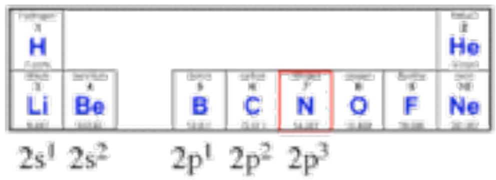
The **troposphere** is the region of the atmosphere closest to the Earth and is the region of all weather events. This layer is heated by the surface of the Earth, which in turn is heated by absorbing visible and infrared electromagnetic radiation from the sun.

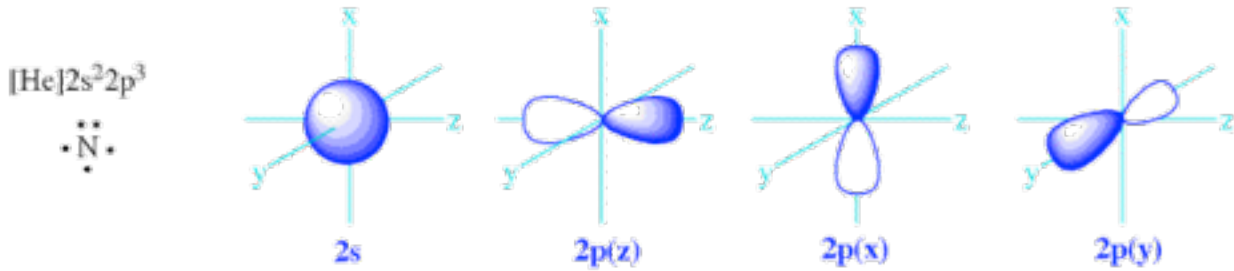
Most of the UV radiation is filtered out by absorption in the stratosphere. Because the heat comes from the Earth, the temperature decreases as altitude increases in this layer.

Nitrogen and Oxygen

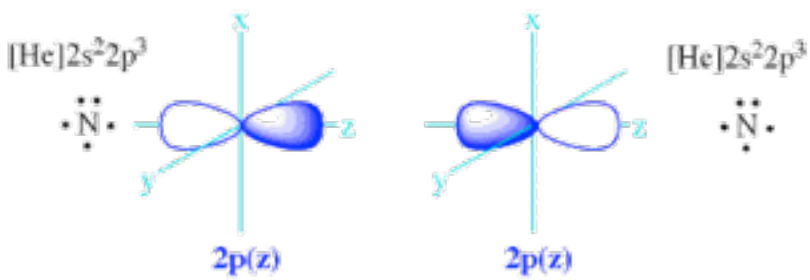
Molecular Nitrogen

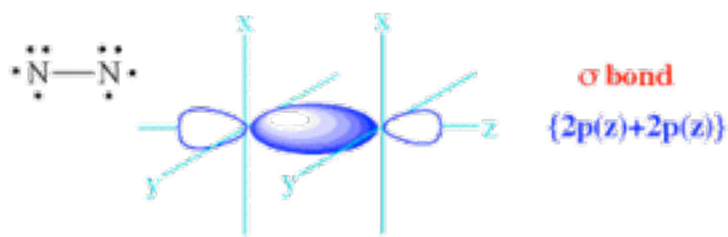
Molecular nitrogen makes up 78% of the gases in the atmosphere. Let's look at this molecule more closely. Molecular nitrogen is made up of 2 nitrogen atoms. From the periodic table we see that N has an electron configuration of $[He]2s^2 2p^3$. It has a filled 2s orbital along with 3, half-filled 2p orbitals. One p orbital is along the z direction, one along the x direction, and the final one along the y direction.



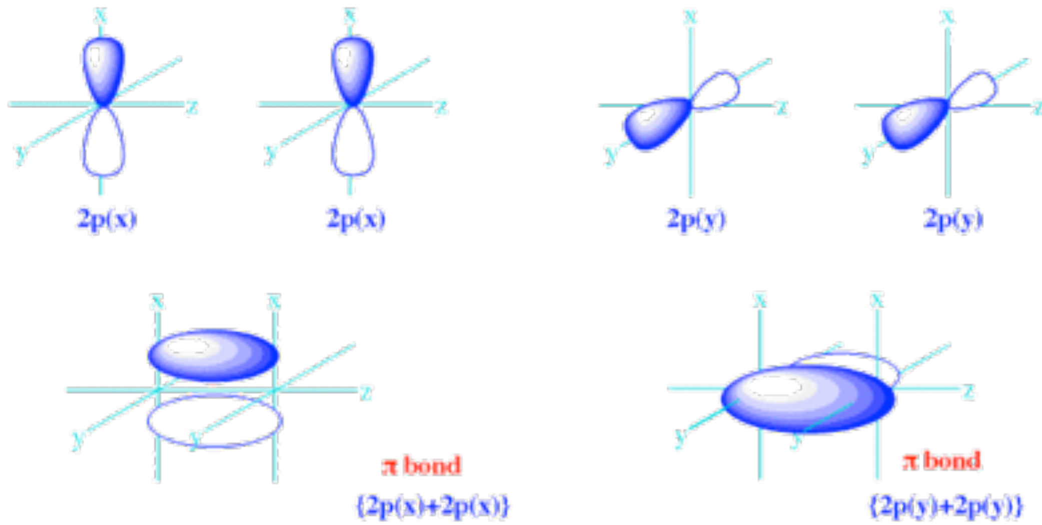


Consider the sharing of electrons in the 2p(z) orbitals of two nitrogen atoms. This type of covalent bond, where the orbitals that share electrons are pointing directly at one another, is called a **sigma bond** (σ).

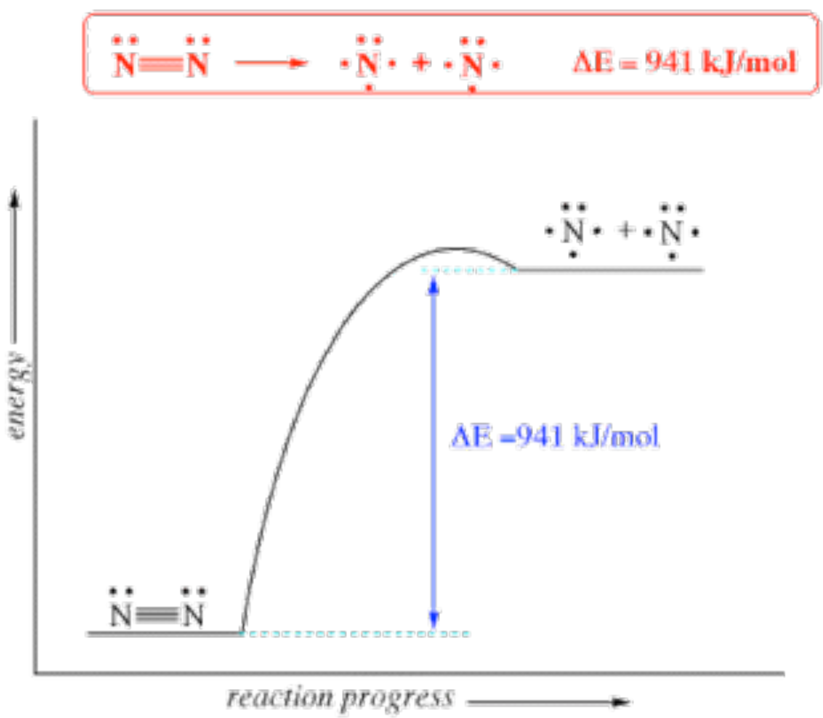




Two 2p(x) orbitals, one from each nitrogen atom, can share an electron side-by-side. The symmetry of this kind of covalent bonding is called a **pi bond** (π). The two 2p(y) orbitals from each nitrogen atom combine in the same way.

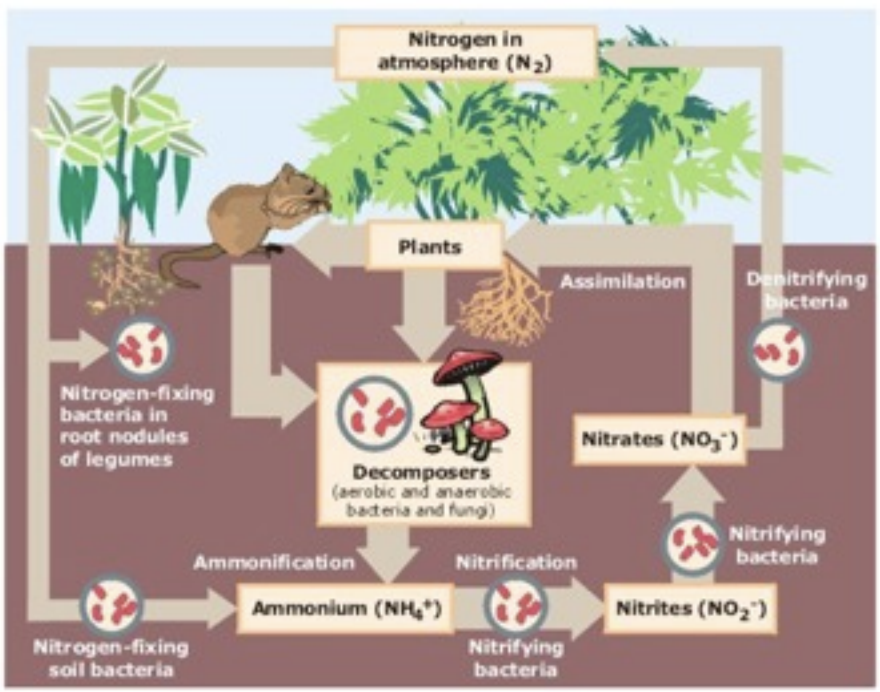


Molecular nitrogen has a triple bond between the two atoms, one sigma bond and two pi bonds. This bond is very strong and requires 941 kJ/mol of energy to break it. This amount of energy is called the **bond energy**.



Let's count the number of electrons around each atom in N_2. Remember that shared electrons are counted for each atom (counted twice). Each nitrogen has an unshared pair of electrons and 3 shared pair of electrons for a total of 8 electrons around each nitrogen atom. This is the same number of electrons as in the next noble gas, neon.

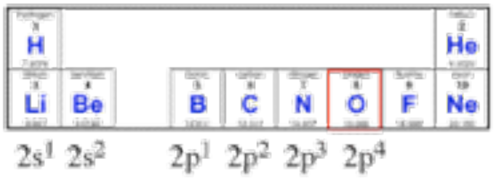
Molecular nitrogen is "fixed" by bacteria associated with some plant roots. This provides NH_3 and NH_4^+ that growing plants can use to make proteins and other biological molecules. When plants decompose, other bacteria in the soil convert the nitrogen-containing molecules back into N_2. The process of recycling the nitrogen is called the nitrogen cycle.

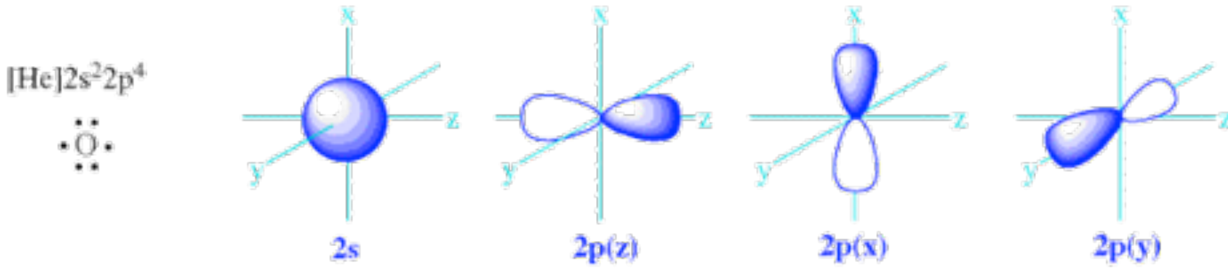


soybean root nodules, nitrogen fixing bacteria

Molecular Oxygen

Molecular oxygen makes up nearly 21% of the atmosphere. The simple electron dot diagram indicates that O_2 has a double bond (one sigma bond and one pi bond) between the two oxygen atoms. Each oxygen also has 2 non-bonding pairs of electrons. When we count the shared electrons and the non-bonding electrons for each oxygen atom, we get 8 electrons. The same number as the filled shell configuration for neon. Based on this, we would expect that O_3 would be very stable and unreactive, just like N_2. This is not the case. Next time we'll go into more depth on the bonding of this molecules in order to explain this.





Oxygen is formed by photosynthesis in green plants, algae, and photosynthetic bacteria.

$$6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2$$

carbon dioxide   water   glucose   oxygen

When plants and the animals that eat them decompose, their carbon containing molecules combine with oxygen in the air. In this way, oxygen and carbon dioxide cycle through living things.

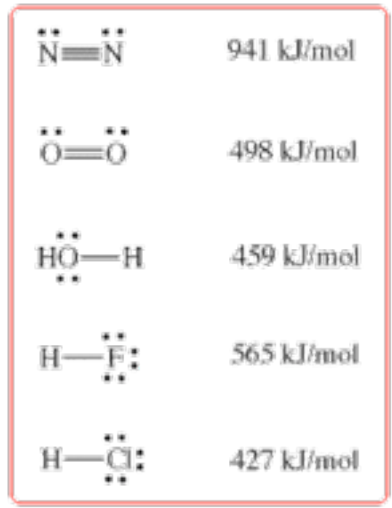
$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O$$

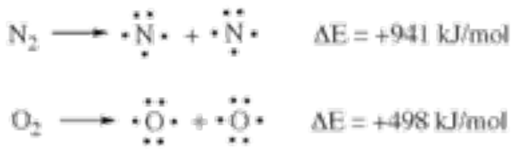
Lightning!

Bond Energy

The N-N triple bond in molecular nitrogen is one of the strongest chemical bonds and, because of this, the N_2 molecule is essentially inert. It doesn't react under normal circumstances with other molecules in the troposphere. However, there is one event in that can provide the energy needed to break the bonds of the N_2 molecule: lightning.

The electric discharge in lightning heats the surrounding air to 30,000 degrees C. This heat energy is more than enough to provide the 941 kJ/mol needed to break the N-N bond. The amount of energy required to break a bond is called the **bond energy**. It is usually reported in kJ/mol. Bond energies for a few other molecules are shown are right.



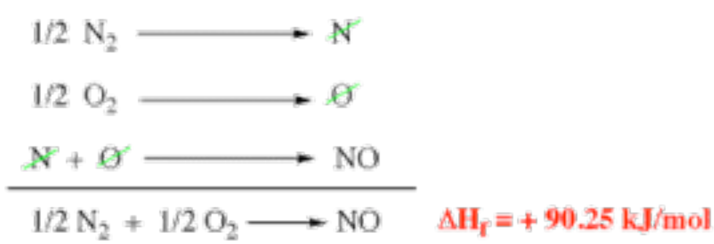


Although bond energies are given here, it is usually easier to measure the bond enthalpies. Remember that **enthalpy change** ΔH is the heat change at constant pressure. Energy is the sum of the heat and the work but the work term for most chemical processes is small.

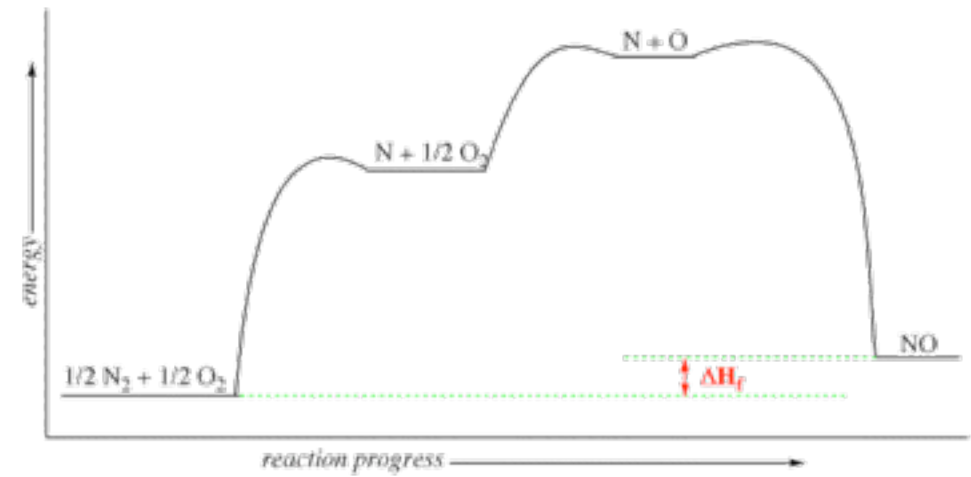
Breaking the N-N bond forms two highly reactive nitrogen atoms. Nitrogen atoms can combine with oxygen atoms that are also formed in the electric discharge to make nitric oxide, NO.

Formation of Nitric Oxide

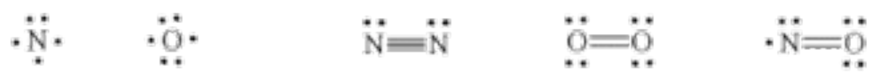
The overall enthalpy change can be measured. It is the sum of the reaction that breaks the N-N bond in N_2, the reaction that breaks the O-O bond in O_2, and the reaction that makes the N-O bond in NO. The enthalpy change for the formation of any molecules from the elements in their standard states in called the **enthalpy of formation**.



The reaction coordinate diagram for the reaction is below. The final product, NO, is at a higher energy than the reactants, 1/2 N_2 and 1/2 O_2. The reaction is called **endothermic** because net heat energy is added to the reaction system.



Let's look at the electron dot structure of the product. Compare it to that of N_2 and O_2.



	N	O	N	N	O	O	N	O
total electrons:	5	6	8	8	8	8	7	8
unshared:	5	6	2	2	4	4	3	4
shared:	0	0	6	6	4	4	4	4

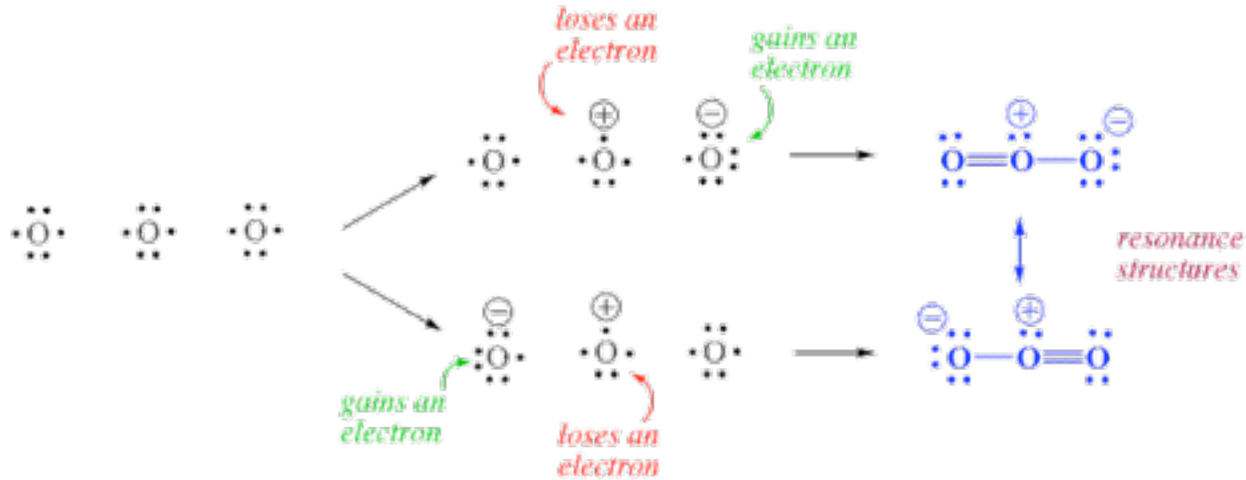
The nitrogen in NO uses 2 of its valence electrons to make 2 bonds (sigma and pi) to the oxygen atom. Oxygen has no more half-filled orbitals so it can't make a triple bond with the nitrogen. The nitrogen atom is left with one of its orbitals half-filled. Any molecule that has an unpaired electron on an atom is called a **radical**. Radicals are much more reactive than other molecules.

Formation of Ozone

After a lightning storm you may detect a sharp odor in the air. This is due to the presence of ozone, O_3. This forms when the oxygen atoms react with oxygen molecule.

$$1/2\ O_2 \longrightarrow O$$
$$O_2 + O \longrightarrow O_3$$
$$\overline{3/2\ O_2 \longrightarrow O_3} \qquad \Delta H_f = +\ 142.7\ \text{kJ/mol}$$

In order to make an electron dot structure of ozone, it is necessary to move an electron from one oxygen atom to another. If oxygen atom #2 donates an electron to oxygen atom #3, it becomes positively charged and #3 becomes negatively charged. Oxygen atom #2 can use two of its electrons to form a double bond (1 sigma bond, 1 pi bond) to oxygen atom #1. It uses another electron to form a sigma bond to oxygen atom #3. Now all three oxygen atoms have a total electron count of 8.



There is another possibility. Oxygen atom #2 could donate an electron to #1. It would form a sigma bond with oxygen atom #1 and form a double bond with oxygen atom #3. The top electron dot structure and the bottom are equivalent. Any time it is possible to make two or more of these equivalent structures (**resonance structures**), the true structure of the molecule is the average of them. In ozone, there is a sigma bond between each oxygen atom and 1/2 of a pi bond.