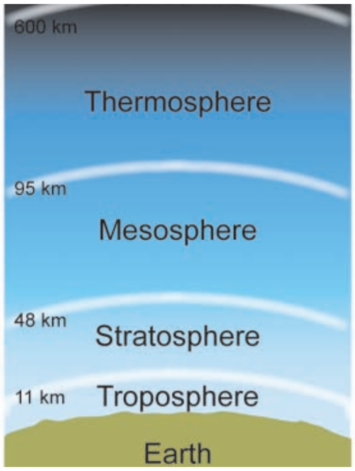
19.1 Chemistry of the Atmosphere

Our atmosphere determines the environment in which we live. Have you ever wondered what is in the air? Or what our atmosphere is made of? Most of us tend to take our atmosphere for granted. We live and breathe it everyday, and for the most part as far as we know it's composition stays the same.

We live in the troposphere

The atmosphere around the earth has four layers of gases that have been given specific names depending on their distance from the earth. The **troposphere** is is the layer closest to the earths surface, and it extends for about 10 kilometers. The weather that we experience all happens in the troposphere. The troposphere is more turbulent than the other layers which causes gases in this layer to mix more rapidly. When you fly on large jet airplanes, you are flying at the top of the troposphere.



The next layer of gases is called the **stratosphere**. The region of gases called the stratosphere begins at approximately 10 km above the earth and goes to about 50 km. Very important chemical reactions take place in the stratosphere. The most significant being the formation of the ozone (O_3) molecule. Approximately ninety percent of the ozone that protects the earth from high energy photons is formed in the stratosphere.

Meteors burn up in the mesosphere

The mesosphere is the "middle" layer of gases around the earth. In this layer the temperatures are very cold. The higher in altitude the colder the temperature becomes, due to decreased heating from the sun. Waves created by gravitational pull in the mesosphere cause gases to circulate around the globe. Meteors burn up in the mesosphere when they collide with the gas particles contained in this layer. The energy created by these collisions produces a lot of heat causing most meteor fragments to vaporize before reaching the earth. The mesosphere contains high concentrations of metal atoms such as iron, Fe, because of these meteor collisions.

The thermosphere, is the outermost layer, beginning at 85 km above the earth. In this layer ultraviolet light from the sun causes ionization of the gases contained there. For example oxygen loses an electron when absorbing UV radiation.
$O_2(g) + \text{photon(hv)} \rightarrow O_2(g)^+ + \text{e-}$ These ionized gases are attracted to the poles of the earth and are responsible for the auroras seen at the polar regions.

Chemistry terms

troposphere - the layer of gases closest to the earth, extending up to approximately 10 km above the earths surface.

stratosphere - the second layer of gases after the troposphere. This region of gases extends from 10 to 50 km above the earth.

Composition of the atmosphere

Heavier gas molecules stay closer to the earth

The atmosphere contains primarily nitrogen(78%) and oxygen(21%) molecules. The remainder of the atmosphere is made up of carbon dioxide and noble gases. Most of the mass of the atmosphere is contained in the troposphere, because the majority of the heavier molecules are found close to the earth's surface. The earths gravitational field causes the lighter molecules and atoms to rise higher in the atmosphere. The sun plays an important role in the chemistry of our atmosphere. The molecules contained in the atmosphere are constantly being hit by radiation from the sun. These energetic collisions have significant chemical effects. We will learn about these in this section.

TABLE 19.1
Composition of dry air

Element	% by Volume
N_2	78.08
O_2	20.95
Ar	0.93
CO_2	0.037
Ne	0.0018
He	0.00052
CH_4	0.00020

Why are these gases so abundant in our atmosphere? Lets look at the four most abundant gases. We think most of the nitrogen gas in our atmosphere was brought out from inside the earth by volcanoes. Nitrogen gas is heavy with a molar mass of 28.02 g/mole causes it tends to stay near the earth's surface and not float up to the higher regions of the atmosphere. Photosynthesis is responsible for the oxygen gas present in our air today. The production of oxygen by plants has greatly influenced the chemistry of the earth. Oxygen is a more reactive molecule than nitrogen, because of this it is responsible for many important chemical reactions in the atmosphere. Argon is also a heavy gas, with a molar mass of about 40 g/mole. Most of the argon in the air was produced by the radioactive decay of other elements in the earths crust such as potassium, (K). Lastly, the carbon dioxide gas present was created during respiration of plants and animals.

Water vapor in the air keeps the earth warm

Water is also present in the atmosphere as moisture. It enters the air through evaporation from the oceans and from the transpiration of plants. Water is an important contributor to the earths relatively moderate temperature, because it absorbs infrared radiation and holds heat near the earth.

The weather patterns we experience in the troposphere are the result of how the sun heats the earth. Different places on the earth are heated at different angles and this unequal heating is what causes the wind and ocean currents to circulate around the earth. Winds are formed when warm air masses rise and cool air sinks, this process sets up movement of air currents around the globe. Weather patterns help to cycle chemicals between the atmosphere, living organisms, and the ocean. This continuous movement of air distributes nutrients to living systems.

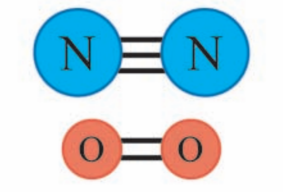
These cycles can be disrupted by pollution or environmental changes, which are cause for much concern. The majority of the pollutants found on the earth come from the widespread use of combustion reactions.

Chemical reactions in the air

Nitrogen and oxygen gas molecules make up about 99% of the atmosphere! These molecules are involved in many of the chemical reactions that take place in our atmosphere, because they are present in such high concentrations. To help you better understand some of the chemical reactions that take place in our atmosphere we will review some of the properties of nitrogen and oxygen molecules.

Nitrogen is nonreactive because of it's triple bond

You may remember that nitrogen, N_2, contains a triple bond and that oxygen, O_2 has a double bond holding its atoms together. The triple bond in nitrogen has a high bond energy and requires 946 kJ/mole of energy to break. The strength of the triple bond makes nitrogen a relatively inert, nonreactive gas close to the earth. Under high temperatures such as in a combustion engine nitrogen can be broken apart. The double bond in oxygen requires significantly less energy to come apart because it has a bond energy of 495 kJ/mole. *In the atmosphere, oxygen is a more reactive molecule than nitrogen because it requires less energy to split apart it's atoms.* Remember, in order to react atoms have to come apart so they can interact with new atoms.



Cars produce nitrous oxide


Courtesy of Steven Buss

In the troposphere, there are several chemical reactions that are important to understand, primarily because they are close to us and we experience their effects directly. For instance, most of us have seen smog. Smog is formed when pollutant gases are trapped in a highly populated city or urban area. The smog effect is created in these areas, because the exhaust emissions contain nitrous oxides. Cars or vehicle engines provide the energy necessary for some of the nitrogen in the air to react with the oxygen in the air producing nitrous oxide, NO(g). $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = 181$ kJ In the air, nitrous oxide, NO is quickly converted to $NO_2(g)$ through oxidation.

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = -113$ kJ

Los Angeles was the first city to experience the full effects of smog. The temperature in the city is hot and the mountains trap the gases down in the valley causing them to become concentrated. When photons from the sun, with wavelengths of 393 nm or less, strike the NO_2 molecules and they dissociate into NO(g) and atomic oxygen O. This atomic oxygen can react with oxygen gas to make ozone, which is another primary pollutant in smog. $O(g) + O_2(g) \rightarrow O_3(g)$ Ground level ozone is very toxic and is dangerous for us to breathe. Ozone in the upper atmosphere protects us, but ozone in the troposphere is a serious health hazard.

Chemical reactions in the troposphere

Formation of sulfur dioxide comes primarily from fossil fuels

Similar to smog other gases in our atmosphere have significant effects even though they are only present in small amounts. Sulfur dioxide, SO_2 is one of the most harmful pollutant gases in our air. How is it formed? The combustion of coal and oil by industry releases significant amounts of sulfur in the form of sulfur dioxide gas. The combustion process causes the sulfur present in these fuels to react with oxygen in the air to produce SO_2. $S(s) + O_2(g) \rightarrow SO_2\ (g)$ Small amounts of sulfur are released naturally into the environment, primarily through the decomposition of organic materials. However, most of the sulfur is released from the use of fossil fuels.

Approximately 80% of the sulfur dioxide in the air comes from the burning of coal used to provide us with electricity. The sulfur dioxide in the air readily reacts with oxygen in the air to form sulfur trioxide, which in turn reacts with water vapor to form sulfuric acid.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4\ (aq)$$

Acid rain is formed from sulfur and nitrogen oxides

Sulfuric acid is a strong acid! This has significant environmental and health impacts. Sulfuric acid is one of the acids responsible for acid rain, which has damaged many ecosystems in the northeast, and great lakes regions of the U.S. For example in New York, there are no fish in hundreds of lakes and ponds because of the low pH caused by acid rain. Certain lakes and streams contain bicarbonate, HCO_3^- , buffer which helps to counteract the effects of acid rain. In areas where the amounts of acid rain are extremely high the pH can get as low as 4.0 pH units. It is important to note that even naturally occurring rain is acidic, having a pH of approximately 5.5-5.8. This happens because natural rain water absorbs carbon dioxide in the air reacting to form the weak acid carbonic acid, H_2CO_3. Carbonic acid is responsible for lowering the pH of our rain water.

Natural rain water is acidic due to the absorption of CO_2

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

Nitrous oxides also react with water vapor to form the strong acid called nitric acid, HNO_3. $3NO_2\ (g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$

On an environmental level, acid rain can damage forests, and crops and it also makes the pH of lakes and streams too low. You may remember that strong acids react with carbonates, like limestone, $CaCO_3$, and this is why it causes damage to stone and buildings. These strong acids also react with many different metals causing corrosion. Overall these effects cause a serious economic impact as well as environmental.

Chemical reactions in the upper atmosphere

The outer layers of the atmosphere absorb dangerous UV radiation

The outer layers of the atmosphere act like a shield protecting us from damaging forms of radiant energy. These outer layers of the atmosphere, beyond the thermosphere, are constantly being struck by high energy particles from the sun. The gas molecules here are exposed to continuous high levels of radiation. The sun produces photons with a wide range of wavelengths. The short wavelength photons in the ultraviolet region of the spectrum(below 400nm) are very damaging to living organisms. These high energy photons can damage cellular DNA causing mutations and possibly cancer. However, the outer layers of our atmosphere are able absorb most of these high energy photons and they do not travel down close to the earth and cause harm.

Chemical changes are caused by high energy photons

How are these photons absorbed? The gas molecules in the upper atmosphere absorb these high energy photons. Chemical changes are caused by high energy photons colliding with the molecules in these layers. One of these important chemical changes is called **photodissociation.** Photodissociation is the breaking of a chemical bond in a molecule caused by the absorption of a photon. Because of nitrogen's high bond energy the oxygen molecule, O_2, is the principle absorber of high energy photons in the upper atmosphere. When a bond is broken by the process of photodissociation, no ions are formed. The bonding electrons are divided equally between the two atoms and two neutral particles are created. The amount of energy required to split the double bond between the oxygen atoms is equal to the bond energy of 495 kJ/mole.

Solved problem

Lets calculate the wavelength of a photon emitted by the sun, that contains enough energy to dissociate the oxygen molecule.

Asked: *Calculate the wavelength of a photon that can split an O_2 molecule.*

Given: *The bond dissociation energy for O_2 is 495 kJ/mole.*

Avogadro's number = 6.022×10^{23} Planks constant=6.63×10^{-34} J.s

Relationships: $E = h\,c / \lambda$.

Solve:

$$\frac{495\text{ kJ}}{mole} \times \frac{\text{mole}}{6.022\text{ x}10^{23}\text{molecules}} = 8.22\text{ x }10^{-22}\frac{kJ}{\text{molecule}} = 8.22\text{ x }10^{-19}\frac{J}{\text{molecule}}$$

$$\lambda = \frac{\text{hc}}{E} = \frac{(6.63\text{ x }10^{-34}\dot{J}s)\left(3.0\text{ x }10^{8}\left(\frac{\text{m}}{s}\right)\right)}{8.22\text{ x }10^{-19}J} = 242\text{ x }10^{-7}m\text{ x }\left(\frac{10^{9}nm}{1\text{ m}}\right) = 242\text{ nm}$$

Discussion: *A photon with a wavelength of 242 nm is energetic enough to break the double bond in the oxygen molecule.*

Chemistry terms

photodissociation - the breaking of a chemical bond in a molecule caused by the absorption of a photon.

Chemical reactions in the upper atmosphere

Molecules absorb short λ of UV light causing them to lose an e^-

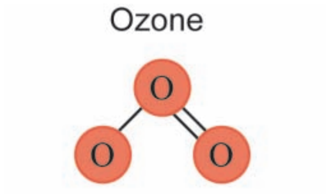
Another type of reaction that is very important in absorbing high energy radiation is called **photoionization**. When a molecule absorbs a photon of sufficient energy it can eject an electron and ionize. Photoionization in the upper atmosphere absorbs photons in the high energy region of the ultraviolet spectrum. These short wavelengths would be very harmful if they reached the earth. It is important to understand that when a molecule absorbs a photon with lots of energy a chemical change is created. Here the change is a loss of an electron. This chemical change in the molecule "uses up" the energy in the photon, so that it no longer has this damaging energy to pass on. Some examples are:

$$O_2(g) + \text{photon}(h\nu) \rightarrow O_2^+(g) + e^-$$

$$N_2(g) + \text{photon}(h\nu) \rightarrow N_2^+(g) + e^-$$

In both of these cases photons with a wavelength between 80 and 100 nm are absorbed, and a positively charged ion is formed.

Stratospheric ozone, O_3, acts as a protective shield against longer λ UV light



The other important chemical reaction that occurs just above the stratosphere is the formation of ozone, $O_3(g)$. Ozone forms when atomic oxygen, formed from photodissociation, collides with molecular oxygen: $O(g) + O_2(g) \rightarrow O_3(g)$. Ozone acts as a shield protecting us from the longer ultraviolet wavelengths. The ozone molecule absorbs high energy radiation that is between 240nm and 310nm. Ozone has a natural cycle of formation and decomposition. Once it collides with a ultraviolet photon it splits apart into atomic oxygen, O and molecular oxygen, $O_2(g)$. These two molecules are then available to react again and form ozone. Basically the ozone molecule splits when it absorbs sufficiently energetic light and then comes back together by undergoing molecular collisions.

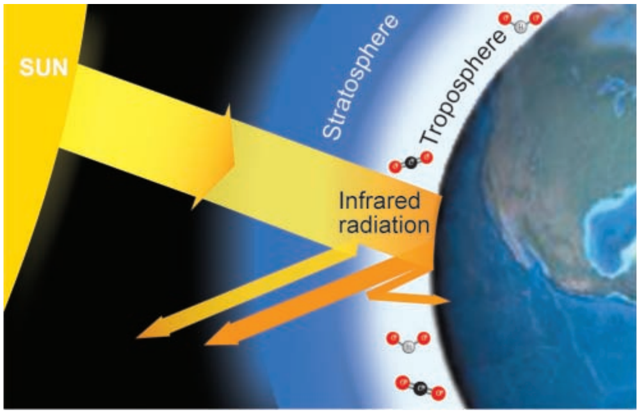
Discussions about the "ozone hole" have been in the news since the late 1980's. The production and use of chlorofluorocarbons in aerosols and air conditioners were causing destruction of the ozone layer. The highest concentrations of ozone are in the stratosphere, here it protects us. Remember near the earth it is toxic and considered a pollutant! But up in the stratosphere we do not breathe it, and it has a useful purpose.

Chemistry terms

photoionization - when a molecule absorbs a photon and ejects an electron causing it to become an ion.

The climate and global warming

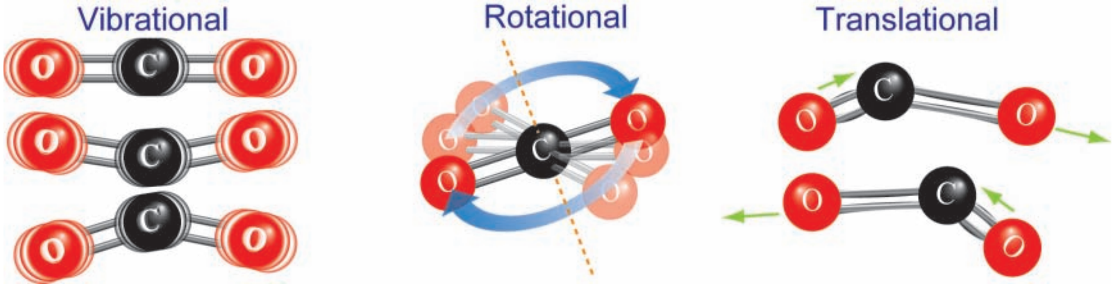
Some greenhouse effect is a good thing



In order for a planet to be inhabited by living organisms it must have a climate that is reasonably moderate so that life forms can adapt. A planet that has extreme temperature fluctuations would not support life. In our atmosphere, carbon dioxide and water are the two most important molecules in maintaining a balanced temperature near the surface of the earth. The earth takes in energy from the sun and it radiates that energy back out through the atmosphere. The greenhouse effect actually is necessary to maintain life on earth. The gases close to the earth allow visible light to enter, but they absorb the longer wavelengths (infrared radiation) of light that are reflected by the earths surface. Now when we discuss the greenhouse effect we are focusing on the fact that the earths gases are trapping too much heat and not allowing it to escape back into the atmosphere. We need the gases to trap some heat, but with the increased use of fossil fuels these gases are trapping too much heat.

Molecules trap infrared radiation in their bonds

How do water and carbon dioxide molecules trap heat? They absorb longer wavelength photons in the infrared region of the spectrum in their bonds. When these molecules absorb the energy their bonds they are able to stretch, vibrate and rotate. These motions allow these molecules to hold onto the energy for a short time before re-radiating it back to the earths surface. When the energy is released, or re-radiated it can go in any direction, about half of it returns to the surface of the earth.



Water molecules in our troposphere keep the earth warm at night, when there is no solar energy. In dry climates, like the desert, it can gets very cold at night because there are few water molecules absorbing warmth from the earth.

Chemistry terms

global warming - the warming of the surface of the earth by gas molecules in the atmosphere which trap heat and reflect it back to the surface of the earth.

Trace amounts of chemicals in our atmosphere

Gases are measure in ppm

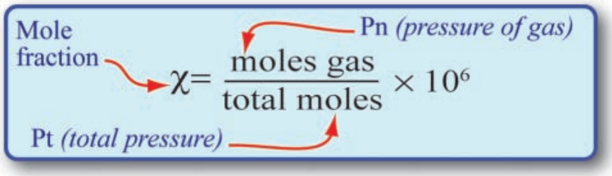
When measuring trace amounts of chemical substances in our air we typically measure them using parts per million (ppm). You many recall we used this same unit to measure amounts of chemicals in aqueous solutions in chapter 2. The difference here is that we are dealing with gases and not water based solutions.

TABLE 19.1. Concentrations of Gases (Natural and man-made)

Molecule	Sources	Typical Concentrations
Carbon dioxide, CO_2	fossil fuel combustion, decomposition of organic materials, ocean	375 ppm in troposphere
Methane, CH_4	decomposition of organic matter	1-2 ppm in troposphere
Carbon monoxide, CO	industrial pollution, fossil fuels, and decomposing organics	0.05 ppm 1- 56 ppm in urban areas
Nitric oxide, NO	combustion, lightning, electricity	0.02 ppm in nonpolluted air; 0.25 ppm in urban areas
Ozone, O_3	photodissociation, electricity	0.55 ppm in urban areas 0.01 ppm in nonpolluted air
Sulfur dioxide, SO_2	fossil fuel combustion, industry, volcanos, fires	0.01 ppm in nonpolluted air 0.15-2 ppm in urban areas

Atmospheric chemists measure the partial pressure of pollutant gases

When we wish to measure the relative amounts of gases we measure the pressure of each individual gas, this is directly related to the moles of the gas given the ideal gas equation, PV = nRT. Atmospheric chemists measure the partial pressure of pollutant gases in our atmosphere and decide whether the amount is dangerous. By using the partial pressure measurements of a gas relative to the total pressure of the atmosphere, scientists can determine the mole fraction of a particular compound in our air. One part per million for a pollutant would be one mole of the compound per one million moles of total gas.



$$\chi = \frac{\text{moles gas}}{\text{total moles}} \times 10^6$$

Amounts of chemicals in our atmosphere

It is helpful to be able to quantitatively measure these small amounts of gases so that we can determine whether or not they are harmful to our health. Lets calculate the concentration in parts per million for carbon monoxide in a small city, that has a total air pressure (P_t) of 702 torr. The partial pressure of CO for that day was measured to be 3.1×10^{-3} torr. To begin we first need to calculate the mole fraction, X. The mole fraction is simply the number of moles of the gas as compared to the total moles in the air sampled. This tells us how much of the gas is present relative to the total gases in the air. Mole fraction means the "fraction" or amount of moles present in the total sample.

How to calculate ppm of CO_2

$X_{CO} = \frac{P_{CO}}{P_{Total}} = \frac{3.1 \times 10^{-3}}{702} = 4.42 \times 10^{-6}$, next we multiply the mole fraction by 10^6 to calculate the parts per million. $4.42 \times 10^{-6} \times 10^{6} =$ 4.42 ppm of CO is the concentration of carbon monoxide in this city.

In the troposphere carbon monoxide is present in small concentrations, as our calculation just showed us. These concentrations vary in different areas due to population differences and industrial activity, refer to table 19.1 on the previous page. In some places the levels are quite low, but the gases can still travel in the air currents and effect more rural regions.

Lets try calculating the concentration of water vapor in the air, in ppm.

Solved problem

Calculate the concentration of water vapor in ppm for a sample of air that contains a pressure of 0.83 torr of water vapor, and a total air pressure of 729 torr.

Asked: *Find the ppm concentration of water vapor*

Given: *Total pressure of air = 729 torr*
Partial Pressure of H_2O vapor = 0.83 torr

Relationships: $X_{H2O} = \frac{P_{H2O}}{P_{Total}}$

Solve: *Find Mole fraction of water.* $X_{H2O} = \frac{0.83\ \text{torr}}{729\ \text{torr}} = 0.0011$

Mole fraction multiplied by 10^6 is the ppm.

$0.0011 \times 10^6 = 1100$ ppm

Answer: *1100 ppm*

Discussion: *The ppm of water vapor in this sample of air is 1100.*