INTRODUCTION OF OXYGEN BINDING AND REDUCTION

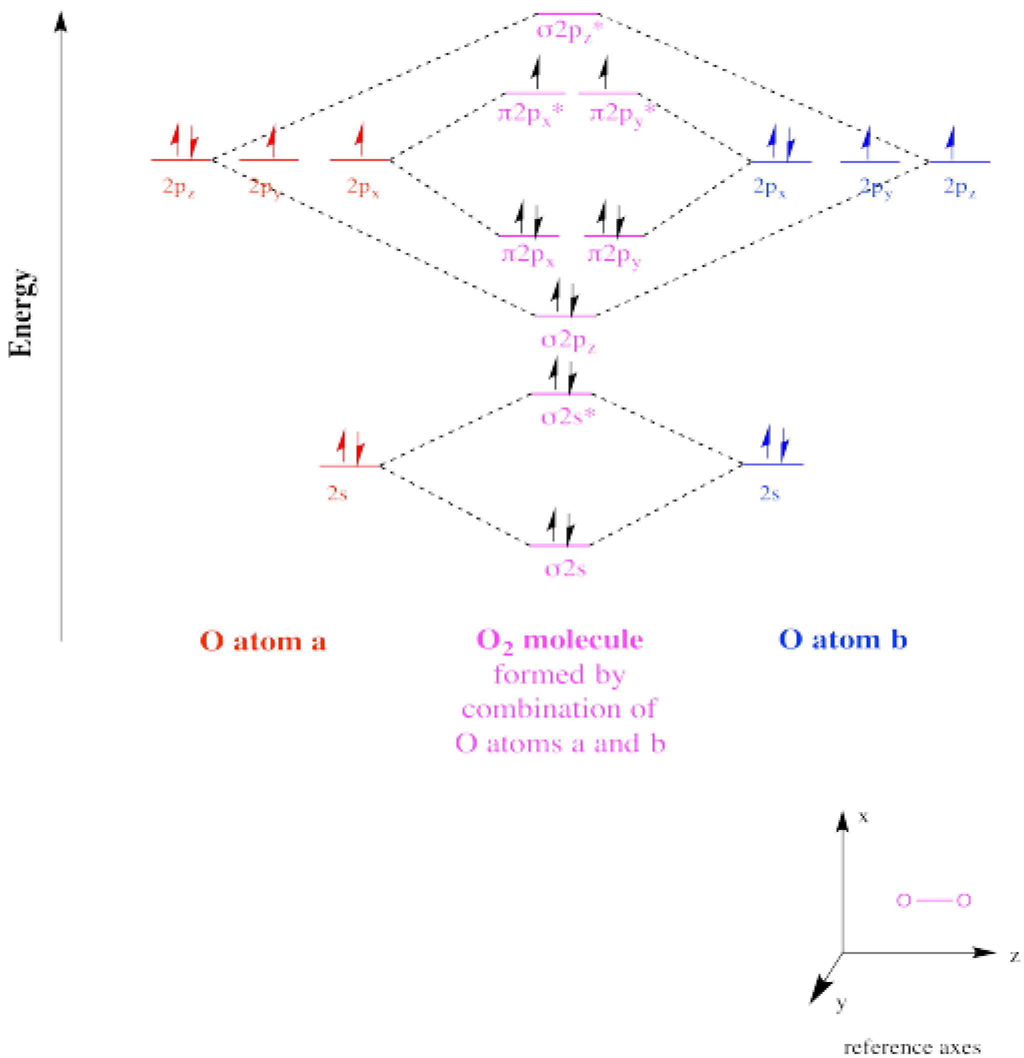
The earth is an oxygen-rich place. Elemental oxygen, O_2, makes up about 20% of the earth's atmosphere by weight. Oxygen atoms, bound in water, make up about 85% of the hydrosphere (the earth's oceans, rivers and lakes). Oxygen atoms also comprise about 45% of the lithosphere (the earth's crust), mostly bound in the form of silicates, aluminosilicates and carbonates.

In this chapter, we will focus on elemental oxygen and the ways nature has evolved to make use of O_2 as a reactant. Dioxygen has a double nature, like Dr. Jeckyll and Mr. Hyde. It is necessary for life, providing a driving force for basic metabolic processes. That driving force ultimately comes from the exergonic conversion of O_2 into water. However, nature has also had to evolve mechanisms to protect itself against reactive oxygen species, which would otherwise cause permanent damage to biomolecules. Those reactive oxygen species arise from the reduction of atmospheric oxygen. They also have dual roles, acting as important cell signalling molecules as well as dangers to the cell, and so their regulation is crucial in biochemistry.

Although da Vinci noted in the 1400's that air contained several components, one of which could support combustion, in a sense oxygen was not "discovered" until the turbulent 1770's. It was first isolated from air in experiments performed by Carl Wilhelm Scheele, a German pharmaceutical chemist (although his homeland of Pomerania was at that time part of Sweden, which extended to the south shores of the Baltic sea). This discovery was soon followed by an independent one by the English scientist and fire-and-brimstone preacher, Joseph Priestley. However, early research on oxygen is often associated with Antoine Lavoisier, whose experiments built upon those of Scheele and Priestley and are generally considered to mark the beginnings of modern chemistry.

These men did not lead long, peaceful lives. Priestley was forced to emigrate to Pennsylvania because of his troublemaking ways, Lavoisier was unfortunately executed during the reign of terror following the French Revolution, and Scheele's habit of tasting his experiments led to an early death from kidney failure. In contrast, a fourth scientist who is closely associated with oxygen, Henry Cavendish, died a wealthy (but remarkably reclusive) man of nearly eighty, having achieved some fame in England for his discoveries. Cavendish established the exact proportion of oxygen and nitrogen in the air, demonstrated in an impressively explosive way how oxygen and his other discovery, hydrogen, could be combined to make water, and even found time to accurately weigh the planet Earth.

Oxygen, present at the birth of modern chemistry, continued to make appearances in the development of the field. In the 1840's, Michael Faraday, the great English chemist and physicist, first demonstrated the O_2 is paramagnetic, meaning it is attracted to a magnetic field. Sixty years later, American chemist and physicist Robert Mulliken explained this property through "molecular orbital theory" (sometimes called Hund-Mulliken theory after its developers). This explanation should be familiar to college-level chemistry students.



The molecular orbital interaction diagram for O_2 shows how two oxygen atoms would combine under symmetry constraints to produce new orbitals in an O_2 molecule. The net four electrons in bonding levels (i.e. at lower energy than they were in the atoms, as opposed to antibonding levels, which are at higher energy than they were in the separate atoms) suggests two bonds, since a bond between two atoms generally has two electrons. This prediction is also predicted by simple Lewis theory (i.e. that's what you would draw in a Lewis structure).

However, in contrast to the Lewis structure, in which all of the electrons in O_2 are paired, Mulliken's MO picture suggests that there are two unpaired electrons. Because species with unpaired electrons are attracted to magnetic fields, this picture provides a compelling explanation for the paramagnetic behaviour of elemental oxygen.

This species is called a triplet state. A triplet is a state in which there are two net spins in the molecule, which has consequences in spectroscopy. If there were no net spins (i.e. they are all paired), the state would be described as a singlet. If there were one net spin (all other spins paired), it would be called a doublet.

Source: http://employees.csbsju.edu/cschaller/Reactivity/oxygen/ORintro.htm