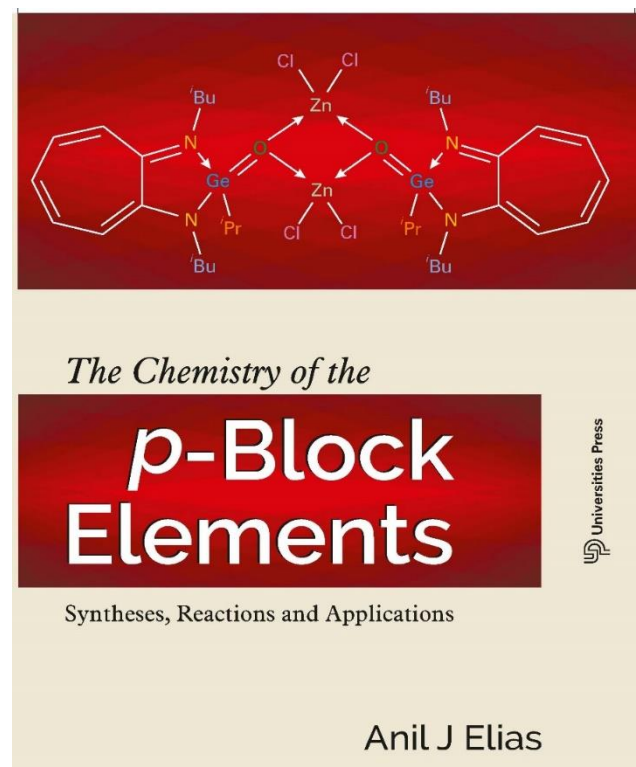


CML 738 : The Chemistry of Oxygen



**For detailed description and problems and exercises
please refer chapter 11 of the book**

Importance of oxygen saturation measurement in the backdrop of COVID-19 !

Blood Oxygen Saturation (SpO₂) (peripheral capillary oxygen saturation)

Your SpO₂ reading is an estimation of the amount of oxygen in your blood. An SpO₂ reading of 95% or greater is generally considered to be a normal oxygen level. However, an SpO₂ reading of 92% or less (at sea level) suggests that your blood is poorly saturated. Insufficient saturation can cause a range of adverse health conditions—including chest pain, shortness of breath and increased heart rate.



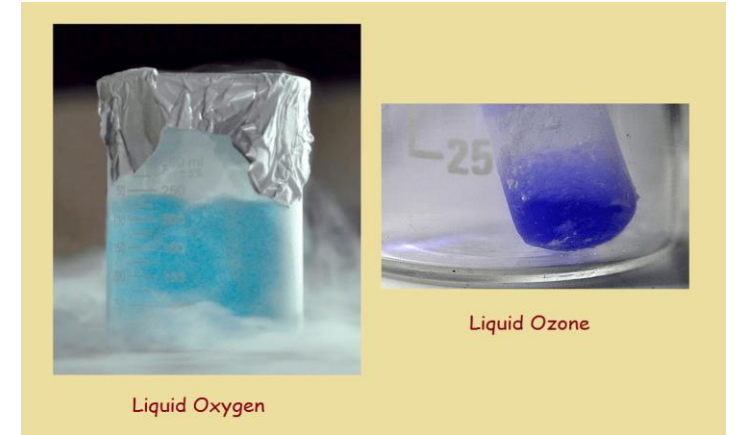
COLOR OF CYLINDER

GAS	USA	INTERNATIONAL
oxygen	Green	White
Carbon dioxide	Gray	Gray
Nitrous oxide	Blue	Blue
helium	Brown	Brown
Nitrogen	Black	Black
air	Yellow	White & black

Unique properties of oxygen and their compounds

Oxygen

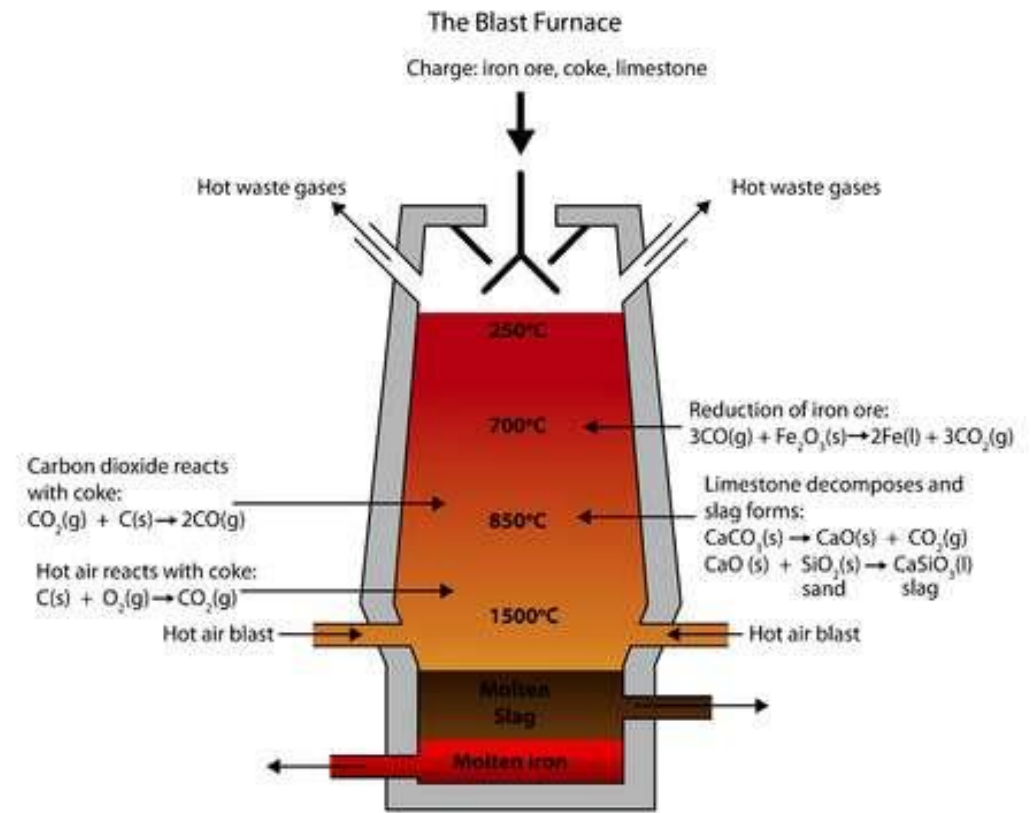
- While oxygen constitutes 20.94% of the earth's atmosphere, its only allotrope ozone constitutes 0.6 ppm of the atmosphere.
- Oxygen is composed of three stable isotopes, ^{16}O , ^{17}O , and ^{18}O , with ^{16}O being the most abundant having 99.762 % natural abundance.
- Oxygen molecule is reversibly bound to the iron centers of hemoglobin which are carried by the red blood cells from lungs to the muscles where it is transferred to myoglobin.
- 25% of the oxygen commercially produced is used by the chemical industry for the synthesis of ethylene oxide which is further converted to ethylene glycol.
- Other industrial uses of oxygen include, medical use, for making oxyacetylene flames for welding and as liquid rocket fuel.
- Plants produce oxygen during photosynthesis by splitting of water molecules.



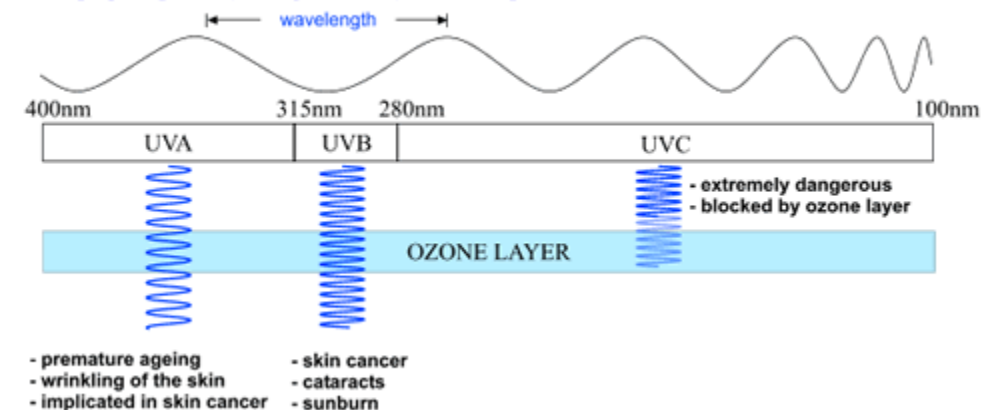
Property	Ozone	Oxygen
Molecular Weight	48	32
Color	light blue	colorless
Smell	smell after lightning storms	odorless
Solubility in water(0°C)	0.64	0.049
Density (g/l)	2.144	1.429
Oxidizing Potential (Volts)	2.07	1.23



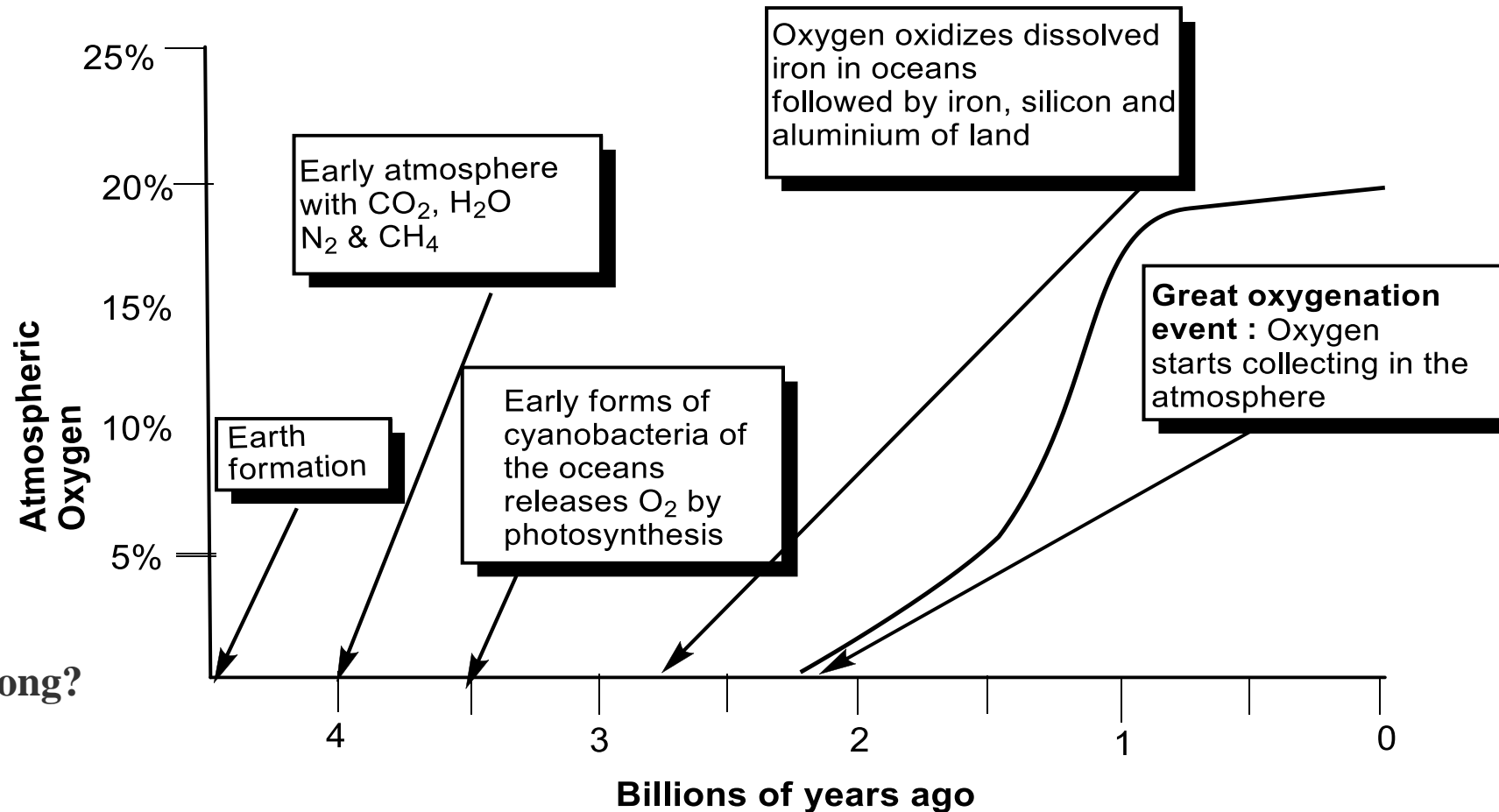
- More than 50% of the commercially produced oxygen is used in the smelting of iron ore to steel. Oxygen injected into molten iron removes sulfur as SO_2 and carbon as CO .
- Ozone strongly absorbs ultraviolet radiation (UV-B & C) and the stratospheric ozone layer helps to protect the earth from harmful UV radiation. Ozone with an oxidation potential of 2.07 V is a stronger oxidizing agent than H_2O_2 , O_2 and KMnO_4 .
- Robert H. Goddard developed a rocket engine that used a liquid fuel with liquid oxygen as the oxidizer. He successfully flew a small rocket to a height of 56 m in 1926 with this fuel.
- Oxygen constitutes 49.2% of the earth's crust by mass as part of oxide compounds such as iron oxides, silicates and aluminosilicates. It is also the major element of the world's oceans (88.8% by mass).
- The importance of breathing oxygen is reflected in the fact that glucose upon oxidation in the presence of O_2 produces 18 times more energy than in the absence of O_2 .
- 65% of the human body consists of oxygen where it is the largest constituent. Sulfur is present in 0.3%. In acidic solutions, H_2O_2 (1.78 V) is one of the most powerful oxidizers known—stronger than KMnO_4 and gets reduced to water. In basic solutions, H_2O_2 (-0.68 V) act as a reducing agent, getting oxidized to O_2 gas.



TYPES OF ULTRAVIOLET RADIATION

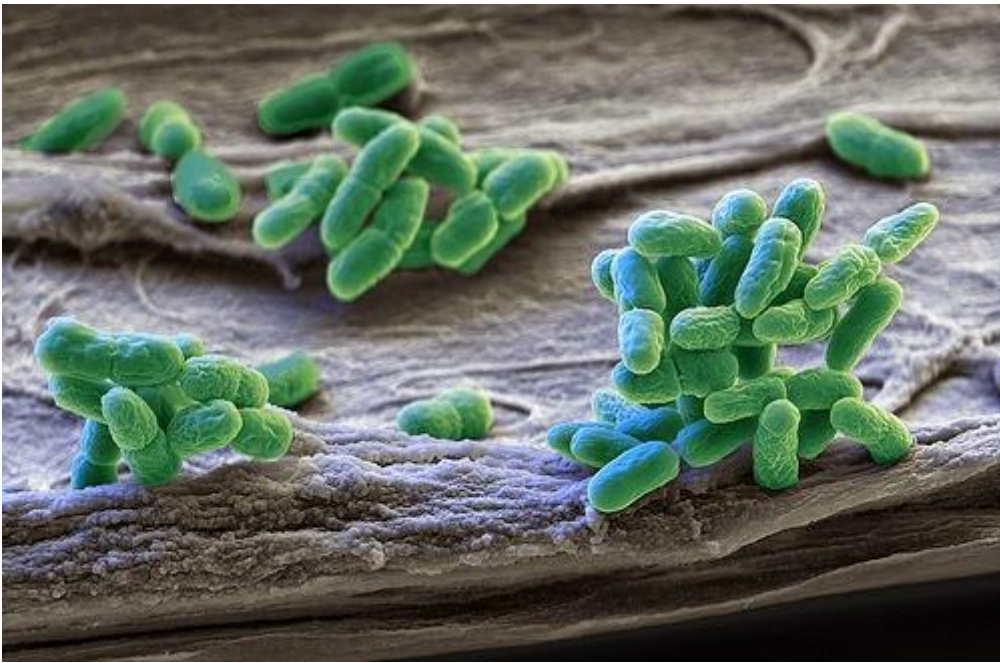


The great oxygenation event



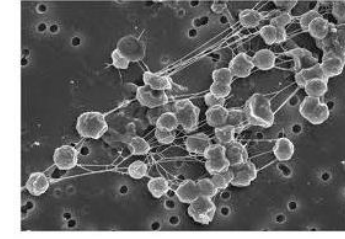
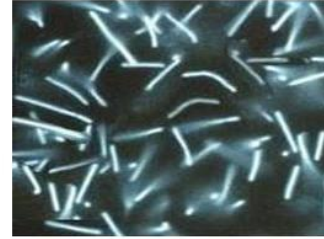
What took it so long?

The cyanobacteria were present long before The Great Oxygenation Event (**GOE**), yet it took millions of years for it to happen. This is because initially the ancient oceans were shared by both cyanobacteria and the methanogens, with the later being the dominant player. The methanogens consumed hydrogen and carbon dioxide releasing methane thereby making the early atmosphere methane rich. Whatever oxygen that was released by the cyanobacteria was being neutralized by the methane forming carbon dioxide and water. However, some 2.7 billion years ago, the **nickel** concentration of the BIFs suddenly started to dwindle and by the time of GOE, the drop was almost 50%. As nickel is required by the metabolic enzymes of the methanogens for the production of methane, they began to starve and their population began to drop.



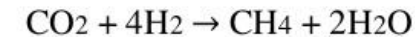
Cyanobacteria or the blue green algae belong to a group of bacteria which derive their energy by the process of photosynthesis. The characteristic color of the organisms gives them their name. They were *the undisputed champions of early life* or *microbial heroes of Earth history* since they were the first to produce oxygen by photosynthesis. Some 2.4 billion years ago, it is believed that the first true global mass extinction was caused by the Cyanobacteria or blue green algae.

1. Methanogens: Convert hydrogen gas and carbon dioxide into methane gas. Oxygen is poisonous for them, so they can live only in places that lack oxygen.



Example: methanogens that live in the intestinal tract of the cow.

- Methanogens produce methane from substrates such as H_2/CO_2 , acetate, formate, methanol and methylamines by a process called methanogenesis.



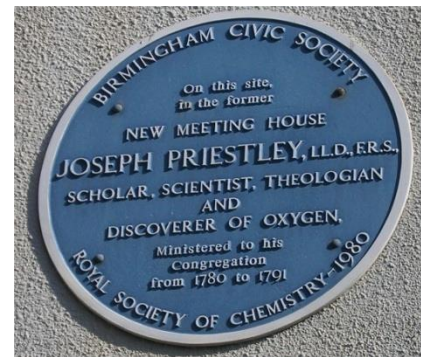
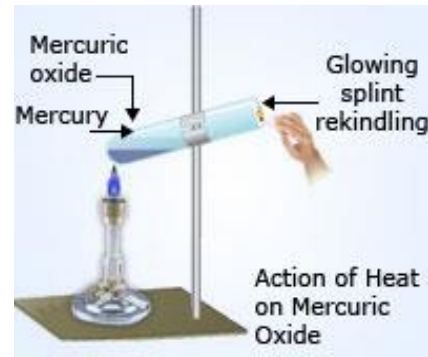
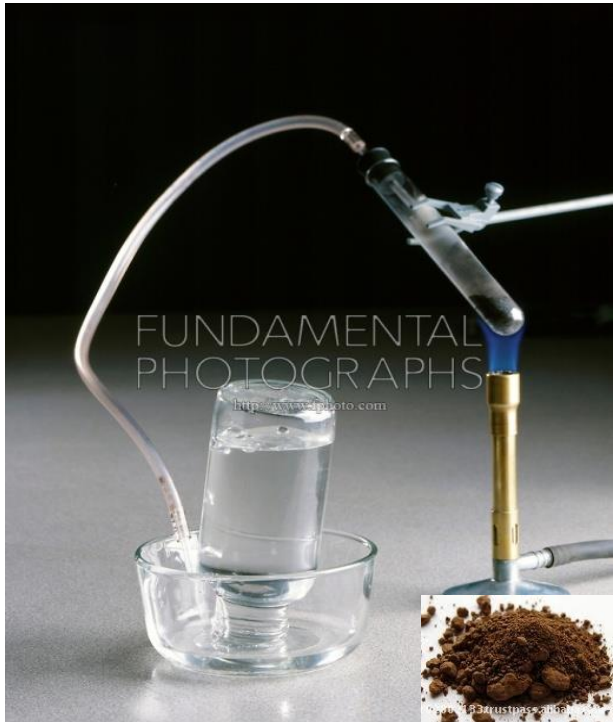
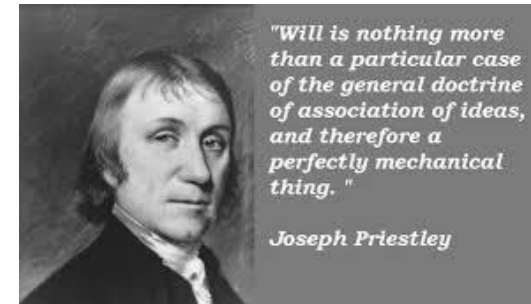
Example: *Methanobacterium bryantii*, *Methanococcus deltae*

Application:

Methane production, biogas production, waste water treatment

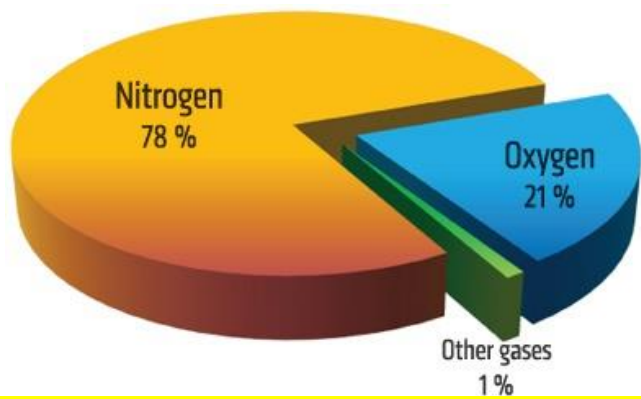


1772



Scheele isolates oxygen gas by heating manganese dioxide (and later potassium nitrate and mercuric oxide) but did not publish his findings immediately. It was also independently discovered by Joseph Priestly by heating and decomposing mercuric oxide in 1774.

<https://www.youtube.com/watch?v=WROdaS82564>



Industrial production of oxygen gas

Pressure Swing Adsorption plant



Two methods:
Liquefaction of air
and PSA



■ nitrogen	78.08%
■ oxygen	20.95%
■ argon	0.93%
■ neon	0.0018%
■ helium	0.0005%
■ krypton	0.00011%

The quadrupole of nitrogen is three times higher than that of oxygen, which leads to a selective adsorption onto the zeolite surface. The most common type of commercial zeolite for oxygen concentration process is zeolite 13X due to its outstanding nitrogen to oxygen adsorption selectivity. However, 13X zeolite modified with Li^+ exchange method exhibits a higher nitrogen adsorption capacity at the active cation sites of the zeolite framework

<https://www.youtube.com/watch?v=LxaoBoOAFak>

The Process

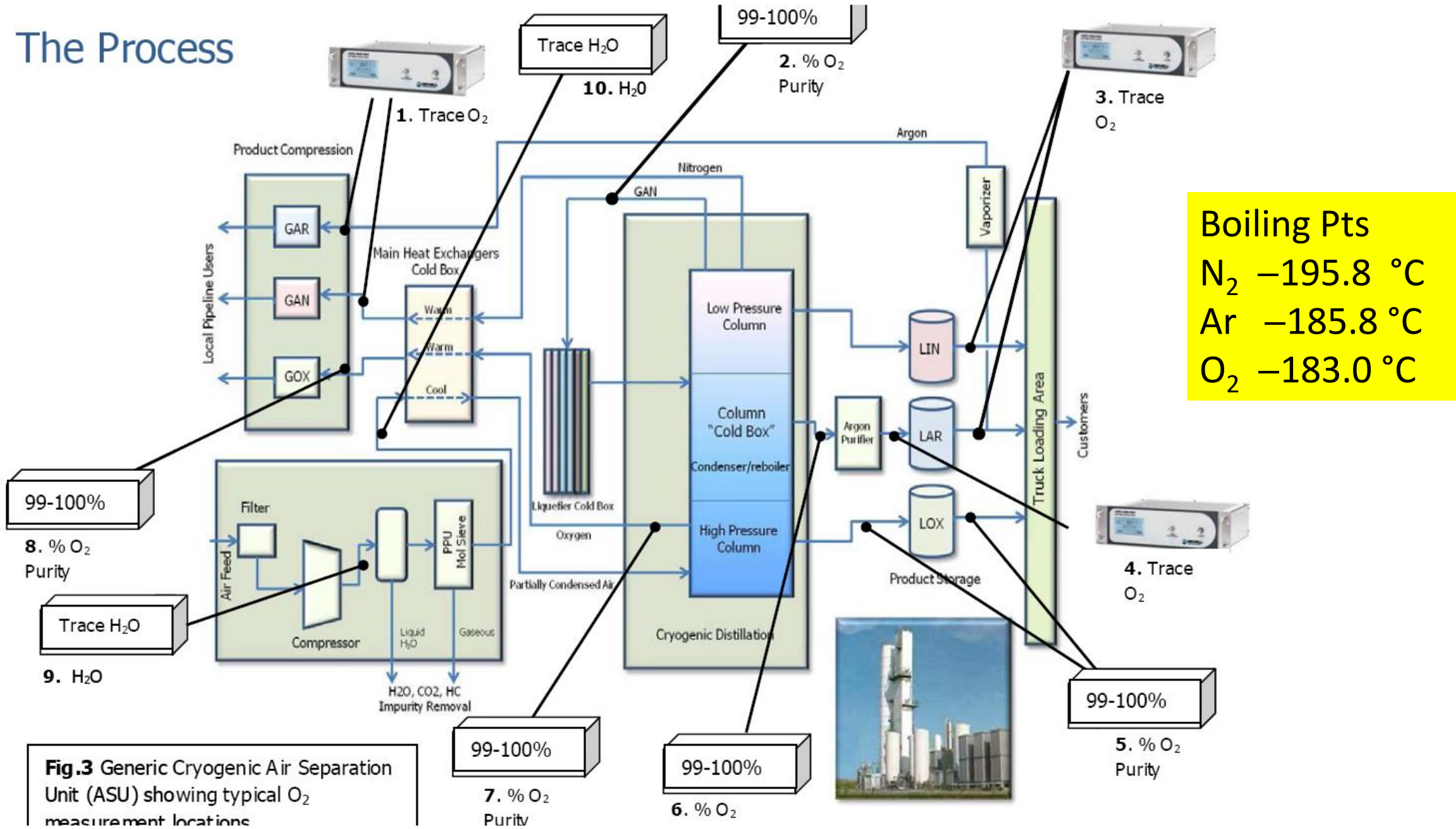
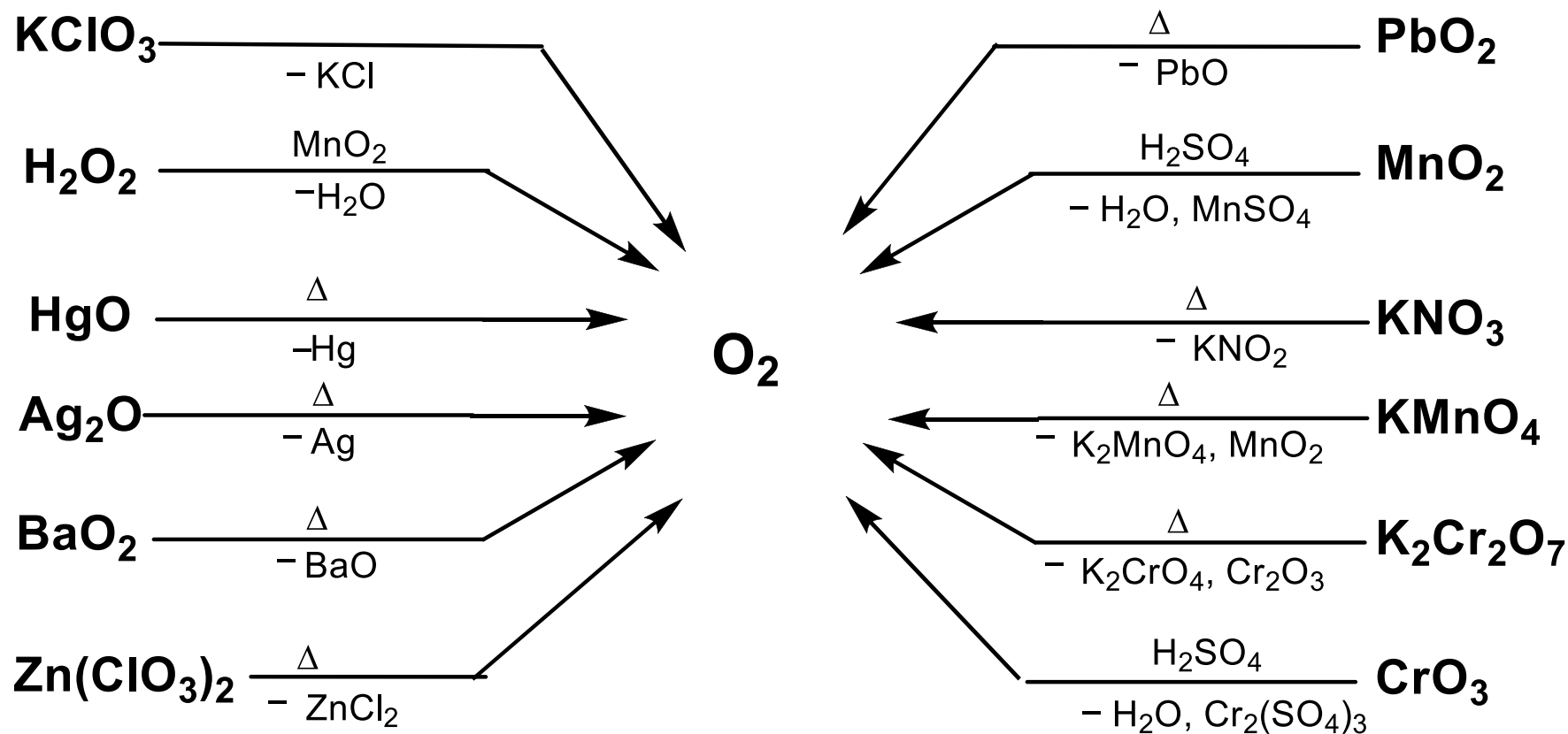
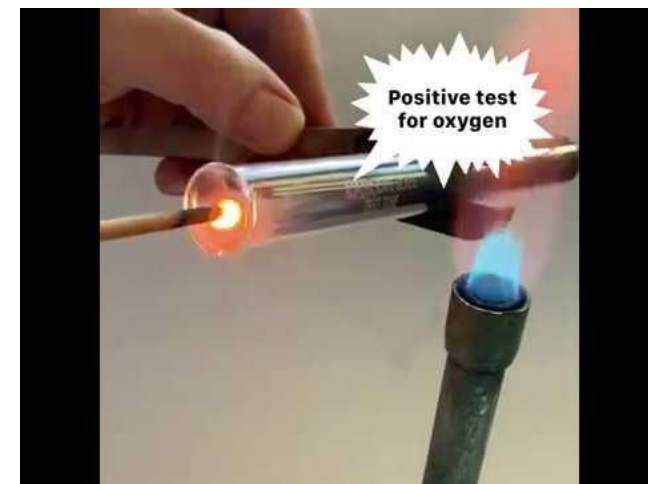
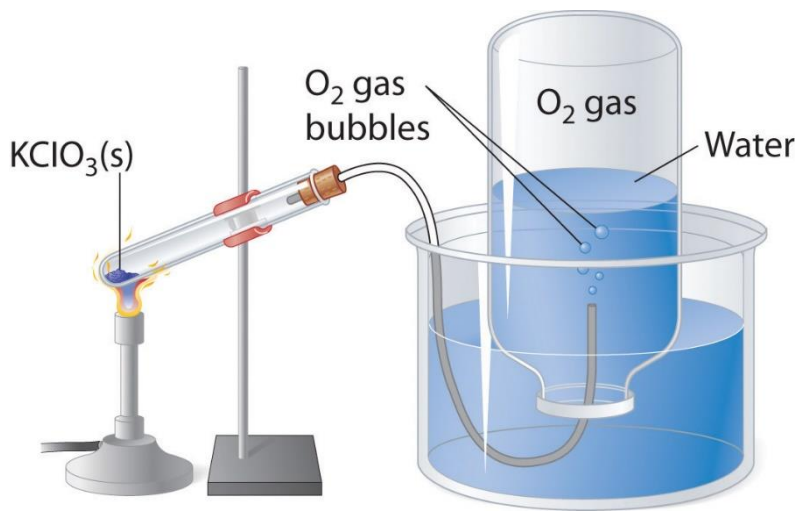


Fig.3 Generic Cryogenic Air Separation Unit (ASU) showing typical O_2 measurement locations

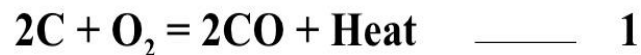
Laboratory Preparation of Oxygen



Industrial uses of oxygen

Chemical Reactions in Blast Furnace

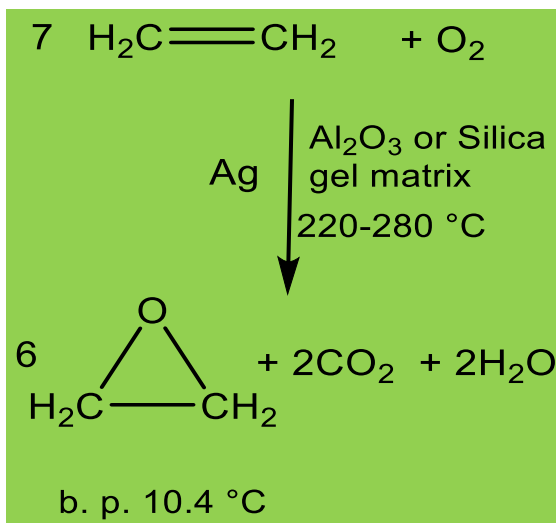
- The **air**, which is blown at the bottom of the furnace causes **partial combustion of the coke**:



- As the **CO**, which is **powerful reducing agent**, rises through the charge, it **chemically reduces the iron oxide** :-



Smelting of
iron ore
50%



Synthesis of
ethylene oxide
25%

Oxygen-acetylene
cutting/welding ($3500 \text{ }^\circ\text{C}$)

Spacecraft fuel

Life support in Hospitals

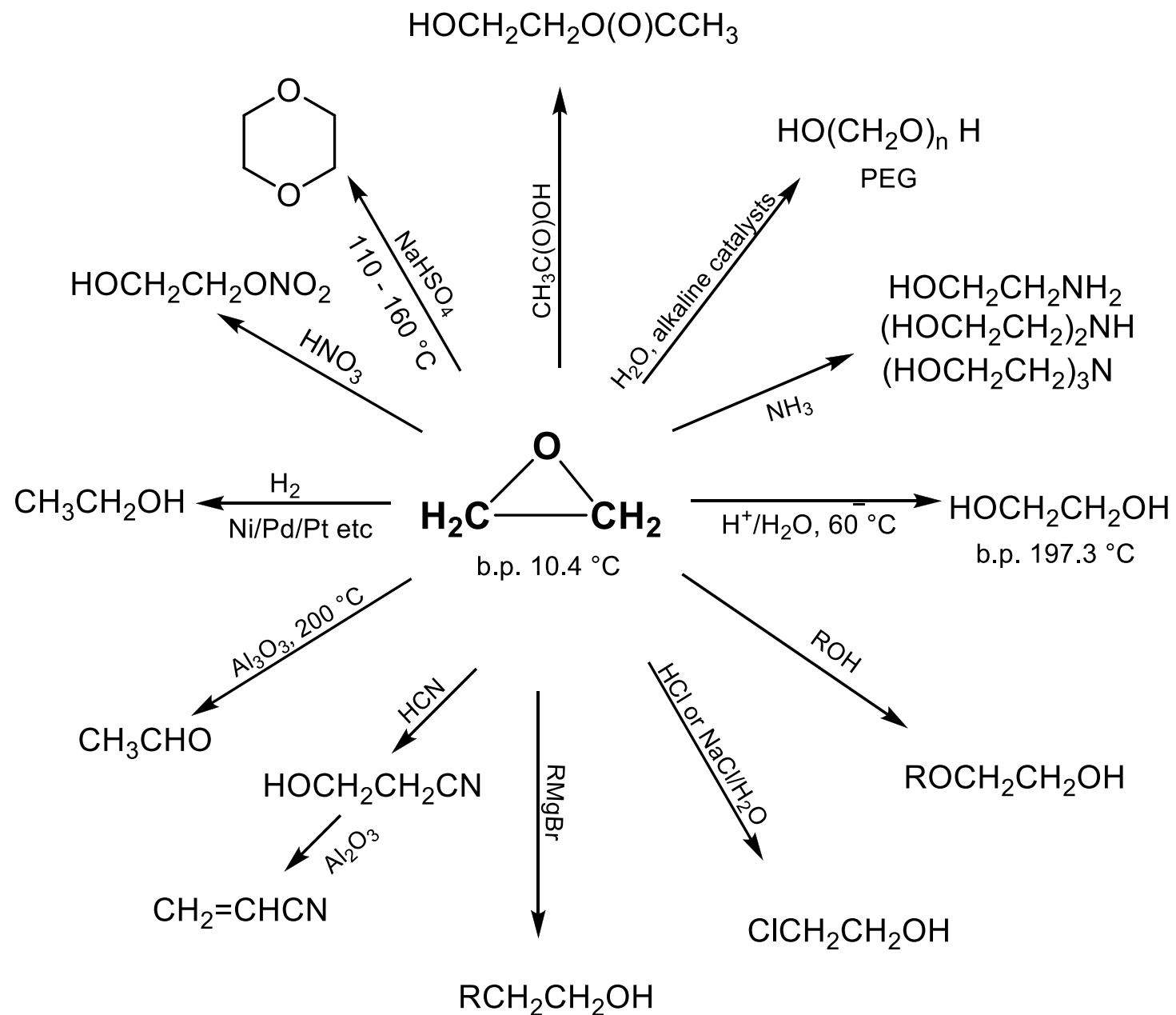
25%

More than 65% of ethylene oxide is used for the synthesis of ethylene glycol which is the most widely used antifreeze in vehicles throughout the world (20 mmt in 2010 while world production of ethylene was 150 mmt).

$\text{HOCH}_2\text{CH}_2\text{OH}$ B.P. $197.3 \text{ }^\circ\text{C}$, freezing point $-13 \text{ }^\circ\text{C}$

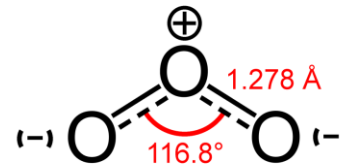
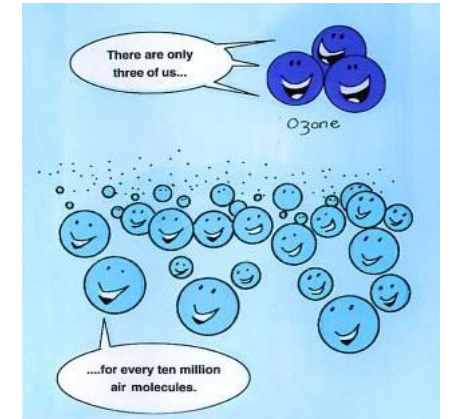


Some reactions of ethylene oxide



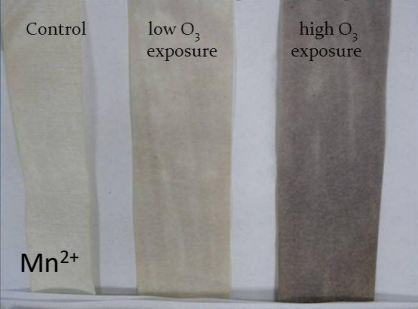
1840 Discovery of ozone

The discovery of ozone is attributed to two scientists. Martinus van Marum from Netherlands while conducting experiments in 1785 involving electrical sparking above water noticed a rather unusual smell. He attributed this smell the electrical reactions, and did not realize that he had created a new allotrope of oxygen. Half a century later, C. F. Schönbein detected the same smell associated with lightning bolts. In 1839, Schönbein was successful in isolating the gaseous chemical and named it "ozone",



Schoenbein Papers

Ozone was discovered by C.F. Schoenbein in 1839. He developed an ozone-sensitive test paper that was widely used historically, and more recently in classrooms. The standard protocol for using the papers calls for an 8-hour exposure to the air out of direct sunlight. Various studies have shown a dependence on humidity, and there are a variety of recommendations for moistening the strips prior to exposure.



Control low O₃ exposure high O₃ exposure

Mn²⁺

C.F. Schoenbein detects and names ozone from its characteristic odour after a lightning storm

Ozone is the only allotrope of oxygen. This pale blue gas with a distinctive pungent smell can be detected by human beings especially after a thunderstorm.

Electric motors using brushes has the ability to generate ozone as a result of the repeated sparking inside the unit. As a result, even traces of O_3 near rubber tyres of cycles parked near electric motors has been found to lead to cracks in the tyres reflecting its high reactivity towards alkene bonds.

Ozone is diamagnetic and on cooling, converts to a dark blue liquid at $-112\text{ }^\circ\text{C}$ and further to a violet black solid on cooling to $-192.2\text{ }^\circ\text{C}$.

Experimental evidence obtained from microwave spectroscopy indicates that ozone is a bent molecule and the O-O distance is 1.272 \AA and the O-O-O angle 116.78° .

Why is doing ozone chemistry difficult?

The relative stability indicated by half life for ozone in distilled water at $25\text{ }^\circ\text{C}$ is about 15 minutes. The half life for ozone gas in a glass container at $20\text{ }^\circ\text{C}$ is 3 days, however, humidity of 50% will cut that down to 11 hours.

Ozone is very **powerful and effective eliminator of different types of smoke and odors** such as tobacco smoke, phenol vapors, cooking odours, smell of pets, mold and other household odors. Turning on an ozone generator in a room with a bad odor removes all odors and converts it into a fresh odor free room often in less than 20-60 minutes. Ozone is an extremely useful tool in the area of fire and flood restoration of buildings. In such a damaged building, ozone will eliminate smoke odors in the carpets, curtains, wood, cupboards, clothing, etc. In a flood damaged building, ozone can be used once all the moisture has been removed. The **ozone will eliminate musty odors and also prevent growth of fungus and other microorganisms**. Odors and bacteria are significantly reduced by ozone in public toilets and washrooms and also kills the germs that can lurk on surfaces of bathroom and toilet fittings. Presence of sulfur in materials can lead to formation of sulfur based compounds such as hydrogen sulfide, carbonyl sulfide, sulfur dioxide, carbon disulfide, and thiols during a fire leading to bad smell. Thiols tend to get adsorbed on surfaces and produce a lingering odor which gets removed once it is oxidized. A systematic analysis of compounds generated from a home on fire indicated presence of aldehydes, ketones, alcohols, carboxylic acids acetophenone, benzyl alcohol, methoxyphenol, hydroxybenzaldehyde, methylphenols and naphthalene. Most of these compounds upon oxidation with ozone lose their characteristic smell.

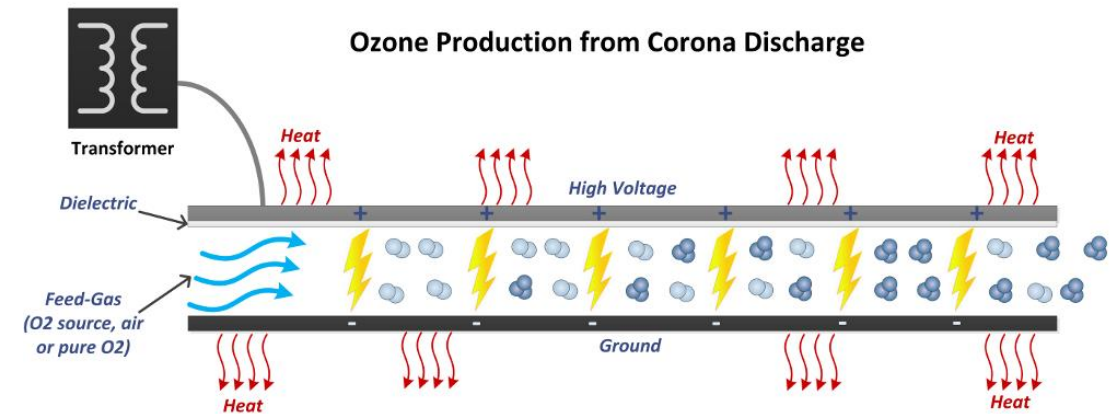
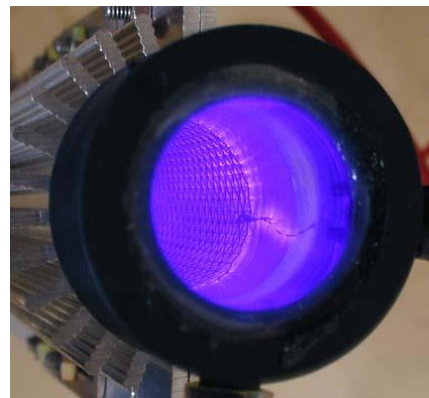


Ozone generators and their working



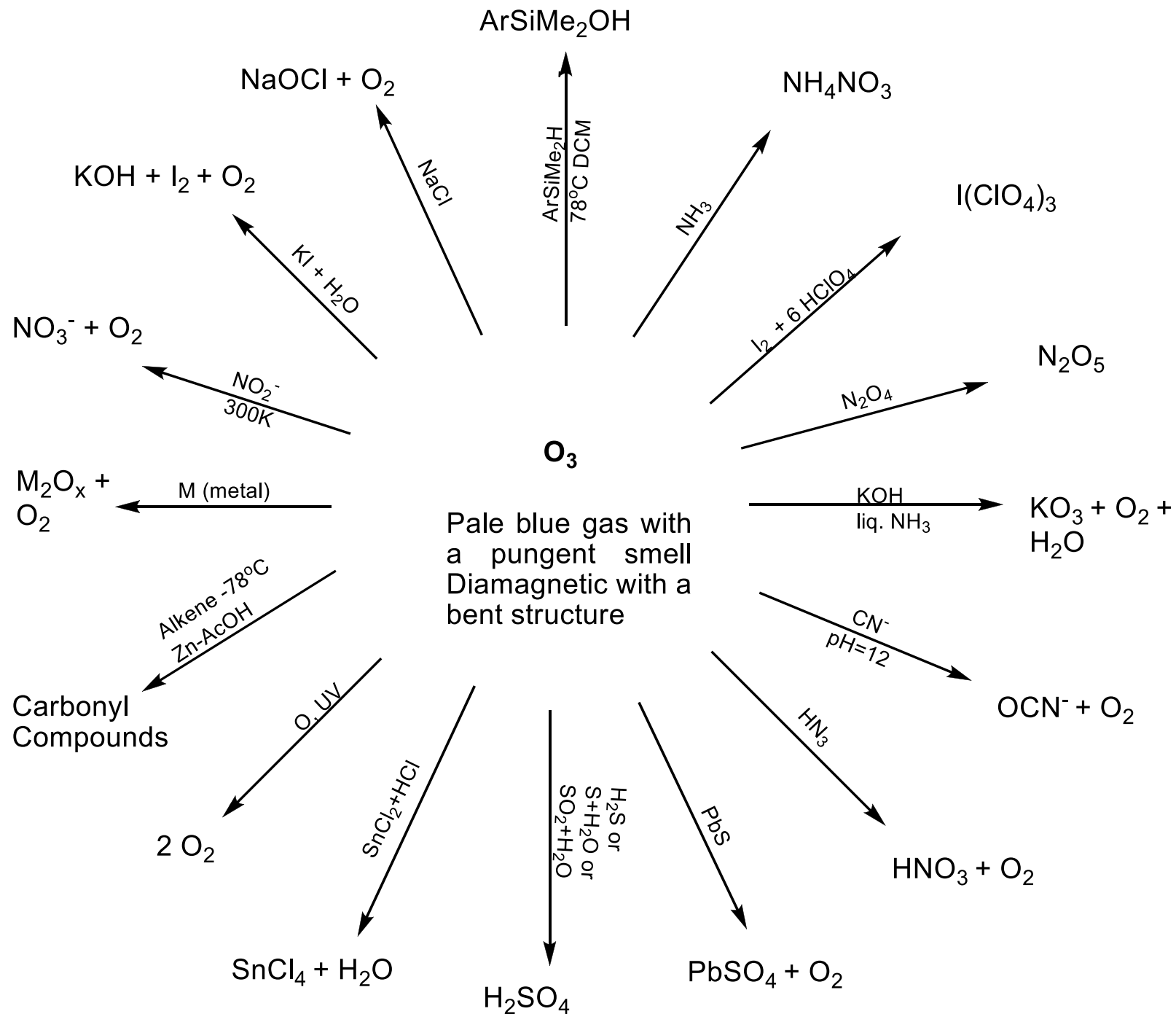
When inhaled, **ozone** can damage the lungs. Relatively low amounts of **ozone** can cause chest pain, coughing, shortness of breath and, throat irritation

Two basic methods of producing ozone namely ultra-violet and corona discharge methods have been developed. Corona discharge makes ozone when a high voltage is applied to a metallic grid sandwiched between two dielectrics. The high voltage travels through the dielectric material to a grounded screen and during the process, creates ozone from oxygen present around the grid. Formation of a corona, seen as a bluish glow, is observed when the electric field strength around a conductor is high enough to form a conductive region, but not enough to cause electrical arcing to nearby objects.



Ozone is formed via an electrical discharge that is diffused over an area using a dielectric to create a corona discharge. Oxygen passed through this corona discharge is converted to ozone.

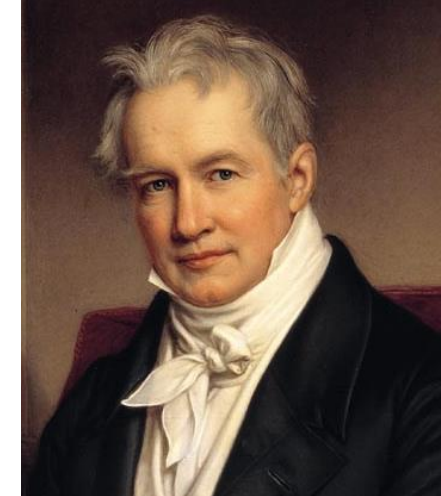
Molecular ozone with an oxidation potential of 2.07 V is among the most powerful oxidizing agents known, more powerful than H_2O_2 (1.78 V), permanganate (1.70 V) and O_2 (1.23 V).



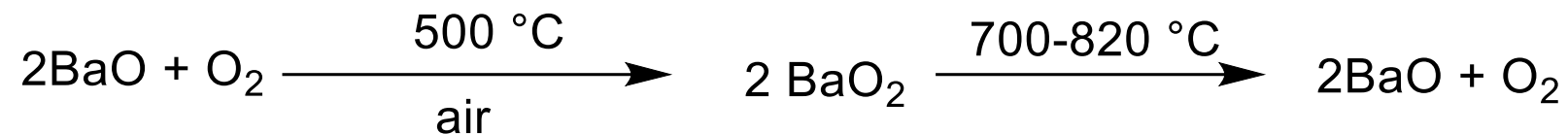
History of Hydrogen Peroxide

Alexander von Humboldt synthesized barium peroxide in 1799 as a byproduct of his attempts to decompose air.

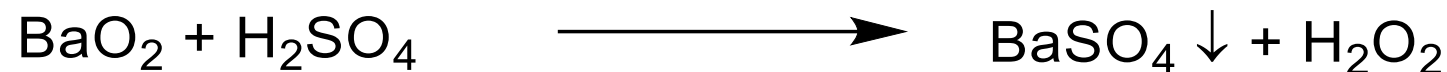
Nineteen years later Louis Jacques Thénard recognized that this compound could be used for the preparation of hydrogen peroxide (1818).



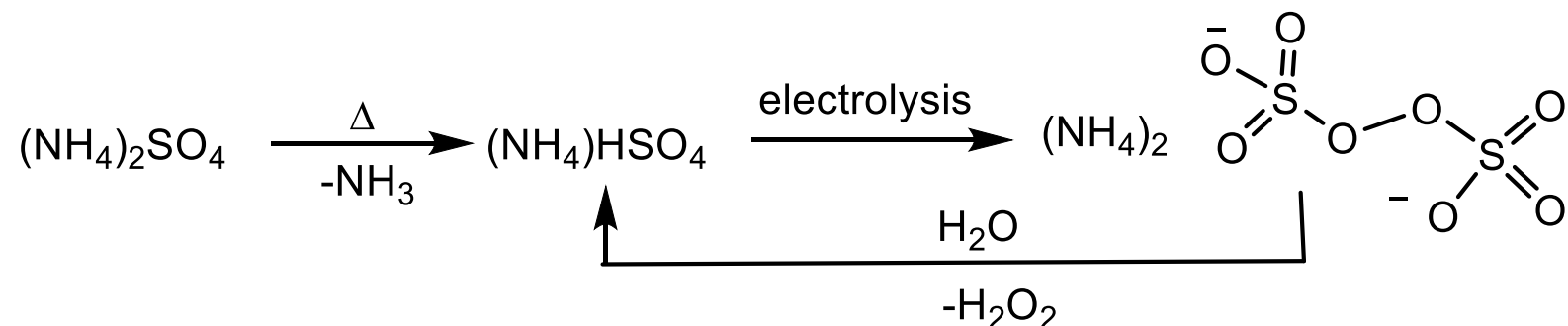
Alexander von Humboldt
Botanical geography, Prussian polymath, geographer, naturalist, explorer, botanist



(also shown by Na_2O and SrO)

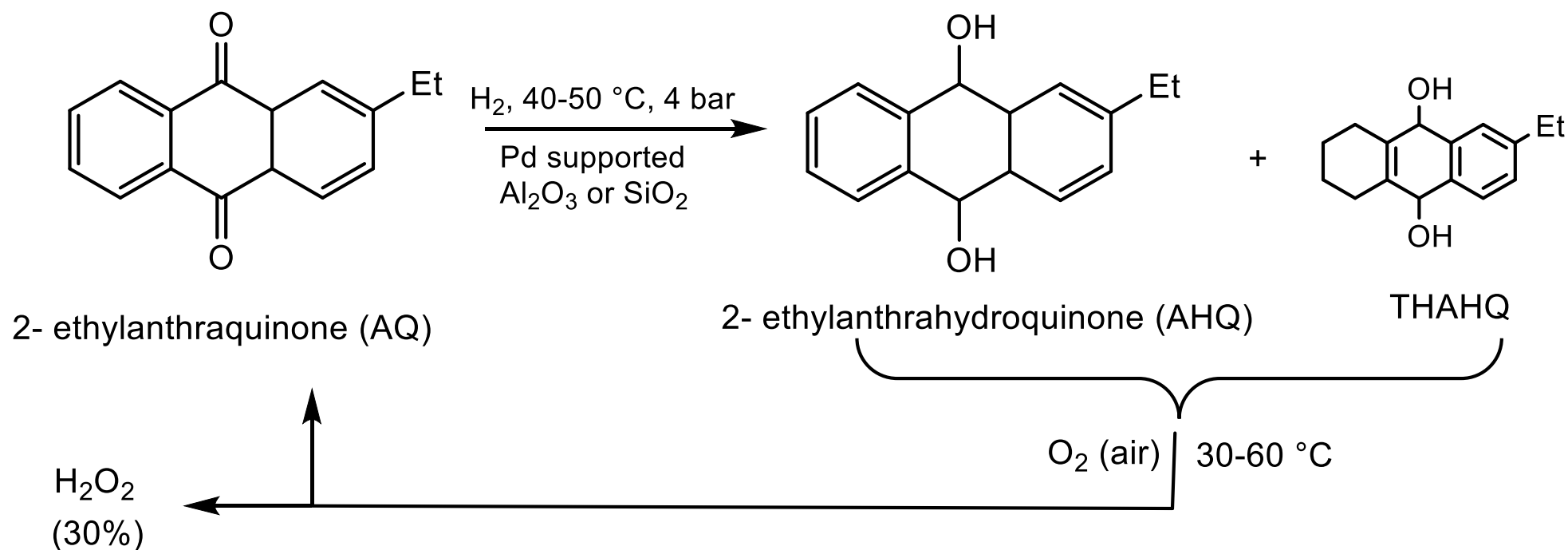


Another earlier method involves the hydrolysis of ammonium peroxydisulfate (persulfate)



Louis Jacques Thénard
One of the 72 names inscribed on Eiffel tower

Today, more than 95% of the world's hydrogen peroxide is manufactured by the anthraquinone process, which was developed by BASF in 1936 and patented in 1939. Many derivatives of anthraquinone can be used but 2-ethylanthraquinone is selected because of its high selectivity. The hydrogenation can reach 90% selectivity by using 2-ethylanthraquinone.



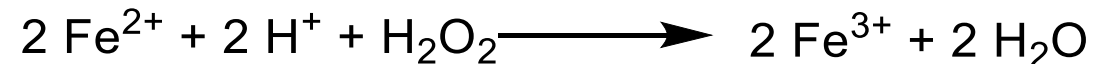
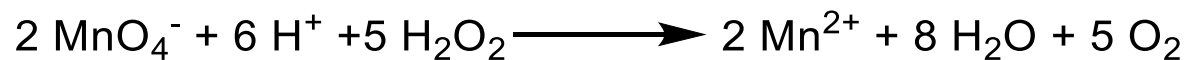
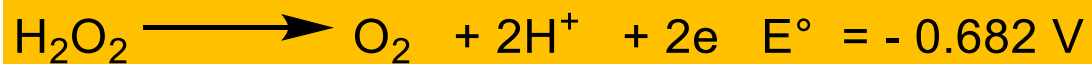
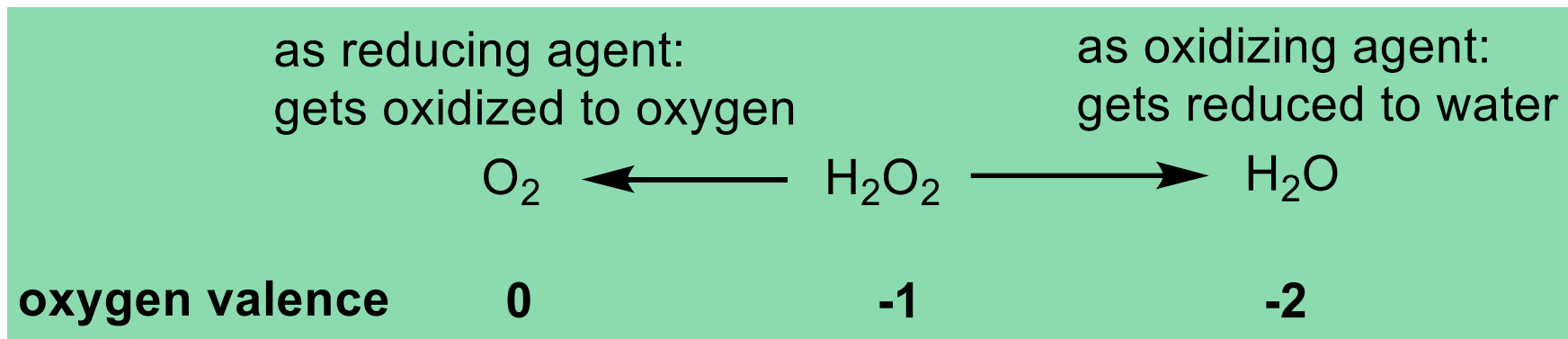
It begins with the reduction of 2-ethylanthraquinone to the corresponding anthrahydroquinone, typically by hydrogenation on a supported palladium catalyst. The anthrahydroquinone then undergoes oxidation by oxygen of air to regenerate the starting anthraquinone, with hydrogen peroxide being produced as a by-product.

Hydrogen peroxide properties

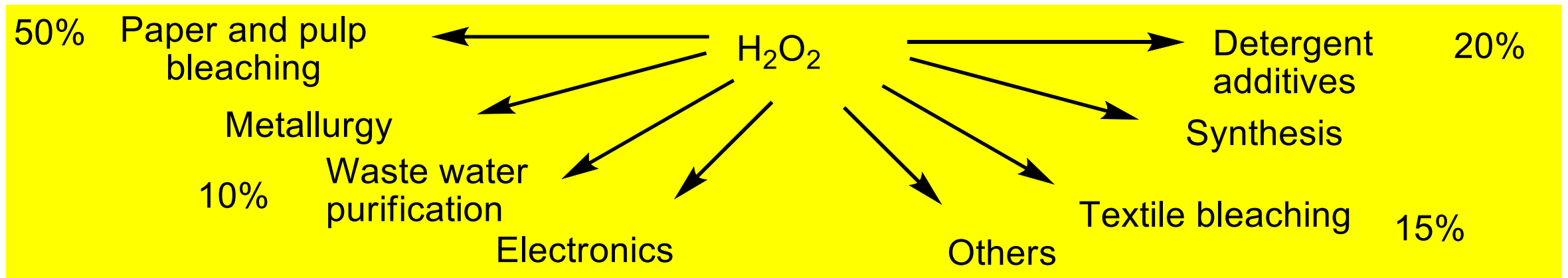
- In the chemical industry, hydrogen peroxide (H_2O_2) is widely used as an oxidant principally as its degradation products are water and oxygen only.
- It is an excellent oxidant which is effective over the whole pH range with high oxidation potential ($E^\circ=1.763 \text{ V}$ at pH 0, $E^\circ=0.878 \text{ V}$ at pH 14).
- An added advantage of using it is that water is the only byproduct of the oxidation reaction.
- The impure hydrogen H_2O_2 is purified and concentrated and is usually marketed with an added stabilizer as aqueous solutions at concentrations of 30, 35, 50, and rarely 70% by weight.
- The most common stabilizer of H_2O_2 is acetanilide.

<https://www.youtube.com/watch?v=Ta4DomSDzF8>

Hydrogen peroxide can act as both oxidizing agent and reducing agent in its reactions



The major industrial uses of H_2O_2 are shown below. Almost 50% of it is used in the manufacture of paper where it is used for bleaching. It is also used for making **perborates** and **percarbonates** which are additives used in detergents especially where bleaching is required to remove stains etc and a chlorine free milder bleach is required.



Hydrogen peroxide is a total chlorine free (TCF) bleaching agent. It is appropriate for chemical, mechanical and recycled pulp to achieve a wide range of brightness

Easy to use, lower production costs, improved paper quality, increased yield percentage and environmental friendly. The brightness of the paper that is made from hydrogen peroxide bleach is more stable.

https://www.youtube.com/watch?v=eH3_vXW2Lnw

<https://www.youtube.com/watch?v=Yta1-EnmMg>

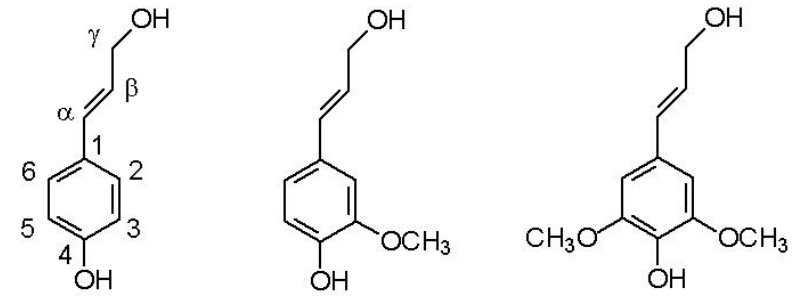
<https://www.youtube.com/watch?v=tPbTWwohqF8>

Pulp bleaching

The dark colour of the pulp is mainly due to residual lignin.
This is removed gradually during bleaching.



The chemistry behind bleaching of wood pulp



p-coumaryl alcohol

Coniferyl alcohol

Sinapyl alcohol

Color causing components of lignin

The objective of bleaching mechanical pulp (also referred to as brightening) is to remove only the chromophores (color-causing groups). This is possible because the structures responsible for color are also more susceptible to oxidation or reduction.

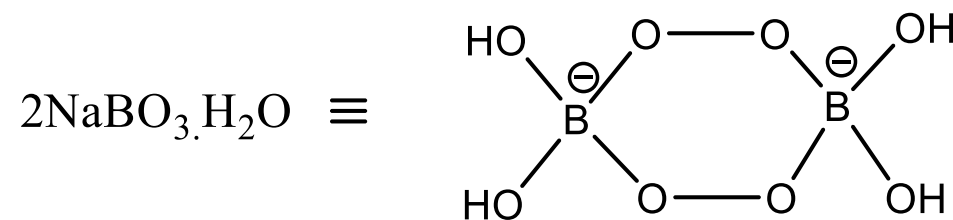
Alkaline hydrogen peroxide is the most commonly used bleaching agent for mechanical pulp. The amount of base such as sodium hydroxide is less than that used in bleaching chemical pulps and the temperatures are lower. These conditions allow alkaline peroxide to **selectively oxidize non-aromatic conjugated groups responsible for absorbing visible light**. The decomposition of hydrogen peroxide is catalyzed by transition metals, and iron, manganese and copper are of particular importance in pulp bleaching. The use of chelating agents like EDTA to remove some of these metal ions from the pulp prior to adding peroxide allows the peroxide to be used more efficiently. Magnesium salts and sodium silicate are also added to improve bleaching with alkaline peroxide.

Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), is the other main reagent used to brighten mechanical pulps. In contrast to hydrogen peroxide, which oxidizes the chromophores, **dithionite reduces these color-causing groups**. Dithionite reacts with oxygen, so efficient use of dithionite requires that oxygen exposure be minimized during its use.

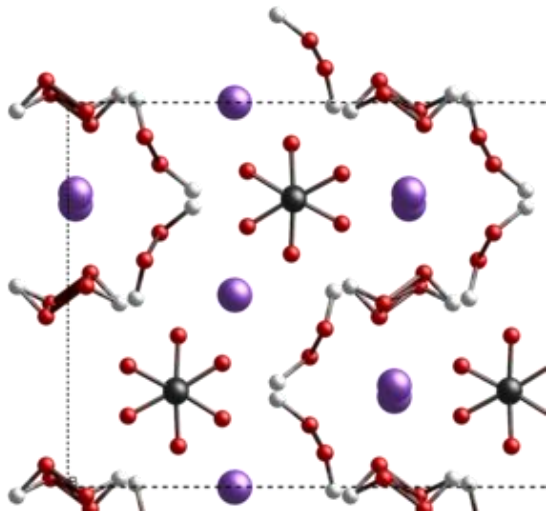
Inorganic Peroxides: Example: Sodium perborate



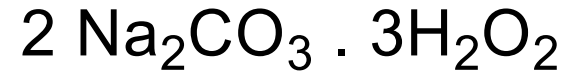
Sodium perborate, $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ is prepared from borax by treatment with NaOH (to convert it to sodium borate, NaBO_2) and further reaction with hydrogen peroxide. The elementary structural unit is a dimeric dianion $\text{B}_2\text{O}_4(\text{OH})_4^{2-}$. It is a source of active oxygen used in teeth whiteners and bleaches and is also a disinfectant. It releases oxygen rapidly above 60°C .



The teeth brightening gel is both legal and safe. It contains the active ingredient Sodium Perborate which forms a very low concentration of Hydrogen Peroxide on your teeth (0.035% Hydrogen Peroxide where the legal limit is 0.1%). This gives great results without any irritation of the gums or teeth sensitivity.



Inorganic Peroxides: Example: Sodium percarbonate



Non flammable white solid

Sodium percarbonate is produced industrially by crystallization of a solution of sodium carbonate and hydrogen peroxide, with proper control of the pH and concentrations.

It is a colorless, crystalline, hygroscopic and water-soluble solid, an adduct of sodium carbonate. It is sometimes abbreviated as SPC. It contains 32.5% by weight of hydrogen peroxide.

It is a chlorine free bleach and a source for anhydrous hydrogen peroxide. World production capacity of this compound was estimated at several hundred thousand tons.



Why do living things age and is there anything we can do to stop ageing?

Two theories :

In the first, the idea is that our genes determine how long we live. We have a gene or some genes that tell our body how long it will live. If you could change that particular gene, we could live longer

The second theory is that over time, our body and our DNA get damaged until we can no longer function properly. The idea here is that how long we last is really just a consequence of small changes in our DNA. These changes add up until the total amount of damage is too much to bear and we die

Which theory is right? Probably reality is a combination of these two ideas. In the past decade, scientists have found evidence to support both theories.

Work in worms, has shown that mutating certain genes can increase lifespan about 4-fold. For humans, that would translate to about 300 years old

One popular scientific hypothesis proposes that **mitochondrial DNA** plays a major role in aging. What is mitochondrial DNA and why would it play an important role in aging?

It turns out that mitochondrial DNA (mtDNA) gets mutations much faster than the DNA in the nucleus. One reason for this is thought to be the presence of ROS or "reactive oxygen species" in the mitochondria. When mitochondria make energy for us, they create ROS that can damage nearby mtDNA. In fact, this might be the reason why eating less leads to longer lives in animals -- less food, fewer ROS.

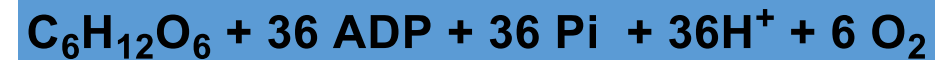
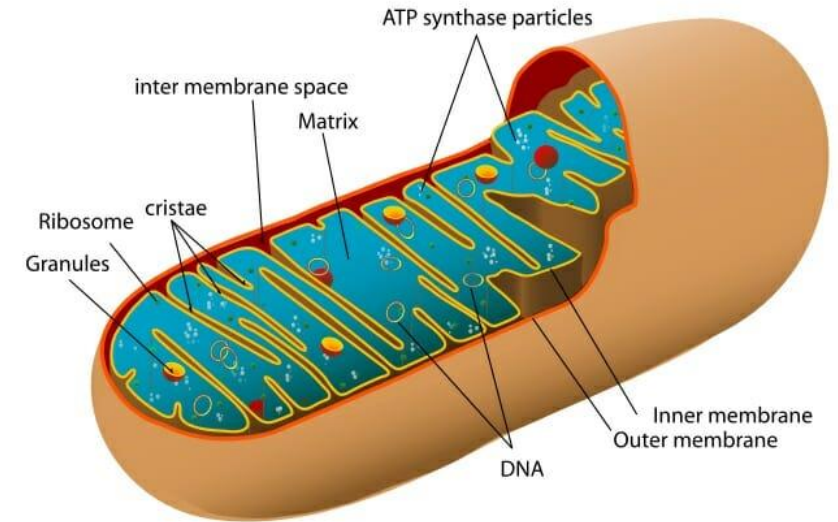
The idea is that as mtDNA becomes more and more damaged, the mitochondria cannot produce energy as well and become dysfunctional. This could lead to aging and ultimately, death.

A group of researchers in Sweden. The researchers mutated a gene in mice so that the mtDNA would get more mutations faster.

At about 25 weeks of age the mutant mice started to display signs of aging that are normally seen in much older mice. The mutant mice lived for less than a year instead of for 2 to 3 years.

What are reactive oxygen species???

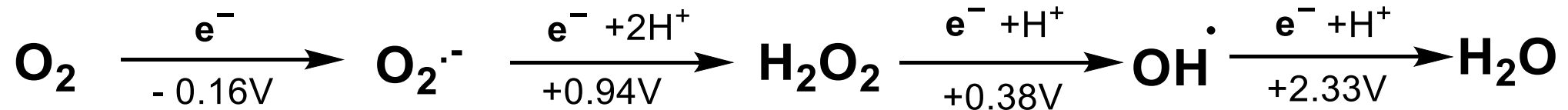
<https://www.youtube.com/watch?v=RrS2uROUjK4>



Oxidative Phosphorylation

<https://www.youtube.com/watch?v=39HTpUG1MwQ>

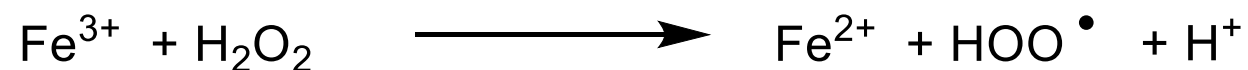
Some oxygen based species are highly toxic and the terms ROS (reactive oxygen species) and ROI (reactive oxygen intermediates) have been coined to address this class of highly reactive, oxygen based species some of which are radicals and radical anions too. According to a more specific classification, the term ROI depict the **chemical species formed upon incomplete reduction of molecular oxygen**, namely superoxide radical anion ($O_2^{\cdot-}$), hydrogen peroxide (H_2O_2), and hydroxyl radicals (OH^{\cdot}), while ROS includes all of the ROI, singlet oxygen (1O_2) and ozone (O_3)



molecular oxygen as such is not very reactive on biomolecules. Despite its high reduction potential of +0.94 V, $O_2^{\cdot-}$ can oxidize very few biological compounds. Under physiological conditions H_2O_2 is relatively stable, although it has a positive one electron reduction potential of 0.38 V. In contrast, **the hydroxyl radical, with a one-electron reduction potential of +2.33 V, is a very strong oxidant reacting with organic matter.**

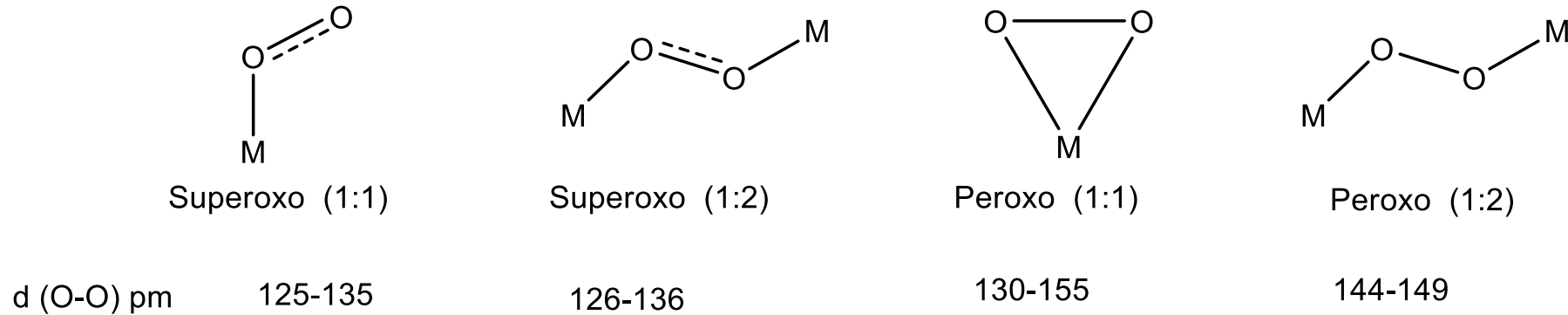
Reactive oxygen species have for quite some time been responsible for the oxidative damage inflicted on fatty acids, DNA, proteins as well as many other cellular components. Diseases such as cancer, cardiovascular, inflammatory, Parkinson's and Alzheimer's diseases have been related to oxidative stress caused by the imbalance between excessive formation of reactive oxygen species and limited antioxidant defenses. According to the "free radical theory of aging" suggested by D. Harman in 1956, the toxic effects of ROS, generated during cellular respiration at the mitochondrial level are directly involved in the processes of ageing.

Fenton's reagent is a solution of hydrogen peroxide (H_2O_2) with ferrous iron (typically iron(II) sulfate, FeSO_4) as a catalyst that is used to oxidize contaminants or waste waters. Fenton's reagent can be used to destroy organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (perchloroethylene, PCE). It was developed in the 1890s by Henry John Horstman Fenton as an analytical reagent



Dioxygen as a ligand in metal complexes

respiration process involves reversible binding of dioxygen to metals

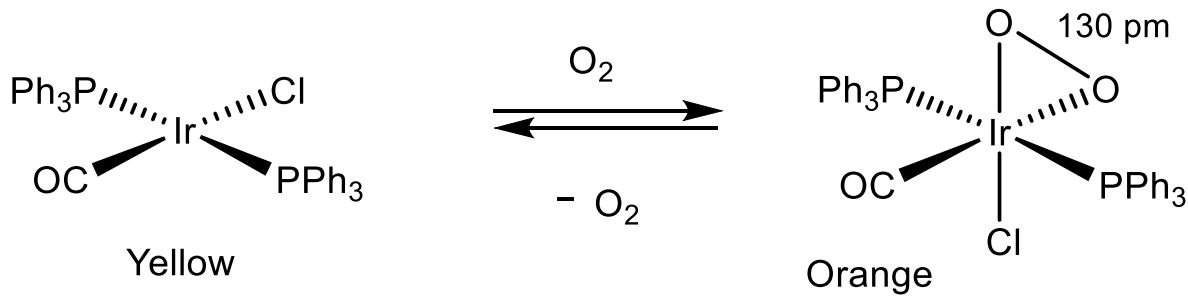


These metal-coordinated species come under the category of superoxo ($M-O_2^-$) or peroxo ($M-O_2^{2-}$).

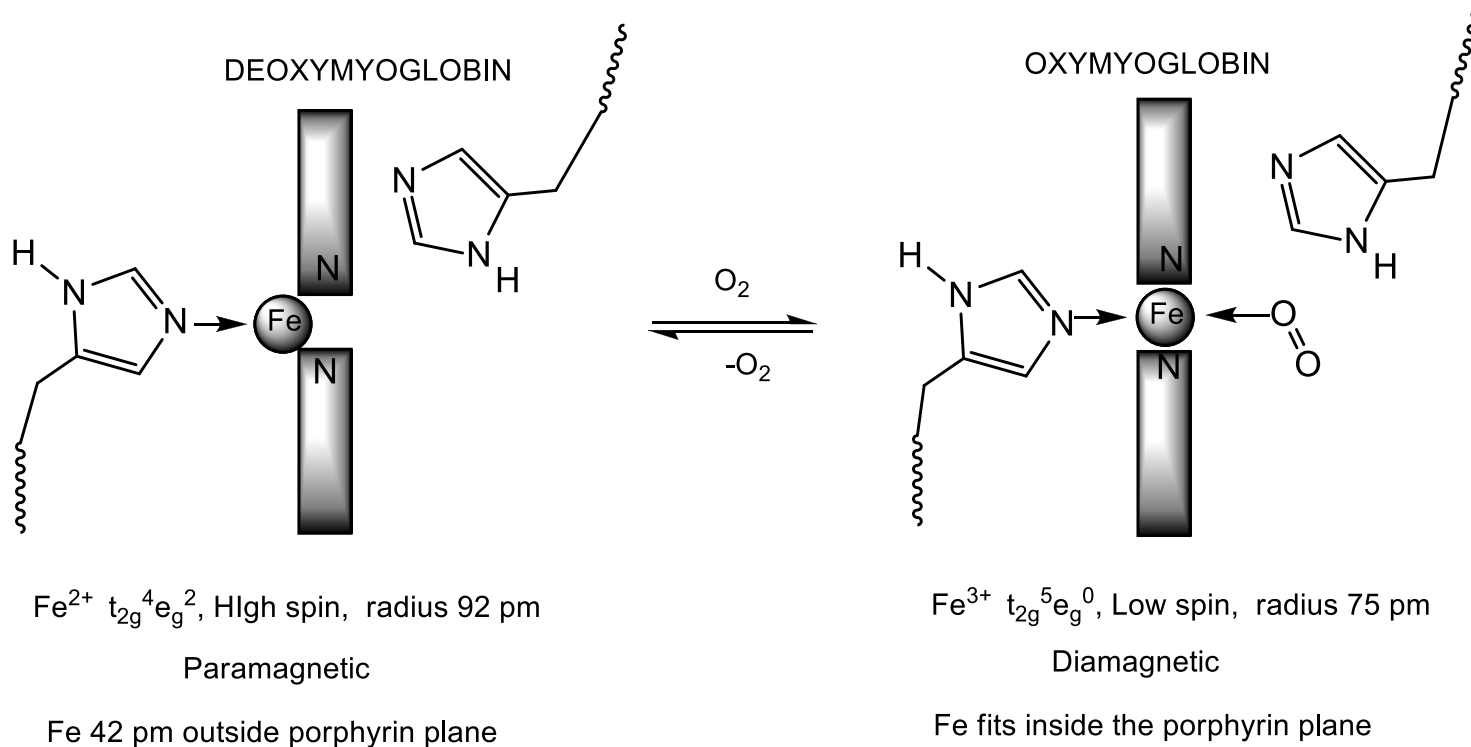
Since reduction of the O_2 involves electron donation to the $2p\pi^*$ antibonding orbitals of dioxygen, the superoxo and peroxo species can be distinguished by the differences in their O-O bond strengths. With respect to the bond order of the O-O bond, molecular dioxygen (O_2), superoxide (O_2^-), and peroxide (O_2^{2-}) have predicted bond orders 2, 1.5, and 1, respectively.

The O-O stretching frequencies vary continually from $1,300\text{ cm}^{-1}$ to 700 cm^{-1} and dioxygen (O_2), superoxide (O_2^-), and peroxide (O_2^{2-}) can have O-O stretching frequencies of 1555 cm^{-1} , $1200\text{--}1070\text{ cm}^{-1}$, and $930\text{--}750\text{ cm}^{-1}$, respectively.

Vaska's complex and haemoglobin: similarities and differences

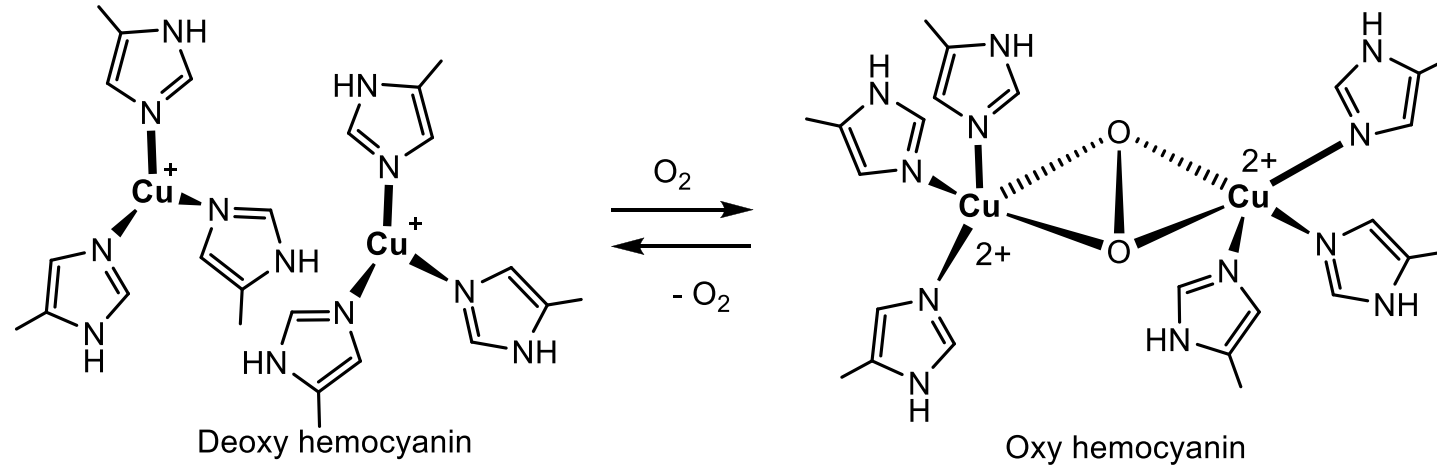


The **peroxo dioxygen** adduct of Vaska's complex reverts to the parent complex upon heating or purging the solution with an inert gas, signaled by a color change from orange back to yellow



The binding of O_2 to the iron of hemoglobin has been envisaged to be as a **superoxide ion**. The presence of superoxide has been found to be a better model and was confirmed by various techniques, including infrared spectra, X-ray absorption spectroscopy and Mössbauer spectroscopy.

Haemocyanin found in spiders, crustaceans, some molluscs, octopuses, squids etc, is copper based and O_2 binds by the side on mode. When deoxygenated, it is colorless and when oxygenated it is blue colored.



Hemerythrin found in some types of marine worms such as peanut worms, brachiopods etc. It is iron based and oxygen binds in the end on mode but one end is bound to the H of a bridging OH unit. It is colorless in the deoxygenated state and violet pink colored in the oxygenated form

