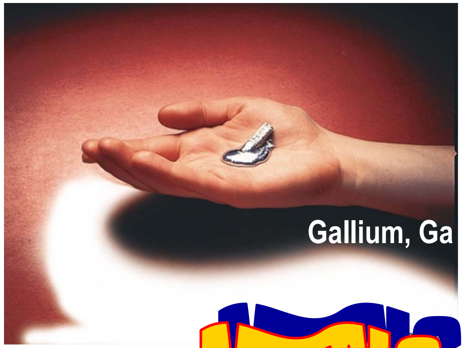
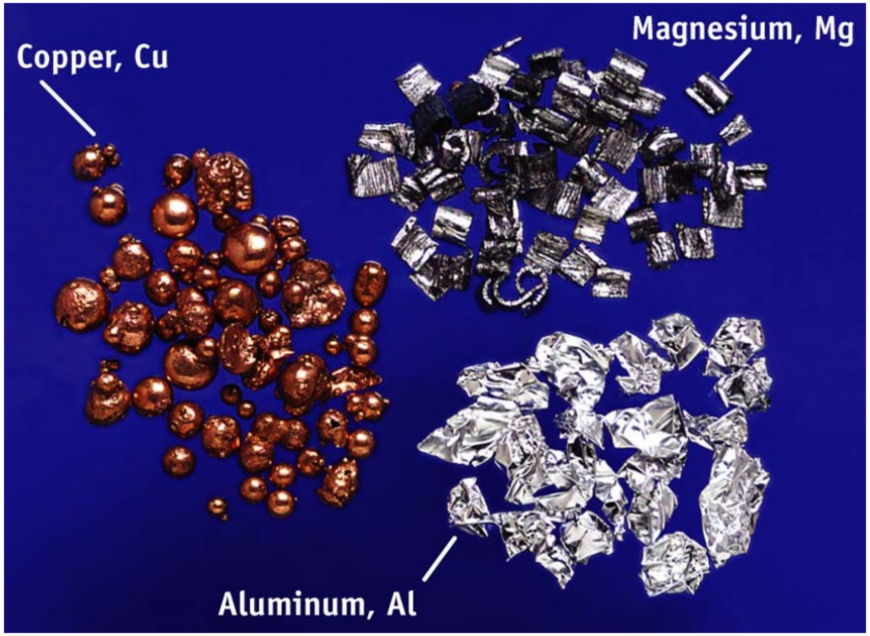


METALS



CHEMISTRY 1000

Topic #2: The Chemical Alphabet

Fall 2020

Dr. Susan Findlay

See Exercises 11.1 to 11.4

NONMETALS


Forms of Carbon

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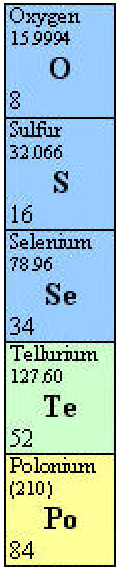
METALLOIDS

The Chalcogens (Group 16)


Oxygen
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O
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Sulfur
32.066
S
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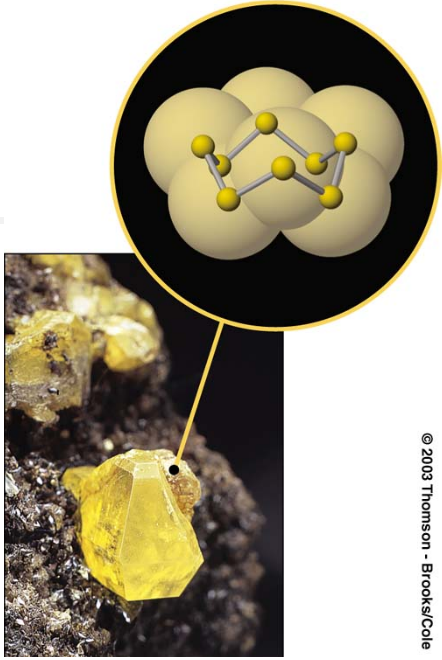
Selenium
78.96
Se
34

Tellurium
127.60
Te
52

Polonium
(210)
Po
84

- What is a chalcogen?
  - Any element in Group 16
  - Nonmetal (O, S, Se), metalloid (Te) or radioactive metal (Po)
  - Has multiple **allotropes** (oxygen is O_2 or O_3; sulfur has many allotropes – most often S_8; selenium can be Se_8 or polymeric)
  - Most form compounds with strong unpleasant odours
  - Forms one monoatomic anion (-2); Po^{2+} and Po^{4+} also exist
  - Has six valence electrons (valence electron configuration $[N.G.]ns^2np^4$) and a large electron affinity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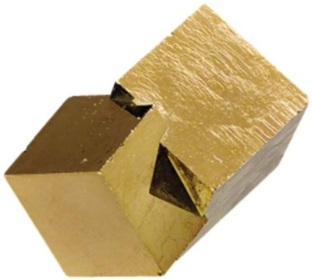
Pyrite, FeS_2

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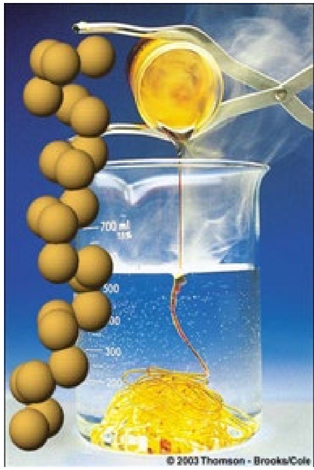
	Melting Point	Boiling Point	State (at 20 °C)	Density (at 20 °C)
Oxygen	-192.5 °C	-111 °C	Gas	0.00143 g/cm^3
Sulfur	113 °C	445 °C	Solid	2.07 g/cm^3
Selenium	221 °C	685 °C	Solid	4.79 g/cm^3
Tellurium	450 °C	1390 °C	Solid	6.24 g/cm^3
Polonium	254 °C	962 °C	Solid	9.32 g/cm^3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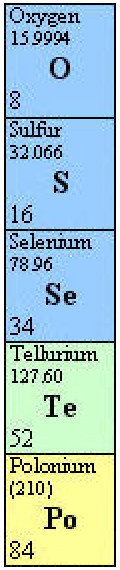
Oxygen and Ozone



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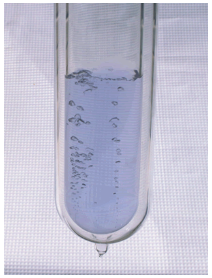
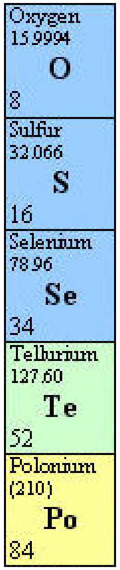
- When we refer to “oxygen”, we are typically referring to diatomic oxygen (O_2), a colourless, odourless, tasteless gas which, when cooled to a low enough temperature, condenses to a pale blue liquid that packs a powerful punch! Solid O_2 is also pale blue.



- Diatomic oxygen is a strong oxidizing agent. As we have seen, it reacts spontaneously with the metals of groups 1, 2 and 13 (as well as some transition metals). Some of these reactions are quite slow unless heat or a catalyst is added – or unless liquid O_2 is used instead of gaseous O_2! Why might that be?
- Another way to increase the reactivity of gaseous O_2 is to add water. Iron rusts much more quickly in damp air than in dry air!

Oxygen and Ozone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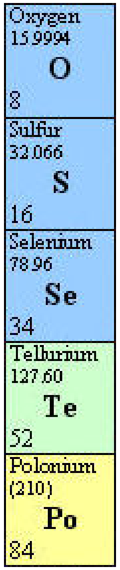
- The other common allotrope of oxygen is ozone (O_3). Ozone is a significant component of "smog"; however it is also an essential component of the upper atmosphere.
- Ozone is formed from O_2 in an endothermic reaction:

  This reaction requires a large input of energy, such as passing an electric current through a sample of oxygen *(as done in a lab if a reaction requires ozone)* or electromagnetic radiation from the sun *(as happens in the upper atmosphere).*
- Ozone is unstable, decomposing to diatomic oxygen (O_2). In order to maintain a constant amount of ozone, it must continually be regenerated.


Photo by the US EPA

Oxygen and Ozone



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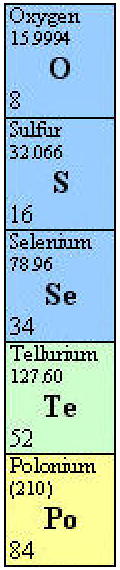
- Ozone in the upper atmosphere absorbs a significant amount of UV radiation from the sun, protecting organisms on Earth from a significant amount of biological damage. In absorbing this radiation, the ozone is broken into O_2 and free oxygen atoms (which react with more ozone to form O_2). This process is exothermic, and helps regulate the Earth's temperature:
- Needless to say, when it became widely recognized that ozone in the atmosphere was disappearing, this was a cause for alarm! This news was first reported by chemists Sherwood Rowland and Mario Molina in 1974. They won the Nobel Prize in Chemistry in 1995.
- The "hole in the ozone layer" over the Antarctic was first reported in 1985 by British scientists Joseph Farman, Brian Gardiner, and Jonathan Shanklin.

Oxygen and Ozone



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- The “hole in the ozone layer” is not actually a region with no ozone, but it is an area in which the ozone has thinned substantially. 70% of the ozone over the Antarctic and 30% of the ozone over the Arctic had disappeared by the early 1980s!
- In 2000, the “hole” over the Antarctic had expanded to cover the southern tip of South America.
- In 2011, we saw the first “hole” over the Arctic.

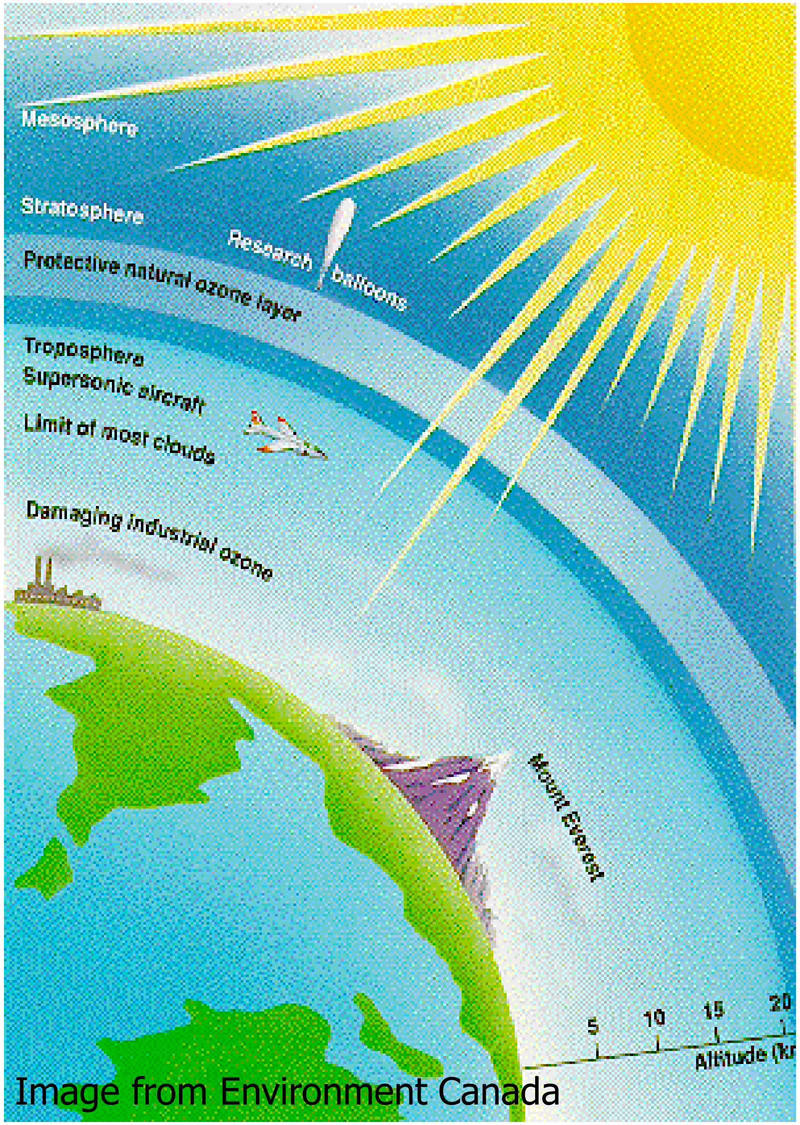
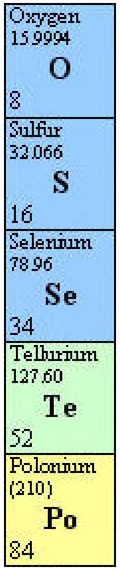


Image from Environment Canada

Oxygen and Ozone



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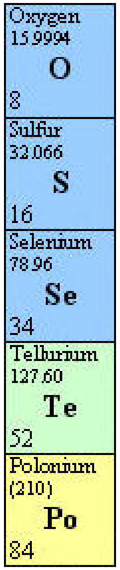
- Where was the ozone going?
  - Certain pollutants – particularly chlorofluorocarbons (CFCs) used as refrigerants – accelerate the decomposition of ozone to O_2. The scheme below is simplified but illustrates the point.
    - First, the CFC absorbs UV radiation to give a free chlorine atom ($Cl \cdot$, a "free radical")
    - This chlorine atom reacts with ozone to form O_2 and $ClO \cdot$
    - The $ClO \cdot$ reacts with a free oxygen atom to form more O_2 and regenerate the free chlorine atom
    - This cycle continues until the chlorine atom finds something to react with other than ozone. That means that one polluted CFC molecule can be responsible for the destruction of millions of ozone molecules!

Sulfur



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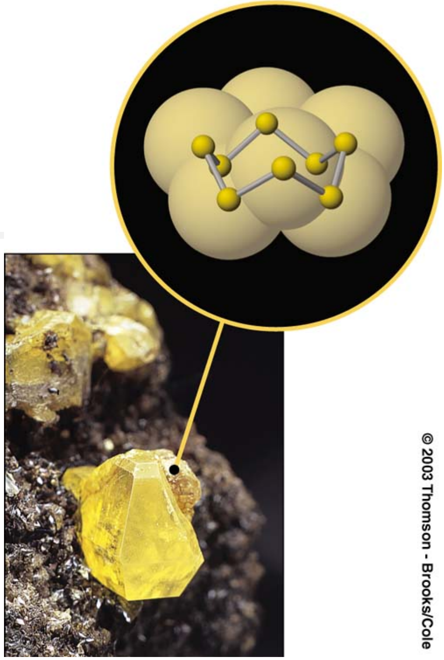

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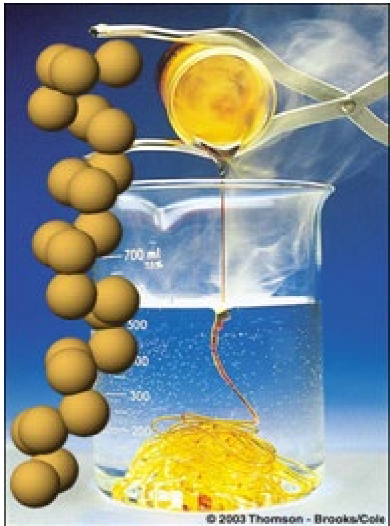
- Sulfur exists as a wide range of allotropes:
  - S_2 is violet
  - S_3 is blue
  - S_4 is red
  - S_5 is red-orange
  - S_6 is yellow-orange
  - S_7 to S_{15} are all shades of yellow as are S_{18}, S_{20} and S_μ (a polymer)
- Some of these allotropes can be further divided into different forms based on their crystal structure (e.g. α-S_8 and β-S_8 have different densities and melting points).
- Naturally occurring sulfur is α-S_8, eight sulfur atoms in a puckered ring often called a crown. This form of sulfur is insoluble in water.
- If sulfur is heated to $400\ °C$ then rapidly cooled *(e.g. by pouring into cold water),* we get "plastic sulfur" which can be pulled into threads.



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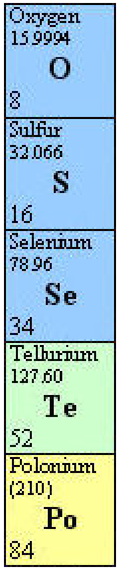
Sulfur



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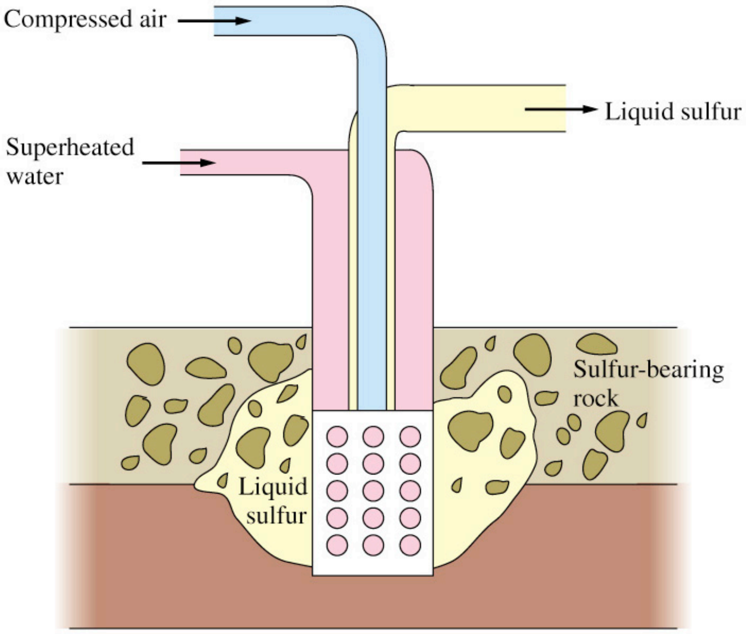
- Two methods of industrially obtaining S_8 are the Frasch process and the Claus process.
  - The Frasch process is an extraction technique.
    - In Texas and Louisiana, sulfur deposits 60-100 meters thick are 400-800 meters underground.
    - Superheated water (160°C liquid, 16 bar) melts the sulfur then hot compressed air (20-25 bar) forces the molten sulfur up a third pipe
    - 10-15 kg of water is needed to extract 1 kg of S_8
    - The sulfur produced is 98-99.5% pure and can be poured into moulds or distributed as a liquid.



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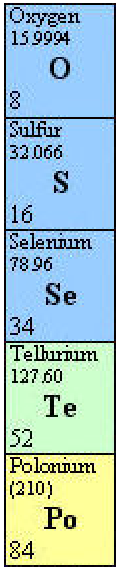

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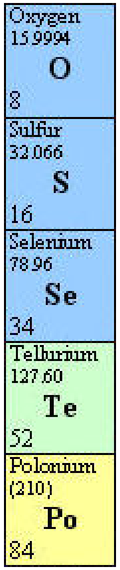
- The Claus process generates S_8 from hydrogen sulfide (H_2S).
  - We need to limit H_2S emissions, a common impurity in oil & gas.
  - To better control the reactions, a two-step process is used.
    - First, hydrogen sulfide is burned in the presence of oxygen. This step is very exothermic.
    - Second, the sulfur dioxide produced in the first step is reacted with more hydrogen sulfide. This step is less exothermic and requires a catalyst.
  - In practice, what is done is to pipe a mixture of H_2S and O_2 into a combustion chamber where most of it reacts to form S_8. The remaining H_2S and SO_2 produced are then piped into two sequential reaction chambers where they complete the second reaction shown above.

Sulfur



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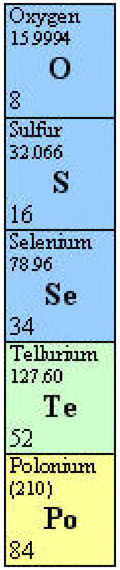
- The oxides of sulfur are strongly acidic. When sulfur trioxide is dissolved in water, sulfuric acid is produced:
- If sulfur trioxide is bubbled through concentrated sulfuric acid, we get “fuming sulfuric acid”:
- When power plants burn sulfur-containing coal or oils, they release sulfur dioxide which reacts with another pollutant, nitrogen dioxide, to produce sulfur trioxide and nitrogen monoxide:

  When the resulting sulfur trioxide dissolves in atmospheric water vapour, we get acid rain!

Sulfur



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- Like the halogens, sulfur forms oxoanions. We've already seen sulfate and sulfite. Sulfur also forms many more complicated oxoanions with bridging sulfur atoms or sulfur atoms replacing one or more oxygen atoms.
- Draw Lewis diagrams for sulfur trioxide and sulfite.

How do are these two species similar? How do they differ? If you dissolved 1 mole of each in a liter of water, which would give you a solution with a lower pH?