**Carbon**

**Discovered:** Known since ancient times. It was first recognized as an element in the second half of the 18th century.

**Name:** A.L. Lavoisier proposed *carbon* in 1789 from the Latin *carbo* meaning "charcoal." A.G. Werner and D.L.G. Harsten proposed *graphite* from the Greek *grafa* meaning "to write," referring to pencils, which were introduced in 1594. *Diamond* is a hybrid word from the Greek meaning "transparent" and "invincible." The blue color of the Hope diamond arises from a trace amount of boron substituting for carbon in the lattice. Likewise, trace nitrogen accounts for the yellow color of the Tiffany diamond. In 1985 a new allotrope of carbon *buckminsterfullerene* was created in the laboratory. It consists of 60 carbon atoms in an arrangement similar to surface of a soccer ball. Its name derives from the inventor of the geodesic dome whose same is very similar and it is found in interstellar space. Other enclosed structures with differing numbers of carbon atoms also exist.

**Occurrence:** Widespread, but not particularly plentiful in nature. Major sources: elemental forms, carbonates, CO₂, living and dead organic matter. (The first two are most important).

**Isolation:** Found naturally (both graphite and diamond); both can also be made artificially.

**Cost for 1 gram, 1 mole:** $0.04, $0.48 (graphite)

**Natural Isotopes:** ¹²C (98.89%) ¹³C (0.11%) ¹⁴C (trace)

**Physical and Chemical Properties:**

<table>
<thead>
<tr>
<th>Graphite</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very soft (Moh's &lt; 1)</td>
<td>Very hard (Moh's = 10)</td>
</tr>
<tr>
<td>Electrical conductor</td>
<td>Electrical insulator</td>
</tr>
<tr>
<td>Black in color</td>
<td>Colorless</td>
</tr>
<tr>
<td>Less dense form</td>
<td>More dense form</td>
</tr>
<tr>
<td>More reactive form</td>
<td>Less reactive form</td>
</tr>
<tr>
<td>Flaky texture</td>
<td></td>
</tr>
</tbody>
</table>

**Reactions:**

- burning: \[ C + O_2 \xrightarrow{\Delta} CO_2 \]
- \[ C + \frac{1}{2} O_2 \xrightarrow{\Delta} CO \]
- \[ H_2O(g) + C(s) \xrightarrow{\Delta} CO(g) + H_2(g) \] ("water-gas shift" reaction)

**Uses:**

**Graphite:**
- Solid lubricant
- Electrodes
- Crucibles
- Neutron moderator in nuclear reactors
- High strength composites
  (in tires, rackets, skis, etc.)

**Diamonds:**
- Grinding/abrasives
- Adornment
Chlorine

**Discovered:** By C.W. Scheele in 1774, but he thought it was a compound. Sir Humphrey Davy demonstrated that Cl₂ was an element in 1810.

**Name:** Proposed by Davy in 1811 it comes from the Greek *chloros* meaning "yellowish or light green" referring to its color.

The word *halogen* was introduced in 1811 by J.S.C. Schweigger to describe the property of chlorine to produce salts when directly reacted with metals. It comes from a hybrid of Greek words meaning "to produce sea salt."

**Occurrence:** Moderate to low abundance, widespread in nature, and never found free. Most chlorine is found in NaCl in either evaporated water pools or the ocean. MgCl₂ and CaCl₂ are also found in substantial quantities.

**Isolation:**

a) Electrolysis of aqueous NaCl (to Cl₂, H₂, and NaOH)
b) Electrolysis of molten NaCl (to Cl₂ and Na)

**Cost of 1 gram, 1 mole:** 0.23, $8.24

**Natural Isotopes:** ³⁵Cl (75.5%) ³⁷Cl (24.5%)

**Physical and Chemical Properties:**

- Yellow-green gas with a sharp odor
- Strong oxidant
- Very electronegative
- Very reactive
- Dissolves in and reacts with water
- Toxic

**Reactions:**

- Cl₂ + H₂ → No reaction
- Cl₂ + H₂ → 2 HCl
- Cl₂ + CO → Cl₂CO (phosgene, WW I poison gas)
- Cl₂ + H₂O ↔ HCl + HClO (gives bleach when NaOH is present)
- Cl₂ reacts with aqueous CaCl₂ at 0 °C to form solid Cl₂•7.3H₂O
- Cl₂ + PhI → cold → PhI•Cl₂ (a “solid form” of chlorine that is easily weighed)

**Uses:**

- Synthesis of chloro organic compounds
- Paper bleaching
- Disinfectants (e.g. of water supplies)
- Synthesis of inorganic chlorides
**Fluorine**

**Discovered:** First isolated by H. Moissan in 1886 after 74 years of efforts by various investigators (The unknown element had been observed as a constituent of minerals.)

**Name:** From the mineral fluorospar (CaF$_2$), suggested in 1812 by A.-M. Ampere (almost 75 years before it was isolated!). Fluorospar is derived from the Latin word *fluor* meaning "to flow." *Note:* Fluorescence was first observed as the light emission from fluorospar in 1852.

**Occurrence:** Moderately abundant, never occurs as the free element. Most common minerals: fluorite (CaF$_2$), cryolite (Na$_3$AlF$_6$), and fluorapatite (Ca$_5$(PO$_4$)$_3$F).

**Isolation:** Interestingly, the only practical method of preparing F$_2$ is the one used to isolate it the first time in 1886 (with safeguards to prevent the fire that happened then). Electrolysis of KF in anhydrous HF (1:2) at 72 ºC. H$_2$ is the by-product gas and must be kept separated from the F$_2$ to prevent explosions. The cells contain no flammable material and have a protective fluoride coating for the same reason.

**Cost of 1 gram, 1 mole:** $1.05, $19.90

**Natural Isotopes:** $^{19}$F (100%)

**Physical and Chemical Properties:**
- Most electronegative element
- Pale yellow gas that condenses to a canary yellow liquid
- Corrosive
- F-F bond energy is low
- Most reactive of the elements
- Finely divided metals, glass, ceramics, carbon, and water(!) spontaneously burn in the presence of F$_2$
- Low melting point
- Binary fluorides are unusually volatile (compared with the corresponding halides or oxides)

**Reactions:**
- U + 3 F$_2$ \[\rightarrow\] UF$_6$ (used to separate U isotopes for nuclear power, accounts for 70-80% of F$_2$ use)
- Cl$_2$ + 3 F$_2$ \[\rightarrow\] 2 ClF$_3$ (used as an incendiary by Germany in WWII)
- F$_2$ + organic compounds \[\rightarrow\] explosion and fire

**Uses:**
- Artificial blood (fully fluorinated long hydrocarbons stores large amounts of oxygen)
- Etching glass (HF)
- Hydrochlorofluorocarbons are used as refrigerants and as inert gases in the computer industry. Originally, chlorofluorocarbons were used for this purpose, but have been phased out of use because they damage the ozone layer. This is ironic as they were originally used because they were completely non-toxic and unreactive towards equipment.
- Dental health. (Fluoride is added to most drinking water supplies and toothpastes. It replaces a surface -OH group on the enamel making it less susceptible to acid attack.)
Nitrogen


Name: Proposed by J.-A.-C. Chaptal in 1790 from the realization that it was a component of HNO₃ and nitrates (from the Greek *niter* and *gen* meaning "to form from salt peter"). A.L. Lavoisier suggested *azote* (meaning "no life" referring to its inability to support aerobic life, c.f. azides, azo compounds, etc.). Likewise, the German term for nitrogen, *Stickstoff*, means "to choke."

Occurrence: N₂ is 75-78 volume %, mole %, and weight % of air. It is non-abundant in the crust, however KNO₃ and NaNO₃ deposits are found in some arid regions of the world.

Isolation: Liquification and distillation of air (b.p. -196 °C, 77 K)

Cost of 1 gram, 1 mole: $0.01, $0.24

Natural Isotopes: \(^{14}\text{N} (99.6\%)^{15}\text{N} (0.4\%)

Physical Properties: Odorless, colorless gas
Chemically inert
Very electronegative
Atomic N can be generated by passing an electrical discharge through a ca. 1 torr sample of N₂. (In spite of the very favorable thermodynamics of recombination, several minutes are required for complete reaction because at low pressure this is a termolecular process.)

Reactions:
\[
\begin{align*}
\text{N}_2 + 3 \text{H}_2 & \xrightleftharpoons[\text{high P}][\text{high T}] \ 2 \text{NH}_3 & \text{(ammonia)} \\
4 \text{NH}_3 + 8 \text{O}_2 & \xrightarrow{\text{\Delta}} 4 \text{HNO}_3 + 4 \text{H}_2\text{O} \\
\text{NH}_4\text{NO}_3 & \xrightarrow{\text{\Delta}} 2 \text{H}_2\text{O} + \text{N}_2\text{O} & \text{(laughing gas)} \\
\text{C}_3\text{H}_5(\text{OH})_3 + 3 \text{HNO}_3 & \xrightarrow{\text{catalyst}} 3 \text{H}_2\text{O} + \text{C}_3\text{H}_5(\text{NO}_3)_3 & \text{(nitroglycerine)}
\end{align*}
\]

Uses: NH₃ is the largest volume chemical produced in the U.S. (by moles) (It is the starting material for many N containing chemicals.) Fertilizers (4 of the top 13 chemicals produced in the U.S. in 1980 contained N and were connected to fertilizer synthesis.) Explosives (1,3,5-trinitrotoluene, nitroglycerin, etc.) Refrigerant (liquid N₂) Anesthetic (laughing gas) Comprises about 15% of proteins by weight
Oxygen

**Discovered:** J. Priestly and C.W. Scheele (independently) in 1773-74.

**Name:** By A.L. Lavoisier in 1777. It is a hybrid word derived from the Greek *oxys* meaning "acid former" from the belief that it was a constituent of all acids. "Ozone" is derived from the Greek word *ozein* meaning "to smell."

**Occurrence:** Comprises about 20% of our atmosphere, 45% of the earth's crust, and 89% of water. It is also by far and away the major component of bodies of water. There are 2 allotropes of oxygen: dioxygen (O\textsubscript{2}) and ozone (O\textsubscript{3}), both of which occur in nature. Almost all of the O\textsubscript{2} found in nature is of biological origin.

**Isolation:** Obtained by the fractional distillation of air. Ozone is formed by exposing dioxygen to an electric discharge or to ultraviolet light. One can often smell ozone near electrical equipment that produces sparks.

**Cost of 1 gram, 1 mole:** $0.07, $0.22

**Natural Isotopes:** $^{16}$O (99.8%) $^{17}$O (0.04%) $^{18}$O (0.2%)

<table>
<thead>
<tr>
<th>Physical and Chemical Properties</th>
<th>Dioxygen</th>
<th>Ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colorless, odorless gas</td>
<td>Safe to breathe</td>
<td>Blue gas with a sharp odor</td>
</tr>
<tr>
<td>Very reactive (reacts with every element except He, Ne, and Ar)</td>
<td>Strong oxidizer</td>
<td>Toxic ([O\textsubscript{3}] &gt; 1 ppm for time &gt; 10 min)</td>
</tr>
<tr>
<td>Fairly soluble in water and organic solvents</td>
<td>Blue when liquefied</td>
<td>Very strong oxidizer</td>
</tr>
<tr>
<td>Bent Structure</td>
<td></td>
<td>Bent Structure</td>
</tr>
</tbody>
</table>

**Reactions:**

**Dioxygen:**
\[ 2 \text{HC}=\text{CH} + 5 \text{O}_2 \xrightarrow{\Delta} 4 \text{CO}_2 + 2 \text{H}_2\text{O} \]
\[ 2 \text{H}_2 + \text{O}_2 \xrightarrow{\Delta} 2 \text{H}_2\text{O} \]

**Ozone:** Ozone is an important component of the stratosphere where it absorbs harmful UV radiation before it reaches the ground. This ozone layer may be in danger because of the slow diffusion of chlorofluorocarbons (freons) into the stratosphere. The reactions that are thought to occur there are shown below.

\[ \text{CF}_3\text{Cl} \xrightarrow{h\nu} \text{CF}_3 + \text{Cl} \]
\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \text{ (Note: This and the next reaction form a repeating chain.)} \]
\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]

**Uses:**
- Blast furnaces in steel making (atmosphere enrichment)
- Industrial NH\textsubscript{3}, MeOH, and ethylene oxide syntheses
- Rocket fuel (with H\textsubscript{2}), used in the space shuttle
Phosphorus

Discovered: By Hanning Brandt in 1669 (by putrefying urine, boiling it to a paste, then reductively distilling it; think about this next you don't like a lab that's been assigned)

Name: From the Greek (fos and fero) meaning “light bearing” because it glows in the dark when exposed to air. Brandt was the first person credited with naming an element. All previous elements had been known since antiquity.

Occurrence: Moderate abundance, widespread distribution, but never found pure. There are over 200 P containing minerals, the apatites (Ca₃(PO₄)₂•CaX₂) being the most significant.

Isolation: \[2\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 + 10\text{C} \rightarrow \text{P}_4 + 6\text{CaSiO}_3 + 10\text{CO}\]

Cost of 1 gram, 1 mole: $0.21, $6.38 (red)

Natural Isotopes: \(^{31}\text{P}\) (100%)

Physical and Chemical Properties:

**White P\(_4\)** - Most common form
- Most reactive form
- Crystalline
- Waxy consistency
- Slow oxidation of vapor emits yellow-green light (phosphorescence)
- Burns in air
- Highly toxic (fatal dose \(ca.\ 50\) mg)

**Red P\(_4\)** - Made by heating white P\(_4\) to \(ca.\ 300\) °C
- Less reactive than white
- Essentially non-toxic
- Polymeric

**Black P\(_4\)** - Made by heating white P\(_4\) under pressure
- Thermodynamically most stable form
- Semi-conductor
- Highly branched polymer

Reactions:
\[\text{P}_4 + \text{O}_2 \rightarrow \text{P}_4\text{O}_6\ or\ \text{P}_4\text{O}_{10}\]
\[\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4\]
\[\text{P}_4 + \text{S} \rightarrow \text{P}_4\text{S}_3\ \text{(matches that will strike anywhere)}\]

Uses:
- Fertilizers (as phosphates)
- Fine china (Ca₃(PO₄)₂)
- Detergents and water softeners (as phosphates)
Silicon

Discovered: J.J. Berzelius in 1824

Name: From the Latin *silex* for “flint.” It ends in -on because of its resemblance to carbon. Prehistoric weapons and tools were made with this silicon containing mineral.

Occurrence: It is the second most abundant element in the earth's crust, but only the seventh most abundant in the universe. It never occurs free and is almost always combined with oxygen. It is a component of many minerals: olivine (Mg$_2$SiO$_4$), quartz (SiO$_2$), amethyst, flint, opal, agate, jasper, granite, asbestos, micas, feldspars, etc.

Isolation: $\text{SiO}_2 + 2 \text{C} \xrightarrow{\Delta} \text{Si} + 2 \text{CO}$

Cost for 1 gram, 1 mole: $0.79, $22.00

Natural Isotopes: $^{28}\text{Si} (92.2\%)$  $^{29}\text{Si} (4.7\%)$  $^{30}\text{Si} (3.1\%)$

Physical and Chemical Properties: Semiconductor

Shiny blue-gray metallic luster
Low tendency towards catenation (doesn't form long chains with itself)
Multiple bonds are much weaker than for carbon analogues (because silicon doesn't use its p-orbitals for $\pi$-bonding)
Chemically inert (attacked by halogens, dilute alkali)
Very oxophilic

Reactions:

$\text{Si} + \text{C} \xrightarrow{2000^\circ\text{C}} (\text{SiC})_x$ (carborundum)

$\text{Si} + 2 \text{Cl}_2 \xrightarrow{\text{red heat}} \text{SiCl}_4$

Uses: Semi-conductors

Construction (SiO$_2$, sand in cement)
Recreation (SiO$_2$, sand on beach)
Glass (SiO$_2$)
Abrasives (SiC)
Synthetic oils, rubbers, and greases (silicones)
**Sulfur**

**Discovered:** By cavemen. First proposed as an element by A.L. Lavoisier in 1777.

**Name:** From the Latin word *sulphyrium*, which is derived from the Sanskrit *sulvere*, meaning "the enemy of copper." and is likely to be an alchemical term. It is called *brimstone* in the Bible, which is a corruption of the German word for sulfur *brennstein* meaning "stone that burns." It is a chalcogen which means "derived from copper (or bronze)" from the Greek.

**Occurrence:** Moderately abundant and widespread in nature, usually found in combined form. Minerals: sulfates [gypsum (CaSO$_4$$•$2H$_2$O), barite (BaSO$_4$), epsom salts (MgSO$_4$)], sulfides [pyrite (FeS$_2$, cinnabar (HgS), galena (PbS), sphalerite (ZnS), chalcopyrite (CuFeS$_2$)]. Elemental sulfur. H$_2$S is found in natural gas. Large deposits of elemental sulfur are located along the Gulf Coast in Texas and Louisiana.

**Isolation:** Hot water and compressed air is forced in the caprock of salt domes melting the sulfur and forcing it out. (The sulfur is probably the result of anaerobic bacteria consuming sulfate deposits.) This sulfur is usually very pure (> 99%). Some sulfur is obtained as a result of contamination of natural gas (CH$_4$) by H$_2$S (up to 30%).

**Cost for 1 gram, 1 mole:** $0.09, $2.87

**Natural Isotopes:** $^{32}$S (95.0%)  $^{33}$S (0.8%)  $^{34}$S (4.2%)  $^{36}$S (0.01%)

**Physical and Chemical Properties:**
- Shows the greatest allotropy of any element
- Has a strong tendency to catenate
- Very reactive, particularly at higher temperatures
- Combines directly with most elements
- Most common allotrope is orthorhombic $\alpha$-cyclo S$_8$
- Good thermal and electrical insulator
- Tasteless with little odor
- Colors of some sulfur allotropes
  - S$_2$ (g) - blue-violet
  - S$_3$ (g) - cherry red
  - S$_6$ - orange-red
  - S$_8$ (s) - yellow

**Reactions:**
- $S + O_2 \overset{\triangle}{\longrightarrow} SO_2$ ("burning")
- $2S + O_2 \overset{\triangle}{\longrightarrow} 2SO_3$
- $SO_3 + H_2O \longrightarrow H_2SO_4$ (a source of acid rain)

**Uses:**
- Fungicides and insecticides
- Vulcanizing rubber
- A component of black (gun)powder
- Almost 90% of sulfur is converted into $H_2SO_4$ (40 million tons/year world wide)
- Most uses of sulfur make use of sulfuric acid as a starting material
- Fertilizer (*ca. 50%* of the $H_2SO_4$)
- Synthetic fabrics
- Paper production