Background

Oxygen is ubiquitous; it comprises approximately 46% of the crust, 21% of the atmosphere, and 61% of the human body. Because of oxygen's high reactivity, it is most often found in compounds. Oxygen's high reactivity is due to its biradical electron configuration. As shown in a molecular orbital drawing of \( \text{O}_2 \), the two unpaired electrons make the molecule highly susceptible to bond formation.

Oxygen has two allotropes (dioxygen, \( \text{O}_2 \), and ozone, \( \text{O}_3 \)), both excellent oxidizing agents (Table P2). Oxygen is typically observed in the -2 oxidation state, in the form \( \text{O}^2^- \), but it can also form other ions such as peroxide, \( \text{O}_2^{2-} \), and superoxide, \( \text{O}_2^- \). With different possible oxidation states, many possible molecular compounds can be formed when an element reacts with oxygen. Many reactions involving oxygen occur in biological processes, including cellular respiration and photosynthesis.

Oxides are chemical compounds that contain at least one oxygen atom and at least one atom of another element. There are four principle oxidation states of oxygen: -2, -1, -1/2, and 0. The oxide ion, \( \text{O}^2^- \), has a oxidation state of -2; the peroxide ion, \( \text{O}_2^{2-} \), has a oxidation state of -1; and the superoxide ion, \( \text{O}_2^- \), has a oxidation state of -1/2. With metals, oxygen forms oxides that are largely ionic in character.

There are general trends in the reactions between main group elements and oxygen:

- Most nonmetals form the oxide with the highest possible oxidation state, with the halides excepted. Most metals form oxides with the oxygen in a -2 oxidation state.
- As a general rule, metal oxides are basic and nonmetal oxides are acidic. Basicity of an oxide increases with increasing ionic (metallic) character. Metal oxides, peroxides, and superoxides dissolve in water actually react with water to form basic solutions. Oxygen also forms covalent oxides with non-metals, that react with water to form acidic solutions.
- Oxygen does not react with fluorine or noble gases.

Exceptions to all of these trends are discussed below.

Reactions with Hydrogen

Oxygen reacts with hydrogen to produce two compounds: water (\( \text{H}_2\text{O} \)) and hydrogen peroxide (\( \text{H}_2\text{O}_2 \)). Water is a versatile compound and participates in acid-base equilibrium and oxidation-reduction reactions. It can act as an acid, base, reducing agent, or oxidizing agent. Water's multifaceted abilities make it one of the most important compounds on earth. The reaction between hydrogen and oxygen to form water is given below:

\[
2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O}\text{(l)}
\]
Hydrogen peroxide's potent oxidizing abilities give it great industrial potential. The following equation shows the reaction of hydrogen and oxygen to form hydrogen peroxide:

\[ \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 \label{2} \]

The product of this reaction is called a peroxide because oxygen is in the \( \text{O}_2^{2-} \) form (hydrogen has a +1 oxidation state). This concept is further explained regarding lithium below.

**Reactions with Group 1 Elements**

Oxygen reacts rapidly with Group 1 elements. All alkali metal oxides form basic solutions when dissolved in water. The principal combustion product is the most stable product with respect to the reactants. For example, with careful control of oxygen, the oxide \( \text{M}_2\text{O} \) (where \( \text{M} \) represents any alkali metal) can be formed with any of the alkali metals. When heated, lithium, sodium, potassium, rubidium, and cesium ignite through combustion reactions with oxygen.

**Lithium**

Lithium, the first metal in Group 1, reacts with oxygen to form \( \text{Li}_2\text{O} \) and burns with a red flame. The oxygen in this compound is an oxide (\( \text{O}^{2-} \)). The formation of \( \text{Li}_2\text{O} \), the principal combustion product, is illustrated by the equation below:

\[ 4 \text{Li}(s) + \text{O}_2(g) \rightarrow 2 \text{Li}_2\text{O}(s) \label{3} \]

However, if there is excess oxygen present, it is possible that a small amount of the compound \( \text{Li}_2\text{O}_2 \) can be formed. Because alkali metals always have a +1 oxidation state, oxygen is in the \( \text{O}_2^{2-} \) form. When oxygen is in this state, the compound is called a peroxide. The formation of this peroxide, the less-likely non-principal combustion product, under excess oxygen is illustrated by the equation below:

\[ 2 \text{Li}(s) + \text{O}_2(g) \rightarrow \text{Li}_2\text{O}_2(s) \label{4} \]

**Sodium**

Sodium burns in air with often little more than an orange glow. Using larger amounts of sodium or burning it in pure oxygen produces a strong orange flame. A white solid mixture of sodium oxide and sodium peroxide is formed. The equation for the formation of the simple oxide is analogous to that for lithium:

\[ 4 \text{Na}(s) + \text{O}_2(g) \rightarrow 2\text{Na}_2\text{O}(s) \label{5} \]

Likewise, the reaction for peroxide formation takes the same form for both metals:

\[ 2 \text{Na}(s) + \text{O}_2(g) \rightarrow \text{Na}_2\text{O}_2(s) \label{6} \]
Potassium

Small pieces of potassium heated in air tend to melt instantly into a mixture of potassium peroxide and potassium superoxide with no visible flame. Larger pieces of potassium burn with a lilac-colored flame. The equation for the formation of the peroxide is identical to that for sodium (click here for more information):

\[ 2K(s) + O_2 (g) \rightarrow K_2O_2 (s) \label{7}\]

The superoxide generating reaction is given below:

\[ K(s) + O_2 (g) \rightarrow KO_2 (s) \label{8}\]

Other alkali metals

The other alkali metals (Rb, Cs, Fr) form superoxide compounds (in which oxygen takes the form \(O_2^-\)) as the principal combustion products. The following equation shows the formation of superoxide, where \(M\) represents K, Rb, Cs, or Fr:

\[ M(s) + O_2(g) \rightarrow MO_2(s) \label{9}\]

These compounds tend to be effective oxidizing agents due to the fact that \(O_2^-\) is one electron short of a complete octet and thus has a strong affinity for another electron. It is easily reduced, and therefore act as an effective oxidizing agent.

Reactions with Group 2 Elements

The elements of Group 2 are beryllium, magnesium, calcium, strontium, barium, and radioactive radium. Alkaline earth metals also react with oxygen, though not as rapidly as Group 1 metals; these reactions also require heating. Similarly to Group 1 oxides, most group 2 oxides and hydroxides are only slightly soluble in water and form basic, or alkaline solutions.
All Group 2 metals all react similarly, burning to form oxides (compounds containing the $O^{2-}$ ion) as shown:

$$2 \, M(s) + O_2(g) \rightarrow 2 \, MO(s) \label{10}$$

Once initiated, the reactions with oxygen are vigorous. The only peroxides (compounds containing the $O_2^{2-}$ ion) that can be formed from alkaline metals are strontium peroxide and barium peroxide. Both reactions require heat and excess oxygen. The general reaction is given below:

$$M(s) + O_2(g) \rightarrow MO_2(s) \label{11}$$

where $M$ represents Sr or Ba.

**Beryllium**

Beryllium is unreactive with air and water. The chemical behavior of beryllium is best attributed to its small size and high ionization energy of its atoms.

**All other group 2 metals**

Except beryllium, the other alkaline earth metals form oxides in air at room temperature.

$$2 \, M(s) + O_2(g) \rightarrow 2 \, MO(s) \label{12}$$

where $M$ represents Be, Mg, Ca, Sr, Ba, or Ra.

Peroxides, of the form $MO_2^-$, are formed for all these elements except beryllium as shown:

$$M(s) + O_2(g) \rightarrow MO_2(s) \label{13}$$

Magnesium, calcium, strontium and barium oxides react with water to form hydroxides:

$$MO(s) + H_2O(l) \rightarrow M(OH)_2(s) \label{14}$$

All the oxides and hydroxides of the group 2 metals, except of those of beryllium, are bases:

$$M(OH)_2(s) \rightarrow M^{2+}(aq) + 2OH^-(aq) \label{15}$$

**Reactions with Group 13 Elements**

**Group 13** consists of the following elements: boron, aluminum, gallium, indium, and thallium. Boron is the only element in this group that possesses no metallic properties. These elements vary in their reactions with oxygen. Recall that oxides of metals are basic and oxides of nonmetals are acidic; this is true for all elements in Group 13, except Al and Ga.

All other Group 13 elements also produce compounds of the form of $M_2O_3$, but adhere to the acid-base rules of metal and nonmetal oxides. Here is the equation of the reaction of oxygen and a Group 13 element:
\[4M(s) + 3O_2(g) \rightarrow 2M_2O_3(s) \label{16}\]

where M is any Group 13 element. At high temperatures, thallium also reacts with oxygen to produce Tl_2O:

\[4Tl(s) + O_2(g) \rightarrow 2Tl_2O \label{17}\]

**Boron:**

The most common oxide form of boron, B_2O_3 or boron trioxide, is obtained by heating boric acid:

\[2B(OH)_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O \label{18}\]

**Aluminum:**

Aluminum occurs almost exclusively in the +3 oxidation state. It rapidly reacts with oxygen in air to give a water-insoluble coating of Al_2O_3. This oxide layer protects the metal beneath from further corrosion. The reaction is shown below:

\[4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3 \label{19}\]

Aluminum trioxide, Al_2O_3, is amphoteric (acts both as an acid and a base):

\[Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l) \label{20}\]

\[Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq) \label{21}\]

Except for thallium in which the +1 oxidation state is more stable than the +3 state, aluminum, gallium, and indium favor +3 oxidation states.

All of group 13 metal elements are known to form a trivalent oxide.

\[4M(s) + 3O_2(g) \rightarrow 2M_2O_3(s) \label{22}\]

with M represents Al, Ga, In, or Tl

Thallium is the only element in this group favors the formation of oxide over trioxide.

\[2M(s) + O_2(g) \rightarrow 2MO(s) \label{23}\]

**Reactions with Group 14 Elements**

**Group 14** is made up of both metals (toward the bottom of the group), metalloids, and nonmetals (at the top of the group). The oxides of the top of Group 4 elements are slightly acidic, and the acidity of the oxides decreases down the group.

- **Non-metal:** The non-metal carbon of Group 14 (and its compounds) burn to form \(CO_{2}(g)\) and, in smaller amounts, \(CO_{(g)}\); both are acidic under different conditions. Carbon monoxide is only slightly soluble in water and does not react with it. Click here for more information.

- **Metalloid:** The metalloid silicon reacts with oxygen to form only one stable compound, \(SiO_{2}\), which dissolves slightly in water and is weakly acidic (Figure 2).
• The three metals in this group have many different oxide compounds due to their extended octets. All of these oxides are amphoteric (exhibit both basic and acidic properties). For example:
  - Germanium: \((\text{GeO}_1), (\text{GeO}_2)\)
  - Tin: \((\text{SnO}_1), (\text{SnO}_2)\)
  - Lead: \((\text{PbO}_1), (\text{PbO}_2), (\text{Pb}_3\text{O}_4)\)

![Figure 2: \((\text{SiO}_2)\): There are various different structures for silicon dioxide. The easiest to remember and draw is based on a diamond structure with each of the silicon atoms being bridged to its other four neighbors via an oxygen atom.]

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**Reactions with Group 15 Elements**

The nitrogen family, Group 15, is capable of reacting with oxygen in many different ways. Nitrogen and phosphorus are nonmetallic, arsenic and antimony are metalloids, and bismuth is metallic.

**Nitrogen**

Nitrogen reacts with oxygen to form many oxides ranging in oxidation states from +1 to +5: All these oxides are gases at room temperature except for \(\text{N}_2\text{O}_5\), which is solid. The nitrogen oxides are given below:

\[\text{NO}, \text{N}_2\text{O}, \text{N}_2\text{O}_3, \text{NO}_2, \text{N}_2\text{O}_5\]

All of these reactions are endothermic, requiring energy for oxygen to react directly with \(\text{N}_2(g)\). The oxides of nitrogen are acidic (because they are nonmetal oxides). \(\text{N}_2\text{O}_3\) and \(\text{N}_2\text{O}_5\) react with water to give acidic solutions of oxoacids. These reactions are shown below:

\[
\text{Nitrous acid: } [\text{N}_2\text{O}_3(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_2(aq) \text{ \label{24}}]\]

\[
\text{Nitric acid: } [\text{N}_2\text{O}_5(s) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(aq) \text{ \label{25}}]\]

**Phosphorus**

There are two forms of allotropes of phosphorus, white phosphorus and red phosphorus. Red phosphorus is less reactive than white phosphorus. Phosphorus reacts with oxygen, usually forming two oxides depending on the amount available oxygen: \(\text{P}_4\text{O}_6\) when reacted with a limited supply of oxygen, and \(\text{P}_4\text{O}_{10}\) when reacted with excess oxygen; the latter is shown below.
On rare occasions, $\text{P}_4\text{O}_7$, $\text{P}_4\text{O}_8$, and $\text{P}_4\text{O}_9$ are also formed, but in small amounts.

Both $\text{P}_4\text{O}_4$ and $\text{P}_4\text{O}_{10}$ react with water to generate oxoacids. Reactions are shown below.

Phosphorous acid: $\text{\textit{27}}$ \[\text{P}_4\text{O}_6(l) + 6\text{H}_2\text{O}(l) \rightarrow 4\text{H}_3\text{PO}_3(aq)\]

Phosphoric acid: $\text{\textit{28}}$ \[\text{P}_4\text{O}_{10}(s) + 6\text{H}_2\text{O}(l) \rightarrow 4\text{H}_3\text{PO}_4(aq)\]

Other Group 15 Elements

Arsenic, antimony and bismuth react with oxygen when burned. The common oxidation states for arsenic, antimony, and bismuth are +3 and +5. There are two main types of oxides for each element:

- Arsenic: $\text{As}_2\text{O}_3$, $\text{As}_2\text{O}_5$
- Antimony: $\text{Sb}_2\text{O}_3$, $\text{Sb}_2\text{O}_5$
- Bismuth: $\text{Bi}_2\text{O}_3$, $\text{Bi}_2\text{O}_5$

There are other oxides, such as $\text{Sb}_4\text{O}_{10}$, that are not formed directly through reaction with oxygen. Arsenic(III) oxide and antimony(III) oxide are amphoteric, whereas bismuth(III) oxide acts only as a base (this is because it is the most metallic element in the group).

Reactions with Group 16 Elements

The elements in Group 16 include oxygen, sulfur, selenium, tellurium, and polonium. Oxygen reacts with the elements in its own group to form various oxides, mostly in the form of $\text{AO}_2$ and $\text{AO}_3$.

Oxygen

Although oxygen is located in Group 16, it is unique in its extreme electronegativity; this allows it to readily gain electrons and create hydrogen bonds. Because it is the smallest element in its group, it is capable of forming double bonds. It has no d-orbitals, and cannot expand its valence shell.

Oxygen is capable of reacting with itself, forming allotropes. One of oxygen's allotropes, ozone ($\text{O}_3$), is formed when oxygen gas, $\text{O}_2$, is subjected to ultraviolet light.

Sulfur

Sulfur dioxide, $\text{SO}_2$, and sulfur trioxide, $\text{SO}_3$, are the only common sulfur oxides.

\[\text{\textit{29}}\] $\text{S(s) + O}_2(g) \rightarrow \text{SO}_2(g)$

Sulfur's reaction with oxygen produces the oxides mentioned above as well as oxoacids. All are powerful oxidizing agents. $\text{SO}_2$ is mainly used to make $\text{SO}_3$, which reacts with water to produce sulfuric acid (recall that nonmetals form acidic oxides). These sequential reactions are shown below:
Selenium and tellurium

Selenium and tellurium adopt compounds of the forms AO₂, AO₃, and AO.

Reactions with Group 17 Elements

The elements in Group 17 include fluorine, chlorine, bromine, and iodine. These elements are called halogens, from Greek roots translating to "salt formers." The halogens react with oxygen, but many of the resulting compounds are unstable, lasting for only moments at a time. They range in structure from X₂O to X₂O₇, where X represents a halogen. Their extended octets allow them to bond with many oxygen atoms at a time.

**Fluorine:**

The most electronegative element adopts the -1 oxidation state. Fluorine and oxygen form OF₂, which is known as oxygen fluoride.

\[2 \text{F}_2 + 2\text{NaOH} \rightarrow \text{OF}_2 + 2 \text{NaF} + \text{H}_2\text{O} \]

**Other Halogens**

The other halogens form oxoacids instead of oxides. For example:

<table>
<thead>
<tr>
<th>Oxidation state of halogen</th>
<th>Chlorine</th>
<th>Bromine</th>
<th>Iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>HOCl</td>
<td>HOBr</td>
<td>HOI</td>
</tr>
<tr>
<td>+3</td>
<td>HClO₂</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>+5</td>
<td>HClO₃</td>
<td>HBrO₃</td>
<td>HIO HIO₃</td>
</tr>
<tr>
<td>+7</td>
<td>HClO₄</td>
<td>HBrO₄</td>
<td>HIO₄; H₅IO₆</td>
</tr>
</tbody>
</table>

Reactions with Group 18 Elements

The Group 18 noble gases include helium, neon, krypton, xenon, and radon. Noble gases are chemically inert with the exception of xenon, which reacts with oxygen to form XeO₃ and XeO₄ at low temperatures and high pressures. The ionization energy of xenon is low enough for the electronegative oxygen atom to capture electrons. XeO₃ is highly unstable, and is known to spontaneously detonate in a clean, dry environment.
References

1. Reactions of Selenium and Oxygen. Matrix Infrared Spectra and Density Functional Calculations of Novel SexOy Molecule
2. G. Dana Brabson and, Lester Andrews, Colin J. Marsden. The Journal of Physical Chemistry 1996 100 (41), 16487-16494

Problems

1. If there are 4.00 g of potassium, how much K$_2$O is created when during combustion (in excess oxygen)?
2. Which noble gas(es), if any, react with oxygen? Why?
3. Complete and balance the following reaction: Al(s) + O$_2$(g) →
4. What is the best environment for nitrogen and oxygen to react in?
5. What are the principal combustion products of each Group 1 element with oxygen?

Solutions

1. 0.00 g K$_2$O. Potassium reacts with oxygen to form K$_2$O$_2$ and KO$_2$ only.
2. Xenon, because the first ionization energy is low enough, allowing oxygen to bond to the xenon atom.
3. 4Al(s) + 3O$_2$(g) → Al$_2$O$_3$(s)
4. High temperatures - it takes energy to cause those reactions.
5. Li generally forms Li$_2$O. Na usually forms Na$_2$O$_2$. The rest of Group 1 elements tend to form compounds in the form of MO$_2$ where M is K, Rb, Cs, or Fr.

Contributors

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