Classification of metal oxides may be done according to structure, as above, or according to acid-base character as shown on the next chart. Classification according to structure type is useful in many ways. Ionic oxides, and related compounds, always react with water to generate basic solutions. Those molecular covalent oxides that react with water (most do, a few do not) always generate acidic solutions. The situation with the polymeric oxides is more complex as indicated in the next chart. However, it is important to realize that there are actually two types of “polymeric” compounds in the above chart, those with truly extended structures like SiO₂ and Al₂O₃, and molecular species such as P₃O₆ and P₄O₁₀ and other Group 15 analogs. There is a very great difference in the rate and extent of the reactivity of some of these species toward water that can be directly related to the nature of their “polymeric” structure.
Basic oxides react with water to generate hydroxide, e.g., \( \text{Na}_2\text{O} + \text{H}_2\text{O} = 2 \text{Na}^+ + 2 \text{OH}^- \)

Similar reactivity is observed for Group 1 and Group 2 salts of anions of other p-block elements. For example, \( \text{Mg}_3\text{N}_2 + 6 \text{H}_2\text{O} = 3 \text{Mg}^{2+} + 6 \text{OH}^- + 2 \text{NH}_3 \).

Amphoteric oxides display both acidic and basic reactivity as illustrated below for \( \text{Al}_2\text{O}_3 \) (alumina).

\[
\text{Al}_2\text{O}_3 + 6 \text{H}_3\text{O}^+ + 3 \text{H}_2\text{O} = 2 \left[ \text{Al(OH}_2\text{)}_6\right]^{3+}
\]

\[
\text{Al}_2\text{O}_3 + 2 \text{OH}^- + 3 \text{H}_2\text{O} = 2 \text{Al(OH)}_4^-
\]

Aluminum is manufactured by the electrolysis of alumina, which is obtained from the mineral Bauxite. Separation of alumina from the other constituents in the mineral is accomplished by dissolution of the alumina according to the above equation. The alumina is recovered by precipitation using \( \text{CO}_2 \), an acidic oxide, to reduce the hydroxide concentration. A stoichiometric reaction can be written involving \( \text{Al(OH)}_4^- \).

\[
2 \text{Al(OH)}_4^- + 2 \text{CO}_2 = \text{Al}_2\text{O}_3 + 2 \text{HCO}_3^- + 3 \text{H}_2\text{O}
\]

All of the elements shown in boldface type in the chart form acidic oxides, sometimes more than one when the element can exist in more than one oxidation state.

Examples of the acidic oxides and their reactions are given on the next page.
Each of the following reactions generates hydronium ion by reaction of the oxide with water. It is important to realize that these reactions can be thought of as involving an initial interaction between the HOMO of a Lewis base (water) and the LUMO of a Lewis acid (the oxide) followed by a proton transfer to another water molecule. In general similar reactions occur with other Lewis bases ($\text{NH}_3$, $\text{OH}^-$, $\text{X}^-$) to give products (adducts) in which there may not be an ionizable hydrogen.

\[
\text{CO}_2 + 2 \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HCO}_3^-
\]

\[
\text{CO}_2 + \text{OH}^- = \text{HOCO}_2^{-}
\]

\[
\text{CO}_2 + 2 \text{OH}^- = \text{CO}_3^{2-} + \text{H}_2\text{O}
\]

It is useful here to ask why is carbon dioxide a monomeric, molecular species whereas silicon dioxide is a polymeric material. The reason is that pi bonds that involve p-orbitals other than 2p orbitals are invariably sufficiently weak that such pi bonds are weaker than two sigma bonds, which is not the case for second row elements.

\[
\begin{align*}
\text{C-O} & \quad 335 \text{ kJ mol}^{-1} \times 2 = 670 \text{ kJ mol}^{-1} \\
\text{C=O} & \quad 715 \text{ kJ mol}^{-1} \\
\text{Si-O} & \quad 420 \text{ kJ mol}^{-1} \times 2 = 840 \text{ kJ mol}^{-1} \\
\text{Si=O} & \quad 590 \text{ kJ mol}^{-1}
\end{align*}
\]

However, although SiO$_2$ does not react with water to generate an acidic solution its acidic properties are exhibited by its reaction with base, i.e.,

\[
\text{SiO}_2 + 4 \text{OH}^- = \text{SiO}_4^{4-} + 2 \text{H}_2\text{O}
\]

$\text{SiO}_4^{4-}$ reacts with protons to generate condensed species. For example,

\[
\text{SiO}_4^{4-} + 2 \text{H}_3\text{O}^+ = \text{O}_3\text{Si-O-SiO}_3^{6-} + 3 \text{H}_2\text{O}
\]
Further condensations lead to more highly polymerized species. When these reactions occur on geological time scales they result in the formation of silicate minerals as illustrated in Figure 21-7 of Oxtoby.

\[
\text{SO}_2 + 2 \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HSO}_3^- \\
\text{SO}_3 + 2 \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HSO}_4^- \\
P_4\text{O}_{10} + 10 \text{H}_2\text{O} = 4 \text{H}_3\text{O}^+ + 4 \text{H}_2\text{PO}_4^{2-}
\]

\(P_4\text{O}_{10}\) is the acid anhydride of phosphoric acid and is such a powerful dehydrating agent and can be used to generate acid anhydrides of other hydroxylic acids, i.e.,

\[
P_4\text{O}_{10} + 12 \text{HONO}_2 = 6 \text{N}_2\text{O}_5 + 4 \text{H}_3\text{PO}_4
\]

\(\text{N}_2\text{O}_5\) will react with water to regenerate \(\text{HONO}_2\).

Some of the nitrogen oxides are not acidic, for example \(\text{NO}\) and \(\text{N}_2\text{O}\). The paramagnetic \(\text{NO}\) and \(\text{NO}_2\) react to give other oxides.

\[
\text{NO} + \text{NO}_2 = \text{N}_2\text{O}_3 \\
2 \text{NO}_2 = \text{N}_2\text{O}_4
\]

Finally some of the nitrogen oxides that are classified as acidic undergo redox reactions to generate the acidic species. This is illustrated by the reaction sequence leading to formation of nitric acid, which is actually based upon hydrogen and nitrogen.

\[
\text{N}_2 + 3 \text{H}_2 = 2 \text{NH}_3 \\
2 \text{NH}_3 + 5/2 \text{O}_2 = 2 \text{NO} + 3 \text{H}_2\text{O} \\
\text{NO} + 1/2 \text{O}_2 = \text{NO}_2 \\
2 \text{NO}_2 + \text{H}_2\text{O} = \text{HONO}_2 + \text{HONO} \\
3 \text{HONO} + = \text{HONO}_2 + 2 \text{NO} + \text{H}_2\text{O} \text{ recycle the NO}
\]