CARBON DIOXIDE, CO₂

Carbon dioxide, CO₂, is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm. Commercially, CO₂ finds uses as a refrigerant (dry ice is solid CO₂), in beverage carbonation, and in fire extinguishers. Because the concentration of carbon dioxide in the atmosphere is low, it is not practical to obtain the gas by extracting it from air. Most commercial carbon dioxide is recovered as a by-product of other processes, such as the production of ethanol by fermentation and the manufacture of ammonia. Some CO₂ is obtained from the combustion of coke or other carbon-containing fuels.

\[
C(\text{coke}) + O₂(g) \rightarrow CO₂(g)
\]

Carbon dioxide is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO₂ in the atmosphere has increased over the past century, now rising at a rate of about 1 ppm per year. Major changes in global climate could result from a continued increase in CO₂ concentration.

In addition to being a component of the atmosphere, carbon dioxide also dissolves in the water of the oceans. At room temperature, the solubility of carbon dioxide is about 90 cm³ of CO₂ per 100 mL of water. In aqueous solution, carbon dioxide exists in many forms. First, it simply dissolves.

\[
CO₂(g) \rightarrow CO₂(aq)
\]

Then, an equilibrium is established between the dissolved CO₂ and H₂CO₃, carbonic acid.

\[
CO₂(aq) + H₂O(l) \leftrightarrow H₂CO₃(aq)
\]

Only about 1% of the dissolved CO₂ exists as H₂CO₃. Carbonic acid is a weak acid which dissociates in two steps.

\[
\begin{align*}
H₂CO₃ & \leftrightarrow H^+ + HCO₃^- & K_{a₁} = 4.2 \times 10^{-7} \\
HCO₃^- & \leftrightarrow H^+ + CO₃^{2-} & K_{a₂} = 4.8 \times 10^{-11}
\end{align*}
\]

As carbon dioxide dissolves in sea water, an equilibrium is established involving the carbonate ion, CO₃^{2-}. The carbonate anion interacts with cations in seawater. According to the solubility rules, “all carbonates are insoluble except those of ammonium and Group IA elements.” Therefore, the carbonate ions cause the precipitation of certain ions. For example, Ca^{2+} and Mg^{2+} ions precipitate from large bodies of water as carbonates. For CaCO₃, the value of K_{sp} is 5 × 10⁻⁹, and for MgCO₃, K_{sp} is 2 × 10⁻⁷. Extensive deposits of limestone (CaCO₃) and dolomite (mixed CaCO₃ and MgCO₃) have been formed in this way. Calcium carbonate is also the main constituent of marble, chalk, pearls, coral reefs, and clam shells.

Although “insoluble” in water, calcium carbonate dissolves in acidic solutions. The carbonate ion behaves as a Bronsted base.

\[
\text{CaCO}_₃(s) + 2 H^+(aq) \rightarrow \text{Ca}^{2+}(aq) + H₂CO₃(aq)
\]

The aqueous carbonic acid dissociates, producing carbon dioxide gas.

\[
H₂CO₃(aq) \rightarrow H₂O(l) + CO₂(g)
\]

In nature, surface water often becomes acidic because atmospheric CO₂ dissolves in it. This acidic water can dissolve limestone:
This reaction occurs in three steps.

\[ \text{CaCO}_3(s) \quad \leftrightarrow \quad \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \]

\[ \text{CO}_2(aq) + \text{H}_2\text{O}(l) \quad \leftrightarrow \quad \text{H}_2\text{CO}_3(aq) \]

\[ \text{H}_2\text{CO}_3(aq) + \text{CO}_3^{2-}(aq) \quad \leftrightarrow \quad 2 \text{HCO}_3^-(aq) \]

In the third step, carbonate ions accept hydrogen ions from carbonic acid. This reaction often occurs underground when rainwater saturated with CO$_2$ seeps through a layer of limestone. As the water dissolves calcium carbonate, it forms openings in the limestone. Caves from which the limestone has been dissolved are often prevalent in areas where there are large deposits of CaCO$_3$ (e.g., Mammoth Cave, Carlsbad Caverns, and Cave of the Mounds). If the water containing dissolved Ca(HCO$_3$)$_2$ reaches the ceiling of a cavern, the water will evaporate. As it evaporates, carbon dioxide escapes, and calcium carbonate deposits on the ceiling.

\[ \text{Ca}^{2+}(aq) + 2 \text{HCO}_3^-(aq) \quad \rightarrow \quad \text{H}_2\text{O}(g) + \text{CO}_2(g) + \text{CaCO}_3(s) \]

Recently, some commercial dry cleaners have begun replacing the dry cleaning solvent perchloroethylene, Cl$_2$C=CCl$_2$, with liquid CO$_2$. Perchloroethylene is a possible carcinogen, and has been linked to bladder, esophageal, and other cancers. Carbon dioxide does not exist in liquid form at atmospheric pressure at any temperature. The pressure-temperature phase diagram of CO$_2$ shows that liquid carbon dioxide at 20°C requires a pressure of 30 atmospheres. The lowest pressure at which liquid CO$_2$ exists is at the triple point, namely 5.11 atm at –56.6°C.

The high pressures needed for liquid CO$_2$ require specialized washing machines. Clothing is immersed in liquid CO$_2$ in a highly pressurized cylinder and agitated by high-velocity fluid jets to remove soils, then dried in a high-velocity spin cycle. Liquid CO$_2$ has drawn high marks in Consumer Reports' tests for its cleaning results, and it is environmentally friendly since it produces no chlorinated pollutants.