Chemical of the Week

CARBON DIOXIDE, CO_2

Carbon dioxide, CO_2, 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, CO_2 finds uses as a refrigerant (dry ice is solid CO_2), 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 CO_2 is obtained from the combustion of coke or other carbon-containing fuels.

$$C(coke) + O_2(g) \longrightarrow CO_2(g)$$

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 CO_2 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 CO_2 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 cm^3 of CO_2 per 100 mL of water. In aqueous solution, carbon dioxide exists in many forms. First, it simply dissolves.

$$CO_2(g) \longrightarrow CO_2(aq)$$

Then, an equilibrium is established between the dissolved CO_2 and H_2CO_3, carbonic acid.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Only about 1% of the dissolved CO_2 exists as H_2CO_3. Carbonic acid is a weak acid which dissociates in two steps.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_{a1} = 4.2 \times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_{a2} = 4.8 \times 10^{-11}$$

As carbon dioxide dissolves in sea water, an equilibrium is established involving the carbonate ion, CO_3^{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 $CaCO_3$, the value of K_{sp} is 5×10^{-9}, and for $MgCO_3$, K_{sp} is 2×10^{-3}. Extensive deposits of limestone ($CaCO_3$) and dolomite (mixed $CaCO_3$ and $MgCO_3$) 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 Brønsted base.

$$CaCO_3(s) + 2\,H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2CO_3(aq)$$

The aqueous carbonic acid dissociates, producing carbon dioxide gas.

$$H_2CO_3(aq) \longrightarrow H_2O(l) + CO_2(g)$$

In nature, surface water often becomes acidic because atmospheric CO_2 dissolves in it. This acidic water can dissolve limestone:

$$CO_2(aq) + H_2O(l) + CaCO_3(s) \longrightarrow Ca^{2+}(aq) + 2\ HCO_3^{-}(aq)$$

This reaction occurs in three steps.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

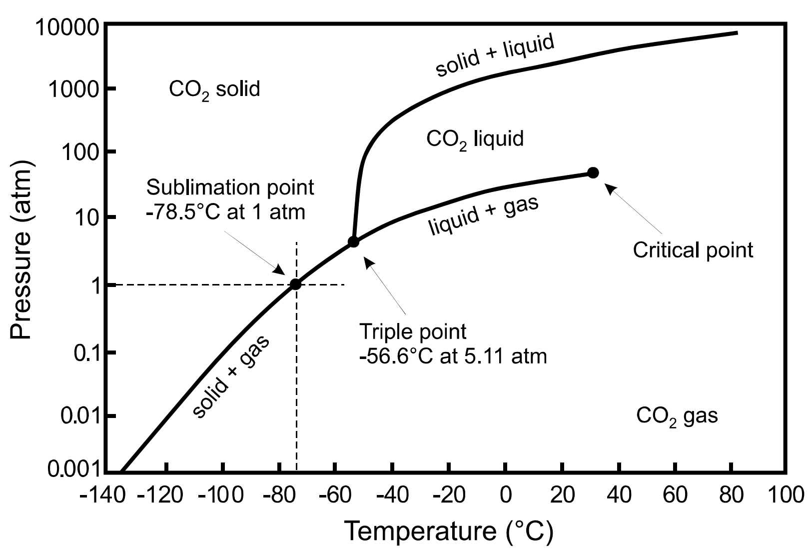
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + CO_3^{2-}(aq) \rightleftharpoons 2\ HCO_3^{-}(aq)$$

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.

$$Ca^{2+}(aq) + 2\ HCO_3^{-}(aq) \longrightarrow H_2O(g) + CO_2(g) + CaCO_3(s)$$

Recently, some commercial dry cleaners have begun replacing the dry cleaning solvent perchloroethylene, $Cl_2C{=}CCl_2$, with liquid CO_2. Perchloroethylene is a possible carcinogen, and has been linked to bladder, esophogeal, 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.



Pressure-Temperature phase diagram for CO_2.

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.