The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, CHCl₃. Considering the role of the solvent’s chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C₆H₁₄, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure 13.5.1). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

![Figure 13.5.1: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.](image)

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water’s ecosystems and, in severe cases, can result in large-scale fish kills (Figure 13.5.2).
The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO$_2$ at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 13.5.3). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become “flat.”

For many gaseous solutes, the relation between solubility, $C_g$, and partial pressure, $P_g$, is a proportional one:

$$C_g = kP_g$$

where $k$ is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry’s law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

**Example 13.5.1: Application of Henry’s Law**

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is $1.38 \times 10^{-3}$ mol L$^{-1}$. Use Henry’s law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth’s atmosphere.
Solution

According to Henry's law, for an ideal solution the solubility, $C_g$, of a gas ($1.38 \times 10^{-3}$ mol L$^{-1}$, in this case) is directly proportional to the pressure, $P_g$, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case).

Because we know both $C_g$ and $P_g$, we can rearrange this expression to solve for $k$.

\[
\begin{align*}
C_g &= kP_g \\
&= \frac{C_g}{P_g} \\
&= \frac{1.38 \times 10^{-3}\text{ mol L}^{-1}}{101.3\text{ kPa}} \\
&= 1.36 \times 10^{-5}\text{ mol L}^{-1}\text{ kPa}^{-1} \\
&= (1.82 \times 10^{-6}\text{ mol L}^{-1}\text{ torr}^{-1})
\end{align*}
\]

Now we can use $k$ to find the solubility at the lower pressure.

\[
\begin{align*}
[C_g] &= kP_g \\
&= (1.36 \times 10^{-5}\text{ mol L}^{-1}\text{ kPa}^{-1}) \times 20.7\text{ kPa} \\
&= (1.82 \times 10^{-6}\text{ mol L}^{-1}\text{ torr}^{-1}) \times 155\text{ torr} \\
&= 2.82 \times 10^{-4}\text{ mol L}^{-1}
\end{align*}
\]

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 13.5.1

Check Your Learning Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of $1.45 \times 10^{-3}$ g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer:

$7.25 \times 10^{-3}$ g

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.

\[
\begin{align*}
\text{H}_3\text{N}^+ + \text{H}_2\text{O} &\rightleftharpoons \left[\text{H}_4\text{N}^+\right]^+ + \left[\text{OH}^-ight]^-
\end{align*}
\]

Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure 13.5.5), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover
due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO$_2$ were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.

Figure 13.5.5: (a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO$_2$ vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)

### Case Study: Decompression Sickness (“The Bends”)

Decompression sickness (DCS), or “the bends,” is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver’s blood are proportionally higher per Henry’s law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver’s blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 13.5.4).

Figure 13.5.4: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.
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