

13.4: Solution Equilibrium and Factors Affecting Solubility

Key Concept Video Solution Equilibrium and Factors Affecting Solubility

The dissolution of a solute in a solvent is an equilibrium process similar to the equilibrium process associated with a state change (discussed in [Chapter 11](#)). Imagine, from a particulate viewpoint, the dissolution of a solid solute such as sodium chloride in a liquid solvent such as water ([Figure 13.8](#)). Initially, water molecules rapidly solvate sodium cations and chloride anions, resulting in a noticeable decrease in the amount of solid sodium chloride in the water. Over time, however, the concentration of dissolved sodium chloride in the solution increases. This dissolved sodium chloride begins to recrystallize as solid sodium chloride. Initially, the rate of dissolution far exceeds the rate of recrystallization, but as the concentration of dissolved sodium chloride increases, the rate of recrystallization also increases. Eventually, the rates of dissolution and recrystallization become equal—**dynamic equilibrium** has been reached:

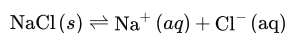
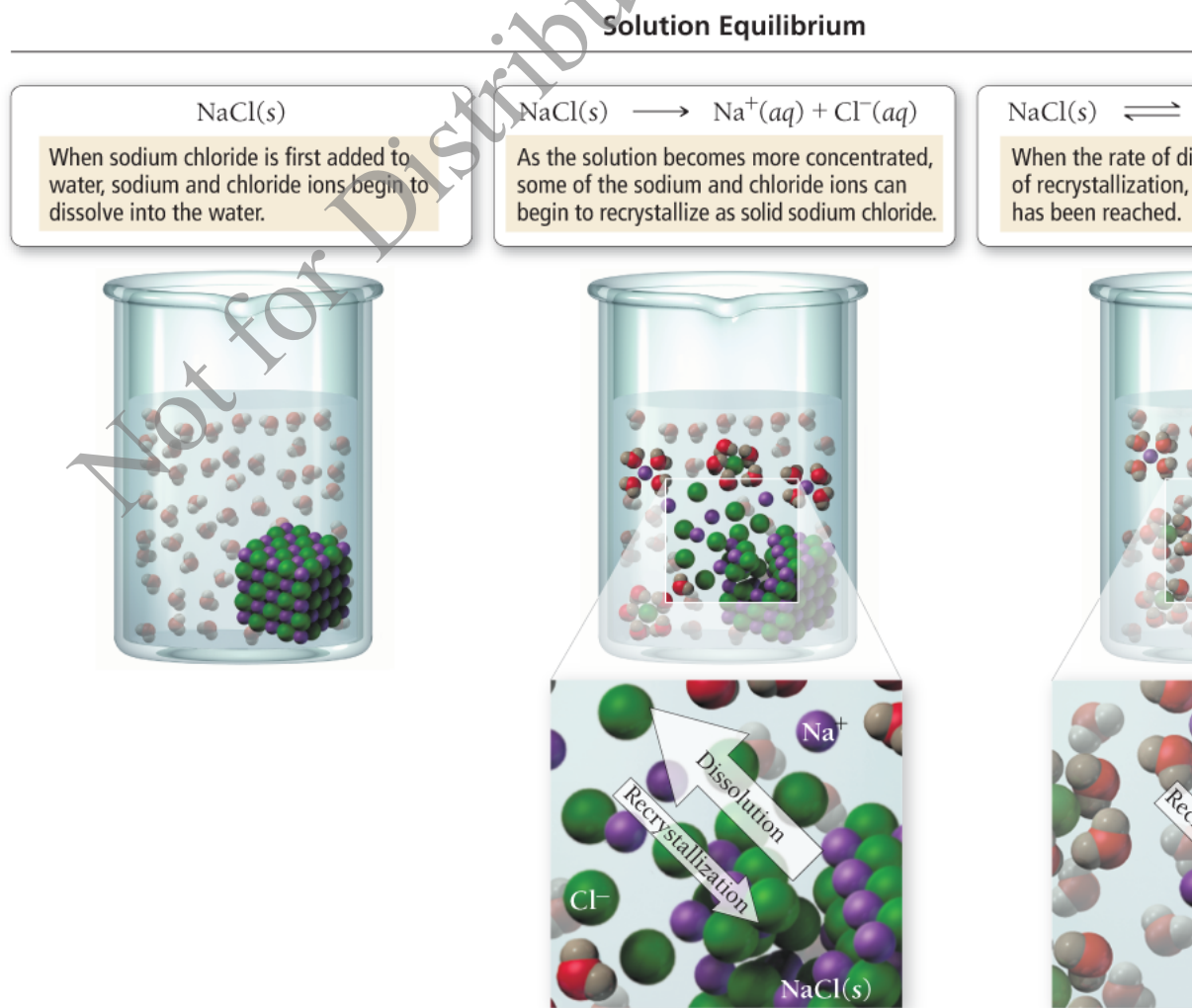


Figure 13.8 Dissolution of NaCl

(a) Initial addition of NaCl, (b) Dissolution, (c) Dynamic equilibrium.



(a) Initial

Rate of dissolution > Rate of recrystallization

(b) Dissolving

Rate of dissolution

(c) Dynamic

A solution in which the dissolved solute is in dynamic equilibrium with the solid (undissolved) solute is a **saturated solution**. If we add additional solute to a saturated solution, the solution concentration will not increase any further. A solution containing less than the equilibrium amount of solute is an **unsaturated solution**. If we add additional solute to an unsaturated solution, the solution concentration increases.

Under certain circumstances, a **supersaturated solution**—one containing more than the equilibrium amount of solute—may form. Supersaturated solutions are unstable, and the excess solute normally precipitates out of the solution. However, in some cases, if left undisturbed, a supersaturated solution can exist for an extended period of time. For example, in a common classroom demonstration, a tiny piece of solid sodium acetate is added to a supersaturated solution of sodium acetate. This triggers the precipitation of the solute, which crystallizes out of solution in a dramatic and often beautiful way (Figure 13.9).

Figure 13.9 Precipitation from a Supersaturated Solution

When a small piece of solid sodium acetate is added to a supersaturated sodium acetate solution, the excess solid precipitates out of the solution.



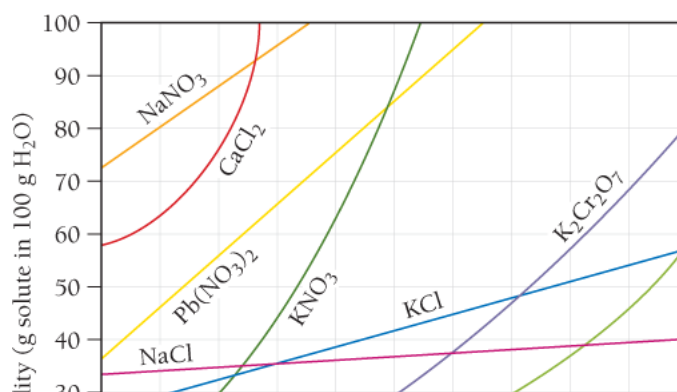
The Effect of Temperature on the Solubility of Solids

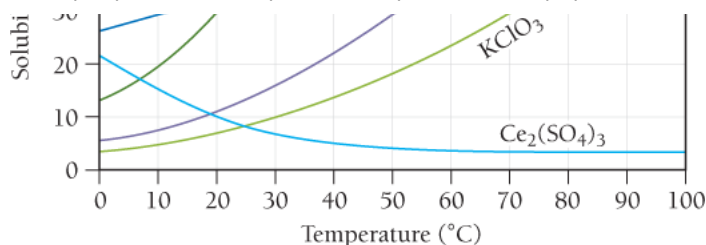
The solubility of solids in water can be highly dependent on temperature. Have you ever noticed how much more sugar you can dissolve in hot tea than in cold tea? Although exceptions exist, *the solubility of most solids in water increases with increasing temperature*, as shown in Figure 13.10. For example, the solubility of potassium nitrate (KNO_3) at room temperature is about 37 g KNO_3 per 100 g of water. At 50 °C, the solubility rises to 88 g KNO_3 per 100 g of water.

In the case of sugar dissolving in water, the higher temperature increases both *how fast* the sugar dissolves and *how much* sugar dissolves.

Figure 13.10 Solubility and Temperature

The solubility of most solids increases with increasing temperature.





A common way to purify a solid is **recrystallization**. In this technique, enough solid is added to water (or some other solvent) to create a saturated solution at an elevated temperature. As the solution cools, it becomes supersaturated and the excess solid precipitates out of the solution. If the solution cools slowly, the solid forms crystals as it comes out of solution. The crystalline structure tends to exclude impurities, resulting in a purer solid.



Rock candy is formed by the recrystallization of sugar.

You can use the temperature dependence of the solubility of solids to make rock candy. Prepare a saturated sucrose (table sugar) solution at an elevated temperature, and allow a string or stick to dangle into the solution for several days. As the solution cools and the solvent evaporates, the solution becomes supersaturated and sugar crystals grow on the string or stick. After several days, beautiful edible crystals or “rocks” of sugar cover the string.

Factors Affecting the Solubility of Gases in Water

Solutions of gases dissolved in water are common. Club soda, for example, is a solution of carbon dioxide and water, and most liquids exposed to air contain dissolved gases. Fish depend on the oxygen dissolved in lake or ocean water for life, and blood contains dissolved nitrogen, oxygen, and carbon dioxide. Even tap water contains dissolved gases. The solubility of a gas in a liquid is affected by both temperature and pressure.

The Effect of Temperature

We can observe the effect of temperature on the solubility of a gas in water when we heat ordinary tap water on a stove. Before the water reaches its boiling point, small bubbles develop in the water. These bubbles are the dissolved air (mostly nitrogen and oxygen) coming out of solution. (Once the water boils, the bubbling becomes more vigorous—these larger bubbles are composed of water vapor.) The dissolved air comes out of the heated solution because—unlike solids, whose solubility generally increases with increasing temperature—the solubility of gases in liquids decreases with increasing temperature.





Cold soda pop

Warm soda pop

Warm soda pop bubbles more than cold soda pop because carbon dioxide is less soluble in the warm solution.

The inverse relationship between gas solubility and temperature is the reason that warm soda pop bubbles more than cold soda pop when you open it and warm beer goes flat faster than cold beer. More carbon dioxide comes out of these solutions at room temperature than at a lower temperature because the gas is less soluble at room temperature. The decreasing solubility of gases with increasing temperature is also the reason that fish don't bite much in a warm lake. The warm temperature results in a lower oxygen concentration. With lower oxygen levels, the fish become lethargic and do not strike as aggressively at the lure or bait you cast their way.

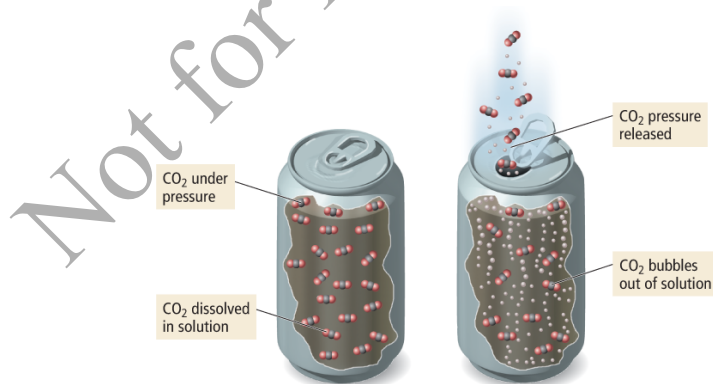
Conceptual Connection 13.3 Solubility and Temperature

The Effect of Pressure

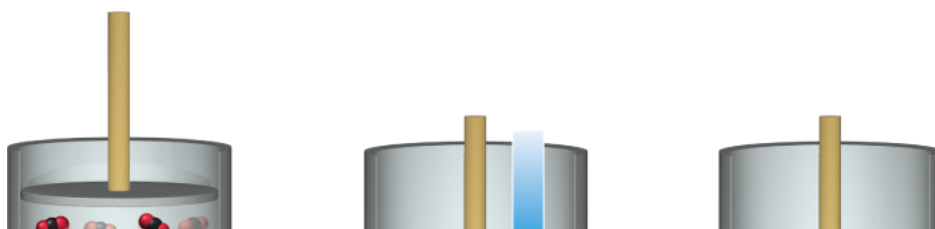
The solubility of gases also depends on pressure. The higher the pressure of a gas above a liquid, the more soluble the gas is in the liquid. In a sealed can of soda pop, for example, the carbon dioxide is maintained in solution by the high pressure of carbon dioxide within the can. When the can is opened, this pressure is released and the solubility of carbon dioxide decreases, resulting in bubbling (Figure 13.11).

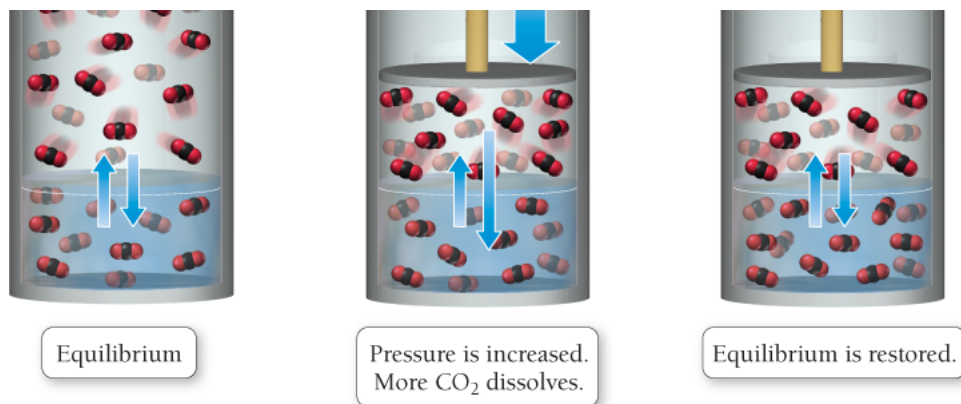
Figure 13.11 Soda Fizz

The bubbling that occurs when a can of soda is opened results from the reduced pressure of carbon dioxide over the liquid. At lower pressure, the carbon dioxide is less soluble and bubbles out of solution.



We can better understand the increased solubility of a gas in a liquid by considering cylinders containing water and carbon dioxide gas.





The first cylinder represents an equilibrium between gaseous and dissolved carbon dioxide—the rate of carbon dioxide molecules entering solution exactly equals the rate of molecules leaving the solution. Now imagine we decrease the volume, as shown in the second cylinder. The pressure of carbon dioxide increases, causing the rate of molecules entering the solution (represented by the longer arrow on the right) to rise. The number of molecules in solution increases until equilibrium is established again, as shown in the third cylinder. However, the amount of carbon dioxide in solution is now greater.

We can quantify the solubility of gases with increasing pressure with **Henry's law**:

$$S_{\text{gas}} = k_{\text{H}} P_{\text{gas}}$$

where S_{gas} is the solubility of the gas (usually in M), k_{H} is a constant of proportionality (called the *Henry's law constant*) that depends on the specific solute and solvent and also on temperature, and P_{gas} is the partial pressure of the gas (usually in atm). The equation shows that the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid. Table 13.4 lists the Henry's law constants for several common gases.

Table 13.4 Henry's Law Constants for Several Gases in Water at 25 °C

Gas	k_{H} (M/atm)
O ₂	1.3×10^{-3}
N ₂	6.1×10^{-4}
CO ₂	3.4×10^{-2}
NH ₃	5.8×10^1
He	3.7×10^{-4}

Conceptual Connection 13.4 Henry's Law

Example 13.2 Henry's Law

What pressure of carbon dioxide is required to maintain the carbon dioxide concentration in a bottle of club soda at 0.12 M at 25 °C?

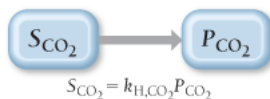
SORT You are given the desired solubility of carbon dioxide and asked to find the pressure required to achieve this solubility.

GIVEN: $S_{\text{CO}_2} = 0.12 \text{ M}$

FIND: P_{CO_2}

STRATEGIZE Use Henry's law to find the required pressure from the solubility. Use the Henry's law constant for carbon dioxide listed in Table 13.4.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$$S_{\text{gas}} = k_{\text{H}} P_{\text{gas}} \text{ (Henry's law)}$$

$$k_{\text{H,CO}_2} = 3.4 \times 10^{-2} \text{ M/atm (from Table 13.4)}$$

SOLVE Solve the Henry's law equation for P_{CO_2} and substitute the other quantities to calculate it.

SOLUTION

$$\begin{aligned} S_{\text{CO}_2} &= k_{\text{H,CO}_2} P_{\text{CO}_2} \\ P_{\text{CO}_2} &= \frac{S_{\text{CO}_2}}{k_{\text{H,CO}_2}} \\ &= \frac{0.12 \text{ M}}{3.4 \times 10^{-2} \frac{\text{M}}{\text{atm}}} \\ &= 3.5 \text{ atm} \end{aligned}$$

CHECK The answer is in the correct units and seems reasonable. A small answer (for example, less than 1 atm) would be suspect because you know that the soda is under a pressure greater than atmospheric pressure when you open it. A very large answer (for example, over 100 atm) would be suspect because an ordinary can or bottle probably could not sustain such high pressures without bursting.

FOR PRACTICE 13.2 Determine the solubility of oxygen in water at 25 °C exposed to air at 1.0 atm. Assume a partial pressure for oxygen of 0.21 atm.

Not for Distribution

Not for Distribution