14.4: Solution Equilibrium and Factors Affecting Solubility

Learning Objectives

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

Effect of Temperature on the Solubility of Solids

Figure 14.4.1 shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and CH_3CO_2Na) exhibit a dramatic increase in solubility with increasing temperature. Others (such as $NaCl$ and K_2SO_4) exhibit little variation, and still others (such as Li_2SO_4) become less soluble with increasing temperature.

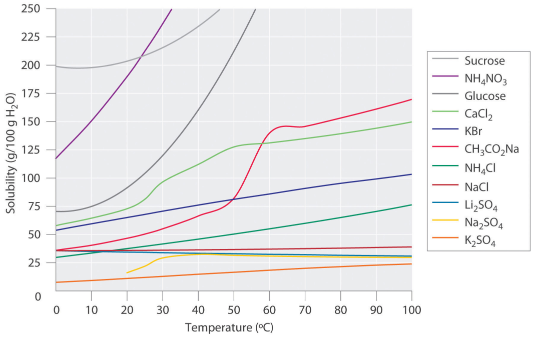

Figure 14.4.1: Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-SA-NC; anonymous)

Graph of solubility against temperature. Plots of sucrose, NH4NO3, glucose, CaCl2, KBr, CH3CO2Na, NH4Cl, Li2SO4, Na2SO4, K2SO4.

Notice in particular the curves for NH_4NO_3 and $CaCl_2$. The dissolution of ammonium nitrate in water is endothermic ($\Delta H_{soln} = +25.7\ kJ/mol$), whereas the dissolution of calcium chloride is exothermic ($\Delta H_{soln} = -68.2\ kJ/mol$), yet Figure 14.4.1 shows that the solubility of both compounds increases sharply with increasing temperature. In fact, the magnitudes of the changes in both enthalpy and entropy for dissolution are temperature dependent. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate (CH_3CO_2Na) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C. According to the temperature curves in Figure 14.4.1, both compounds dissolve in water at 80°C, and all 50 g of KBr remains in solution at 0°C. Only about 36 g of CH_3CO_2Na are soluble in 100 g of water at 0°C, however, so approximately 114 g (150 g − 36 g) of CH_3CO_2Na crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original CH_3CO_2Na in essentially pure form in only one step.

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 14.4.1 and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be more soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

Effect of Temperature on the Solubility of Gases

The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 14.4.2. Attractive intermolecular interactions in the gas phase are essentially zero for most substances. When a gas dissolves, it does so because its molecules interact with solvent molecules. Because heat is released when these new attractive interactions form, dissolving most gases in liquids is an exothermic process ($\Delta H_{soln} < 0$). Conversely, adding heat to the solution provides thermal energy that overcomes the attractive forces between the gas and the solvent molecules, thereby decreasing the solubility of the gas. The phenomenon is similar to that involved in the increase in the vapor pressure of a pure liquid with increasing temperature. In the case of vapor pressure, however, it is attractive forces between solvent molecules that are being overcome by the added thermal energy when the temperature is increased.

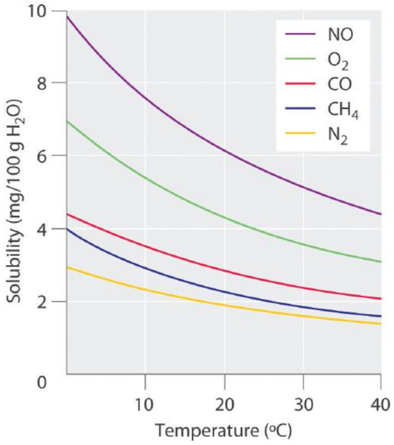

Figure 14.4.2: Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm. The solubilities of all gases decrease with increasing temperature. (CC BY-SA-NC; anonymous)

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called “boiler scale,” a deposit that can seriously decrease the capacity of hot water pipes (Figure 14.4.3). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex and will be described elsewhere, but the driving force is the loss of dissolved CO_2 from solution. Hard water contains dissolved Ca^{2+} and HCO_3^- (bicarbonate) ions. Calcium bicarbonate ($Ca(HCO_3)_2$) is rather soluble in water, but calcium carbonate ($CaCO_3$) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

$$2\,HCO_3^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l) + CO_2(aq) \tag{14.4.1}$$

Heating the solution decreases the solubility of CO_2, which escapes into the gas phase above the solution. In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.

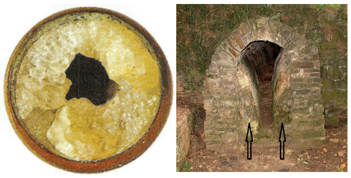

Figure 14.4.3: Calcium carbonate deposits (left) Calcium carbonate ($CaCO_3$) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved CO_2 is driven into the gas phase at high temperatures. (right) Highly calcified remains of Eiffel aqueduct near Euskirchen-Kreuzweingarten, Germany. (Wikipedia)

Thermal Pollution

In **thermal pollution**, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of O_2 at higher temperatures (Figure 14.4.2), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water.

There are many causes of fish kill, but oxygen depletion is the most common cause. (Public Domain; United States Fish and Wildlife Service)

A similar effect is seen in the rising temperatures of bodies of water such as the k0oi89Chesapeake Bay, the largest estuary in North America, where \lobal warming has been implicated as the cause. For each 1.5°C that the bay’s water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter feeders, which then decreased light transmission to allow the eelsgrass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

Effect of Pressure on the Solubility of Gases: Henry’s Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 14.4.4, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

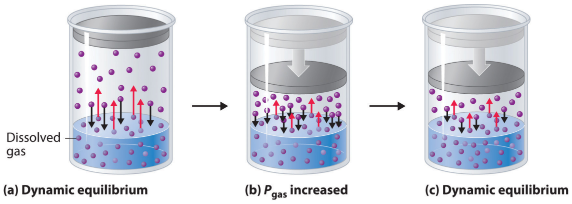

Figure 14.4.4: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established. (CC BY-SA-NC; anonymous)

The relationship between pressure and the solubility of a gas is described quantitatively by Henry’s law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = kP \tag{14.4.2}$$

where

- C is the concentration of dissolved gas at equilibrium,
- P is the partial pressure of the gas, and
- k is the Henry’s law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry’s law constant are therefore mol/(L·atm) = M/atm. Values of the Henry’s law constants for solutions of several gases in water at 20°C are listed in Table 14.4.1.

As the data in Table 14.4.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the Group 18 elements, the Henry's law constants increase smoothly from He to Ne to Ar.

Table 14.4.1: Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
He	3.9
Ne	4.7
Ar	15
H_2	8.1
N_2	7.1
O_2	14
CO_2	392

Oxygen is Especially Soluble

Nitrogen and oxygen are the two most prominent gases in the Earth's atmosphere and they share many similar physical properties. However, as Table 14.4.1 shows, O_2 is twice as soluble in water as N_2. Many factors contribute to solubility including the nature of the intermolecular forces at play. For a details discussion, see "The O_2/N_2 Ratio Gas Solubility Mystery" by Rubin Battino and Paul G. Seybold (J. Chem. Eng. Data 2011, 56, 5036–5044),

Gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S, and NH_3, do **not** obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $\mathrm{H^+(aq)}$ and $\mathrm{Cl^-(aq)}$, not dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

> *Gases that react with water do not obey Henry's law.*

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

A Video Discussing Henry's Law. Video Link: Henry's Law (The Solubility of Gases in Solvents), YouTube(opens in new window) [youtu.be]

✓ Example 14.4.1

The Henry's law constant for O_2 in water at 25°C is $1.27 \times 10^{-3} M/atm$, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at 25°C at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of O_2, and pressure

Asked for: solubility

Strategy:

A. Use Dalton's law of partial pressures to calculate the partial pressure of oxygen. (For more information about Dalton's law of partial pressures)
B. Use Henry's law to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2:

$$\begin{aligned} P_A &= \chi_A P_t \\ &= (0.21)(1.00\ atm) \\ &= 0.21\ atm \end{aligned}$$

B From Henry’s law, the concentration of dissolved oxygen under these conditions is

$$\begin{aligned}[\mathrm{CO_2}] &= kP_{\mathrm{O_2}} \\ &= (1.27\times 10^{-3}\ M/\ \cancel{atm})(0.21\ \ \cancel{atm}) \\ &= 2.7\times 10^{-4}\ M\end{aligned}$$

Exercise 14.4.1

To understand why soft drinks “fizz” and then go “flat” after being opened, calculate the concentration of dissolved CO_2 in a soft drink:

a. bottled under a pressure of 5.0 atm of CO_2
b. in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately $3\times 10^{-4}\ atm$). The Henry’s law constant for CO_2 in water at 25°C is $3.4\times 10^{-2}\ M/atm$.

Answer a

$0.17M$

Answer b

$1\times 10^{-5}M$

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry’s law describes the relationship between the pressure and the solubility of a gas.

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