

# **CHEMISTRY IN ACTION**

# \*\* Solid Hydrates-Salt + Water

If you add salt to water, you would expect it to dissolve and form a solution. But some ionic compounds attract water strongly enough to hold on to water molecules even when crystalline, forming what are called  $solid\ hydrates$ . For example, the plaster of Paris used to make decorative objects and casts for broken limbs is calcium sulfate hemihydrate, CaSO $_4 \cdot \frac{1}{2} H_2 O$ . The dot between CaSO $_4$  and  $\frac{1}{2} H_2 O$  in the formula indicates that for every two CaSO $_4$  formula units in the crystal there is also one water molecule present.

$$CaSO_4 \cdot \frac{1}{2}H_2O$$
 A solid hydrate

After being ground up and mixed with water to make plaster,  $CaSO_4 \cdot \frac{1}{2}H_2O$  gradually changes into the crystalline dihydrate  $CaSO_4 \cdot 2H_2O$ , known as *gypsum*.

During the change, the plaster hardens and expands in volume, causing it to fill a mold or shape itself closely around a broken limb. Still other ionic compounds attract water so strongly that they pull water vapor from humid air to become hydrated. Compounds that show this behavior, such



as calcium chloride ( $CaCl_2$ ), are called hygroscopic and are often used as drying agents. You might have noticed a small bag of a hygroscopic compound (probably silica gel,  $SiO_2$ ) included in the packing material of a new MP3 player, camera, or other electronic device to keep humidity low during shipping. These and other ionic compounds that are handled primarily as hydrates are listed in the following table.

#### Some Common Solid Hydrates

Formula	Name	Uses
AICI <sub>3</sub> · 6H <sub>2</sub> O	Aluminum chloride hexahydrate	Antiperspirant
CaSO <sub>4</sub> • 2H <sub>2</sub> O	Calcium sulfate dihydrate (gypsum)	Cements, wallboard molds
CaSO <sub>4</sub> • ½H <sub>2</sub> O	Calcium sulfate hemihydrate (plaster of Paris)	Casts, molds
CuSO <sub>4</sub> • 5H <sub>2</sub> O	Copper(II) sulfate pentahydrate (blue vitriol)	Pesticide, germicide, topical fungicide
MgSO <sub>4</sub> ·7H <sub>2</sub> O	Magnesium sulfate heptahydrate (epsom salts)	Laxative, anticonvulsant
NaB <sub>4</sub> O <sub>7</sub> • 10H <sub>2</sub> O	Sodium tetraborate decahydrate (borax)	Cleaning compounds, fireproofing agent
$Na_2S_2O_3 \cdot 5H_2O$	Sodium thiosulfate pentahydrate (hypo)	Photographic fixer

**CIA Problem 9.1** Write the formula of sodium sulfate decahydrate, known as Glauber's salt and used as a laxative.

**CIA Problem 9.2** What mass of Glauber's salt must be used to provide 1.00 mol of sodium sulfate?

### PROBLEM 9.2

Which of the following pairs of substances would you expect to form solutions?

- (a) CCl<sub>4</sub> and water
- (b) Benzene  $(C_6H_6)$  and MgSO<sub>4</sub>
- (c) Hexane  $(C_6H_{14})$  and heptane  $(C_7H_{16})$
- (d) Ethanol ( $C_2H_5OH$ ) and heptanol ( $C_7H_{15}OH$ )

# 9.3 Solubility

#### Learning Objective:

• Define the properties of a solution, including miscibility, saturation, and solubility.

We learned in Section 9.2 that ethanol is soluble in water because hydrogen bonding is nearly as strong between water and ethanol molecules as it is between water molecules alone or ethanol molecules alone. So similar are the forces in this

particular case, in fact, that the two liquids are **miscible** or mutually soluble in all proportions. Ethanol will continue to dissolve in water no matter how much is added.

Most substances, however, reach a solubility limit beyond which no more will dissolve in solution. Imagine, for instance, that you are asked to prepare a saline solution (aqueous NaCl). You might measure out some water, add solid NaCl, and stir the mixture. Dissolution occurs rapidly at first but then slows down as more and more NaCl is added. Eventually the dissolution stops because an equilibrium is reached when the numbers of Na<sup>+</sup> and Cl<sup>-</sup> ions leaving a crystal and going into solution are equal to the numbers of ions returning from solution to the crystal. At this point, the solution is said to be **saturated.** A maximum of 35.8 g of NaCl will dissolve in 100 mL of water at 20 °C (293 K). Any amount above this limit simply sinks to the bottom of the container and sits there.

The equilibrium reached by a saturated solution is like the equilibrium reached by a reversible reaction (Section 7.7). Both are dynamic situations in which no *apparent* change occurs because the rates of forward and backward processes are equal. Solute particles leave the solid surface and reenter the solid from solution at the same rate.

The maximum amount of a substance that will dissolve in a given amount of a solvent at a given temperature, usually expressed in grams per 100 mL (g/100 mL), is called the substance's **solubility**. Solubility is a characteristic property of a specific solute–solvent combination, and different substances have greatly differing solubilities. Only 9.6 g of sodium hydrogen carbonate will dissolve in 100 mL of water at  $20 ^{\circ}\text{C}$  (293 K), for instance, but 204 g of sucrose will dissolve under the same conditions.

Miscible Mutually soluble in all proportions.

Saturated solution A solution that contains the maximum amount of dissolved solute at equilibrium.

Solid solute 
$$\stackrel{\text{Dissolve}}{\longleftarrow}$$
 Solution

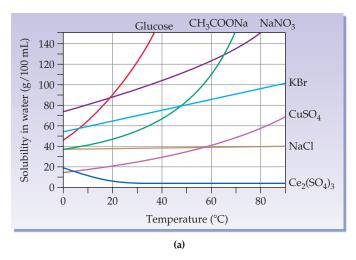
**Solubility** The maximum amount of a substance that will dissolve in a given amount of solvent at a specified temperature.

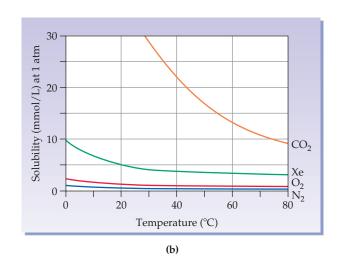
# 9.4 The Effect of Temperature on Solubility

## Learning Objective:

• Determine the effect of temperature changes on the solubility of a solute in a solution.

As anyone who has ever made tea or coffee knows, temperature often has a dramatic effect on solubility. The compounds in tea leaves or coffee beans, for instance, dissolve easily in hot water but not in cold water. The effect of temperature is different for every substance, however, and is usually unpredictable. As shown in Figure 9.3a, the solubilities of most molecular and ionic solids increase with increasing temperature, but the





▲ Figure 9.3
Solubilities of some (a) solids and (b) gases in water as a function of temperature.

Most solid substances become more soluble as temperature rises (although the exact relationship is usually complex), whereas the solubility of gases decreases.



▲ Figure 9.4 A supersaturated solution of sodium acetate in water.

When a tiny seed crystal is added, larger crystals rapidly grow and precipitate from the solution until equilibrium is reached.

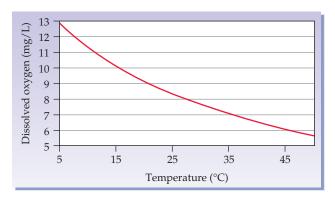
solubilities of others (NaCl) are almost unchanged, and the solubilities of still others  $[Ce_2(SO_4)_3]$  decrease with increasing temperature.

Solids that are more soluble at high temperature than at low temperature can sometimes form **supersaturated solutions**, which contain even more solute than a saturated solution. Suppose, for instance, that a large amount of a substance is dissolved at a high temperature. As the solution cools, the solubility decreases and the excess solute should precipitate to maintain equilibrium. But if the cooling is done very slowly, and if the container stands quietly, crystallization might not occur immediately and a supersaturated solution might result. Such a solution is unstable, however, and precipitation can occur dramatically when a tiny seed crystal is added to initiate crystal growth or when the container is disturbed (Figure 9.4).

Unlike solids, the influence of temperature on the solubility of gases *is* predictable: Addition of heat decreases the solubility of most gases, as seen in Figure 9.3b (helium is the only common exception). One result of this temperature-dependent decrease in gas solubility can sometimes be noted in a stream or lake near the outflow of warm water from an industrial operation. As water temperature increases, the concentration of dissolved oxygen in the water decreases, killing fish that cannot tolerate the lower oxygen levels.

# Worked Example 9.2 Solubility of Gases: Effect of Temperature

From the following graph of solubility versus temperature for  $O_2$ , estimate the concentration of dissolved oxygen in water at 25 °C and at 35 °C. By what percentage does the concentration of  $O_2$  change?



**ANALYSIS** The solubility of  $O_2$  (on the y-axis) can be determined by finding the appropriate temperature (on the x-axis) and extrapolating. The percent change is calculated as

$$\frac{\text{(Solubility at 25 °C)} - \text{(Solubility at 35 °C)}}{\text{(Solubility at 25 °C)}} \times 100$$

#### **SOLUTION**

From the graph, we estimate that the solubility of  $O_2$  at 25 °C is approximately 8.3 mg/L and at 35 °C is 7.0 mg/L. The percent change in solubility is

$$\frac{8.3 - 7.0}{8.3} \times 100 = 16$$

**Supersaturated solution** A solution that contains more than the maximum amount of dissolved solute; a nonequilibrium situation.

### PROBLEM 9.3

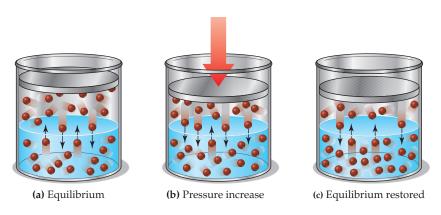
A solution is prepared by dissolving 12.5 g of KBr in 20 mL of water at 60  $^{\circ}$ C (see Figure 9.3). Is this solution saturated, unsaturated, or supersaturated? What will happen if the solution is cooled to 10  $^{\circ}$ C?

# 9.5 The Effect of Pressure on Solubility: Henry's Law

### Learning Objective:

• Determine the effect of a change in pressure on the solubility of a gas in solution.

Pressure has virtually no effect on the solubility of a solid or liquid, but it has a strong effect on the solubility of a gas. According to **Henry's law**, the solubility (or concentration) of a gas in a liquid is directly proportional to the partial pressure of the gas over the liquid. If the partial pressure of the gas doubles, solubility doubles; if the gas pressure is halved, solubility is halved (Figure 9.5).



**Henry's law** The solubility (or concentration) of a gas is directly proportional to the partial pressure of the gas if the temperature is constant. That is, concentration (*C*) divided by pressure (*P*) is constant when *T* is constant, or

$$\frac{C}{P_{\text{gas}}} = k$$
 (At a constant temperature)

Henry's law can be explained using Le Châtelier's principle. In the case of a saturated solution of a gas in a liquid, an equilibrium exists whereby gas molecules enter and leave the solution at the same rate. When the system is stressed by increasing the pressure of the gas, more gas molecules go into solution to relieve that increase. Conversely, when the pressure of the gas is decreased, more gas molecules come out of solution to relieve the decrease.

As an example of Henry's law in action, think about the fizzing that occurs when you open a bottle of soft drink or champagne. The bottle is sealed under greater than 1 atm of  $CO_2$  pressure, causing some of the  $CO_2$  to dissolve. When the bottle is opened, however,  $CO_2$  pressure drops and gas comes fizzing out of solution.

Writing Henry's law in the form  $P_{\rm gas}=C/k$  shows that partial pressure can be used to express the concentration of a gas in a solution, a practice especially common in health-related sciences. Table 9.3 gives some typical values and illustrates the convenience of having the same unit for concentration of a gas in both air and blood. Compare the oxygen partial pressures in saturated alveolar air (air in the lungs) and in arterial blood, for instance. The values are almost the same because the gases dissolved in blood come to equilibrium with the same gases in the lungs.

If the partial pressure of a gas over a solution changes while the temperature is constant, the new solubility of the gas can be found easily. Because C/P is a constant value at constant temperature, Henry's law can be restated to show how one variable changes if the other changes.

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} = k$$
 (Where *k* is constant at a fixed temperature)

Worked Example 9.3 gives an illustration of how to use this equation.

CONCEPTS TO REVIEW Recall from Section 8.11 that each gas in a mixture exerts a partial pressure independent of other gases present (Dalton's law of partial pressures).

### **◄ Figure 9.5**

#### Henry's law.

The solubility of a gas is directly proportional to its partial pressure. An increase in pressure causes more gas molecules to enter solution until equilibrium is restored between the dissolved and undissolved gas.

Le Châtelier's principle states that when a system at equilibrium is placed under stress, the equilibrium shifts to relieve that stress (Section 7.9).

[Pressure increases  $\longrightarrow$ ]

Gas + Solvent  $\Longrightarrow$  Solution

		Partial Pressure (Pa)		
Sample	$P_{N_2}$	$P_{0_2}$	$P_{CO_2}$	P <sub>H2</sub> 0
Inspired air (dry)	$79.6 \times 10^3$	$21.2 \times 10^3$	40.0	493
Alveolar air (saturated)	$76.3 \times 10^3$	$13.3 \times 10^3$	$5.33 \times 10^3$	$6.27 \times 10^3$
Expired air (saturated)	$75.9 \times 10^3$	$15.5 \times 10^3$	$3.7 \times 10^3$	$6.27 \times 10^3$
Arterial blood	$76.4 \times 10^3$	$12.7 \times 10^3$	$5.33 \times 10^3$	
Venous blood	$76.4 \times 10^3$	$5.33 \times 10^3$	$6.0 \times 10^3$	
Peripheral tissues	$76.4 \times 10^3$	$5.33 \times 10^3$	$6.0 \times 10^3$	

Table 9.3 Partial Pressures and Normal Gas Concentrations in Body Fluids

# Worked Example 9.3 Solubility of Gases: Henry's Law

At a partial pressure of oxygen in the atmosphere of  $21.2 \times 10^3$  Pa, the solubility of oxygen in blood is 0.44 g/100 mL. What is the solubility of oxygen in blood at 7925 m, where the partial pressure of  $O_2$  is  $7.5 \times 10^3$  Pa?

ANALYSIS According to Henry's law, the solubility of the gas divided by its pressure is constant.

$$\frac{C_1}{P_1} = \frac{C_2}{P_2}$$

Of the four variables in this equation, we know  $P_1$ ,  $C_1$ , and  $P_2$ , and we need to find  $C_2$ .

**BALLPARK ESTIMATE** The pressure drops by a factor of about 3 (from  $21.2 \times 10^3$  Pa to  $7.5 \times 10^3$  Pa). Since the ratio of solubility to pressure is constant, the solubility must also drop by a factor of 3 (from 0.44 g/100 mL to about 0.15 g/100 mL).

### **SOLUTION**

STEP 1: Identify known information. We have values for  $P_1$ ,  $C_1$ , and  $P_2$ .

STEP 2: Identify answer and units. We are looking for the solubility of  $O_2(C_2)$  at a partial pressure  $P_2$ .

STEP 3: Identify conversion factors or equations. In this case, we restate Henry's law to solve for  $C_2$ .

**STEP 4: Solve.** Substitute the known values into the equation and calculate  $C_2$ .

$$P_1 = 21.2 \times 10^3 \,\text{Pa}$$
  
 $C_1 = 0.44 \,\text{g}/100 \,\text{mL}$   
 $P_2 = 7.5 \times 10^3 \,\text{Pa}$   
Solubility of  $O_2$ ,  $C_2 = ?? \,\text{g}/100 \,\text{mL}$ 

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} \Rightarrow C_2 = \frac{C_1 P_2}{P_1}$$

$$C_2 = \frac{C_1 P_2}{P_1} = \frac{(0.44 \text{ g}/100 \text{ mL})(7.5 \times 10^3 \text{ Pá})}{21.2 \times 10^3 \text{ Pá}} = 0.16 \text{ g}/100 \text{ mL}$$

BALLPARK CHECK The calculated answer matches our estimate.

#### **PROBLEM 9.4**

At 20 °C (293 K) and a partial pressure of  $10^5$  Pa, the solubility of  $CO_2$  in water is 0.169 g/100 mL. What is the solubility of  $CO_2$  at  $33.3 \times 10^5$  Pa?

#### PROBLEM 9.5

At a total atmospheric pressure of  $10^5$  Pa, the partial pressure of  $CO_2$  in air is approximately  $4.0 \times 10^{29}$  Pa. Using the data in Problem 9.4, what is the solubility of  $CO_2$  in an open bottle of seltzer water at 20 °C (293 K)?

### 9.6 Units of Concentration

### Learning Objective:

• Define units of concentration, and calculate the concentration of a solute in solution.

Although we speak casually of a solution of, say, orange juice as either "dilute" or "concentrated," laboratory work usually requires an exact knowledge of a solution's concentration. As indicated in Table 9.4, there are several common methods for expressing concentration. The units differ, but all the methods describe how much solute is present in a given quantity of solution.

Table 9.4 Some Units for Expressing Concentration

Concentration Measure	Solute Measure	Solution Measure
Percent  Mass/mass percent, (m/m)%  Volume/volume percent, (v/v)%  Mass/volume percent, (m/v)%	Mass (g) Volume* Mass (g)	Mass (g) Volume* Volume (mL)
Parts per million, ppm	Parts*	10 <sup>6</sup> parts*
Parts per billion, ppb	Parts*	10 <sup>9</sup> parts*
Molarity, M	Moles	Volume (L)

<sup>\*</sup>Any units can be used as long as they are the same for both solute and solution.

Let us look at each of the concentration measures listed in Table 9.4 individually, beginning with *percent concentrations*.

#### **Percent Concentrations**

Percent concentrations express the amount of solute in 100 units of solution. The amount of solute and the amount of solution can be represented in units of mass or volume. For solid solutions, such as a metal alloy, concentrations are typically expressed as mass/mass percent concentration, (m/m)%.

$$(m/m)\%$$
 concentration =  $\frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 100$ 

For example, the mass percent of copper in a red-gold ring that contains 19.20 g of gold and 4.80 g of copper would be calculated as

$$(m/m)\%$$
 Cu =  $\frac{\text{mass of Cu (g)}}{\text{mass of Cu (g)} + \text{mass of Au (g)}} \times 100$   
=  $\frac{4.80 \text{ g}}{4.80 \text{ g} + 19.20 \text{ g}} \times 100 = 20.0$ 

The concentration of a solution made by dissolving one liquid in another is often given by expressing the volume of solute as a percentage of the volume of final solution—the volume/volume percent concentration, (v/v)%.

$$(\mathbf{v/v})\%$$
 concentration =  $\frac{\text{Volume of solute (mL)}}{\text{Volume of solution (mL)}} \times 100$ 

For example, if 10.0 mL of ethanol is dissolved in enough water to give 100.0 mL of solution, the ethanol concentration is  $(10.0 \text{ mL}/100.0 \text{ mL}) \times 100 = 10.0\% \text{ (v/v)}$ .

A third common method for expressing percent concentration is to give the number of grams (mass) as a percentage of the number of milliliters (volume) of the final solution—called the mass/volume percent concentration, (m/v)%.

mass/mass percent concentration, (m/m)% Concentration expressed as the number of grams of solute per 100 g of solution.

volume/volume percent concentration, (v/v)% Concentration expressed as the number of milliliters of solute dissolved in 100 mL of solution.

mass/volume percent concentration, (m/v)% Concentration expressed as the number of grams of solute per 100 mL of solution.