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These rules should be taken as guidelines only, since there are exceptions; they are not all-inclusive. However, they do serve as aids and you should become familiar with them. It should also be noted here that the term *soluble* is somewhat arbitrary. As a guideline, substances with solubility (section 12.2) greater than 1 g per 100 g H₂O are considered soluble; those between 0.1 g and 1 g per 100 g H₂O are slightly soluble; and those whose solubilities are less than 0.1 g per 100 g H₂O are considered insoluble.

Section Review 12.1

- In each of the following solutions, indicate which substance is the solute and which is the solvent.
 - a solution containing 5.6 g KBr and 55.4 g H₂O
 - a solution containing 3.9 g paraffin wax and 100. g benzene
 - a solution containing 25.0 g methanol and 15.0 g H₂O
 - a solution containing 50.0 g silver and 13.0 g mercury
- Describe the behavior of the following pairs of substances as soluble, insoluble, miscible, or immiscible.
 - 1.00 g AgCl is shaken with 100.0 g H₂O to give a milky mixture which separates into a clear liquid and a white sediment.
 - 10.0 g CuSO₄ · 5 H₂O and 150 g H₂O are mixed to give a blue solution that is clear (i.e., not cloudy) and of one phase.
 - 10.0 g chloroform and 25.0 g H₂O are shaken together; the mixture quickly separates into two layers.
 - 500 g ethylene glycol and 500 g H₂O are shaken together; the mixture is clear and colorless and does not separate into layers.
- What is meant by each of the following terms?
 - solvated
 - hydrated
- Differentiate between *dissociation* and *ionization*.
- List three things that could be done to hasten the rate of solution of a large crystal of CuSO₄ · 5 H₂O in water.



Figure 12.4

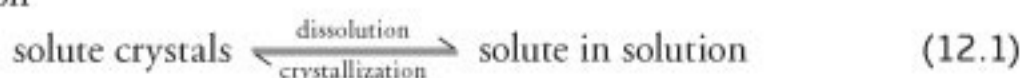
Solution equilibrium analogy

As long as the amount of water flowing into the bucket equals that flowing out of the bucket, the water level remains constant. Similarly, the concentration of a solution remains constant as long as the rate of dissolution equals the rate of crystallization.

12.2 Behavior of Solutions

Solution Equilibrium

When crystals of a substance such as table salt are first placed in water, many of the particles leave the surfaces of the crystals and go into solution. As the number of particles in solution increases, the number that collide with the surfaces of the undissolved crystals and remain there also increases; this is called **crystallization**. If there is sufficient solute present, eventually *the rate of crystallization becomes equal to the rate of dissolution* and the amount of undissolved solid remains constant at that temperature; a condition of **solution equilibrium** exists. This may be represented by the equation



However, since the processes of crystallization and dissolution are *continuously occurring, though at equal rates so they offset each other*, the situation is referred to as a state of **dynamic equilibrium**.

A solution such as that just described is known as a **saturated solution**—it *contains all the solute possible under equilibrium conditions at a given temperature*. The amount of solute present in the saturated solution is known as the **solubility** of the solute. Since solubility varies with temperature, the temperature must be specified when solubilities are given; if not specified, 25 °C is generally assumed. Table 12.3 gives the solubilities of several substances in water at 20 °C. These values must be experimentally determined. A solution that contains less solute than it could at equilibrium at a specific temperature is said to be **unsaturated**.

Many solutes have greater solubilities at temperatures higher than room temperature. If a saturated solution is prepared at an elevated temperature and the solution allowed to cool slowly without being disturbed, all of the solute may remain dissolved. Such a solution *contains more solute than it could under equilibrium conditions* and is said to be **supersaturated**. This is an unstable condition and usually requires a dust-free solvent and a container with a smooth interior surface. Crystallization is aided by the presence of a rough surface and can also be initiated by a sudden disturbance or by scratching the surface of the container with a stirring rod. If a small crystal of the substance that is dissolved in the supersaturated solution is added to the solution—a process known as “seeding,” the excess solute will usually crystallize out of solution immediately; a saturated solution results. This occurs because the seed crystal provides a surface on which the particles in solution can orient themselves and crystallize.

Honey is an example of a supersaturated solution of sugars, primarily glucose and fructose; crystallization often occurs when honey stands for a time. Heating the jar of honey will dissolve the crystals and return it to its supersaturated condition.

Effects of Pressure and Temperature on Solubility

Pressure. The solubility of liquid or solid solutes in liquid solvents is virtually unaffected by ordinary pressure changes. In addition, since all gaseous mixtures are totally miscible solutions, pressure has no effect on gas-in-gas solubility. However, the solubility of a gas in a liquid is greatly affected by changes in pressure.

Gas molecules in contact with a liquid can collide with molecules at its surface and become solvated, much as solid solutes do. The number of collisions by gas molecules is related to the partial pressure of the particular gas being considered (section 5.4). Initially, more gas molecules will enter the solution than will escape, but eventually a dynamic equilibrium is established with the same number of molecules leaving as entering the solution. *At a given temperature, the equilibrium concentration of a dissolved gas is directly proportional to the partial pressure of that gas.* This statement is known as



Figure 12.5 **Crystallization of a supersaturated solution**
Addition of a “seed crystal” to a supersaturated solution of sodium thiosulfate (a) will cause the excess solute to crystallize (b), resulting in a saturated solution.

Table 12.3
Solubilities of several compounds in water at 20 °C

Compound	Solubility (g/100 g H ₂ O)
AgNO ₃	216
AgCl	0.000194
BaSO ₄	0.00024
LiCl	83
NaCl	35.9
NH ₄ Cl	37.2
Pb(NO ₃) ₂	54.3

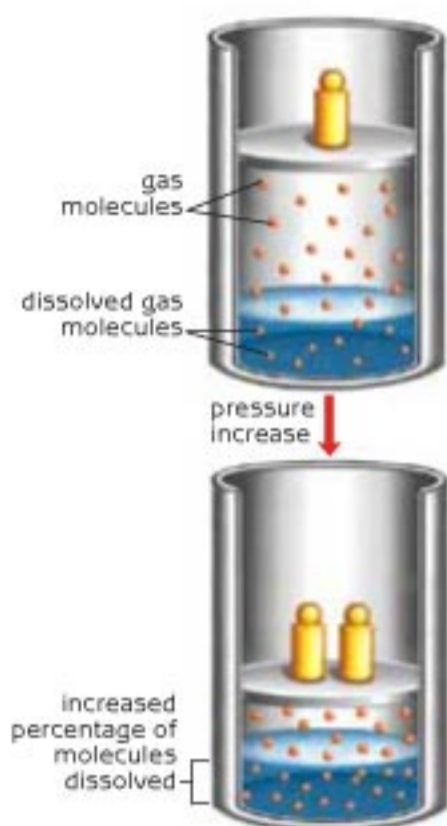


Figure 12.6
Illustration of Henry's law
The solubility of a gas in a solution is greater as the pressure of the gas increases.

Henry's law. Thus, *the higher the partial pressure of a gas, the greater the solubility of the gas at a given temperature.* This law also applies to *each* gas in a mixture of gases such as air.

Probably the most familiar example of a gas-in-liquid solution is that of CO_2 in water—a carbonated beverage. At the bottling company, the flavored water is saturated with CO_2 at a partial pressure of 5–10 atmospheres. When the bottle or can is opened, all of the “excess” CO_2 does not immediately come out of solution because CO_2 tends to readily form supersaturated solutions. Disturbing this unstable supersaturated solution by stirring or shaking it, however, does hasten the rate at which it reaches equilibrium with the atmospheric CO_2 partial pressure (about 4×10^{-4} atm) and becomes “flat.” A similar situation occurs if a can or bottle of carbonated beverage is shaken or dropped shortly before it is opened. Unless it is given time to “recover” from this disturbance under the pressure at which it was bottled, a “geyser” of foamy beverage may erupt from the can or bottle.

The increased solubility of gases under pressure can be a problem for deep-sea divers who breathe ordinary air. More nitrogen from the air than normal is able to dissolve in the bloodstream of a diver under pressure; unless his rise to the surface is slow enough for the nitrogen to gradually escape from solution without forming bubbles, a painful and possibly fatal condition known as the “bends” results. This condition is caused by the formation of nitrogen gas bubbles in the bloodstream, which can obstruct blood flow and cause strokelike symptoms. Replacing nitrogen with helium can help alleviate this problem because helium is less soluble than nitrogen in blood.

Temperature. As the temperature of an equilibrium gas-in-liquid solution is raised, more gas molecules will leave the solution than enter it, resulting in an overall decrease in the amount of dissolved gas. Thus, *the solubilities of gases decrease with increasing temperature.* For this reason, the solubility of oxygen in rivers, streams, and lakes becomes less as the temperature of the water increases. A warm can of carbonated beverage “fizzes” more when opened than does a cold can because CO_2 is less soluble in warm water than in cold water.

Table 12.4
Solubility as a function of temperature (g per 100 g H_2O)

Substance	Temperature, °C			
	0°	20°	60°	100°
AgNO_3	122	216	440	733
$\text{Ba}(\text{OH})_2$	1.67	3.89	20.94	101.40 (80°)
$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	179.2	203.9	287.3	487.2
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	37.4	34.7	32.7	29.7
$\text{Ce}_2(\text{SO}_4)_3$	21.4	9.84	3.87	---
CuSO_4	23.1	32.0	61.8	114
KCl	280	342	45.8	56.3
KI	128	144	176	206
KNO_3	13.9	31.6	106	245
$\text{NaC}_2\text{H}_3\text{O}_2$	36.2	46.4	139	170.15
NaCl	35.7	35.9	37.1	39.2
NaNO_3	73.0	87.6	122	180
NH_4NO_3	118	192	421	871

Most solid solutes have greater solubility in a liquid such as water as the temperature is raised, but a few show a decreased solubility with increased temperature. For example, the solubility of silver nitrate in 100. g water *increases* from 122 g at 0 °C to 440 g at 60 °C, but the solubility of cerium sulfate *decreases* from 20.8 g to 3.9 g, respectively. The effects of temperature on solubility can be seen in Table 12.4 and in the solubility curves of Fig. 12.7.

Heats of Solution

The solution process described in section 12.1 may be divided into the following three steps: (1) the solute particles are separated from the crystal; (2) the solvent molecules are moved apart to make room for the solute particles that will enter the liquid environment; and (3) the solvent and solute particles interact and attract each other. The first two steps require an input of energy (they are endothermic); the third step releases energy (it is exothermic). Depending on the amounts of energy involved in each step, the net energy change may be negative or positive; the heat of solution, ΔH_{soln} , may thus be negative or positive. Thus, we may define **heat of solution** as the total heat energy absorbed or released when one substance dissolves in another. Most solids are found to have a $+\Delta H_{\text{soln}}$ (the solution process is an *endothermic* process), and most gases have a $-\Delta H_{\text{soln}}$ (an *exothermic* process).

When a solid dissolves, its particles are usually more randomly distributed in the solution than they were in the crystal; there is therefore an increase in disorder or entropy (ΔS_{soln} is *positive*). For those solids with a negative ΔH_{soln} (an exothermic process), the degree of hydration is apparently so high that there is more order (*less* disorder) in the solution than in the solid and liquid separately (ΔS_{soln} is *negative*).

In the case of gases, there is an increase in order (a *decrease* in disorder) when the randomly distributed gas molecules become more organized by being solvated; ΔS_{soln} is therefore negative. A negative ΔH_{soln} for gases results.

Diluting a more concentrated solution may cause an absorption or liberation of heat energy, depending on the solute. Thus, the enthalpy change of solution (ΔH_{soln}) depends on the amount of solvent present—that is, the concentration of the final solution. Tabulated ΔH_{soln} data must therefore be given for a specified concentration (Table 12.5).

Table 12.5
Heat of solution (kJ/mole solute in 200 moles H_2O)

Substance	ΔH_{soln}	Substance	ΔH_{soln}
$\text{AgNO}_3(s)$	+22.8	$\text{KNO}_3(s)$	+35.6
$\text{CaCl}_2(s)$	-82.8	$\text{KOH}(s)$	-54.6
$\text{CO}_2(g)$	-19.9	$\text{LiCl}(s)$	-35.0
$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}(s)$	+11.5	$\text{Li}_2\text{CO}_3(s)$	-12.8
$\text{HC}_2\text{H}_3\text{O}_2(l)$	-1.59	$\text{NaCl}(s)$	+4.27
$\text{HCl}(g)$	-74.2	$\text{NaNO}_3(s)$	+21.0
$\text{HI}(g)$	-29.4	$\text{NaOH}(s)$	-41.6
$\text{H}_2\text{SO}_4(l)$	-74.3	$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}(s)$	+78.5
$\text{KCl}(s)$	+17.6	$\text{NH}_3(g)$	-34.6
$\text{KClO}_3(s)$	+42.0	$\text{NH}_4\text{Cl}(s)$	+16.2
$\text{KI}(s)$	+21.4	$\text{NH}_4\text{NO}_3(s)$	+25.4

Positive values mean heat is absorbed (endothermic); negative values mean heat is released (exothermic).

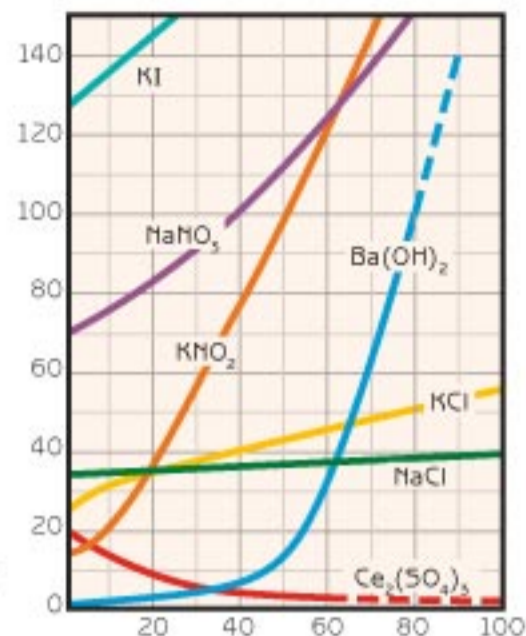


Figure 12.7 **Solubility curves**
The solubility of most solutes in grams per 100. grams water increases with temperature.



Figure 12.8 **Heat of solution of ammonium nitrate**

When ammonium nitrate (NH_4NO_3) is dissolved in water, it absorbs about 25.4 kJ of heat energy per mole of solute, cooling the solution. In this example, the temperature of the water in the beaker dropped by 9 °C when ammonium nitrate was added.

Chemistry in Action

Instant Hot Packs and Cold Packs

A practical use for negative and positive heats of solution is in instant hot packs and cold packs, used in first-aid treatment of sprains and other injuries. They typically contain a dry chemical, such as magnesium sulfate, calcium chloride, or ammonium nitrate, and a pouch of water inside the pack. When the pack is struck or squeezed, the pouch of water ruptures. The temperature of the pack will either rise or fall, depending on what chemical it contains and whether its heat of solution is exothermic or endothermic. For example, a pack containing 20 g of calcium chloride and 100 g of water at 20 °C will rise in temperature to about 55 °C when the pack is used; one containing 30 g of ammonium nitrate and 100 g of water at 20 °C will fall in temperature to about 0 °C. Thus, an instant cold pack usually contains NH_4NO_3 , while a single-use hot pack might contain CaCl_2 or MgSO_4 .



Reusable hot packs and long-lasting warmers are based upon different chemical principles than other hot packs. Most reusable hot packs contain supersaturated solutions of sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) or sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$); the heat released when the pack is activated is due to heat of crystallization (section 6.3), and the pack may be “recharged” by heating it in a microwave to redissolve the chemical. Mitten and boot warmers generally use exothermic chemical reactions, such as the slow oxidation of powdered iron in an aqueous solution, to generate heat for several hours.

Section Review 12.2

1. What is meant by the term *solution equilibrium*?
2. What is a dynamic equilibrium?
3. What is meant when a solution is described as saturated, unsaturated, and supersaturated, respectively?
4. Relating pressure to solubility, explain why deep-sea divers often replace the nitrogen in their air tanks with helium.
5. Based on what you have read, would you expect the cool waters of the Atlantic Ocean to contain more or less dissolved oxygen than the waters of a tropical lagoon? What effect might this have on the abundance of sea life?
6. What is meant by the term *heat of solution*?

12.3 Measuring Solution Concentration

To a chemist, the nebulous terms *dilute* and *concentrated* mean very little if he is interested in knowing the actual quantity of solute particles present in a solution. More precise relationships can be given in terms of **concentration**—*an expression of the amount of solute present in a given amount of solution (or solvent)*.

$$\text{concentration} = \frac{\text{amount of solute}}{\text{amount of solution (or solvent)}} \quad (12.2)$$

Since many reactions are carried out in solution, it is often important to know the amounts of the various reactants present.