



# Ch. 2. Physical properties of solutions

**S**OLUTIONS are homogeneous mixtures of a solvent and one or more solutes. In your everyday life, you will encounter numerous liquid-based mixtures, from recovery drinks to fancy champagne or plain milk. However, solutions are not just liquid-based as you can also find solid solutions such as an alloy, and even gas solutions such as the air. This chapter will cover the physical properties of solutions—boiling, freezing, and melting—and in particular, we will gain insight into the impact of the solute on the physical properties of the solvent. The chapter will also address the meaning of different concentration units and the relationship between them, as well as the properties of colloids—a special type of unstable mixture.

## 2.1 Solutions and colloids

A solution is a homogeneous mixture of a solvent and one or more solutes. Homogeneous means that a solution consists of only one visible phase (e.g. wine) in contrast to heterogeneous which means that a mixture would be composed of two or more distinct phases (e.g. a chocolate chip cookie).

*Solutions in terms of phase and solubility* One can find gas, liquid, or solid solutions depending on the final phase of the resulting solutions. For example, brass is a solid solution of copper and zinc and the air is a gaseous solution of oxygen, nitrogen, and other components. Solutions can be classified in terms of solubility. The solubility of a given solute in a solvent is the maximum amount of solute one can dissolve in a volume of solvent. Solutions can be saturated when they contain the maximum amount of solute one can fit, unsaturated when they contain less than the maximum amount of solute one can fit, or supersaturated when they contain more than a saturated solution. Supersaturated solutions tend to be unstable and the solute tends to eventually precipitate. Table 2.1 reports different types of solutions with examples.

Table 2.1 Types of solutions

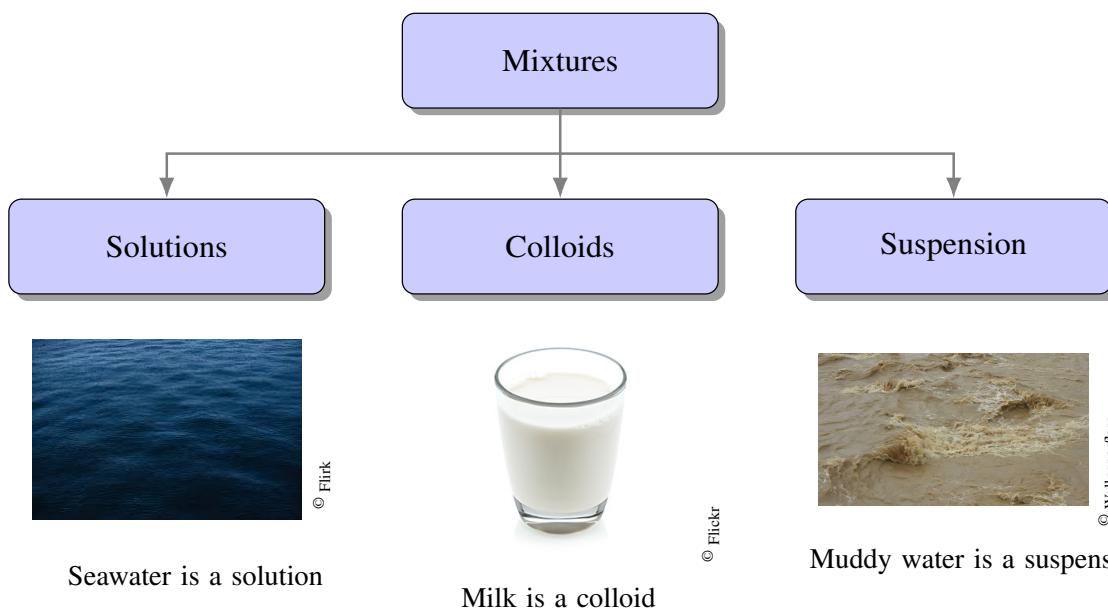
Solute	Solvent	Solution state	Example
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Club soda
Gas	Solid	Solid	H <sub>2</sub> in Pd
Liquid	Liquid	Liquid	Acetone in water
Liquid	Solid	Solid	Easy light charcoal
Solid	Liquid	Liquid	Saltwater
Solid	Solid	Solid	Brass



Table 2.1 reports different types of solutions with examples.

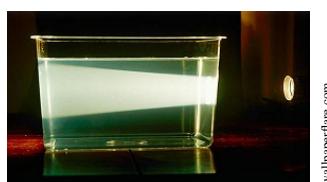
**Solutions** In solutions, the solute particles are dispersed evenly throughout the solvent giving homogeneous mixtures. As such, in a solution such as seawater, the solute cannot be visually distinguished from the solvent. The mixture appears transparent even when it may have a certain color. The solute particles are so small that they can go through filters and membranes.

**Suspensions** Suspensions are heterogeneous mixtures. The particles of a suspension are so large that they can often be visually seen and they can be trapped using filters and membranes. Because of its weight, suspended particles tend to segregate and settle out on the bottom of suspensions. Examples of suspensions are antacid mixtures or liquid penicillin (see Figure 2.1).



**Figure 2.1** Classification of the mixtures

▼The Tyndall effect of a liquid



▼The Tyndall effect of a gas



**Colloids** We have that solutions are homogeneous mixtures in the form of only one visible phase. If we add an ionic solute to a solvent, the solute particles would break down into ions and these ions would be solvated by the solvent molecules. As such, the solute in solution exists in a different state than the solid solute. We also have that a heterogeneous mixture would result from mixing sand and water. The particles of sand will suspend on the liquid but eventually, they will deposit on the bottom of the container. Between homogeneous and heterogeneous mixtures we have colloids or *colloidal dispersions*. Colloids are special types of homogeneous mixtures. Colloids are suspensions of two components that are indeed immiscible in a non-homogeneous way. Think for example of milk, which is a colloid containing small particles of fat and protein suspended in a liquid. The particles of fat are called the dispersed phase and the liquid matrix is called the dispersing medium. The suspended particles of a colloid are larger than the particles of a normal homogeneous solution. Also, and perhaps more importantly, the particles of a colloid can be separated and for example, by adding a few drops of lemon to a glass of milk you will be able to separate both the fat and the liquid. In contrast, solutions are made of inseparable components and the only way to separate the solvent and solute in a solution is by boiling it. Colloids are named depending on the nature of the dispersed and dispersant phases: aerosols (e.g. fog), foams (e.g. whipped cream), emulsions (e.g. mayonnaise), sols (e.g. milk of magnesia), and gels (e.g. jelly) are just a few examples of different types of colloids. How to differentiate a solution and a colloid? The Tyndall effect exposes the differences between solutions and



colloids. A focused beam of light can easily pass through a solution as the particles of the solute are smaller than the light wavelength. Differently, when a colloid is exposed to the same light it will be scattered by the dispersed phase of the colloid which has a larger size. Therefore, you will be able to see the beam passing through the colloid. An example of the Tyndall effect is the scattering of light from the car headlights on a foggy day. Many factors stabilize a colloid, allowing two very different phases to coexist. In particular, electrostatic repulsions are known to play a key role in colloidal stability, hence avoiding coagulation. Colloidal particles are electrically neutral. Still, when applying an electrical field experiment demonstrates that all particles migrate towards the same electrode. Hence, all particles seem to have the same electrical charge. How can these particles coexist together? Experiments indicate that colloidal particles can be surrounded by several layers of electrically charged particles. These layers can impede coagulation. For example, colloidal particles can surround themselves with a layer of positive particles, and at the same time, this positive layer surrounds with another layer of negative charges. This series of external layers of charged particles exert repulsion among colloidal particles avoiding coagulation. Colloids can be destructed in a process called *coagulation*, which can be accomplished either by heating or by adding an electrolyte. On one hand, heating increases the average speed of colloidal particles which helps coagulation. On the other hand, adding electrolytes impacts the charged, protective layer that stabilizes colloidal particles, hence inducing coagulation (e.g. think what happens when you add lemon juice to a glass of milk). An example of colloid coagulation happens when a river reaches the salty ocean depositing. Sea electrolytes help produce clay particles. Similarly, electrostatic precipitators improve the air quality of industrialized cities by removing soot from smoke. Table 2.2 reports all different types of colloids one can encounter with examples for each of them.

**Table 2.2 Types of colloids**

Dispersing medium	Dispersed medium	name	Example
Gas	Liquid	Aerosol	Fog
Gas	Solid	Aerosol	Smoke
Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Emulsion	Mayonnaise
Liquid	Solid	Sol	Milk of magnesia
Solid	Gas	Foam	Styrofoam
Solid	Liquid	Gel	jelly
Solid	Solid	Solid sol	alloys

## 2.2 Units of concentration

There are numerous units to express concentration. Here, we will cover molarity, molality, percent of the mass, and mole fraction. We will also review the concept of density under a new light. More importantly, we will also learn how to interchange different concentration units.

*The concept of solution* Mind that solution results of adding a solute to a solvent.

$$\text{solution} = \text{solvent} + \text{solute} \quad (2.1)$$



*Molarity, M* Molarity, M, is defined as the moles of solute divided by the liters of solution. In this chapter, it is critical to specify the nature of the moles and the volume, as one can think of moles of solute or moles of solvent, as well as liters of solution or liters of solvent.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (2.2)$$

For example, if we mix 0.4 moles of NaCl and we fill the beaker until we reach a 100mL (0.1L) mark, the molarity of the solution will be 4M.

*Mole fraction,  $\chi$*  The mole fraction of a solute is the ratio of the moles of solute over the moles of solution—that is moles of solute plus the moles of solvent.

$$\chi = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}} \quad (2.3)$$

For example, if we mix 0.4 moles of NaCl and 0.6 moles of water, the mole fraction of solute will be 0.4. We can define a similar mole fraction of solvent and both, the mole fraction of solvent and solute should add up to 1.

*Percent by mass,  $\%_m$*  The percent by mass (or percent by weight) of a solute is the ratio of the grams of solute over the grams of solution—that is grams of solute plus the grams of solvent—multiplied by 100.

$$\%_m = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100 \quad (2.4)$$

There is an equivalent concentration measure to the solute percent by mass but based on volume called the solute percent by volume.  $\%_v$  is calculated as the ratio of the solute volume and the solution volume in percent form. This percentage is useful when the solute and solvent are both liquids and can be measured in terms of volume. For example, if we mix 5 grams of NaCl and 100 grams of water, the percent by mass of solute will be 5%. We can define a similar percent by mass of solvent and both, the percent by mass of solvent and solute should add up to 100.

*Molality, m* The molality of a solution is the number of moles of solute per kilogram of solvent.

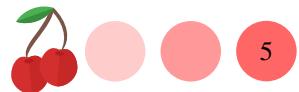
$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} \quad (2.5)$$

For example, if we mix 5 grams of NaCl and 100 grams (0.1 kg) of water, the molality of the solution will be 50m. The properties of molarity and molality are different. In particular, molarity (M) depends on temperature. As the volume of a liquid slightly increases with temperature, molarity decreases with temperature. Differently, molality (m) is temperature-independent.

*Density of a solution, d* The density of a solution—often expressed in g/mL—is the ratio of the grams of solution and the mL of solution.

$$d = \frac{\text{grams of solution}}{\text{mL of solution}} \quad (2.6)$$

Density is used to convert the mass of solution into the volume of solution, or the opposite. In the case of pure water, the density of water is 1g/mL that is the mass in grams of water equals its volume in mL.



*Normality of a solution, N* Normality is another way to express concentration. This unit is normally used for acid, bases, oxidizing, or reducing agents. *Normality* is defined as the number of equivalents per liter of solution and is related to molarity

$$N = n_{eq} \cdot M$$

where  $M$  is molarity and  $n_{eq}$  is the number of equivalents. Still, the definition of an equivalent changes based on the species in solution. In an acid-base reagent, the number of equivalents is the number of protons or hydroxyls an acid or base can produce. For example, for  $\text{H}_2\text{SO}_4$   $n_{eq}$  is 2 and for  $\text{H}_3\text{PO}_4$   $n_{eq}$  is 3. Therefore, a 1M solution of  $\text{H}_2\text{SO}_4$  will be 2 normal. For redox reactions, the equivalent is defined as the quantity of redox agents that can exchange one mole of electrons. For example, permanganate exchanges  $5e^-$  during redox reaction based in the reaction below:  $\text{MnO}_4^- + 5e^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$  therefore 1M solution of  $\text{KMnO}_4$  will be 5 normal. When dealing with normality, historically one speaks about the *equivalent mass* or equivalent weight of a reagent, defined as the molar mass divided by the number of equivalents.

### Sample Problem 1

A solution is prepared by mixing 1g of NaCl (MW=59g/mol) in 100g of water to give a final volume of 120mL. Calculate: (a) The percent by mass of solute (b) The mole fraction of solute (c) The molarity of the solution (d) The molality of the solution (e) The density of the solution

#### SOLUTION

In this example it is convenient to recall all the parameters we have in terms of solute, solvent and solution. Regarding the solute, we have the mass of solute ( $m_{\text{solute}} = 1\text{g}$ ), and the moles of solute ( $n_{\text{solute}} = 1\text{g} \times \frac{1\text{ mol of NaCl}}{59\text{ g of NaCl}} = 0.017\text{ moles}$ ). Regarding the solvent, we have the mass of solvent ( $m_{\text{solvent}} = 100\text{g}=0.1\text{kg}$ ), the moles of water ( $n_{\text{solvent}} = 100\text{g} \times \frac{1\text{ mol of H}_2\text{O}}{18\text{ g of H}_2\text{O}} = 5.6\text{ moles}$ ), and the volume of solvent ( $v_{\text{solvent}} = 100\text{mL}$ ). Mind that in the case of water, very normally, its mass in grams equals to its volume in mL. In terms of solution, we can compute the mass of solution ( $m_{\text{solution}} = 1 + 100 = 101\text{g}$ ), the moles of solution ( $n_{\text{solution}} = 0.017 + 5.6 = 5.617\text{ moles}$ ), and the volume of solution ( $v_{\text{solution}} = 120\text{mL}=0.12\text{L}$ ). Now, we are ready to compute all concentration units of the solution. The percent by mass of solute is the ration between the mass of solute and the mass of solution times 100:

$$\%_m = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100 = \frac{1\text{g of solute}}{101\text{g of solution}} \times 100 = 0.99\%$$

The mole fraction is the ration between the moles of solute and moles of solution:

$$\chi = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}} = \frac{0.017\text{ moles of solute}}{5.617\text{ moles of solution}} = 3.02 \times 10^{-3}$$

The molarity of the solution is the ration between the moles of solute and the liters of solution:

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{5.617\text{ moles of solution}}{0.12\text{L of solution}} = 46.8\text{M}$$

The molality is the ration between the moles of solute and the kg of solvent:

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.017\text{ moles of solute}}{0.1\text{kg of solvent}} = 0.17\text{m}$$

Finally, density of the solution is the ration of the grams of solution and the volume of solution:

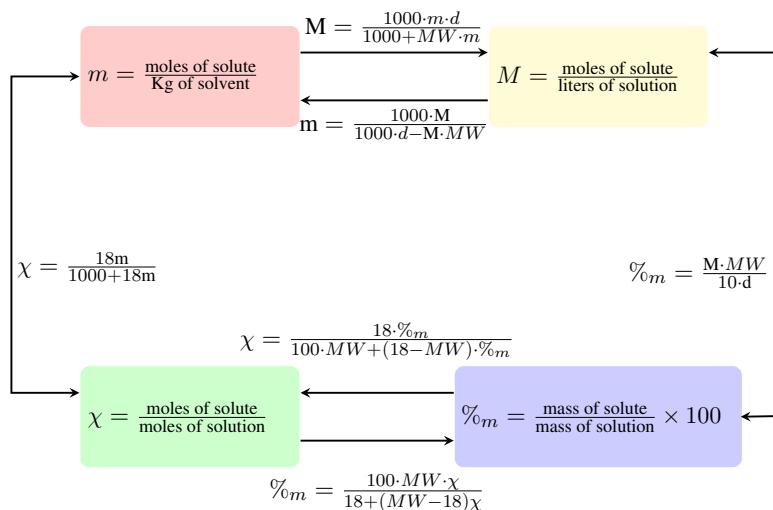
$$d = \frac{\text{grams of solution}}{\text{mL of solution}} = \frac{101\text{g of solution}}{120\text{mL of solution}} = 0.84\text{g/mL}$$



### ◆ STUDY CHECK

A solution is prepared by mixing 1g of glucose (MW=180g/mol) in 50g of water to give a final volume of 100mL. Calculate: (a) The percent by mass of solute (b) The mole fraction of solute (c) The molarity of the solution (d) The molality of the solution (e) The density of the solution

►Answer: (a) 1.96% (b)  $2 \times 10^{-3}$  (c) 0.05M (d) 0.11m (e) 0.51g/mL



**Figure 2.3** Diagram displaying the set of formulas used to relate, from left to right, molality with molarity, mass percent of solute, and mole fraction. In some of these formulas, the solution density  $d$  (in g/mL) is needed as well as the molar mass of the solute ( $MW$ ). The solvent in all these equations is assumed to be water and hence the 18 value in some of the formulas.

## 2.3 Relating units of concentration

When you prepare a solution you normally weigh a given amount of solute and add some volume of solvent. That will give you a given concentration that you can compute in terms of for example molarity. Often, you encounter a solution already prepared, for example, a 2M solution and you need to know a different type of concentration unit, such as its molality. That is why relating concentration units is important. In the next sections, we will cover how the different concentration units are related. Figure displays all formulas used to relate different units of concentration.

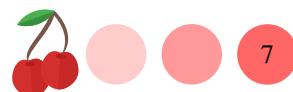
*Relating molarity and molality,  $M \longleftrightarrow m$*  We can use the following formula to relate Molarity and molality

$$m = \frac{1000 \cdot M}{1000 \cdot d - M \cdot MW} \quad \text{or} \quad M = \frac{1000 \cdot m \cdot d}{1000 + MW \cdot m} \quad (2.7)$$

where:

$M$  is the molarity of the solution

$m$  is the molality of the solution



$d$  is the density of the solution

$MW$  is the molecular weight of the solute

Mind that this formula only works for water as a solvent and uses 1g/mL as the density of water.

*Relating molarity and the percent by mass of solute,  $M \longleftrightarrow \%_m$*

We can use the following formula to relate Molarity and percent by mass of solute

$$M = \frac{\%_m \cdot d \cdot 10}{MW} \quad \text{or} \quad \%_m = \frac{M \cdot MW}{10 \cdot d} \quad (2.8)$$

where:

$M$  is the molarity of the solution

$\%_m$  is the percent by mass of solute

$d$  is the density of the solution

$MW$  is the molecular weight of the solute

*Relating percent by mass and mole fraction of solute,  $\chi \longleftrightarrow \%_m$*

We can use the following formula to relate Molarity and percent by mass of solute

$$\chi = \frac{18 \cdot \%_m}{100 \cdot MW + (18 - MW) \cdot \%_m} \quad \text{or} \quad \%_m = \frac{100 \cdot MW \cdot \chi}{18 + (MW - 18)\chi} \quad (2.9)$$

where:

$\chi$  is the solute mole fraction

$\%_m$  is the solute percent by mass

$MW$  is the molecular weight of the solute

18 is the molar weight of water

Mind that this formula only works for water as a solvent. If using a different solvent you just need to update the 18 value and use the molar weight of the new solvent instead.

### Sample Problem 2

A 2M NaCl (MW=59g/mol) solution has a density of 1.2g/mL. Calculate:

- (a) The molality of the solution
- (b) The mass percent of solute
- (c) The mole fraction of solute

#### SOLUTION

We will first convert molarity into molality using density and the molar mass of the solute.

$$m = \frac{1000 \cdot M}{1000 \cdot d - M \cdot MW} = \frac{1000 \cdot 2}{1000 \cdot 1.2 - 2 \cdot 59} = 1.84m$$

We will then convert molality into mass percent:

$$\%_m = \frac{M \cdot MW}{10 \cdot d} = \frac{2 \cdot 59}{10 \cdot 1.2} = 9.83\%$$

We will finally convert the mass percent of solute into mole fraction:

$$\chi = \frac{18 \cdot \%_m}{100 \cdot MW + (18 - MW) \cdot \%_m} = \frac{18 \cdot 9.83\%}{100 \cdot 59 + (18 - 59) \cdot 9.83\%} = 0.03$$

#### ❖ STUDY CHECK

For a 0.11m glucose (MW=180g/mol) solution with density 0.51g/mL, calculate:



- (a) The percent by mass of solute (b) The mole fraction of solute (c) The molarity of the solution

►Answer: (a) 1.76% (b)  $1.78 \times 10^{-3}$  (c) 0.05M

*Compute molecular masses from molality and molarity* In numerous applications, one needs to compute the molecular weight of a solute using a given molality or molarity. It is useful to remember that the molality of a solution is related to the moles of solute and the kilograms of solvent, in contrast to the molarity of a solution that depends on the liters of solution. When we prepare a solution we normally know the mass of the solute used and the mass of the solvent or the volume of the solution. We can compute the molar mass of the solute using:

$$MW = \frac{\text{g of solute}}{\text{m} \cdot \text{kg of solvent}} \quad \text{or} \quad MW = \frac{\text{g of solute}}{\text{M} \cdot \text{L of solution}} \quad (2.10)$$

where:

MW is the molar mass of the solute

g of solute is the mass of solute

kg of solvent is the mass of solvent

L of solution is the volume of solution

m is the molality of the solution

### Sample Problem 3

We prepare a solution by weighting 5g of solute and adding 10g of solvent in order to prepare a 0.1m solution. Calculate the molar mass of the solute.

#### SOLUTION

In this example, we are given molality ( $m=0.1$ ), the mass of solute ( $m_{\text{solute}}=5\text{g}$ ) and the mass of solvent ( $m_{\text{solvent}}=0.01\text{kg}$ ). In order to calculate the molar mass of a solute by means of molality we have that:

$$MW = \frac{\text{g of solute}}{\text{m} \cdot \text{kg of solvent}} = \frac{5}{0.1 \cdot 0.01} = 5000\text{g/mol}$$

#### ◆ STUDY CHECK

We prepare a solution by weighting 10g of solute and adding liquid until 100mL of solution in order to prepare a 2M solution. Calculate the molar mass of the solute.

►Answer: 50g/mol

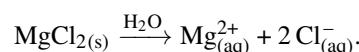
## 2.4 Solutions of electrolytes and effective solute particles

Chemicals can be classified based on their electrolyte character in strong electrolytes and non-electrolytes. Non-electrolytes do not dissociate in solution so each non-electrolyte molecule becomes a solute particle. Differently, strong electrolytes dissociate in solution

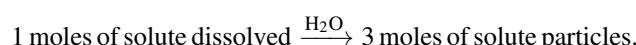


so that each strong electrolyte molecule gives more than one solute particle. This section covers the concept of effective solute particles and the idea of Van't Hoff factor  $i$  that relates the amount of moles of solute dissolved and the moles of solute particles.

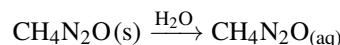
**Strong electrolytes** Strong electrolytes completely dissociate in water. Hence, in a solution of a strong electrolyte, you will mostly contain ions. Strong electrolytes are typically ionic compounds such as MgCl<sub>2</sub> or NaCl (table salt). We represent the dissociation of a strong electrolyte with a single arrow, meaning that the reaction proceeds to completion. For the example below, in the solution, we will only have ions (Mg<sup>2+</sup><sub>(aq)</sub> + 2 Cl<sup>-</sup><sub>(aq)</sub>) and not magnesium chloride molecules (MgCl<sub>2(s)</sub>):



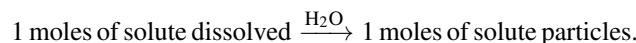
For this electrolyte, in terms of solute dissolved and solute particles, we have that one mole of solute dissolved will give three moles of solute particles:



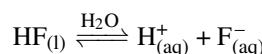
**Nonelectrolytes and weak electrolytes** Nonelectrolytes do not dissociate in water. Hence a solution of a nonelectrolyte will mostly contain molecules of that electrolyte and not ions. Examples of nonelectrolytes are carbon-based chemicals such as methanol, ethanol, urea, or sucrose. The dissociation of urea for example CH<sub>4</sub>N<sub>2</sub>O proceeds as:



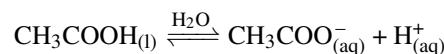
For this electrolyte, in terms of solute dissolved and solute particles, we have that one mole of solute dissolved gives one mole of solute particle:



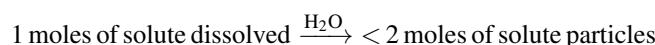
Weak electrolytes partially dissociate in water, and on paper, this is indicated using a chemical reaction with a double arrow. Hence in a solution of a weak electrolyte, you will have both ions as well as molecules of the electrolyte. Examples of weak electrolytes are hydrofluoric acid, water, ammonia, or acetic acid. The dissociation of hydrochloric acid (HF) proceeds as:



Acetic acid (CH<sub>3</sub>COOH) is an important weak electrolyte and its dissociation proceeds somehow in a peculiar way:



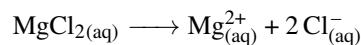
For this electrolyte, in terms of solute dissolved and solute particles, we have that one mole of solute dissolved will give less than two moles of solute particles:



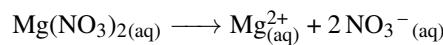
**Breaking down electrolytes into ions** Electrolytes—in particular strong electrolytes—dissociate producing ions. This way, a solution of for example NaCl does not contain NaCl molecules but Na<sup>+</sup><sub>(aq)</sub> cations and Cl<sup>-</sup><sub>(aq)</sub> anions. Hence it is important



to correctly break down electrolytes into ions. To do this, you need to revert the combination of ions that produce a given chemical while making sure the charges are balanced. For example, let us break magnesium chloride  $MgCl_{2(aq)}$  into ions. This is a strong electrolyte formed by magnesium cations and chloride anions. The valence of magnesium is +II and the valence of chlorine is -I. The  $MgCl_2$  formula also tells us we have one magnesium and two chlorines. The overall process is:



Another example is magnesium nitrate  $Mg(NO_3)_2$ . This strong electrolyte—as this is an ionic salt—is made of lithium with valence +I and nitrate with valence -I. The formula indicates we have one  $Mg_{(aq)}^{2+}$  and two  $NO_3^-_{(aq)}$ . Hence:



#### Sample Problem 4

Break down the following chemicals into ions, if possible:

Chemical	Particles in solution
$K_2CrO_4(aq)$	
$Ba(NO_3)_2(aq)$	
$BaCrO_4(s)$	
$KNO_3(aq)$	

#### SOLUTION

We can only break down into ions ionic compounds and oxosalts that are not solid. From the list of chemicals in the example, we will not be able to break down  $BaCrO_4(s)$  into ions as it is a solid. From the other chemicals,  $K_2CrO_4(aq)$  is named potassium chromate and contains  $2K_{(aq)}^+$  and  $CrO_4^{2-}_{(aq)}$  ions. Barium nitrate— $Ba(NO_3)_2(aq)$ —will produce  $Ba_{(aq)}^{2+}$  and  $2NO_3^-_{(aq)}$ . Finally, potassium nitrate— $KNO_3(aq)$ —will produce  $K_{(aq)}^+$  and  $NO_3^-_{(aq)}$ . In the table:

Chemical	Particles in solution
$K_2CrO_4(aq)$	$2K_{(aq)}^+ + CrO_4^{2-}_{(aq)}$
$Ba(NO_3)_2(aq)$	$Ba_{(aq)}^{2+} + 2NO_3^-_{(aq)}$
$BaCrO_4(s)$	$BaCrO_4(s)$
$KNO_3(aq)$	$K_{(aq)}^+ + NO_3^-_{(aq)}$

#### ❖ STUDY CHECK

Break down the following chemicals into ions, if possible:  $H_2O(l)$ ,  $NH_3(l)$ ,  $AgNO_3(aq)$ .

►Answer:  $H_2O(l)$ ,  $NH_3(l)$ ,  $Ag_{(aq)}^+$ ,  $NO_3^-_{(aq)}$ .

**Table 2.3 Expected and observed Van't Hoff factors for different concentrations.**

Solute	$i^{\text{Observed}}$			$i^{\text{Expected}}$	$i^{\text{Observed}} / i^{\text{Expected}} * 100$		
	0.1m	0.01m	0.001m		0.1m	0.01m	0.001m
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	1.00	1.00	1.00	1.00	100%	100%	100%
NaCl	1.87	1.94	1.97	2.00	93.5%	97.0%	98.5%
K <sub>2</sub> SO <sub>4</sub>	2.32	2.70	2.84	3.00	77.3%	90.0%	64.6%
MgSO <sub>4</sub>	1.21	1.53	1.82	2.00	60.5%	76.5%	91.0%

Table 2.3 reports observed and expected  $i$  values for different salts and different concentrations.

*Van't Hoff factor  $i$*  This factor for a given electrolyte is related the number of dissolved particles and the number of solute particles:

$$i = \frac{\text{moles of solute particles}}{\text{moles of dissolved particles}} \quad (2.11)$$

For example, all non-electrolytes produce only a single solute particle, as they do not break down in solution and therefore for all non-electrolytes  $i$  is 1. Differently, the  $i$  values for a strong electrolyte depend on the salt stoichiometry. For example, for NaCl  $i$  is two, as one mole of salt produces two moles of ions, and for CaCl<sub>2</sub>  $i$  is 3, as one mole of calcium fluoride produces three moles of ions, overall. It is important to notice the research has found that the Van't Hoff factor indeed depends on the concentration of the salt and for large concentrations the expected  $i$  value not always correspond to the observed value, due to the formation of ion pairs, pairs of ions that associate on solution reducing the effective ion concentration.

At low concentrations, the effect of ion pairs is less pronounced and the expected value tends to resemble the observed value:  $i^{\text{Expected}} \approx i^{\text{Observed}}$ . The Van't Hoff factor is reported for strong electrolytes. A property called percent dissociation of an electrolyte,  $\alpha$ , is helpful to describe the dissociation of weak electrolytes. Strong electrolytes dissociate completely and hence the effective concentration of ions is the same as the nominal concentration of solute particles. Weak electrolytes, on the other hand, do not completely dissociate in solution and the effective concentration of solute particles tends to be smaller than the nominal concentration. We have that:

$$\alpha = \frac{c^{\text{effective}}}{c^{\text{Nominal}}} \times 100 \quad (2.12)$$

Percent dissociation is zero for nonelectrolytes as no ions are produced and hence the effective ion concentration is null. Finally, percent dissociation for strong electrolytes is 100% as the nominal and effective ion concentrations are the same. Note that the percent dissociation can change with concentration. Table 2.3 reports observed and expected  $i$  values for different salts and different concentrations.

### Sample Problem 5

A solution that is 0.02M in HF has a effective ion concentration of 0.015M. Calculate the percent dissociation of the electrolyte.

#### SOLUTION

The percent dissociation,  $\alpha$ , is the ration between the effective ion concentration (the amount of ions in solution) and the nominal concentration (the amount of



▼ Streets are salted to reduce the freezing point of ice



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▼ A solution of ethyleneglycol is used as antifreeze in cars



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▼ Any salt would reduce the intensity of a perfume



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▼ Salting fish kills bacteria by removing water inside its cells



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▼ Adding salt to boiling water increases the boiling point of water



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solute added to the solution). We have that the nominal concentration is 0.02M and the effective concentration is 0.015M. As usual for weak electrolytes, the effective concentration is lower than the nominal one as some molecules did not dissociate. We can calculate the percent dissociation:

$$\alpha = \frac{c^{\text{effective}}}{c^{\text{Nominal}}} \times 100 = \frac{0.015}{0.02} \times 100 = 75\%$$

The results indicate that only the 75% of the solute dissociate in solution.

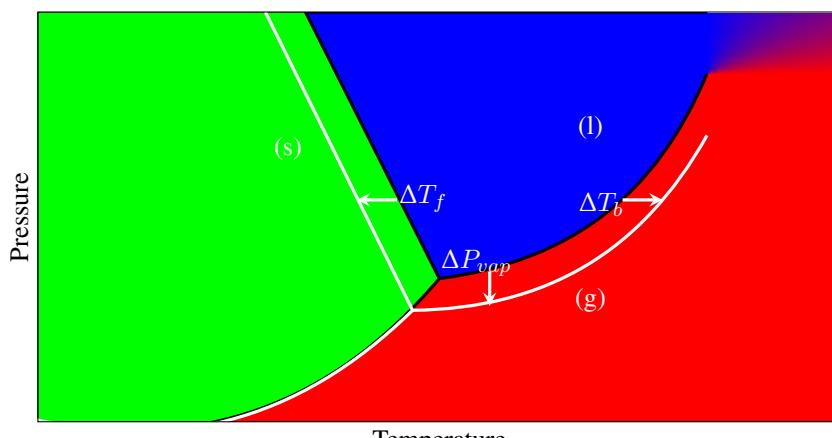
#### ◆ STUDY CHECK

The percent dissociation of a 0.1M weak electrolyte is 40%. Calculate the effective concentration of the electrolyte.

► Answer: 0.04M

## 2.5 Colligative properties

Colligative properties of solutions are properties that depend on the concentration of solute but not on the nature of this solute. In the following, we will elaborate more on the idea of colligative properties. Indeed, there are four colligative properties of the solutions: the freezing point decrease, the boiling point increase, the osmotic pressure, and the vapor pressure. Mind that these are all properties of solutions and not of pure substances. Figure 2.3 displays the effect of the solute concentration on the phase diagram of water.



**Figure 2.3** Effect of the solute concentration on the phase diagram of water

**Boiling point elevation** Solutions are made of a solute dissolved in a solvent.

Pure solvents have a specific boiling point. When we made a solution, the solution boils at a different temperature than the pure solvent, and in particular, a solution boils at a higher temperature than the solvent. This effect is called the boiling point elevation of a solution in comparison with the pure solvent. The boiling point elevation does not depend on the nature of the solute and only depends on the molality (m) of the solution using the following formula:

$$T_b^{\text{solution}} = T_b^{\text{solvent}} + k_b \cdot i \cdot m \quad \text{or} \quad \Delta T_b = k_b \cdot i \cdot m \quad (2.13)$$

where:



$T_b^{\text{solution}}$  is the boiling point of the solution

$T_b^{\text{solvent}}$  is the boiling point of the pure solvent

$k_b$  is called molal boiling point elevation constant in units of  $^{\circ}\text{C}/m$

$m$  is the molality of the solution

$i$  is van't Hoff factor of the solute

$\Delta T_b$  is the boiling point increase, that is  $T_b^{\text{solution}} - T_b^{\text{solvent}}$

$i \cdot m$  is the effective concentration of solute particles

Mind that  $i \cdot m$  represents the effective solute-particle concentration in the solution. For the case of NaCl  $i$  is 2 as every NaCl unit dissociates producing 2 ions or two solute-particles. The value of  $k_b$  depends on the solvent and in general boiling point increases tend to be modest. For example, a water-based solution containing NaCl boils at a higher temperature than pure water which boils at  $100^{\circ}\text{C}$ . A 1m NaCl solution boils at  $101.04^{\circ}\text{C}$  which is one degree higher than pure water. The boiling point elevation formula establishes a linear relationship between the boiling point of a solution and molality in which the slope of the relationship is positive and gives the value of  $k_b$ , the  $x$  variable is  $m$  and the  $y$  variable is  $T_b^{\text{solution}}$ . In other words, by plotting  $T_b^{\text{solution}}$  vs.  $m$  we should obtain a straight line with a slope that equals to  $k_b$  and an intercept equals to  $T_b^{\text{solvent}}$ .

*Freezing point depression* A pure solvent freezes at a specific temperature and for example, water freezes at  $0^{\circ}\text{C}$ . Solutions freeze at a lower temperature than the pure solvent. We call this effect the freezing point depression. This decrease in the freezing point depends only on the molality of the solution and not on the solute. The freezing point depression—or decrease—is given by the formula:

$$T_f^{\text{solution}} = T_f^{\text{solvent}} - k_f \cdot i \cdot m \quad \text{or} \quad \Delta T_f = -k_f \cdot i \cdot m \quad (2.14)$$

where:

$T_f^{\text{solution}}$  is the freezing point of the solution

$T_f^{\text{solvent}}$  is the freezing point of the pure solvent

$k_f$  is called molal freezing point depression constant in units of  $^{\circ}\text{C}/m$

$m$  is the molality of the solution

$i$  is van't Hoff factor of the solute

$\Delta T_f$ , a negative value, is the freezing point depression, that is

$T_f^{\text{solution}} - T_f^{\text{solvent}}$

$i \cdot m$  is the effective concentration of solute particles

Mind that  $i \cdot m$  represents the effective solute-particle concentration in the solution. For the case of NaCl  $i$  is 2 as every NaCl unit dissociates producing 2 ions, or 2 solute particles. For example, pure water freezes at  $0^{\circ}\text{C}$  but a 1m NaCl solution freezes at  $-3.72^{\circ}\text{C}$ , which is almost four degrees lower than pure water. The freezing point depression formula establishes a linear relationship between the freezing point of a solution and molality in which the slope of the relationship is negative and gives the value of  $k_f$ , the  $x$  variable is  $m$  and the  $y$  variable is  $T_f^{\text{solution}}$ . In other words, by plotting  $T_f^{\text{solution}}$  vs.  $m$  we should obtain a straight line with a slope in absolute value that equals  $k_f$  and an intercept equals  $T_f^{\text{solvent}}$ . Table 2.4 reports values for the boiling-point elevation and freezing-point depression for various solvents.

**Table 2.4 Boiling-point elevation and freezing-point depression for various solvents**

Solvent	$T_b^{\text{solvent}}$ (°C)	$k_b$ (°C/m)	$T_f^{\text{solvent}}$ (°C)	$k_f$ (°C/m)
Acetic acid	117.9	3.07	16.6	3.90
Benzene	80.1	2.53	5.5	4.90
Carbon disulfide	46.2	2.34	-111.5	3.83
Carbon tetrachloride	76.5	5.03	-23	30
Chloroform	61.7	3.63	-63.5	4.70
Diethyl ether	34.5	2.02	-116.2	1.79
Ethanol	78.5	1.22	-117.3	1.99
Water	100	0.512	0	1.86
Cyclohexane	80.7	2.79	6.5	20.1

Table 2.4 reports values for the boiling-point elevation and freezing-point depression for various solvents.

### Sample Problem 6

For a solution of 5 g of I<sub>2</sub> (MW=254g/mol) in 100 g of benzene, C<sub>6</sub>H<sub>6</sub>: (a) Calculate its molality (b) Given that benzene boiling point is 80°C, and that  $k_b = 2.53$  °C/m, calculate the boiling point and the boiling point elevation of the solution. (c) Given that benzene freezing point is 5°C, and that  $k_f = 5.10$  °C/m, calculate the freezing point and the freezing point depression of the solution.

#### SOLUTION

In order to calculate the molality of the solution, we need the moles of solute ( $5\text{g} \times \frac{1\text{mol}}{254\text{g}} = 0.019\text{moles}$ ) and the kilograms of solvent (100g=0.1kg). We have that molality is

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.019}{0.1} = 0.19m$$

With the molality, we can calculate the freezing and boiling point of the solution. Mind that the pure solvent freezes at 5°C and boils at 80°C. The solution will freeze at a lower temperature and will boil at a higher temperature—that is, it will experience a freezing depression and boiling elevation. We will calculate first the freezing point (and freezing point depression):

$$T_f^{\text{solution}} = T_f^{\text{solvent}} - k_f \cdot i \cdot m = 5 - 5.10 \cdot 1 \cdot 0.19 = 4.031^\circ\text{C}$$

In other words the freezing depression will be

$$\Delta T_f = -k_f \cdot i \cdot m = -5.10 \cdot 1 \cdot 0.19 = -0.969^\circ\text{C}$$

We will now calculate the boiling point elevation:

$$T_b^{\text{solution}} = T_b^{\text{solvent}} + k_b \cdot i \cdot m = 80 + 2.53 \cdot 1 \cdot 0.19 = 80.48^\circ\text{C}$$

In other words the boiling elevation will be

$$\Delta T_b = k_b \cdot i \cdot m = 2.53 \cdot 1 \cdot 0.19 = 0.4807^\circ\text{C}$$

#### ◆ STUDY CHECK

For a solution of 5 g of NaCl (MW=58g/mol) in 100 g of acetic acid, CH<sub>3</sub>COOH:



(a) Calculate its molality (b) Given that the boiling point of acetic acid is 118°C, and that  $k_b = 3.08 \text{ } ^\circ\text{C}/\text{m}$ , calculate the boiling point and the boiling point elevation of the solution. (c) Given that the freezing point of acetic acid is 17°C, and that  $k_f = 3.59 \text{ } ^\circ\text{C}/\text{m}$ , calculate the freezing point and the freezing point depression of the solution.

►Answer: (a) 0.86m (b) 123.3°C ; 5.29°C (c) 10.82°C ; -6.17°C

**Vapor-pressure lowering** Every liquid exerts a certain vapor pressure that depends on temperature. The molecules on the surface of the liquid are less tied than the molecules of the interior part of the liquid called the bulk. As such, they can escape producing what we call the vapor pressure of the liquid. Solutions exert lower vapor pressure than pure solvents. The vapor-pressure lowering is a colligative property that depends on the solute mole fraction:

$$P_{vap}^{\text{solution}} = P_{vap}^{\text{solvent}} - \chi \cdot P_{vap}^{\text{solvent}} \quad \text{or} \quad \Delta P_{vap}^{\text{solution}} = -\chi \cdot P_{vap}^{\text{solvent}} \quad (2.15)$$

where:

$P_{vap}^{\text{solution}}$  is the vapor pressure of the solution

$P_{vap}^{\text{solvent}}$  is the vapor pressure of the pure solvent

$\chi$  is the solute mole fraction

$\Delta P_{vap}^{\text{solution}}$ , a negative value, is the vapor-pressure lowering, that is,  
 $P_{vap}^{\text{solution}} - P_{vap}^{\text{solvent}}$

For example, the vapor pressure of water at 25°C is 0.03 atm. If we make a solution with a 0.5 solute mole fraction by adding table salt to the water, the vapor pressure of this solution would be 0.015 atm. In other words, the vapor pressure is lower than the one from pure water. Equation 2.15 is called Raoult's Law. Raoult's Law establishes a linear relationship between the vapor pressure of a solution and the mole fraction in which the slope of the relationship gives the vapor pressure of the pure solvent, the  $x$  variable is  $1 - \chi$  and the  $y$  variable is  $P_{vap}^{\text{solution}}$ . Simply put, by plotting  $P_{vap}^{\text{solution}}$  vs.  $1 - \chi$  we obtain a straight line with a slope equals to  $P_{vap}^{\text{solvent}}$ .

### Sample Problem 7

Given that the vapor pressure of water at 25°C is 0.03 atm, calculate the vapor pressure and the vapor pressure lowering of a 20% of mass NaCl (MW=59g/mol) solution at that temperature.

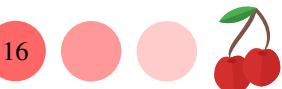
#### SOLUTION

In order to calculate the vapor pressure of a solution or the vapor-pressure lowering of a solution we need to calculate the mole fraction of the solute. We can calculate  $\chi$  by means of the solution of the solute mass percent:

$$\chi = \frac{18 \cdot \%_m}{100 \cdot MW + (18 - MW) \cdot \%_m} = \frac{18 \cdot 20}{100 \cdot 59 + (18 - 59) \cdot 20} = 0.07$$

Now, with the mole fraction of the solute and given that the vapor pressure of the solvent is 0.03atm, we can compute first the vapor pressure of the solution

$$P_{vap}^{\text{solution}} = (1 - \chi) \cdot P_{vap}^{\text{solvent}} = (1 - 0.07) \cdot 0.03 = 0.028 \text{ atm}$$



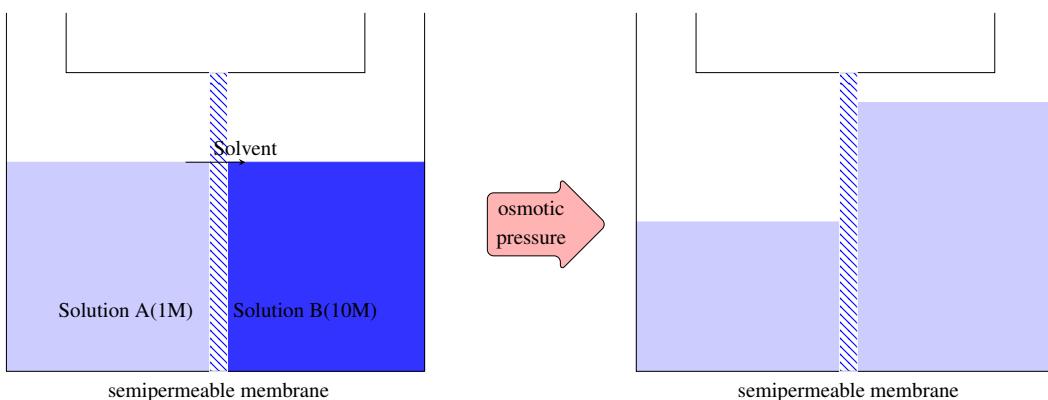
and then the vapor-pressure lowering

$$\Delta P_{vap}^{\text{solution}} = -2.1 \times 10^{-3} \text{ atm}$$

### ❖ STUDY CHECK

For a 3m I<sub>2</sub> (MW=254g/mol) solution in cyclohexane (MW=84g/mol) at 279K given given that the vapor pressure of cyclohexane at that temperature is 5.164kPa and the solution density is 1.3g/mL: (a) calculate the solute mole fraction. (b) calculate the vapor-pressure lowering in kPa.

►Answer: (a)  $\chi = 0.24$  (b)  $\Delta P_{vap} = -1.23 \text{ kPa}$



**Figure 2.4** In the left diagram, we put in contact two solutions with different concentrations by means of a semipermeable membrane. The left solution is more diluted than the right solution. The difference in osmotic pressure between the membrane creates a water flow that goes from the more diluted to the more concentrated solution that minimizes the pressure gradient. As a result the liquid level changes.

*Osmotic pressure of a solution* The pressure of gas results from the movement of the gas particles as they hit the walls of their container. The higher the hitting frequency the higher pressure. More specifically, the pressure of a gas depends on the force exerted by the gas molecules per unit of container area. Solutions can also exhibit pressure as solute molecules also hit the walls of their container. This pressure is called osmotic pressure,  $\Pi$ . The higher the molarity, that is the number of moles per liter in the solution, the higher the osmotic pressure of a solution:

$$\boxed{\pi = i \cdot M \cdot RT} \quad (2.16)$$

where:

$\pi$  is the osmotic pressure of the solution in atm

$M$  is the molarity of the solution

$R$  is the constant of the gases: 0.082 atm·L/(mol· K) (62.363577 torr·L/(mol· K))

$T$  is the temperature of the solution in K

$i$  is van't Hoff factor of the solute

$i \cdot M$  is the effective concentration of solute particles

The osmotic pressure of solutions is responsible for an effect called *osmosis*. First, let us talk about what is a semipermeable membrane. These are a type of membranes that allow the passing of solvent molecules without allowing the passing of solute molecules. We could set up an experiment in which we separate two solutions of



different concentrations by a semipermeable membrane and we will certainly see that the level of liquid in the most concentrated solution will rise, whereas the level of liquid in the most dilute will reduce. This effect results from the travel of water molecules from the less to the more concentrated solution equilibrating the osmotic pressure at the semipermeable membrane. Solute diffusion normally occurs against the concentration gradient. Solute diffuses from more to less concentrated solution. The more concentrated solution is referred to as the hypertonic solution, whereas the less concentrated solution is referred to as the hypotonic solution. Differently, solvent diffusion occurs following the concentration gradient (Low M → High M). On one hand, osmosis can be prevented by applying external pressure to the most concentrated solution. The minimum pressure that stops the osmosis is the osmotic pressure of the solution. On the other hand, osmotic pressure is regularly employed to experimentally obtain molar masses of soluble solutes. This colligative property is particularly useful on top of the others as small molarities cause relatively large osmotic pressures. Figure 2.4 displays how differences in osmotic pressure between the membrane create a water flow that goes from the more diluted to the more concentrated solution that minimizes the pressure gradient.

### Sample Problem 8

Calculate the osmotic pressure in torr of a 0.0125M KCl solution at 25°C.

#### SOLUTION

We have that the osmotic pressure of a solution is the pressure needed to stop the osmotic flow of water when the solution is placed in contact with pure solvent by means of semipermeable membrane. It depends on the number of ions in solution—KCl produces two ions and therefore  $i=2$ , molarity, and on temperature. Employing the value of the R constant in torr (62.363577 torr·L/(mol·K)) we have:

$$\Pi = i \cdot M \cdot R \cdot T = 2 \cdot 0.0125 \cdot 62.363577 \cdot 298 = 465 \text{ torr}$$

This result indicates that we would have to apply a 465 torr pressure to the solution in order to stop the osmotic flow of water.

#### ❖ STUDY CHECK

Calculate the osmotic pressure in torr of a 0.0345M K<sub>2</sub>CO<sub>3</sub> solution at 25°C.

►Answer: 1923 torr

*Colligative properties review* As you can see from the equations previously presented here, the vapor-pressure lowering, the freezing-point depression, the boiling-point elevation, and the osmotic pressure are all controlled by the concentration of the solute particles, in terms of molality, molarity, or mole fraction and they are unaffected by the nature of the solute. As such, a 1m NaCl solution will experience the same boiling-point increase as a 1m KCl solution, even if the solute is different. Colligative properties are associated with the nature of the solvent and the concentration of solute but not the nature of the solute. Furthermore, these formulas work well for very diluted solutions. We call these solutions, in general, ideal solutions.

## 2.6 Application of colligative properties



*Graphical method to calculate colligative constants* The formulas for the different colligative properties represent linear relationships. Therefore using plotting, we can calculate some of the colligative constants. The next example explains how to obtain colligative constants using a graphical method. To obtain any colligative constants, the plot involved in the calculation should represent a good-quality linear trend, and the statistic tool used to assess the goodness of a linear plot is called linear correlation or linear regression. Linear regression uses a linear correlation coefficient,  $r^2$ , to assess the quality of the fit. Good linear plots, in general, are characterized by values of linear correlation coefficient between 0.99 and 1. Differently,  $r^2$  values lower than 0.99 in general do not result from a truly linear relationship. No accurate colligative constants should be calculated from a set of data characterized by a poor linear correlation coefficient. Is important to keep in mind:

$$\begin{array}{ll} 0.99 \leq r^2 \leq 1.00 & \text{(Good linear regression)} \\ r^2 < 0.99 & \text{(Poor linear regression)} \end{array} \quad (2.17)$$

You can fit a linear regression to a set of experimental data either using a graphic calculator or using specialized [internet websites](#).

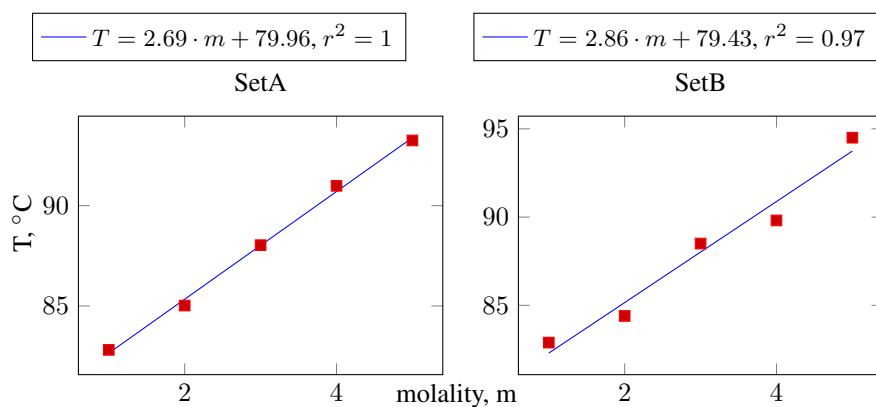
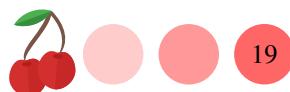
### Sample Problem 9

The following two sets of data report the change in boiling point of a solution. Assess the data to calculate the boiling elevation constant, and if possible, calculate colligative constant and the boiling point of the pure solvent.

Set A		Set B	
T(°C)	m	T(°C)	m
82.81	1	82.89	1
85.02	2	84.4	2
88.03	3	88.5	3
90.99	4	89.81	4
93.25	5	94.5	5

### SOLUTION

In order to ensure that the data is good enough to calculate the boiling elevation constant we need to assess the quality of the linear regression. By means of two regression analysis displayed below, we have that for Data set A,  $r^2$  is larger than 0.99 and hence this data set fits well a linear regression. On the other hand, the Data set B is not good enough in order to calculate the boiling point elevation constant as  $r^2$  is lower than 0.99. In another words, the Data set B does not represent a real linear relationship between boiling temperature and molality. Therefore, we will use Data set A in order to calculate the boiling elevation constant. From the slope of the line we will calculate  $k_b=2.69\text{°C/m}$  and from the intersect we will calculate the boiling point of the pure solvent  $T_b^{\text{solvent}} = 79.96\text{°C}$ .



### ❖ STUDY CHECK

The following two sets of data report the change in boiling point of a solution. Assess the quality of the data to calculate graphically the boiling elevation constant, and if possible, calculate colligative constant and the boiling point of the pure solvent.

Set A		Set B	
T(°C)	m	T(°C)	m
17.02	1	17.21	1
15.21	2	14.42	2
11.10	3	11.63	3
7.65	4	8.84	4
6.05	5	6.05	5

►Answer: Data set B,  $k_f = 2.79^\circ\text{C}$ ,  $T_f^{\text{solvent}} = 20^\circ\text{C}$

*Use of colligative properties to calculate  $\alpha$*  Colligative measurements can be used to calculate the percent dissociation ( $\alpha$ ) of an electrolyte. The idea is to compare the nominal concentration based on the preparation of the electrolyte solution and the effective concentration of ions and molecules in the solution obtained using the colligative measurements. Remember these measurements directly depend on the total number of particles in the solution: ions and molecules. However, in a weak electrolyte, the nominal concentration used to prepare the solution is not the same as the effective concentration of ions and molecules. This is because the concentration of ions and molecules in solution as weak electrolytes break down based on the degree of dissociation and, at the same time, the number of ions produced depends on the Van't Hoff factor  $i$ . The following equation gives the effective concentration of solute particles in the solution for a weak electrolyte in terms of the Van't Hoff factor and the nominal concentration:

$$c^{\text{effective}} = c^{\text{Nominal}} \cdot (1 + (i - 1) \frac{\alpha}{100})$$

For example, imagine we prepare a 0.1M ( $c^{\text{Nominal}}$ ) solution of a weak electrolyte with a 98% degree of dissociation ( $\alpha$ ) and the electrolyte dissociates into two different ions ( $i=2$ ). The number of solute particles in the solution, that is the effective concentration of particles, will be 0.198M. As you can see this number is larger than 0.1M as it accounts not only for molecules (0.002M) but also for ions (0.196M). The following



example demonstrates how to compute an electrolyte's degree of dissociation using osmotic pressure measurements.

### Sample Problem 10

A solution of 0.07M HF—a weak electrolyte—has a osmotic pressure of 2atm at 298K. Calculate: (a) The nominal solute concentration. (b) The effective ion concentration. (c) The percent dissociation of the acid.

#### SOLUTION

(a) The nominal solute concentration is 0.07M. (b) The osmotic pressure depends on molarity and temperature. We know the temperature, R is 0.082atmL/Kmol, and the value of the osmotic pressure. With this information we can calculate the effective concentration of particles in solution:

$$i \cdot M = \frac{\pi}{RT} = \frac{2}{0.082 \cdot 298} = 0.08M$$

This value accounts for the overall concentration of solute particles in the form of molecules and ions. (c) The osmotic pressure is related to the effective molarity and given that we know the nominal solute concentration, we can calculate the degree of dissociation of the acid:

$$c^{\text{effective}} = c^{\text{Nominal}} \cdot (1 + (i - 1) \frac{\alpha}{100})$$

Plugging the given values we have:

$$0.08 = 0.07 \cdot (1 + (2 - 1) \frac{\alpha}{100})$$

We can solve for  $\alpha$ :

$$\alpha = 100 \cdot (0.08 / 0.07 - 1) = 14.28\%$$

This results indicated that 14% of the electrolyte dissociates forming  $H^+ + F^-$ , whereas 86% stays in the form of HF.

#### ❖ STUDY CHECK

We prepare a 0.1M solution of a weak electrolyte with  $i=3$ . Given that the degree of dissociation of the electrolyte is 95%, calculate the osmotic pressure of the solution at 298K.

►Answer: 7.09atm

*Use of colligative properties to calculate MW* Colligative properties measurements are also useful to calculate molar masses of solutes as most of these properties are related to concentration and concentration is related to the molar mass of the solute. The method is based on carrying any colligative measurement, for example, the boiling point elevation, the freezing point depression, or the osmotic pressure, and with these measurements computing the corresponding concentration, molarity or molarity. Once we have the concentration we can use Equation 2.10 to compute the molar mass of the solute. We will work on an example:

### Sample Problem 11

We prepare a solution by adding 1g of solute—a non-electrolyte—into 100mL of water. The solution experience a freezing point depression of  $2.1^\circ C$ . Given



than the freezing depression constant of water is  $0.512^{\circ}\text{C}/\text{m}$ , calculate the molar mass of the solute.

### SOLUTION

We will first calculate the molality of the solution by means of the freezing point depression.

$$\Delta T_f = -i \cdot k_f \cdot m$$

We will use the freezing point depression ( $\Delta T_f = -2.1^{\circ}\text{C}$ ), Van't Hoff's factor ( $i=1$ ) and the freezing point depression constant ( $k_f = 0.512^{\circ}\text{C}/\text{m}$ ):

$$-2.1 = -1 \cdot 0.512 \cdot m$$

we have that the molality of the solution is  $m = 4.10\text{m}$ . Now that we have the molality we will calculate the molar mass of the solute using the information provided regarding the solution preparation: mass of solute ( $m_{\text{solute}} = 1\text{g}$ ) and volume of water ( $m_{\text{solvent}} = 0.1\text{kg}$ ), taking into account that the density of water is  $1\text{g/mL}$ . We have that the molar mass of the solute is:

$$MW = \frac{\text{g of solute}}{\text{m} \cdot \text{kg of solvent}} = \frac{1}{4.10 \cdot 0.1} = 2.44\text{g/mol}$$

### ◆ STUDY CHECK

We prepare a solution by adding 5g of solute—a non-electrolyte—into 50mL of water. The solution experience a boiling point elevation of  $5.3^{\circ}\text{C}$ . Given the boiling elevation constant of water,  $1.86^{\circ}\text{C}/\text{m}$ , calculate the molar mass of the solute. Mind the density of water is  $1\text{g/mL}$ .

►Answer: 35.09g/mol

*Osmosis* The solute concentration impacts the movement of water in and out of the animal and vegetal cells. This important process is called osmosis. Osmosis occurs when two solutions of different concentrations—a more concentrated and a more diluted solution—are connected using a semipermeable membrane, that is a membrane that only allows the movement of small water molecules. Osmosis refers to the flow of water through a semipermeable membrane, from the most diluted to the most concentrated solution. The flow follows a gradient of osmotic pressure from the most diluted solution with lower osmotic pressure to the most concentrated with a larger osmotic pressure. Water molecules flow to reduce the concentration of the most concentrated solution and hence to minimize the difference in concentration across the semipermeable membrane. Due to the flow of liquid, the liquid level of the most concentrated side rises and the level of the most diluted side decreases.

In a process called *reverse osmosis*, external pressure is applied to a concentrated solution in contact with a container with pure solvent, to force the reverse flow of water against the concentration gradient. This way solutions drie up while solvent transfers out of it. This principle is applied in desalination plants that obtain pure water from salty water. Still, the pressure applied is so much that this process is not economically feasible in most parts of the world.

*Dialysis* Dialysis is a process that resembles osmosis in which a semipermeable membrane—referred to as the dialyzing membrane—is used to separate water and small molecules from larger molecules such as proteins. This process indeed occurs in most

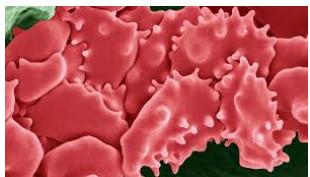


▼Normal red cells



© www.wallpaperflare.com

▼Shriveled red cell



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▼Dialysis is based on the principles of osmosis



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plant and animal cells, with the difference that these membranes allow the pass not only of the solvent but also of small solutes and ions. This process is also used in artificial kidney machines that purify blood with the help of a cellophane membrane. In this process, a dialyzing solution with the same composition as blood but without any waste product is used to clean up blood. Hence, a movement of waste molecules from the solution cleanses blood.

**Osmolarity** The molarity of a solution is directly related to the number of moles of solute molecules in the solution. However, the osmotic pressure of a solution depends on the number of moles of ions and not the number of moles of solute molecules. The osmolarity (Osm) is defined as the number of osmoles per liter of solution, being the number of osmoles the number of moles times the number of particles on solution  $i$ :

$$Osm = i \cdot M \quad (2.18)$$

where:

$M$  is the molarity

$i$  is the number of ions produced per mole of solute

For example, the osmolarity of a 2M NaCl solution would be 4Osm as NaCl contains two ions ( $i = 2$ ).

**Isotonic, hypotonic and hypertonic solutions** The cells in biological systems contain semipermeable membranes. *Isotonic solutions*—the prefix iso means the same—exert the same osmotic pressure as biological fluids such as blood. In hospitals, most intravenous solutions are made of isotonic solutions. Examples of isotonic solutions are a 1M NaCl solution or a 2M glucose ( $C_6H_{12}O_6$ ) solution. Both have the same osmolarity of 2 Osm. If we place a red blood cell in an isotonic solution it will not experience any changes in its shape as the osmotic pressure inside and outside would be the same. The osmotic pressure of blood at  $25^\circ C$  is  $\Pi=7.70\text{atm}$ . *Hypotonic solutions*—the prefix hypo means lower than—have a lower osmolarity than biological fluids. As such, if we place a red blood cell in a hypotonic solution it will swell and burst as water from the outside will flow inside the cell to compensate for the higher osmotic pressure. This phenomenon is called hemolysis. Differently, *hypertonic solutions*—the prefix hyper means higher than—have a higher osmolarity than biological solutions. A red blood cell placed in such a solution will shrink as water will flow out of the cell into the solution to compensate for the higher osmotic pressure outside the cell. This phenomenon is called crenation. Crenation is regularly used in the food industry to preserve food. By treating food with a solution hypertonic to bacteria one can kill these types of germs. This is why salt is used to protect meat and sugar to preserve fruits.

## 2.7 Ideal and real solutions

We have considered the impact of a solute on the vapor pressure of a liquid assuming that the solute with null vapor pressure. How about mixing two liquids? In this case, both liquids with different vapor pressures will contribute to the overall vapor pressure of the mixture using an expression equivalent to Raoul's law:

$$P_{vap}^{\text{solution}} = \chi_A \cdot P_{vap,A} + \chi_B \cdot P_{vap,B} \quad (2.19)$$

where:



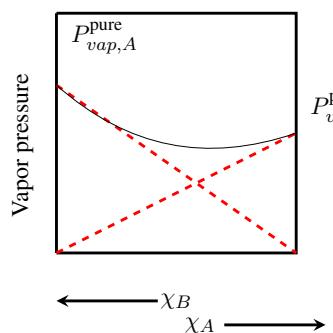
$P_{vap}^{\text{solution}}$  is the vapor pressure of the mixture

$P_{vap,A}$ ,  $P_{vap,B}$  is the vapor pressure of the pure solvent A and B

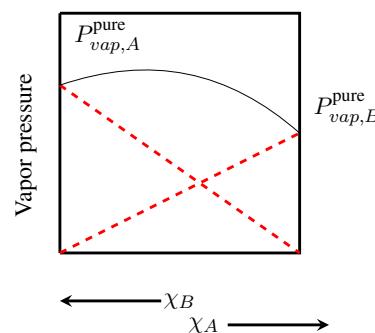
$\chi_A$ ,  $\chi_B$  is the mole fraction of A and B

Ideal mixtures will follow Equation 2.19. In other words, when the vapor pressure of the mixtures results from adding the vapor pressure of both liquids the mixture will be ideal. For some mixtures, the overall vapor pressure is lower or higher than the pressure resulting from adding the vapor pressure of both liquids. These mixtures are called real mixtures. We can encounter positive or negative deviations from the ideal behavior. When the interaction between the two liquids is exothermic and hence favorable ( $\Delta H_{sol} < 0$ ), the resulting vapor pressure of the mixture will be lower than the resulting combined vapor pressure and the mixture will experience negative deviations from ideality (e.g. water and acetone). When the interaction between the two liquids is endothermic ( $\Delta H_{sol} > 0$ ) and hence energetically unfavorable, the resulting vapor pressure of the mixture will be higher than the resulting combined vapor pressure and the mixture will experience positive deviations from ideality (e.g. hexane and ethanol). Mixtures of very similar liquids (e.g. benzene and toluene) with very small enthalpy of solution ( $\Delta H_{sol} \approx 0$ ) tend to behave as ideal mixtures, without deviating from Raoult's law.

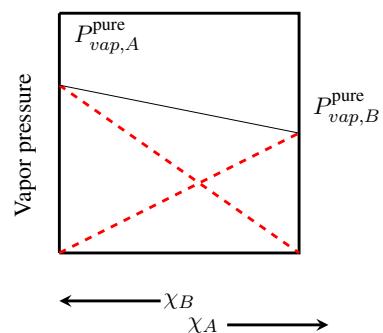
Favorable solute-solvent interaction



Unfavorable solute-solvent interaction



Ideal mixture



**Figure 2.5** Different patterns for the vapor pressure of mixtures of two liquids. When the interaction is favorable, the resulting vapor pressure is lower than combined the pressure of both components. Differently, when the interaction is unfavorable, the resulting vapor pressure is higher than combined the pressure of both components. Finally, the vapor pressure of an ideal mixture is the result of combining the vapor pressure of both components.

## 2.8 Factors affecting the solubility of solids and gases

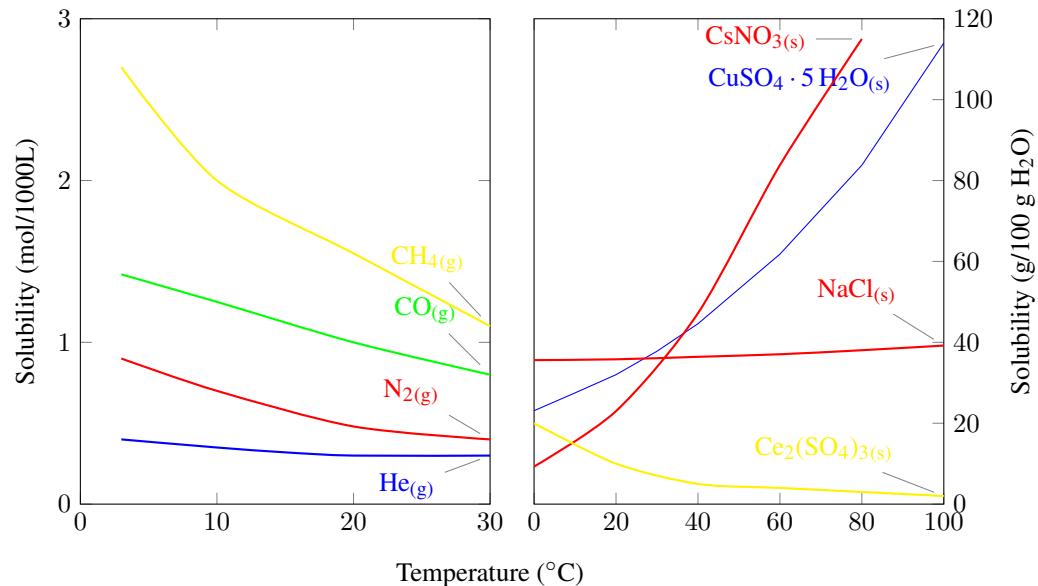
In this section, we will address the impact of temperature on the solubility of solids and gases on liquids and the impact of pressure on the solubility of gases on liquids. Figure 2.6 displays solubility vs. temperature plots for gases and solids in water.

*Impact of the molecular structure on solubility* The solubility of a solute into a solvent is intimately related to how the molecules of both compounds interact with each other. Polar solutes will tend to dissolve in polar solvents whereas nonpolar solutes will be more soluble in nonpolar solvents. Still, polarity only does not explain why a polar solute is more soluble in some polar solvents than others, and ultimately is the interaction between molecules and the energy associated with this interaction that determines solubility.

*Impact of temperature on solubility* The solubility of a solute in a solvent is the maximum amount of solute that one can dissolve in a solvent at a given



temperature. Solubility is affected by the state of matter of the solute—solids dissolve differently than gases—and by temperature. The nature of the temperature impact depends on the nature and state of matter of the solute (see Figure 2.6). The temperature has a strong impact on the solubility of solids. On one hand, temperature speeds up the dissolution process so that solids dissolve more rapidly at higher temperatures. On the other hand, the amount of solid that can be dissolved in a solvent can increase or decrease with temperature, depending on the nature of the solid. The solubility of sugar increases with temperature. That means the higher temperature the more solute one can dissolve. However, solid solutes like  $\text{Ce}_2(\text{SO}_4)_3$  or  $\text{Li}_2\text{SO}_4$  follow the opposite trend with lower solubility at higher temperatures. The change of solubility with temperature is more homogeneous for gases. We have that the solubility of gas solutes normally decreases with temperature (at least for low temperatures), that is, the higher the temperature the less amount of gas will be dissolved in a liquid. If you warm up a can of soda it goes flat as the gas comes out of the liquid—we call this desorption. Solubility changes with temperature have numerous applications in everyday life. For example, the decrease of gas solubility with temperature is responsible for the formation of boiler scale that occurs at the walls of kettles and industrial boilers. When increasing temperature, the solubility of carbon dioxide decreases, and this gas is released from water. To compensate for this effect, more carbon dioxide is absorbed in water leading to the formation of bicarbonate ions that can react with calcium leading to solid calcium carbonate, the boiler scale. Another example is thermal pollution. When water is used in cooling systems and returned to the rivers, it can be returned with higher temperatures. As the solubility of gases decreases with temperature, warm water floats on top of cold water and impedes access to oxygen.



**Figure 2.6** Solubility vs. Temperature plots for gases and solids in water.

#### Impact of pressure on the solubility of gases on liquids

Pressure does not impact the solubility of solids or liquids in a liquid solvent. However, gas pressure impacts the solubility of a gas solute on a liquid at a fixed temperature. In particular, the higher pressure the higher solubility. The law that related gas solubility with pressure is called Henry's law:

$$s = k \cdot P \quad (2.20)$$

where:



$s$  is the solubility of a gas in a liquid solvent in M units

$k$  is Henry's law constant with units of M/atm

$P$  is the gas pressure in atm

Henry's law constant is characteristic of a solution at a fixed temperature. This law is obeyed for very diluted solutions of gases that do not dissociate or react with water (e.g. O<sub>2</sub> in water). For example, HCl<sub>g</sub> does not follow this law as it can dissociate in water. An everyday life application of Henry's law is the production of carbonated beverages. These beverages are produced in contact with a liquid with an atmosphere of CO<sub>2</sub> of typical pressures of 5 atm. When you open a can container, the CO<sub>2</sub> in the drink comes out of the liquid in the form of bubbles to equilibrate the high gas pressure on the liquid and the low gas pressure in the atmosphere.

### Sample Problem 12

For the dissolution of CO<sub>2</sub> in water, Henry's constant is  $3.4 \times 10^{-2}$  M/atm.

Calculate: (a) the CO<sub>2</sub> pressure needed to achieve a gas concentration of 0.04M.  
 (b) If we open a carbonated can until it goes flat and given that the partial pressure of CO<sub>2</sub> in the air is  $4 \times 10^{-4}$  atm at 25°C, calculate the final gas concentration in the drink.

#### SOLUTION

(a) We will apply Henry's law given that we know solubility and Henry's constant:

$$s = k \cdot P \quad 0.04 = 3.4 \times 10^{-2} \cdot P$$

Solving for the pressure we have: 1.17atm. (b) We will also apply Henry's law, this time knowing the partial pressure of CO<sub>2</sub> and again Henry's constant:

$$s = k \cdot P \quad s = 3.4 \times 10^{-2} \cdot 4 \times 10^{-4}$$

The solubility is  $1.36 \times 10^{-5}$ M.

#### ◆ STUDY CHECK

Calculate the solubility of nitrogen in water after exposing water to a 5 atm nitrogen pressure, given that Henry's constant is  $6.1 \times 10^{-4}$ M/atm.

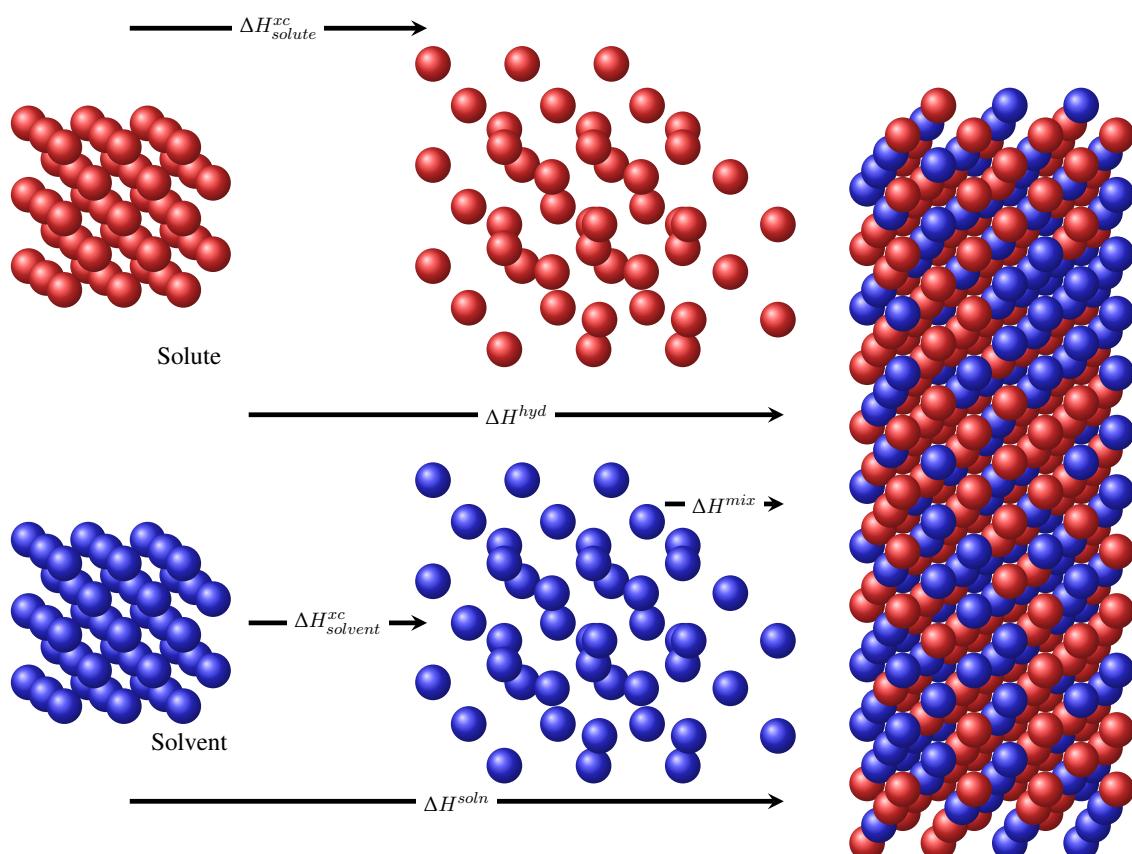
►Answer:  $3.05 \times 10^{-3}$ M

★★★★★ NEW FEATURE!

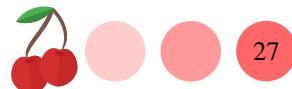


Table 2.5 Enthalpy of solution in KJ/mol for several compounds*			
Compound	$\Delta H^{sol}$	Compound	$\Delta H^{sol}$
$\text{HF(g)}$	-61.50	$\text{HCl(g)}$	-74.84
$\text{HClO}_4\text{(l)}$	-88.76	$\text{HClO}_4 \cdot \text{H}_2\text{O(s)}$	-32.95
$\text{HBr(g)}$	-85.14	$\text{HI(g)}$	-81.67
$\text{HIO}_3\text{(s)}$	+8.79	$\text{HNO}_3\text{(l)}$	-33.28
$\text{HCOOH(l)}$	-0.86	$\text{CH}_3\text{COOH(l)}$	-1.51
$\text{NH}_3\text{(g)}$	-30.50	$\text{NH}_4\text{Cl(s)}$	+14.78
$\text{NH}_4\text{ClO}_4\text{(s)}$	+33.47	$\text{NH}_4\text{Br(s)}$	+16.78
$\text{NH}_4\text{I(s)}$	+13.72	$\text{NH}_4\text{IO}_3\text{(s)}$	+31.80
$\text{NH}_4\text{NO}_2\text{(s)}$	+19.25	$\text{NH}_4\text{NO}_3\text{(s)}$	+25.69
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2\text{(s)}$	-2.38	$\text{NH}_4\text{CN(s)}$	+17.57
$\text{NH}_4\text{CNS(s)}$	+22.59	$\text{CH}_3\text{NH}_3\text{Cl(s)}$	+5.77
$(\text{CH}_3)_3\text{NHCl(s)}$	+1.46	$\text{N}(\text{CH}_3)_4\text{Cl(s)}$	+4.08
$\text{N}(\text{CH}_3)_4\text{Br(s)}$	+24.27	$\text{N}(\text{CH}_3)_4\text{I(s)}$	+42.07
$\text{AgClO}_4\text{(s)}$	+7.36	$\text{AgNO}_2\text{(s)}$	+36.94
$\text{AgNO}_3\text{(s)}$	+22.59	$\text{LiOH(s)}$	-23.56
$\text{LiOH} \cdot \text{H}_2\text{O(s)}$	-6.69	$\text{LiF(s)}$	+4.73
$\text{LiCl(s)}$	-37.03	$\text{LiCl} \cdot \text{H}_2\text{O(s)}$	-19.08
$\text{LiClO}_4\text{(s)}$	-26.55	$\text{LiClO}_4 \cdot 3 \text{H}_2\text{O(s)}$	+32.61
$\text{LiBr(s)}$	-48.83	$\text{LiBr} \cdot \text{H}_2\text{O(s)}$	-23.26

\* Parker, V. B., Thermal Properties of Uni-Univalent Electrolytes  
Natl. Stand. Ref. Data Series - Natl. Bur. Stand.(U.S.), No.2, 1965.



**Figure 2.7** Representation of the steps involved in dissolution



## 2.9 Enthalpy of solution

Some chemicals favorably mix. For example, table salt and water or oil and cyclohexane. Others such as water and cyclohexane do not mix. Like dissolves like is the rule behind miscibility. Understanding why chemicals mix at the molecular level is the key to understanding solubility. Thermodynamics can give some insight into why chemicals mix. In particular, an enthalpy analysis of mixing, and understanding the energy effects involved in solubility can give some partial insight into solubility. Still, it is important to acknowledge that energetics—energy considerations—is only part of the answer, and the spreading of energy has to be included in this analysis to achieve a complete picture of solubility.

NEW FEATURE!

*Dissolution steps* We will address here the steps involved in the process of dissolution of a compound in a general solvent such as water. This process involves the disaggregation of the molecules of the solute into dissolved particles, that is, particles solvated by the molecules of the solvent. The molecules of the solute and the solvent interact through intermolecular forces. These forces play a key role in dissolution. In the case of the solute, strong intermolecular forces hinder dissolution. It takes more energy to separate the solute particles when intermolecular forces in the solute are strong. Similarly, for the solvent, intermolecular forces also hinder dissolution. It takes more energy to separate the solvent particles when intermolecular forces in the solvent are strong. Once the solute is disaggregated into dissolved particles, the energetics involved in the hydration play a role in dissolution. Particles that do not hydrate easily are less soluble than particles with a large tendency to be surrounded by water molecules. This way, we can understand the dissolution process, characterized by the enthalpy of solution ( $\Delta H^{soln}$ ), using three steps: first, the energy involved in expanding the solute into separate entities ( $\Delta H_{solute}^{xp}$ ); second, the energy involved in expanding the solvent into separate entities ( $\Delta H_{solvent}^{xp}$ ); third, the energy involved in mixing the separate solute and solvent particles into hydrated ions ( $\Delta H^{mix}$ ). Overall we have that

$$\Delta H^{soln} = \Delta H_{solute}^{xp} + \Delta H_{solvent}^{xp} + \Delta H^{mix} = \Delta H_{solute}^{xp} + \Delta H^{hyd}$$

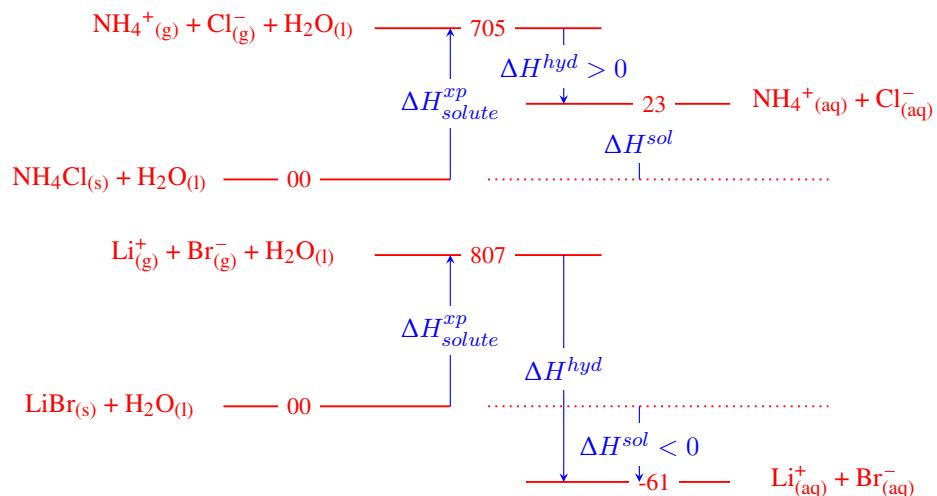
Steps two and three combined represent the energy of hydrating ( $\Delta H^{hyd}$ ) of the solute:

$$\Delta H^{hyd} = \Delta H_{solvent}^{xp} + \Delta H^{mix}$$

At the same time, the energy of expanding the solute has a clear meaning when the solute is ionic. This is called the negative value of the lattice energy ( $\Delta H_{lattice}$ ), the energy needed to form a solid ionic lattice from the separated ions:

$$\Delta H_{solute}^{xp} = -\Delta H_{lattice}$$

Figure 2.8 displays enthalpy profiles for an endo and exothermic dissolution process.



**Figure 2.8** Enthalpy diagrams for the dissolution process. (Top) an endothermic dissolution; (Bottom) an exothermic dissolution. Enthalpy values are listed in KJ/mol.

▼ Heat pads contain a supersaturated solution of sodium acetate in water.

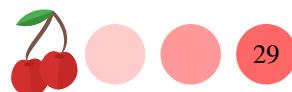


▼ Instant cold packs contain ammonium nitrate and water.



**Enthalpy of solution** Large, positive  $\Delta H_{soln}$  values correspond to endothermic solution processes, that is, the solute would absorb energy when dissolving (e.g.  $\text{NH}_4\text{Cl}$ ). Small, negative  $\Delta H_{soln}$  values correspond to exothermic solution processes, that is, the solute would release energy when dissolving (e.g.  $\text{LiBr}$ ).  $\Delta H_{soln}$  values for numerous solutes are given in Table 2.5. For the case of  $\text{LiBr}$  we have that the enthalpy of solution is  $-61\text{ kJ/mol}$ , while the energy needed to expand the solute is  $807\text{ kJ/mol}$  (the lattice energy of  $\text{LiBr}$  is  $-807\text{ kJ/mol}$ ). The enthalpy of hydration for  $\text{Li}^+$  is  $-520\text{ kJ/mol}$  and for  $\text{Br}^-$  is  $-348\text{ kJ/mol}$ . The overall enthalpy of hydration ( $-682\text{ kJ/mol}$ ) is smaller in absolute value than the energy needed to expand the solute giving an overall, negative enthalpy of solution. Therefore, the large solvation energy of the salt makes the dissolution of  $\text{LiBr}$  exothermic.

**Enthalpy of hydration** The enthalpy of hydration represents the energy involved in the reaction of an ion with water to produce an hydrated ion. For single ions, this property is impossible to measure directly, as we cannot recreate the process of dissolution of a single ion, those are found in the form of ionic compounds and not separate ions. Still, simulations can give insight into the factors that impact these properties. In general terms, the electronegativity of the ion impacts hydrations: more electronegative ions tend to have smaller, more negative, hydration energies.  $\Delta H_{hyd}$  values for numerous solutes are given in Table 2.6. We can see that  $\Delta H_{hyd}$  for  $\text{F}^-$  is  $-524\text{ kJ/mol}$ , while being  $-308\text{ kJ/mol}$  for  $\text{I}^-$ , a less electronegative ion.

**Table 2.6 Enthalpy of hydration in KJ/mol for several ions \***

Ion	$\Delta H^{hyd}$	Ion	$\Delta H^{hyd}$	Ion	$\Delta H^{hyd}$	Ion	$\Delta H^{hyd}$
H <sup>+</sup>	-1091	Li <sup>+</sup>	-520	Na <sup>+</sup>	-406	K <sup>+</sup>	-320
Rb <sup>+</sup>	-296	Cs <sup>+</sup>	-264	In <sup>+</sup>	-344	Tl <sup>+</sup>	-328
Cu <sup>+</sup>	-593	Ag <sup>+</sup>	-473	Au <sup>+</sup>	-615	NH <sub>4</sub> <sup>+</sup>	-307
Be <sup>2+</sup>	-2484	Mg <sup>2+</sup>	-1926	Ca <sup>2+</sup>	-1579	Sr <sup>2+</sup>	-1446
Ba <sup>2+</sup>	-1309	Ti <sup>2+</sup>	1862	Cr <sup>2+</sup>	-1908	Mn <sup>2+</sup>	-1851
Fe <sup>2+</sup>	-1950	Co <sup>2+</sup>	-2010	Ni <sup>2+</sup>	-2096	Cu <sup>2+</sup>	-2099
Pt <sup>2+</sup>	-2100	Zn <sup>2+</sup>	-2047	Cd <sup>2+</sup>	-1809	Pb <sup>2+</sup>	-1485
Hg <sup>2+</sup>	-1829	Sn <sup>2+</sup>	-1554	Y <sup>3+</sup>	-4105	Tl <sup>3+</sup>	-4108
Al <sup>3+</sup>	-4680	Sc <sup>3+</sup>	-3930	NO <sub>3</sub> <sup>-</sup>	-314	OH <sup>-</sup>	-460
F <sup>-</sup>	-524	Cl <sup>-</sup>	-378	Br <sup>-</sup>	-348	I <sup>-</sup>	-308

\* D.W. Smith, J. Chem. Educ., 54, 540 (1977).

*Heat packs* Athletes take advantage of the energetics of dissolution by using hot and cold packs to treat injuries. Both packs consist on a solid chemical that dissolves in a pouch of water when the pack is squeezed. Calcium chloride or magnesium sulfate is used in hot packs, whereas ammonium nitrated is mainly used on cold packs.

