

# 1

## Physical properties of solutions



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SOLUTIONS 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.

### 1.1 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.

- GOALS
- 1 Compute different concentration units
  - 2 Interconvert concentration units
  - 3 Predict freezing and boiling point of solutions
  - 4 Predict the vapor pressure of solutions
  - 5 Identify colloids

Discussion: What does it mean the term colligative, like in colligative properties of solutions? List four colligative properties of a solution.

Table 1.1 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 1.1 reports different types of solutions with examples.

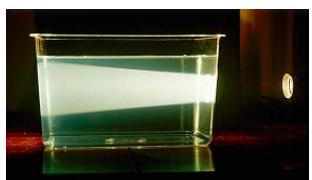
*Solutions* In solutions, the solute particles are dispersed evenly throughout the solvent giving homogeneous mixtures. As such, in a solution such as seawater, the solute cannot be visually distinguished from the solvent. The mixture appears transparent even when it may have a certain color. The solute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



**Figure 1.1** Classification of the mixtures

▼The Tyndall effect of a liquid



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▼The Tyndall effect of a gas



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40 *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. 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, that is a colloid containing small particles of fat and protein suspended on 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 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.

65

**Table 1.2 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

Table 1.2 reports all different types of colloids one can encounter with examples for each of them.

▼Clouds are an aerosol



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▼Smoke is an aerosol



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▼whipped cream is a foam.

Cream needs to be whipped to let the air in



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▼Ketchup is an emulsion



© wikipedia

▼mayonnaise is an emulsion



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▼Styrofoam is a foam



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**Figure 1.2** Different colloids

## 1.2 Units of concentration

70

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 sol-

75

vent.

$$\text{solution} = \text{solvent} + \text{solute} \quad (1.1)$$

*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.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (1.2)$$

For example, if we mix 0.4 moles of NaCl and we fill 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.

$$\chi = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}} \quad (1.3)$$

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.

$$\%_m = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100 \quad (1.4)$$

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.

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} \quad (1.5)$$

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 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* Density of a solution—often expressed in g/mL—is the ration of the grams of solution and the mL of solution.

$$d = \frac{\text{grams of solution}}{\text{mL of solution}} \quad (1.6)$$

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

**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

110

*Why relating units of concentration* When you prepare a solution you normally weight 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

115

different concentration units are related.

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

$$m = \frac{1000 \cdot M}{1000 \cdot d - M \cdot MW} \quad \text{or} \quad M = \frac{1000 \cdot m \cdot d}{1000 + MW \cdot m} \quad (1.7)$$

<sup>120</sup> 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

<sup>125</sup> Mind that this formula only works for water as solvent and used 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 in order to relate Molarity and percent by mass of solute

$$M = \frac{\%_m \cdot d \cdot 10}{MW} \quad \text{or} \quad \%_m = \frac{M \cdot MW}{10 \cdot d} \quad (1.8)$$

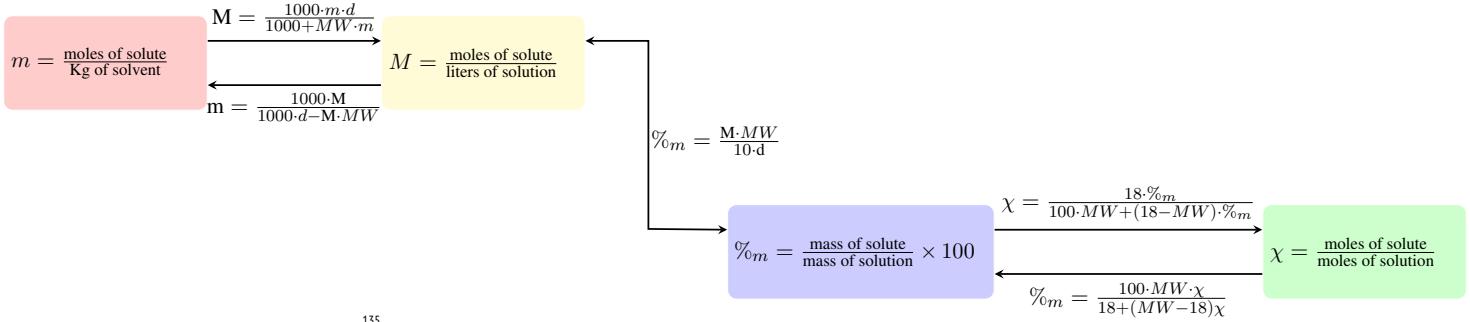
<sup>130</sup> where:

$M$  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 in order to relate Molarity and percent by mass of solute

$$\chi = \frac{18 \cdot \%_m}{100 \cdot MW + (18 - MW) \cdot \%_m} \quad \text{or} \quad \%_m = \frac{100 \cdot MW \cdot \chi}{18 + (MW - 18) \cdot \chi} \quad (1.9)$$

where:

<sup>140</sup>  $\chi$  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 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

*Compute molecular masses from molality and molarity* In numerous applications one needs to compute the molecular weight of a solute by means of 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 solute used and the mass of the solvent or the volume of solution. We can compute the molar mass of the solute by means of:

150

$$MW = \frac{\text{g of solute}}{\text{m} \cdot \text{kg of solvent}} \quad \text{or} \quad MW = \frac{\text{g of solute}}{\text{M} \cdot \text{L of solution}} \quad (1.10)$$

where:

MW is the molar mass of the solute

155

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

160

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 1g of solute and adding liquid until 100mL of solution in order to prepare a 2M solution. Calculate the molar mass of the solute.

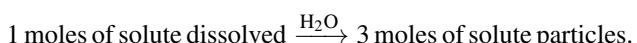
## 1.3 Solutions of electrolytes and effective solute particles

Chemicals can be classified based on their electrolyte character in strong electrolytes and non-electrolytes. Non-electrolytes do not dissociate in solution so that 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 particles. This section covers the concept of effective solute particle and the idea of Van't Hoff factor  $i$  that related the amount of moles of solute dissolved and the moles of solute particles.

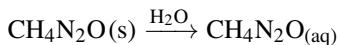
*Strong and non-electrolytes* Strong electrolytes completely dissociate in water. Hence, in a solution of a strong electrolyte you will only have ions and never molecules. Strong electrolytes are typically ionic compounds such as MgCl<sub>2</sub> or NaCl (table salt). We represent the dissociation of a strong electrolyte with a single arrow, meaning that the reaction proceeds to completion and 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 molecules (MgCl<sub>2(s)</sub>):



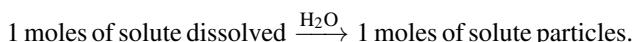
In terms of solute dissolved and solute particles, we have that one mole of solute dissolved gives three moles of solute particle:



*Nonelectrolytes* Nonelectrolytes do not dissociate in water. Hence a solution of a nonelectrolyte will only contain molecules 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:



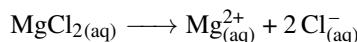
In terms of solute dissolved and solute particles, we have that one mole of solute dissolved gives one mole of solute particle:



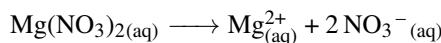
*Breaking down electrolytes into ions* Electrolytes—in particular strong electrolytes—dissociate producing ions. This way, a solution of for example NaCl does not contain NaCl molecules but Na<sup>+</sup><sub>(aq)</sub> cations and Cl<sup>-</sup><sub>(aq)</sub> anions. Hence it is important to correctly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

195



Another example, 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 indicated we have one  $Mg_{(aq)}^{2+}$  and two  $NO_3^{-}_{(aq)}$ . Hence:



200

#### 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:  $H_2O(l)$ ,  $NH_3(l)$ ,  $AgNO_3(aq)$ .

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

$$i = \frac{\text{moles of solute particles}}{\text{moles of dissolved particles}} \quad (1.11)$$

For example, all non-electrolytes produce only a single solute particles, as they do not break down in solution and therefore for all non-electrolytes *i* is 1. Differently, the

205

*i* values for a strong electrolyte depends 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 corresponds to the observed value, due to the formation of ion pairs, pairs of ions that associate on solution reducing the effective ion concentration.

**Table 1.3 Expected and observed Van't Hoff factors for different concentrations.**

Solute	<i>i</i> <sup>Observed</sup>			<i>i</i> <sup>Expected</sup>	<i>i</i> <sup>Observed</sup> / <i>i</i> <sup>Expected</sup> * 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 1.3 reports observed and expected *i* values for different salts and different concentrations. At low concentration the effect of ion pairs is less pronounced and the expected value tend to resemble the observed value: *i*<sup>Expected</sup>  $\approx$  *i*<sup>Observed</sup>. 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 tend to be smaller than the nominal concentration. We have that:

$$\alpha = \frac{c^{\text{effective}}}{c^{\text{Nominal}}} \times 100 \quad (1.12)$$

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 concentration are the same. Note that the percent dissociation can change with concentration.

### Sample Problem 5

A solution that is 0.02M in HF has an effective ion concentration of 0.015M.

Calculate the percent dissociation of the electrolyte.

#### SOLUTION

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

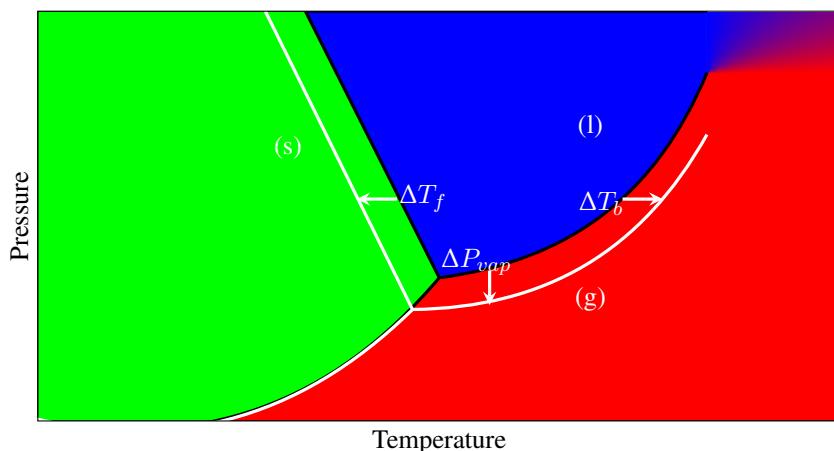
#### ◆ STUDY CHECK

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

## 1.4 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.

230



**Figure 1.3** Effect of the solute concentration on the phase diagram of water

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

235

Pure solvent 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 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 by means of the following formula:

240

$$T_b^{\text{solution}} = T_b^{\text{solvent}} + k_b \cdot i \cdot m \quad \text{or} \quad \Delta T_b = k_b \cdot i \cdot m \quad (1.13)$$

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

245

$m$  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-particles 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  $101.04^{\circ}\text{C}$  that 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

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▼ 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



© Pngwing

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



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© Pngwing

*x* variable is  $m$  and the *y* variable is  $T_b^{\text{solution}}$ . In another 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°C. Solutions freeze at a lower temperature than the pure solvent. We call this effect the freezing point depression. This decrease on 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:

$$T_f^{\text{solution}} = T_f^{\text{solvent}} - k_f \cdot i \cdot m \quad \text{or} \quad \Delta T_f = -k_f \cdot i \cdot m \quad (1.14)$$

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 freezing point depression constant in units of °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-particles 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°C but a 1m NaCl solution freezes at -3.72°C, that 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 another words, by plotting  $T_f^{\text{solution}}$  vs.  $m$  we should obtain a straight line with a slope in absolute value that equals to  $k_f$  and an intercept equals to  $T_f^{\text{solvent}}$ .

**Table 1.4 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

Table 1.4 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  $k_b = 2.53 \text{ } ^\circ\text{C}/\text{m}$ , calculate the boiling point and the boiling point elevation of the solution. (c) Given that benzene freezing point is 5°C, and that  $k_f = 5.10 \text{ } ^\circ\text{C}/\text{m}$ , 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.

**Vapor-pressure lowering** Every liquid exerts a certain vapor pressure that depends on temperature. The molecules of 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 vapor pressure of the liquid. Solutions exert lower vapor pressure than the pure solvent. The vapor-pressure lowering is a colligative property that depends on the solute mole fraction:

$$P_{vap}^{\text{solution}} = P_{vap}^{\text{solvent}} - \chi \cdot P_{vap}^{\text{solvent}} \quad \text{or} \quad \Delta P_{vap} = -\chi \cdot P_{vap}^{\text{solvent}} \quad (1.15)$$

where:

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$P_{vap}^{\text{solution}}$  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

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

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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 1.15 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 0.03 atm, we can compute first the vapor pressure of the solution

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

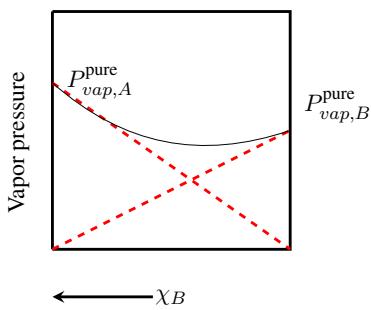
and then the vapor-pressure lowering

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

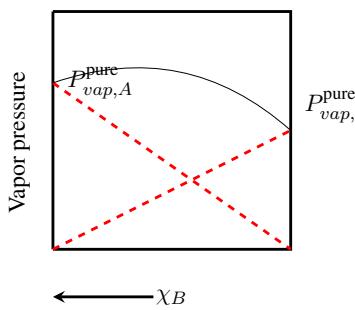
#### ◆ STUDY CHECK

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

Favorable solute-solvent interaction



Unfavorable solute-solvent interaction



Ideal mixture

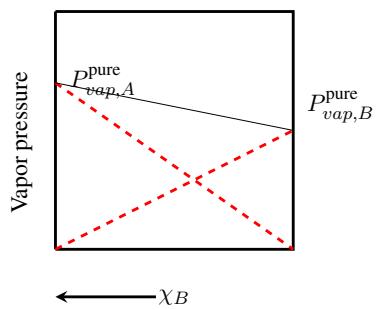


Figure 1.4 Different patterns for the vapor pressure of mixtures of two liquids

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*Ideal and real liquid mixtures* 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 pressure will contribute to the overall vapor pressure of the mixture by means of an expression equivalent to Raoul's law:

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$$P_{vap}^{\text{solution}} = \chi_A \cdot P_{vap,A} + \chi_B \cdot P_{vap,B} \quad (1.16)$$

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 1.16. 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 real. We can encounter positive or negative deviations from the ideal behavior. When the interaction between the two liquids is exothermic and hence favorable, 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. When the interaction between the two liquids is endothermic 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.

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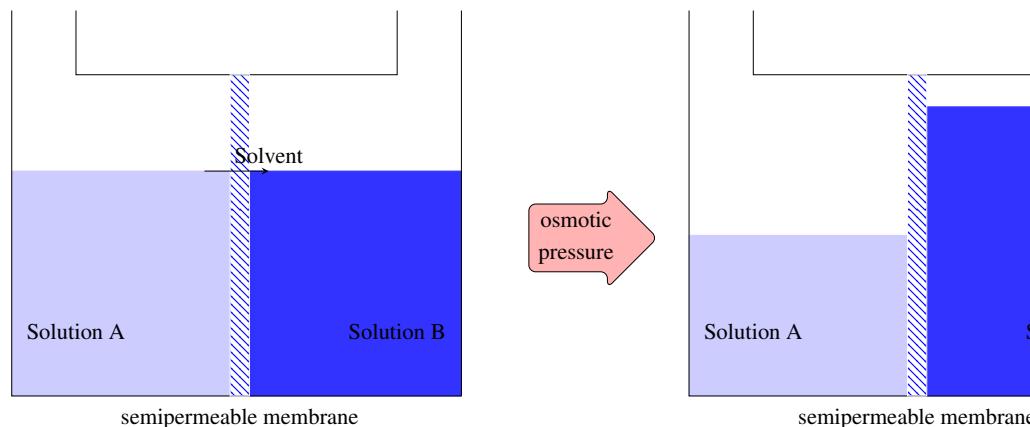
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*Osmosis* The solute concentration impacts the movement of water in and out of the animal and vegetal cells. This important process is called osmosis. Osmosis occurs when two solutions of different concentrations—a more concentrated and a more diluted solution—are connected by means of a semipermeable 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 in order 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 up and the level of the most diluted side decreases. In a process called reverse osmosis, external pressure is applied to the most concentrated solution in order to force the reverse flow of water against the concentration gradient. This principle is applied in desalination plants in order to 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.

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**Figure 1.5** Osmotic pressure

<sup>350</sup> *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 5% NaCl solution or a 0.9% glucose ( $C_6H_{12}O_6$ ) solution. Both have the same osmolarity of 0.3 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. 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 in order to compensate for the higher osmotic pressure outside the cell. This phenomenon is called crenation.

<sup>365</sup> *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.

<sup>370</sup> *Osmotic pressure of a solution* The pressure of a gas result 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. The higher molarity, that is the number of moles per liter in the solution, the higher the osmotic pressure of a solution:

$$\pi = i \cdot M \cdot RT \quad (1.17)$$

<sup>375</sup> 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 atmL/Kmol

$T$  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 pass of solvent molecules without allowing the pass of solute molecules. We could set up and experiment in which we separate two solutions of different concentrations by a semipermeable membrane and we will certainly see that the level of liquid on 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 the 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). Osmosis is responsible for many every-day life phenomena such as salting as a method to preserve food: by adding salt one can kill bacteria and preserve fish by extracting the water from their inside.

*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 liters of solution, being the number of osmoles the number of moles times the number of particles on solution  $i$ :

$$Osm = i \cdot M \quad (1.18)$$

where:

$M$  is the molarity

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

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

*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. A such, a 1m NaCl solutions will experience the same boiling-point increase than 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.

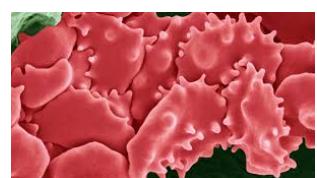
*Graphical method to calculate colligative constants* The formulas for the different colligative properties represent linear relationships. Therefore by means of plotting, we can calculate some of the colligative constants. The next example explains how to obtain colligative constants by means of a graphical method. In order 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 a 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

▼Normal red cells



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▼Shriveled red cell



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▼Dialysis is based on the principles of osmosis



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relationship. No accurate colligative constants should be calculated from a set of data characterized by poor linear correlation coefficient. Is important to keep in mind:

$$\begin{aligned} r^2 \leq 0.99 & \quad (\text{Good linear regression}) \\ r^2 < 0.99 & \quad (\text{Poor linear regression}) \end{aligned} \quad (1.19)$$

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

### Sample Problem 8

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

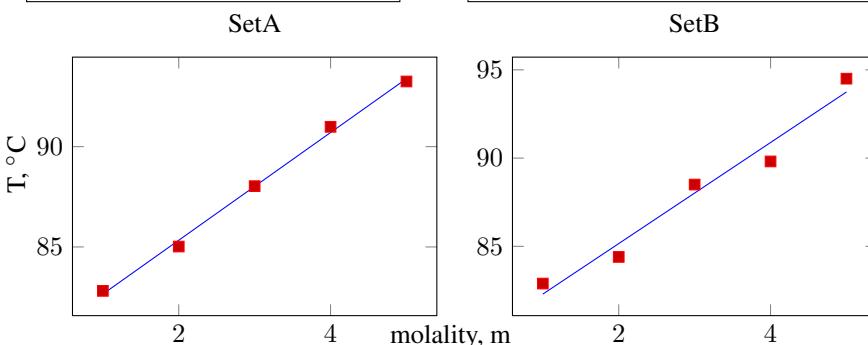
Set A		Set B	
T(°C)	m	T(°C)	m
82.81	1	82.89	1
85.02	2	84.4	2
88.03	3	88.5	3
90.99	4	89.81	4
93.25	5	94.5	5

### 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  $k_b = 2.69^\circ\text{C}/\text{m}$  and from the intersect we will calculate the boiling point of the pure solvent  $T_b^{\text{solvent}} = 79.96^\circ\text{C}$ .

$$T = 2.69 \cdot m + 79.96, r^2 = 1$$

$$T = 2.86 \cdot m + 79.43, r^2 = 0.97$$



### ❖ STUDY CHECK

The following two sets of data report the change in boiling point of a solution. Assess the date 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
17.02	1	817.21	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

*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 electrolyte's degree of dissociation using osmotic pressure measurements.

#### Sample Problem 9

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 vale 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  $\text{H}^+$  +  $\text{F}^-$ , 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.

*Use of colligative properties to calculate MW* Colligative properties measurements are also useful in order 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 1.10 in order to compute the molar mass of the solute. We will work on an example:

#### Sample Problem 10

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

$$MW = \frac{\text{g of solute}}{\text{m} \cdot \text{kg of solvent}} = \frac{1}{4.10 \cdot 0.1} = 5.12\text{g/mol}$$

#### ❖ 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°C. Given the boiling elevation constant of water, 1.86°C/m, calculate the molar mass of the solute. Mind the density of water is 1g/mL.

## 1.5 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. 465

*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. 470

*Impact of temperature on solubility* The solubility of a solute on a solvent is the maximum amount of solute that one can dissolve in a solvent at a given temperature. The temperature has a strong impact on solubility. However, the nature of the impact depends on the nature and state of matter of the solute. Normally, the solubility of solids increases with temperature. That means the higher temperature the more solute one can dissolve. However, this trend is not true for all solid solutes. Solid solutes like  $\text{Ce}_2(\text{SO}_4)_3$  or  $\text{Li}_2\text{SO}_4$  follow the opposite trend the higher temperature the lower solubility. The solubility of gas solutes normally decreases with temperature, that is, the higher 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. 475

*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. In particular, the higher pressure the higher solubility. The law that related gas solubility with pressure is called Henry's law: 485

$$s = k \cdot P \quad (1.20)$$

where: 490

$s$  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

An every-day 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  $\text{CO}_2$  of typical pressures of 5 atm. When you open a can container, the  $\text{CO}_2$  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. 495

**Sample Problem 11**

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.

# CHAPTER 1

## SOLUTIONS AND COLLOIDS

**1.1** For the following colloids, indicate the nature of the dispersed and dispersing medium (liquid, solid or gas) :  
 (a) soda water (b) cake (c) midst (d) smoke (e) froth

**1.2** For the following colloids, indicate the nature of the dispersed and dispersing medium (liquid, solid or gas) :  
 (a) pumice stone lava (b) cheese (c) paint (d) clouds

## UNITS OF CONCENTRATION

**1.3** Calculate: (a) the percent by mass of a solution made of 5g of NaBr in 70g of solution (b) the percent by mass of a solution made of 5g of NaBr with 20g of water(c) the percent by mass of a solution made of 5g of NaBr with 10mL of water

**1.4** Calculate the molality for: (a) a solution made of 5moles of NaBr(MW=103g/mol) in 200g of water (b) a solution made of 20g of NaBr(MW=103g/mol) in 200g of water (c) a solution made of 10g of NaBr(MW=103g/mol) in 20mL of water

**1.5** Calculate the density of a solution: (a) containing 3g of solute and 100g of water in 101mL (b) containing 1g of solute and 100mL of water in 103mL

**1.6** Calculate the mole fraction of solute of a solution:  
 (a) containing 3g of solute (MW=16g/mL) and 100g of water (b) containing 2 moles of solute and 30 moles of solvent (c) containing 4 moles of solute and 45 moles of solution

**1.7** Calculate: (a) the molarity of a 0.2m solution of density 1.2g/mL made of a NaCl(MW=58g/mol) (b) the molality of a 0.2M solution of density 1.2g/mL made of a NaCl(MW=58g/mol) (c) the percent by mass of a 0.1M solution of density 1.2g/mL made of a NaCl(MW=58g/mol)

**1.8** Calculate: (a) the molarity of a 20% solution of density 1.1g/mL made of a Na<sub>2</sub>SO<sub>4</sub>(MW=142g/mol)  
 (b) the mole fraction of a 20% aqueous solution of density 1.1g/mL made of a Na<sub>2</sub>SO<sub>4</sub>(MW=142g/mol) (c) the percent by mass of an aqueous solution of density 1.1g/mL and 0.4mole fraction, made of a Na<sub>2</sub>SO<sub>4</sub>(MW=142g/mol)

**1.9** We prepare an C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> (MW=180g/mL) solution by mixing 5g of solute in 100mL of water giving 102mL of solution. Calculate: (a) the molarity (b) the molality (c) the percent by mass (d) the mole fraction

**1.10** Calculate the molar weight of the solute of a solution with 0.9g/mL density, 2M and 1.9m.

**1.11** Calculate the molar weight of the solute of a solution with 0.9g/mL density, 0.5 mole fraction and 90% of solute by mass.

## SOLUTIONS OF ELECTROLYTES AND EFFECTIVE SOLUTE PARTICLES

**1.12** Break down the following electrolytes in ions, if possible: (a) CaI<sub>2</sub> (b) KNO<sub>3</sub> (c) CaSO<sub>4</sub> (d) FeSO<sub>4</sub>

**1.13** Break down the following electrolytes in ions, if possible: (a) SnCl<sub>4</sub> (b) CuCl<sub>2</sub> (c) Ba(OH)<sub>2</sub> (d) CuSO<sub>3</sub> (e) MgSO<sub>4</sub>

**1.14** Calculate the *i* factor for the following chemicals:  
 (a) NaNO<sub>3</sub> (b) NaCl (c) CaI<sub>2</sub> (d) MgCl<sub>2</sub>

**1.15** Calculate the *i* factor for the following chemicals:  
 (a) Mg(NO<sub>3</sub>)<sub>2</sub> (b) CuSO<sub>4</sub> (c) FeCl<sub>3</sub>

**1.16** We dissolve 3 moles of solute in 1L of solution. Given that Van't Hoff factor of the solute is 3, calculate the nominal solute concentration and the effective concentration of particles on solution.

**1.17** We dissolve 0.5 moles of solute in 1L of solution reaching a effective concentration of solute particles of 0.9M. Calculate the Van't Hoff factor.

**1.18** Can the percent dissociation of a electrolyte be negative? Elaborate.

## COLLIGATIVE PROPERTIES

**1.19** Calculate the boiling point of a 3m C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> aqueous solution.  $T_b^{solvent}=100^{\circ}\text{C}$  and  $k_b=0.512^{\circ}\text{C}/\text{m}$ .

**1.20** Calculate the boiling point increase of a 8m  $C_6H_{12}O_6$  aqueous solution.  $T_b^{solvent}=100^{\circ}\text{C}$  and  $k_b=0.512^{\circ}\text{C}/\text{m}$ .

**1.21** Calculate the boiling point of a 3m  $\text{CaCl}_2$  aqueous solution.  $T_b^{solvent}=100^{\circ}\text{C}$  and  $k_b=0.512^{\circ}\text{C}/\text{m}$ .

**1.22** Calculate the boiling point increase of a 8m  $\text{KCl}$  aqueous solution.  $T_b^{solvent}=100^{\circ}\text{C}$  and  $k_b=0.512^{\circ}\text{C}/\text{m}$ .

**1.23** Calculate the freezing point of a 2m  $I_2$  solution on benzene.  $T_f^{solvent}=5.5^{\circ}\text{C}$  and  $k_f=4.9^{\circ}\text{C}/\text{m}$ .

**1.24** Calculate the freezing point depression of a 2m  $I_2$  solution on benzene.  $T_f^{solvent}=5.5^{\circ}\text{C}$  and  $k_f=4.9^{\circ}\text{C}/\text{m}$ .

**1.25** The vapor pressure of cyclohexane is 100hPa at  $20^{\circ}\text{C}$ . Calculate the vapor pressure of the solution resulting of mixing 3moles of cyclohexane and 4 moles of  $I_2$ .

**1.26** The vapor pressure of cyclohexane is 100hPa at  $20^{\circ}\text{C}$ . Calculate the vapor pressure lowering of the solution resulting of mixing 3moles of cyclohexane and 4 moles of  $I_2$ .

**1.27** The vapor pressure of cyclohexane is 100hPa at  $20^{\circ}\text{C}$ . Calculate the vapor pressure lowering of the solution resulting of mixing 3moles of cyclohexane and 3 moles of  $I_2$ .

**1.28** The vapor pressure of cyclohexane is 100hPa at  $20^{\circ}\text{C}$ . Calculate the vapor pressure of the solution resulting of mixing 6moles of cyclohexane and 1 moles of  $I_2$ .

**1.29** The vapor pressure of cyclohexane is 100hPa at  $20^{\circ}\text{C}$ . Calculate the vapor pressure lowering of the solution resulting of mixing 6moles of cyclohexane and 1 moles of  $I_2$ .

**1.30** Calculate the osmotic pressure of a 3M  $\text{NaCl}$  solution at 298K.

**1.31** A semipermeable membrane separate two  $\text{NaCl}$  solutions with concentration 0.2M (on the left) and 0.1M (on the right). What side of the membrane will receive an osmotic flow of water?

**1.32** A semipermeable membrane separate two solutions, 0.2M  $\text{NaCl}$  (on the left) and 0.1M  $\text{CaCl}_2$  (on the right). What side of the membrane will receive an osmotic flow of water?

#### FACTORS AFFECTING THE SOLUBILITY OF SOLIDS AND GASES

**1.33** The solubility of Ar in water at 298K when the partial pressure of Ar is 0.9atm is  $1.26 \times 10^{-3}\text{M}$ . Calculate: (a) Henry's law constant at that temperature (b) The solubility of Ar at a partial pressure of 0.5atm

**Answers**

**1.1** (a) soda water (dispersed: gas ; dispersing: liquid) (b) cake (dispersed: gas ; dispersing: solid) (c) midst (dispersed: liquid ; dispersing: gas) (d) smoke (dispersed: solid ; dispersing: gas) (e) froth (dispersed: gas ; dispersing: liquid)

**1.2** (a) pumice stone lava (dispersed: gas ; dispersing: solid) (b) cheese (dispersed: liquid ; dispersing: solid) (c) paint (dispersed: solid ; dispersing: liquid) (d) clouds (dispersed: liquid ; dispersing: gas)

**1.3** (a) 7.14% (b) 20% (c) 33.3%

**1.4** (a) 25m (b) 0.97m (c) 4.85m

**1.5** (a) 1.02g/mL (b) 0.98g/mL

**1.6** (a) 0.03 (b) 0.06 (c) 0.09

**1.7** (a) 0.26M (b) 0.27M (c) 0.45%

**1.8** (a) 1.55M (b) 0.03 (c) 84%

**1.9** (a) 0.27M (b) 0.28m (c) 4.76% (d) 0.005

**1.10** 155g/mol

**1.11** 162g/mol

**1.12** (a)  $\text{CaI}_2$  ( $\text{Ca}^{2+} + 2\text{I}^-$ ) (b)  $\text{KNO}_3$  ( $\text{K}^+ + \text{NO}_3^-$ ) (c)  $\text{CaSO}_4$  ( $\text{Ca}^{2+} + \text{SO}_4^{2-}$ ) (d)  $\text{FeSO}_4$  ( $\text{Fe}^{2+} + \text{SO}_4^{2-}$ )

**1.13** (a)  $\text{SnCl}_4$  ( $\text{Sn}^{4+} + 4\text{Cl}^-$ ) (b)  $\text{CuCl}_2$  ( $\text{Cu}^{2+} + 2\text{Cl}^-$ ) (c)  $\text{Ba}(\text{OH})_2$  ( $\text{Ba}^{2+} + 2\text{OH}^-$ ) (d)  $\text{CuSO}_3$  ( $\text{Cu}^{2+} + \text{SO}_3^{2-}$ ) (e)  $\text{MgSO}_4$  ( $\text{Mg}^{2+} + \text{SO}_4^{2-}$ )

**1.14** (a)  $\text{NaNO}_3$  (b)  $\text{NaCl}$  (c)  $\text{CaI}_2$  (d)  $\text{MgCl}_2$

**1.15** (a)  $\text{Mg}(\text{NO}_3)_2$  (b)  $\text{CuSO}_4$  (c)  $\text{FeCl}_3$

**1.16**  $c^{nominal}=9\text{M}$ ;  $c^{effective}=9\text{M}$

**1.17** 1.8

**1.18** No as the maximum value should be one.

**1.19**  $101.5^\circ\text{C}$

**1.20**  $4.01^\circ\text{C}$

**1.21**  $104.07^\circ\text{C}$

**1.22**  $8.19^\circ\text{C}$

**1.23**  $-4.3^\circ\text{C}$

**1.24**  $-4.3^\circ\text{C}$

**1.25** 42.8hPa

**1.26** -42.85hPa

**1.27** -50hPa

**1.28** 85.71hPa

**1.29** -14.28hPa

**1.30** 146.62atm

**1.31** The more concentrated (left side).

**1.32** none

**1.33** (a)  $1.4 \times 10^{-3} \text{ M/atm}$  (b)  $7.00 \times 10^{-4}\text{M}$