

## Unit 8: When Chemicals Meet Water—The Properties of Solutions



### Unit Overview

Solutions are all around us, from the air we breathe to the blood in our veins to the steel frames of many buildings. While solutions don't have to be liquids, aqueous, or water based, solutions are fundamental to life and common in inorganic chemistry: The majority of biochemical reactions happen in aqueous solutions. The formation of a solution depends upon the interactions between the solute (the substance that gets dissolved) and the solvent (the substance that does the dissolving); in turn, the interactions

of solute and solvent are heavily influenced by their concentrations, temperature, and pressure. Solution chemistry is behind the extraction of materials for a variety of applications, for example, making a great cup of coffee.

*by Adam Brunet*

### Sections

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## Unit 8: *When Chemicals Meet Water—The Properties of Solutions*

### Section 1: Introduction

Solutions are mixtures of substances that are uniform throughout. They are found all around us, from the apple juice in our refrigerator to the fillings in our teeth, from the plasma of our blood to the air we are breathing. Solutions are fixtures of our daily lives and a critical subject in chemistry.

In this unit, we will define solutions and learn about their important characteristics and some of the techniques that chemists use to determine those properties. Next, we will examine the physical properties of solutions, with a special focus on the interaction of gases and liquids. Finally, we'll look at some methods of separating and purifying materials after they have been mixed together.



**Figure 8-1. Food Coloring in Water**

Yellow food coloring is added into a glass of water. Initially, we see that the dark yellow color is spreading out into the water. Eventually, it will form one distributed homogeneous solution that is all pale yellow and more dilute than the original food coloring.

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Understanding the chemistry of solutions is important because most chemical reactions, both in the laboratory and in nature, take place in solutions. Because water is one of the most ubiquitous chemicals on Earth and is necessary for life, many important biological reactions involve aqueous solutions, which consist of substances dissolved in water. (Figure 8-1) In this case, the water is what we call the "**solvent**," and the substances dissolved in it are referred to as the "**solutes**." For example, water accounts for more than half of an average person's body weight, and a number of electrolytes (mineral salts) that regulate important physical functions are dissolved in it. If a person does not drink enough water and becomes dehydrated, his or her electrolyte concentrations can be thrown out of balance, which may cause symptoms such as dizziness, cramps, or irregular heartbeat.

Solutions chemistry is also central to many industrial processes. It can be a challenge to dissolve all of the reagents needed for a reaction into the same solution so they can react with one another in a timely manner. With an understanding of solutions, we can analyze problems such as how to blend medicines at appropriate concentrations for infants, children, and adults, or how to make industrial processes greener by making better solvents, recovering the solvents after the reaction is done, or eliminating solvents all together.

## **Glossary**

### ***Solutes***

In a solution, the substances that are dissolved.

### ***Solvent***

In a solution, the substance in which the solute is dissolved.

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### Section 2: What Is a Solution?

Whenever we combine two or more different substances, we create a mixture. As we saw in Unit 1 of this course, chemists used terms like mixture, compound, and element rather loosely through the 18th century, but later these words acquired more precise meanings. A mixture can be **homogenous** or **heterogeneous**. In a homogenous mixture, particles are dispersed uniformly throughout the solution. For example, in homogenized milk, naturally occurring clumps of fat are broken down into smaller sizes so that they will stay *evenly dispersed* throughout the milk. Without homogenization, the fat separates out, causing the cream to rise to the top. Unhomogenized milk is a heterogeneous mixture because the fat floats on top, not uniformly dispersed throughout the liquid.

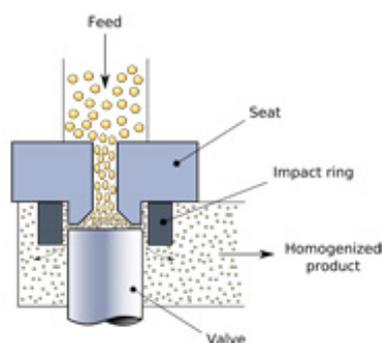
#### Homogenized Milk

Holstein or Guernsey? If we live in cow country, this is a burning question. Why? Because the Holstein breed of dairy cows produces more milk, but the milk from the Guernsey breed has more fat in it. Because farmers get paid based on the fat content of their milk as well as the volume, figuring out which cow to go with is no simple matter.



Different breeds of cows produce different concentrations of fat in their milk. © Left: Holstein Cow, Wikimedia Commons, Public Domain. Right: Guernsey Cows, Wikimedia Commons, Creative Commons License 2.0. Author: Evelyn Simak, 16 September 2009.

But we never see milk marketed as "100% Holstein." This is because, unless we purchase milk straight from a farmer, the dairy industry takes all the milk it buys from all of its farmers and mixes it together to get the desired fat content. But, the fat in that huge vat of mixed milk doesn't stay in solution. Instead, the fat (in the form of cream) floats to the top. If we skim off this fat, we get "skim milk," which is a solution. But if we want to keep all or most of the fat in the milk, we have to get that fat to stay dispersed in the mixture, which we call a "colloid." This is accomplished through the process of homogenization.



Homogenization. © Wikimedia Commons, Creative Commons License 3.0. Author: Daniele Pugliesi, 17 April 2010.

Milk is processed to decrease the size of the fat particles. It is pushed through tiny holes under great pressure, which allows the small groups of fat molecules to mix evenly throughout the milk, creating a consistent colloidal mixture with a known fat concentration.

A **solution** is more than just a homogenous mixture. It is a homogenous mixture down to the molecular level. So, even if it looks homogeneous to the human eye, there can still be groups of molecules clumped together that make it not a solution. Homogenized milk isn't a solution. Rather, it is a **colloid**—a mixture in which very small particles of one substance are distributed evenly throughout another substance. The clumps of fat in the milk, while small, are still in groups of fat molecules. If individual fat molecules were uniformly spread throughout the milk, homogenized milk would be a solution. Salad dressing can be made by mixing olive oil with vinegar. At first they don't mix; but if we shake them for a long time, they "look like" they make a solution. However, it is a colloid with very small oil droplets suspended in the dressing. Several hours later, it will separate back into the two layers.

Household rubbing alcohol is a good example of a solution. It contains a homogenous mixture of isopropanol (alcohol) and water. So, if we took one milliliter of liquid from the top of the bottle of rubbing alcohol and another milliliter from the bottom of the bottle, both of these samples would contain exactly the same components in the same proportion and would have identical properties: They would weigh the same, boil and freeze at the same temperature, taste the same, and so on. Uniformity in solution is extremely important in chemical experiments. We need to know exactly what is in the sample that we're working with, no matter where we take it from in the container.



**Figure 8-2. Mixture vs. Solution**

Sand will not dissolve in the ocean, but the force of crushing waves may intermingle sand with water to form a mixture. Sugar and water, on the other hand, begin as a mixture until the sugar dissolves. Once the sugar evenly disperses throughout the water, it becomes a solution. This process is called "dissolution."

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Pure water is not a solution because it is not a mixture of different types of molecules; rather, it contains just one type of molecule. But suppose we add a few tablespoons of sugar to the water. At first the sugar will settle at the bottom of the glass, so the mixture is not uniform—there will be less sugar in a milliliter of water from the top of the glass than in a milliliter from the bottom. After a while, however, the sugar molecules will dissolve and spread themselves uniformly throughout the water. At this point, when water molecules surround each individual sugar molecule, the mixture has become a solution. The process of molecules spreading out evenly through a mixture is called **dissolution**, and when it is complete the sugar is said to be dissolved in the water. (Figure 8-2)

## **Glossary**

### ***Colloid***

A mixture in which very small particles of one substance are distributed evenly throughout another substance.

### ***Dissolution***

The process of creating a homogeneous solution of solute molecules in a solvent.

### ***Heterogeneous***

Describing a mixture consisting of ingredients with various physical and chemical properties, like a pepperoni pizza.

### ***Homogenous***

Describing a mixture having the same physical and chemical properties throughout, like salt water.

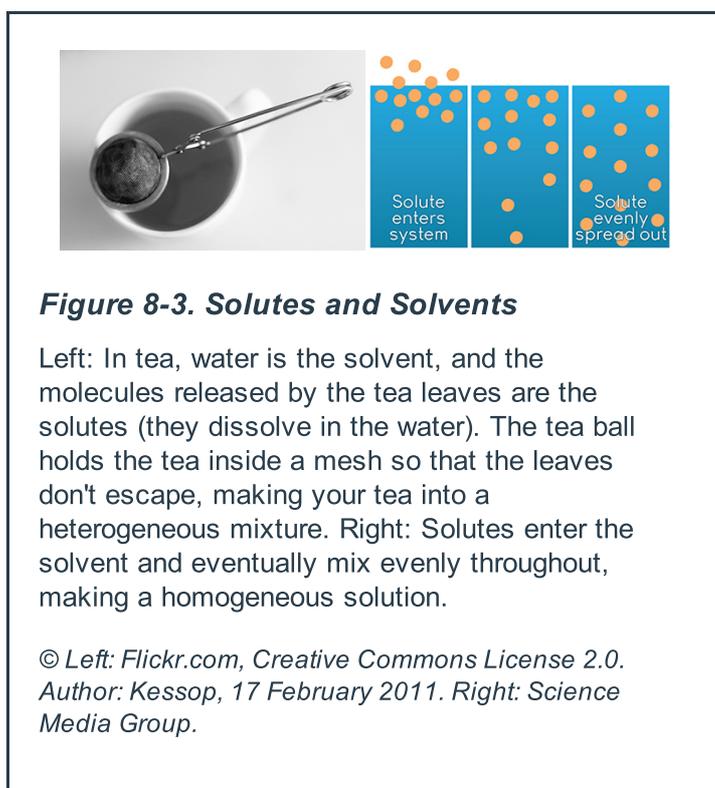
### ***Solution***

A mixture of substances in which one substance, the solute, distributes its molecules evenly throughout a second substance, the solvent.

## Unit 8: When Chemicals Meet Water—The Properties of Solutions

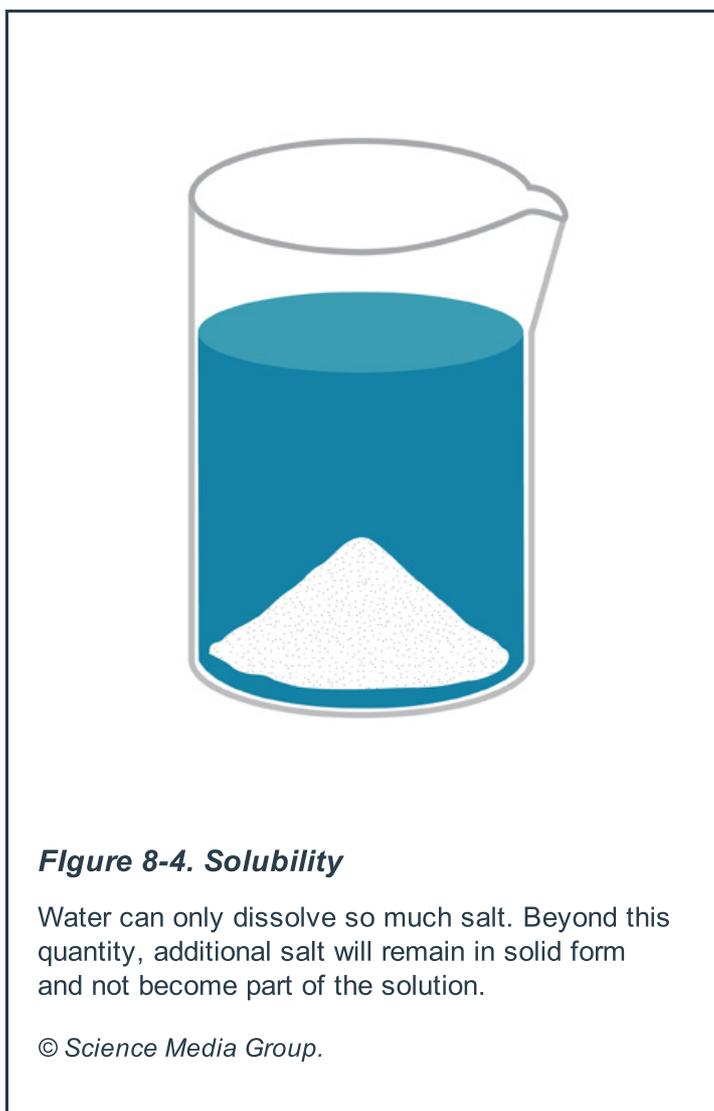
### Section 3: Solutions and Solubility

Solutions can be made of liquids, gases, or even solids. However, when we speak of solutions, we commonly think of the solution being in the liquid phase, such as coffee, tea, juice, household bleach, shampoo, gasoline, and ink. Some solutions are also in the gas phase; air is a gaseous solution consisting mainly of nitrogen and oxygen, plus much smaller amounts of argon, carbon dioxide, and a few other gases, all mixed evenly together at the molecular level. There can even be solutions that are in the solid phase; a good example of these are metal alloys, like dental fillings, and these will be revisited in Unit 13.



The component that represents the largest fraction of a solution is called the "solvent," and its other components are called the "solutes." The solvent is the substance in which other materials (the solutes) dissolve. For example, the solvent in tea is water, and the solutes are all of the various molecules released by the tea leaves. (Note that the tea leaves themselves do not dissolve and become part of the solution—they are steeped to release flavor, then filtered out.) (Figure 8-3)

## Solubility



A solvent cannot always dissolve a given amount of a solute. When table salt (sodium chloride,  $\text{NaCl}$ ) is added to water, it makes a salty solution. But if we keep adding salt, it doesn't keep getting saltier beyond a certain point. The salt that was initially added to the water dissolves, but eventually additional salt just sits in a pile on the bottom of the container. At this point when no more solute can dissolve, we say the solution is **saturated**. At a given temperature, a particular solvent can dissolve a set amount of a particular solute, and then no more. This amount, usually measured in grams per volume of solvent, is said to be the **solubility** of the solute in the solvent at that temperature.

For example, table salt has a solubility of 36 grams per 100 mL of water at room temperature. This means that we can dissolve 36 grams of salt in every 100 mL of water we have. If more salt is added to the solution, it will just sit on the bottom of the container. (Figure 8-4) Solubilities are always given for a particular temperature of solvent. For table salt, if the temperature is raised, the 100 mL of water can dissolve more salt; if it is lowered, the water will hold less salt. This is not true for all solutes. Some of them are actually more soluble at lower temperatures.

## Precipitation



**Figure 8-5. Precipitation**

When molecules of a solid begin to disperse throughout a solvent, the substance is said to be "dissolving." When the opposite process occurs, and molecules in a solution collect themselves back into a solid state, they are said to be "precipitating." In this picture, sugar crystals are precipitating out of solution to form rock candy.

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If we prepared a saturated solution of salt at 25°C and then cooled the solution, we would see little salt crystals begin to appear in the liquid. This process of molecules coming together to form crystals is called "**precipitation**." (Figure 8-5) By cooling the solution, we have made the solution supersaturated, which means there is more solute than the solution normally can dissolve. The process of precipitation creates a solid that is called the "precipitate." Precipitation is the opposite of dissolution. When a substance dissolves, its molecules spread themselves out throughout the solvent. When it precipitates, the scattered molecules come together to form solid particles or, in some cases, crystals.

## Glossary

### **Precipitation**

The formation of solid crystals by dissolved solute molecules coalescing out of solution. This process is the opposite of dissolution.

### **Saturated**

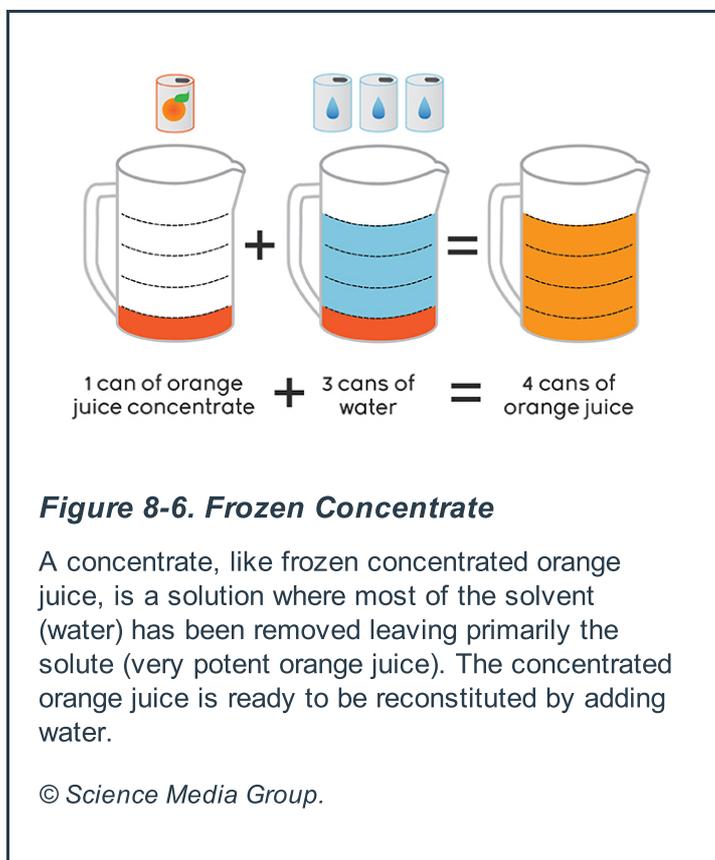
An adjective used to describe a solution that has dissolved as much of a particular solute as it can at its current temperature.

### **Solubility**

The extent to which a solute is able to dissolve in a solvent. Often the solubility is given as the specific quantity of solute it takes to saturate 100 mL of solvent. For example, the solubility of sugar in water is 67 grams per 100 mL.

## Unit 8: When Chemicals Meet Water—The Properties of Solutions

### Section 4: Solution Concentrations



In making and using solutions, a key question is how strong each solution should be—that is, how much solute should be mixed with the solvent. A parent needs to know just how much orange juice concentrate to add to water to make a refreshing drink. (Figure 8-6) To keep a pool clean, we need to know exactly how much chlorine to dissolve in a given amount of water. A doctor prescribing a drug for a patient needs to know exactly how much of that drug is contained in each pill or injection of medication. The amount of solute dissolved in a given amount of solution is called the **concentration** of the solution.

How the concentration is measured or described for a solution depends on the nature of the solutes in the solution, how concentrated the solution is, and what we plan on using this concentration for. The simplest concentrations we see are the ones we can find listed on the bottles of household chemicals that come in different strengths. These are usually given as percentages.

### ***Parts per Million and Parts per Billion***

When a solution has a very low concentration of solute, it is said to be dilute. In discussing the concentrations of very dilute solutions of gases or liquids, percentages or molarities are not convenient units. This becomes very important when creating regulations for the environment or for food safety. When there are toxins present in food and drinking water, the maximum limits that humans can tolerate are very small.

In other cases, environmental pollutants might be of unknown identity. So, if we have a large sample of ocean water, let's say a million grams, we might find that it contains 2 grams of some unknown compound. We cannot convert those 2 grams into moles, because we have no idea what it is, so environmental chemists use another term called "parts per million (ppm)." They would say that there are two parts per million of that compound present or 2 ppm. For even smaller amounts, we can use the parts per billion (ppb) term, where 1 part per billion means that there is 1 gram of something present out of 1 billion total grams present. Technically, ppm and ppb are what scientists call "unitless," because we divided grams by grams, which would then cancel out.

For example, in 2001 the U.S. Environmental Protection Agency (EPA) issued a stringent regulation limiting the maximum concentration of arsenic in drinking water to 10 ppb. This would mean that at most 10 grams of arsenic present in a billion grams of water could be present, but that's a lot of water. On a smaller scale, it must be less than 0.000001 grams of solute in 100 grams of water solution. Arsenic appears in water sometimes as a trace contaminant, but EPA deemed exposure to concentrations below this limit to be harmless. This concentration is 0.000001% (m/m). Rather than writing all those zeroes, we can use a more convenient unit—the grams of solute per billion mL of solution.

### ***Mass and Volume Percentages***

If we were to look in the bathroom or kitchen of our house, we would probably find a bottle of peroxide for disinfecting cuts or bleach for cleaning that have a percentage listed prominently on the front of the bottle. This percentage is a form of concentration to tell how strong that solution of peroxide or bleach is. Most household bleach will be listed at 5%. This is a **mass percentage** or (m/m) percent, or the (mass of the solute/mass of solution)  $\times$  100%. This means if we were to measure out 100 grams of bleach, 5% or 5 grams of that would be the bleach molecules (which is also called "sodium hypochlorite," which is a solid solute).

When two liquids are mixed together, the calculation is a bit different. This is called a "**volume/volume percent solution**" or (v/v) percent solution, which means that it is the (volume of the solute/volume of the solution)  $\times$  100%. Note that this is the percent volume of solute per volume of solution, *not* just per volume of solvent. The peroxide we find in our bathroom in a brown bottle is usually a 3% (v/v) solution, which means if we poured out 100 milliliters of it, it would contain about 3 milliliters of liquid hydrogen peroxide, with the remainder being the water solvent.

### ***Molarity***

For chemists in the lab, the most common way to measure concentration is in moles of solute per liter of solution, or **molarity** (designated by the letter M). One mole of solute in one liter of solution is said to be "1.0 M" or 1 molar. Molarity is commonly used by both chemists and biologists, and special containers called "volumetric flasks" exist in a variety of sizes to help scientists prepare solutions of a specific molarity that they need. (Figure 8-7)



**Figure 8-7. Using a Volumetric Flask**

Chemists want solutions of specific molarities, and they use volumetric flasks to accomplish this. The line etched into the stem of the flask represents a very precise volume if the liquid is exactly at that level. So, chemists will measure out how much solute they need and put it into the bottom of the flask, and then slowly add solvent until the total volume of the solution is exactly at that line. Now the molarity is known because the number of moles of solute are in exactly the volume of the solution written on the outside of the volumetric flask.

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One of the problems with molarity, because it is based on the volume of the solution, is that it is temperature dependent. This is because all substances, including liquid solutions, expand and contract as they are heated and cooled. Because of this, there are two other common measures of solution concentrations that are independent of temperature. One of them is called "**molality**." This concentration is calculated by dividing the moles of the solute by the mass of the solvent in kilograms, since mass doesn't change when the temperature changes. Another unit used is called the "**mole fraction**." In the mole fraction, the moles of the solute are divided by the total moles of everything present, both solvent and solute. Mole fractions are interesting because they can only have values between 0 and 1. Molality and mole fractions are important for measuring some of the properties of solutions that will be discussed in the later sections of this unit.

## Glossary

### **Concentration**

The amount of solute in a given amount of solution.

### **Mass percentage or (m/m) percent**

The mass of the solute divided by the mass of solution multiplied by 100%.

### **Molality**

The concentration of dissolved solute in a solution, expressed as the number of moles of solute per kilogram of mass of the solvent.

**Molarity**

The concentration of dissolved solute in a solution, expressed as the number of moles of solute per liter of the solution.

**Mole fraction**

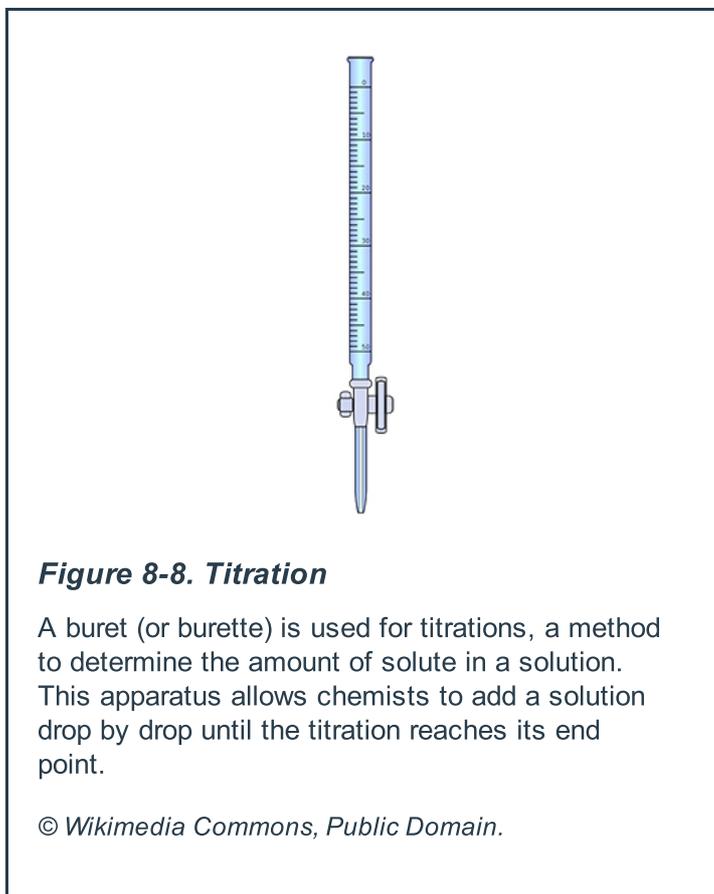
The fraction of a mixture that is comprised of a particular molecule. It is expressed as the number of moles of the molecule of interest divided by the total number of moles of all the molecules in the mixture.

**Volume/volume or (v/v) percent solution**

The volume of the solute divided by the volume of the solution multiplied by 100%.

## Unit 8: When Chemicals Meet Water—The Properties of Solutions

### Section 5: Analyzing Solutions—Titrations



Using a volumetric flask, it is straightforward to create a solution of a particular concentration. But if we want to find the concentration of an unknown solution, we have to analyze it. This could be to determine the concentration of a solution formed from an industrial reaction or it could be to analyze a sample of water from the environment for toxins. The preferred method for chemists who want to analyze a solution to determine its concentration is called a "**titration**." A titration is a form of volumetric analysis because the only thing that gets measured is the volume of the solution that is added during the titration experiment.

To perform a titration, we need to find a reaction that the solute (S) to be analyzed will undergo with another molecule (T), which we can add or titrate into the solution. These two chemicals should react together to make a product (P). In an ideal setup, we want to find a way to make sure we add exactly enough T to the solution to react with all of the S. In other words, a titration is just a controlled chemical reaction where there is no limiting reagent, because it should end exactly when both S and T are consumed by the reaction. The point when this reaction is complete is called the "**end point**" of the titration.

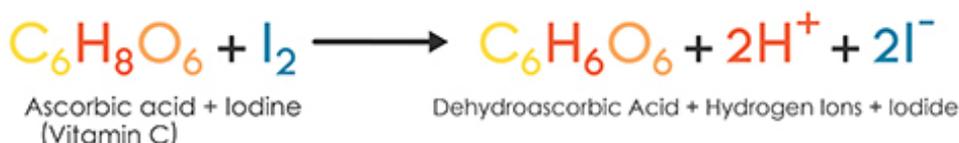


So, to do a titration, a solution of T is slowly added drop by drop into a solution of S using a buret (or burette), which marks the exact volume of the solution of T that is added. (Figure 8-8) Before starting the titration, a solution of T is prepared where the concentration is known exactly. So, once exactly enough of solution T has been added to react with solution S, the stoichiometry of the balanced chemical reaction can be used. Since the volume of solution T is known, as is its concentration, the number of moles of S that were in the solution that was being titrated is now known. However, the tricky part of a titration is being able to tell exactly when the reaction is complete.

### A Practical Titration: Vitamin C in Grapefruit Juice

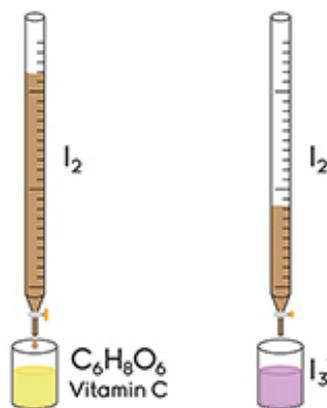
How much vitamin C is in grapefruit juice? We use a titration to figure this out. Here's how that works. In this case, the solution is the grapefruit juice, and the dissolved solute we are interested in is the vitamin C.

To start, we need another molecule that we can add to the grapefruit juice that will react with the vitamin C. We'll use iodine ( $I_2$ ). When we add iodine to vitamin C, it produces iodide ( $I^-$ ) as shown in this equation:



To titrate the grapefruit juice, we add a known amount of iodine ( $I_2$ ) drop by drop until all the vitamin C is gone and the reaction ceases. Then, we figure out how much iodine we added to determine the amount of vitamin C. Simple, right? But how will we know when the reaction has stopped and we have reached the end point?

We need an indicator. The trick we need to know for this titration is that if there is even the smallest amount of excess iodine around, it can react with iodide to form triiodide ( $I_3^-$ ). Triiodide turns dark purple when it is in the presence of starch. Starch is a complex sugar common in nature (potatoes, for example, are made almost entirely of starch). So, we add starch to our grapefruit juice. Now, if even the smallest fraction of a drop is added past the end of the reaction, the color purple will appear in our sample. Ideally, it would be the faintest color purple possible that the eye can see. If it were dark purple, it might mean that we added excess iodide, which would ruin the data from the experiment.



Titration of Grapefruit Juice with Iodine. © Science Media Group.

### Indicators

For the titration described above to work, we must have some way of determining exactly when the reaction has stopped occurring, since molecules are too small to monitor with the human eye. Therefore, it would be perfect if there were a visual change when the exact amount of solution T has been added to completely react with solution S. If either S or T is a colored compound, we can keep adding the solution of T drop by drop until the color disappears; unfortunately, most of the chemicals used in titrations are colorless. Therefore, a common way to determine the point at which the chemical reaction is complete is to use a

substance called an "**indicator**." An indicator is a molecule that changes color to indicate when the reaction is over. When we see the color change, we know that exactly enough of solution T has been added to react with solution S.

So long as the indicator changes color when the reaction is over, it can be useful. There are many things to consider when picking an indicator. We will further address indicators in Unit 10.

## **Glossary**

### ***End point***

The point in a titration where the reaction ceases to occur. It indicates that all of the reactant in the flask is used up.

### ***Indicator***

A substance that undergoes a change, usually in color, that indicates the endpoint of a titration.

### ***Titration***

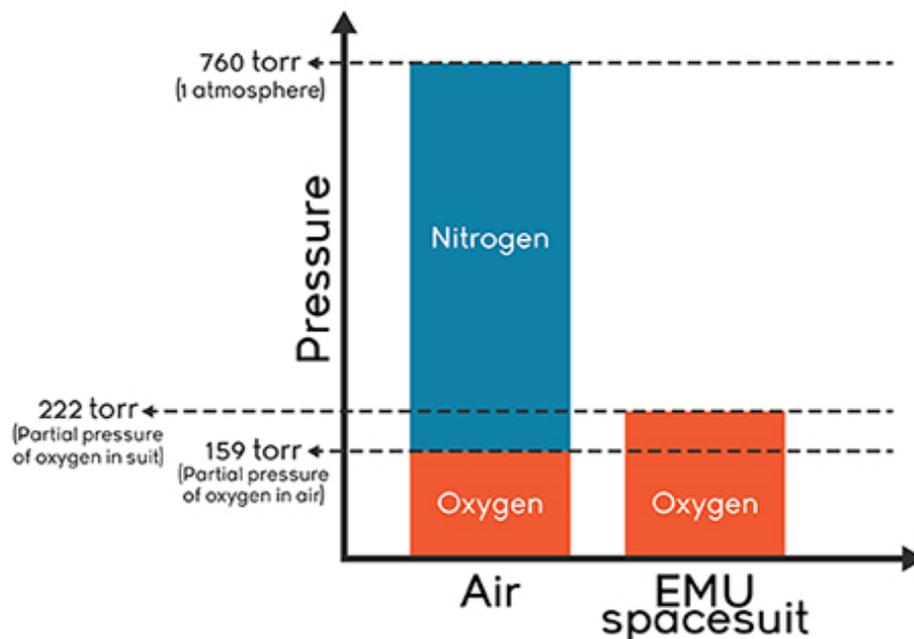
A technique for measuring the concentration of a solute in a solution by carefully measuring how much of a second molecule, called the "titrant," reacts with it. As titrant is added to the solution, the reaction takes place until the solute is used up; the amount of titrant required to reach this point (see End Point) can be used to deduce how much solute was in the solution.

## Unit 8: When Chemicals Meet Water—The Properties of Solutions

### Section 6: Solutions and the Gases above Them—Raoult's Law

#### *Partial Pressures and Spacesuits*

Dalton's Law shows why we need special air mixtures to breathe under certain conditions. Earth's atmosphere consists mostly of a mix of nitrogen and oxygen; the partial pressure of the nitrogen is 593 torr and that of oxygen is 159 torr. This is the partial pressure of oxygen to which our bodies are adapted. Airplanes contain oxygen masks that drop down to passengers if their cabins lose pressure because the atmosphere outside of the plane is at lower pressure than is on Earth's surface. In other words, the partial pressure of oxygen at high altitudes is not high enough for humans to breathe. When astronauts on the International Space Station do spacewalks, they often use spacesuits referred to as "EMUs" (extravehicular maneuvering units) that operate at only 222 torr—less than 30% normal atmospheric pressure! But these suits offer the astronauts pure oxygen to breathe so the partial pressure of the oxygen is the entire 222 torr, well above the amount needed to keep the astronauts alive and comfortable. It is also important to know that humans cannot breathe gases with a partial pressure much higher than 159 torr for long periods of time or the body will begin to overheat.



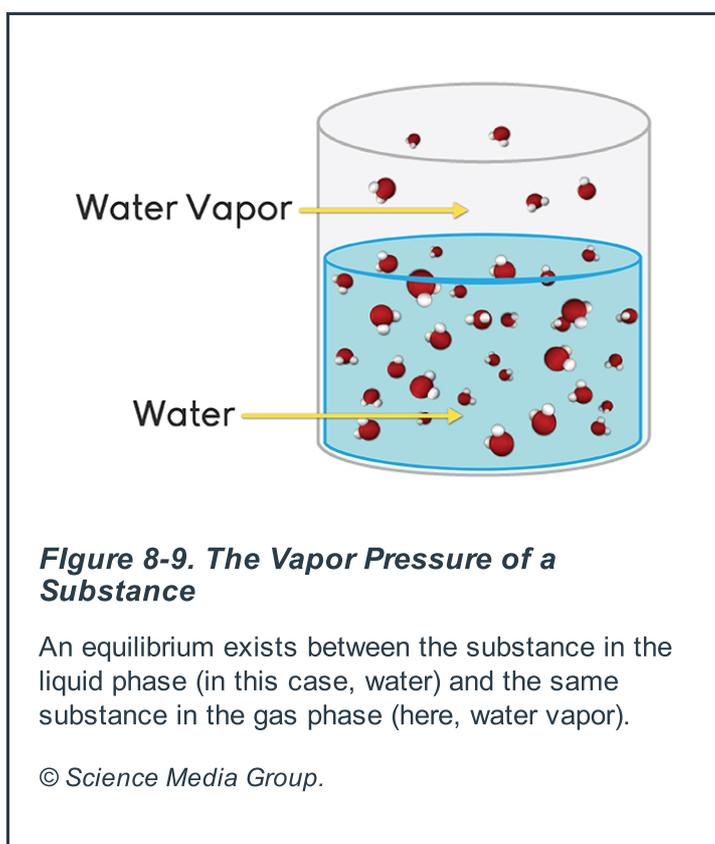
*How a Low-Pressure Spacesuit Works. © Science Media Group.*

Before learning about Raoult's Law and what that tells us about solutions, we need to introduce and review a few terms. Raoult's Law is all about the relationship between a solution and how it affects the gases above the solution. So, we need to refer back to **partial pressure** of gases and review what a **vapor pressure** is.

In Unit 1, partial pressures were introduced as part of the history of John Dalton, the founder of modern atomic theory. He discovered that if we have a mixture of gases, then each of the gases exerts a part of the total pressure, relative to its amount in the mixture. This rule is known as Dalton's Law of Partial Pressures, named for its discoverer. The partial pressure of oxygen ( $O_2$ ) in air is 0.20 atm and that of nitrogen ( $N_2$ ) is 0.78 atm. There are also trace amounts of argon (Ar), carbon dioxide ( $CO_2$ ), and other gases, but their partial pressures are very small. Together, they will add up to the 1.00 atm of normal atmospheric pressure at sea level. This is because 20% of the molecules in air are oxygen molecules, and 78% of the molecules in air are nitrogen molecules.

### Vapor Pressure

Imagine we fill a jar halfway with water, and seal it. (Figure 8-9) Some of the water will start evaporating until the air above the container has some water vapor in it. On a normal temperature day, the partial pressure from just the water vapor is about 3% of the pressure of the air in the jar. This partial pressure of the vapor of a liquid is called the "vapor pressure." Any liquid placed in a jar will produce a vapor pressure in this way, but the vapor pressures will vary for different substances.



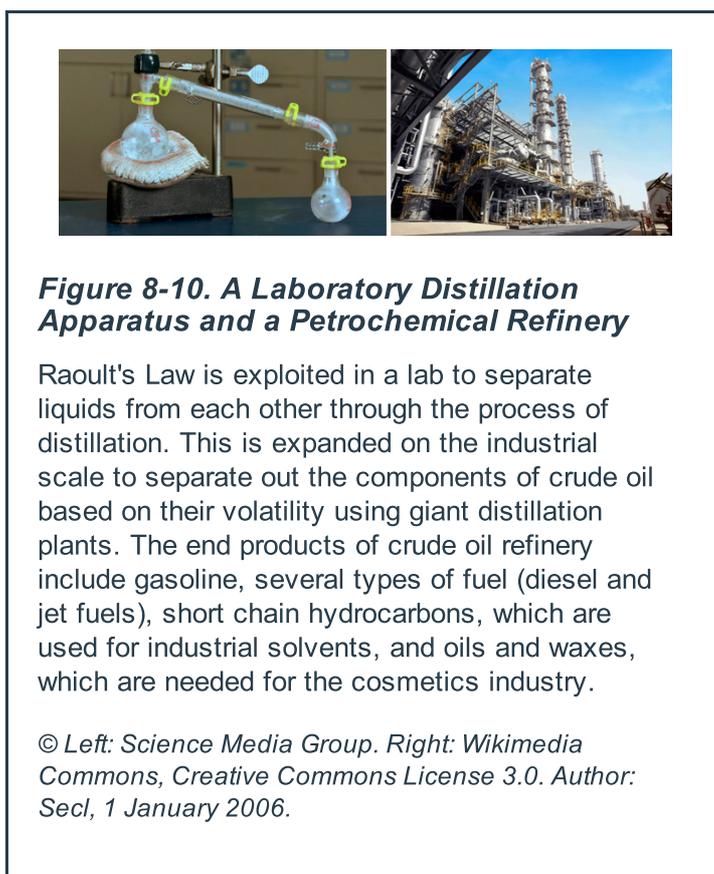
If attractive forces between particles of a liquid are relatively strong, the liquid's evaporation rate will be low and it will have a low vapor pressure. If the forces are weak, it will evaporate more readily and have a high vapor pressure. Liquids with a high propensity to evaporate are called "volatile." If we were to open a container of a volatile liquid, like gasoline, within a minute, we could smell its vapors throughout the room. However, a liquid like baby oil, which isn't very volatile, has such a low vapor pressure that we can only smell it by putting our noses right into the container. Vapor pressure for a given liquid increases as temperature increases, because adding heat increases the kinetic energy of molecules in the liquid, making it easier for the liquid to overcome attractive forces and change to a gas. The higher the temperature, the more liquid evaporates and the higher the vapor pressure. This will be important later when we discuss the process of boiling.

So, now that we know what partial pressure and vapor pressure are, what is **Raoult's Law**? Raoult's Law usually applies to solutions when two different volatile liquids are mixed together into a solution. It can also be used for mixtures of multiple volatile liquids or in cases where one of the components is a solid; solids and Raoult's Law will be discussed in the next section. It turns out that each volatile liquid will have a vapor pressure above the solution, and its vapor pressure is proportional to what fraction of the solution that liquid is.

$$P_A = X_A P_A^\circ$$

Vapor Pressure of A above the solution = Mole Fraction of A in the solution x Standard Vapor Pressure for A

While that might sound complicated, in reality it means this: If we have two liquids that are both volatile in a solution, the vapors above them will always be richer in the more volatile component. So, if we were able to take the vapors above the solution and cool them and recondense those vapors into a new solution, that solution would have a higher percentage of the more volatile component. If we could repeat that over and over again, it would allow us, in theory, to separate a more volatile compound from the less volatile one. Doing this in multiple steps isn't practical, but it can be done easily in a laboratory or in an industry using special equipment. This process of exploiting Raoult's Law to separate two or more volatile compounds is called "distillation."



Distillation is used widely in the oil industry. When crude oil is pumped out of the ground, it consists of a mixture of many different hydrocarbon molecules. At an oil refinery, it is distilled repeatedly to separate out different components according to their different vapor pressures. From crude oil, one can separate out and produce gasoline, kerosene, liquid petroleum gas (LPG), diesel fuel, waxes, and tar. Distillation is also used to prepare medicines from certain plants, produce perfumes, and purify beverages. (Figure 8-10)

## Glossary

### ***Partial pressure***

The part of the total pressure exerted by one of the gases in a mixture of gases. Each gas exerts the pressure it would exert if it were by itself in the same volume at the same temperature as the mixture; the total pressure is the sum of these partial pressures.

### ***Raoult's Law***

The partial pressure of a gas over a liquid mixture is equal to the vapor pressure of the pure substance multiplied by the mole fraction of that substance in the liquid mixture.

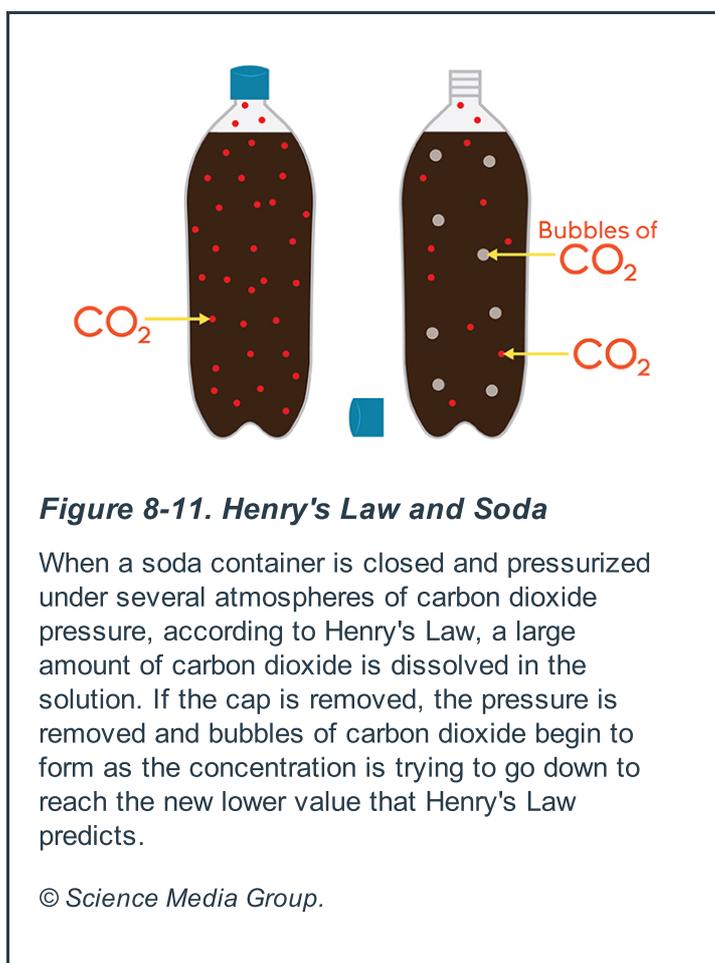
### ***Vapor pressure***

The gas pressure, defined at a given temperature, due to the evaporation from the surface of a liquid phase.

## Unit 8: When Chemicals Meet Water—The Properties of Solutions

### Section 7: Henry's Law

As we learned earlier in this unit, there are limits to the amount of any given solid that can be dissolved in a specific liquid before the solution becomes saturated. Similarly, the same thing is true if the solute is a gas; the liquid can only absorb a certain amount of the gas before it becomes saturated. In daily life, many liquids have gases dissolved in them; the most common example of this is carbonated sodas. Colas and root beer are composed of flavoring and sugars added to a solution of carbon dioxide gas dissolved in water. (Figure 8-11)



In 1803, English chemist William Henry (1774–1836) published a paper on his experiments dissolving different quantities of gases in water at varying temperatures and pressures. Henry's Law states that the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid. (See the equation below.) The greater the partial pressure of a gas, the more of that gas will dissolve in the liquid. Understanding Henry's Law allows us to manipulate the amount of gas that dissolves in liquid. In the health field, this means that we can expose the body to higher pressures of oxygen to increase the amount of oxygen in the blood. Or vice versa, we can remove toxic gases like carbon monoxide from the air to which a patient is exposed, to remove it from the solution of blood.

$$c = kP$$

concentration of the gas in the solution = Henry's Law constant x partial pressure of the gas above the solution

So, this is really just a simple relationship between the amount of gas that dissolves in the liquid and the partial pressure of the gas above the liquid solution. The constant in that equation is also affected by three other factors. The first is temperature. Henry's Law constants are a function of temperatures. If we leave a glass of tap water out for a long time, bubbles form as the water warms up to room temperature because the air dissolved in the water is actually more soluble when the water is colder. It also depends on what gas is being dissolved and what solvent or liquid is being used. Henry's Law explains why diving with compressed air is dangerous; nitrogen makes up 78 percent of air, and it has a very high Henry's Law constant compared to other gases. Therefore, if we dive down with compressed air for a while, nitrogen begins to dissolve significantly into our blood under the increased pressure of the water. However, returning to the surface quickly removes that pressure; "the bends" occurs when this happens so fast that small bubbles of nitrogen gas form in the small blood vessels. In order to prevent death if this occurs, a diver needs to get to a hospital quickly to get repressurized in a chamber, so that the bubbles will redissolve and the pressure can be released slowly.

### **Liquid Breathing**

Henry's Law states that we can alter the amount of gas dissolved in a liquid by changing the partial pressure of that gas on the liquid. However, we can also have an effect by changing the solvent. There is an experimental approach to respiratory medicine, with applications in deep sea diving, that hopes to put this into practice. The liquid perfluorodecalin has the ability to dissolve large amounts of oxygen gas (49 ml/100 ml at room temperature). It is theorized that applying liquid perfluorodecalin to wounds would accelerate healing by saturating the tissue with oxygen. It is also hoped that breathing perfluorodecalin into the lungs would be useful in treating pulmonary or cardiac trauma, as this compound was originally developed by the Navy for deep sea diving.



*Deep Sea Divers. © Wikimedia Commons, Public Domain.*

Henry's Law tells us that if we put pure water in a jar, the nitrogen and oxygen in the air will dissolve into the water in proportion to their partial pressures. This is important for lakes, streams, and other water reservoirs. The fish and other creatures that live in these bodies of water need certain levels of oxygen to survive. As the water moves around, and comes in constant contact with the air above the surface, a level of oxygen is maintained that allows fish to survive. However, in the ocean, where the depths of the water can be miles deep, only the water near the surface will be in contact with the air, while the water farther down will have little oxygen dissolved in it and can support very little aquatic life. In a fish tank, we have to use a bubbler to force enough oxygen to dissolve in the water so certain types of fish will have enough oxygen to survive. But in the natural world, fish don't need bubblers. The natural motions of certain bodies of water and Henry's Law take care of that.

## Unit 8: When Chemicals Meet Water—The Properties of Solutions

### Section 8: Colligative Properties—Vapor Pressure and Osmosis

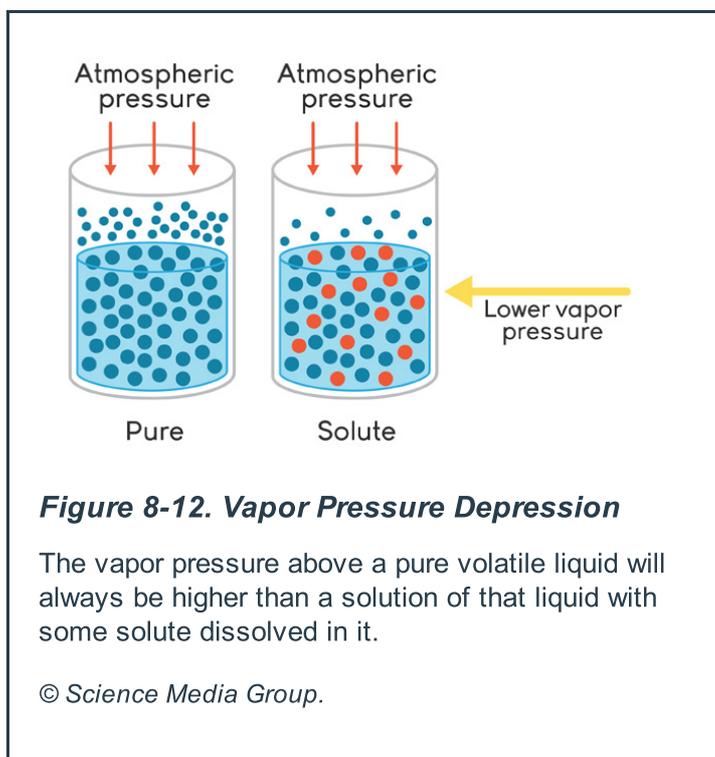
Chemists typically work with solutions that are **dilute**, meaning that they consist mostly of solvent with only a little solute. In these cases, the mole fraction of the solvent is high and may be close to one. Of course, it is not actually one, because then we would have a pure substance instead of a solution.

Many physical properties of solutions depend only on the concentration or amount of the solute in the solution, not on the identity of the solute. In these, the concentration can be measured as a mole fraction, molarity or molality. These properties are called "**colligative properties**" and include:

- Vapor pressure depression
- Osmotic pressure
- Boiling point elevation
- Freezing point depression

These four properties are bound together by the fact that they each vary in proportion to the *amount* of solute and not the *type* of solute present. They are also closely related to chemistry behind Raoult's Law. Let's look separately at the first two in this section.

#### Vapor Pressure Depression



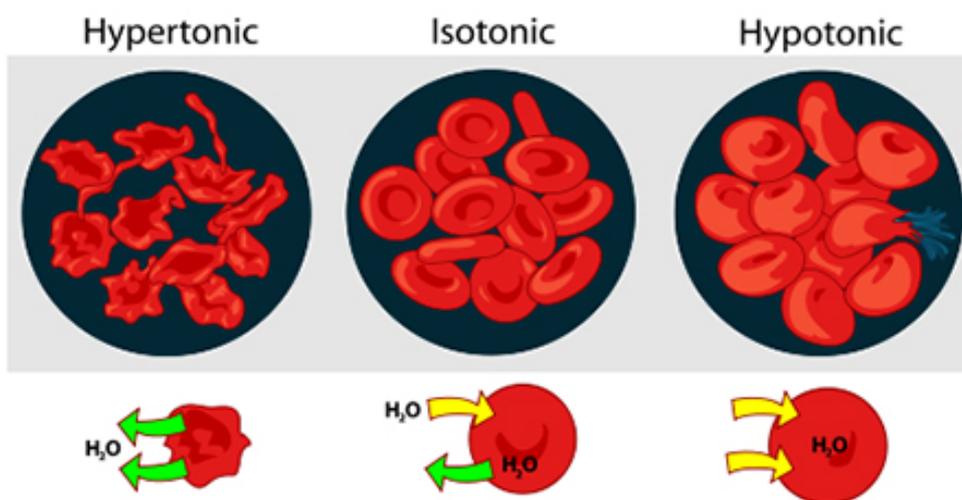
From Raoult's Law, we know that the partial pressure of a gas above a mixture is proportional to the mole fraction of that component in the liquid. If the solution consists of a solute that is nonvolatile (that is, it doesn't evaporate) and a solvent that *is* volatile (it will produce vapor), then the only vapor above the liquid will be that of the solvent. An example would be an aqueous solution of sodium chloride: The sodium chloride will not evaporate to form a gas above the solution, but the water will.

Because the solvent has a solute dissolved in it, the mole fraction of the solvent is less than one, so the partial pressure is less than the vapor pressure of pure solvent. The amount by which it is less is called the "**vapor pressure depression.**" The more concentrated the solute, the greater the vapor pressure depression. (Figure 8-12) This means that if we take a glass of water from the tap and some salt water from the ocean and leave them sitting out, the salt water will evaporate much more slowly than the pure water. As the salt water evaporates, the concentration of the salt will rise, the vapor pressure of the water will keep falling, and it will take longer and longer to evaporate the same amount of water.

## Osmotic Pressure

### Osmotic Pressure and Cells

When we have two solutions separated by a semipermeable membrane, the one with the greater concentration of dissolved solute—and thus the higher osmotic pressure—is said to be "hypertonic" to the other (from the Greek *hyper* meaning "over," and *tonikos* meaning "stretched"). The solution with less dissolved solute—thus, lower osmotic pressure—is said to be "hypotonic" to the other (from the Greek *hypo* meaning "under.") If the two solutions have an equal number of dissolved particles—hence, equal osmotic pressure—they are said to be isotonic to each other.



*Hypertonic, Hypotonic, and Isotonic Solutions.* © Wikimedia Commons, Public Domain.

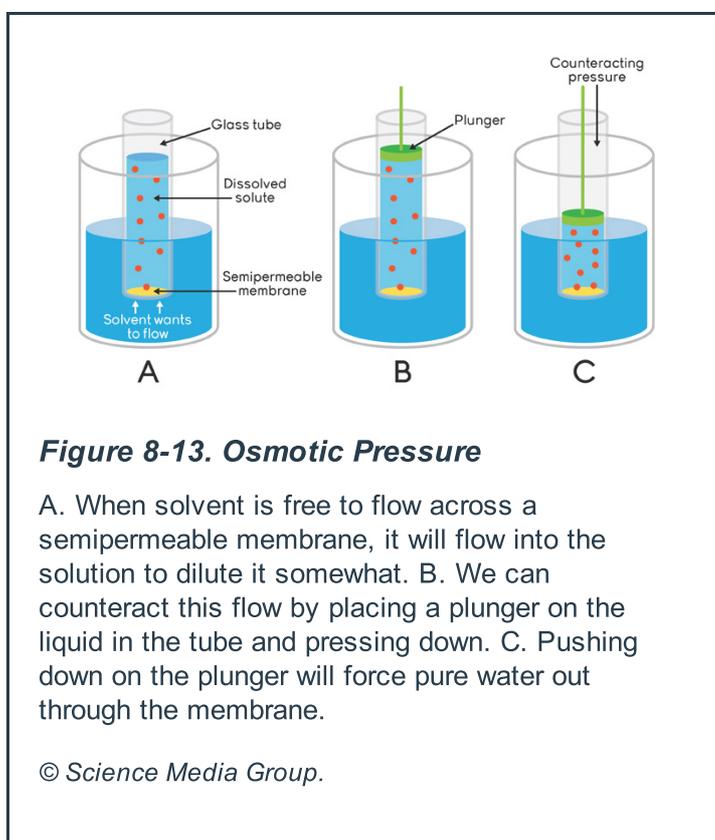
An erythrocyte, or red blood cell, is sensitive to the osmotic pressure of its environment. The membrane of the cell is a semipermeable membrane. In a hypertonic environment, where there is more dissolved salt outside the cell than inside, water flows out of the cell and it shrivels up. In a hypotonic environment, with more dissolved particles inside the cell than outside, the water flows in causing the cell to swell up. If this goes far enough, the cell will burst. In an isotonic environment, the flow of water across the membrane is balanced and the cell has its normal size and shape.

Plant cells do not have to worry about bursting when placed in a hypotonic solution, because they have strong cell walls on the outside of the cell membrane that prevent that type of rupture. Humans are not so fortunate. Why does our skin become wrinkled when we take baths or swim for long periods of time. What has actually happened is that we were placed in pure or nearly pure water that was hypotonic relative to the inside of our skin cells, and they all began to swell with water. And now, with our skin increasing in size, it starts to buckle or wrinkle like a carpet that is too big for a room. If we leave the water, our cells will pump out that water, it will evaporate, and our skin will return to normal. However, if we stay in water for too long, our skin cells will be

permanently destroyed. This is why swimmers who are crossing large bodies of water, like the English Channel, wear wet suits or coat their bodies with grease to prevent the water from coming in contact with their skin.

When a membrane or similar barrier allows the passage of some molecules but not others, it is called a "**semipermeable membrane**." If a semipermeable membrane is placed in a solution, generally the solvent flows freely across the membrane and the solute is blocked. When this happens, solvent will flow through the membrane toward the side on which there is a higher concentration of solute. The sidebar on how cells behave in solutions shows some of the interesting effects of osmotic pressure. (See the *Osmotic Pressure and Cells* sidebar.)

In Figure 8-13, we have placed solvent in a jar and set a glass tube in it with a semipermeable membrane at the bottom. Some solute particles are dissolved in the solvent inside the tube, where they are confined because they cannot pass through the semipermeable membrane. Because the solution in the tube is more concentrated, solvent will flow through the membrane into the tube to try to dilute it. This won't happen forever, just until the liquid reaches a certain height. The height of this column of water can be related to what we call its **osmotic pressure**, which has forced the liquid up to that height.



This pressure can affect cells in the body making them swell or shrink, but it has a practical industrial use: reverse osmosis. If a pressure higher than the osmotic pressure of solution is applied to it, as by pushing down on a plunger, pure water can be forced out of the semipermeable membrane. This is one of the common ways, not involving filters or evaporation, to purify water.

## Glossary

### ***Colligative properties***

Properties of solutions that vary with the concentration of dissolved solute particles, but are indifferent to the particular chemical identity of the solute.

### ***Dilute***

To make a solution less concentrated by adding more solvent.

### ***Hypertonic***

The property a solution is said to have when it contains a higher concentration of dissolved particles than another solution to which it is being compared. For example, the salt in seawater makes it hypertonic to the fresh water of a lake.

### ***Hypotonic***

The property a solution is said to have when it contains a lower concentration of dissolved particles than another solution to which it is being compared.

### ***Isotonic***

The property a solution is said to have when it contains the same concentration of dissolved particles as another solution to which it is being compared.

### ***Osmotic pressure***

The pressure required to prevent the flow of solvent across a semipermeable membrane due to different concentrations of dissolved particles on each side of the membrane.

### ***Semipermeable membrane***

A membrane that allows only certain types of molecules to pass through it.

### ***Vapor pressure depression***

The decrease in vapor pressure seen between the gas over a pure liquid substance and the gas over the same liquid containing dissolved solute particles.

## Unit 8: When Chemicals Meet Water—The Properties of Solutions

### Section 9: Colligative Properties—Freezing and Boiling

#### *Boiling Point Elevation*

As mentioned earlier, vapor pressure increases as we raise the temperature. This means that we can compensate for the vapor pressure depression by increasing the temperature. For a particular decrease in vapor pressure due to the presence of dissolved solutes, there will be some increase in temperature that will raise the vapor pressure back up to what it was for the pure solvent. This is important for understanding the next colligative property, boiling point elevation.



**Figure 8-14. Boiling Point Elevation**

A solution has a higher boiling point than the corresponding pure solvent. Dissolving a solute in the solvent decreases the mole fraction of the solvent relative to what it would be if it were pure. This decreases the vapor pressure at any given temperature. Since the boiling point is the temperature at which the vapor pressure equals the atmospheric pressure, the solution must therefore be heated to a higher temperature to reach this equivalence. This is referred to as "boiling point elevation."

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When we increase the temperature of a liquid, the vapor pressure above it increases. At some point, the vapor pressure of the liquid equals the pressure of the atmosphere above it. When this happens, the liquid stops merely evaporating from the surface of the liquid and begins to bubble vigorously and rapidly turn into the vapor phase. This is called "boiling," and the temperature at which it happens is called the "**boiling point**." As we saw in Unit 2, for pure water the boiling point occurs at 100°C.

Since decreasing the mole fraction of a solvent lowers the vapor pressure, salt water will not boil at 100°C. Because the mole fraction of the water is less than one, the vapor pressure of salt water at 100°C is lower than what it would be for pure water, and so it is less than atmospheric pressure.

We can compensate for this, though, by heating the water to a higher temperature until the vapor pressure increases to equal atmospheric pressure again. Salt water will boil at some temperature above 100°C; exactly how much above depends on how much we have lowered the mole fraction of the water (in other

words, how much salt we have added). This phenomenon is called "**boiling point elevation**." (Figure 8-14)

### **Freezing Point Depression**

While dissolving a solute in solvent increases the boiling point, dissolving a solute in solvent decreases the freezing point. As the mole fraction of solvent goes down, the freezing point of the solution goes down as well.



**Figure 8-15. Freezing Point Depression**

Just as adding solute to a solvent raises the boiling point, it also lowers the freezing point. This means that solutions will melt at a colder temperature than the pure solvent. This is why putting a sand/salt mixture on roads prevents them from icing up.

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This phenomenon is called "**freezing point depression**," and it is what makes salt water freeze at a lower temperature than pure water. This is why we salt roads in the winter: By lowering the freezing point of the water, any ice will melt at a higher temperature. (Figure 8-15)

For salt in water, freezing point depressions are more dramatic than are boiling point elevations. A 36 percent solution of sodium chloride (which is saturated) boils at about 109°C, an increase of only nine degrees from the boiling point of pure water (100°C). In contrast, this same saturated salt solution freezes at about -22°C, a decrease of more than 20 degrees from the freezing point of pure water (0°C).

## **Glossary**

### **Boiling point**

The temperature at which a liquid begins to boil, i.e., its phase changes from liquid to gas. At this temperature, the vapor pressure of the liquid is equal to the pressure of the atmosphere.

### **Boiling point elevation**

The increase in boiling point of a solution due to an increased concentration of dissolved solute.

### **Freezing point depression**

The decrease in freezing point of a solution due to an increased concentration of dissolved solute.

## Unit 8: When Chemicals Meet Water—The Properties of Solutions

### Section 10: Separation and Purification



**Figure 8-16. Purification by Filtration**

When making coffee, we use a filter to separate the coffee solution from the solid particles (the coffee grounds). When camping, we pump water from a stream through a filter to remove dirt particles and microorganisms like *Giardia*, which leaves us with clean drinking water as the purified product.

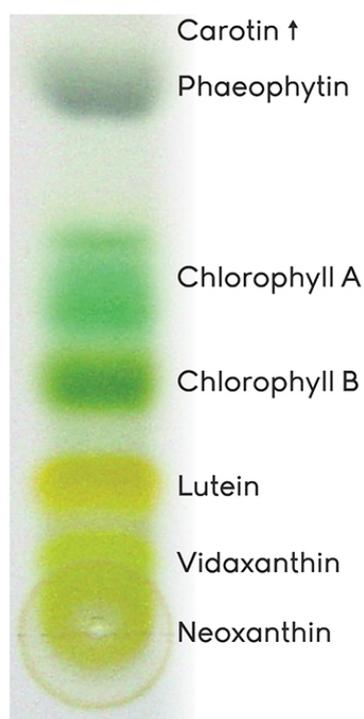
© Left: Science Media Group. Right: National Park Service.

Often, we want to remove a solute from a solution, either because the solute is desirable and we want to extract it and use it, or because the solute is undesirable and we want to purify the solvent by getting rid of it. There are a number of ways to do this.

#### **Filtration**

**Filtration** is a familiar process for anyone who has made coffee. Ground coffee beans are mixed with hot water, and the molecules in the beans dissolve into solution. But the solid residue of grounds is still mixed in with the coffee. To remove it, we pour the coffee through a special piece of paper called a "coffee filter." The liquid and any dissolved molecules pass through the material of the paper, while the larger, solid particles are caught and stay inside the filter. In this way, the coffee is purified from the grounds. (Figure 8-16)

If the molecules of solute can be turned into solid crystals, filtration can be used to remove the solute from a solution. This method of analysis involves precipitating the solute out as a solid. For example, if we had a solution of silver nitrate, but we wanted to collect the silver, we could add sodium chloride to the solution. It would form insoluble silver chloride precipitate, and then we could filter the solution and collect the precious silver that is now separated from the solution it was originally in.



**Figure 8-17. Chromatography**

The pigments in leaves have been separated by paper chromatography. The pigments that have relatively more affinity for the solvent than the paper have migrated upward faster than those that have relatively more affinity for the paper than the solvent. The result is that the various molecules of different colors are spread out into the pattern seen here.

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Another method of separating and purifying compounds from solutions is called "**extraction**." Some solutes are more soluble in some solvents as compared to others. For example, if we were to make a strong cup of tea, there would be some caffeine, some flavors, and some brown colorant molecules that could be extracted from the tea leaves into the solution of tea in water. But it turns out that the caffeine is very soluble in organic solvents. If we shook together the tea and an organic solvent, the caffeine would move into the organic solvent and leave behind the flavors and colors in the water. Conveniently, organic solvents and water are immiscible, meaning they won't mix together. We can now say that we have extracted the caffeine from the tea using an organic solvent.

### **Chromatography**

**Chromatography** is a way of separating the components out of mixtures or solutions. In chromatography, a solution is passed over or through a solid material. Different solute molecules will have differing degrees of molecular attraction for the solid material and so they will move through it at different speeds. The more attracted a molecule is to the solid material, the less quickly it will move. The different rates at which the solutes pass through the solid material are what allow them to separate. In chromatography, the solvent is called the "**mobile phase**," because it migrates through the solid material, and the unmoving material is called the "**stationary phase**." (Figure 8-17)

## **Glossary**

### ***Chromatography***

A technique for separating different types of molecules from a solution. The solution, called the "mobile phase," is passed over a material called the "stationary phase"; the different solute molecules have different affinities for the stationary phase and move through it at different rates, allowing for their separation.

### ***Extraction***

The removal of a solute, or solutes, from a solution, for example: filtration.

### ***Filtration***

The process of passing a liquid through a filter. The filter allows the passage of solvent and dissolved solute molecules, but blocks the passage of undissolved large particles.

### ***Mobile phase***

The substance in a chromatography experiment that carries the dissolved molecules of interest through the stationary phase.

### ***Stationary phase***

The substance in a chromatography experiment that remains in place while the mobile phase carries the molecule of interest through it.

## **Unit 8: *When Chemicals Meet Water—The Properties of Solutions***

### **Section 11: Conclusion**

With an understanding of solutions chemistry, we can see how to dissolve one substance into another, separate solvents from solutions, and purify them. These processes are central to many modern industries, from oil refining to the development of new pharmaceutical products. Concepts like solubility and saturation are relevant to many tasks, from inventing new sports drinks to cleaning up hazardous waste spills. In the next unit, we will apply these concepts to the equilibrium behavior of molecules in solution and explore how the thermodynamics of these reactions explain their equilibrium behavior.

## **Unit 8: When Chemicals Meet Water—The Properties of Solutions**

### **Section 12: Further Reading**

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