

Chapter 15 Lecture Outline

A. Definition of a Solution

A *solution* is a homogeneous mixture of two or more substances. A solution consists of a *solvent*, the substance which other substances are dissolved, and one or more *solutes*, substances which are dissolved in the solvent. How does one identify the solvent in a particular solution? If the solvent and solutes are all in the same physical state, then the solvent is the substance present in greatest quantity. For example, in air, which is a mixture of several gases, nitrogen is the most abundant and is the solvent. In alcoholic beverages, water is the solvent if the % alcohol is less than 50% and alcohol is the solvent if the % alcohol is more than 50%. If the solvent and solute are in different physical states, then whichever substance has the same physical state as the final solution is the solvent. For example, a saturated solution of sugar in water consists of 67% sugar. However, since the solution is a liquid (syrup), the water is still considered the solvent.

B. Types of Solutions

Since the solvent and solute can exist as either solids, liquids, or gases, there are nine possible combinations in a *binary solution* (a solution consisting of one solvent and one solute). Of these nine, only seven are actually possible and are shown below with examples of each.

1. Solid in liquid: salt in water
2. Liquid in liquid: alcohol in water
3. Gas in liquid: CO₂ in water (carbonated beverages)
4. Gas in gas: Oxygen in nitrogen (air)
5. Liquid in solid: Mercury in silver (dental amalgam)
6. Solid in solid: zinc in copper (brass)
7. Gas in solid: hydrogen in palladium (strange but true)

Neither solids nor liquids dissolve in gases, because they would first have to be converted into gases in order to mix with a gas.

C. Why Do Solutions Form?

Solutions form for the same reason that any process takes place. Because it is favored energetically. Remember our earlier discussions throughout the semester which described the driving force behind chemical processes and many physical processes as the formation of stronger bonds and thus more stable states. Solutions are no different. A solute will dissolve if the bonds it forms with the

solvent are stronger than the bonds between the solvent molecules or the solute molecules separately.

There are three steps in the formation of any solution: the breaking of the bonds between the solvent particles, the breaking of the bonds between the solute particles, and the formation of new bonds between the solvent and solute particles. As an example, consider the dissolution of CaCl_2 in water. First, the water molecules must be separated from each other to make room for the solute. Second, the calcium and chloride ions must dissociate to mix with the water. And third, the ions and polar water molecules will form bonds due to their electrical charges. The first two steps, as with all bond breaking processes, will be endothermic. The third step, as with all bond forming processes, will be exothermic. Since we know that CaCl_2 is soluble in water, and since we learned earlier that all spontaneous processes are exothermic, we must assume that the overall sum of these three steps will be exothermic. If we add CaCl_2 to water, we observe that the solution becomes quite hot, proving this point.

Now consider the similar formation of a solution of NH_4NO_3 in water. Again, since the solution does form spontaneously, we must assume that the process is exothermic. When we dissolve NH_4NO_3 in water, it instead becomes quite cold! Thus we have an endothermic spontaneous process. How is this possible? This process is moving up the energy hill spontaneously. It is no different than a dead battery recharging itself or a ball rolling uphill on its own!

Fortunately there is a logical explanation. It turns out that the energy involved in a process is not the only factor we must consider. There is a second factor that also determines if a process will be spontaneous, and that is *entropy*.

D. What is Entropy?

Entropy has often been described as a measure of disorder. This is not really accurate, but is a useful analogy for students just beginning to learn about it. In reality, entropy is based on probability, or random chance. In any given process, entropy will favor the one with the highest probability of taking place. Consider what happens when you flip two coins. Of the four possible outcomes, there is one chance of getting two heads, one of getting two tails, and two chances of getting one head and one tail. Probability (and entropy) favors one head and one tail. What if you flipped 100 coins? There are now approximately 10^{37} possible outcomes! Would you be more likely to get all heads or all tails, or more likely to get a mixture of heads and tails. While there is only one way to have all coins land the same, there are millions of ways for them to land with a mix of heads and tails.

Thus probability (and entropy) favor the most likely outcome, a mixture of heads and tails.

Now how does this apply to solutions? When a solute such as sugar is first mixed with water, the sugar molecules are all packed together in solid crystals, a very organized arrangement. The water molecules are also linked with other water molecules. Now ask yourself this. Are there more ways to arrange the sugar in the water as large crystals, or if the sugar were broken down into individual molecules and mixed throughout the water? Of course, the mixture would offer more possibilities and thus be more probable. You would also likely describe the mixture as more disorganized than a pile of sugar sitting in the bottom of a beaker of water. Thus, from a probability point of view or based on disorder, entropy favors mixing and forming solutions.

Some factors that influence entropy are as follows. Increasing temperature will increase entropy, since molecules and atoms have more freedom of movement. Breaking something into more pieces will increase entropy. There are more ways to arrange the pieces of a broken glass than the intact glass. A change in state from solid to liquid or liquid to gas will increase entropy as the volume and freedom of movement increases. Forming a solution usually increases entropy, because there are more ways to mix particles together than when they are separate. The exception would be dissolving a gas in a liquid or solid, since the entropy of the gas would decrease greatly. This explains why the NH_4NO_3 dissolved in water, even though the process is endothermic. The increase in entropy offset the absorption of energy.

E. Predicting if a Process Will Be Spontaneous

Earlier in the semester, we used energy to predict if a process would be spontaneous or not. Exothermic processes would be spontaneous and endothermic processes would not. We now must consider both the energy change in a process as well as the entropy change. With two factors, there are four possible outcomes.

1. **Energy is released and entropy increases.** Both favor the process and it will always be spontaneous. An example would be the explosion of dynamite.
2. **Energy is absorbed and entropy decreases.** Both oppose the process and it will never occur spontaneously. Like all processes, however, it can be made to happen if energy is provided. An example would be the growth of a plant or any living thing.

3. **Energy is released and entropy decreases.** This process may or may not be spontaneous, depending on which is greater. An example would be water freezing. It does not occur spontaneously above 0 °C but does below 0 °C.

4. **Energy is absorbed and entropy increases.** This process also may or may not be spontaneous, again depending on the magnitude of the energy and entropy changes. NH_4NO_3 dissolves in water because the energy absorbed is more than offset by the increase in entropy. CaCO_3 does not dissolve in water because the energy required is greater than the increase in entropy. Can you suggest why CaCO_3 behaves differently than NH_4NO_3 ?

F. Polar and Nonpolar Solvents

Not all solutes dissolve in the same solvents. Sugar is very soluble in water but does not dissolve in CCl_4 . Grease will wash off in gasoline but not in water. Determining what solutes will dissolve in which solvents is actually quite simple. The rule we use is “Like Dissolves Like”. Simply put, polar substances will dissolve best in polar solvents and nonpolar substances will dissolve best in nonpolar solvents. Ionic compounds also dissolve in polar solvents, since they have positive and negative charges as do polar solvents.

G. Degrees of Solubility

Even if a substance is soluble in a solvent, there is a limit as to how much will dissolve. For example, the maximum solubility of sugar in water at 20 °C is 204 g of sugar in 100 g of water. A solution which contains the maximum amount of solute is called *saturated*. If the amount of solute is less than the maximum, it is *unsaturated*, and if more than the maximum solute is dissolved, it is *supersaturated*. The solubility of most solutes vary with temperature, and in the case of solids and liquids, solubility normally increases with increasing temperatures.

The solubility of sugar in water increases to 260 g/100 g water at 50 °C. If we took a saturated solution of 204 g/100 g at 20 °C and heated it to 50 °C, what kind of solution would we now have? What if we then added an additional 56 g of sugar? If we take the new solution of 260 g of sugar in 100 g of water at 50 °C and then cool it back down to 20 °C, what should then take place? If you believe that the excess sugar should precipitate out as sugar crystals, you are correct. Sugar solutions are unusual, however, because this precipitation process is very slow, sometimes requiring several days to occur. Thus, the solution actually contains more than the maximum amount of sugar which should be possible to dissolve. This type of solution is called *supersaturated*.

Supersaturated solutions are usually not stable. For example, honey is a supersaturated solution of sugar in water. If stored too long or cooled, the honey will crystallize, forming solid crystals of sugar. Syrup will often exhibit the same behavior.

H. Factors Affecting Solubility

As illustrated with the sugar water, the solubility of most solids in liquids increases at higher temperatures. This has to do with the energy changes involved in these processes. Can you suggest an explanation for why solubility of solids is usually higher at higher temperatures?

In the cases where the solute is a gas, this is no longer true. Gases are always more soluble at lower temperatures. To understand this we must examine the nature of a gas/liquid solution. Oxygen dissolves in water, which is necessary for fish and other aquatic life to survive. When an oxygen molecule strikes the surface of water, it may bond to the water molecules and dissolve. As dissolved oxygen molecules move through the water, they sometimes reach the surface, and if they have sufficient energy, escape back into the atmosphere. If we increase the temperature of the water, the oxygen molecules have more energy and are more likely to escape, reducing the amount of dissolved oxygen. If the water is colder, the oxygen molecules have less energy and are more likely to remain dissolved.

This is another example of dynamic equilibrium. When the rate of gas entering the liquid is equal to the rate of gas leaving, the amount of dissolved gas remains constant. By cooling the water, we reduce the rate of the gas leaving, allowing the amount of gas entering the water to increase the concentration of dissolved gas. Of course, as the amount of the dissolved gas increases, more molecules begin to leave, until we reach a new balance at the higher concentration.

Pressure can also affect the solubility of gases, again due to the dynamic equilibrium process. If we were to double the air pressure above water, there would be twice as many oxygen molecules colliding with the surface of the water. Thus the number of molecules entering the water would double. Over time, as the concentration of dissolved oxygen increases, the rate that they leave the water will increase as well. The two rates will eventually even out, with twice as many molecules entering and leaving, and twice the concentration of oxygen in the water. This is the way in which carbonated beverages are made. Soft drinks have about 4 atm of CO_2 pressure above the liquid, which is about 120 times the amount of CO_2 in the atmosphere. This causes a large amount of CO_2 to dissolve in the beverage. When you open a can of pop, the concentration of CO_2 in the liquid is much greater than that in the atmosphere. Molecules of CO_2 will leave the liquid much faster than they enter, and the carbonation will slowly be lost.

Fortunately, this process is slow, so the carbonation remains long enough for us to enjoy the beverage.

Pressure does not affect the solubility of solids or liquids. Since the molecules in these are already packed together, they cannot be compressed and their concentrations do not change as do gases.

I. Quantitative Measures of Solubility

It is very important to be able to measure the precise concentration of various solutes in solutions. Drugs, for example, must be administered in the appropriate amounts of they may be either ineffective or worse, be hazardous to the patient. Concentrations of solutions are generally represented as the amount of solute divided by the amount of solution.

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}}$$

There are two basic ways to calculate concentrations, percent concentration and molarity. Percent concentration is commonly used in everyday applications. The amount of solute and solution are usually represented by either mass of volume,

$$\% \text{ Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}} \times 100 \%$$

with mass expressed in grams and volume in mL. Three of these combinations are generally used. These are volume/volume (v/v), weight/volume (w/v), and weight/weight (w/w).

The alcohol content of beverages is normally given as a v/v %. This is because both the solute and solution are liquids. A bottle of wine that is 11 % alcohol by volume contains 11 mL of alcohol in every 100 mL of wine. The concentration of an I.V. solution of glucose is 5 % (w/v), meaning that there are 5 g of glucose in every 100 mL of solution. In chemistry, solubility is commonly expressed as a (w/w) percent.

Each of these percentages can be converted from one to the other. Since they all involve units of either grams or mL, it is simply a matter of using density to relate the two. For example, the density of alcohol is 0.7893 g/mL. By converting the volume of the alcohol in our 11 % wine to grams, we can calculate the w/v %.

$$\frac{11 \text{ mL alcohol}}{100 \text{ mL wine}} \times \frac{0.7893 \text{ g alcohol}}{1 \text{ mL alcohol}} \times 100\% = 8.68 \% \text{ alcohol}$$

The w/w % can also be calculated by converting the volume of the wine into grams as well. The density of the wine is 0.9822 g/mL.

$$\frac{11 \text{ mL alcohol}}{100 \text{ mL wine}} \times \frac{0.7893 \text{ g alcohol}}{1 \text{ mL alcohol}} \times \frac{1 \text{ mL wine}}{0.9822 \text{ g wine}} \times 100\% = 8.84 \% \text{ alcohol}$$

Thus, it is very simple to convert between the three types of percent concentrations. All it requires is to change grams into mL or mL into grams.

Chemists commonly measure solution concentrations in *molarity*, which is simply the number of moles of solute divided by the number of liters of solution. The units for molarity are then mole/L, which can be expressed simply with a capital M. Thus a solution which contains 0.55 moles of solute per liter of solutions is simply written as 0.55 M.

How would we determine the molarity of the wine in the previous problem. Since the amounts of both the solute and solution are initially in units of mL, the numerator must be changed to moles and the denominator to liters, as shown below.

$$\frac{11 \text{ mL alcohol}}{100 \text{ mL wine}} \times \frac{0.7893 \text{ g alcohol}}{1 \text{ mL alcohol}} \times \frac{1 \text{ mole alcohol}}{46.0 \text{ g alcohol}} \times \frac{1000 \text{ mL}}{1 \text{ l}} = 1.89 \text{ M}$$

The same approach can be used in reverse. The molarity of dilute HCl used in the laboratory is 6.0 M. Calculate the w/v % of the solution.

$$\frac{6.0 \text{ mole HCl}}{\text{liter}} \times \frac{36.5 \text{ g HCl}}{\text{mole HCl}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 100 \% = 21.9 \% \text{ (w/v)}$$

The w/v % can be further converted to the w/w % using the density of the solution.

$$\frac{21.9 \text{ g HCl}}{100 \text{ mL solution}} \times \frac{1 \text{ mL solution}}{1.1 \text{ g solution}} \times 100\% = 19.9 \% \text{ (w/w)}$$