CONCENTRATIONS

©2008, 2012, 2023 Mark E. Noble

In this Chapter, we take on a different tack and we concentrate on concentration. We'll look at various units which are commonly encountered and, in the next Chapter, we'll talk about a few processes which depend on concentration.

For the most part, molarity has served as our primary solution concentration term ever since we first talked about it back in Chapter 9.

molarity =
$$M = \frac{\text{mol solute}}{\text{L soln}}$$

We will still use molarity in numerous applications but it's not the only unit in all normal and formal applications. We will now look at other concentration units which are used. Some of these received brief mention in prior chapters but we'll broaden that coverage here.

42.1 Molality

Molality. The word is close to the word molarity, so you need to be careful with the distinction. The definition of molality is also close to that of molarity but with a key difference in the denominator. Both molarity and molality involve moles of solute upstairs but they differ in the downstairs: molality is relative to the mass in kg of solvent.

molality =
$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

With molarity, the actual amount of solvent used was not necessarily known. Here's what was said in Chapter 9 for molarity.

Motice that I said you use just enough water to make the final volume 1.0 L. You actually don't have to measure the volume of the solvent by itself. It doesn't matter because the solute can affect the volume anyway. It's very common for the <u>solution</u> volume to be different from the <u>solvent</u> volume. The only thing that matters for molarity is the <u>final</u> volume of the whole solution.

That was molarity. Now for the case of molality, the amount of the <u>solvent only</u> is used and it's used as a mass. Total solution volume does not matter to molality.

Although they are somewhat similar, molarity (M) and molality (m) have advantages over each other in different aspects. For example, molarity (M) is easier for conducting a reaction in solution when a reactant is already in solution; you simply pour out a certain volume of solution and molarity gives you the moles of that reactant. Molality (m) is easier when temperature changes are involved. The reason for this is that solution volumes change with T; thus, the molarity (M) of a solute in a given solution also changes with T. That's a bit of a nuisance if you make a solution at one temperature and use the solution at other temperatures. On the other hand, the value for molality (m) does not change with temperature because mass does not change with T.

The unit of molality is symbolized by lower case m and it's called a molal (" $m\bar{o}$ -lal"). If you have one mole of solute per kg of solvent, then the concentration is one molal.

Here's a simple molality example. Calculate the molality of a solution prepared from 13.1~g lithium sulfate and 200.0~g water.

First, recognize that your starting information is already a concentration term: the unit is g Li_2SO_4 per g H_2O .

Unfortunately, those units aren't the concentration units which you need. For molality, you need mol Li_2SO_4 per kg H_2O . The denominator here is an easy fix.

The numerator is also an easy fix using the molar mass for Li₂SO₄.

$$\frac{13.1 \text{ g Li}_2 \text{SO}_4}{0.2000 \text{ kg H}_2 \text{O}} \quad \times \quad \frac{\text{mol Li}_2 \text{SO}_4}{109.94 \text{ g Li}_2 \text{SO}_4}$$

This gets you what you want.

$$\frac{13.1 \text{ g Li}_2 \text{SO}_4}{0.2000 \text{ kg H}_2 \text{O}} \times \frac{\text{mol Li}_2 \text{SO}_4}{109.94 \text{ g Li}_2 \text{SO}_4} = 0.596 \frac{\text{mol Li}_2 \text{SO}_4}{\text{kg H}_2 \text{O}} = 0.596 \text{ m Li}_2 \text{SO}_4$$

This setup is much like the setup for the sample molarity calculations back in Chapter 9 but now with a different denominator.

Your turn. **Example 1.** Consider a sugar solution which contains 2.84 g sucrose (table sugar), $C_{12}H_{22}O_{11}$, in 100.0 g water. What is the molality of the sugar in the solution?

If you want to check your setup, it's in Section 43.3. It's in the next Chapter because we will use this same setup for an application of molality at that time.

We made brief reference to molality back in Chapter 19 when we were setting up standard conditions for thermodynamics.

For a solute, the standard for concentration is one mole of solute per kg of solvent. For dilute solutions with water as solvent, one kg of solvent is close to one L, so standard concentration is acceptably close to one mole of solute per L of solution. That's molarity. As such, we will use one molar as our unit for standard concentration. (There's a reason for using kg of solvent. It involves another concentration unit, which we'll get to later in Chapter 42.)

Later is now. The standard concentration for a solute in thermodynamics is typically one molal and not one molar. As indicated in the quote, molal and molar can be similar in aqueous solution. At typical temperatures and for approximation to two sigfigs, the density of pure water is 1.0 g/mL or 1.0 kg/L. For dilute solutions, one L of aqueous solution is still close to one kg of solution, although this does not apply at moderate and/or high concentrations. Although there are approximations here, these approximations are commonly made for aqueous solutions because they do not change the thermodynamic values substantially. On the other hand, in more detailed work, you must go with molality. Furthermore, these approximations are OK with aqueous solution but they are not OK with a nonaqueous solvent. For those, molality and molarity are likely to have very different values because most other solvents do not have a density of 1.0 kg/L.

Let me make a final point about molality, one which sets it aside from all other concentration units discussed here. The denominator for molality <u>only involves the solvent</u>. The denominator in all of the other units in this Chapter, including good old molarity, <u>involves the solution as a whole</u>, which means solvent plus solute(s). This is a key distinction for molality. Remember this distinction; it's important.

Let's go on to other units.

42.2 Percents

Percent concentrations come in different forms. These are very common in various sciences and they are also found in commercial applications. I briefly mentioned some percent concentrations back at the star in Chapter 9.

" Concentration can be expressed in many different ways. Rubbing alcohol is commonly 70% C_3H_8O along with some H_2O . That's a concentration. The hydrogen peroxide they sell in stores is 3% H_2O_2 dissolved in H_2O . That's a concentration. Both of these are examples of percent concentration. Percent concentrations are based on mass and/or volume relationships between a solute and the grand sum of all components in the solution.

percent concentration =
$$\frac{\text{mass-or-volume of solute}}{\text{sum of masses-or-volumes of all components}} \times 100\%$$

Later, when we did gas mixtures in Chapter 16, we talked about mole fraction and mole percent.

There's another useful relationship to introduce at this time with respect to mixtures. It's called mole fraction and it's abbreviated x. The term applies to one component which is present in a homogeneous mixture. It's just a ratio of that component's moles to the total moles.

$$x = \text{mole fraction of some component} = \frac{\text{moles of that component}}{\text{sum of moles of all components}}$$

In other words, for some compound A in the sample,

mol fraction of A =
$$x_A = \frac{n_A}{n_{\text{total}}}$$

Mole fraction can be expressed as a decimal or as a percent. For percent, just place " \times 100%" after the equations above. The solution can be a gas solution or it can be a liquid solution; it doesn't matter. Right now we are doing gases, so that's what we'll stick with here. We'll do liquids later in Chapter 42. 9

Later is now.

Let's summarize all of the percent terms so far.

$$mass percent = \frac{mass of solute}{sum of masses of all components} \times 100\%$$

$$volume percent = \frac{volume of solute}{sum of volumes of all components} \times 100\%$$

$$mole percent = \frac{moles of solute}{sum of moles of all components} \times 100\%$$

Notice that all denominators for the percents are for the total of all components, which includes solutes plus solvent. The denominator includes everything. The numerator includes only the one component of interest.

There's a subtle but important point to be made here although it only affects volume percent. The denominator is the sum of the volumes of all components PRIOR to mixing. This is important because volumes are not additive for different substances. For example, as quoted above, rubbing alcohol is 70% C_3H_8O and that is a volume percent; it's also 30% H_2O . If you mix 70. mL of C_3H_8O with 30. mL of H_2O , you get 97 mL of 70.% H_2O with 30. mL of 90 and 100 mL of solution. The individual volumes of H_2O and H_2O don't add numerically for the solution, and that's typical. In general, the final volume of a solution can be less than or greater than the sum of the volumes of the components prior to mixing. It just depends on the compounds involved. Volumes are NOT additive due to the way that different molecules of different sizes and of different interactions congregate around each other in different solutions. On the other hand, masses and moles ARE additive, so this business is not an issue with mass percent or mole percent. In other words, the sum of the masses before and after mixing is the same; likewise, the sum of the moles before and after mixing is the same.

Mass percent is often abbreviated as %m/m, for mass over mass. Sometimes you'll see it as %w/w, for weight over weight, and it really doesn't matter which is used. Volume percent is often abbreviated as %v/v, for volume over volume. Sometimes a label will just say "percent by mass", "percent by weight" or "percent by volume", respectively. Sometimes a label won't say either way, so then you're not even sure. There are even more variations to these units but that's more than we need here. For mole percent, the abbreviation is simply mol%. This can still be expressed as mole fraction (x) instead of percent, as was done for gas mixtures.

Mass percent and mole percent are fairly general for any phase of solute. Volume percent usually involves liquid phase solutes; this one is common in commerce such as rubbing alcohol and even alcohol content in beverages.

A mass percent problem was done in Chapter 15 as the first example for titration (Example 5); it was for acetic acid in vinegar. Here's how we ended that problem.

$$\frac{\text{mass of CH}_3\text{CO}_2\text{H}}{\text{masses of all components}} \times 100\% = \frac{0.1775 \text{ g}}{4.00 \text{ g}} \times 100\% = 4.44\%$$

This calculation tells us that acetic acid is 4.44% by mass in that sample of vinegar. **

That was our first application of %m/m.

Let's do a new calculation with percent. We did the molality problem earlier for a solution of Li_2SO_4 ; now we'll find the mass percent of Li_2SO_4 in that solution.

For this, you want the mass of the item of interest in the numerator; here, it's the 13.1 g Li_2SO_4 . You want the total solution mass in the denominator; here, it's the 13.1 g Li_2SO_4 plus the 200.0 g H_2O for a total of 213.1 g solution.

mass percent =
$$\frac{13.1 \text{ g}}{213.1 \text{ q}} \times 100\%$$

Plug in, punch out, round off; you get 6.15% (or 6.15%m/m) Li_2SO_4 for the answer.

Volume percent and mole percent are pretty much the same calculation as for mass percent, although mole percent can be a bit more involved. Just be sure to get the correct units in the numerator and denominator. Here's an example of a mole percent problem. Given the solution of 13.1 g Li_2SO_4 per 200.0 g H_2O , calculate the mole percent of lithium sulfate in the solution.

You'll need mol Li_2SO_4 in the numerator; we did that upstairs for molality. For the denominator, you need total moles which is mol Li_2SO_4 plus mol H_2O . Here's the whole setup.

mole percent
$$\text{Li}_2\text{SO}_4 = \frac{\frac{13.1 \text{ g}}{109.94 \text{ g/mol}}}{\frac{13.1 \text{ g}}{109.94 \text{ g/mol}} + \frac{200.0 \text{ g}}{18.02 \text{ g/mol}}} \times 100\%$$

By our method for sigfigs, the overall denominator has mixed arithmetic operations and that can get confusing. Here's how that is handled. Do both divisions in the denominator and then round each; then add them together and round off the sum; then divide into the numerator and round off for the final answer. This is one of the more tedious sigfig manipulations and your instructor may choose for you to execute the whole thing and then round. Go with what s/he says. For this particular problem, it doesn't matter: the final answer is 1.06% (or 1.06 mol%) either way. Work this through and check it out.

Your turn. **Example 2.** Consider the sugar water from earlier: $2.84 \text{ g C}_{12}H_{22}O_{11}$ in 100.0 g H_2O . Calculate the %m/m and the mol% of sucrose in the solution.

The answers are 2.76%m/m and 0.149 mol%. Be sure you can get these numbers.

42.3 pp terms

By the standard definition of percent, all percent concentration terms are parts-per-hundred. For example, in the %m/m example above for Li_2SO_4 , the solution is 6.15% Li_2SO_4 ; this means the concentration by mass is 6.15 parts of solute per hundred parts of solution. We can also say the concentration is 6.15 g Li_2SO_4 per hundred grams solution.

While percents are parts-per-hundred or pph, there are several other "parts-per" terms. Two of the most common pp terms are ppm and ppb, which stand for parts-per-million and parts-per-billion. There's also a ppt, but this one gets confusing because it can mean parts-per-thousand or parts-per-trillion. I'll

just stick with ppm and ppb here. Although you can do pp volume (v/v) ratios, I'll only work with pp mass (m/m) ratios for our coverage.

The pp terms are set up the same way as for percent but with a different multiplier on the end.

parts-per-million =
$$\frac{\text{mass of solute}}{\text{total mass of soln}} \times 10^6 \text{ ppm}$$

parts-per-billion = $\frac{\text{mass of solute}}{\text{total mass of soln}} \times 10^9 \text{ ppb}$

These ppm and ppb terms are commonly used for trace levels of solutes. One ppm is one gram of solute per million grams of solution. One ppb is one gram of solute per billion grams of solution. Those are very dilute ranges; we can put this on a more familiar scale by the following equivalent relationships.

$$ppm = \frac{mg \text{ solute}}{kg \text{ soln}} \qquad ppb = \frac{\mu g \text{ solute}}{kg \text{ soln}}$$

Although these are very small concentrations, they can be still very important. One example is your tap water: it will have many things dissolved in it at ppm and ppb levels. Many municipal water companies make this information available to their customers and you can check yours out some time. For example, there may be 14 ppm Mg^{2+} and 62 ppm Ca^{2+} and 5 ppb Pb^{2+} and who knows what else. Of course, there are anions also in tap water, such as 6 ppm NO_3^- and 4 ppm F^- and who knows what else. There are also molecular compounds, such as 18 ppb of $CHCl_3$ and 2 ppm of $CINH_2$ and who knows what else.

Notice that some amounts are given for one particular ion. That is not unusual in these applications. The amount cited is for the total amount of that ion in whatever ionic compounds happen to be present in solution.

So how much of what do you actually drink? Consider $CINH_2$ at 2.0 ppm in your drinking water. Let's say you have a glass of 227 g (8.00 oz) water. What mass of $CINH_2$ is present in that glass of water?

Take the above ppm equation and set it up for the problem.

parts-per-million = 2.0 ppm =
$$\frac{??? \text{ g}}{227 \text{ g}} \times 10^6 \text{ ppm}$$

Re-arrange; the ppm units cancel.

$$\frac{2.0 \times 227 \,\mathrm{g}}{10^6} = ??? \,\mathrm{g}$$

Solve. You get 0.00045 g (or 0.45 mg) for the $CINH_2$. That's how much you would drink in that glass of water. So how did that stuff get into your water? They may have put it there deliberately as a microbicide. $CINH_2$ is chloramine, which I mentioned in Section 6.4 within the context of the hydrazine example back then. Most solutes in tap water are present from the water source itself although some are not. Chloramine (or chlorine in many cases) is a deliberate additive, and so also are a fluoride compound and acid/base regulators. Copper and lead ions are also present in tap water but those come primarily from the plumbing itself, namely from the pipes and solder. Modern plumbing standards do not use lead solder anymore due to the problems with lead toxicity. So how much lead do you think you drink?

Example 3. If your tap water has 4.7 ppb Pb^{2+} , then how many μg of Pb^{2+} ions do you drink in 227 g (8.00 oz) of tap water?

......

The answer is $1.1 \mu g$. Time to get the lead out?

Interestingly, many compounds considered "insoluble" will often saturate at these very small amounts. Our very first insoluble example back in Chapter 10, $BaSO_4$, was stated to have a solubility of 0.00022 g per 100 mL of H_2O . How many ppm is this? For this problem, use 1.00 g/mL for the density of water; this gives a solution mass of 100. g solution.

parts-per-million =
$$\frac{0.00022 \text{ g}}{100. \text{ g}} \times 10^6 \text{ ppm}$$

That comes to 2.2 ppm for $BaSO_4(aq)$ at saturation.

The parts-per-billion cases are more dilute by 10^3 than are the parts-per-million cases. In other words, one ppm equals one thousand ppb. Thus, a saturated solution of BaSO₄ contains 2,200 ppb of BaSO₄.

Although these numbers are small, they can be very important. Many insolubles constitute environmental hazards, so these concentrations are significant even if "insoluble". If there's an oil or gasoline spill into a body of water, you can trap and skim the material floating on the surface but traces of it will dissolve into the water. Let's consider our toilet bowl sanitizer from Chapter 36, p-dichlorobenzene, $C_6H_4Cl_2$. Those deodorizers eventually disappear, partly due to sublimation and partly due to trace dissolving. Let's consider the latter for now. $C_6H_4Cl_2$ is insoluble in water, to the tune of 83 ppm. For some city or region, consider 1.0×10^4 (10,000) flushes of 1.0 gallon each from toilets with $C_6H_4Cl_2$ as a sanitizer; in metric numbers, this corresponds to a total mass of 3.8×10^7 g for the combined flushes. If the water was saturated each time with $C_6H_4Cl_2$, how many grams of $C_6H_4Cl_2$ are going down those toilets and eventually into the waterways?

To solve this, set up the ppm expression.

83 ppm =
$$\frac{??? g}{3.8 \times 10^7 g} \times 10^6 ppm$$

Re-arrange and solve. It comes to $3,200 \text{ g C}_6\text{H}_4\text{Cl}_2$ going down the drain. That's not such a small amount, is it?

When dealing with ppm and ppb for aqueous solutions, there are two shortcuts commonly taken. The first shortcut deals with the masses in solution. In typical ppm and ppb ranges, the solute mass has no significant impact on the solution mass to the correct sigfigs. Let me illustrate this. For saturated $BaSO_4(aq)$, you have 0.00022 g of $BaSO_4$ in 100. g total solution. If the solution only contains $BaSO_4$ and H_2O , then what is the total solution mass?

Mass of H_2O :100. gMass of $BaSO_4$:0.00022 gTotal solution mass:100. g

This shows that, to the correct sigfigs, the solute is not a significant contributor to the solution mass. Thus, for small ppm and ppb ranges, we can take the mass of the solution to be the mass of the solvent. Now, keep in mind that this is for small ppm and ppb ranges. In some applications, you can find solutes listed as 20,000 ppm or so. In those extreme cases, then the solute mass can become significant to the total mass. But that's not the range for our shortcut here.

A second shortcut for aqueous solutions is to bring in the density approximation for water, noted in the very beginning of this Chapter.

At typical temperatures and for approximation to two sigfigs, the density of pure water is 1.0 g/mL or 1.0 kg/L. For dilute solutions, one L of aqueous solution is still close to one kg of solution, although this does not apply at moderate and/or high concentrations.

We combine this with the relationships upstairs,

$$ppm = \frac{mg \text{ solute}}{kg \text{ soln}} \qquad ppb = \frac{\mu g \text{ solute}}{kg \text{ soln}}$$

and, together, these provide the following relationships for water as solvent.

$$ppm = \frac{mg \text{ solute}}{L \text{ soln}} \qquad ppb = \frac{\mu g \text{ solute}}{L \text{ soln}}$$

These relationships are useful for putting things into a nicely workable perspective. For example, if your tap water has 18 ppb CHCl₃ (chloroform), then you consume 18 μ g of CHCl₃ in a liter of water.

Alright, we've completed the introduction to new concentration units. Let's look at some interconversions between various units.

42.4 Concentration conversions

Conversions among the various concentration units can be straightforward or they can be a royal pain. It just depends on which ones are involved. A number of illustrations were contained in the definitions and coverage above. We'll show some more conversions here. To do these, you need to keep in mind what each concentration unit is. You need to keep in mind that each has a numerator and a denominator, and you need to be able to convert among those. Sometimes, density can enter into the picture.

Let's get to it.

Hydrochloric acid is commonly available in hardware and home improvement stores under its commercial name of muriatic acid. A typical concentration is 20%. Let's assume only HCl and H_2O are present and that the solution is 20.0%m/m of HCl with density d=1.098 g/mL. Calculate (A.) the molarity, (B.) the molality, and (C.) the mole percent of the acid.

A. Molarity

OK, what exactly do you need?

You need $\frac{\text{mol HCl}}{\text{L soln}}$

Do you have mol HCl or L soln in the given information? No. For the sake of the problem, however, we can choose to work with one L of solution as a sample size.

How do you determine mol HCl in that one L? We can go through mass. Since we chose one L sample size and we know d=1.098 g/mL, then we can say there are 1098 g of solution per L solution.

1,098 g soln L soln

Now, the important connection lies in the mass percent, 20.0%m/m. This says that there are 20.0 g of HCl for exactly 100 g solution. This is a conversion factor.

 $\frac{1,098 \text{ g soln}}{\text{L soln}} \times \frac{20.0 \text{ g HCl}}{100 \text{ g soln}}$

This cancels g soln and leaves the numerator at g HCI; it is a simple task to take that to mol HCI.

 $\frac{\text{1,098 g soln}}{\text{L soln}} \hspace{0.2cm} \times \hspace{0.2cm} \frac{\text{20.0 g HCl}}{\text{100 g soln}} \hspace{0.2cm} \times \hspace{0.2cm} \frac{\text{mol HCl}}{\text{36.46 g HCl}}$

Now, the remaining units are mol HCl/L soln, which is what we want. That gives 6.02 M. Done with Part A.

Let me just make a quick note about sigfigs and percents using this example. 20.0%m/m means 20.0 g (three sigfigs) per 100 g (exact number). The 100 is part of the definition of percent, so it is an exact number and does not enter into round-off decisions.

B. Molality

OK, what exactly do you need?

You need $\frac{\text{mol HCl}}{\text{kg H}_2\text{O}}$

Since molality has only the solvent in the denominator, then this is a simple ratio of the two components which are present. Do you have mol HCl or kg $\rm H_2O$ in the given information? No, not directly, but we do have the 20.0%m/m term. The 20.0%m/m means 20.0 g HCl per 100 g solution. So, out of exactly 100 g of solution, 20.0 g are HCl.

What's the rest? Since we are told that only HCl and H_2O are present, the rest is H_2O . That means that, in exactly 100 g solution, if there are 20.0 g HCl then there are 80.0 g H_2O . We can now say that there are 20.0 g HCl per 80.0 g H_2O . This now gives us a ratio of the two components, but not quite the correct units for molality. The denominator is a simple matter to change

and the numerator just needs a molar mass conversion.

$$\frac{20.0 \text{ g HCl}}{0.0800 \text{ kg H}_2\text{O}} \times \frac{\text{mol HCl}}{36.46 \text{ g HCl}}$$

That gives molality: 6.86 m. Done with Part B.

C. Mole Percent

OK, what exactly do you need?

You need

Do you have mol HCl or total mol in the given information? Once again, it's in there but you have to dig it out. Let's look at 20.0%m/m again.

$$\frac{20.0 \text{ g HCl}}{100 \text{ g soln}}$$

Break the denominator into its separate components.

Now, take each mass to moles.

That will give you mole fraction; you need to add the " \times 100%" part in the end for mole percent. Plug, chug, and you get 11.0 mol%. (Watch the sigfigs. The sum of moles in the overall denominator comes to 4.99 mol.)

OK, we're done with these.

As you can see, some of these can be a bit tricky, but break them down as needed. It may take a while to get used to interconversion problems, but that takes practice. You can try a different one.

Example 4. Consider again the sucrose solution from earlier in the Chapter, 2.84 g $C_{12}H_{22}O_{11}$ in 100.0 g H_2O , for which the mass percent was found to be 2.76%m/m. If the density of the solution is

1.010 g/mL, what is the molarity of the sucrose?

The answer is 0.0814 M. If you can't get this, look at Part A for HCl above.

Problems

- A municipal water company reports 1.1 ppm NO₃⁻ in its tap water. If the density of the tap water is 1.0 g/mL, how many moles of NO₃⁻ are present in 100. L of this tap water?
- 2. A solution contains 9.19 g water (d = 0.997 g/mL) and 19.6 g CH₃OH (d = 0.787 g/mL).
 - a. What is the mass percent of water in the solution?

- b. What is the volume percent of water in the solution?
- 3. A solution is made from 40.0 g C_6H_6 , 26.4 g C_5H_{12} and 49.1 g C_2Cl_6 . What is the mole percent of each component in the solution?
- 4. 250. L of a solution with density = 0.862 g/mL were found to be contaminated with 14.3 ppm H₂S. How many grams of H₂S are present in the solution?
- 5. A solution is composed of 6.03 g disulfur dichloride in 50.0 g carbon tetrachloride. What is the molality of the disulfur dichloride in this solution?
- 6. Consider an aqueous ammonia solution which is 8.0% m/m NH_3 and which has a density of 0.965 g/mL.
 - a. What is the molarity of the ammonia?
 - b. What is the molality of the ammonia?
 - c. What is the mole percent of ammonia?
- 7. Consider an aqueous solution of 0.305 m KBr which has a density of 1.026 g/mL.
 - a. What is the mole percent of KBr?
 - b. What is the mass percent of KBr?
 - c. What is the molarity of KBr? (Clue: You can use the answer from Part b.)