Scientific Soapmaking

The Chemistry of Handcrafted Soap

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Introduction

Chemistry is not widely viewed with admiration by the general public. Astronomy has the stars, twinkling suns of unimaginably distant planets from which, perhaps, alien stargazers peer into the night sky and ponder our existence as we ponder theirs. Biology has ornate birds and fragrant flowers and glow-in-the-dark creatures of the ocean depths. Paleontology has myriad monsters both large and small which have emerged, thrived, and vanished over eons which dwarf our conceptions of eternity. Archeology has mummies, skeletons, lost tombs, splendid treasures of ancient civlizations, and the romance of dust left undisturbed by the passage of time. These are the sciences which inspire fiction. By contrast, there is no quicker end to a coctail-party conversation than to confess a passing acquaintance with the Periodic Table. It is no wonder, then, that students shun chemistry in favor of her more personable sisters.

To The Student: Many of the handcrafted soapmakers I have met confess that they wish they had paid more attention to high school chemistry. The arcane formulas and exotic glassware, the undecipherable names and brown glass bottles of stink seemed boring, dangerous, or irrelevant at the time. But these folks now find themselves determined to learn concepts they vaguely remember resisting in their youth. If you are such a person, I have written this book for you. In my mind, it is the textbook for the chemistry course you now wish you had taken in high school or college. I hope you enjoy it.

To The Teacher: You can lead a horse to water but you can't make her drink. We chemistry teachers live this proverb every day, leading reluctant students to water for which they have not yet acquired at taste. If twenty years of teaching has taught me anything it is that I cannot teach anyone anything if they don't want to know it. Much of my time and effort, then, is spent in motivating students, in helping them to understand that some of the things I want to teach them are worth knowing. Student who are motivated by a desire to make soap will find that every bit of chemical theory and practice in this book advances them toward that goal. If we teachers can simply convince students that soap is as interesting as it is useful, they will become thirsty for the water we have to offer.

Chapter 1. Weights and Measures

The cook and the chemist place different requirements on their balances. The cook needs to know whether the turkey weighs 10 or 12 pounds; the chemists needs to know whether the sample of diethyl biglongnameate weighs 126 or 127 milligrams. The soapmaker lives somewhere in between. In order to use the balance to best advantage, the soapmaker needs to become familiar with two terms which specify the capabilities of a balance: capacity and readability. The *capacity* of a balance is the largest weight it can accurately register. A bathroom scale may have a capacity of several hundred pounds, a kitchen scale may hold a few pounds, and a jeweler's balance may buckle under the weight of a few ounces. The *readability* of a balance is the smallest increment it can display. The bathroom scale reads to the nearest pound, the kitchen scale to a tenth of an ounce, and the jeweler's balance to a thousandth of an ounce.

Accuracy and Precision

Most people use the terms *accuracy* and *precision* interchangeably, but there is a subtle difference between them. Consider the weight of a hypothetical person visiting a friend. He goes to the bathroom and can't resist the temptation to step on the scale, which registers 185 pounds. "That's odd," he thinks, "I didn't think I weighed that much." When he gets home he weighs himself and finds his weight to be 173 pounds. Which weight should he believe? Unless he has a way of callibrating his scale he has no good reason to believe one over the other. But let's imagine that he has an item which is certified to weigh exactly 100 pounds. He puts it on his scale and adusts a screw on the side of the scale until it reads 100 pounds. He then reweighs himself and finds his weight to be 180 pounds. We would say that the weight of 180 pounds is *accurate*. The first weight,185 pounds, is 5 pounds higher than the actual weight and we can express this as a *relative error* of

An equation

We are interested only in the size of the error so we round it off to +3%. The second weight, 173 pounds, is 7 pounds lower than the actual weight and the relative error in this measurment is -4%.

Now suppose that our hypothetical person, still on the scale, picks up a toothbrush. The scale continues to read 180 pounds. Why? Because the toothbrush weighs less than a pound. Now it is certainly true that he weighs more with the toothbrush than without, but the scale is unable to register the difference. Even if the callibrated scale reads 180 pounds, all we can really say is that his weight is higher than 179 pounds and less than 181 pounds. We would say that the scale weighs to within 1 pound of the actual weight. We can also say that the scale is *precise* to within ±1 pound. This translates into a *relative precision* of ±0.5 percent or ±5 *parts per thousand.*[1]

Units

While American cooks are most familiar with units of pounds and ounces, there are good reasons for the soapmaker to prefer units of grams. You might think that a chemist would have philosophical reasons for preferring the metric system, but when it comes to making soap my preference is determined on strictly practical grounds. Consider a typical kitchen scale, the MyWeigh KD-600, with a capacity of 13 pounds and a readability of 0.1 ounce. Suppose my soap recipe calls for 18 ounces of lye. I weigh out "exactly" 18.0 ounces, but even if the scale is accurately calibrated, I do not know the precise weight. All I know is that the lye weighs more than 17.9 ounces and less than 18.1 ounces. The oil might weigh 17.95 or 18.04 ounces and I wouldn't know it because the balance does not read that extra digit. With a readability of 0.1 ounce and a weight of 18 ounces, the relative precision in the weight amounts to 0.6%, or 6 parts per thousand (ppt). But if we switch the scale over to metric mode, the capacity is 6000 grams and the readability is 1 gram. The same soap recipe would call for 511 grams of lye and with this mode I know the actual weight is somewhere between 510 and 512 grams. With a readability of 1 gram and a weight of 511 grams, the relative precision in the weight amounts to 0.2%, or 2 ppt. Bear in mind that we are using the same scale for both measurements. We may even be weighing the exact same object. But because a gram is smaller than a tenth of an ounce, this scale will register more precise weights in metric mode than in English mode.

Weighing Carefully

In this book you are going to be weighing smaller amounts of materials than you may be used to and you need to be able to weigh them accurately and precisely. The method I'm going to teach you will seem needlessly complicated at first, but it will allow you to weigh soapmaking materials to within 2 ppt of the target weight. Let's suppose that you need to weigh 26.80 grams of water. Your first instinct would be to put a cup on the balance, note its weight, say 10.24 g, and pour water into the cup until the balance reads 10.24 + 26.80, or 37.04 g. But what if you got a little carried away and the weight went to 38.77 g? Well, you'd probably use a medicine dropper to remove some of the water. Everything would be fine as long as there was nothing in the cup to begin with. But if the cup had something in it, salt or sugar or sodium hydroxide, you'd be sunk because the medicine dropper would be removing salt or sugar or sodium hydroxide as well as water. By changing the procedure just a little bit, we can weigh 26.80 g of water into a glass jar quickly and accurately.

Weighing a Liquid

1. *Gather your materials:*
   - A balance with capacity of at least 50 g and readability of at least 0.01 g
   - Goggles or glasses
   - Distilled water (best) or tap water (OK)
   - A medicine dropper, or *pipette*
   - A glass jar (A)
   - A plastic cups (B)
   - Your soapmaking notebook and a pen
2. *Arrange your workspace:* Note that glass jar (A) may exceed the capacity of the balance, so putting it on the balance is not an option. Instead, place the plastic cup (B) onto the balance and glass jar (A)

next to the balance. Put on your safety glasses. OK, it seems silly when you are just weight water, but you should get in the habit of doing so.

3. *Tare the balance:* The plastic cup (B) has a weight and you might be tempted to write it down so you can add 26.80 to it. No need! The balance has a button on it marked *Zero* or *Tare*. If your balance has both buttons, press the *Tare* button. The balance will read 0.00 g.
4. *Fill the cup:* Pour water into cup (B) until it the balance reads *more than* 27 g. It might be 32.74 or 45.23 or 52.71 g, it doesn't matter a bit as long as cup (B) has more than enough water in it.
5. *Tare the balance:* Press the *Tare* button and the balance once again reads 0.00 g.
6. *Weigh from the balance:* Use the medicine dropper, or *pipette*, to suck up a little water from cup (B) and squirt it into glass jar (A). The balance now reads a negative number, say -3.75 g. This is the amount of water you have removed from cup (B). Use the pipette to transfer a second and a third batch of water from (B) to (A). Eventually you will get to the last pipette-full and the balance will go past your target weight. Suppose the balance now reads -27.25 g. Stop! You have passed your target but the water in the pipette is still pure water—it hasn't been anywhere yet. Return water from the pipette, drop by drop, *back into cup (B)* until the balance reads as close to -26.80 as possible. When you are satisfied, deliver the water remaining in the pipette into glass jar (A). Now all of the water is either in cup (B), jar (A), or in the pipette. Since you know the weight of the water in the cup and the pipette is as close to empty as you can make it, the weight of water in the jar must be equal and opposite to the reading on the balance. Record in your notebook the weight of the water that you delivered to the jar.

How close were you able to get to your target of 26.80 g? I know that it's hard to hit the target exactly. Let's suppose that your actual weight was 26.85 g. You have made an error of 0.05 in 26.80. We can express this as a relative error of

An equation

We are only interested in the size of the relative error, so we round off to one digit and express it as a percentage:

An equation

More usually, however, we express relative error in *parts per thousand*, or *ppt:*

An equation

Weighing to a couple of parts per thousand is a reasonable goal for a soapmaker. Try weighing 26.80 g of water a few more times until you can do it quickly, accurately, and precisely. For each trial record the actual weight of water delivered and compute the relative error in ppt. Now try weighing 75.77 g of water. How does your relative error for this larger target compare to that for the smaller target?

What is the precision of this measurement? When the balance reads 26.85 g, it is telling you that the weight is more than 26.84 and less than 26.86 g. The uncertainty is ±0.01 in 26.85 and the relative precision is ±0.04 percent or ±0.4 ppt.

Weighing a Solid

Weighing a solid is not much different from weighing a liquid. Modify the procedure of the Section called *Weighing a Liquid*, using a stainless steel spoon instead of a pipette. When you overshoot the target, just sprinkle a little of the solid from the spoon back into cup (B). Here is the modified procedure for weighing 13.40 g of salt into a glass jar.

1. *Gather your materials:*
   - A balance with capacity of at least 50 g and readability of at least 0.01 g
   - Goggles or glasses
   - Table salt (sodium chloride)
   - A stainless steel teaspoon or *spatula*
   - A glass jar cup (A)
   - A plastic cups (B)
   - Your soapmaking notebook and a pen
2. *Arrange your workspace:* Place the plastic cup (B) onto the balance and glass jar (A) next to the balance. Put on your safety glasses. Don’t make me tell you again.
3. *Tare the balance:* Press the *Tare* button. The balance will read 0.00 g.
4. *Fill the cup:* Pour salt into cup (B) until it the balance reads *more than* 14 g.
5. *Tare the balance:* Press the tare*Tare* button and the balance once again reads 0.00 g.
6. *Weigh from the balance:* Use the teaspoon or *spatula* to pick up a little salt and dump it into glass jar (A). The balance now reads a negative number, say -2.23 g. Continue transferring salt from cup (B) to cup (A) until you get to the spoonful and the balance will go past your target weight. Suppose the balance now reads -14.27 g. Stop! You have passed your target but the salt in the spoon is still pure salt--it hasn’t been anywhere yet. Return salt from the spoon *back into cup (B)* until the balance reads as close to your target weight as possible. When you are satisfied, deliver the salt remaining in the spoon into glass jar (A). Record in your notebook the weight of the salt you delivered into glass jar (A) and compute the relative error in ppt.

As a final exercise, try weighing 26.80 grams of water into a glass jar and 13.40 grams of salt into the same glass jar. Note that you will need one plastic cup (B) to hold the water and another (C) to hold the salt. Write out a procedure in your notebook, record the actual weights, and compute the relative error in ppt for each measurement.

Batch Size

The most critical measurement in soapmaking is the weight of the sodium hydroxide used to make a batch of soap. The general rule is that if an object weighs more than 1000 times the readability of a callibrated balance, we can be confident that the displayed weight is within ± 1 ppt of the actual value. A balance with a readability of 0.01 g, for example, may be used to precisely weigh as little as 10 g of sodium hydroxide. Since a typical soap requires about seven times as much oil as sodium hydroxide and twice as much water as sodium hydroxide, we could use this balance to produce as little as 100 g of soap,[2] about the weight of a typical bar and a convenient size for an experimental sample. We could produce an even smaller bar if we were satisfied with a relative precision of ± 2 ppt, a reasonable target for soapmaking. Table 1-1 shows the readability you need for soap batches of different sizes. Note that if you make a batch smaller than the minimum, your precision will be poorer than ± 2 ppt; if you make a batch larger than the minimum your precision will be better than ± 2 ppt.

Table 1-1. Balances for Soapmaking

Readability	Minimum Soap Batch for $\pm$ 2 ppt Precision
0.01 g	50 g (half bar)
0.1 g	500 g (5 bars)
1 g	5000 g (50 bars)
0.01 kg	50 kg (500 bars)
0.05 kg	250 kg (2500 bars)

Notes

1. Think of a percent as one part per hundred. A part per thousand is ten times smaller than a percent. 1 ppt = 0.1%; 1% = 10 ppt.
2. 100 g of raw soap is produced from 70 g of oil, 20 g of water, and 10 g of lye.

Chapter 2. Residual Alkali

There are two problems with the residual alkali tests described so far. First, they are qualitative tests, that is, they give a thumbs-up or thumbs-down determination of soap alkalinity, but they provide no means of comparing soaps of differing compositions or ages. Second, the soap itself interferes with all of the previous tests; it has a bitter taste of its own and interacts with indicators, masking the effect of residual caustic soda. The test described here, while more time-consuming than the others, yields a quantitative measure of the residual alkali content, that is, it assigns a numerical value which may be tracked as the soap ages. The residual alkali content may also be compared from one soap to another. Thus the residual alkali titration provides a powerful tool for answering questions about soap formulation and processing.

Materials

- A 10 g sample of the soap to be tested
- 200 g of distilled water (best) or tap water (OK)
- Two microwave-safe glass jars and a plastic spoon
- A microwave oven and oven mits
- 80 g of table salt
- A coffee filter and rubber band
- A toothpick
- Phenolphthalein solution
- A bottle of household vinegar
- A medicine dropper

1. *Dissolve the soap:* Tare one of the jars and add 200 g of water to it. *Weigh carefully* 10 g of soap and add it to the water in the jar. Microwave on high until the water begins to boil, but do not allow it to boil over. Set your microwave oven[1] to its lowest setting and continue heating for another 5 minutes or until the soap is completely dissolved. Pay careful attention and be prepared to stop heating if the water threatens to boil over. The soap solution will be *hot!* Allow it to rest in the oven for a minute before removing it with a pair of oven mits. Then stir it with a plastic spoon until it is completely dissolved.
2. *Add the salt:* Add 80 g of table salt to the soap solution. The solution will turn milky as the soap curdles and separates from the solution. Stir with the plastic spoon and then allow the solution to stand and cool for 10 minutes. The soap curd will rise to the top, the excess salt will sink to the bottom, leaving a clear solution in the middle. This solution contains the residual alkali to be tested.
3. *Filter the solution:* Place a coffee filter over the mouth of the jar and use a rubber band to seal it to the mouth. Carefully pour the liquid from the first jar into the second, leaving the soap curd and salt behind. If the filtration slows, you may use a toothpick to poke a hole in the filter paper near the top. This will allow air into the jar and speed the filtration. The water collecting in the second jar should be clear. If it is cloudy, you probably filtered too soon. Pour the water back into the first jar, let it settle, and filter again. The filtered solution contains most of the residual alkali and very little of the soap.
4. *Titrate the solution:* Add a drop or two of phenolphthalein solution to the solution; it should turn pink. Fill your medicine dropper with vinegar, add a drop of vinegar to the solution, and stir it with the spoon. Continue to add vinegar, counting the drops and stirring after each drop. The pink color will fade and then disappear entirely at the *endpoint.* If you are unsure whether the pink color is

gone, add another drop of vinegar and watch for a further color change. If the color fades, you were not at the endpoint but you may be now.

5. *Record the result:* The number of drops of vinegar required to neutralize the residual alkali in a 10 g sample of soap is a reliable measure of the soap's alkalinity. Record this number in your notebook in the entry for the soap being analyzed. Household vinegar is approximately 5% acetic acid in water, but its concentration may vary considerably from one bottle to the next. For this reason, you should label the vinegar with the number of drops required to neutralize a mild and fully-cured soap. If you squirrel this vinegar away and use it only for residual alkali titrations, it will last a very long time and you will be able to compare the alkalinity of soaps made months, and perhaps years apart.

So how many drops should it take to titrate a mild and fully-cured soap? The specification given in (Give Reference) is that soap should have a residual alkali content of less than 0.1%, that is, 1 g of alkali in 1000 g of of soap. We can convert this to drops of vinegar by the following calculation: NEEDS WORK

Figure 2-1. LATEX

Made with gnuplot

The titration just described takes between 30 and 40 minutes to perform and so you probably won't use it as a routine test for every batch of soap you make. But if you are developing a new soap formula this test will allow you to quantitatively evaluate the results. In the next chapter we shall vary the *alkali ratio* in order to determine the effective saponification value.

Notes

1. You may dissolve your soap using a saucepan on a conventional range. Just be careful that it doesn't boil over.

Chapter 3. Saponification Value

The determination of SAP

Glossary

Accuracy

The difference between a measured value and either the true value or the target value. If your goal is to weigh out 173 g of oil and you actually weigh out 171 g of oil, you are accurate to within 2 g. If all of the digits of the measured value are correct, the measurement is said to be accurate.

Acid

A material which contributes H^+ to an aqueous solution. Acids taste sour and neutralize alkalis. Examples include acetic acid, the acid present in vinegar, and oleic acid, the major fatty acid in olive oil.

Alkali

A material which contributes OH^- to an aqueous solution. Alkalis taste bitter and neutralize acids. Examples include sodium hydroxide, the alkali used to make solid soap, and potassium hydroxide, the alkali used to make liquid soap. *Alkali* and *base* are synonyms.

Alkali Ratio

The number of grams of alkali used to saponify 1000 grams of oil. In practice, the alkali ratio should not exceed the saponification value.

Base

A material which contributes OH^- to an aqueous solution. Bases taste bitter and neutralize acids. Examples include sodium hydroxide, the alkali used to make solid soap, and potassium hydroxide, the alkali used to make liquid soap. *Base* and *alkali* are synonyms.

Capacity

The maximum weight that a balance can register.

Lye

An alkali, or, more commonly, and alkaline solution. Examples include sodium hydroxide, the alkali used to make solid soap, and potassium hydroxide, the alkali used to make liquid soap.

Lye Discount

Official Website

CavemanChemistry.com (http://cavemanchemistry.com)

Parts per Thousand (ppt)

The number of parts of one thing in 1000 parts of something else. For example, when we say that a soap contains 1 ppt residual alkali, we mean that there is 1 gram of alkali in 1000 grams of soap. 1 ppt is 0.1%.

Percent

The number of parts of one thing in 100 parts of something else. For example, when we say that an oil blend is 25% olive oil by weight, we mean that there are 25 grams of olive oil in 100 grams of mixed oil. 1% is 10 ppt.

Precision

The magnitude of the last digit used to express a measured value. When a weight is given as 173 grams, it is assumed to be between 172 g and 174 g and it is said to be precise to within 1 g. When a weight is given as 173.2 g, it is assumed to be between 173.1 g and 173.3 g and it is said to be precise to within 0.1 g. We say that 173.2 is more precise than 173.

Readability

The smallest incremental weight that a balance can register. If it can read 10.1 g the readability is 0.1 g. If it can read 10.05 the readability is 0.01 g. The readability of a balance is also referred to as its resolution.

Relative Error

The accuracy of a measured value divided by the actual value. Relative error is often expressed in percent or parts per thousand.

Relative Precision

The precision of a measured value divided by the measured value itself. Relative precision is often expressed in percent or parts per thousand.

Saponification

The chemical reaction by which oil is turned into soap. Three moles of alkali react with each mole of oil to produce three moles of soap and one mole of glycerol.

Saponification Value (SAP)

The number of grams of alkali needed to *completely* saponify 1000 grams of oil. Whereas the alkali ratio is the actual ratio of alkali to oil in a given formula, the saponification value is the maximum value of the alkali ratio that may be used without producing an excessively alkaline soap.

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