Chapter

13

RECRYSTALLIZATION

- *Too much solvent and your crystals don't come back.*

The essence of a recrystallization is **purification.** Messy, dirty compounds are cleaned up, purified, and can then hold their heads up in public again. The sequence of events you use will depend a lot on how messy your crude product is and on just how soluble it is in various solvents.

In any case, you'll have to remember a few things.

1. Find a solvent that will *dissolve the solid while hot.*
2. The same solvent *should not dissolve it while cold.*
3. The *cold solvent* must keep impurities dissolved in it *forever or longer.*

This is the major problem. And it requires some experimentation. That's right! Once again, art over science. Usually, you'll know what you should have prepared, so the task is easier. It requires a trip to **your notebook** and, possibly, the **internet** (see Chapter 2, "Keeping a Notebook," and Chapter 3, "Mining Your Own Business"). You have the data on the solubility of the compound in your notebook. What's that, you say? *You don't have the data in your notebook?* Congratulations, you get the highest F in the course.

Information in the notebook (which came from the internet) for your compound might say, for alcohol (meaning *ethyl* alcohol), **s.h**. Since this means soluble in hot alcohol, it implies that it is insoluble (**i.**) in cold alcohol. Then alcohol is probably a good solvent for recrystallization of that compound. Also, check on the **color** or **crystalline form**. This is important since:

1. A color in a supposedly white product is an impurity.
2. A color in a colored product is *not* an impurity.
3. The *wrong color* in a product is an impurity.

You can usually assume that impurities are present in small amounts. Then you don't have to guess what possible impurities might be present or what they might be soluble or insoluble in. If your sample is really dirty, the assumption can be fatal. This doesn't usually happen in an undergraduate lab, but you should be aware of it.

FINDING A GOOD SOLVENT

If the solubility data for your compound is not readily available, then:

1. Place 0.10 g of your solid (weighed to 0.01 g) in a test tube.
2. Add 3 mL of a solvent, stopper the tube, and shake the bejesus out of it. If *all of the solid dissolves at room temperature,* then your solid is **soluble**. Do *not* use this solvent as a recrystallization solvent. (You must make note of this in your notebook, though.)
3. If none (or very little) of the solid dissolved at room temperature, unstopper the tube and heat it (*careful—no flames and get a boiling stone!*) and shake it and heat it and shake it. You may have to heat the solvent to a gentle boil. (*Careful!* Solvents with low boiling points often boil away.) If it does *not* dissolve at all, then do not use this as a recrystallization solvent.
4. If the sample *dissolved when hot,* and *did not dissolve at room temperature,* you're on the trail of a good recrystallization solvent. One last test.
5. Place the test tube (no longer hot) in an ice-water bath, and cool it about 5°C or so. If lots of crystals come out, this is good, and this is your recrystallization solvent.
6. Suppose your crystals don't come back when you cool the solution. Get a glass rod into the test tube, stir the solution, rub the inside of the tube with the glass rod, and agitate that solution. If crystals still don't come back, perhaps you'd better find another solvent.
7. Suppose, after all this, you still haven't found a solvent. Look again. Perhaps your compound *completely* dissolved in ethanol at room temperature and would *not* dissolve in water. Aha! Ethanol and water are **miscible** (i.e., they mix in all proportions). You will have to perform a **mixed-solvent recrystallization** (see "Working with a Mixed-Solvent System" later in this chapter).

GENERAL GUIDELINES FOR A RECRYSTALLIZATION

Here are some general rules to follow for purifying any solid compound.

1. Put the solid in an Erlenmeyer flask, not a beaker. If you recrystallize compounds in beakers, you may find the solid climbing the walls of the beaker to get at you as a reminder. A 125-mL Erlenmeyer usually works. Your solid should look comfortable in it, neither cramped nor with too much space. You probably shouldn't fill the flask more than one-fifth to one-fourth full.
2. Heat a large quantity of a proven solvent (see preceding section) to the boiling point, and *slowly add the hot solvent* to the sample in the Erlenmeyer. *Slowly!* A word about solvents: *Fire!* Solvents burn! *No flames!* A hot plate here would be better. You can even heat solvents in a *steam or water bath*. But—*no flames!*
3. Carefully add the hot solvent to the solid to just dissolve it. In parts. Your first shot of solvent *must* not dissolve all of the solid. Or else you might have gone too far and have more solvent in that flask than to just dissolve your solid. This can be tricky, since hot solvents evaporate, cool down, and so on. Ask your instructor.
4. Add a slight excess of the hot solvent to keep the solid dissolved.
5. If the solution is only slightly colored, the impurities will stay in solution. Otherwise, the big gun, **activated charcoal**, may be needed (see "Activated Charcoal" later in this chapter). Remember, if you were working with a colored compound, it would be silly to try to get rid of all the color, since you would get rid of all the compound and probably all your grade.
6. Keep the solvent hot (*not boiling*) and look carefully to see if there is any trash in the sample. This could be old boiling stones, sand, floor sweepings, and so on. Nothing you'd want to bring home to meet the folks. *Don't confuse real trash with undissolved good product!* If you add more hot solvent, good product will dissolve, and trash will not. If you have trash in the sample, do a **gravity filtration** (see following section).
7. Let the Erlenmeyer flask and the hot solution cool. Slow cooling gives better crystals. Garbage doesn't get trapped in them. But this can take what seems to be an interminable length of time. (I know, the entire lab seems to take an interminable length of time.) So, after the flask cools and it's just *warm* to the touch, then put the flask in an ice-water bath to cool. *Watch it!* The flasks have a habit of turning over in the water baths and letting all sorts of water destroy all your hard work! Also, a really hot flask will shatter if plunged into the ice bath, so again, watch it.

Why everyone insists on loading up a bucket with ice and trying to force a flask into this mess, I'll never know. How much cooling do you think you're going to get with just a few small areas of the flask barely touching ice?

Ice bath really means ice-water bath.

8. **"Is it cool enough yet?"** Hey, cool it, yourself. When the solution gets down to the temperature of the ice-water bath (and you should know what that is, eh?), then filter the crystals on a **Buchner funnel** or **Hirsch funnel**.
9. Dry them and take a melting point, as described in Chapter 12, "The Melting-Point Experiment."

My Product Disappeared

If you don't get any crystals back after cooling, remember: They're in there. Now is NOT the time to despair and throw anything away. First, see about getting a glass rod down into the flask, and, with a bit of vigorous scratching of the flask walls and stirring of the solution, crystals may appear. Waiting awhile after the stirring may help, but this is problematic; you can't wait all day.

You could just have too much solvent, and the crystals won't come out. Time to evaporate some of the solvent—start with about half—then go back to #7 above, cooling the solution again. Still no crystals? Don't throw anything away. You might have to evaporate solvent again. Remember—they're in there . . .

GRAVITY FILTRATION

If you find yourself with a flask full of hot solvent and your product dissolved in it, along with all sorts of trash, this is for you. You'll need more hot solvent, a ring stand with a ring attached, possibly a clay triangle, some filter paper, a clean, dry flask, and a **stemless funnel**. Here's how **gravity filtration** works.

1. Fold up a **filter cone** from a piece of filter paper (Fig. 13.1). It should fit nicely, within a single centimeter or so of the top of the funnel. For those who wish to filter with more panache, try using **fluted filter paper** (see "Finishing the final fluted fan," Fig. 13.12).

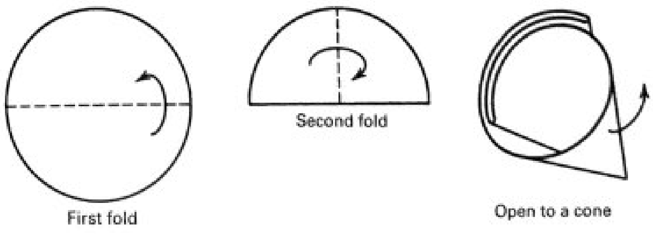

FIGURE 13.1 Folding filter paper for gravity filtration.

2. Get yourself a **stemless funnel** or, at least, a **short-stem funnel**, or even a **powder funnel**. Why? Go ahead and *use* a long-stem funnel and watch the crystals come out in the stem as the solution cools, blocking up the funnel (Fig. 13.2).
3. Put the **filter paper cone** in the **stemless funnel**.
4. Support this in a ring attached to a ring stand (Fig. 13.3). If the funnel is too small and you think it could fall through the ring, you may be able to get a **wire** or **clay triangle** to support the funnel in the ring (Fig. 13.4).

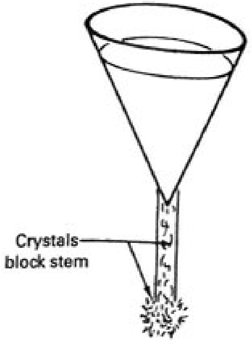

FIGURE 13.2 The "too long a funnel stem—oops!" problem.

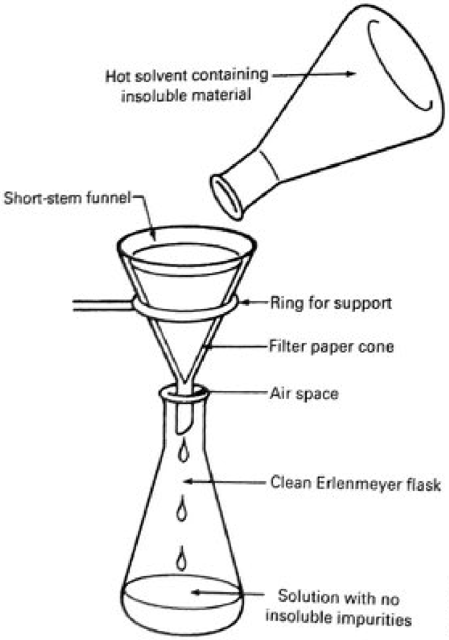

FIGURE 13.3 The gravity filtration setup with a funnel that fits the iron ring.

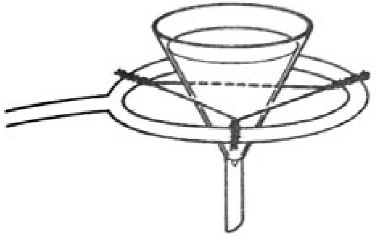

FIGURE 13.4 A wire triangle holding a small funnel in a large iron ring for gravity filtration.

5. Put the new, *clean, dry flask* under the funnel to catch the hot solution as it comes through. All set?
6. Get that flask with the solvent, product, and trash hot again. (*No flames!*) You should get some fresh, clean solvent hot as well. (*No flames!*)
7. Carefully pour the hot solution into the funnel. As it is, some solvents evaporate so quickly that product will probably come out on the filter paper. It is often hard to tell the product from the insoluble trash. Then—
8. Wash the filter paper down with *a little hot solvent.* The product will redissolve. The trash won't.
9. Now, you let the *trash-free* solution cool, and clean crystals should come out. Since you have probably added solvent to the solution, *don't be surprised if no crystals come out of solution. Don't panic, either!* Just boil away some of the solvent (not out into the room air, please), let your solution cool, and wait for the crystals again. If they *still* don't come back, just repeat the boiling.

Do not boil to dryness!

Somehow, lots of folks think recrystallization means dissolving the solid, then boiling away all the solvent to dryness. No! There must be a way to convince these lost souls that *the impurities will deposit on the crystals.* After the solution has cooled, crystals come out, sit on the bottom of the flask, and *must be covered by solvent!* Enough solvent to keep those nasty impurities dissolved and off the crystals.

THE BUCHNER FUNNEL AND FILTER FLASK

The **Buchner funnel** (Fig. 13.5) is used primarily for separating crystals of product from the liquid above them. If you have been *boiling your recrystallization solvents dry, you should be horsewhipped* and forced to reread these sections on recrystallization!

1. Get a piece of filter paper large enough to cover all of the holes in the bottom plate, and yet *not* curl up the sides of the funnel. It is placed *flat* on the plate (Fig. 13.5).

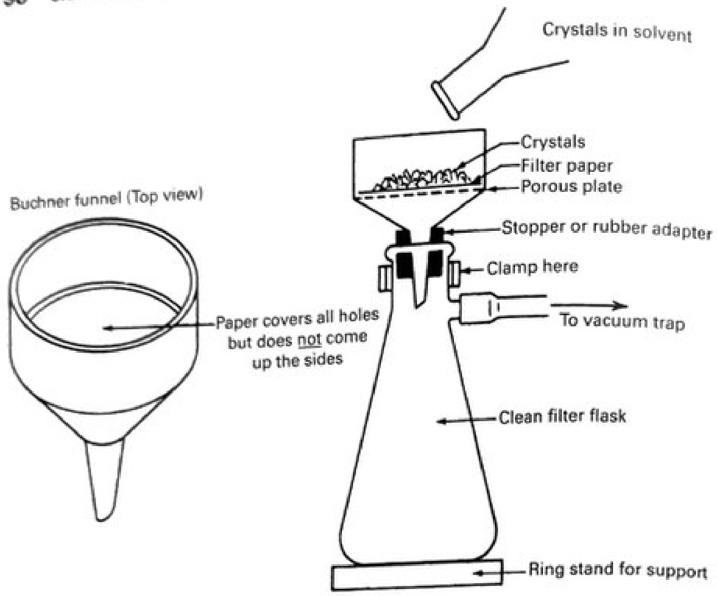

FIGURE 13.5 The Buchner funnel at home and at work.

2. Clamp a **filter flask** to a ring stand. This filter flask, often called a **suction flask**, is a very heavy-walled flask that has a side arm on the neck. A piece of heavy-walled tubing connects this flask to the **water trap** (see Fig. 13.6).
3. Now use a **rubber stopper** or **filter adapter** to stick the Buchner funnel into the top of the filter flask. The Buchner funnel makes the setup top-heavy and prone to be prone—and broken. Clamp the flask first, or go get a new Buchner funnel to replace the one you'll otherwise break.
4. The **water trap** is in turn connected to a source of vacuum, most likely a **water aspirator** (see Fig. 13.7).
5. The faucet on the **water aspirator** should be turned on *full blast!* This should suck down the filter paper, which you now *wet with some of the* ***cold*** *recrystallization solvent.* This will make the paper stick to the plate. You may have to push down on the Buchner funnel a bit to get a good seal between the rubber adapter and the funnel.
6. Swirl and pour the crystals and solvent *slowly and directly into the center of the filter paper,* as if to build a small mound of product there. *Slowly!* Don't flood the funnel by filling it right to the brim and waiting for the level to go down. If you do that, the paper may float up, ruining the whole setup.
7. Use a very small amount of the same *cold* recrystallization solvent and a spatula to remove any crystals left in the flask. Then you can use some of the *fresh, cold recrystallization solvent* and slowly pour it over the crystals to wash away any old recrystallization solvent and dissolved impurities.

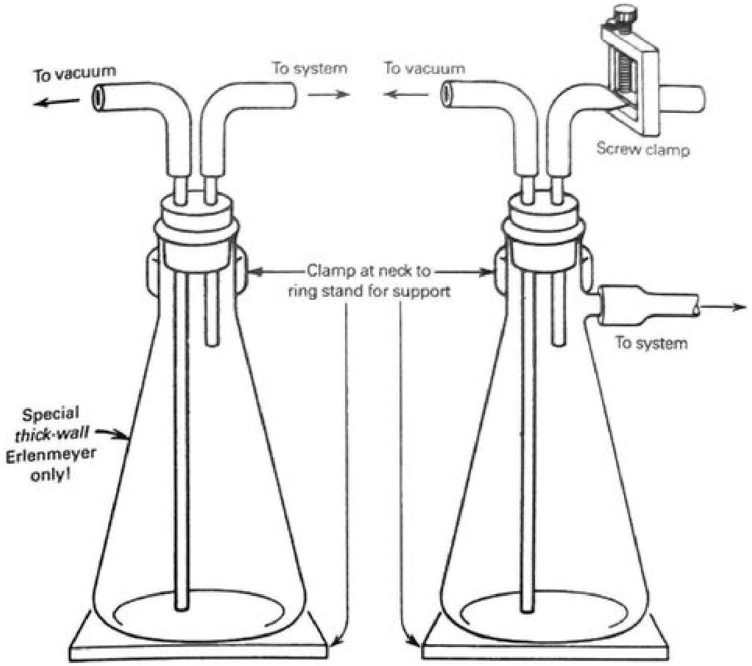

FIGURE 13.6 A couple of water traps hanging around.

8. Leave the aspirator on, and let air pass through the crystals to help them dry. You can put a thin rubber sheet, a **rubber dam**, over the funnel. The vacuum pulls it in, and the crystals are pressed clean and dry. You won't have air or moisture blowing through, and possibly decomposing, your product. Rubber dams are neat.
9. When the crystals are dry *and you have a* **water trap**, just turn off the water aspirator. Water won't back up into your flask. (If you've been foolhardy and have filtered without a water trap, just remove the rubber tube connected to the filter flask side arm [Fig. 13.5].)
10. At this point, you may have a *cake of crystals* in your **Buchner funnel**. The easiest way to handle this is to *carefully lift the cake* of crystals out of the funnel *along with the filter paper,* plop the whole thing onto a larger piece of filter paper, and let everything dry overnight. If you are pressed for time, *scrape the damp filter cake from the filter paper, but don't scrape any filter paper fibers into the crystals.* Repeatedly press the crystals between dry sheets of

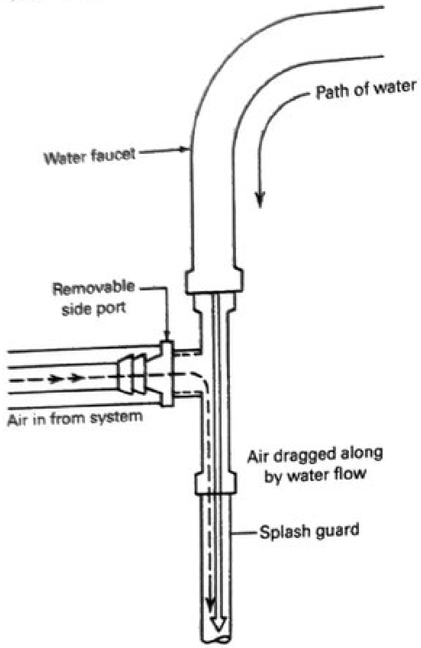

FIGURE 13.7 A water aspirator.

filter paper, and change sheets until the crystals no longer show any solvent spot after pressing. Those of you who use **heat lamps** may find your white crystalline product turning into instant charred remains.

11. When your cake is *completely dry,* weigh a vial, put in the product, and weigh the vial again. Subtracting the weight of the vial from the weight of the vial and sample gives the weight of the product. This **weighing by difference** is easier and less messy than weighing the crystals directly on the balance. This weight should be included in the label on your **product vial** (see Chapter 5, "Microscale Jointware," and Chapter 11, "On Products").

Just a Note

I've said that a Buchner funnel is used primarily for separating crystals of product from the liquid above them. And in the section on drying agents, I tell people to use a gravity filtration setup to separate a drying agent from a liquid product. Recently, I've had some people get the notion that you can Buchner-filter liquid products from drying agents. I don't advise that. You will probably lose a lot of your product, especially if it has a low boiling point (<100°C). Under this *vacuum filtration,* your product simply evaporates along with your grade.

THE HIRSCH FUNNEL AND FRIENDS

You can think of the **Hirsch funnel** (Fig. 13.8) as a smaller, sloping-sided Buchner funnel, and, for the most part, you use it in the same way.

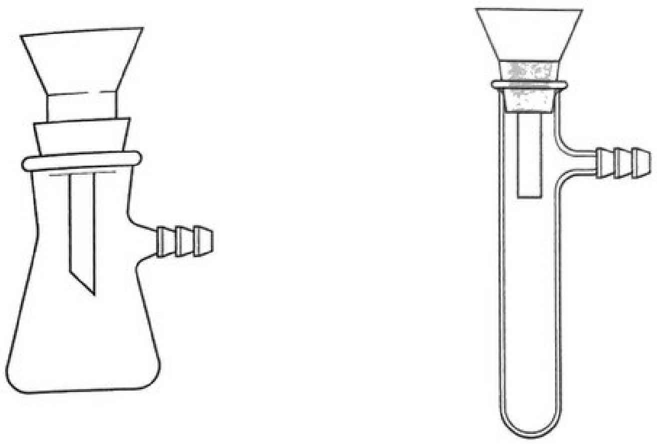

FIGURE 13.8 The Hirsch funnel and friends.

ACTIVATED CHARCOAL

Activated charcoal is ultrafinely divided carbon with lots of places to suck up big, huge, polar, colored impurity molecules. Unfortunately, if you use too much, it'll suck up *your product!* And, if your product was white or yellow, it'll have a funny gray color from the excess charcoal. Sometimes the impurities are untouched and only the product is absorbed. Again, it's a matter of trial and error. Try not to use too much. Suppose you've got a *hot solution* of some solid, *and the solution is highly colored.* Well,

1. First, *make sure your product should not* ***be*** *colored!*
2. Take the flask with your filthy product off the heat, and swirl the flask. This dissipates any superheated areas so that when you add the activated charcoal, the solution doesn't foam out of the flask and onto your shoes.
3. *Add the activated charcoal.* Put a small amount, about the size of a pea, on your spatula; then throw the charcoal in. Stir. The solution should turn black. Stir and heat.
4. Set up the **gravity filtration** and filter off the carbon. It is especially important to *wash off any product caught on the charcoal,* and it is really hard to see anything here. You should take advantage of **fluted filter paper**. It should give a more efficient filtration.

5. Yes, have some extra fresh solvent heated as well. You'll need to add a few milliliters of this to the hot solution to help keep the crystals from coming out on the filter paper. And you'll need more to help wash the crystals off the paper when they come out on it anyway.
6. The filtered solution should be *much cleaner* than the original solution. If not, you'll have to *add charcoal and filter again*. There is a point of diminishing returns, however, and one or two treatments is usually all you should do. Get some guidance from your instructor.

Your solid products should not be gray. Liquid products (yes, you can do liquids!) will let you know that you didn't get all the charcoal out. Often, you can't see charcoal contamination in liquids while you're working with them. The particles stay suspended for awhile, but after a few days, you can see a layer of charcoal on the bottom of the container. Sneaky, those liquids. By the time the instructor gets to grade all the products—*voilà*—the charcoal has appeared.

THE WATER ASPIRATOR: A VACUUM SOURCE

Sometimes you'll need a vacuum for special work like **vacuum distillation** and **vacuum filtration** as with the Buchner funnel. The **water aspirator** is an inexpensive source of vacuum (Fig. 13.7).

When you turn the water on, the water flow draws air in from the side port on the aspirator. The faster the water goes through, the faster the air is drawn in. Pretty neat, huh? I've shown a plastic aspirator, but many of the older metal varieties are still around.

You may have to pretest some aspirators before you find one that will work well. It'll depend on the water pressure in the pipes, too. Even the number of people using aspirators on the same water line can affect the performance of these devices. You can test them by going to an aspirator and turning the faucet on *full blast*. It does help to have a sink under the aspirator. If water leaks out the side port, *tell your instructor and find another aspirator.* Wet your finger and place it over the hole in the side port to feel if there is any vacuum. If there is *no vacuum,* tell your instructor and find another aspirator. Some of these old, wheezing aspirators produce a very weak vacuum. You must decide for yourself if the suction is "strong enough." There should be a **splash guard** or rubber tubing leading the water stream directly into the sink. This will keep the water from going all over the room. If you check and don't find such protection, see your instructor. All you have to do with a fully tested and satisfactory aspirator is to hook it up to the **water trap**.

THE WATER TRAP

Every year, I run a chem lab, and when someone is doing a **vacuum filtration**, suddenly I'll hear a scream and a moan of anguish, as water backs up into someone's filtration system. Usually there's not much damage, since the filtrate in the suction flask is generally thrown out. For **vacuum distillations**, however, this **suck-back** is disaster. It happens whenever there's a pressure drop on the water line big enough to cause the flow to decrease so that there is a *greater vacuum in the system than in the aspirator.* Water, being water, flows into the system. Disaster.

So, for your own protection, make up a **water trap** from some stoppers, rubber tubing, a thick-walled Erlenmeyer or filter flask, and a screw clamp (Fig. 13.6). *Do not use garden-variety Erlenmeyers; they may implode without warning.* Two versions are shown. I think the setup using the filter flask is more flexible. The screw clamp allows you to let air into your setup at a controlled rate. You might clamp the water trap to a ring stand when you use it. The connecting hoses have been known to flip unsecured flasks two out of three times.

WORKING WITH A MIXED-SOLVENT SYSTEM—THE GOOD PART

If, after sufficient agony, you cannot find a single solvent to recrystallize your product from, you may just give up and try a *mixed-solvent system.* Yes, it does mean you mix more than one solvent and *recrystallize using the mixture.* It should only be so easy. Sometimes you are told what the mixture is and the correct proportions. Then it is easy.

For an example, I could use "solvent 1" and "solvent 2," but that's clumsy. So I'll use the ethanol–water system and point out the interesting stuff as I go along.

The Ethanol–Water System

If you look up the solubility of water in ethanol (or ethanol in water), you find an ∞. This means they mix in all proportions. Any amount of one dissolves completely in the other—no matter what. Any volumes, any weights. You name it. The special word for this property is **miscibility**. Miscible solvent systems are the kinds you should use for mixed solvents. They keep you out of trouble. You'll be adding amounts of water to the ethanol, and ethanol to the water. If the two weren't miscible, they might begin to separate and form two layers as you changed the proportions. Then you'd have REAL trouble. So, go ahead. You *can* work with mixtures of solvents that aren't miscible. But don't say you haven't been warned.

The ethanol–water mixture is useful because:

1. *At high temperatures, it behaves like alcohol!*
2. *At low temperatures, it behaves like water!*

From this, you should get the idea that it would be good to use a mixed solvent to recrystallize compounds that are *soluble in alcohol* yet *insoluble in water.* You see, each solvent alone cannot be used. If the material is soluble in alcohol, not many crystals come back from alcohol alone. If the material is insoluble in water, you cannot even begin to dissolve it. So, you have a *mixed solvent,* with the best properties of *both* solvents. To actually perform a *mixed-solvent recrystallization,* you:

1. Dissolve the compound in the smallest amount of *hot ethanol.*
2. Add *hot water* until the solution turns cloudy. This **cloudiness** is *tiny crystals of compound coming out of solution.* Heat this solution to dissolve the crystals. If they do not dissolve completely, add *a very little hot ethanol* to force them back into solution.
3. Cool and collect the crystals on a **Buchner funnel**.

Any solvent pair that behaves the same way can be used. The addition of hot solvents to one another can be tricky. It can be *extremely dangerous* if the boiling points of the solvents are very different. For the *water–methanol mixed solvent*, if 95°C water hits *hot methanol* (bp 65.0°C), watch out!

There are other miscible, mixed-solvent pairs—petroleum ether and diethyl ether, methanol and water, and ligroin and diethyl ether among them.

A MIXED-SOLVENT SYSTEM—THE BAD PART

Every silver lining has a cloud. More often than not, compounds "recrystallized" from a mixed-solvent system don't form crystals. Your compound may form an *oil* instead.

Oiling out is what it's called; more work is what it means. Compounds usually oil out if *the boiling point of the recrystallization solvent is higher than the melting point of the compound*, although that's not the only time. In any case, if the oil solidifies, the impurities are trapped in the now-solid "oil," and you'll have to purify the solid again.

Don't think you won't ever get oiling out if you stick to single, unmixed solvents. It's just that with two solvents, there's a greater chance you'll hit on a composition that will cause this.

Temporarily, you can:

1. Add more solvent. If it's a mixed-solvent system, try adding more of the solvent the solid is NOT soluble in. Or add more of the OTHER solvent. No contradiction. The point is to *change the composition*. Whether single solvent or mixed solvent, changing the composition is one way out of this mess.
2. Redissolve the oil by heating; then shake up the solution as it cools and begins to oil out. When these smaller droplets finally freeze out, they may form crystals that are relatively pure. They may not. You'll probably have to clean them up again. Just don't use the same recrystallization solvent.

Sometimes, once a solid oils out it doesn't want to solidify at all, and you might not have all day. Try removing a sample of the oil with an eyedropper or a disposable pipet. Then get a glass surface (watch glass) and add a few drops of a solvent that the compound is known to be *insoluble* in (usually water). Then use the rounded end of a glass rod to *triturate the oil with the solvent*. **Trituration** can be described loosely as beating an oil into a crystalline solid. Then you can put these crystals back into the rest of the oil. Possibly they'll act as seed crystals and get the rest of the oil to solidify. Again, you'll still have to clean up your compound.

SALTING OUT

Sometimes you'll have to recrystallize your organic compound from water. No big deal. But sometimes your organic compound is more than ever-so-slightly insoluble in water, and not all the compound will come back. Solution? Salt solution! A pinch of salt in the water raises the **ionic strength**. There are now charged ions in the water. Some of the water that solvated your compound goes with the salt ions. Your organic compound does not particularly like charged ions anyway, so more of your organic compound comes out of the solution.

You can dissolve about 36 g of common salt in 100 mL of cold water. That's the upper limit for salt. You can estimate how much salt you'll need to practically saturate the water with salt. Be careful, though—if you use too much salt, you may find yourself collecting salt crystals along with your product. (See also the application of salting out when you have to do an extraction, "Extraction Hints," in Chapter 15.)

WORLD-FAMOUS FAN-FOLDED FLUTED PAPER

Some training in origami is *de rigueur* for chemists. It seems that the regular filter paper fold is inefficient, since very little of the paper is exposed. The idea here is to **flute** or **corrugate** the paper, increasing the surface area that is in contact with your filtrate. You'll have to do this several times to get good at it.

Right here let's review the difference between **fold** and **crease**. Folding is folding; creasing is folding, then stomping on it, and running fingers and fingernails over a fold over and over and over. Creasing so weakens the paper, especially near the folded point, that it may break at an inappropriate time in the filtration.

1. Fold the paper in half, then in half again, then in half again (Fig. 13.9). Press on this wedge of paper to get the fold lines to stay, but *don't crease. Do this in one direction only.* Always fold either toward you or away from you, but don't do both.

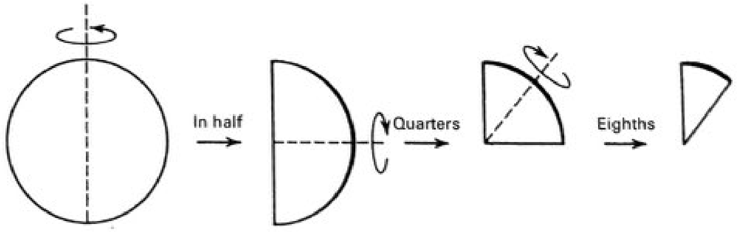

FIGURE 13.9 Folding filter paper into eighths.

2. Unfold this cone *twice* so it looks like a semicircle (Fig. 13.10), and then put it down on a flat surface. Look at it and think for not less than two full minutes the first time you do this.
3. OK. Now try a "fan fold." You alternately fold, first in one direction and then the other, every individual eighth section of the semicircle (Fig. 13.11).
4. Open the fan and play with it until you get a fairly fluted filter cone (Fig. 13.12).
5. It'll be a bit difficult, but try to find the two opposing sections that are not folded correctly. Fold them inward (Fig. 13.12), and you'll have a fantastic fan-folded fluted filter paper of your very own.

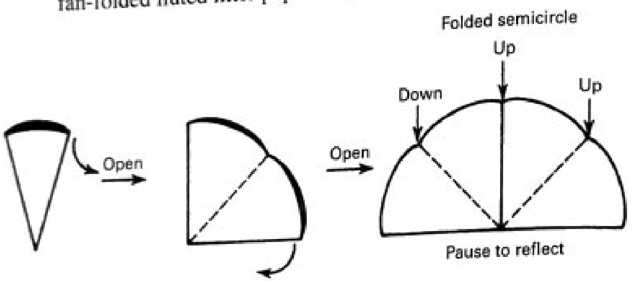

FIGURE 13.10 Unfolding to a sort of bent semicircle.

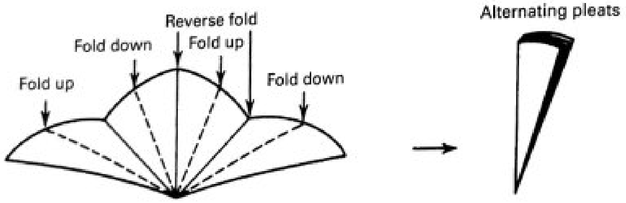

FIGURE 13.11 Refolding to a fan.

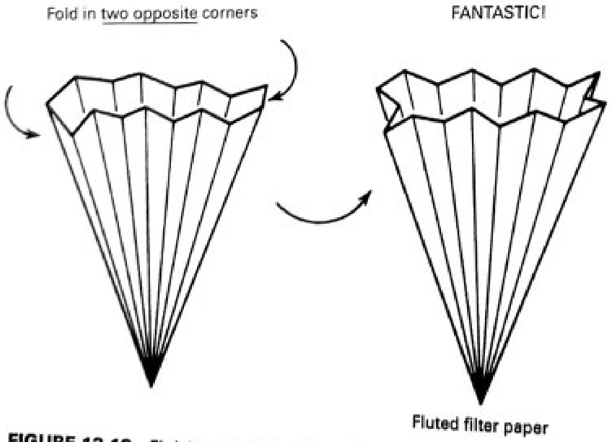

FIGURE 13.12 Finishing the final fluted fan.

P. S. For those with more money than patience, prefolded fan-folded fluted filter paper is available from suppliers.

EXERCISES

1. An impatient lab student plunges his hot, totally dissolved solution into his ice-water bath to get the crystals out quickly. Comment on the purity of his recrystallized product.
2. You perform the recrystallization procedure and get no crystals. What might you do to rectify this situation? Would it help to recall a Prego spaghetti sauce commercial that, talking about the composition of the sauce, stated, "It's in there!"?
3. OK, you have an oil, and you have to change the composition of your mixed-solvent system to get to a different point on the phase diagram. Do you add more of the more-polar solvent or the less-polar solvent?