GENERAL LAB TECHNIQUES

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CHAPTER OVERVIEW

General Lab Techniques

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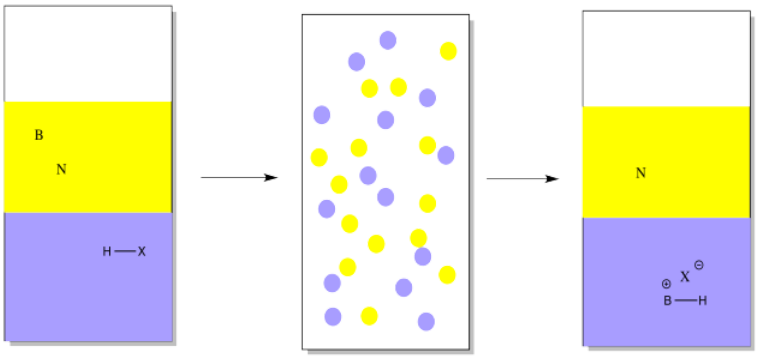
Acid-Base Extraction

An acid-base extraction is a type of liquid-liquid extraction. It typically involves different solubility levels in water and an organic solvent. The organic solvent may be any carbon-based liqiuid that does not dissolve very well in water; common ones are ether, ethyl acetate, or dichloromethane.

Acid-base extraction is typically used to separate organic compounds from each other based on their acid-base properties. The method rests on the assumption that most organic compounds are more soluble in organic solvents than they are in water. However, if the organic compound is rendered ionic, it becomes more soluble in water than in the organic solvent. These compounds can easily be made into ions either by adding a proton (an H^+ ion), making the compound into a positive ion, or by removing a proton, making the compound into a negative ion.

Suppose you have a mixture of two compounds. There is a neutral one which doesn't react with any acids or bases. There is also a basic one, which reacts with acids by picking up a proton. In this case, a proton might be added via reaction with a strong mineral acid (represented by HX in the drawing). Suppose an aqueous solution of mineral acid, such as HCl, were shaken vigorously with an ethereal solution of an organic base and an organic neutral. The proton would be transferred to a basic compound, but not to a neutral one. The basic compound would become ionic, and more water-soluble.

Note that in the drawing, the ether is represented in yellow, whereas the water is shown in blue. The water is on the bottom in this case because water has a higher density than ether, so it will sink to the bottom (along with anything dissolved in it). Some organic solvents do have a higher density than water, so the aqueous solution would float to the top in those case.



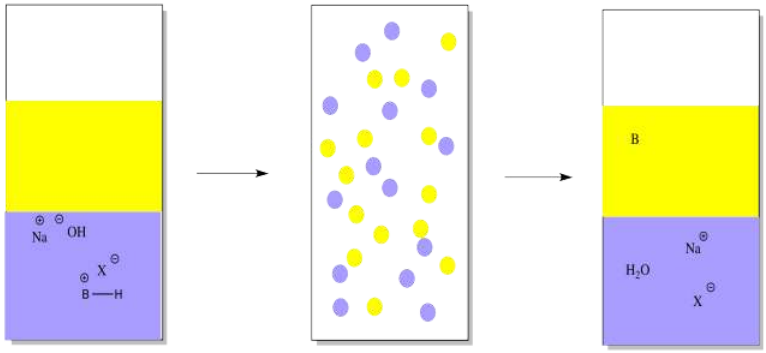
As a result, the ethereal solution would contain only the neutral compound, not the basic one. The neutral compound could be isolated simply by evaporating the ether.

However, as a practical matter, the ether would have to be dried first. What's the difference between evaporating and drying? Have you ever been to the beach or taken a shower? Drying refers to the removal of water. This step is necessary because ether tends to dissolve a lot of water in it. Once the ether has been evaporated, there would be some neutral compound, but it would be mixed with water.

Water removal is most easily done by adding a drying agent, such as magnesium sulfate or sodium sulfate. The water sticks to these solids, which are then filtered off.

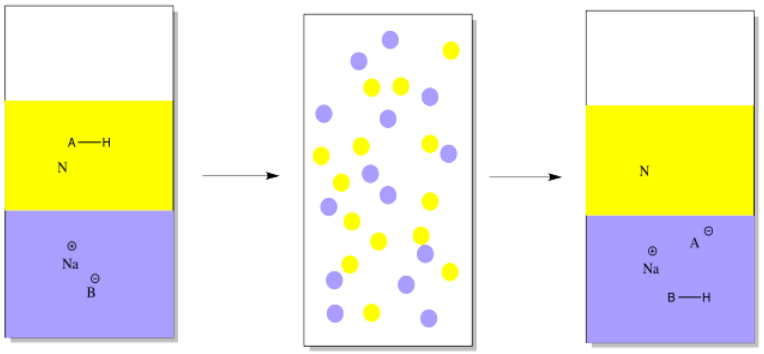
Now the neutral compound is alone in the ether. Evaporation of the ether gives the pure, neutral compound.

However, the basic compound is stuck in the water, and it isn't the same compound anymore. It's an ion, now. If we want the original compound in a pure form, we need to take that proton away. That can be done by adding a mineral base, such as sodium hydroxide.



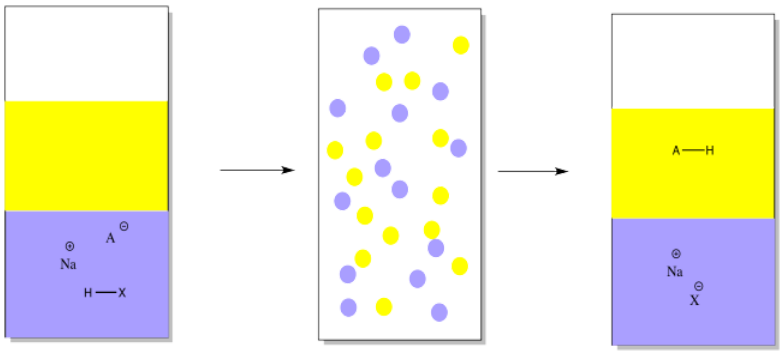
The mineral base will remove the proton, leaving the original organic compound. The organic compound is uncharged and not as soluble in water anymore. It will go back into the ether layer.

Conversely, we might have a mixture of an acidic organic compound and a neutral compound to start out with. In that case, we would add a mineral base in the first place, to take a proton away from the acidic compound. The mineral base might be something like sodium hydroxide or sodium bicarbonate. In the drawing, it is just represented as Na^+ B^-.



The acidic compound becomes ionic and water-soluble when it loses a proton. That leaves the neutral compound alone.

To get that acidic compound back, we would add a mineral acid such as hydrochloric acid in order to restore the missing proton.



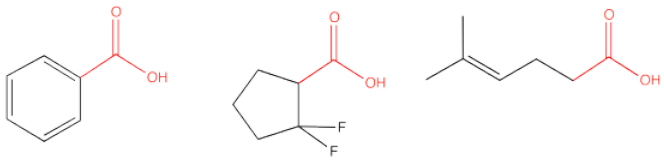
Just as in the other case, the ether layer containing a pure compound could be separated, dried and evaporated in order to provide the pure compound.

Acidity

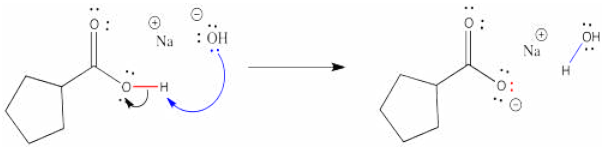
But how do we know whether something is an organic acid or a base? Common structural features of organic acids and bases are displayed below.

Note that the terms, "strong acid" and "weak acid", are relative with organic compounds. Sometimes, the term, "strong acid", designates a compound that completely ionizes in solution, so that it automatically gives up a H^+ ion and forms an ionic compound. Hydrochloric acid, HCl, in water is a good example. That isn't true here; none of these acids ionize very easily on their own, and they appear in solution just as they do above, with just a small minority of molecules forming H^+ and an anion. In this case, the term just compares one group of acidic compounds (called carboxylic acids) to another group of acidic compounds (called phenols). Carboxylic acids are more likely to give up protons than are phenols, so carboxylic acids are referred to in this context as "strong" and phenols as "weak".

The carboxylic acid group contains a C=O (a carbonyl) with an additional OH group attached to the carbon. Examples are shown below.

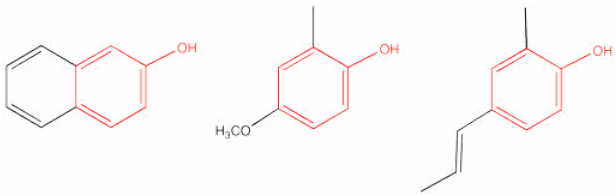


When carboxylic acids are treated with mineral bases such as sodium hydroxide, the carboxylic OH group gives up a proton to the hydroxide, forming a water molecule. The electrons in the O-H bond stay behind, putting a negative charge on the resulting carboxylate anion. The salt that forms is much more water soluble.

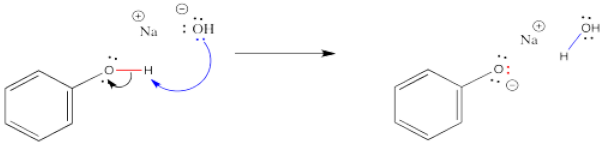


This reaction is completely reversible. A mineral acid, such as HCl, could provide protons to the carboxylate anion. The carboxylate ion would use a pair of electrons to bind to a proton, and the compound would become a neutral (as in uncharged) carboxylic acid again.

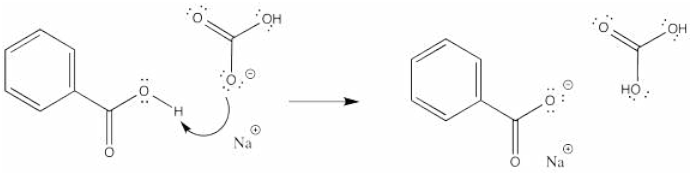
Phenols also contain an OH group, but instead of being attached to a C=O group, the OH is attached to a benzene (a six-carbon ring with three double bonds). Examples are shown below.



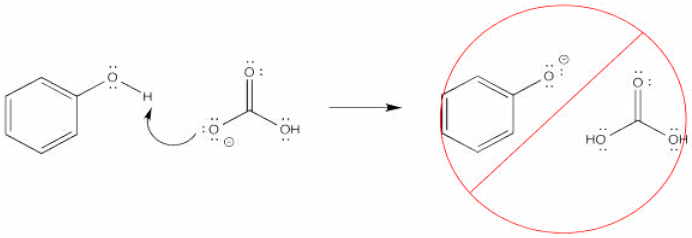
Phenols react with bases in the same way as do carboxylic acids, just not so as easily.



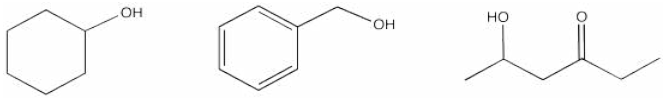
Because phenols do not react as easily as carboxylic acids, there are situations in which a carboxylic acid would react with a base but a phenol would not. For example, carboxylic acids react even with weak bases such as sodium bicarbonate (baking soda).



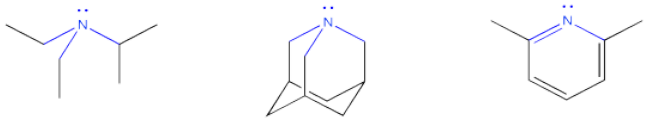
Phenols, on the other hand, do no such thing.



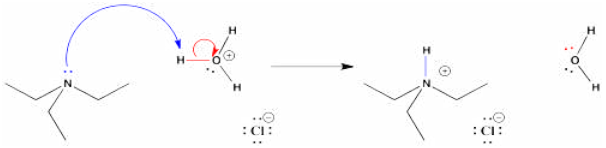
If the OH is attached to a carbon in an organic compound, but it is not attached to either a C=O or a benzene ring, it is not acidic enough to be removed to an appreciable extent. That is true even if there is a carbonyl or a benzene somewhere else in the molecule. As a result, acid-base extraction is not possible in these cases.



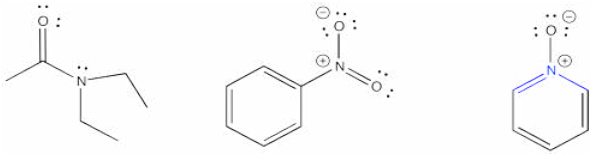
Organic bases are compounds that contain nitrogen atoms. In order to be basic, the nitrogen atom must have a lone pair. The lone pair is needed in order to make a bond with the proton.



Once the lone pair has donated to the proton to form a bond with it, the nitrogen compound becomes positively charged. It then becomes more water-soluble.



If the nitrogen does not have a lone pair, it is unable to bond to a proton. However, some compounds that do have a lone pair on the nitrogen still can't donate their lone pair to make a bond to the hydrogen. Most often that's because of a very electronegative oxygen atom nearby. The attraction of the oxygen for the lone pair makes the lone pair less able to donate to another atom. There can also be other reasons, especially involving electron delocalization or aromaticity that makes the lone pair unavailable for bonding.



Contributors

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Calibration of a Buret

Discussion and Procedure

To carry out this procedure you will require, in addition to a volumetric buret, two clean, dry 125 mL Erlenmeyer flasks and one #5 rubber stopper.

Select a 50 mL buret from the buret cabinet in the north-west corner of the lab. After you have cleaned this buret attach a piece of tape with your name to the open end of the buret. This will serve to identify it. You will be using this buret for this calibration and for the two volumetric analyses. Proceed with the calibration as described below.

1. Disassemble the stopcock, noting carefully how it is assembled, then clean the bore of the buret with a warm solution of Alconox. The teflon stopcock usually does not require much cleaning; however it might be necessary to soak it in warm Alconox solution. Do not use a brush on the stopcock since it will scratch the relatively soft teflon. These scratches are the primary reason for leaking burets. Rinse the buret and stopcock well with water and distilled water. Reassemble the stopcock.

2. Fill the buret with distilled water and check to see that no bubbles of air are entrapped in the tip. Drain water slowly until the meniscus is at the 0.00 mL mark. Touch the tip of the buret to the side of a beaker to remove the drop hanging from the tip. After about a minute, to allow for drainage, make an initial reading of the meniscus, estimating the volume to the nearest 0.01 mL. Record the initial reading. Allow the buret to stand for 5 minutes and recheck the reading. If the stopcock is tight, there should be no noticeable change in the reading. If the reading has changed tighten the blue (or orange) nut on the stopcock and let stand for another 5 minutes. Check the reading again. If the buret continues to leak consult your instructor. Click here for guidance on reading a buret.

3. You will need to prepare a "buret card" to be used every time you read your buret. Obtain a 3"x5" card from your instructor and using a black felt tip pen make a horizontal mark on your card, one inch thick and practically the length of the card. When the top of the black band is held just below the bottom of the meniscus you will see a reflection of the band in the meniscus against the white of the card behind. This offers you a repeatable method of determining the position of the meniscus. You must make sure during your readings that your line of sight is perpendicular to the buret so as to avoid *parallax* due to the center of the meniscus being a greater distance from your eye than the scale against which you are reading it. If your line of sight is looking downward or looking upward, the meniscus will appear to be higher or lower, respectively, than its true value. It is extremely important that you learn how to read a buret with a repeatable precision of ±0.01 mL so as to eliminate this source of errors in all of the volumetric analyses that you perform. What is the volume of the liquid in the buret shown above? Does that volume agree to within 0.01 mL of the volume proposed by your instructor?

4. While checking the buret, weigh, to the nearest 1 mg, a dry 125 mL Erlenmeyer flask fitted with a #5 rubber stopper. Once the tightness of the buret stopcock has been established, record the level of the meniscus (which should be at ***0.00 mL***). Run an accurately measured volume of about 10 mL into the weighed flask at a flow rate of approximately 10 mL per minute. Touch the tip to the wall of the flask. Wait 1 minute, record the meniscus level. The difference between the two readings is the "apparent volume". Now stopper the Erlenmeyer flask with the #5 rubber stopper and then weigh it to the nearest 1 mg. The difference between the two weights gives the mass of water equivalent to the apparent volume. Record the temperature of the water in the flask. With the aid of the table below convert this mass of water into the true volume at 20 ^{o}C.

Volume occupied by 1.000 g of water weighed in air using stainless steel weights. Corrections for the buoyancy of stainless steel and the thermal expansion of the glass buret have been applied.

T, in ^{o}C	Volume at T	Volume corrected to 20 ^{o}C
10	1.0013	1.0016
11	1.0014	1.0016
12	1.0015	1.0017
13	1.0016	1.0018
14	1.0018	1.0019
15	1.0019	1.0020
16	1.0021	1.0022
17	1.0022	1.0023
18	1.0024	1.0025
19	1.0026	1.0026
20	1.0028	1.0028
21	1.0030	1.0030
22	1.0033	1.0032
23	1.0035	1.0034
24	1.0037	1.0036
25	1.0040	1.0037

T, in ^{o}C	Volume at T	Volume corrected to 20 ^{o}C
26	1.0043	1.0041
27	1.0045	1.0043
28	1.0048	1.0046
29	1.0051	1.0048
30	1.0054	1.0052

This is accomplished by multiplying the value, corresponding to your temperature, in the right-most column of the table, by the mass of water in the flask. The correction that must be applied is obtained by subtracting the apparent volume from the true volume. Notice that this correction may be either positive or negative and is an additive correction term applied to the apparent volume. We use Class A burets in this class. The tolerance allowed by the National Institute of Standards and Technology for Class A 50 mL burets is ±0.05 mL. Your correction ought not to exceed this deviation from 0 to 50 mL. Continuing the delivery of water into the same flask, add water in increments of 10.00 mL to 20, 30, 40 and 50 mL. Weigh the flask after the delivery of each increment. While you are carrying out the procedure, dry a second flask. When you have finished the drainage to 50 mL in the first flask and made your final weighing, repeat the entire procedure using the second flask as your receiving vessel. The deviations you observe between the first and second run will give you important information about the reproducibility of your buret readings.

5. Calculate the correction value for each volume. If any of your readings exceed a 10 mL increment by a few hundredths of a mL, there is salvation. For example, if for the 10 mL reading your meniscus was at 10.02 mL, you should subtract 10.02 from your true volume and then plot the resulting value. Make an accurate plot of correction value vs. apparent volume in your lab notebook. Don't average the values (yet) for the two runs, but superimpose them on the same graph. Place the correction value on the ordinate and the volume on the abscissa. Make this graph as large as possible on one page of the notebook. Use the long side of the page as the volume coordinate and the short side for the correction terms. Keep in mind that the correction values may be either positive or negative, make allowance for this when you lay out your graph. Connect the points on the graph by straight lines. Correction values for intermediate volumes may now be read off the graph. The two plots should "shadow" each other. Any pair of points ought not to differ by more than 0.04 mL. The similarity between the two plots will give you confidence about the trustworthiness of your data. Now, use the average correction value for each pair of readings as your final buret correction.

6. You need not submit a report for this calibration but write in your laboratory notebook the answers to the questions posed below.

Questions on Buret Calibration

1. Your weight of water is converted to the true volume using data from Table 27-3 of SHW. What are the three corrections that are embodied in those values?
2. Explain why it is not necessary to weigh the water samples on the analytical balance.
3. When the glass of a buret expands due to an increase in temperature does the diameter of the bore increase or decrease?
4. Most volumetric glassware is calibrated at what temperature?
5. What do the letters T.D. and T.C., that are found on various types of volumetric glassware, signify?

Contributors

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Condensing Volatile Gases

Ever had to run a reaction with a volatile gas? It's not a very common thing to have to do, but every once in a while, it needs to be done.

Introduction

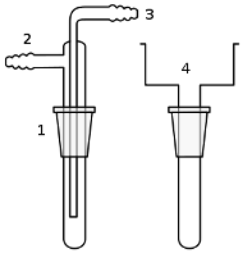
Assuming the volatile gas is coming from a lecture bottle, there are a few ways to do this:

Bubbling into solvent: Add solvent into a reaction flask (with stirbar?) and pre-weigh. Bubble gas into stirring solvent (cooled?), stop when the weight matches the desired amount. I've been concerned about suckback into lecture bottles (although I suspect I'm very paranoid, so there are other ways to skin this cat.)

Just doing it: From the brass adapter (that you can buy special from Aldrich!) that's screwed onto the lecture bottle fitting, attach a tube and direct it into a pre-chilled tared round-bottom flask. When you think you're done adding, turn down the gas and quickly weigh the flask.

Using a coldfinger

The methods above work fine, but you run the risk of allowing a lot of evaporation of your gas to happen. So, when you move to a higher scale (>20 grams of condensed liquid), you might want to try a coldtrap. Assuming that you have one (see 1st picture below), it's pretty self-explanatory: just a glass coldfinger with a place for dry ice/acetone to cool down the incoming gas, a gas inlet above and a 24/40 ground glass joint at the bottom.



Coldfingers in the lab

You prepare your lecture bottle pretty mundanely: screw your brass fitting onto the inlet and attach whatever tubing that you prefer. I like stiff plastic tubing, but that's just an affectation more than anything. Obviously, 1/4 inch Tygon is best for good seals between tubing and fittings. If you have something that's particularly dangerous (it is, after all, a pressurized gas), you should probably clamp that thing down. While it's not pictured below, it's probably still a good diea.

1. Take your coldfinger and mate it to the multi-neck round bottom of your choice. You'll note that below (3rd picture), the picture shows a three-neck flask with two septa and a needle for venting. It has been pre-weighed (with the septa and needle). Clamp the RBF and the coldfinger.
2. Hook your Tygon tubing from the lecture bottle to your coldfinger.
3. Cool the coldfinger to the desired temperature; in this case, -78°C.
4. Slowly add the gas by opening the knob on the pre-weighed lecture bottle (slowly!) You will note that the bubbling of the coldfinger will get faster as the gas is condensing to liquid. Hopefully, the liquid is collecting on the coldfinger and you're seeing it drip into your reaction flask. Add as much as you need. You can check your progress by 1) looking 2) checking the weight of the lecture bottle or 3) checking the weight of your reaction flask (tedious). Stop when you think you're done by tightening the knob on the lecture bottle.
5. You can add reaction solvent slowly by either adding it by squeeze bottle through the top inlet of the coldfinger or (for larger amounts) performing a cold cannulation. If you're experiencing clogging of the cannula (due to water (?) freezing at the tip of the cannula), you can place it deep enough into your reaction flask that it gets jarred by the stirbar.

Concerns about losing gas

When I was running these reactions, I was always concerned about losing gas. Using the "just do it" method, I think I was losing up to 30% of the gas I was trying to condense. The cold trap method dropped that significantly (<5%).

Contributors

- ChemJobber

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Cooling baths

Cooling baths are used extensively in organic chemistry for a variety of reasons. The low temperature of these baths is determined both by the appropriate use of solvent as well as a cryogenic agent such as liquid nitrogen, dry ice (CO_2) or ice. Most of these methods require continuous monitoring to ensure the temperature remains steady. For longer or unmonitored reactions, it may be best to invest in a cryocooler. Temperatures between -20 and -80° can be obtained using varied mixtures of ethylene glycol and ethanol over dry ice. A little more detailed list taken from the Hoveyda group website at Boston College.

Temperature	Mixture Composition
13 °C	p-Xylene/ dry ice
12 °C	Dioxane/ dry ice
6 °C	Cyclohexane/ dry ice
5 °C	Benzene/ dry ice
2 °C	Formamide/ dry ice
0 °C	Crushed Ice
-5 -> -20 °C	Ice/Salt: Equal amounts of ice and NaCl. The actual temperature obtained will depend on how finely crushed and well mixed the components are, and could be as high as -10°. A dewar is recomended. Brine/ dry ice produces an identical mixture.
-10.5 °C	Ethylene Glycol/ dry ice
-12 °C	Cycloheptane/ dry ice
-15 °C	Benzyl alcohol/ dry ice
-22 °C	Tetrachloroethylene/ dry ice
-22.8 °C	Carbon Tetrachloride/ dry ice
-25°C	1,3-Dichlorobenezene/ dry ice
-29 °C	o-Xylene/ dry ice
-32 °C	m-Toluidine/ dry ice
-41 °C	Acetonitrile/ dry ice: Put the acetonitrile into the Dewar with your thermocouple, slowly add dry ice until you hit your desired temperature. Do not add too much dry ice or you'll freeze the MeCN solid.
-42 °C	Pyridine/ dry ice
-47 °C	m-Xylene/ dry ice
-56 °C	n-Octane/ dry ice
-60 °C	Isopropyl Ether/ dry ice
-77 °C	Acetone/ dry ice: Slowly adding acetone to dry ice will minimize the amount of dry ice you need to handle. Alternatively, you must slowly add dry ice to the acetone or the large volumes of carbon dioxide produced will cause rapid bubbling.
-77 °C	Butyl Acetate/ dry ice
-83 °C	Propyl Amine/ dry ice
-83.6 °C	Ethyl Acetate/Liq N2
-89 °C	n-Butanol/Liq N2
-94 °C	Hexane/Liq N2
-94.6 °C	Acetone/Liq N2
-95.1 °C	Toluene/Liq N2

Temperature	Mixture Composition
-98 °C	Methanol/Liq N2
-100 °C	Ethyl Ether/dry ice
-104 °C	Cyclohexane/Liq N2
-116 °C	Ethanol/Liq N2
-116 °C	Ethyl Ether/Liq N2
-131 °C	n-Pentane/Liq N2
-160 °C	Isopentane/Liq N2
-196 °C	Liq N2

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1. Blatchley, Ronald C. " The Joys of Liquid Nitrogen. " *J. Chem. Educ.* **1997** *74* 616.
2. Nolan, William R.; Gish, Thaddeus J. " The authors reply to "The Joys of Liquid Nitrogen." *J. Chem. Educ.* **1997** *74* 617.
3. Nolan, William T.;Gish, Thaddeus J. " The Joys of Liquid Nitrogen. " *J. Chem. Educ.* **1996** *73* 651.

Contributors

- Chemotoplex, Burk, Kiwi

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Distillation

Distillation of compounds is a method of separation which exploits the differences in boiling point of a crude mixture. Several methods exist:

Short Path (simple) distillation

1. Clamp the distillation apparatus to monkey bars in a well ventilated hood.
2. Run water through the condenser such that it fills from the bottom first (when using a Liebing, Allihn or Graham condenser condenser. It is not quite as important when using a Dimroth condenser.)
3. Place flask (1) in a cool bath of oil, sand or on a heating mantle.
4. Place receiving flask 6 away from heat source - sometimes it is advantageous to place it in ice.
5. If your distillation setup allows for the inclusion of a thermometer, insert it. Make sure your thermometer goes to temperatures HIGHER than the ones you will be boiling to prevent damage to the thermometer.
6. Slowly heat flask 1 and allow the condensation to collect into flask 6.
7. Do not heat oil baths above 200 C. Consider Vacuum Distillation for high boiling compounds to prevent injury and facilitate separation.

Fractional Distillation

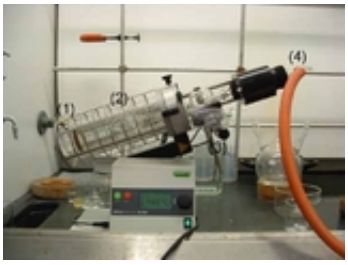
Fractional Distillation involves the use of a fractionating column.

Vacuum Distillation

When preparing to perform a vacuum distillation, use a *pressure-temperature nomograph* to determine what the adjusted boiling point of your compound will be.

1. The vacuum will quickly remove air from porous boiling chips, so a magnetic stir bar or gas bubbler is required in flask 1 to keep the rate of boiling under control.
2. Apply vacuum to the rig via 5 before heating flask 1. Heating the sample first may cause it to bump over into 6 when vacuum is applied.
3. Slowly heat flask 1 and allow distillation to occur as you would with a simple distillation. Often times during vacuum distillation the boiling point range is greater that it is during a simple distillation.
4. Release the vacuum before attempting to remove any flasks from the rig

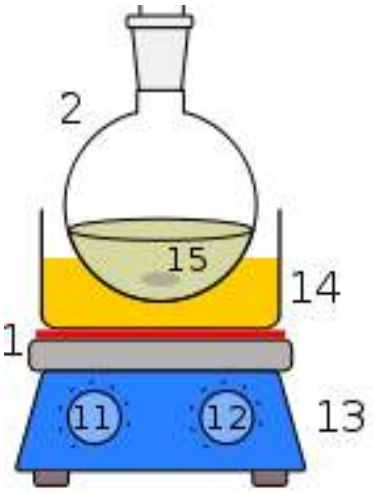
Kugelrohr Distillation



Separation of small amounts of compounds with close boiling points is difficult in a fractional distillation setup and can alternatively be performed via Kugelrohr Distillation. The setup is shown in the image above. Typically high boiling compounds are used and vacuum is applied. To perform a Kugelrohr Distillation:

1. Place compound mixture in small round bottom flask (see figure to right). The amount of compound should be small enough that, when the round bottom is tilted horizontally, it does not spill out.
2. Attach Kugelrohr flasks - typically two additional flasks are used.
3. Assemble Kugelrohr, placing the round bottom flask inside the heating jacket, keeping the two Kugelrohr flasks outside. Typically there is a "shutter" that can be used to reduce the amount of heat transfer from the heating jacket to the first Kugelrohr flask - this should be closed.

4. Induce vacuum, if desired. If your Kugelrohr is so equipped, you can cool the external Kugelrohr flasks with an ice bath. Alternatively, the outer bulb can be cooled by slowly dripping dichloromethane onto the outer bulb with a seperating funnel (fumehood!).
5. Heat the Kugelrohr and start rotating motor until distillation occurs. If needed, most Kugelrohr setups will allow you to "insert" the second Kugelrohr flask into the heating jacket - by doing this and reducing the temperature slightly, it is possible to produce a more pure distillation. This can be repeated until you have run out of Kugelrohr flasks.



Contributors

- Kiwi, ChemJobber

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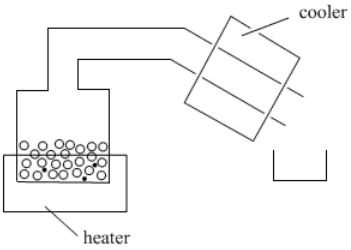
Distillation II

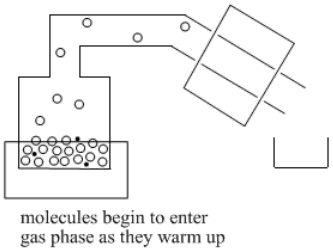
Distillation is a method of purifying organic compounds. It takes advantage of the fact that two different compounds probably have two different boiling points. Suppose two different liquids are present in a homogeneous mixture (they are completely miscible, or they mix completely together, like water and alcohol). If they have two different boiling points, one of the compounds will evaporate before the other one does. The more volatile compound (the one that evaporates easily) will leave the less volatile compound behind.

Distillation is probably a familiar word. Distilleries are factories that produce alcoholic beverages, such as whiskey, from the fermentation of grains, such as corn or rye. At the heart of the distillery is a large distillation apparatus. This "still' is used to purify the alcohol/water mixture by evaporation, leaving behind most of the other components of the grain. That process is slightly more complicated than the one described here, but it is similar.

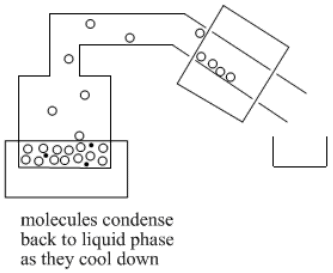
In distillation, a mixture is put into a container and the container is placed on a heat source. A tube leads away from the container. Sometimes this tube is cooled by cold, running water or ice; sometimes it is just left to cool in the air. There is also a second container to collect the liquid that distills.



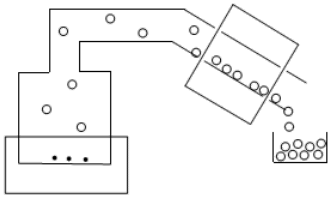
As the container or "pot" is heated, the volatile liquid begins to evaporate. Molecules enter the gas phase and begin to float through the tube leading away from the pot. In the lab, the tube above the pot is called the "still head."



Once molecules get past the still head, they reach the "condensor." Often the condensor is cooled by cold water that flows along outside of it. When molecules reach the cold condensor, they give up some heat energy and condense back into the liquid phase.



As enough molecules condense into the liquid phase, they begin to form drops of liquid. This liquid collects in a "receiver flask".



molecules collect in a receiver;
molecules with a higher boiling
point remain behind

Contributors

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Drying Solvents

As a general rule, consult a copy of *Perrin* (*Purification of Laboratory Chemicals, 4th Ed;* http://books.google.com/books?id=SYzm1tx2z3QC) for further details on how to purify your solvents. These days many laboratories will use a commercially available solvent purification system, others will distil solvents using more traditional techniques.

Tetrahydrofuran, dichloromethane, dimethylformamide, chloroform, acetonitrile, methanol, diethyl ether and toluene are all commonly used solvents, and in many cases they are required in anhydrous form. In some cases there are multiple ways to dry a given solvent. Here are some suggestions:

Specific solvents

- **THF** (Tetrahydrofuran): distilled from sodium benzophenone ketyl. Add sodium wire and benzophenone to a volume of THF (pre-dried over calcium hydride or 4A molecular sieves), heat at reflux/under nitrogen for several hours until the solvent turns deep blue in colour. This indicates the solvent is dry, and you can distill off the volume you require. With time (weeks-maybe months if used correctly) the still will turn orange, this indicates that it is time to make a new one!
- **DCM** (Dichloromethane): pre-dry over calcium hydride, then distil over calcium hydride... unfortunately no colorimetric indicator to tell you when the solvent is dry.
- **MeCN** (Acetonitrile): pre-dry by shaking with type 4A molecular sieves, the distil over calcium hydride. Dried acetonitrile can be stored over 4A molecular sieves.
- **Diethyl ether**: distilled from sodium benzophenone ketyl (see THF), will turn a deep purple/blue colour when dry.
- **Methanol**: For most purposes, drying over 3A molecular sieves overnight followed by distillation is sufficient. Alternatively, the methanol can be dried from magnesium methoxide. Magnesium turnings (5 g) and iodine (0.5 g) are refluxed in a small (50-100 mL) quantity of dry methanol (from a previous batch) until all of the magnesium has reacted. The mixture is diluted (up to 1 L) with reagent grade methanol, refluxed for 2-3 hours then distilled under nitrogen.
- **DMF** (*N*,*N*-dimethylformamide): Decomposes slowly at room temperature and more rapidly at reflux, releasing dimethylamine and carbon monoxide. This decomposition is catalysed by acidic and basic impurities, and standing DMF for several hours at room temperature with basic drying agents such as calcium hydride or sodium hydroxide leads to noticeable decomposition. Dry DMF can be prepared by drying overnight over barium oxide or 4A molecular sieves, followed by decantation of the drying agent and vacuum distillation (~20 mmHg is a sufficient vacuum to lower the boiling point over DMF to a reasonable value). Dry DMF can be stored over 4A molecular sieves.

General Precautions

As a general precaution ethers can produce explosive peroxides, making distillation of these solvents hazardous. If one is available, use a blast guard (really thick piece of pyrex? attached to a stand), and do not use stills once they have passed their use-by date. The process of distillation also removes the stabilisers that are added to the ethers, consquently distilled ethers should not be stored for long periods of time. For directions on handling sodium etc. consult 'reagant specific hazards'.

How to quench a solvent still

Stills that use metals (THF) should be quenched by pouring any excess solvent into a large container fileld with isopropanol or tert-butanol. The reaction may become exothermic, so addition of the solvent to the alcohol must be done slowly. The remaining metal in the still can be quenched like normal.

You can reuse 4A molecular sieves from most applications, though you should discard those used in the perperation of DMF. Sieves can be regenerated by heating at 350° C for 24 hours or under vacuum. The seives should cool in a desicator or they will become saturated with moisture again.

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Fractional crystallization

Fractional crystallization is a method of refining substances based on differences in solubility. It fractionates via differences in crystallization (forming of crystals). If a mixture of two or more substances in solution are allowed to crystallize, for example by allowing the temperature of the solution to decrease, the precipitate will contain more of the least soluble substance. The proportion of components in the precipitate will depend on their solubility products. If the solubility products are very similar, a cascade process will be needed to effectuate a complete separation. This technique is often used in chemical engineering to obtain very pure substances, or to recover saleable products from waste solutions.

Contributors

- Wikipedia

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Heating a Crucible to Constant Weight

As part of the procedure for the determination of the sulfate content of an unknown sample it will be necessary to accurately determine the empty weights of a set of crucibles. This is accomplished by first cleaning the crucible and then heating them in the flame of a Tirrel burner. They are then cooled and weighed. This process of heating and cooling is repeated until successive weighings agree to within 0.2mg. The procedure will, in addition, acquaint the student with the use of the analytical balance and the proper use of the desiccator. Be sure that you read the appendix section dealing with the use of desiccator.

Procedure

Wash and rinse four 10 ml crucibles and their lids. Identify each of the crucibles by means of existing visual differences. Carefully note in your lab notebook what these identifying marks are and assign a number to each crucible. Do not use marking pens or pencils to mark your crucibles. The high heat which will be used to take them to constant weight will obliterate such markings and more importantly will affect their weight in an unpredictable manner. The lids to the crucibles do not need to be taken to constant weight, however, they should be clean.

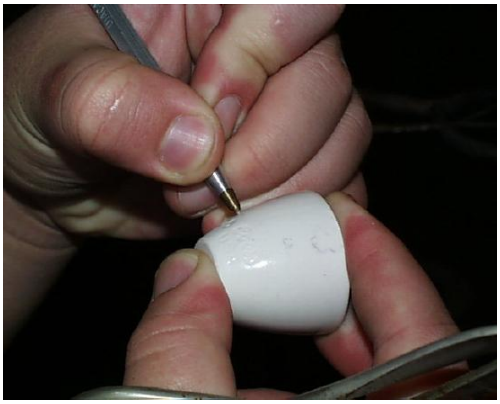
Place a Tirrel burner under the crucible and adjust the flame of the burner to give a non-luminous flame with a full gas supply. The tip of the flame cone should be just below but not touching the crucible. Heat the crucible at red heat in this manner for 5-10 minutes. Allow it to cool for a few minutes and then place it in the desiccator. When it has reached room temperature weigh the crucible accurately, to ± 0.1 mg, and then put it back into the desiccator. Reheat and reweigh it until successive weighings agree to within 0.2 mg.

NOTES

1. Both the hot and cool crucibles should only be handled with tongs. It is therefore imperative that the tips of the tongs be very clean. If they appear dirty or rusty be sure that you clean them. Dipping them into some dilute HCl is helpful in removing rust. Never allow the tips to come in contact with the desk top.
2. Never touch a red hot crucible with the tongs. The high heat used will soften the enamel enough so that some it will stick to the tongs and thereby lead to erratic weights.
3. Crucibles should never be placed directly on your desk. Obtain a piece of aluminum foil which can be used to place the crucibles and tongs.
4. Make sure that the plate in the desiccator is completely clean. Also check to see that crucibles sitting in the holes of the plate do not touch any part of the wire gauze which separates the desiccant from the rest of the desiccator.

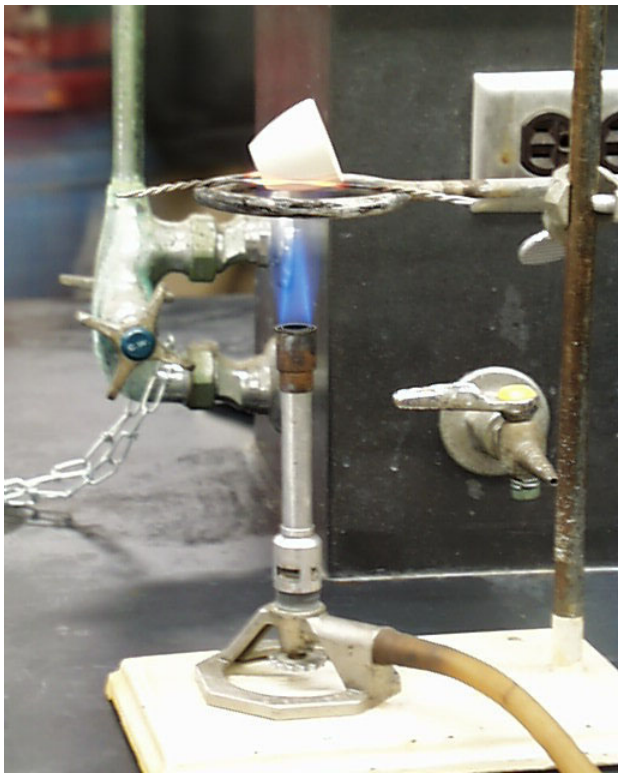
Demonstration

Your first exercise teaches you some skills on the proper use of the laboratory burner (in this case called a Tirill Burner), the adjustment of the flame and the proper placement of a crucible which is to be heated to constant weight.

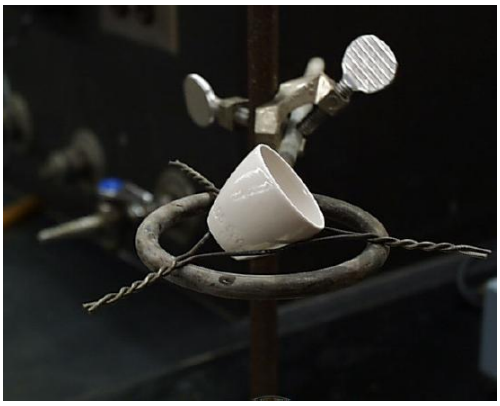
You ought to make sure at the outset that the crucibles you use have indelible identifying marks on them. Sometimes there are indentations left during the manufacture of a crucible which will allow you to distinguish one from another. More likely, there will

be a letter or number written into the side by a former student, such as the one shown at the left. Note the "A" scratched into the glossy surface. This can be done with the diamond pencil available in the lab, as shown at the right .

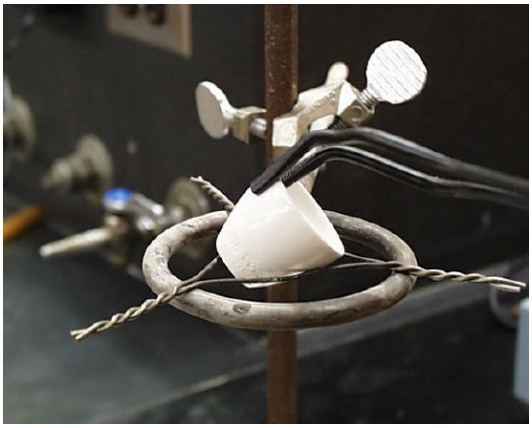



The hottest part of the flame is at the top of the bright cone of oxidation. The zone beneath the sharp point of the cone is filled with a rising mixture of cool gases not yet in the process of combustion. Although the rim around this zone is quite hot, the gases inside are essentially at room temperature. See that placement on the left. Such a placement is not recommended Note the correct placement of the crucible in the photograph at the right.


The crucible may be placed right side up, as in the left photo, or on its side, as in the right photo. Heating it on its side is preferred because the overall strain on the ceramic material at the high temperatures used is somewhat less.

The crucible ought to be heated to incandescence for 5-10 minutes (left). At the end of this time, remove the flame and allow the crucible to cool on the iron triangle for a few minutes (right)

When transferring a crucible to the dessicator tongs must be used. If the crucible has been allowed to cool, you may use bare tongs (left), but if you must transfer a hot crucible, make sure that you cover the ends of the tongs with aluminum foil (right) as the paint on the tongs might melt onto the crucible and change its weight. Make sure you grab the crucible on the edge as shown. Don't try to pick up a crucible by squeezing the tongs on the outer rim both because the crucible may slip from your grip owing to its slick walls. There is also the possibility of breaking a hot crucible that way.

Place the cool crucible into one of the holes in the plate in your dessicator and cover until it has reached room temperature. At that time you may remove it for weighing.

If a crucible is not at the temperature of the balance compartment it will likely show a weight different from that it would show were it at the same temperature. If it is hotter the weight will be slightly less, if colder slightly more owing to the production of convection currents which affect the apparent mass. Here are some photos to prove the point. (Please note that two separate analytical balances had to be used for this sequence of photos so as not to interfere with student use. The final agreement is within that which is routinely observed for two separate balances.) A dry cold crucible is weighed to the nearest 0.0001 g.

The crucible is then heated to incandescence for five minutes, as shown at the left. The fire is extinguished and the crucible is allowed to cool for five minutes.

Its apparent weight is less by more than four milligrams.

It is allowed to cool for an additional five minutes.

Its exhibited weight is still 0.0003 g less than that of the cold crucible, above.

Finally, after an additional five minutes of cooling, the crucible exhibits a weight slightly greater than that of the cold crucible, above. The agreement here is within that which is routinely observed for two separate balances. This cooling sequence took place outside the dessicator. The amount of time necessary to achieve thermal equilibrium with the environment will likely be somewhat longer when you let the crucible cool in the dessicator.

Contributor

- Oliver Seely (Professor of Chemistry, Emeritus; California State University Dominguez Hills). This content are in the public domain and may be copied without restriction.

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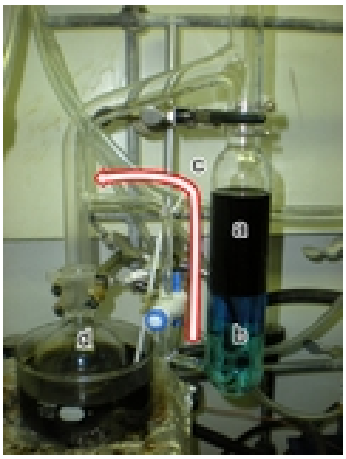
Liquid-Liquid Extraction

Liquid-Liquid extraction is a method by which a compound is pulled from solvent A to solvent B where solvents A and B are not miscible. The most common method of liquid-liquid extraction is performed using a *separatory funnel*.

Liquid-Liquid Extractor

Compounds which are poorly miscible in organic solvents but highly miscible in water can be extracted into organic compounds either by (1) repetitive extraction with a separatory funnel or (2) by using a liquid-Liquid extractor.

Extraction methods differ depending upon the *density* of the solvent being used. Solvents more dense than water will require different glassware (or supplemental glassware) vs. solvents that are less dense than water. There are presently a number of setups that can do both. By adding a removable fritted glass tube, and closing the solvent return tap, the setup below can be used to extract water continuously with a solvent less dense than water (such as diethyl ether).



Liquid-Liquid Extraction with solvents more dense than water

Using a setup purchased from Sigma-Aldrich, the method can be accomplished as depicted below in the extraction of methylene blue from water into methylene chloride:

1. The stopcock is closed.
2. Methylene chloride is poured poured into the trap until it is to the level of the stopcock (b).
3. The aqueous solution of methylene blue is then added to the top of that layer of methylene blue (a).
4. The stop cock is then opened.
5. Methlyene chloride is added until it flows into the round bottom flask (d) through path (c).
6. As the methylene chloride is evaporated it will condense by a water condenser (not shown, above the image) The liquid will follow through the aqueous solution and then through the glass path into the round bottom flask (c).
7. This process will continue for several hours to days.

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Solvent Partitioning (Liquid - Liquid Extraction)

This method is often called "extraction." Extraction means drawing a compound out of a mixture using a solvent. Solvent partitioning is more specific. It means compounds have a "choice" of two solvents that they can dissolve in. Some compounds dissolve in one solvent. Some compounds dissolve in the other solvent. That way the compounds in the mixture become separated into two groups.

Solvent partitioning depends on solubility. It depends on the solubility in two different solvents, though. It depends on an equilibrium: does the compound dissolve more in solvent A, or solvent B?

Solvent partitioning requires two solvents that are not miscible in each other. Usually one of the solvents is water. The other solvent is a liquid that does not dissolve very well in water, such as diethyl ether (this is the most common type of ether, and it is often called simply "ether"). If you look closely at a mixture of ether and water, you will see two layers because the two compounds do not dissolve very well in each other.

It's important that the two solvents are immiscible, because then it is easy to separate them from each other. The top liquid can be drawn off with a pipet, or the bottom layer can be drained out via a stopcock. The compounds that dissolved in the ether have thus been separated from the water-soluble compounds. Because ether evaporates very easily, the compounds that dissolved in the ether can also be separated from the ether (see "distillation"). As a result, purer compounds can be obtained.

Contributors and Attributions

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Packing Columns

Column chromatography in chemistry is a chromatography method used to purify individual chemical compounds from mixtures of compounds. It is often used for preparative applications on scales from micrograms up to kilograms.

- Packing Normal Phase Columns
- Packing Reverse Phase Columns
- Packing Size Exclusion Columns

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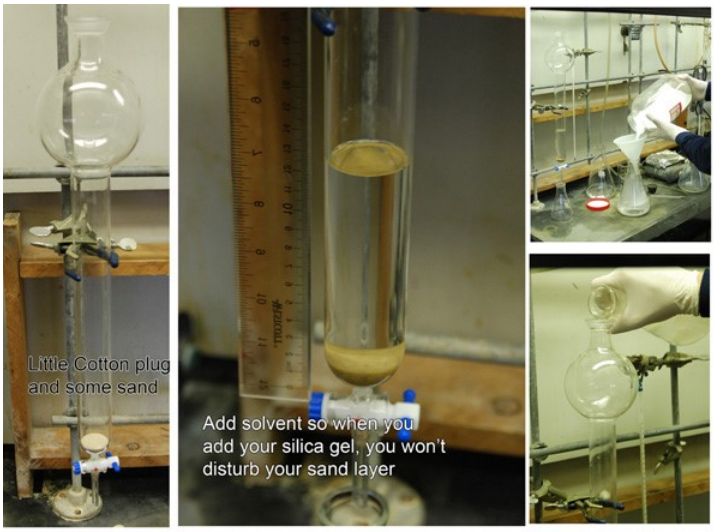
Packing Normal Phase Columns

"**Normal Phase" chromatography** is used to seperate compounds on the basis of their polarity, the the least polar eluting first. This is typically accomplished by using silica gel, which is avaliable in various qualities and particle sizes. The phrase "Normal phase" is meant to distinguish it from reverse phase.

Packing the Column

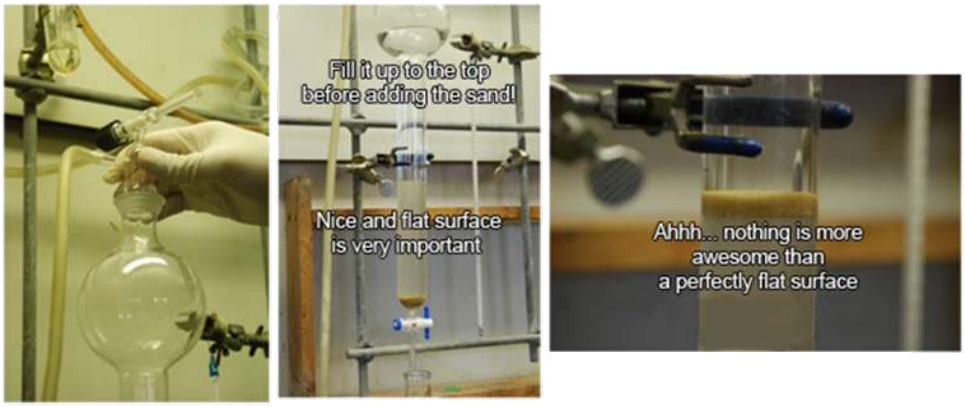
The most important part of running a column is packing it, though I don't think that's where the bulk of the confusion comes in. I think most people, when they enter into a lab, just don't know what size column to use for the sample they're running - and I'll get to that this week. But first, a photo montage on how I pack my columns:

Phase 1: Preparing the Column



From the above photo, you can see that I like to start out with a cotton and sand plug. The cotton keeps the sand from grinding on the stopcock. You can get these things fitted with a glass frit if you take it to your glassblower… but I have never seen the need for that and don't find establishing this plug to be particularly challenging. Second step is adding enough solvent (in this case 13 cm) such that when you pour stuff into your column, you won't molest the nice sand layer at the bottom. For this column, I was running chloroform. Nasty stuff, but it's fun to run columns on. On the far right, you can see how one prepares the slurry - just dump silica gel into an Erlenmeyer flask filled with solvent. Stir it up good, (you don't want chunks) and dump it in! w00t.

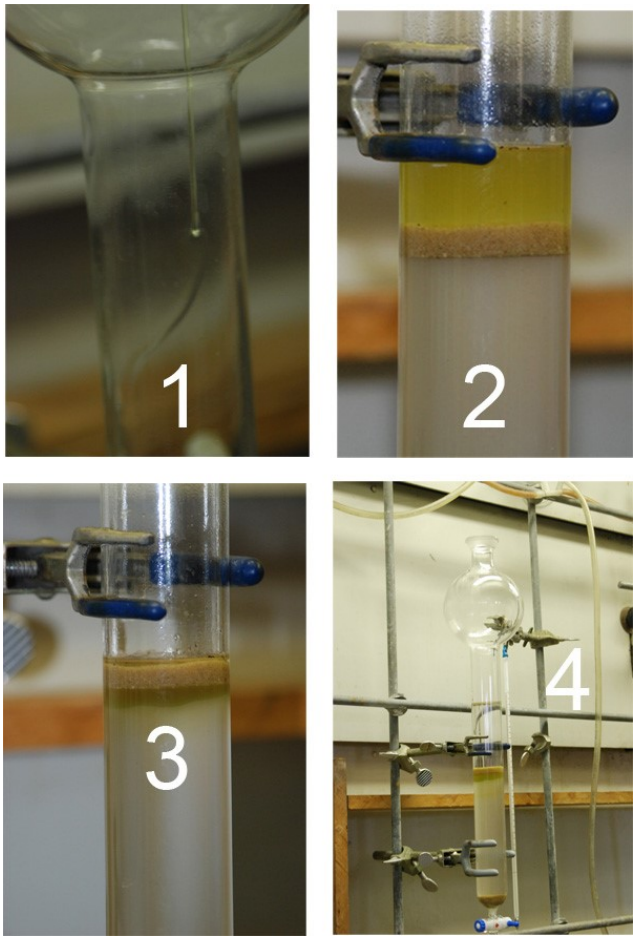
Phase 2: Packing the Column



Pressurize the column to pack it. Hopefully you added enough silica gel. If not, just add more. Nothing big about that. Once you're satisfied with the amount of silica gel you have, fill the column up with solvent to the top - make sure your silica layer is FLAT -

and add sand gently. If you have enough solvent, the sand will gently float down to the surface of the silica, where it will provide a comfortable layer of protection against splashing solvents. Blow the solvent all the way down to the sand level. Running solvent through the column at modest pressure will help you prevent cracking later on. Don't over pressurize a column - it's still made of glass.

Phase 3: Loading the Column



So, in the 3rd and final photo montage, we can see how one loads a column. This isn't too surprising, I think, since it involves just adding your sample (dissolved in toluene or the least polar solvent you can dissolve it in) to the sand layer. You can see in photo 3, the material is allowed to load onto the column. I usually do this via gravity until the column stops dripping. *MOST* of the time, your column will stop dripping once the solvent level reaches the silica gel (it will dry out the sand, but that's fine). Volatile solvents like pet ether and pentane cause problems with this, but it's not a big deal. Rinse the sides of the columns with a pipette of whatever you used to load it, allowing it to load the sample fully into the **silica gel** (not the sand!) and then top it up (gently at first) with your solvent.

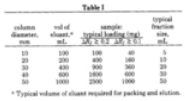
This method gives me separation essentially every time for me on the first run, even with obnoxious Rf's. This obviously doesn't address dry packing samples or the myriad of other ways you can pack a column…

Choosing a column based upon size

This is possibly the toughest aspect of column chromatography and the least important. Selecting the appropriate sized column, imho, falls way behind the ability to properly pack and load a column. You could, even in practice, use the same column for everything from 100 mg to 5 g samples. Through the years I've heard that there's a 20:1 silica to sample mass ratio that you should employ (not substaniated) or that the length of the column is the inverse of the Rf in decimeters (?!) or some other nonsense like that. What I have posted below are 5 "typical" column sizes that can be used from everything from 40 mg to 20 g. I have used each one to great affect for sample sizes in between.

Column 1, you can see, has the inner diameter of a pencil whilst column 5 has the inner diameter of… hugeness. Let's say, for our purposes, all the columns are filled to about half the column length.

Scientists, many centuries ago published a table on this stuff and it is shown to the right. You can read the full article here. Having said that scientists have determined the best size I'm going to now say that there are no real rules to the picking of the column, since the amount of silica gel you use, the length of the column, your solvent system… all these things go into making a decision. One thing you should avoid is making a lot of compounds that are really hard to separate on a column. Maybe this isn't avoidable? I dunno. There's nothing wrong with running two columns, if you must, but you certainly don't want to run more than that.



There is also the issue of the "pipette column." You can run those, you know, if you want. I tried to run one on a 40 mg sample once, but I found that short packing column 1 is way easier - even if you can't just chuck the column into the glass box when you finish it.

You can usually get columns made by your lazy glass blower for cheap - typically far cheaper than if you had ordered them from Aldrich. We get ours made for about $6 plus the cost of the glass and the stop cock (usually another $20.)

That's about all I can really offer on this subject. I myself use columns 1, 3 or 5 for almost everything I run between 200 mg and 3 g when I need to run a column.

To recap, **things I don't do:**

- I don't weigh out silica gel. That's just gross and you'll get silica gel lungs.
- I don't really stress over the size of the column because it's not *that* important.
- I don't believe anyone can create hard-and-fast rules on column sizes. Though I gave it my best shot.
- I don't do massive scale on compounds that is hard to separate on a column.

Mobile Phase Selection

A discussion on column chromatography wouldn't be complete without touching on the subject of the mobile phase. What is it that makes us choose a mobile phase? It becomes almost instinct, sorta like what kind of solvent you should run a reaction in to get the best yields. But it's not instinct we are born with, it's instinct we must develop. If you take it into consideration that there are many different solvent systems you can run, then you should appreciate that I can't possibly cover them all.

Normal phase silica can run a host of solvents - from the least polar, like cyclohexane (an expensive column…) to outrageously polar like methanol/water. The solvent systems can also become incredibly complex, with the addition of acids or bases, depending on how you need to move a product. For instance, it wouldn't be outrageous to run a column on some cyclodextrin containing molecule in 5:4:3:2 - butanol:ethanol:water:ammonium hydroxide. You could substitute the ammonium hydroxide for acetic acid (depending on how protonated you want to run your column.)

You can also pre-neutralize an acidic column by running a 3% solution of triethylamine in hexanes on it… but you have to keep in mind that chloroform will reverse any hard work you put into neutralizing it (unless, of course, you run the chloroform through activated neutral alumina).

And then there's the perpetual myths that surround solvents - like methanol eating silica[1] or water not working on normal phase silica (It's not an ideal mobile phase at 100%, that's true).

But, here are some good solvent mixtures I have come across that are always a good first shot:

- *Hexanes:Ethyl acetate* - so standard it hardly needs mentioning. Greasy stuff works great on this.
- *Methylene Chloride:Ethyl acetate* - again, pretty standard. More polar than the above, but it's good

- *Chloroform:Methanol* - at about 2-3% methanol, this solvent system is the tits for almost everything I do, which usually involves separation and isolation of macrolactams.

Compounds sensitive to heat

pet ether:ethyl ether - the solvent system your grandpa would have used. Light boiling solvents are wonderful when you're working with sensitive compounds that decompose under the heat of a rotavap. You can also use pentanes and methylene chloride in this instance, too.

I keep bottles of all those solvents on my bench in squirt bottles and a handy 10 mL graduated cylinder,which helps me make a number of solvent systems for quick TLC tests. Don't forget to make a quick reusable TLC spotter. (the needle in that link is too large. I use a much smaller needle).

Gradients:

Because no one has had the foresight to create a great gradient TLC chamber, the use of a gradient is arrived at after realizing that good separation on a static system appears not to work. Tight Rfs being a clear sign that a gradient may be useful. Gradients are convenient because sometimes a family of related compounds will work with just one gradient solvent system, if you ramp the gradient up slowly enough, you'll almost always get some separation. Of course, ramp it up too much (and too quickly), *any nice seperation you had will disappear*. The key is simply not to suddenly go from, say, 0% ethyl acetate in hexane to a 50% mixture. For various reasons, this could cause your column to crack, most specifically any resolution you were trying to obtain with running pure hexanes will likely be lost by such a huge polarity jump.

I dunno if there's a rule of thumb, but I generally limit myself to an increase of 10-20% of the total concentration each time I add solvent to a column - for instance, If I'm running a chloroform:methanol column (5% MeOH), I'll start at 0% methanol and increase the mobile phase by half to one percent each time I add more solvent. Methanol is particularly tricky, because adding too much too quick will crack your column due to exotherm effects. Other solvents seem to be more forgiving.

Amines

I have run very few columns with amines on them, but have run enough to know that the more you have, the worse the column gets. You can cut back on streaking by deprotonating your column with a solution of TEA in base or running with some ammonium hydroxide (if you have a polar compound.) Keep in mind that halogenated solvents (in particular chloroform) can be acidic and are generally bad news for compounds with amines. You could also just run a column in basic or neutral alumina.[2]

References

1. Silica appears to be mildly soluble in methanol. Unless the column heats up because the solvent is suddenly switched to methanol, I've never found it to be a problem…
2. Don't buy alumina TLC plates on glass. Buy the ones on Aluminum. The alumina falls right off the glass when you cut the plates.

Contributors

- Kyle Finchsigmate

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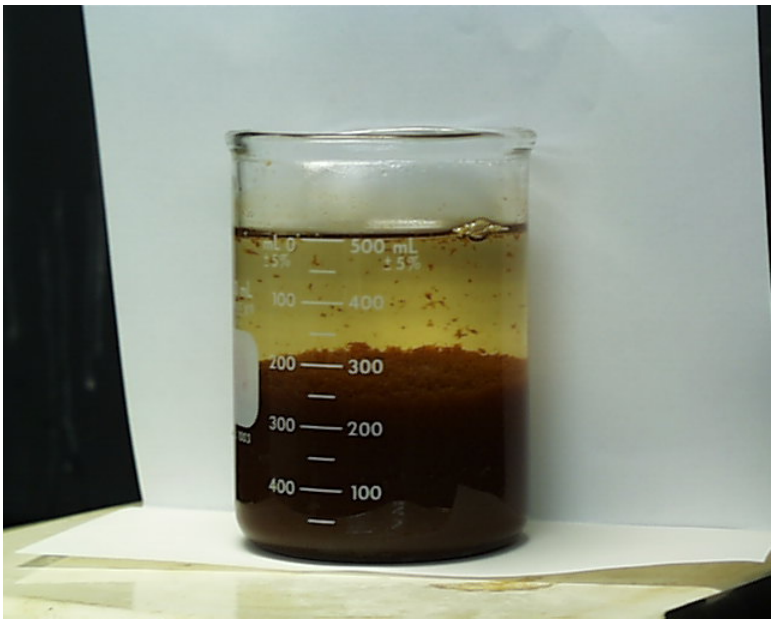
Precipitation from a Homogeneous Solution

If a precipitating agent is produced over a long period of time in a homogeneous solution the level of supersaturation remains low and compact crystal precipitates usually result instead of coagulated colloids. The resulting suspension of precipitate is compact, crystalline and easily filtered, whereas a precipitate formed by the addition of a precipitating agent is not easily filtered owing to a high level of relative supersaturation at the point where the reagent is added.

500 mL 0.02 M $Fe_2(SO_4)_3$ was prepared and 20 mL 12 M NH_4OH(aq) was added to complete the precipitation of $Fe(OH)_3$ (s) according to the equation

$$Fe^{3+} + 3NH_4OH_{(aq)} \rightarrow Fe(OH)_3(s) + 3NH_4^+ \quad (1)$$



The resulting solution is shown in the photograph at the left. A second sample of 500 mL 0.02 M $Fe_2(SO_4)_3$ was prepared and 7.2 g urea, $(NH_2)_2CO$, was dissolved in the ferric sulfate solution. On the addition of heat the generation of ammonium hydroxide occurs according to the reaction

$$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4OH \quad (2)$$

After two hours at a temperature just below the boiling point, the resulting precipitate settles in a thin layer on the bottom (photo at right). This precipitate has a texture considerably different from that on the left which is flocculent and of low density. Note: this reaction seems to be pH sensitive. A first attempt at preparing the demonstration on the right included adding a small amount of hydrochloric acid to the ferric sulfate so as to assure that all ferric ion would remain in solution. After two hours of heating no precipitate had formed. From this experience one would presume that if this method were to be used as part of a quantitative analysis the pH would have to be adjusted to a point just below that which is high enough to initiate precipitation of ferric hydroxide before starting the process of heating the solution with urea added.

Here here are two time lapse videos of the process.

- ,@api,deki,files,127122,homogen2.wmv
- @api,deki,files,127123,homogen1.wmv

Contributor

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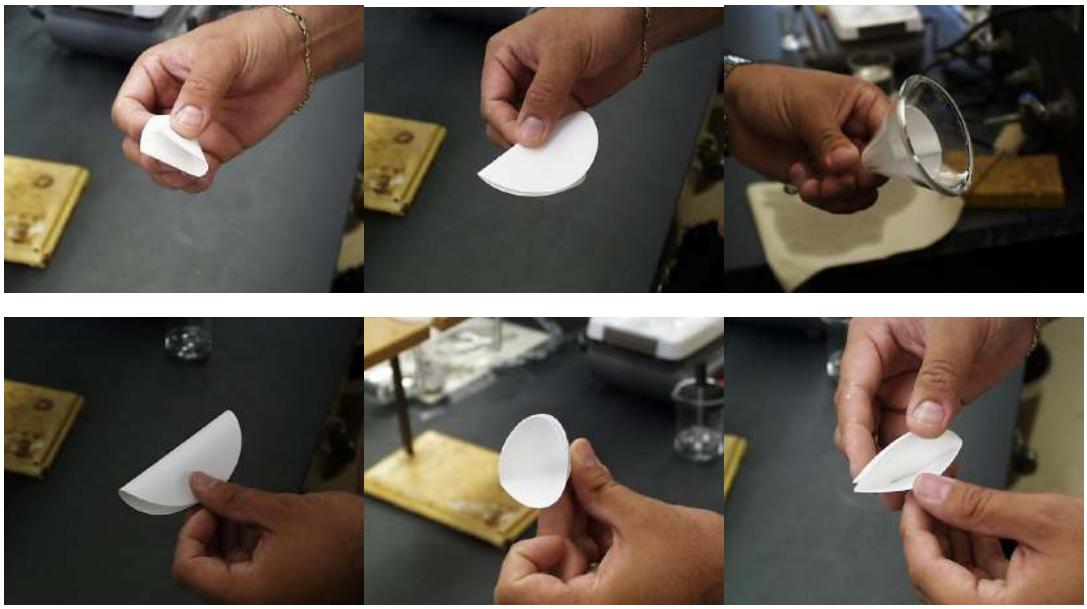
Preparing your Filter Paper

Folding a piece of filter paper for insertion into a conical filter consists of a simple set of steps shown here in the six photographs below. From left to right and top to bottom, one first folds the round piece of filter paper in half and creases it. Then it is folded again and creased to produce a quarter circle. One outer layer of paper is separated from the other three (not two and two!) and the opening made wider by squeezing slightly together at the creases. The conical shaped piece of filter paper is placed into a glass or plastic funnel and wetted slightly with distilled water from your wash bottle:



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Proper Use of a Buret

The volumetric analysis exercises will make use of a 50 mL buret.

Storing Buret Tubes

First of all, you MUST learn how to put your buret away properly in the buret cabinet. Here's a picture of the buret cabinet on the left. On the right we have three burets stored properly. Note the arrows pointing to the holes into which one "ear" of the petcock valve is placed. Placing the buret in the cabinet this way assures that the buret will not fall out when the cabinet is opened.

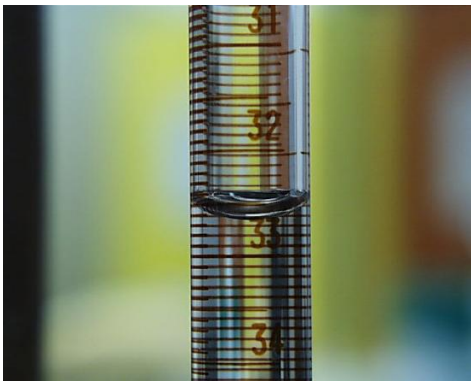

But get a load of these two pictures below. Notice how the burets have been placed precariously so that just a quick opening of the door will allow either to slip out, fall on the floor and break. So make sure that you exercise due care in the storage of your buret. I want everyone to know how to store their burets safely after the first period during which they are used.


The "petcock" or draining valve which allows titrant to flow out the nozzle is made of teflon. On one end is a handle for opening and closing it. On the other is a tightening nut, a rubber o-ring and a teflon spacer. Your buret ought to be assembled as shown in the photo at the left with the teflon spacer rubbing against the buret and the rubber o-ring between the spacer and the nut. Otherwise there is a tendency for the nut to loosen with repeated turns of the petcock.

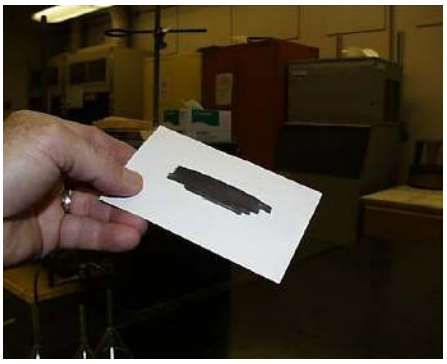
Read Buret Tubes

When reading a buret it is important that your line of sight be in a direction perpendicular to the buret column. Note in this photograph that although the bottom of the meniscus is clearly outlined, the variability of the background does not always offer

such visibility. More likely than not, the bottom of the mensicus is lightened by random reflections in the laboratory. Such variability can produce errors of several hundredths of a milliliter. All buret reading should be done using a buret card.

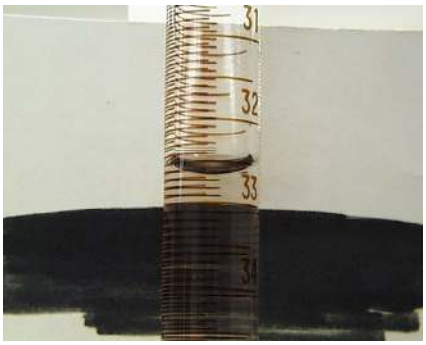


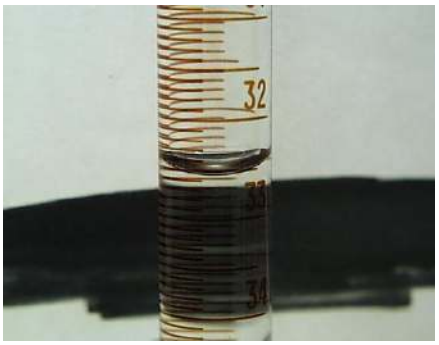
The black streak is produced using a felt tipped pen and offers the student a constant dark reflection against a white background for higher precision in determining relative titrant volumes.



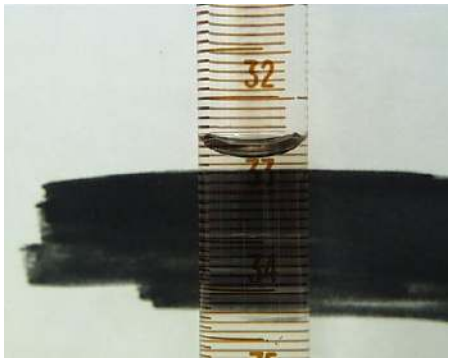
Another problem often encountered by students is poor drainage. Note that this buret has droplets which stick to the inner wall. If your buret shows such droplets, use one of the buret brushes and Alconox to wash the inner surface. If that doesn't improve the drainage, ask your instructor to draw some dichromate/sulfuric acid cleaning solution into the buret for more thorough cleaning.

A 50 mL buret can be read to ±0.01 mL, but in order to be able to interpolate to the last digit, the perpendicular line of sight must be followed with meticulous care.

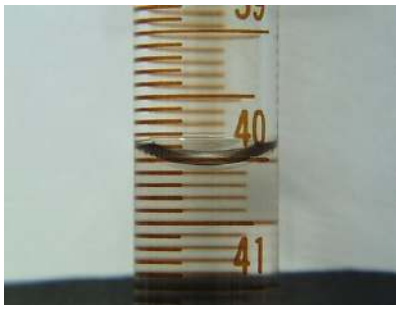




Note in these two photographs, one in which the line of sight is slightly upward and the other in which it is downward, that an interpolation is difficult because the calibration lines don't appear to be parallel.

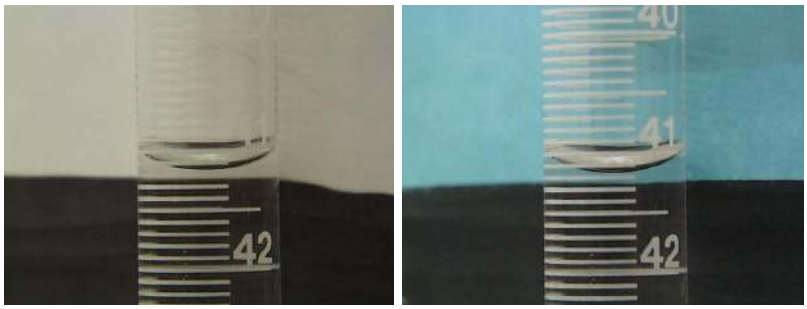


The use of a buret card and a line of sight perpendicular to the buret column are techniques which must be adopted to achieve maximum precision. Note the final photograph in which the level of the meniscus bottom can be determined to within ±0.01 mL. What reading would you report for this buret volume?



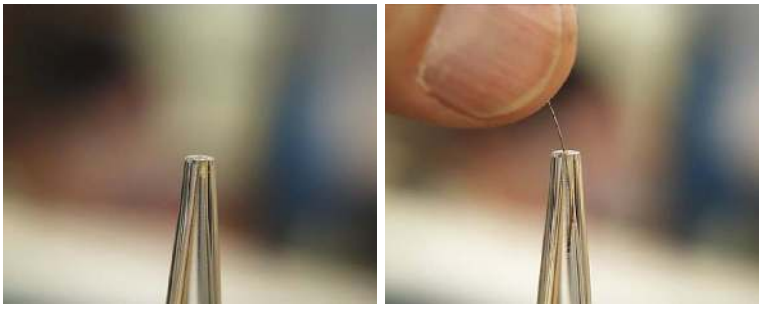
A buret card ought to have a black streak with a distinct horizontal zone of black against white. Moreover, when held behind the buret, the upper limit of the black streak ought to be placed just under the meniscus, so that the bottom of the meniscus can be seen distinctly against a narrow zone of white. Note in the photo at the left that the apparent level of the meniscus is different from that on the right. Since placing the black streak just under the meniscus is more repeatable than at some variable distance, the close placement is recommended.

If you are assigned a buret with a white instead of a blue or red scale, a buret card other than white ought to be used. Notice in the photo at the left the white scale is rendered invisible by the white card but can be seen more clearly with the pastel blue card on the right.

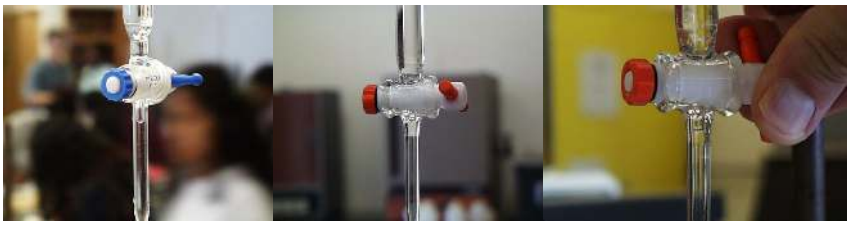


Cleaning Buret Tubes

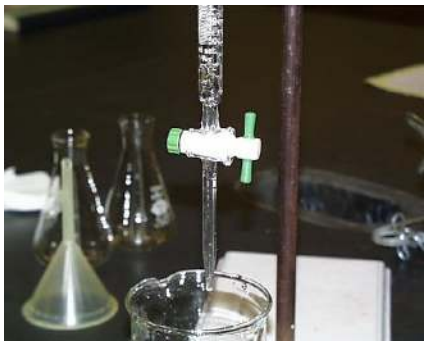
Pipettes and burettes accumulate inert solid material which must be removed from time to time. Here at the left is the nozzle of a burette which has material which will not pass through. You may have to use a wire, available on the lower ledge of the burette case, to clean out this material. It is best to do it with the petcock valve removed so that when you do a reverse wash after poking it free, the material can be washed out at the point of the valve instead of at the other end of the burette cylinder.



A bubble in the nozzle of a buret will produce an inaccurate volume reading if the bubble escapes during a titration. Bubbles may be large and visible as shown above left or so small as not to be seen, above center. During a titration such small bubbles begin to move in the direction of the nozzle but may remain in place even though there is a moderate flow of titrant (above right). Even when the buret valve is wide open some bubbles remain in place until you take your eyes off them. Then they sneak through the nozzle and ruin your titration.

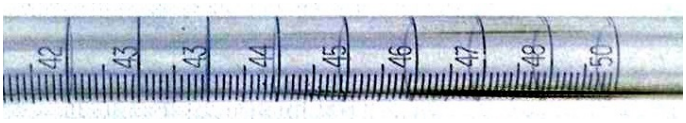


The quickest way to get rid of nozzle bubbles is to fill the buret with titrant and open the valve. The pressure of the titrant in a full buret is often enough to force all bubbles out. If that doesn't work, two other methods can be used. The first is to use some chaotic suction. The student on the left has first rinsed then filled her buret with titrant. Her attempt to force out all bubbles by the first method didn't work, so she opens the buret valve, letting the contents begin to drain into a beaker. She uses her bulb momentarily to suck air through the nozzle. The mixture of small bubbles which are produced reenter the nozzle. The chaos and production of small bubbles (right) is often capable of driving out all bubbles from the nozzle

If that doesn't work, immerse the nozzle of the buret in a small beaker of titrant and while using the bulb to reverse the flow of titrant, open the valve (right). The bubble will emerge from the top of the valve and rise to the top of the column of titrant, but no air will be able to enter the mouth of the nozzle.

Finally, a brand new buret, just taken out of the box, ought to be examined carefully, as ought a buret returned to service after having been in storage a long time. Production errors are rare but they do occur. Burets in storage may be there for reasons not connected with a lack of need. The image below shows a buret found at the University of Kentucky by Professor Jim O'Reilly a number of years ago. Its particular aberration is that it has two "43" mL designations and continues on to 48 (which is really 49 mL), then it jumps to 50. It is thought to have been made in the 1950s.



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Proper Use of a Desiccator

A desiccator is an airtight container which maintains an atmosphere of low humidity through the use of a suitable drying agent which occupies the bottom part of the desiccator. It is used both for the cooling of heated objects and for the storage of dry objects that must not be exposed to the moisture normally present in the atmosphere.

The desiccator you will be using is made of aluminum. The desiccant we will be using is anhydrous $CaCl_2$. An airtight seal is maintained by applying silicone grease to the surfaces where the lid and body of the desiccator meet. Be careful not to add too much grease. Once the desiccant has been added, the lid to the desiccator should not be removed any more than is necessary.

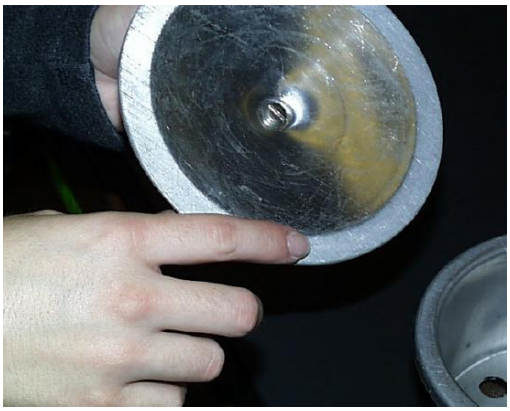
An ignited crucible or other very hot object should be cooled for about one minute before being placed into the desiccator. In either case, the lid of the desiccator should be slightly ajar for 30 seconds prior to complete closing. This will prevent a partial vacuum from forming as the heated air cools. If such a vacuum forms it might become very difficult to remove the lid without upsetting the samples within.

A dried sample should remain in the desiccator for at least 5 minutes before being weighed. If the sample is to remain in the desiccator for an extended period of time before weighing, the top of the weighing bottle of the lid of the vial should be put in place after 10 minutes of cooling.

Discussion

Several experiments will require some skill in using a desiccator. To open the desiccator, slide the lid gently as shown at left. If you feel or hear metal scraping against metal when you slide off the lid, then a small amount of silicon grease needs to be rubbed around the flat surface of the lid. Squeeze a VERY small amount of grease onto your finger, as at the right,


and rub it all around the flat surface of the lid.




The desiccator contains a plate with holes over a screen which covers granulated anhydrous calcium sulfate, a desiccating or dehydrating agent. The desiccator ought not to be left open except to transfer samples in or out of it.


The holes may be used to store samples in a dry environment.

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Proper Use of Balances

During the course you will be asked to make a variety of weighings. It is important for you to realize with what sort of accuracy these weighings should be made. Depending on the desired accuracy you should use the proper balance to make your weighings. There are two types of balances available to you in this course:

Top-loading balances

Located in the room adjacent to the laboratory. These will weigh to an accuracy of ± 1 mg and are suitable for most weighings of amounts that are specified to only two or three significant figures. Directions for the use of these balances are posted in the balance room.

Analytical balances

Also located in the room adjacent to the laboratory. These will weigh to an accuracy of ± 0.1 mg and must be used whenever you desire four or more significant figure accuracy. This will be the case when you weigh out samples of an unknown, primary standards or when taking crucibles to constant weight. Directions for the use of these balances are posted in the balance room.

VARIOUS TYPES OF WEIGHING

When mass amounts are specified in chemical procedures the following terms are commonly used:

a. "Weigh out about 2 g of ..... " This statement means that you are required to weigh an amount of approximately two grams. The accuracy to which this mass amount needs to known is not high and the top-loading balance will suffice.

b. "Accurately weigh out about 0.2 g of ...." This statement means that you should, with the aid of the analytical balance, weigh out an amount that is close to 0.2 g, but you must know the exact amount to an accuracy of ± 0.1 mg. Note that this does not mean that you must weigh out exactly 0.2000 g. An amount between 0.1900 g and 0.2100 g is perfectly acceptable. However, you must know the exact amount to the nearest tenth of a milligram. When weighing out triplicate samples it is not necessary that all three weights be exactly the same, indeed, it is poor procedure to attempt to do so.

RULES FOR ANALYTICAL BALANCES

The following rules summarize those procedures which must be followed in order to obtain accurate and reliable mass measurements with a single-pan analytical balance. Adherence to these rules will, at the same time, prevent damage to the balance.

1. Close the balance door, while weighing an object, in order to prevent air currents from disturbing the reading. When finished, the operator should close the balance door to prevent dust and dirt from entering the balance.
2. Only glass, ceramic, metal or plastic objects and containers should be placed in direct contact with the balance pan.
3. Do not handle objects to be weighed with bare hands. Moisture, grease and dirt on you fingers will affect the weight of the objects.
4. To be weighed accurately, all objects must be at room temperature. A warm object sets up convection currents inside the balance enclosure, which will make an object appear lighter than it really is. Also, warm air inside the enclosure is less dense than the air that it displaces and this also leads to a negative determinate error.
5. Never weigh chemicals directly in contact with the balance pan. Use containers such as beakers, flasks and weighing bottles.
6. All objects and materials that have recently been removed from a desiccator will absorb moisture and thereby gain weight. It is therefore good practice to record weights after identical time intervals. For example if you are taking crucibles to constant weight. Always record the weight of the crucible exactly 5 seconds after having placed the crucible on the balance pan. Using this technique it is possible to minimize the effect of moisture absorption.
7. The use of weighing paper must be strictly avoided when using an analytical balance.
8. Do not spill chemicals inside the balance enclosure. If a spill occurs, clean it up immediately.

Discussion

The images shown on this page are supplementary to the information given on the use of laboratory balances in your text book. This Web page and all direct links on it are in the public domain and may be copied without restriction.

One of the electronic analytical balances we shall be using is shown at the right.

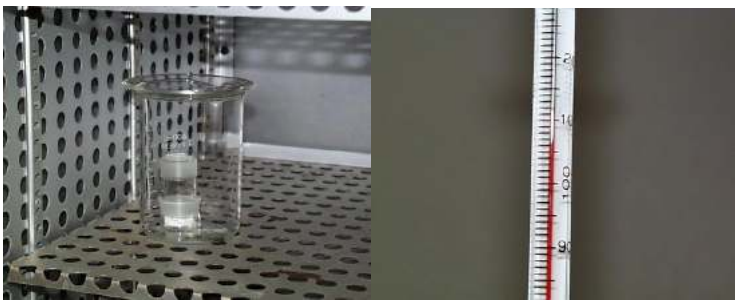
Your objective is to develop techniques which allow you to transfer samples of material from one container to another and to have confidence that you know the amounts transferred to a precision of one tenth of a milligram or one ten-thousanth of a gram, ±0.0001 g.

First, before weighing anything on this analytical balance, it needs to be "tared," or recalibrated to read 0.0000 g. When first turned on, or when left by the previous user, the balance may indicate something other than 0.0000 g. The Tare button needs to be pressed and released to effect this recalibration. The four images below illustrate this process.

An analytical balance is so sensitive that it can detect the mass of a single grain of a chemical substance. Thus, if a method of direct weighing is used, the substance ought to be added to the tared container which will hold it, NEVER directly to the pan or even to weighing paper placed on the pan. The container used should be completely dry and at room temperature, never at an elevated or reduced temperature. Even slight temperature differences can produce APPARENT changes in mass of the container. Finally, the container ought to be completely dry, inside and out. All that having been said, here are some images showing various correct ways of carrying out weighings using an analytical balance.

Regardless of which method illustrated below is used accurately to weigh a sample, the sample, placed in a weighing bottle set in the upturned cap in a beaker with a watch glass placed on top, must be first dried in the oven. You may identify your sample by marking the beaker but DO NOT mark the weighing bottle.

The ovens are kept at 110^{o}C, but our ovens may show slightly lower temperatures owing to the doors being opened repeatedly during normal laboratory activities.



The tried-and-true method of transferring a precisely weighed sample uses "weighing by difference," shown here. The empty balance is tared, then the weighing bottle with cap is placed on the pan and weighed to ±0.0001 g.

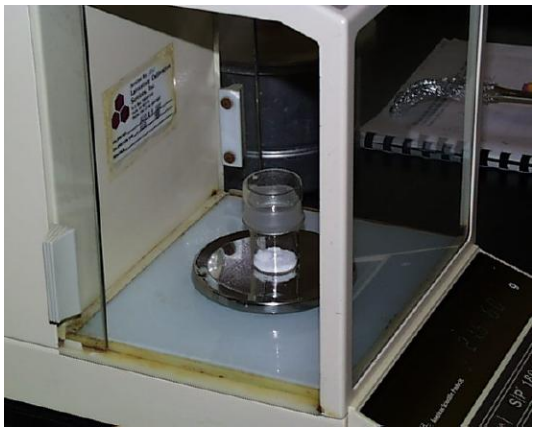
The weighing bottle is removed in a manner which avoids the transference of oil or other matter from one's fingers.

The cap is likewise removed from the weighing bottle.

The weighing bottle is tipped above the container to receive the sample and a small amount is allowed to fall out of the weighing bottle. The weighing bottle is tipped back up and tapped gently to make sure all of the substance falls back in the bottle and doesn't remain on the bottle rim. The cap is replaced and the bottle weighed once again. The difference between the first and second weighings represents the amount transferred. If your sample has a tendency to absorb water and thus to gain weight when exposed to the moisture of the air, this method MUST be used to minimize exposure to the atmosphere. Still, the method is not foolproof and has its own perils:

1. several transfers may be necessary until an amount close to that needed is added to the receiving container,
2. too much may be transferred the first time, forcing one to discard the entire sample ("Drat and blast, I have to start over," is a common epithet heard in weighing rooms),
3. sample which remains on the weighing bottle rim may be lost and produce a weighing error. This peril is repeated each time a transfer is attempted.



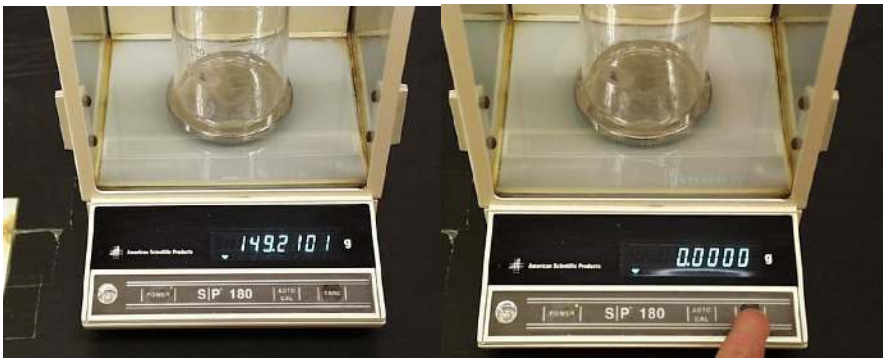


The direct transfer of samples to receiving containers is possible using modern analytical balances which allow one to tare a receiving container before the transfer is begun. Note the Erlenmeyer flask on the pan. The Erlenmeyer flask needs to be completely dry so that there will be no systematic error due to the evaporation of water.

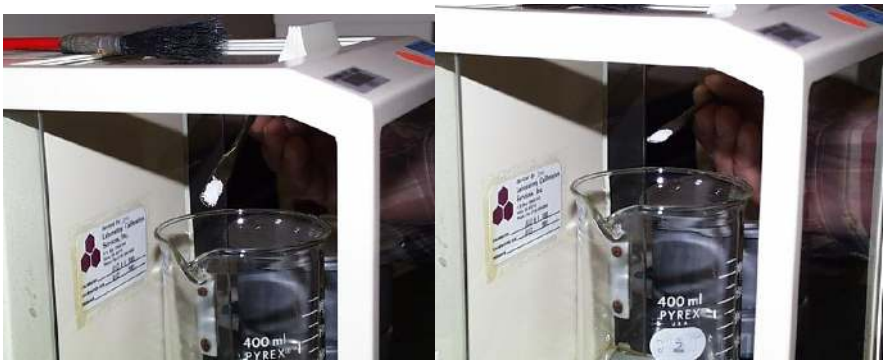
A spatula can be used to remove a sample from the weighing bottle and the sample placed directly into the flask.


This method has some perils associated with it: (1) one risks losing the sample on the outside of the Erlenmeyer flask due to the small diameter of the flask neck and (2) the point of entry is rather high; one must have good coordination to orient the spatula above the mouth of the flask. Advantage: The sample is placed directly into the flask and the mass read is that of the sample added. Eternal vigilance being the price of good results, note in the image at the right the particles of sodium carbonate which didn't quite make it to the bottom of the flask. The titration yielding the molarity of the hydrochloric acid standard for the percent sodium carbonate in soda ash experiment showed a precision within one part per thousand with the other titrated samples but only because both the stopper, which was removed gently before the titration, and the inside of the flask neck were rinsed carefully to dissolve the particles of carbonate and to allow them to drain into the body of the flask.

The mass limit of our analytical balances beyond which one receives an error message is 200.0000 grams. Even this 400 mL beaker can be placed on the pan. Note that its mass is just above 149 g.



Once tared, the sample may be placed directly into the beaker, as shown below.



The perils using this method are similar to those encountered during a direct transfer to an Erlenmeyer flask. The beaker must be clean, dry and at the same temperature as the room and the balance. The mouth of the beaker is rather high, so one must have good coordination to orient the spatula over the mouth without knocking it against the beaker or the windows of the balance, thus losing the sample.

You can still weigh your sample directly but do it in a manner which doesn't require as much care and coordination as that illustrated above by removing the beaker from the pan, adding your sample and replacing the beaker on the pan. The advantage of this method is that you have more room for sample addition and the placement of your hands, arms and the transfer spatula is less awkward, but the disadvantage is that you must check the weight of your beaker and sample after each addition; it is not good practice to remove excess sample from the beaker if you add too much. You must be sure that the removed beaker is placed on a clean and dry part of the bench so to avoid picking up any particles which will change your weight and decrease your accuracy. The removal and replacement of the beaker must also be done with a small folded piece of paper or paper towel so as to avoid adding weight to the beaker in the form of fingerprints.

Using the Top Loading Balance

Several top loading balances, precise to ±0.001 g, are available for your use in the balance room. Many professors of Quantitative Analysis do not allow them to be placed in the same room where the analytical balances are kept because students often use them to save time when they ought to be using the analytical balances.
First of all, the top loading balances are less precise by a factor of 10 and secondly, air currents around the pan can reduce that precision by as much as another factor of 3 or 4. But the top loading balance is the instrument of choice where precision is not of great importance. Here is one our top loading balances. It can be "tared" by pressing the front bar, as shown at the right

In the drawer below the top loading balances you will find weighing paper. This paper must be used ONLY on the top loading balances, NEVER on the analytical balances, because there is always the chance that some of the substance being weighed will stick to the weighing paper after the weight has been recorded thus producing an error on the low side. The precision of the top loading balances is ±0.001 and it is possible to see particles which have a mass of 0.001 g. Moreover, often one wants to weigh a reagent which is to be used in excess, and a precision of ±0.001 is well beyond what is needed for such a weighing.

Once a piece of weighing paper has been placed on the pan, and the balance set to 0.000 by taring it, a sample can be removed from the container holding it and placed on the pan, repeating the process as many times as are necessary until the weight of material needed is achieved, as shown here.

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SECTION OVERVIEW

Quenching Reactions

Quenching a reaction refers to the deactivate any unreacted reagents.

Topic hierarchy

Quenching Reactions: Grignards

Quenching Reactions: Lithium Aluminium Hydride

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Quenching Reactions: Grignards

Quenching Grignards

1. Remove your RBF from the oil bath, and place it in an ice bath. This tends to make the quench less angry. Leave the condenser on if you have one attached.
2. Add water, DROPWISE. Dropwise means dropwise! Be very patient, or you will create a volcano.[1] Continue adding water until what's in the RBF is no longer angry. Let stir about another five minutes.
3. Add 10% sulfuric acid, DROPWISE. Again, be patient. Keep adding--very very slowly--until the anger subsides. At this point, I usually let it stir for between 20 minutes and an hour or two, depending on what's convenient. Give any leftover magnesium and associated salts a chance to dissolve.
4. Extract into the solvent of your choice (often ether), dry, evaporate, do whatever else is necessary.

[1] Respect the induction period! Generally, it takes several seconds for the Grignard to unleash its wrath upon the water. If you happen to add MORE water during this period, you may end up painting your hood ceiling.

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Quenching Reactions: Lithium Aluminium Hydride

There are several ways to quench lithium aluminium hydride.

- **Dropwise** addition of a saturated aqueous sodium sulfate (Na_2SO_4).
- For each (one) gram of lithium alumninium hydride used, add **dropwise** one ml water followed by one ml of 15% aqeuous NaOH and, finally, 3 ml of water. Filter the resulting solid through a pad of celite. Rinse with solvent.
    - Alternatively, after the final water addition, the mixture can be diluted with diethyl ether and dried (anh. sodium sulfate, stir 15 minutes) to produce an easily filtered mixture, capable of being filtered through paper, if so desired. Evaporation of the filtrate gives the crude product. This method is especially useful for polar products with appreciable water solubility.
- Add 3 equivalents of sodium fluoride (NaF) followed by **dropwise** addition of a 9:1 THF:Water mixture.
    - Filter the resulting white solid through a pad of celite. Rinse with THF. This method will sometimes produce a finner solid that traps less of the desired product.
- **Dropwise** addition of an aqueous solution of Rochelle's salt (sodium potassium tartrate, $KNaC_4H_4O_6$)
- Recrystallize sodium sulfate from water and grind this with an equal volume of celite using a mortar and pestle. This mixture may be stored indefinitely. To quench your LAH reduction, add the celite/ hydrated sodium sulfate mixture to your reaction mixture one spatula full at a time. This will be exothermic and might cause the reaction to temporarily stop stirring, but keep adding the solid until the mixture resumes stirring. Once the solution has been quenched and freely stirs, filter through a fritted funnel, wash the solid with a small amount of THF or diethyl ether, and evaporate the solvent to obtain your product.

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Recrystallization (Advantages)

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This technique is no longer as widely used as it was before the advent of flash chromatography, but it's still quite useful! A particular advantage is that compounds can be recrystallized in amounts that are somewhere between streaky and impossible to column. Do you have over 50 mg of a compound that should be a solid?[1] Can you find something in the lab that will dissolve it? If the answer to both questions is yes, hie thee to the oil bath and get to work![2]

1. ***Find a solvent.*** If your compound has been previously published, you may get lucky here. If you have Beilstein access, check under the melting point section--appropriate recrystallization solvents are sometimes listed. Otherwise, group lore and common sense prevail. If a particular solvent works for a similar compound, give it a shot. What you want is for your material of interest to be minimally soluble in cold solvent but reasonably soluble in hot solvent. The ideal solvent should boil higher than, say, DCM or ether, but you can use solubility in the low-boiling stuff to point you in the direction of something more appropriate. If DCM seems like it may work, try recrystallizing in 1,2-dichloroethane. If pentane (or hexane or pet ether) looks good, use heptane.
2. ***Set up***. Common sense should dictate the size of glassware you use. Plan on the total volume of your solution taking up at least, like, a fifth of the total volume, but no more than about half or two thirds--head space is your friend. You're going to want an appropriately sized stir bar, too, and an oil bath. While heat gun recrystallizations may seem quick and easy, I don't recommend them--it's easy to scorch small amounts of very precious materials with a heat gun. Use an oil bath. Add your compound to the flask, and add a smallish amount of solvent. Heat to about 10-20 degrees above the boiling point of the solvent.[3]
3. ***Just enough solvent--not too much.*** If you screw up anything, it'll probably be this step, so be patient and go slowly. Wait until your initial amount of solvent has been refluxing for at least 5 minutes. Check to see if your stuff has dissolved. If not, add a little more solvent, wait, and check again. Repeat as needed. If you happen to notice that a stubborn bit of material just won't dissolve no matter how much solvent you add, you're probably going to have to start over--you have an insoluble impurity. Take a hot coarse frit (use a heat gun or oven to get it nice and toasty) and vacuum filter your hot solution. This will remove the insoluble crud you don't want.[4] Once all your material is in solution, you're ready to go on.
4. ***Cool down***. As a side note, some people recommend a hot filtration every time. If you see anything solid, or suspect that there is any dust or other crud that could serve as a nucleation hotspot, you need to take your stuff through a hot frit. If your material absorbs like mad, and the solution is so dark it's opaque, swirl the flask and see if any little chunks are visible--some usually stick to the glassware. If you see them, you need to hot filter. If no solids are visible, you can just turn off the stirring, pull out of the oil bath a little, and let the solution settle for a minute. Then decant very carefully. Whatever you decant or filter into should ideally be as pristine and unscratched as possible. Once the solution is in the nice unscratched glassware, cover it (do not use parafilm! it will melt) and place it in an out-of-the-way hiding spot. You are hiding it from yourself. Leave it alone for at least an hour or two. Do not pick it up. Do not disturb the solution. You may gently feel the side of the flask after it has been sitting neglected for an hour. Wait until it's room temperature--not remotely warm!--before you do anything else.
5. ***Wait for shiny things.*** Once your solution is room temperature, you may relocate it to a refrigerator. Be careful that your solvent won't FREEZE in said refrigerator--this can be a problem when water is the solvent, but seldom otherwise. If freezing is a possibility, or you have no refrigerator, use an ice bath. Either way, let it sit in the cold for a good long while. Overnight in an ice bath won't work so well because the ice will melt, but I like to do at least overnight if in the refrigerator. Be very patient and leave your growing crystals alone. Slow growth is best! If you're recrystallizing something colorful, you can watch as the solution becomes more and more pale--and then you know it's ready. Watch for shiny solids.
6. ***Harvest.*** Filter, and rinse with a little bit of very cold recrystallization solvent. Let dry and TLC or NMR to ensure that they are sufficiently pure--sometimes more than one recrystallization is necessary.

References

1. Superior synthetic ninjas may be able to work with less material--I can't. Conveniently, the upper limit of the amount of material that can be made shiny in a single batch is determined by the size of your glassware.
2. A very important caveat: If your material is too dirty, this just won't work. If the TLC shows any spots of comparable intensity to your goodies, take the stuff through a silica plug before you even try to get it shiny. If other spots are there but much fainter, you have a good chance.

3. UNLESS you have a good reason to keep the temperature lower. If you strongly suspect that your material isn't thermally stable at, say, 140 ºC, and you're using toluene, don't heat that high. You'll be fine only going to, say, 70 ºC--I've done this before on many occasions.
4. Check to make sure it is not your compound of interest. Sometimes it is. It is quite confusing when this occurs, and you could be very sad if you happen to toss anything without making sure it's junk.

Contrubutors

- psi*psi

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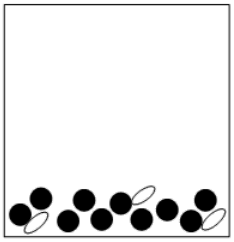
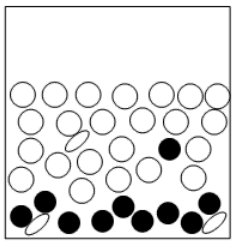
Recrystallization

Recrystallization is used to purify solids. Usually this method works best when there is only a small amount of impurity in the solid.



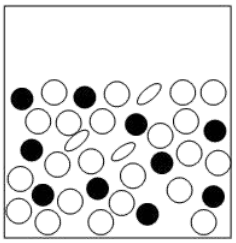
an impure solid

The method involves addition of a cold solvent to the material.



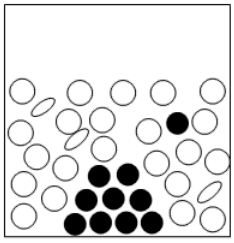
some of the solid dissolves
when solvent is added

The mixture that results is heated until the solids dissolve.



all of the solid dissolves
when the solvent is heated

The mixture is slowly cooled again until a pure solid is obtained.



some materials
remain dissolved

when cooled, one of the solids
slowly packs together in an
organized, crystalline form.

Recrystallization depends on different solubilities of the target compound and other compounds present in the impure mixture. The goal of this method is to have one compound dissolved in a solvent while the other compound is not dissolved. If one compound is an undissolved solid, it can be filtered out of the solution in order to separate it from all the other things that are in solution.

Solubility in a solvent is a physical property of a material, just like its boiling point or melting point. Sodium chloride (table salt) has a particular solubility in cold water (35.7 g will dissolve in 100 mL) while sodium oleate (found in some soaps) has a different

solubility in cold water (10 g per 100 mL). That difference can be exploited to separate these two compounds.

STOP AND THINK

1. Suppose you were trying to go into the soap business. Maybe you find you can easily produce a mixture of equal parts (weight:weight) of sodium chloride and sodium oleate. Describe how you could get pure sodium oleate.

2. Look at the structures of sodium chloride and sodium oleate. Can you qualitatively explain the difference between their solubilities in water?

It's possible that a mixture of sodium chloride and sodium oleate could be purified through the addition of water. If the right amount of water were added and the resulting slurry were stirred together and filtered, much of the sodium chloride would be removed because it is more soluble in water than is sodium oleate. Sodium oleate is less soluble in water than is sodium chloride, so most of it would not dissolve. It could be gathered or "isolated" by filtration.

The technique described above is not recrystallization. It is referred to as "washing". The sodium oleate was washed with water to remove sodium chloride. Washing is simple to do. Sometimes it can increase the purity of a compound, but it is not always very effective.

Sometimes in a mixture the two compounds are mixed very tightly together. Suppose there is a pile of powder that contains sodium oleate and sodium chloride. Instead of having individual grains of sodium chloride and individual grains of sodium oleate, the grains of powder contain both compounds. There might be a small nugget of sodium chloride surrounded by a coating of sodium oleate. This situation is very common, especially when the two compounds have formed together. Washing might remove most of the exposed sodium chloride, but it wouldn't touch the hidden or "occluded" sodium chloride that was surrounded by sodium oleate molecules.

STOP AND THINK

3. How can you get all of the sodium chloride out of this mixture? In other words, how can you make sure there is no sodium chloride covered by sodium oleate?

It would be convenient if there were a switch that could be turned on and off to control dissolution. When the switch is on, all the sodium oleate dissolves, and any sodium chloride trapped inside can get dissolved, too. When the switch is off, the sodium oleate comes out of solution again so that you can filter it out.

This switch exists. It is found on the front of your hot plate in the organic lab. Solubility is temperature-dependent. For example, the solubility of sodium chloride is different in cold water (35.7 g per 100 mL at 0 C) than in hot water (39.12 g per 100 mL at 100 C).

It's possible that, in the right amount of hot water, all the sodium oleate and all the sodium chloride dissolves. If the resulting solution is cooled to room temperature, the sodium oleate is no longer soluble. The sodium oleate forms a solid again. This solid can be filtered away from the water.

STOP AND THINK

4. After filtration, list the contents of the solution.

5. Instead of filtering, can the solution be allowed to evaporate to leave the sodium oleate behind?

There is one more part of this process that would make it a complete recrystallization. If the sodium oleate forms an amorphous solid when it comes back out of solution, we have precipitation. If the sodium oleate forms a crystalline solid when it comes back out of solution, we have recrystallization. An amorphous solid contains molecules that are packed together in random ways. A crystalline solid contains molecules that are ordered in a specific way.

An amorphous solid is like a pile of boxes that were thrown across the room and piled in the corner. A crystalline solid is like a set of boxes that were stacked neatly in the corner.

There are many open spaces between the boxes in the "amorphous" pile. Impurities could get trapped in those spaces; in that case we are back where we were at the beginning.

There are not really spaces between the boxes in the “crystalline” pile. No impurities can be trapped. Crystallization safeguards against the inclusion of impurities in the material.

STOP AND THINK

6. There are many variations on most purification techniques. One problem that could happen in a recrystallization is that there is a very insoluble impurity. How could this very insoluble impurity be separated from the rest of the sample? What precautions must be taken in doing so?

7. Suppose you are trying to recrystallize a sample of borneol. You think it should be recrystallized from methanol. You add a couple of mL of cold methanol and the sample all dissolves. Evaluate the prognosis of your recrystallization: is it working well? If not, what do you need to do?

8. Suppose you are trying to recrystallize a sample of borneol. You think it should be recrystallized from methanol. You add a couple of mL of cold methanol and only about half the sample dissolves. Evaluate the prognosis of your recrystallization: is it working well? If not, what do you need to do?

9. Suppose you are trying to recrystallize a sample of borneol. You think it should be recrystallized from methanol. You add a couple of mL of hot methanol and only about half the sample dissolves. Evaluate the prognosis of your recrystallization: is it working well? If not, what do you need to do?

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Reflux

So, you need to drive a chemical reaction by heating it at reflux. You will need to heat the reaction at the boiling point of your solvent(s) and fit a reflux condenser to the RBF. The condenser has cold water flowing through it; the solvent which has evaporated from the reaction will condense on the surface of the condenser and drip back down into the reaction, thus preventing your reaction from drying out.

1. Make sure all of your glassware is clean. Rinse with water and acetone at the very least; even small amounts of impurities can act as catalysts that can drive other reactions different from your desired reaction and lower your yield.
2. Clamp your round-bottom flask on your heating pad and stirrer. Make sure your stir bar is in the round-bottom before you add liquid. If you are not using a stir bar, add boiling stones. You may also use a teflon sleave at the junction of the RBF and the condenser to prevent the ground glass joints from fusing together.
3. Set the reflux condenser in the round bottom.
4. Start heating your reaction. Gradually increase the temperature until the solvent boils. Some heating mantles take quite a while to heat up.

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Rotary Evaporation

Rotary evaporation is the process of reducing the volume of a solvent by distributing it as a thin film across the interior of a vessel at elevated temperature and reduced pressure. This promotes the rapid removal of excess solvent from less volatile samples. Most rotary evaporators have four major components: heat bath, rotor, condenser, and solvent trap. Additionally an aspirator or vacuum pump needs to be attached, as well as a bump trap and round bottom flask containing the sample to be concentrated.

Flask, Bump Trap, and Bath Temperature

Selecting a flask that accommodates approximately twice the starting volume. If proper caution is exercised, the volume of the bump trap is irrelevant, but one should always be used as it prevents you from having to recover your sample from the condenser and solvent trap if bumping occurs. A low-vac pump or sink aspirator and temperatures between 25 and 50°C suffice for most common lab solvents. Lower temperatures make for a slower process but reduce the likelihood of bumping. Use common sense when selecting a temperature unless you lack common sense or are crippled with self doubt. In such a case a manometer and distillation nomograph can be utilized.

How to Commence a Rotary Evaporation

1. Let the heat bath get hot and the condenser get cold. The inverse situation often yields suboptimal results. Empty the solvent trap given that the previous user almost certainly did not. Take care when the trap is filled with unknown solvent as almost invariably the previous user left it brimming with pyridine or trifluoroacetic acid.
2. Secure the bump trap and sample flask using clamps. Alternatively, see the page on how to extract 5 mg of advanced intermediate from several liters of algae-infested hard water.
3. Activate the rotor. It should spin fast enough to create an even coating on the inner surface of the flask. Use this time to study the effects of coriolis force.
4. Activate the vacuum pump. Close the stopcock on the condenser to the point where you can no longer hear it whistling, but that there is an audible “pop” if you cover and release it with your thumb. Allow the sample to spin under vacuum for approximately a minute. Very likely it will soon begin to boil. Don’t panic. Boiling is not the same as bumping. As long as the bubbles do not reach the neck of the flask it may be allowed to boil. If the bubbles do reach the neck you have allowed it to bump: congratulations. If the bubbles seem to be in danger of reaching the neck, repressurize the system by fully opening the stopcock to cease boiling. Repeat until boiling has ceased and solvent is steadily streaming from the condenser; only then do you fully close the stopcock. When condensation begins to form on the exterior surface of the flask, lower it into the heat bath approximately half way.
5. Continue to monitor the situation for another minute or two. If there is danger of bumping, open the stopcock. Once again, repeat until boiling has ceased and solvent is steadily streaming from the condenser. At this point it is safe to leave the rotary evaporator unattended.
6. Occasionally check to ensure nothing has gone heinously wrong.

How to Halt a Rotary Evaporation

1. Remove the flask from the heat bath.
2. Open the stopcock.
3. Halt the rotor.
4. Turn off the vacuum/aspirator.
5. Disconnect the flask.
6. Drop flask in heat bath.
7. Hope that you serendipitously extract the cure for cancer from the crud in your heat bath.

Omission of any of these steps may result in an undesired outcome, e.g: filling the rotary evaporator with tap water when turning off the aspirator before opening the stop cock, bulk transport of your sample into the deepest recesses of the rotary evaporator when disconnecting the flask before opening the stopcock, and broken glassware as well as lacerations and the derision of fellow lab members when attempting to remove the flask before halting the rotor.

If at any point in this process bumping occurs, remove the flask and bump trap as a unit and rinse the interior with several mL of solvent. If your trap has drain holes the sample will flow back into the flask. Depending on the configuration of you trap, if it lacks drain holes you may have a Gordian monstrosity on your hands.

When you have finished your rotary evaporation do not empty the solvent trap, that is for suckers. So is washing and drying the bump trap.

Reagent/solvent-specific Considerations

Care should be taken to avoid damaging the pump and/or releasing toxic volatiles into the lab atmosphere. Acids and chlorinated solvents do not belong in your lungs, and even if you don't mind/care, I guarantee that your lab-mates will. Be aware that in some cases (expecially for highly volatile liquids) not all of the solvent removed on the rotovap will condense in the traps. You can try venting through a fume hood if the apparatus is in an appropriate position, if not attach a scrubber filled with paraffin oil.

If you really must remove corrosive materials such as propionic/acetic acid, make sure you attach a second liquid nitrogen trap before the solvent passes through the vacuum. This will prolong the life of the pump.

Some solvents/reagents are not really suitable for rotary evaporation, unless the exhaust from your vacuum pump is vented into a fumehood. Pyridine is one. Try extracting it out instead (dilute HCl will help), or remove *in vacuo* in your fume hood. The spermies of the males in your lab are susceptible to pyridine and you don't want an accidental leak of this fertility-killing stuff.

Lastly, be aware of any potentially reactive solvent combinations. Thionyl chloride and water is a good example. If you really must take off thionyl chloride on the rotovap (there are better alternatives!) be aware that if your apparatus contains moisture you may end up with a nasty stream of HCl/SO_2 gas coming from the pump, a combination that is both bad for the pump, and bad for the unfortunate souls who share a lab with you.

Advanced techniques

Cracking the vacuum: If you're rotovapping off ether, you won't need the same power as you will if you're rotovapping toluene. If you can figure out a way of breaking the vacuum just a little bit, it can be awesome. There are special glass/plastic rigs for this -- basically a tube attached somewhere between your pump/aspirator where you can screw it all the way shut (full vacuum - toluene, etc.) or leave it unscrewed just a little bit (ether, other bump-happy solvents), you can make your life easier.

Continuous rotary evaporation without breaking vacuum: It can be done! Basically, you need 1) a tube that goes from the airvent (?) near the stopcock to your Erlenmeyer full of solution to be rotovapped, 2) an internal tube from the stopcock that reaches down past the condenser tubing, through the rotating shaft and into your bump trap and 3) an appropriate bump trap that allows your solution to reach your attached rotating round bottom. (One of these works fine (http://www.safetyemporium.com/?CG-1319-04) -- basically, you can't have the "standard" bump trap.) Fire up your rotovap with the vacuum open and slowly open the stopcock to allow it to pull solution from your Erlenmeyer into your bump trap. Do not let solvent accumulate in the evaporation flask faster than it is evaporating! That's a good way to fill up your evaporating flask all the way full and you'll look pretty silly. This is a great way to rotovap off liters of solvent (limited by your receiving flask, of course) without ever turning off your pump.

Concerned about the environment because of your water aspirator?: As others have noted, one of the problems with using a water aspirator is that all solvents (especially low boiling ones) can be pulled into the vacuum and down the drain. A simple solution to this problem is A) to empty your bump trap faithfully and 2) to cool down your condenser water. How to do that? Buy a Gatorade-type cooler and a fish-tank pump. Add ice and water to the cooler, hook your fish-tank pump to your Tygon tubing to the condenser, plug in the pump and drop it in the ice water! Assuming that you've hooked it up correctly, you can guarantee that your condenser coils are at or around 0°C, which should catch most low-boiling solvents.

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Thin Layer Chromatography

Thin layer chromatography (TLC) is a chromatographic technique used to separate the components of a mixture using a thin stationary phase supported by an inert backing. It may be performed on the analytical scale as a means of monitoring the progress of a reaction, or on the preparative scale to purify small amounts of a compound. TLC is an analytical tool widely used because of its simplicity, relative low cost, high sensitivity, and speed of separation.TLC functions on the same principle as all chromatography: a compound will have different affinities for the mobile and stationary phases, and this affects the speed at which it migrates. The goal of TLC is to obtain well defined, well separated spots.

Retention Factor

After a separation is complete, individual compounds appear as spots separated vertically. Each spot has a retention factor (Rf) which is equal to the distance migrated over the total distance covered by the solvent. The R_f formula is

$$R_f = \frac{\text{distance traveled by sample}}{\text{distance traveled by solvent}} \tag{1}$$

The R_f value can be used to identify compounds due to their uniqueness to each compound. When comparing two different compounds under the same conditions, the compound with the larger R_f value is less polar because it does not stick to the stationary phase as long as the polar compound, which would have a lower R_f value.

R_f values and reproducibility can be affected by a number of different factors such as layer thickness, moisture on the TLC plate, vessel saturation, temperature, depth of mobile phase, nature of the TLC plate, sample size, and solvent parameters. These effects normally cause an increase in R_f values. However, in the case of layer thickness, the R_f value would decrease because the mobile phase moves slower up the plate.

If it is desired to express positions relative to the position of another substance, x, the R_x (relative retention value) can be calculated:

$$R_x = \frac{\text{distance of compound from origin}}{\text{distance of compound x from origin}} \tag{2}$$

While R_f can never be greater than 1, R_x can be (i.e., faster than the reference compound x.

Apparatus

Plates (Stationary Phase)

As stated earlier, TLC plates (also known as chromatoplates) can be prepared in the lab, but are most commonly purchased. Silica gel and alumina are among the most common stationary phases, but others are available as well. Many plates incorporate a compound which fluoresces under short-wave UV (254 nm). The backing of TLC plates is often composed of glass, aluminum, or plastic. Glass plates are chemically inert and best withstand reactive stains and heat, but are brittle and can be difficult to cut. Aluminum and plastic plates can be cut with scissors, but aluminum may not withstand strongly acidic or oxidizing stains, and plastic does not withstand the high heat required to develop many stains. Aluminum and plastic plates are also flexible, which may result in flaking of the stationary phase. Never under any circumstances touch the face of a TLC plate with your fingers as contamination from skin oils or residues on gloves can obscure results. Instead, always handle them by the edges, or with forceps.

The properties of your sample should be considered when selecting the stationary phase. As shown below in Table 1, silica gel can be exclusively used for amino acids and hydrocarbons. It is also important to note that silica gel is acidic. Therefore, silica gel offers poor separation of basic samples and can cause a deterioration of acid-labile molecules. This would be true for alumina plates in acidic solutions as well. It is important to note that there are differences between silica gel and alumina. Alumina is basic and it will not separate sample sizes as large as silica gel would at a given layer thickness. Also, alumina is more chemically reactive than silica gel and as a result, would require more care of compounds and compound classes. This care would avoid decomposition and rearrangement of the sample.

Table 1: Stationary phase and mode of separation

Stationary Phase	Chromatographic Mechanism	Typical Application
Silica Gel	adsorption	steroids, amino acids, alcohols, hydrocarbons, lipids, aflaxtoxin, bile, acids, vitamins, alkaloids
Silica Gel RP	reversed phase	fatty acids, vitamins, steroids, hormones, carotenoids
Cellulose, kieselguhr	partition	carbohydrates, sugars, alcohols, amino acids, carboxylic acids, fatty acids
Aluminum oxide	adsorption	amines, alcohols, steroids, lipids, aflatoxins, bile acids, vitamins, alkaloids
PEI cellulose	ion exchange	nucleic acids, nucleotides, nucelosides, purines, pyrimidines
Magnesium silicate	adsorption	steroids, pesticides, lipids, alkaloids

Chromatographic Columns is a good reference to learn more about the different types of columns and stationary phases.

Solvent (Mobile Phase)

Proper solvent selection is perhaps the most important aspect of TLC, and determining the best solvent may require a degree of trial and error. As with plate selection, keep in mind the chemical properties of the analytes. A common starting solvent is 1:1 hexane:ethyl acetate. Varying the ratio can have a pronounced effect of R_f. R_f values range from 0 to 1 with 0 indicating that the solvent polarity is very low and 1 indicating that the solvent polarity is very high. When performing your experiment, you do not want your values to be 0 or 1 because your components that you are separating have different polarities. If the value is 0, you need to increase your solvent polarity because the sample is not moving and sticking to the stationary phase. If the value is 1, you need to decrease your solvent polarity because the compound was not able to separate.

If you know that one component of a mixture is insoluble in a given solvent, but another component is freely soluble in it, it often gives good separations. How fast the compounds travel up the plate depends on two things:

- If the compound is soluble in the solvent, it will travel further up the TLC plate
- How well the compound likes the stationary phase. If the compound likes the stationary phase, it will stick to it, which will cause it to not move very far on the chromatogram.

You should be able to determine which by looking at the R_f value.

Acids, bases, and strongly polar compounds often produce streaks rather than spots in neutral solvents. Streaks make it difficult to calculate an \(R_f\) and may occlude other spots. Adding a few percent of acetic or formic acid to the solvent can correct streaking with acids. Similarly for bases, adding a few percent triethylamine can improve results. For polar compounds adding a few percent methanol can also improve results.

The volatility of solvents should also be considered when chemical stains are to be used. Any solvent left on the plate may react with the stain and conceal spots. Many solvents can be removed by allowing them to sit on the bench for a few minutes, but very nonvolatile solvents may require time in a vacuum chamber. Volatile solvents should only be used once. If the mobile phase is used repeatedly, results will not be consistent or reproducible.

Useful Solvent Mixtures

- A solvent that can be used for separating mixtures of strongly polar compounds is ethyl acetate : butanol : acetic acid : water, 80:10:5:5.
- To separate strongly basic components, make a mixture of 10% NH_4OH in methanol, and then make a 1 to 10% mixture of this in dichlormethane.
- Mixtures of 10% methanol or less in DCM can be useful for separating polar compounds.

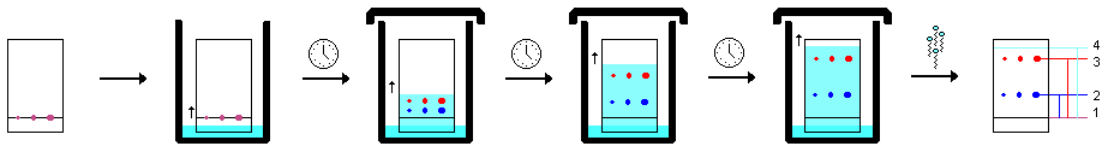
Pipettes

- Spots are applied to the plate using very thin glass pipettes. The capillary should be thin enough to apply a neat spot, but not so thin as to prevent the uptake of an adequate quantity of analyte. Here is a popular method of producing TLC pipettes.
- Heat a glass capillary in the very tip of a Bunsen burner flame just until it becomes pliable and then pull the ends apart until the center of the capillary is significantly narrower. Snap this in half and use the thin end to apply spots.

Spotting and Developing

Developing a TLC plate requires a developing chamber or vessel. This can be as simple as a wide-mouth jar, but more specialized pieces of glassware to accommodate large plates are available. The chamber should contain enough solvent to just cover the bottom. It should also contain a piece of filter paper, or other absorbent material to saturate the atmosphere with solvent vapors. Finally, it should have a lid or other covering to minimize evaporation.

1. Cut the plate to the correct size and using a pencil (never ever use a pen), gently draw a straight line across the plate approximately 1 cm from the bottom. Do not use excessive forces when writing on a TLC plate as this will remove the stationary phase. It is important to use a pencil rather than a pen because inks commonly travel up the plate with the solvent. An example of how black ink separates is shown in the section labeled "examples".
2. Using TLC pipettes, apply spots of analyte to the line. Make sure enough sample is spotted on the plate. This can be done by using the short-wave UV. A purple spot should be seen. If the spot is not visible, more sample needs to be applied to the plate. If a standard of the target compound is available, it is good practice to produce a co-spot by spotting the standard onto a spot of the unknown mixture. This ensures the identity of the target compound.
3. Place the plate into the chamber as evenly as possible and lean it against the side. Never allow the bulk solvent to rise above the line you drew. Allow capillary action to draw the solvent up the plate until it is approximately 1 cm from the end. Never allow the solvent to migrate all the way to the end of the plate.
4. Remove the plate and immediately draw a pencil line across the solvent front.
5. Use a short-wave UV light and circle the components shown with a pencil.



The sequence involved in TLC. Image used with permission (CC BY-SA 3.0; Wikipedia).

Visualizing

If fluorescent plates are used, a number of compounds can be seen by illuminating the plate with short-wave UV. Quenching causes dark spots on the surface of the plate. These dark patches should be circled with a pencil. For compounds which are not UV active, a number of chemical stains can be used. These can be very general, or they can be specific for a particular molecule or functional group.

Iodine is among the most common stains. Plates are placed in a jar containing iodine crystals, or covered in silica gel with iodine dispersed throughout, for approximately one minute. Most organic compounds will be temporarily stained brown. Some popular general use stains are Permanganate, ceric ammonium molybdate (CAM), and p-anisaldehyde. These can be kept in jars which plates are dipped into, or in spray bottles.

To develop a plate with permanganate, spray or dip the plate and heat it with a heat-gun. Hold the plate face up 10 to 20 cm above the heat gun until the bulk water evaporates. Then move the plate to 5 to 10 cm above the heat gun and heat it until white/yellow/brown spots appear. Overheating will turn the entire plate brown, obscuring the spots. If glass plates are used it is often easier to see spots through the backing because it is harder to overheat. CAM and p-anisaldehyde stained plates are developed similarly. Overheating CAM stained plates turns everything blue.

Common Problems in TLC

There are common problems in TLC that should be avoided. Normally, these problems can be solved or avoided if taught proper techniques.

- **Over-large Spot**s: Spotting sizes of your sample should be not be larger than 1-2 mm in diameter. The component spots will never be larger than or smaller than your sample origin spot. If you have an over-large spot, this could cause overlapping of other component spots with similar R_f values on your TLC plate. If overlapping occurs, it would prove difficult to resolve the different components.
- **Uneven Advance of Solvent Front**: Uneven advance of the mobile phase is a common problem encountered in TLC. Consequences would be inaccurate R_f values due to the uneven advance of sample origin spots. This uneven advance can be caused by a few factors listed below.

    1. *No flat bottom*. When placing the TLC plate into the chamber, place the bottom of the plate on the edge of the chamber (normally glass container (e.g. beaker)) and lean the top of the plate along the other side of the chamber. Also, make sure that the TLC plate is placed in the chamber evenly. Do not tilt the plate or sit it at an angle.
    2. *Not enough solvent*. There should be enough solvent (depends on size of the chamber) to travel up the length of the TLC plate.
    3. *Plate is not cut evenly*. It is recommended that a ruler is used so that the plate is cut evenly.

Rarely, water is used as a solvent because it produces an uneven curve front which is mainly accounted for by its surface tension.

- **Streaking**: If the sample spot is too concentrated, the substance will travel up the stationary phase as a streak rather than a single separated spot. In other words, the solvent can not handle the concentrated sample and in result, moves as much of the substance as it can up the stationary phase. The substance that it can not move is left behind. This can be eliminated by diluting the sample solution. To ensure that you have enough solution, use a short-wave UV light to see if the spot is visible (normally purple in color), as stated earlier.
- **Spotting**: The sample should be above the solvent level. If the solvent level covers the sample, the sample spot will be washed off into the solvent before it travels up the TLC plate. An example is shown below.

Example: Analyzing Commercial Analgesics

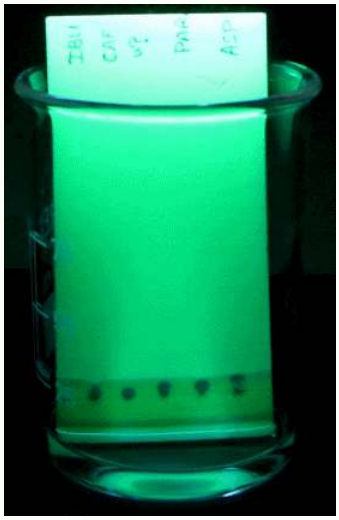
Thin layer chromatography of three analgesics and caffeine under U.V. light was carried out in order to show the separation taking place. It is **not a recommended technique** in the laboratory. Due to the nature of the uv hazard polycarbonate safety spectacles (which absorb short wavelength U.V. light) and rubber gloves were worn throughout.

Five samples were run on a single TLC plate. The samples were (left to right on the plate):

- Ibuprofen (ICU)
- caffeine (CAF)
- u? = a commercial ‘pain relief’ medicine, used as an unknown
- Acetominophen (PAR)
- Aspirin (ASP)

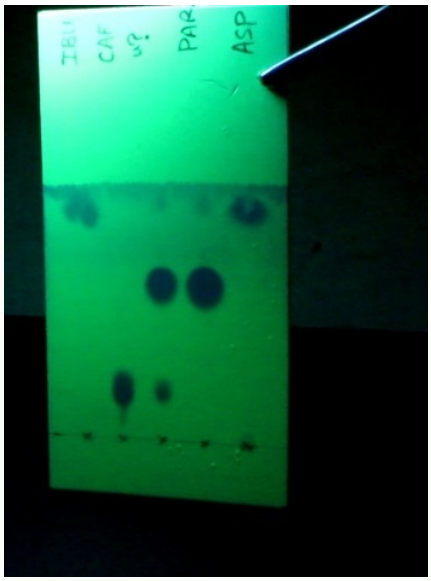
Five samples prior to elution. Image used with permission (Free for education use, Nigel Baldwin via chemligin).

The samples were dissolved in ethanol for spotting onto the plate. The TLC plate was run in an open beaker under short wavelength u.v. light using ethyl ethanoate as the eluting solvent.



Separation of the samples. (Free for education use, Nigel Baldwin via chemligin).

The movement of the dark purple spots (samples) during the running of the plate can be observed in the animation. The original movie can be viewed here.



R_f values can be measured. (Free for education use, Nigel Baldwin via chemligin).

It is easy to see which are the two active ingredients in the unknown commercial pain relief medicine by comparison of the spots with the standard reference materials running on either side (caffeine and acetominophen).

Advantages and Disadvantages of TLC

TLC is very simple to use and inexpensive. Undergraduates can be taught this technique and apply its similar principles to other chromatographic techniques. There are little materials needed for TLC (chamber, watch glass, capillary, plate, solvent, pencil, and UV-light). Therefore, once the best solvent is found, it can be applied to other techniques such as High performance liquid chromatography. More than 1 compound can be separated on a TLC plate as long as the mobile phase is preferred for each compound. The solvents for the TLC plate can be changed easily and it is possible to use several different solvents depending on your desired results. As stated earlier, TLC can be used to ensure purity of a compound. It is very easy to check the purity using a UV-light. The identification of most compounds can be done simply by checking R_f literature values. You can modify the chromatography conditions easily to increase the optimization for resolution of a specific component.

TLC plates do not have long stationary phases. Therefore, the length of separation is limited compared to other chromatographic techniques. Also, the detection limit is a lot higher. If you would need a lower detection limit, one would have to use other chromatographic techniques. TLC operates as an open system, so factors such as humidity and temperature can be consequences to the results of your chromatogram.

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2. Geiss, Friedrich. *Fundamentals of thin layer chromatography planar chromatography*. Heidelberg: A. Hüthig, 1987. Print.
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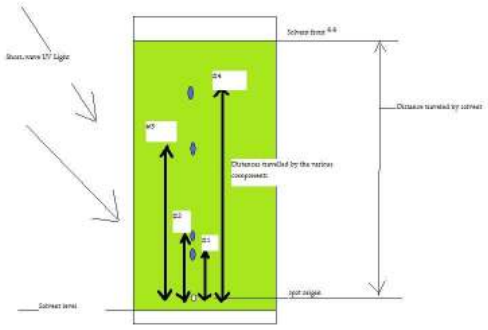
Problems and Solutions

Figure 3: TLC plate under UV light with values for distance traveled of solvent and components.



Given:

#1=1.4 cm

#2= 1.5 cm

#3= 3.1 cm

#4= 3.6 cm

Using only the given information and the above figure, answer the problems listed below.

1. What is the R_f value for component #2?
2. What is the R_f value for component # 3?
3. What is the relative retention value for components #1 and # 4, with # 4 being compound x?
4. Using the answers from questions 1 and 2 and assuming that components 2 and 3 are different compounds, which component would be considered more polar? Explain.

Answers

1. 1.5/4.4=0.34
2. 3.1/4.4=0.70
3. 1.4/3.6=0.39
4. Component # 2 would be considered more polar because it has the lower R_f value, which means that it sticks to the stationary phase a lot stronger than component #3 and therefore moves slower in the mobile phase.

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Chromatography Columns

Thin layer chromatography (TLC) can be used to separate many different mixtures. It is very flexible because several different compounds can be separated from each other in one experiment. Practically speaking, TLC is often used only as an analytical tool rather than as a method of purification. It is used to quickly determine if a mixture is pure, how many compounds it may contain, and what combination of eluent and stationary phase can be used to separate the compounds. However, TLC often works best with a very small amount of material. Isolating useful amounts of compound sometimes requires other kinds of chromatography.

Column chromatography is another kind of liquid chromatography. It works just like TLC. The same stationary phase and the same mobile phase can be used. Instead of spreading a thin layer of the stationary phase on a plate, the solid is packed into a long, glass column either as a powder or a slurry. Sometimes these columns are several inches wide and a few feet long. A large amount of material can be purified on a chromatography column.

Instead of letting eluent wick up through the stationary phase, the solvent is poured into the top of the column and allowed to run through by gravity. The same factors of adhesion and solution in TLC apply here. If the same solid phase and liquid phase from TLC are used in a column, the compounds will elute through the column in the same order that they elute across a TLC plate.

Sometimes, instead of letting the eluent run through the column via gravity, the eluent can be pushed through more quickly using an inert gas or an air pump. This method is called flash chromatography. There is sometimes a trade-off between quality of separation and the time it takes to run the column, though.

STOP AND THINK

1. Why might there be less separation between two compounds if they move through the column faster?
2. Suppose you are in the middle of separating a mixture on a chromatography column when you remember that you left the oven on in your apartment. Your apartment is a half hour from lab. You turn off the stopcock at the bottom of the column so that the eluent stops flowing. When you get back, you finish the column. You find that you didn't get very good separation between the compounds. What happened?
3. a) Suppose you are working with a chromatography column that can hold about 20 mL of solvent. You know that a sample is usually dissolved and then poured onto the top of the column before eluting with solvent. You dissolve your sample in 20 mL of solvent and proceed with the experiment. You get very poor results. What went wrong?
    1. b) Meanwhile, Alicia, the annoyingly perfect student in the next hood, dissolves her sample in 1 mL of solvent and runs her column. She gets three pure compounds at the end and the instructor immediately gives her an A in the course. What did she do right?
4. 4. TLC shows that the white powder you received in lab contains three compounds. All of them are colorless. You dissolve the sample, load it onto a chromatography column and begin to collect 0.5 mL samples in small test tubes. After twenty test tubes, you get tired and stop the column. How can you use TLC to determine which test tubes have which compounds in them?

Silica and alumina are not the only possible solid phases. Stationary phases can be purchased that have long carbon chains bonded to silica beads. For example, a C18 column contains beads that have 18-carbon chains attached to them. These stationary phases are powders, like silica, and they can be loaded into a column just like silica can.

A C18 column is an example of a "reverse phase" column. Reverse phase columns are often used with more polar solvents such as water, methanol or acetonitrile.

STOP & THINK

5. In a normal column, the stationary phase is more polar than the mobile phase. Is that true in a reverse phase column?
6. In a normal column, three compounds were eluted in the following order: p-dimethylbenzene, p-dimethoxybenzene, then p-methoxyphenol. What might you expect the order of elution would be on a C18 column?
7. You are trying to elute a sample on a C18 column using 20:80 mixture of water:acetontrile, but the compounds are taking too long to come through the column. What should you do?

There are additional methods of chromatography that you might not do in an organic lab. If you do, it will probably be under specific conditions in which your instructor has developed an exact protocol for carrying out the chromatography. These methods are more time-consuming to get working properly. They also use more expensive equipment that may require special training in advanced courses.

Liquid chromatography is often done with more sophisticated equipment. This kind of method is called "high performance liquid chromatography" or HPLC. Rather than packing stationary phase into a glass column, a steel column containing the stationary phase can be purchased. The column can be plumbed into a system that contains a solvent pump to push eluent through the column. After passing through the column, the liquid may go into a UV spectrometer so you can detect when compounds are eluting from the column. The whole apparatus is controlled by a computer. By clicking a button, you can change how quickly the solvent flows. You can easily change the ratio of solvents in the eluent by clicking a button, too.

In addition to a UV spectrometer, other instruments can be used with an HPLC system to get information about compounds being eluted . One of the most important is mass spectrometry (MS). Liquid chromatography-mass spectrometry (LC-MS) can be used to determine the molecular weights of the compounds as they elute. That infromation can be used to help identify the compound.

Gas chromatography is an important variation that you should know about. Instead of passing a liquid over the stationary phase, an inert gas moves over the stationary phase. The inert gas may be helium or nitrogen. The equilibrium here is between compounds absorbed onto the stationary phase and compounds moving in the gas phase. Intermolecular attractions with the stationary phase play a role in GC, but so does the boiling point of the compounds.

Because most compounds are not very volatile, they would spend all their time sitting on the solid phase under normal conditions. For that reason, the column in a gas chromatograph is placed inside an oven. The temperature in this oven is carefully controlled so that compounds will spend a greater fraction of time in the gas phase.

The eluent can't be varied in GC. It is just an inert gas. To control separation of compounds in GC, we can change the pressure of the inert gas, which controls how quickly the gas flows. We can also control the temperature, which influences how much time compounds spend moving along in the gas phase . We can also choose different kinds of columns with different stationary phases.

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Chromatography I: TLC

Solvent partitioning involves an equilibrium between dissolving in one liquid and dissolving in another. Our first look at chromatography involves a similar equilibrium between dissolving in a liquid and sticking to a solid.

Sticking to a solid, or adhesion, occurs through intermolecular attractions between the solid and the compound adhering to it.

A grass stain on the knee of your jeans goes into the washing machine and enters into this sort of equilibrium. The equilibrium constant involving these materials (grass stain compounds such as chlorophyll, the cellulose in the cotton of the jeans, and the soapy water) determines whether your jeans will become clean or remain stained.

The great advantage of chromatography is flexibility. It does not matter whether the compound you wish to purify is a solid or liquid. Even gases can be purified by chromatography, as you will see in a later section. As long as the compound is able to dissolve in one liquid and stick to one solid, chromatography can be used to purify it.

There is a very similar type of chromatography called paper chromatography. In a typical paper chromatography demonstration, a sample of ink is spotted onto a piece of filter paper. The filter paper is made of cellulose, like jeans. The paper is dipped into a beaker of water. The water begins to wick up along the paper. As it water seeps up past the spot of ink, the spot begins to move. If the ink is made from a mixture of pigments, it separates out into different, coloured compounds.

STOP AND THINK

1. Look at the structures of paper (cellulose) and water. Why is water able to spread up through a piece of paper that is dipped into it?
2. Why does the ink separate into different components as the water seeps up the paper?

In liquid chromatography, there is a solid that stays put, called the stationary phase, and a liquid that moves over the solid, called the mobile phase or the eluent.

The solid is usually silica (SiO_2) or alumina (Al_2O_3). Both are polar compounds capable of hydrogen bonding. Usually they have hydroxyl groups on their surfaces.

The eluent is usually an organic solvent or mixture of solvents. The eluent can be more polar or less polar. It should not be so polar that it would dissolve the alumina or silica. If it did, the stationary phase would not stay put, but would move with the liquid phase. For that reason, methanol and water are not normally used as the eluent.

If the solid phase is stationary, then when compounds are absorbed onto the solid, they will not move either. If the liquid phase is moving, then when compounds dissolve in the liquid, they will move along, too. If there is an equilibrium between solid-phase adhesion and liquid-phase solution, compounds will spend some time moving and some time staying still.

Different compounds may have different equilibria between solution and adhesion. That means different compounds will spend different amounts of time moving or staying still. As a result, the compounds will separate from each other over time.

Thin layer chromatography is often done in the organic lab. Thin layer chromatography is like paper chromatography. A solid sheet or plate is dipped into a solution. As the solution moves up the surface of the solid, the compounds on the plate move along to different extent based on their polarity.

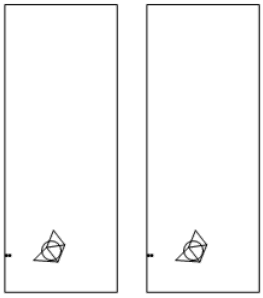
A thin layer chromatography (TLC) plate can be made of metal, glass or plastic. The alumina or silica is sprayed onto the plate and it is allowed to dry, like paint. Very often, TLC plates are purchased already prepared, with the stationary phase already "painted" onto them. Sometimes students need to make the plates themselves.

STOP AND THINK

3. Suppose you place a spot of sample on a TLC plate. You have pentane and 2-butanone to use as eluent. First you try the pentane. After the pentane elutes (or wicks up) all the way to the top of the plate, none of the compounds in your mixture have moved. What is wrong? How will you fix the problem?
4. Suppose you place a spot of sample on a TLC plate. You have pentane and 2-butanone to use as eluent. First you try the 2-butanone. After the 2-butanone elutes (or wicks up) all the way to the top of the plate, all of the compounds in your mixture

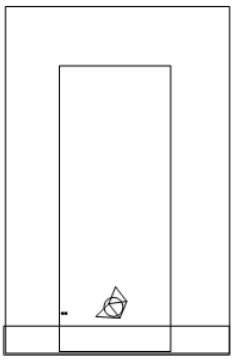
have moved to the top of the plate, too. They have not separated from each other. What is wrong? How will you fix the problem?

5. Suppose you finally succeed in getting your mixture separated into three spots on a TLC plate. You want to isolate these three pure compounds and put them each in a labeled vial. Come up with a series of steps that you could do to accomplish this task.

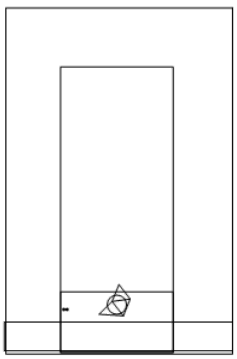


a mixture is spotted on a TLC plate

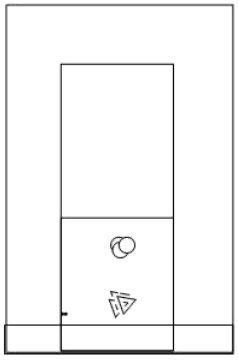
a mixture is spotted on a TLC plate



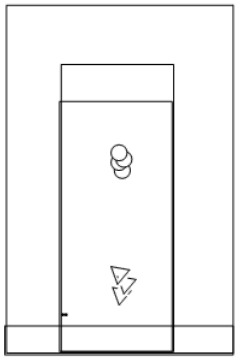
the plate is placed in a container with a small amount of solvent



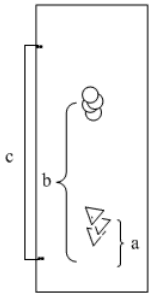
the solvent begins to wick up the plate



as the solvent wicks up the plate, compounds in the mixture equilibrate between adsorbing onto the surface of the plate and dissolving in the mixture



the farther the solvent goes, the farther the spots of compound move (unless they run out of TLC plate)



the direction of this equilibrium depends on each compound's polarity; **b** spent most of its time moving with the solvent, while **a** spent most of its time adsorbed on the plate

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SECTION OVERVIEW

Titration

Titration is the slow addition of one solution of a known concentration (called a titrant) to a known volume of another solution of unknown concentration until the reaction reaches neutralization, which is often indicated by a color change. The solution called the titrant must satisfy the necessary requirements to be a primary or secondary standard. In a broad sense, titration is a technique to determine the concentration of an unknown solution.

Topic hierarchy

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Acid-Base Titrations

Acid-Base titrations are usually used to find the amount of a known acidic or basic substance through acid base reactions. The analyte (titrand) is the solution with an unknown molarity. The reagent (titrant) is the solution with a known molarity that will react with the analyte.

Procedure

The analyte is prepared by dissolving the substance being studied into a solution. The solution is usually placed in a flask for titration. A small amount of indicator is then added into the flask along with the analyte. The reagent is usually placed in a burette and slowly added to the analyte and indicator mixture. The amount of reagent used is recorded when the indicator causes a change in the color of the solution.

Some titrations requires the solution to be boiled due to the CO_2 created from the acid-base reaction. The CO_2 forms carbonic acid (H_2CO_3) when dissolved in water that then acts as a buffer, reducing the accuracy of data. After boiling water, most of the CO_2 will be removed from the solution allowing the solution to be titrated to a more accurate endpoint. The endpoint is the point where all of the analyte has be reacted with the reagent.

Indicator

A useful indicator has a strong color that changes quickly near its pKa. These traits are desirable so only a small amount of an indicator is needed. If a large amount of indicator is used, the indicator will effect the final pH, lowering the accuracy of the experiment. The indicator should also have a pKa value near the pH of the titration's endpoint. For example a analyte that is a weak base would require an indicator with a pKa less than 7. Choosing an indicator with a pKa near the endpoint's pH will also reduce error because the color change occurs sharply during the endpoint where the pH spikes, giving a more precise endpoint.

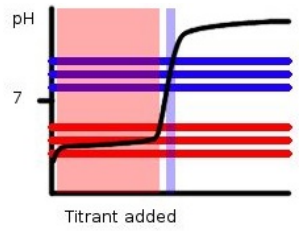

***Figure 1**: A Basic Titration Curve, The horizontal lines show the range of pH in which phenolphthalein (blue) and methyl orange (red) changes color. The middle line represents the pKa, while the two outer lines represent the end or start of the color changes. The peak and light blue highlights show the range in which the color changes will occur based on the amount of titrant added.*

Notice that this reaction is between a weak acid and a strong base so phenolphthalein with a pKa of 9.1 would be a better choice than methyl orange with a pKa of 3.8. If in this reaction we were to use methyl orange as the indicator color changes would occur all throughout the region highlighted in pink. The data obtained would be hard to determine due to the large range of color change, and inaccurate as the color change does not even lie with the endpoint region. Phenolphthalein on the other hand changes color rapidly near the endpoint allowing for more accurate data to be gathered.

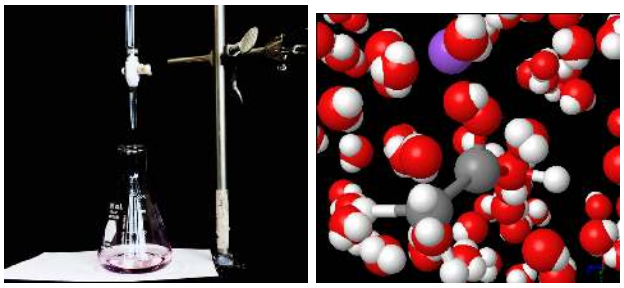

***Figure 2**: Titration Demonstration, The picture was taken during a vinegar titration lab. $C_2H_4O_2(aq)$ - acetic acid- was titrated against NaOH (aq) - sodium hydroxide - using phenolphthalein as indicator. The image on the right is submicroscopic view of the*

titration reaction featuring $C_2H_4O_2(aq)$, which is partially dissociated and NaOH (aq) that is completely dissociated into $Na^+(aq)$ in purple and $OH^-(aq)$.

Multiply the volume of reagent added to get to the endpoint, with the molarity of the reagent to find the moles of reagent used. With the balanced equation of the acid-base reaction in question to find the moles of unknown substance. Then the original molarity can be calculated by dividing through with the initial volume.

Note

For example an unknown molarity of HCl acts as the analyte. 50 mL of it is placed into a flask and a 0.1 M solution of $NaOH$ will be the reagent. The endpoint is $pH = 7$ so litmus, with a pKa of 6.5 is chosen. The color of the solution changes when 10 mL of 0.1 M $NaOH$ is added.

The balanced neutralization reaction:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(l)} + Na^+ + Cl^- \tag{1}$$

Or just the net ionic equation

$$H^+ + OH^- \rightarrow H_2O_{(l)} \tag{2}$$

The following equation can then be derived

$$X = (0.1\ M\ \ NaOH)(10\ mL)\left(\frac{1\ L}{1000\ mL}\right)\left(\frac{1\ mol\ NaOH}{1\ mol\ OH^-}\right) \tag{3}$$

$$H^+ = X\ \ HCl \tag{4}$$

$$X = 0.0010\ mol\ of\ HCl$$

The molarity is now easily solved for

$$\frac{0.0010\ mol\ HCl}{0.050\ L} = 0.020\ M\ HCl \tag{5}$$

References

1. Reactions of Acids and Bases in Analytical Chemistry. Hulanicki, A. and Masson, M.R. New York: Halsted Press, 1987.
2. Aqueous Acid-Base Equilibria and Titrations. Levie, Robert De. New York : Oxford University Press, 1999.

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Complexation Titration

The earliest examples of metal–ligand **complexation titrations** are Liebig's determinations, in the 1850s, of cyanide and chloride using, respectively, Ag^+ and Hg^{2+} as the titrant. Practical analytical applications of complexation titrimetry were slow to develop because many metals and ligands form a series of metal–ligand complexes. Liebig's titration of CN^- with Ag^+ was successful because they form a single, stable complex of $Ag(CN)_2^-$, giving a single, easily identified end point. Other metal–ligand complexes, such as CdI_4^{2-}, are not analytically useful because they form a series of metal–ligand complexes (CdI^+, $CdI_2(aq)$, CdI_3^- and CdI_4^{2-}) that produce a sequence of poorly defined end points.

> **Note**
>
> Recall that an acid–base titration curve for a diprotic weak acid has a single end point if its two K_a values are not sufficiently different. See Figure 9.11 for an example.

In 1945, Schwarzenbach introduced aminocarboxylic acids as multidentate ligands. The most widely used of these new ligands—ethylenediaminetetraacetic acid, or EDTA—forms strong 1:1 complexes with many metal ions. The availability of a ligand that gives a single, easily identified end point made complexation titrimetry a practical analytical method.

9.3.1 Chemistry and Properties of EDTA

Ethylenediaminetetraacetic acid, or EDTA, is an aminocarboxylic acid. EDTA, which is shown in Figure 9.26a in its fully deprotonated form, is a Lewis acid with six binding sites—four negatively charged carboxylate groups and two tertiary amino groups—that can donate six pairs of electrons to a metal ion. The resulting metal–ligand complex, in which EDTA forms a cage-like structure around the metal ion (Figure 9.26b), is very stable. The actual number of coordination sites depends on the size of the metal ion, however, all metal–EDTA complexes have a 1:1 stoichiometry.

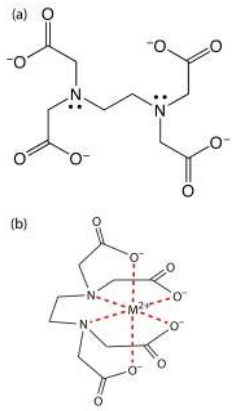

Figure 9.26 Structures of (a) EDTA, in its fully deprotonated form, and (b) in a six-coordinate metal–EDTA complex with a divalent metal ion.

Metal–ED TA Formation Constants

To illustrate the formation of a metal–EDTA complex, let's consider the reaction between Cd^{2+} and EDTA

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq) \tag{9.9}$$

where Y^{4-} is a shorthand notation for the fully deprotonated form of EDTA shown in Figure 9.26a. Because the reaction's formation constant

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]} = 2.9 \times 10^{16} \tag{9.10}$$

is large, its equilibrium position lies far to the right. Formation constants for other metal–EDTA complexes are found in Table E4.

EDTA is a Weak Acid

In addition to its properties as a ligand, EDTA is also a weak acid. The fully protonated form of EDTA, H_6Y^{2+}, is a hexaprotic weak acid with successive pK_a values of

$pK_{a1} = 0.0$	$pK_{a2} = 1.5$	$pK_{a3} = 2.0$
$pK_{a4} = 2.66$	$pK_{a5} = 6.16$	$pK_{a6} = 10.24$

The first four values are for the carboxylic acid protons and the last two values are for the ammonium protons. Figure 9.27 shows a ladder diagram for EDTA. The specific form of EDTA in reaction 9.9 is the predominate species only at pH levels greater than 10.17.

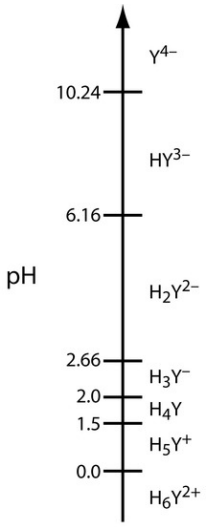

Figure 9.27 Ladder diagram for EDTA.

Conditional Metal–Ligand Formation Constants

The formation constant for CdY^{2-} in equation 9.10 assumes that EDTA is present as Y^{4-}. Because EDTA has many forms, when we prepare a solution of EDTA we know it total concentration, C_{EDTA}, not the concentration of a specific form, such as Y^{4-}. To use equation 9.10, we need to rewrite it in terms of C_{EDTA}.

At any pH a mass balance on EDTA requires that its total concentration equal the combined concentrations of each of its forms.

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}] \quad (1)$$

To correct the formation constant for EDTA's acid–base properties we need to calculate the fraction, $\alpha_{Y^{4-}}$, of EDTA present as Y^{4-}.

$$\alpha_{Y^{4-}} \frac{[Y^{4-}]}{C_{EDTA}} \quad (9.11)$$

Table 9.10 Values of $\alpha_{Y^{4-}}$ for Selected pH Levels

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
1	1.9×10^{-18}	8	5.6×10^{-3}
2	3.4×10^{-14}	9	5.4×10^{-2}
3	2.6×10^{-11}	10	0.37
4	3.8×10^{-9}	11	0.85
5	3.7×10^{-7}	12	0.98
6	2.4×10^{-5}	13	1.00
7	5.0×10^{-4}	14	1.00

> **Note**
>
> Problem 9.42 from the end of chapter problems asks you to verify the values in Table 9.10 by deriving an equation for $\alpha_{Y^{4-}}$.

Table 9.10 provides values of $\alpha_{Y^{4-}}$ for selected pH levels. Solving equation 9.11 for $[Y^{4-}]$ and substituting into equation 9.10 for the CdY^{2-} formation constant

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\alpha_{Y^{4-}} C_{EDTA}} \tag{2}$$

and rearranging gives

$$K_f' = K_f \times \alpha_{Y^{4-}} = \frac{[CdY^{2-}]}{[Cd^{2+}]C_{EDTA}} \tag{9.12}$$

where K_f' is a pH-dependent **conditional formation constant**. As shown in Table 9.11, the conditional formation constant for CdY^{2-} becomes smaller and the complex becomes less stable at more acidic pHs.

Table 9.11 Conditional Formation Constants for CdY^{2-}

pH	K_f'	pH	K_f'
1	5.5×10^{-2}	8	1.6×10^{14}
2	1.0×10^{3}	9	1.6×10^{15}
3	7.7×10^{5}	10	1.1×10^{16}
4	1.1×10^{8}	11	2.5×10^{16}
5	1.1×10^{10}	12	2.9×10^{16}
6	6.8×10^{11}	13	2.9×10^{16}
7	1.5×10^{13}	14	2.9×10^{16}

EDTA Competes With Other Ligands

To maintain a constant pH during a complexation titration we usually add a buffering agent. If one of the buffer's components is a ligand that binds Cd^{2+}, then EDTA must compete with the ligand for Cd^{2+}. For example, an NH_4^+/NH_3 buffer includes NH_3, which forms several stable Cd^{2+}–NH_3 complexes. Because EDTA forms a stronger complex with Cd^{2+} it will displace NH_3, but the stability of the Cd^{2+}–EDTA complex decreases.

We can account for the effect of an **auxiliary complexing agent**, such as NH_3, in the same way we accounted for the effect of pH. Before adding EDTA, the mass balance on Cd^{2+}, C_{Cd}, is

$$C_{Cd} = [Cd^{2+}] + [Cd(NH_3)^{2+}] + [Cd(NH_3)_2^{2+}] + [Cd(NH_3)_3^{2+}] + [Cd(NH_3)_4^{2+}] \tag{3}$$

and the fraction of uncomplexed Cd^{2+}, $\alpha_{Cd^{2+}}$, is

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{C_{Cd}} \tag{9.13}$$

> **Note**
>
> The value of $\alpha_{Cd^{2+}}$ depends on the concentration of NH_3. Contrast this with $\alpha_{Y^{4-}}$, which depends on pH.

Solving equation 9.13 for $[Cd^{2+}]$ and substituting into equation 9.12 gives

$$K_f' = K_f \times \alpha_{Y^{4-}} = \frac{[CdY^{2-}]}{\alpha_{Cd^{2+}} C_{Cd} C_{EDTA}} \tag{4}$$

Because the concentration of NH_3 in a buffer is essentially constant, we can rewrite this equation

$$K_f'' = K_f \times \alpha_{Y^{4-}} \times \alpha_{Cd^{2+}} = \frac{[CdY^{2-}]}{C_{Cd} C_{EDTA}} \tag{9.14}$$

to give a conditional formation constant, K_f'', that accounts for both pH and the auxiliary complexing agent's concentration. Table 9.12 provides values of $\alpha_{M^{2+}}$ for several metal ion when NH_3 is the complexing agent.

Table 9.12 Values of $\alpha_{M^{2+}}$ for Selected Concentrations of Ammonia

$[NH_3]$(M)	$\alpha_{Ca^{2+}}$	$\alpha_{Cd^{2+}}$	$\alpha_{Co^{2+}}$	$\alpha_{Cu^{2+}}$	$\alpha_{Mg^{2+}}$	$\alpha_{Ni^{2+}}$	$\alpha_{Zn^{2+}}$
1	5.50×10^{-1}	6.09×10^{-8}	1.00×10^{-6}	3.79×10^{-14}	1.76×10^{-1}	9.20×10^{-10}	3.95×10^{-10}
0.5	7.36×10^{-1}	1.05×10^{-6}	2.22×10^{-5}	6.86×10^{-13}	4.13×10^{-1}	3.44×10^{-8}	6.27×10^{-9}
0.1	9.39×10^{-1}	3.51×10^{-4}	6.64×10^{-3}	4.63×10^{-10}	8.48×10^{-1}	5.12×10^{-5}	3.68×10^{-6}
0.05	9.69×10^{-1}	2.72×10^{-3}	3.54×10^{-2}	7.17×10^{-9}	9.22×10^{-1}	6.37×10^{-4}	5.45×10^{-5}
0.01	9.94×10^{-1}	8.81×10^{-2}	3.55×10^{-1}	3.22×10^{-6}	9.84×10^{-1}	4.32×10^{-2}	1.82×10^{-2}
0.005	9.97×10^{-1}	2.27×10^{-1}	5.68×10^{-1}	3.62×10^{-5}	9.92×10^{-1}	1.36×10^{-1}	1.27×10^{-1}
0.001	9.99×10^{-1}	6.09×10^{-1}	8.84×10^{-1}	4.15×10^{-3}	9.98×10^{-1}	5.76×10^{-1}	7.48×10^{-1}

9.3.2 Complexometric EDTA Titration Curves

Now that we know something about EDTA's chemical properties, we are ready to evaluate its usefulness as a titrant. To do so we need to know the shape of a complexometric EDTA titration curve. In section 9B we learned that an acid–base titration curve shows how the titrand's pH changes as we add titrant. The analogous result for a complexation titration shows the change in pM, where M is the metal ion, as a function of the volume of EDTA. In this section we will learn how to calculate a titration curve using the equilibrium calculations from Chapter 6. We also will learn how to quickly sketch a good approximation of any complexation titration curve using a limited number of simple calculations.

Calculating the Titration Curve

Let's calculate the titration curve for 50.0 mL of 5.00×10^{-3} M Cd^{2+} using a titrant of 0.0100 M EDTA. Furthermore, let's assume that the titrand is buffered to a pH of 10 with a buffer that is 0.0100 M in NH_3.

Note

Step 1: Calculate the conditional formation constant for the metal–EDTA complex.

Because the pH is 10, some of the EDTA is present in forms other than Y^{4-}. In addition, EDTA must compete with NH_3 for the Cd^{2+}. To evaluate the titration curve, therefore, we first need to calculate the conditional formation constant for CdY^{2-}. From Table 9.10 and Table 9.11 we find that $\alpha_{Y^{4-}}$ is 0.35 at a pH of 10, and that $\alpha_{Cd^{2+}}$ is 0.0881 when the concentration of NH_3 is 0.0100 M. Using these values, the conditional formation constant is

$$K_f'' = K_f \times \alpha_{Y^{4-}} \times \alpha_{Cd^{2+}} = (2.9 \times 10^{16})(0.37)(0.0881) = 9.5 \times 10^{14} \tag{5}$$

Because K_f'' is so large, we can treat the titration reaction

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightarrow CdY^{2-}(aq) \tag{6}$$

as if it proceeds to completion.

Note

Step 2: Calculate the volume of EDTA needed to reach the equivalence point.

The next task in calculating the titration curve is to determine the volume of EDTA needed to reach the equivalence point. At the equivalence point we know that

$$\text{moles EDTA} = \text{moles } Cd^{2+} \tag{7}$$

$$M_{EDTA} \times V_{EDTA} = M_{Cd} \times V_{Cd} \tag{8}$$

Substituting in known values, we find that it requires

$$V_{eq} = V_{EDTA} = \frac{M_{Cd}V_{Cd}}{M_{EDTA}} = \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{0.0100\ \text{M}} = 25.0\ \text{mL} \tag{9}$$

of EDTA to reach the equivalence point.

Note

Step 3: Calculate pM values before the equivalence point by determining the concentration of unreacted metal ions.

Before the equivalence point, Cd^{2+} is present in excess and pCd is determined by the concentration of unreacted Cd^{2+}. Because not all the unreacted Cd^{2+} is free—some is complexed with NH_3—we must account for the presence of NH_3. For example, after adding 5.0 mL of EDTA, the total concentration of Cd^{2+} is

$$C_{Cd} = \frac{\text{initial moles } Cd^{2+} - \text{moles EDTA added}}{\text{total volume}} = \frac{M_{Cd}V_{Cd} - M_{EDTA}V_{EDTA}}{V_{Cd} + V_{EDTA}} \tag{10}$$

$$= \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL}) - (0.0100\ \text{M})(5.0\ \text{mL})}{50.0\ \text{mL} + 5.0\ \text{mL}} = 3.64 \times 10^{-3}\ \text{M} \tag{11}$$

To calculate the concentration of free Cd^{2+} we use equation 9.13

$$[Cd^{2+}] = \alpha_{Cd^{2+}} \times C_{Cd} = (0.0881)(3.64 \times 10^{-4}\ \text{M}) = 3.21 \times 10^{-4}\ \text{M} \tag{12}$$

which gives a pCd of

$$\text{pCd} = -\log[Cd^{2+}] = -\log(3.21 \times 10^{-4}) = 3.49 \tag{13}$$

Note

Step 4: Calculate pM at the equivalence point using the conditional formation constant.

At the equivalence point all the Cd^{2+} initially in the titrand is now present as CdY^{2-}. The concentration of Cd^{2+}, therefore, is determined by the dissociation of the CdY^{2-} complex. First, we calculate the concentration of CdY^{2-}.

$$[CdY^{2-}] = \frac{\text{initial moles } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}} \tag{14}$$

$$= \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 25.0\ \text{mL}} = 3.33 \times 10^{-3}\ \text{M} \tag{15}$$

Next, we solve for the concentration of Cd^{2+} in equilibrium with CdY^{2-}.

$$K_f'' = \frac{[CdY^{2-}]}{C_{Cd}C_{EDTA}} = \frac{3.33 \times 10^{-3} - x}{(x)(x)} = 9.5 \times 10^{14} \tag{16}$$

$$x = C_{Cd} = 1.9 \times 10^{-9}\ \text{M} \tag{17}$$

Note

At the equivalence point the initial moles of Cd^{2+} and the moles of EDTA added are equal. The total concentrations of Cd^{2+}, C_{Cd}, and the total concentration of EDTA, C_{EDTA}, are equal.

Once again, to find the concentration of uncomplexed Cd^{2+} we must account for the presence of NH_3; thus

$$[Cd^{2+}] = \alpha_{Cd^{2+}} \times C_{Cd} = (0.0881)(1.9 \times 10^{-9}\ \text{M}) = 1.70 \times 10^{-10}\ \text{M} \tag{18}$$

and pCd is 9.77 at the equivalence point.

Note

Step 5: Calculate pM after the equivalence point using the conditional formation constant.

After the equivalence point, EDTA is in excess and the concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. First, we calculate the concentrations of CdY^{2-} and of unreacted EDTA. For example, after adding 30.0 mL of EDTA

$$[CdY^{2-}] = \frac{\text{initial moles } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}} \tag{19}$$

$$= \frac{(5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 30.0\ \text{mL}} = 3.13 \times 10^{-3}\ \text{M} \tag{20}$$

$$C_{EDTA} = \frac{M_{EDTA}V_{EDTA} - M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}} \tag{21}$$

$$= \frac{(0.0100\ \text{M})(30.0\ \text{mL}) - (5.00 \times 10^{-3}\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 30.0\ \text{mL}} \tag{22}$$

$$= 6.25 \times 10^{-4}\ \text{M} \tag{23}$$

Substituting into equation 9.14 and solving for $[Cd^{2+}]$ gives

$$\frac{[CdY^{2-}]}{C_{Cd}C_{EDTA}} = \frac{3.13 \times 10^{-3}\ \text{M}}{C_{Cd}(6.25 \times 10^{-4}\ \text{M})} = 9.5 \times 10^{14} \tag{24}$$

$$C_{Cd} = 5.4 \times 10^{-15}\ \text{M} \tag{25}$$

$$[Cd^{2+}] = \alpha_{Cd^{2+}} \times C_{Cd} = (0.0881)(5.4 \times 10^{-15}\ \text{M}) = 4.8 \times 10^{-16}\ \text{M} \tag{26}$$

a pCd of 15.32. Table 9.13 and Figure 9.28 show additional results for this titration.

Note

After the equilibrium point we know the equilibrium concentrations of CdY^{2-} and EDTA. We can solve for the equilibrium concentration of C_{Cd} using K_f'' and then calculate $[Cd^{2+}]$ using $\alpha_{Cd^{2+}}$. Because we use the same conditional formation constant, K_f'', for all calculations, this is the approach shown here.

There is a second method for calculating $[Cd^{2+}]$ after the equivalence point. Because the calculation uses only $[CdY^{2-}]$ and C_{EDTA}, we can use K_f' instead of K_f''; thus

$$\frac{[CdY^{2-}]}{[Cd^{2+}]C_{EDTA}} = \alpha_{Y^{4-}} \times K_f \tag{27}$$

$$\frac{3.13 \times 10^{-3}\ \text{M}}{[Cd^{2+}](6.25 \times 10^{-4}\ \text{M})} = (0.37)(2.9 \times 10^{16}) \tag{28}$$

Solving gives $[Cd^{2+}] = 4.7 \times 10^{-16}$ M and a pCd of 15.33. We will use this approach when learning how to sketch a complexometric titration curve.

Table 9.13 Titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10 and in the Presence of 0.0100 M NH_3

Volume of EDTA (mL)	pCd	Volume of EDTA (mL)	pCd
0.00	3.36	27.0	14.95
5.00	3.49	30.0	15.33
10.0	3.66	35.0	15.61
15.0	3.87	40.0	15.76
20.0	4.20	45.0	15.86
23.0	4.62	50.0	15.94

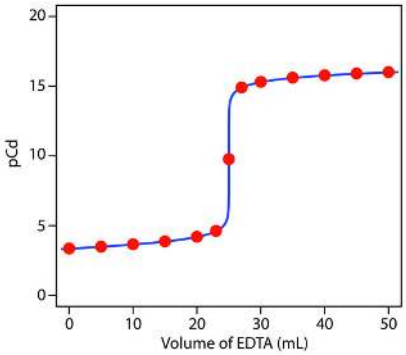

Figure 9.28 Titration curve for the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M NH_3. The red points correspond to the data in Table 9.13. The blue line shows the complete titration curve.

Practice Exercise 9.12

Calculate titration curves for the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7. Neither titration includes an auxiliary complexing agent. Compare your results with Figure 9.28 and comment on the effect of pH and of NH_3 on the titration of Cd^{2+} with EDTA.

Click here to review your answer to this exercise.

Sketching an EDTA Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point, we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a complexation titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA in the presence of 0.0100 M NH_3 to illustrate our approach.

Note

This is the same example that we used in developing the calculations for a complexation titration curve. You can review the results of that calculation in Table 9.13 and Figure 9.28.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 25.0 mL. Next, we draw our axes, placing pCd on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 25.0 mL of EDTA. Figure 9.29a shows the result of the first step in our sketch.

Before the equivalence point, Cd^{2+} is present in excess and pCd is determined by the concentration of unreacted Cd^{2+}. Because not all the unreacted Cd^{2+} is free—some is complexed with NH_3—we must account for the presence of NH_3. The calculations are straightforward, as we saw earlier. Figure 9.29b shows the pCd after adding 5.00 mL and 10.0 mL of EDTA.

Note

See Table 9.13 for the values.

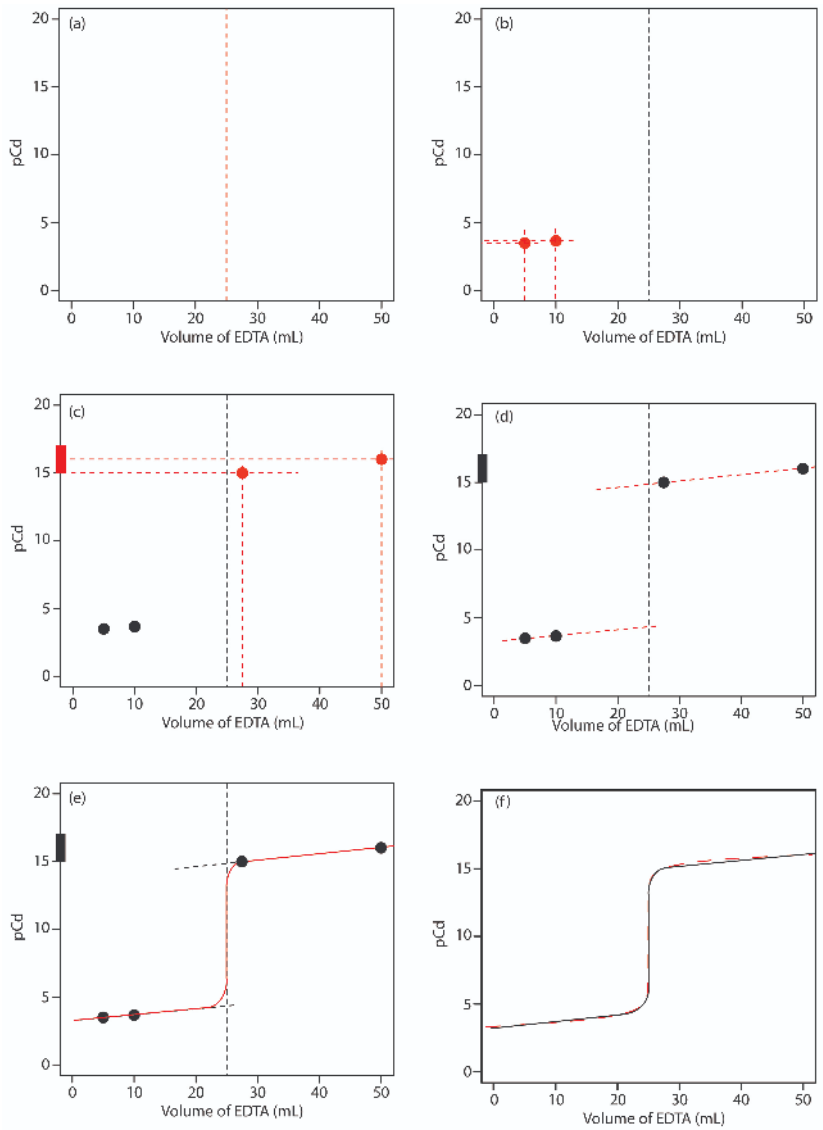

Figure 9.29 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA in the presence of 0.0100 M NH_3: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

The third step in sketching our titration curve is to add two points after the equivalence point. Here the concentration of Cd^{2+} is controlled by the dissociation of the Cd^{2+}–EDTA complex. Beginning with the conditional formation constant

$$K_f' = \frac{[CdY^{2-}]}{[Cd^{2+}]C_{EDTA}} = \alpha_{Y^{4-}} \times K_f = (0.37)(2.9 \times 10^{16}) = 1.1 \times 10^{16} \tag{29}$$

we take the log of each side and rearrange, arriving at

$$\log K_f' = -\log[Cd^{2+}] + \log \frac{[CdY^{2-}]}{C_{EDTA}} \tag{30}$$

$$pCd = \log K_f' + \log \frac{C_{EDTA}}{[CdY^{2-}]} \tag{31}$$

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> **Note**
>
> See the final side comment in the previous section for an explanation of why we are ignoring the effect of NH_3 on the concentration of Cd^{2+}.

Note that after the equivalence point, the titrand's solution is a metal–ligand complexation buffer, with pCd determined by C_{EDTA} and $[CdY^{2-}]$. The buffer is at its lower limit of pCd = $\log K_f' - 1$ when

$$\frac{C_{EDTA}}{[CdY^{2-}]} = \frac{\text{moles EDTA added} - \text{initial moles } Cd^{2+}}{\text{initial moles } Cd^{2+}} = \frac{1}{10} \tag{32}$$

Making appropriate substitutions and solving, we find that

$$\frac{M_{EDTA}V_{EDTA} - M_{Cd}V_{Cd}}{M_{Cd}V_{Cd}} = \frac{1}{10} \tag{33}$$

$$M_{EDTA}V_{EDTA} - M_{Cd}V_{Cd} = 0.1 \times M_{Cd}V_{Cd} \tag{34}$$

$$V_{EDTA} = \frac{1.1 \times M_{Cd}V_{Cd}}{M_{EDTA}} = 1.1 \times V_{eq} \tag{35}$$

Thus, when the titration reaches 110% of the equivalence point volume, pCd is $\log K_f' - 1$. A similar calculation should convince you that pCd = $\log K_f'$ when the volume of EDTA is $2 \times V_{eq}$.

> **Note**
>
> Our derivation here is general and applies to any complexation titration using EDTA as a titrant.

Figure 9.29c shows the third step in our sketch. First, we add a ladder diagram for the CdY^{2-} complex, including its buffer range, using its $\log K_f'$ value of 16.04. Next, we add points representing pCd at 110% of V_{eq} (a pCd of 15.04 at 27.5 mL) and at 200% of V_{eq} (a pCd of 16.04 at 50.0 mL).

Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point's volume (Figure 9.29d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.29e). A comparison of our sketch to the exact titration curve (Figure 9.29f) shows that they are in close agreement.

> **Practice Exercise 9.13**
>
> Sketch titration curves for the titration of 50.0 mL of 5.00×10^{-3} M Cd^{2+} with 0.0100 M EDTA (a) at a pH of 10 and (b) at a pH of 7. Compare your sketches to the calculated titration curves from Practice Exercise 9.12.
>
> Click here to review your answer to this exercise.

9.3.3 Selecting and Evaluating the End point

The equivalence point of a complexation titration occurs when we react stoichiometrically equivalent amounts of titrand and titrant. As is the case with acid–base titrations, we estimate the equivalence point of a complexation titration using an experimental end point. A variety of methods are available for locating the end point, including indicators and sensors that respond to a change in the solution conditions.

Finding the End point with an Indicator

Most indicators for complexation titrations are organic dyes—known as **metallochromic indicators**—that form stable complexes with metal ions. The indicator, In^{m-}, is added to the titrand's solution where it forms a stable complex with the metal ion, MIn^{n-}. As we add EDTA it reacts first with free metal ions, and then displaces the indicator from MIn^{n-}.

$$MIn^{n-} + Y^{4-} \rightarrow MY^{2-} + In^{m-} \tag{36}$$

If MIn^{n-} and In^{m-} have different colors, then the change in color signals the end point.

The accuracy of an indicator's end point depends on the strength of the metal–indicator complex relative to that of the metal–EDTA complex. If the metal–indicator complex is too strong, the change in color occurs after the equivalence point. If the metal–indicator complex is too weak, however, the end point occurs before we reach the equivalence point.

Most metallochromic indicators also are weak acids. One consequence of this is that the conditional formation constant for the metal–indicator complex depends on the titrand's pH. This provides some control over an indicator's titration error because we can adjust the strength of a metal–indicator complex by adjusted the pH at which we carry out the titration. Unfortunately, because the indicator is a weak acid, the color of the uncomplexed indicator also changes with pH. Figure 9.30, for example, shows the color of the indicator calmagite as a function of pH and pMg, where H_2In^-, HIn^{2-}, and In^{3-} are different forms of the uncomplexed indicator, and $MgIn^-$ is the Mg^{2+}–calmagite complex. Because the color of calmagite's metal–indicator complex is red, its use as a metallochromic indicator has a practical pH range of approximately 8.5–11 where the uncomplexed indicator, HIn^{2-}, has a blue color.

Note

Figure 9.30 is essentially a two-variable ladder diagram. The solid lines are equivalent to a step on a conventional ladder diagram, indicating conditions where two (or three) species are equal in concentration.

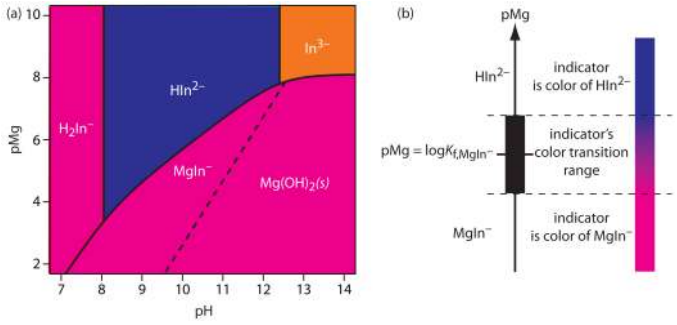

Figure 9.30 (a) Predominance diagram for the metallochromic indicator calmagite showing the most important form and color of calmagite as a function of pH and pMg, where H_2In^-, HIn^{2-}, and In^{3-} are uncomplexed forms of calmagite, and $MgIn^-$ is its complex with Mg^{2+}. Conditions to the right of the dashed line, where Mg^{2+} precipitates as $Mg(OH)_2$, are not analytically useful for a complexation titration. A red to blue end point is possible if we maintain the titrand's pH in the range 8.5–11. (b) Diagram showing the relationship between the concentration of Mg^{2+} (as pMg) and the indicator's color. The ladder diagram defines pMg values where $MgIn^-$ and HIn^- are predominate species. The indicator changes color when pMg is between $\log K_f - 1$ and $\log K_f + 1$.

Table 9.14 provides examples of metallochromic indicators and the metal ions and pH conditions for which they are useful. Even if a suitable indicator does not exist, it is often possible to complete an EDTA titration by introducing a small amount of a secondary metal–EDTA complex, if the secondary metal ion forms a stronger complex with the indicator and a weaker complex with EDTA than the analyte. For example, calmagite gives poor end points when titrating Ca^{2+} with EDTA. Adding a small amount of Mg^{2+}–EDTA to the titrand gives a sharper end point. Because Ca^{2+} forms a stronger complex with EDTA, it displaces Mg^{2+}, which then forms the red-colored Mg^{2+}–calmagite complex. At the titration's end point, EDTA displaces Mg^{2+} from the Mg^{2+}–calmagite complex, signaling the end point by the presence of the uncomplexed indicator's blue form.

Table 9.14 Selected Metallochromic Indicators

Indicator	pH Range	Metal Ions[a]
calmagite	8.5–11	Ba, *Ca*, Mg, Zn
eriochrome Black T	7.5–10.5	Ba, *Ca*, Mg, Zn
eriochrome Blue Black R	8–12	*Ca*, Mg, Zn, Cu
murexide	6–13	Ca, Ni, Cu
PAN	2–11	Cd, Cu, Zn
salicylic acid	2–3	Fe

[a] metal ions in *italic* font have poor end points

Note

Two other methods for finding the end point of a complexation titration are a thermometric titration, in which we monitor the titrand's temperature as we add the titrant, and a potentiometric titration in which we use an ion selective electrode to monitor the metal ion's concentration as we add the titrant. The experimental approach is essentially identical to that described earlier for an acid–base titration, to which you may refer.

See Chapter 11 for more details about ion selective electrodes.

An important limitation when using an indicator is that we must be able to see the indicator's change in color at the end point. This may be difficult if the solution is already colored. For example, when titrating Cu^{2+} with EDTA, ammonia is used to adjust the titrand's pH. The intensely colored $Cu(NH_3)_4^{2+}$ complex obscures the indicator's color, making an accurate determination of the end point difficult. Other absorbing species present within the sample matrix may also interfere. This is often a problem when analyzing clinical samples, such as blood, or environmental samples, such as natural waters.

If at least one species in a complexation titration absorbs electromagnetic radiation, we can identify the end point by monitoring the titrand's absorbance at a carefully selected wavelength. For example, we can identify the end point for a titration of Cu^{2+} with EDTA, in the presence of NH_3 by monitoring the titrand's absorbance at a wavelength of 745 nm, where the $Cu(NH_3)_4^{2+}$ complex absorbs strongly. At the beginning of the titration the absorbance is at a maximum. As we add EDTA, however, the reaction

$$Cu(NH_3)_4^{2+}(aq) + Y^{4-}(aq) \rightarrow CuY^{2-}(aq) + 4NH_3(aq) \tag{37}$$

decreases the concentration of $Cu(NH_3)_4^{2+}$ and decreases the absorbance until we reach the equivalence point. After the equivalence point the absorbance remains essentially unchanged. The resulting **spectrophotometric titration curve** is shown in Figure 9.31a. Note that the titration curve's *y*-axis is not the actual absorbance, A, but a corrected absorbance, A_{corr}

$$A_{corr} = A \times \frac{V_{EDTA} + V_{Cu}}{V_{Cu}} \tag{38}$$

where V_{EDTA} and V_{Cu} are, respectively, the volumes of EDTA and Cu. Correcting the absorbance for the titrand's dilution ensures that the spectrophotometric titration curve consists of linear segments that we can extrapolate to find the end point. Other common spectrophotometric titration curves are shown in Figures 9.31b-f.

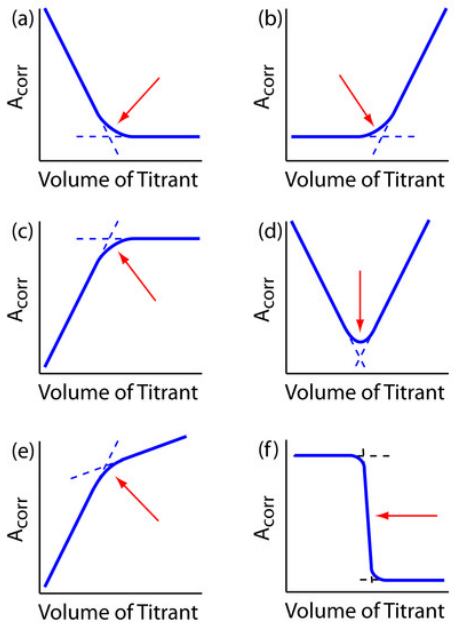

Figure 9.31 Examples of spectrophotometric titration curves: (a) only the titrand absorbs; (b) only the titrant absorbs; (c) only the product of the titration reaction absorbs; (d) both the titrand and the titrant absorb; (e) both the titration reaction's product and the titrant absorb; (f) only the indicator absorbs. The red arrows indicate the end points for each titration curve.

Note

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical complexation titrimetric method. Although each method is unique, the following description of the determination of the hardness of water provides an instructive example of a typical procedure. The description here is based on Method 2340C as published in *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., American Public Health Association: Washington, D. C., 1998.

Representative Method 9.2

Determination of Hardness of Water and Wastewater

Description of the Method

The operational definition of water hardness is the total concentration of cations in a sample capable of forming insoluble complexes with soap. Although most divalent and trivalent metal ions contribute to hardness, the most important are Ca^{2+} and Mg^{2+}. Hardness is determined by titrating with EDTA at a buffered pH of 10. Calmagite is used as an indicator. Hardness is reported as mg $CaCO_3$/L.

Procedure

Select a volume of sample requiring less than 15 mL of titrant to keep the analysis time under 5 minutes and, if necessary, dilute the sample to 50 mL with distilled water. Adjust the sample's pH by adding 1–2 mL of a pH 10 buffer containing a small amount of Mg^{2+}–EDTA. Add 1–2 drops of indicator and titrate with a standard solution of EDTA until the red-to-blue end point is reached (Figure 9.32).

Questions

1. Why is the sample buffered to a pH of 10? What problems might you expect at a higher pH or a lower pH?

Of the cations contributing to hardness, Mg^{2+} forms the weakest complex with EDTA and is the last cation to be titrated. Calmagite is a useful indicator because it gives a distinct end point when titrating Mg^{2+}. Because of calmagite's acid–base properties, the range of pMg values over which the indicator changes color is pH–dependent (Figure 9.30). Figure 9.33 shows the titration curve for a 50-mL solution of 10^{-3} M Mg^{2+} with 10^{-2} M EDTA at pHs of 9, 10, and 11. Superimposed on each titration curve is the range of conditions for which the average analyst will observe the end point. At a pH of 9 an early end point is possible, leading to a negative determinate error. A late end point and a positive determinate error are possible if we use a pH of 11.

2. Why is a small amount of the Mg^{2+}–EDTA complex added to the buffer?

The titration's end point is signaled by the indicator calmagite. The indicator's end point with Mg^{2+} is distinct, but its change in color when titrating Ca^{2+} does not provide a good end point. If the sample does not contain any Mg^{2+} as a source of hardness, then the titration's end point is poorly defined, leading to inaccurate and imprecise results.

Adding a small amount of Mg^{2+}–EDTA to the buffer ensures that the titrand includes at least some Mg^{2+}. Because Ca^{2+} forms a stronger complex with EDTA, it displaces Mg^{2+} from the Mg^{2+}–EDTA complex, freeing the Mg^{2+} to bind with the indicator. This displacement is stoichiometric, so the total concentration of hardness cations remains unchanged. The displacement by EDTA of Mg^{2+} from the Mg^{2+}–indicator complex signals the titration's end point.

3. Why does the procedure specify that the titration take no longer than 5 minutes?

A time limitation suggests that there is a kinetically controlled interference, possibly arising from a competing chemical reaction. In this case the interference is the possible precipitation of $CaCO_3$ at a pH of 10.

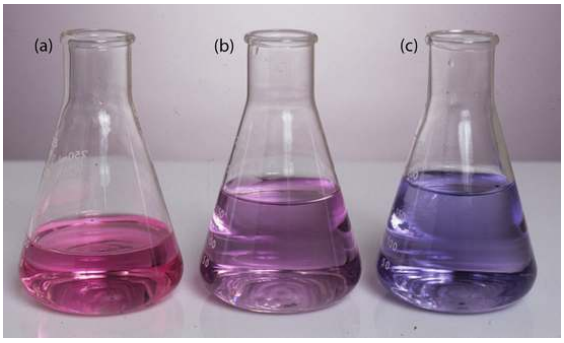

Figure 9.32 End point for the titration of hardness with EDTA using calmagite as an indicator; the indicator is: (a) red prior to the end point due to the presence of the Mg^{2+}–indicator complex; (b) purple at the titration's end point; and (c) blue after the end point due to the presence of uncomplexed indicator.

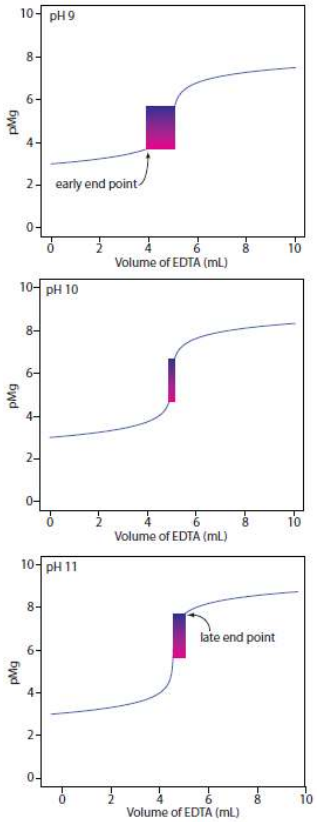

Figure 9.33 Titration curves for 50 mL of 10^{-3} M Mg^{2+} with 10^{-3} M EDTA at pHs 9, 10, and 11 using calmagite as an indicator. The range of pMg and volume of EDTA over which the indicator changes color is shown for each titration curve.

9.3.4 Quantitative Applications

Although many quantitative applications of complexation titrimetry have been replaced by other analytical methods, a few important applications continue to be relevant. In the section we review the general application of complexation titrimetry with an emphasis on applications from the analysis of water and wastewater. First, however, we discuss the selection and standardization of complexation titrants.

Selection and Standardization of Titrants

EDTA is a versatile titrant that can be used to analyze virtually all metal ions. Although EDTA is the usual titrant when the titrand is a metal ion, it cannot be used to titrate anions. In the later case, Ag^{+} or Hg^{2+} are suitable titrants.

Solutions of EDTA are prepared from its soluble disodium salt, $Na_2H_2Y•2H_2O$ and standardized by titrating against a solution made from the primary standard $CaCO_3$. Solutions of Ag^+ and Hg^{2+} are prepared using $AgNO_3$ and $Hg(NO_3)_2$, both of which are secondary standards. Standardization is accomplished by titrating against a solution prepared from primary standard grade NaCl.

Inorganic Analysis

Complexation titrimetry continues to be listed as a standard method for the determination of hardness, Ca^{2+}, CN^-, and Cl^- in waters and wastewaters. The evaluation of hardness was described earlier in Representative Method 9.2. The determination of Ca^{2+} is complicated by the presence of Mg^{2+}, which also reacts with EDTA. To prevent an interference the pH is adjusted to 12–13, precipitating Mg^{2+} as $Mg(OH)_2$. Titrating with EDTA using murexide or Eriochrome Blue Black R as the indicator gives the concentration of Ca^{2+}.

Cyanide is determined at concentrations greater than 1 mg/L by making the sample alkaline with NaOH and titrating with a standard solution of $AgNO_3$, forming the soluble $Ag(CN)_2^-$ complex. The end point is determined using *p*-dimethylaminobenzalrhodamine as an indicator, with the solution turning from a yellow to a salmon color in the presence of excess Ag^+.

Chloride is determined by titrating with $Hg(NO_3)_2$, forming $HgCl_2(aq)$. The sample is acidified to a pH of 2.3–3.8 and diphenylcarbazone, which forms a colored complex with excess Hg^{2+}, serves as the indicator. A pH indicator—xylene cyanol FF—is added to ensure that the pH is within the desired range. The initial solution is a greenish blue, and the titration is carried out to a purple end point.

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. For a titration using EDTA, the stoichiometry is always 1:1.

Example 9.7

The concentration of a solution of EDTA was determined by standardizing against a solution of Ca^{2+} prepared using a primary standard of $CaCO_3$. A 0.4071-g sample of $CaCO_3$ was transferred to a 500-mL volumetric flask, dissolved using a minimum of 6 M HCl, and diluted to volume. After transferring a 50.00-mL portion of this solution to a 250-mL Erlenmeyer flask, the pH was adjusted by adding 5 mL of a pH 10 NH_3–NH_4Cl buffer containing a small amount of Mg^{2+}–EDTA. After adding calmagite as an indicator, the solution was titrated with the EDTA, requiring 42.63 mL to reach the end point. Report the molar concentration of EDTA in the titrant.

(Note that in this example, the analyte is the titrant.)

Solution

The primary standard of Ca^{2+} has a concentration of

$$\frac{0.4071\text{ g }CaCO_3}{0.5000\text{ L}} \times \frac{1\text{ mol }Ca^{2+}}{100.09\text{ g }CaCO_3} = 8.135 \times 10^{-3}\text{ M }Ca^{2+} \tag{39}$$

The moles of Ca^{2+} in the titrand is

$$8.135 \times 10^{-3}\text{ M }Ca^{2+} \times 0.05000\text{ L }Ca^{2+} = 4.068 \times 10^{-4}\text{ mol }Ca^{2+} \tag{40}$$

which means that 4.068×10^{-4} moles of EDTA are used in the titration. The molarity of EDTA in the titrant is

$$\frac{4.068 \times 10^{-4}\text{ mol EDTA}}{0.04263\text{ L EDTA}} = 9.543 \times 10^{-3}\text{ M EDTA} \tag{41}$$

Practice Exercise 9.14

A 100.0-mL sample is analyzed for hardness using the procedure outlined in Representative Method 9.2, requiring 23.63 mL of 0.0109 M EDTA. Report the sample's hardness as mg $CaCO_3$/L.

Click here to review your answer to this exercise.

As shown in the following example, we can easily extended this calculation to complexation reactions using other titrants.

Example 9.8

The concentration of Cl^- in a 100.0-mL sample of water from a freshwater aquifer was tested for the encroachment of sea water by titrating with 0.0516 M $Hg(NO_3)_2$. The sample was acidified and titrated to the diphenylcarbazone end point, requiring 6.18 mL of the titrant. Report the concentration of Cl^-, in mg/L, in the aquifer.

Solution

The reaction between Cl^- and Hg^{2+} produces a metal–ligand complex of $HgCl_2(aq)$. Each mole of Hg^{2+} reacts with 2 moles of Cl^-; thus

$$\frac{0.0516 \text{ mol } Hg(NO_3)_2}{\text{L}} \times 0.00618 \text{ L } Hg(NO_3)_2 \times \frac{2 \text{ mol } Cl^-}{\text{mol } Hg(NO_3)_2} \times \frac{35.453 \text{ g } Cl^-}{\text{mol } Cl^-} = 0.0226 \text{ g } Cl^- \quad (42)$$

are in the sample. The concentration of Cl^- in the sample is

$$\frac{0.0226 \text{ g } Cl^-}{0.1000 \text{ L}} \times \frac{1000 \text{ mg}}{\text{g}} = 226 \text{ mg/L} \quad (43)$$

Practice Exercise 9.15

A 0.4482-g sample of impure NaCN is titrated with 0.1018 M $AgNO_3$, requiring 39.68 mL to reach the end point. Report the purity of the sample as %w/w NaCN.

Click here to review your answer to this exercise.

Finally, complex titrations involving multiple analytes or back titrations are possible.

Example 9.9

An alloy of chromel containing Ni, Fe, and Cr was analyzed by a complexation titration using EDTA as the titrant. A 0.7176-g sample of the alloy was dissolved in HNO_3 and diluted to 250 mL in a volumetric flask. A 50.00-mL aliquot of the sample, treated with pyrophosphate to mask the Fe and Cr, required 26.14 mL of 0.05831 M EDTA to reach the murexide end point. A second 50.00-mL aliquot was treated with hexamethylenetetramine to mask the Cr. Titrating with 0.05831 M EDTA required 35.43 mL to reach the murexide end point. Finally, a third 50.00-mL aliquot was treated with 50.00 mL of 0.05831 M EDTA, and back titrated to the murexide end point with 6.21 mL of 0.06316 M Cu^{2+}. Report the weight percents of Ni, Fe, and Cr in the alloy.

Solution

The stoichiometry between EDTA and each metal ion is 1:1. For each of the three titrations, therefore, we can easily equate the moles of EDTA to the moles of metal ions that are titrated.

Titration 1: moles Ni = moles EDTA

Titration 2: moles Ni + moles Fe = moles EDTA

Titration 3: moles Ni + moles Fe + moles Cr + moles Cu = moles EDTA

We can use the first titration to determine the moles of Ni in our 50.00-mL portion of the dissolved alloy. The titration uses

$$\frac{0.05831 \text{ mol EDTA}}{\text{L}} \times 0.02614 \text{ L EDTA} = 1.524 \times 10^{-3} \text{ mol EDTA} \quad (44)$$

which means the sample contains 1.524×10^{-3} mol Ni.

Having determined the moles of EDTA reacting with Ni, we can use the second titration to determine the amount of Fe in the sample. The second titration uses

$$\frac{0.05831 \text{ mol EDTA}}{\text{L}} \times 0.03543 \text{ L EDTA} = 2.066 \times 10^{-3} \text{ mol EDTA} \quad (45)$$

of which 1.524×10^{-3} mol are used to titrate Ni. This leaves 5.42×10^{-4} mol of EDTA to react with Fe; thus, the sample contains 5.42×10^{-4} mol of Fe.

Finally, we can use the third titration to determine the amount of Cr in the alloy. The third titration uses

$$\frac{0.05831 \text{ mol EDTA}}{\text{L}} \times 0.05000 \text{ L EDTA} = 2.916 \times 10^{-3} \text{ mol EDTA} \quad (46)$$

of which 1.524×10^{-3} mol are used to titrate Ni and 5.42×10^{-4} mol are used to titrate Fe. This leaves 8.50×10^{-4} mol of EDTA to react with Cu and Cr. The amount of EDTA reacting with Cu is

$$\frac{0.06316 \text{ mol } Cu^{2+}}{\text{L}} \times 0.00621 \text{ L } Cu^{2+} \times \frac{1 \text{ mol EDTA}}{\text{mol } Cu^{2+}} = 3.92 \times 10^{-4} \text{ mol EDTA} \quad (47)$$

leaving 4.58×10^{-4} mol of EDTA to react with Cr. The sample, therefore, contains 4.58×10^{-4} mol of Cr.

Having determined the moles of Ni, Fe, and Cr in a 50.00-mL portion of the dissolved alloy, we can calculate the %w/w of each analyte in the alloy.

$$\frac{1.524 \times 10^{-3} \text{ mol Ni}}{50.00 \text{ mL}} \times 250.0 \text{ mL} \times \frac{58.69 \text{ g Ni}}{\text{mol Ni}} = 0.4472 \text{ g Ni} \quad (48)$$

$$\frac{0.4472 \text{ g Ni}}{0.7176 \text{ g sample}} \times 100 = 62.32\% \text{ w/w Ni} \quad (49)$$

$$\frac{5.42 \times 10^{-4} \text{ mol Fe}}{50.00 \text{ mL}} \times 250.0 \text{ mL} \times \frac{55.847 \text{ g Fe}}{\text{mol Fe}} = 0.151 \text{ g Fe} \quad (50)$$

$$\frac{0.151 \text{ g Fe}}{0.7176 \text{ g sample}} \times 100 = 21.0\% \text{ w/w Fe} \quad (51)$$

$$\frac{4.58 \times 10^{-4} \text{ mol Cr}}{50.00 \text{ mL}} \times 250.0 \text{ mL} \times \frac{51.996 \text{ g Cr}}{\text{mol Cr}} = 0.119 \text{ g Cr} \quad (52)$$

$$\frac{0.119 \text{ g Cr}}{0.7176 \text{ g sample}} \times 100 = 16.6\% \text{ w/w Fe} \quad (53)$$

Practice Exercise 9.16

A indirect complexation titration with EDTA can be used to determine the concentration of sulfate, SO_4^{2-}, in a sample. A 0.1557-g sample is dissolved in water, any sulfate present is precipitated as $BaSO_4$ by adding $Ba(NO_3)_2$. After filtering and rinsing the precipitate, it is dissolved in 25.00 mL of 0.02011 M EDTA. The excess EDTA is then titrated with 0.01113 M Mg^{2+}, requiring 4.23 mL to reach the end point. Calculate the %w/w Na_2SO_4 in the sample.

Click here to review your answer to this exercise.

9.3.5 Evaluation of Complexation Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a complexation titration are similar to those described earlier for acid–base titrations. Complexation titrations, however, are more selective. Although EDTA forms strong complexes with most metal ion, by carefully controlling the titrand's pH we can analyze samples containing two or more analytes. The reason we can use pH to provide selectivity is shown in Figure 9.34a. A titration of Ca^{2+} at a pH of 9 gives a distinct break in the titration curve because the conditional formation constant for CaY^{2-} of 2.6×10^9 is large enough to ensure that the reaction of Ca^{2+} and EDTA goes to completion. At a pH of 3, however, the conditional formation constant of 1.23 is so small that very little Ca^{2+} reacts with the EDTA.

Suppose we need to analyze a mixture of Ni^{2+} and Ca^{2+}. Both analytes react with EDTA, but their conditional formation constants differ significantly. If we adjust the pH to 3 we can titrate Ni^{2+} with EDTA without titrating Ca^{2+} (Figure 9.34b). When the titration is complete, we adjust the titrand's pH to 9 and titrate the Ca^{2+} with EDTA.

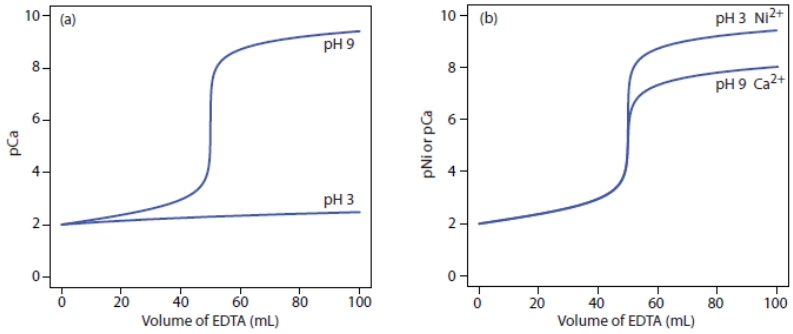

Figure 9.34 Titration curves illustrating how we can use the titrand's pH to control EDTA's selectivity. (a) Titration of 50.0 mL of 0.010 M Ca^{2+} at a pH of 3 and a pH of 9 using 0.010 M EDTA. At a pH of 3 the CaY^{2-} complex is too weak to successfully titrate. (b) Titration of a 50.0 mL mixture of 0.010 M Ca^{2+} and 0.010 M Ni^{2+} at a pH of 3 and a pH of 9 using 0.010 M EDTA. At a pH of 3 EDTA reacts only with Ni^{2+}. When the titration is complete, raising the pH to 9 allows for the titration of Ca^{2+}.

A spectrophotometric titration is a particularly useful approach for analyzing a mixture of analytes. For example, as shown in Figure 9.35, we can determine the concentration of a two metal ions if there is a difference between the absorbance of the two metal-ligand complexes.

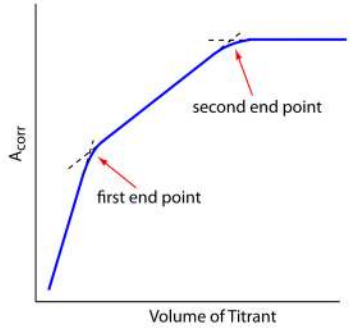

Figure 9.35 Spectrophotometric titration curve for the complexation titration of a mixture of two analytes. The red arrows indicate the end points for each analyte.

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Precipitation Titration

Thus far we have examined titrimetric methods based on acid–base, complexation, and redox reactions. A reaction in which the analyte and titrant form an insoluble precipitate also can serve as the basis for a titration. We call this type of titration a **precipitation titration**.

One of the earliest precipitation titrations—developed at the end of the eighteenth century—was the analysis of K_2CO_3 and K_2SO_4 in potash. Calcium nitrate, $Ca(NO_3)_2$, was used as the titrant, forming a precipitate of $CaCO_3$ and $CaSO_4$. The titration's end point was signaled by noting when the addition of titrant ceased to generate additional precipitate. The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag^+ and halide ions.

9.5.1 Titration Curves

A precipitation titration curve follows the change in either the titrand's or the titrant's concentration as a function of the titrant's volume. As we have done with other titrations, we first show how to calculate the titration curve and then demonstrate how we can quickly sketch a reasonable approximation of the titration curve.

Calculating the Titration Curve

Let's calculate the titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$. The reaction in this case is

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \tag{1}$$

Because the reaction's equilibrium constant is so large

$$K = (K_{sp})^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^9 \tag{2}$$

we may assume that Ag^+ and Cl^- react completely.

> **Note**
>
> Step 1: Calculate the volume of $AgNO_3$ needed to reach the equivalence point.

By now you are familiar with our approach to calculating a titration curve. The first task is to calculate the volume of Ag^+ needed to reach the equivalence point. The stoichiometry of the reaction requires that

$$\text{moles } Ag^+ = \text{moles } Cl^- \tag{3}$$

$$M_{Ag} \times V_{Ag} = M_{Cl} \times V_{Cl} \tag{4}$$

Solving for the volume of Ag^+

$$V_{eq} = V_{Ag} = \frac{M_{Cl}V_{Cl}}{M_{Ag}} = \frac{(0.0500\text{ M})(50.0\text{ mL})}{(0.100\text{ M})} = 25.0\text{ mL} \tag{5}$$

shows that we need 25.0 mL of Ag+ to reach the equivalence point.

> **Note**
>
> Step 2: Calculate pCl before the equivalence point by determining the concentration of unreacted NaCl.

Before the equivalence point the titrand, Cl^-, is in excess. The concentration of unreacted Cl^- after adding 10.0 mL of Ag^+, for example, is

$$[Cl^-] = \frac{\text{initial moles } Cl^- - \text{moles } Ag^+ \text{ added}}{\text{total volume}} = \frac{M_{Cl}V_{Cl} - M_{Ag}V_{Ag}}{V_{Cl} + V_{Ag}} \tag{6}$$

$$= \frac{(0.0500\text{ M})(50.0\text{ mL}) - (0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 2.50 \times 10^{-2}\text{ M} \tag{7}$$

which corresponds to a pCl of 1.60.

Note

Step 3: Calculate pCl at the equivalence point using the K_{sp} for AgCl to calculate the concentration of Cl^-.

At the titration's equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. To calculate the concentration of Cl^- we use the K_{sp} expression for AgCl; thus

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = 1.8 \times 10^{-10} \tag{8}$$

Solving for x gives $[Cl^-]$ as 1.3×10^{-5} M, or a pCl of 4.89.

Note

Step 4: Calculate pCl after the equivalence point by first calculating the concentration of excess $AgNO_3$ and then calculating the concentration of Cl^- using the K_{sp} for AgCl.

After the equivalence point, the titrant is in excess. We first calculate the concentration of excess Ag^+ and then use the K_{sp} expression to calculate the concentration of Cl^-. For example, after adding 35.0 mL of titrant

$$[Ag^+] = \frac{\text{moles } Ag^+ \text{ added} - \text{initial moles } Cl^-}{\text{total volume}} = \frac{M_{Ag}V_{Ag} - M_{Cl}V_{Cl}}{V_{Cl} + V_{Ag}} \tag{9}$$

$$= \frac{(0.100 \text{ M})(35.0 \text{ mL}) - (0.0500 \text{ M})(50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}} = 1.18 \times 10^{-2} \text{ M} \tag{10}$$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8} \text{ M} \tag{11}$$

or a pCl of 7.81. Additional results for the titration curve are shown in Table 9.18 and Figure 9.43.

Table 9.18: Titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$

Volume of $AgNO_3$ (mL)	pCl	Volume of $AgNO_3$ (mL)	pCl
0.00	1.30	30.0	7.54
5.00	1.44	35.0	7.82
10.0	1.60	40.0	7.97
15.0	1.81	45.0	8.07
20.0	2.15	50.0	8.14
25.0	4.89		

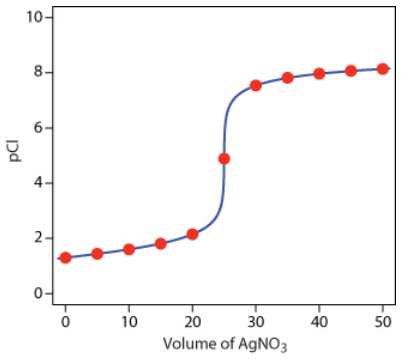

Figure 9.43 *Titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$. The red points corresponds to the data in Table 9.18. The blue line shows the complete titration curve.*

Practice Exercise 9.22

When calculating a precipitation titration curve, you can choose to follow the change in the titrant's concentration or the change in the titrand's concentration. Calculate the titration curve for the titration of 50.0 mL of 0.0500 M $AgNO_3$ with 0.100 M NaCl as pAg versus V_{NaCl}, and as pCl versus V_{NaCl}.

Click here to review your answer to this exercise.

Sketching the Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a precipitation titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$.

Note

This is the same example that we used in developing the calculations for a precipitation titration curve. You can review the results of that calculation in Table 9.18 and Figure 9.43.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 25.0 mL. Next we draw our axes, placing pCl on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 25.0 mL of $AgNO_3$. Figure 9.44a shows the result of this first step in our sketch.

Before the equivalence point, Cl^- is present in excess and pCl is determined by the concentration of unreacted Cl^-. As we learned earlier, the calculations are straightforward. Figure 9.44b shows pCl after adding 10.0 mL and 20.0 mL of $AgNO_3$.

Note

See Table 9.18 for the values.

After the equivalence point, Ag^+ is in excess and the concentration of Cl^- is determined by the solubility of AgCl. Again, the calculations are straightforward. Figure 4.43c shows pCl after adding 30.0 mL and 40.0 mL of $AgNO_3$.

Note

See Table 9.18 for the values.

Next, we draw a straight line through each pair of points, extending them through the vertical line representing the equivalence point's volume (Figure 9.44d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.44e). A comparison of our sketch to the exact titration curve (Figure 9.44f) shows that they are in close agreement.

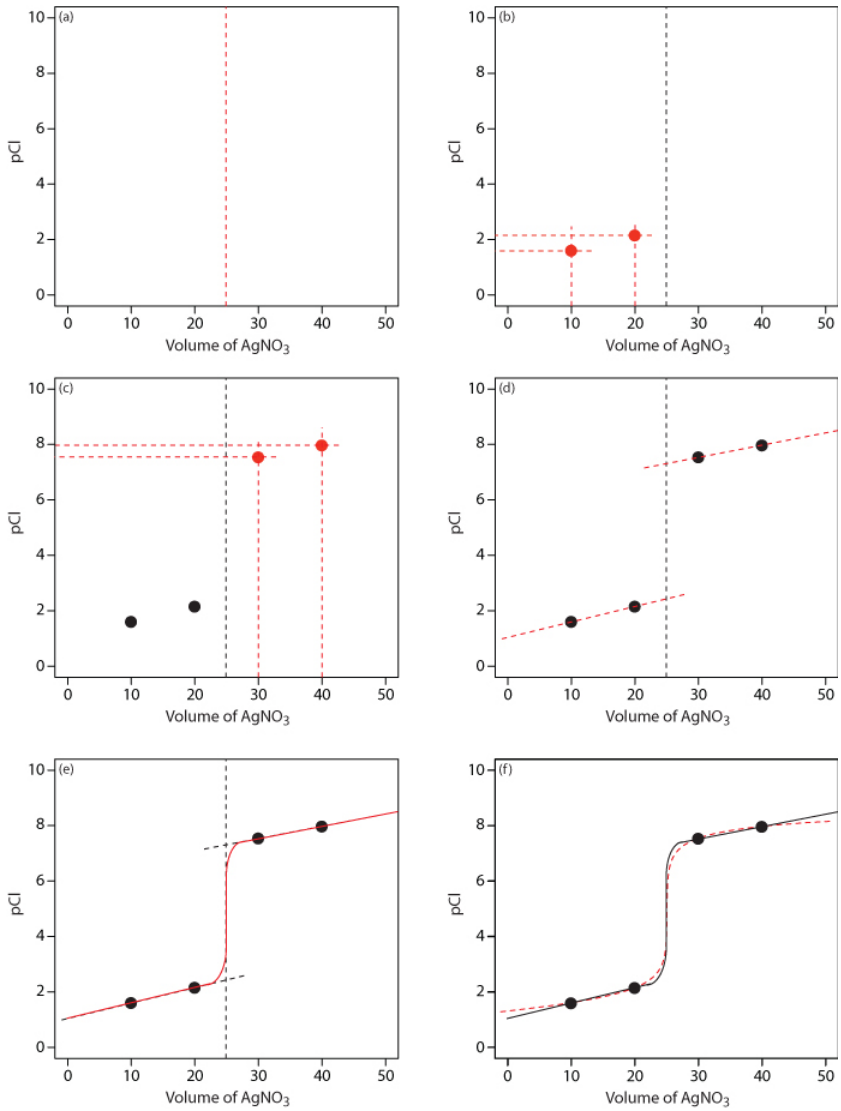

Figure 9.44 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.0500 M NaCl with 0.100 M $AgNO_3$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details. A better fit is possible if the two points before the equivalence point are further apart—for example, 0 mL and 20 mL— and the two points after the equivalence point are further apart.

9.5.2 Selecting and Evaluating the End point

At the beginning of this section we noted that the first precipitation titration used the cessation of precipitation to signal the end point. At best, this is a cumbersome method for detecting a titration's end point. Before precipitation titrimetry became practical, better methods for identifying the end point were necessary.

Finding the End point With an Indicator

There are three general types of indicators for precipitation titrations, each of which changes color at or near the titration's equivalence point. The first type of indicator is a species that forms a precipitate with the titrant. In the **Mohr method** for Cl^- using Ag^+ as a titrant, for example, a small amount of K_2CrO_4 is added to the titrand's solution. The titration's end point is the formation of a reddish-brown precipitate of Ag_2CrO_4.

> **Note**
>
> The Mohr method was first published in 1855 by Karl Friedrich Mohr.

Because CrO_4^{2-} imparts a yellow color to the solution, which might obscure the end point, only a small amount of K_2CrO_4 is added. As a result, the end point is always later than the equivalence point. To compensate for this positive determinate error, an analyte-free reagent blank is analyzed to determine the volume of titrant needed to affect a change in the indicator's color. Subtracting the end point for the reagent blank from the titrand's end point gives the titration's end point. Because CrO_4^{2-} is a weak base, the titrand's solution is made slightly alkaline. If the pH is too acidic, chromate is present as $HCrO_4^-$ instead of CrO_4^{2-}, and the Ag_2CrO_4 end point is delayed. The pH also must be less than 10 to avoid the precipitation of silver hydroxide.

A second type of indicator uses a species that forms a colored complex with the titrant or the titrand. In the **Volhard method** for Ag^+ using KSCN as the titrant, for example, a small amount of Fe^{3+} is added to the titrand's solution. The titration's end point is the formation of the reddish-colored $Fe(SCN)^{2+}$ complex. The titration must be carried out in an acidic solution to prevent the precipitation of Fe^{3+} as $Fe(OH)_3$.

> *The Volhard method was first published in 1874 by Jacob Volhard.*

The third type of end point uses a species that changes color when it adsorbs to the precipitate. In the **Fajans method** for Cl^- using Ag^+ as a titrant, for example, the anionic dye dichlorofluoroscein is added to the titrand's solution. Before the end point, the precipitate of AgCl has a negative surface charge due to the adsorption of excess Cl^-. Because dichlorofluoroscein also carries a negative charge, it is repelled by the precipitate and remains in solution where it has a greenish-yellow color. After the end point, the surface of the precipitate carries a positive surface charge due to the adsorption of excess Ag^+. Dichlorofluoroscein now adsorbs to the precipitate's surface where its color is pink. This change in the indicator's color signals the end point.

> *The Fajans method was first published in the 1920s by Kasimir Fajans.*

Finding the End point Potentiometrically

Another method for locating the end point is a potentiometric titration in which we monitor the change in the titrant's or the titrand's concentration using an ion-selective electrode. The end point is found by visually examining the titration curve. A further discussion of potentiometry is found in Chapter 11.

9.5.3 Quantitative Applications

Although precipitation titrimetry is rarely listed as a standard method of analysis, it may still be useful as a secondary analytical method for verifying other analytical methods. Most precipitation titrations use Ag^+ as either the titrand or the titration. A titration in which Ag^+ is the titrant is called an **argentometric titration**. Table 9.19 provides a list of several typical precipitation titrations.

Table 9.19: Representative Examples of Precipitation Titrations

Titrand	Titrant[a]	End Point[b]
AsO_4^{3-}	$AgNO_3$, KSCN	Volhard
Br^-	$AgNO_3$ $AgNO_3$, KSCN	Mohr or Fajans Volhard
Cl^-	$AgNO_3$ $AgNO_3$, KSCN	Mohr or Fajans Volhard*
CO_3^{2-}	$AgNO_3$, KSCN	Volhard*
$C_2O_4^{2-}$	$AgNO_3$, KSCN	Volhard*
CrO_4^{2-}	$AgNO_3$, KSCN	Volhard*
I^-	$AgNO_3$ $AgNO_3$, KSCN	Fajans Volhard
PO_4^{3-}	$AgNO_3$, KSCN	Volhard*
S^{2-}	$AgNO_3$, KSCN	Volhard*
SCN^-	$AgNO_3$, KSCN	Volhard*

[a] When two reagents are listed, the analysis is by a back titration. The first reagent is added in excess and the second reagent used to back titrate the excess.

[b] For those Volhard methods identified with an asterisk (*) the precipitated silver salt must be removed before carrying out the back titration.

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. If you are unsure of the balanced reaction, you can deduce the stoichiometry from the precipitate's formula. For example, in forming a precipitate of Ag_2CrO_4, each mole of CrO_4^{2-} reacts with two moles of Ag^+.

Example 9.14

A mixture containing only KCl and NaBr is analyzed by the Mohr method. A 0.3172-g sample is dissolved in 50 mL of water and titrated to the Ag_2CrO_4 end point, requiring 36.85 mL of 0.1120 M $AgNO_3$. A blank titration requires 0.71 mL of titrant to reach the same end point. Report the %w/w KCl in the sample.

Solution

To find the moles of titrant reacting with the sample, we first need to correct for the reagent blank; thus

$$V_{Ag} = 36.85\ \text{mL} - 0.71\ \text{mL} = 36.14\ \text{mL} \tag{12}$$

$$(0.1120\ \text{M}\ AgNO_3) \times (0.03614\ \text{L}\ AgNO_3) = 4.048 \times 10^{-3}\ \text{mol}\ AgNO_3 \tag{13}$$

Titrating with $AgNO_3$ produces a precipitate of AgCl and AgBr. In forming the precipitates, each mole of KCl consumes one mole of $AgNO_3$ and each mole of NaBr consumes one mole of $AgNO_3$; thus

$$\text{moles KCl} + \text{moles NaBr} = 4.048 \times 10^{-3} \tag{14}$$

We are interested in finding the mass of KCl, so let's rewrite this equation in terms of mass. We know that

$$\text{moles KCl} = \frac{\text{g KCl}}{74.551\ \text{g KCl/mol KCl}} \tag{15}$$

$$\text{moles NaBr} = \frac{\text{g NaBr}}{102.89\ \text{g NaBr/mol NaBr}} \tag{16}$$

which we substitute back into the previous equation

$$\frac{\text{g KCl}}{74.551\ \text{g KCl/mol KCl}} + \frac{\text{g NaBr}}{102.89\ \text{g NaBr/mol NaBr}} = 4.048 \times 10^{-3} \tag{17}$$

Because this equation has two unknowns—g KCl and g NaBr—we need another equation that includes both unknowns. A simple equation takes advantage of the fact that the sample contains only KCl and NaBr; thus,

$$\text{g NaBr} = 0.3172\ \text{g} - \text{g KCl} \tag{18}$$

$$\frac{\text{g KCl}}{74.551\ \text{g KCl/mol KCl}} + \frac{0.3172\ \text{g} - \text{g KCl}}{102.89\ \text{g NaBr/mol NaBr}} = 4.048 \times 10^{-3} \tag{19}$$

$$1.341 \times 10^{-2}(\text{g KCl}) + 3.083 \times 10^{-3} - 9.719 \times 10^{-3}(\text{g KCl}) = 4.048 \times 10^{-3} \tag{20}$$

$$3.69 \times 10^{-3}(\text{g KCl}) = 9.65 \times 10^{-4} \tag{21}$$

The sample contains 0.262 g of KCl and the %w/w KCl in the sample is

$$\frac{0.262\ \text{g KCl}}{0.3172\ \text{g sample}} \times 100 = 82.6 \tag{22}$$

The analysis for I^- using the Volhard method requires a back titration. A typical calculation is shown in the following example.

Example 9.15

The %w/w I^- in a 0.6712-g sample was determined by a Volhard titration. After adding 50.00 mL of 0.05619 M $AgNO_3$ and allowing the precipitate to form, the remaining silver was back titrated with 0.05322 M KSCN, requiring 35.14 mL to reach the end point. Report the %w/w I^- in the sample.

Solution

There are two precipitates in this analysis: $AgNO_3$ and I^- form a precipitate of AgI, and $AgNO_3$ and KSCN form a precipitate of AgSCN. Each mole of I^- consumes one mole of $AgNO_3$, and each mole of KSCN consumes one mole of $AgNO_3$; thus

$$\text{moles } AgNO_3 = \text{moles } I^- + \text{moles KSCN} \tag{23}$$

Solving for the moles of I^- we find

$$\text{moles } I^- = \text{moles } AgNO_3 - \text{moles KSCN} \tag{24}$$

$$\text{moles } I^- = M_{Ag} \times V_{Ag} - M_{KSCN} \times V_{KSCN} \tag{25}$$

$$\begin{aligned}\text{moles } I^- = {} & (0.05619\ \text{M } AgNO_3) \times (0.05000\ \text{L } AgNO_3) \\ & - (0.05322\ \text{M KSCN}) \times (0.03514\ \text{L KSCN})\end{aligned} \tag{26}$$

that there are 9.393×10^{-4} moles of I^- in the sample. The %w/w I^- in the sample is

$$\frac{(9.393 \times 10^{-4}\ \text{mol } I^-) \times 126.9\ \text{g } I^-/\text{mol } I^-}{0.6712\ \text{g sample}} \times 100 = 17.76\%\ \text{w/w } I^- \tag{27}$$

Practice Exercise 9.23

A 1.963-g sample of an alloy is dissolved in HNO_3 and diluted to volume in a 100-mL volumetric flask. Titrating a 25.00-mL portion with 0.1078 M KSCN requires 27.19 mL to reach the end point. Calculate the %w/w Ag in the alloy.

Click here to review your answer to this exercise.

9.5.4 Evaluation of Precipitation Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a precipitation titration is similar to those described elsewhere in this chapter for acid–base, complexation, and redox titrations. Precipitation titrations also can be extended to the analysis of mixtures provided that there is a significant difference in the solubilities of the precipitates. Figure 9.45 shows an example of a titration curve for a mixture of I^- and Cl^- using Ag^+ as a titrant.

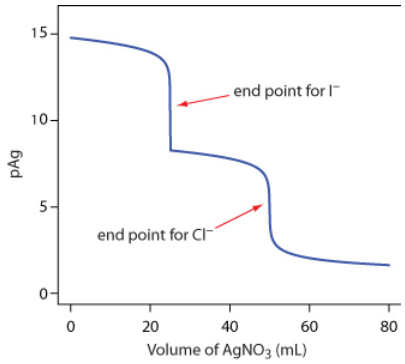

Figure 9.45 Titration curve for the titration of a 50.0 mL mixture of 0.0500 M I^- and 0.0500 M Cl^- using 0.100 M Ag^+ as a titrant. The red arrows show the end points. Note that the end point for I^- is earlier than the end point for Cl^- because AgI is less soluble than AgCl.

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Redox Titration

Analytical titrations using redox reactions were introduced shortly after the development of acid–base titrimetry. The earliest **Redox titration** took advantage of the oxidizing power of chlorine. In 1787, Claude Berthollet introduced a method for the quantitative analysis of chlorine water (a mixture of Cl_2, HCl, and HOCl) based on its ability to oxidize indigo, a dye that is colorless in its oxidized state. In 1814, Joseph Gay-Lussac developed a similar method for determining chlorine in bleaching powder. In both methods the end point is a change in color. Before the equivalence point the solution is colorless due to the oxidation of indigo. After the equivalence point, however, unreacted indigo imparts a permanent color to the solution.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO_4^-, $Cr_2O_7^{2-}$, and I_2 as oxidizing titrants, and of Fe^{2+} and $S_2O_3^{2-}$ as reducing titrants. Even with the availability of these new titrants, redox titrimetry was slow to develop due to the lack of suitable indicators. A titrant can serve as its own indicator if its oxidized and reduced forms differ significantly in color. For example, the intensely purple MnO_4^- ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colorless. Other titrants require a separate indicator. The first such indicator, diphenylamine, was introduced in the 1920s. Other redox indicators soon followed, increasing the applicability of redox titrimetry.

Redox Titration Curves

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction's potential instead of the concentration of one species.

You may recall from Chapter 6 that the Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which a titrand in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

$$A_{red} + B_{ox} \rightleftharpoons B_{red} + A_{ox} \tag{1}$$

where A_{ox} is the titrand's oxidized form, and B_{red} is the titrant's reduced form. The reaction's potential, E_{rxn}, is the difference between the reduction potentials for each half-reaction.

$$E_{rxn} = E_{B_{ox}/B_{red}} - E_{A_{ox}/A_{red}} \tag{2}$$

After each addition of titrant the reaction between the titrand and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the titrand's and the titrant's reduction potentials are identical.

$$E_{B_{ox}/B_{red}} = E_{A_{ox}/A_{red}} \tag{3}$$

This is an important observation because we can use either half-reaction to monitor the titration's progress.

Before the equivalence point the titration mixture consists of appreciable quantities of the titrand's oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand's half-reaction

$$E_{rxn} = E^o_{A_{ox}/A_{red}} - \frac{RT}{nF} \ln \frac{[A_{red}]}{[A_{ox}]} \tag{4}$$

> Although the Nernst equation is written in terms of the half-reaction's standard state potential, a matrix-dependent **formal potential** often is used in its place. See Appendix 13 for the standard state potentials and formal potentials for selected half-reactions.

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{rxn} = E^o_{B_{ox}/B_{red}} - \frac{RT}{nF} \ln \frac{[B_{red}]}{[B_{ox}]} \tag{5}$$

Calculating the Titration Curve

Let's calculate the titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$. The reaction in this case is

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq) \tag{9.15}$$

In 1 M $HClO_4$, the formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of Ce^{4+} to Ce^{3+} is +1.70 V.

Because the equilibrium constant for reaction 9.15 is very large—it is approximately 6×10^{15}—we may assume that the analyte and titrant react completely.

Step 1

Calculate the volume of titrant needed to reach the equivalence point.

The first task is to calculate the volume of Ce^{4+} needed to reach the titration's equivalence point. From the reaction's stoichiometry we know that

$$\text{moles } Fe^{2+} = \text{moles } Ce^{4+} \tag{6}$$

$$M_{Fe} \times V_{Fe} = M_{Ce} \times V_{Ce} \tag{7}$$

Solving for the volume of Ce^{4+} gives the equivalence point volume as

$$V_{eq} = V_{Ce} = \frac{M_{Fe}V_{Fe}}{M_{Ce}} = \frac{(0.100\text{ M})(50.0\text{ mL})}{(0.100\text{ M})} = 50.0\text{ mL} \tag{8}$$

Step 2:

alculate the potential before the equivalence point by determining the concentrations of the titrand's oxidized and reduced forms, and using the Nernst equation for the titrand's reduction half-reaction.

Before the equivalence point, the concentration of unreacted Fe^{2+} and the concentration of Fe^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction.

$$E = E^o_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.767\text{V} - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]} \tag{9.16}$$

For example, the concentrations of Fe^{2+} and Fe^{3+} after adding 10.0 mL of titrant are

$$[Fe^{2+}] = \frac{\text{initial moles } Fe^{2+} - \text{moles } Ce^{4+}\text{ added}}{\text{total volume}} = \frac{M_{Fe}V_{Fe} - M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}} \tag{9}$$

$$= \frac{(0.100\text{ M})(50.0\text{ mL}) - (0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 6.67 \times 10^{-2}\text{ M} \tag{10}$$

$$[Fe^{3+}] = \frac{\text{moles } Ce^{4+}\text{ added}}{\text{total volume}} = \frac{M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}} \tag{11}$$

$$= \frac{(0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 1.67 \times 10^{-2}\text{ M} \tag{12}$$

Substituting these concentrations into equation 9.16 gives a potential of

$$E = +0.767\text{ V} - 0.05916\log\frac{6.67 \times 10^{-2}\text{ M}}{1.67 \times 10^{-2}\text{ M}} = +0.731\text{ V} \tag{13}$$

Step 3:

Calculate the potential after the equivalence point by determining the concentrations of the titrant's oxidized and reduced forms, and using the Nernst equation for the titrant's reduction half-reaction.

After the equivalence point, the concentration of Ce^{3+} and the concentration of excess Ce^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Ce^{4+}/Ce^{3+} half-reaction.

$$E = E^o_{Ce^{4+}/Ce^{3+}} - \frac{RT}{nF}\log\frac{[Ce^{3+}]}{[Ce^{4+}]} = +1.70\text{ V} - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]} \tag{9.17}$$

For example, after adding 60.0 mL of titrant, the concentrations of Ce^{3+} and Ce^{4+} are

$$[Ce^{3+}] = \frac{\text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Fe}V_{Fe}}{V_{Fe}+V_{Ce}} \tag{14}$$

$$= \frac{(0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 60.0\text{ mL}} = 4.55\times10^{-3}\text{ M} \tag{15}$$

$$[Ce^{4+}] = \frac{\text{moles } Ce^{4+}\text{ added} - \text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Ce}V_{Ce} - M_{Fe}V_{Fe}}{V_{Fe}+V_{Ce}} \tag{16}$$

$$= \frac{(0.100\text{ M})(60.0\text{ mL}) - (0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 60.0\text{ mL}} = 9.09\times10^{-3}\text{ M} \tag{17}$$

Substituting these concentrations into Equation 9.17 gives a potential of

$$E = +1.70\text{ V} - 0.05916\log\frac{4.55\times10^{-2}\text{ M}}{9.09\times10^{-3}\text{ M}} = +1.66\text{ V} \tag{18}$$

Step 4

Calculate the potential at the equivalence point.

At the titration's equivalence point, the potential, E_{eq}, in equation 9.16 and equation 9.17 are identical. Adding the equations together to gives

$$2E_{eq} = E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]} \tag{19}$$

Because $[Fe^{2+}] = [Ce^{4+}]$ and $[Ce^{3+}] = [Fe^{3+}]$ at the equivalence point, the log term has a value of zero and the equivalence point's potential is

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Ce^{4+}/Ce^{3+}}}{2} = \frac{0.767\text{ V} + 1.70\text{ V}}{2} = 1.23\text{ V} \tag{20}$$

Additional results for this titration curve are shown in Table 9.15 and Figure 9.36.

Table 9.15: *Data for the Titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}*

Volume of Ce^{4+} (mL)	*E* (V)	Volume Ce^{4+} (mL)	*E* (V)
10.0	0.731	60.0	1.66
20.0	0.757	70.0	1.68
30.0	0.777	80.0	1.69
40.0	0.803	90.0	1.69
50.0	1.23	100.0	1.70

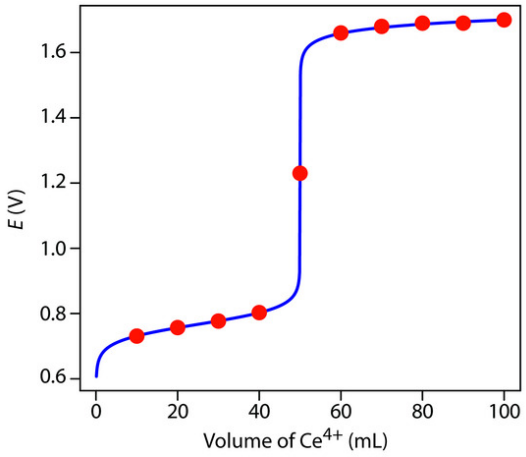

Figure 9.36 *Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The red points correspond to the data in Table 9.15. The blue line shows the complete titration curve.*

Exercise 1

Calculate the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}(aq) + Tl^{3+}(aq) \rightarrow Sn^{4+}(aq) + Tl^{+}(aq) \quad (21)$$

Click here to review your answer to this exercise.

Sketching a Redox Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a redox titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$.

This is the same example that we used in developing the calculations for a redox titration curve. You can review the results of that calculation in Table 9.15 and Figure 9.36.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 50.0 mL. Next, we draw our axes, placing the potential, *E*, on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 50.0 mL of Ce^{4+}. Figure 9.37a shows the result of the first step in our sketch.

Before the equivalence point, the potential is determined by a redox buffer of Fe^{2+} and Fe^{3+}. Although we can easily calculate the potential using the Nernst equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a redox buffer operates over a range of potentials that extends approximately ±(0.05916/*n*) unit on either side of $E^{o}_{Fe^{3+}/Fe^{2+}}$. The potential is at the buffer's lower limit

$$E = E^{o}_{Fe^{3+}/Fe^{2+}} - 0.05916 \quad (22)$$

when the concentration of Fe^{2+} is 10× greater than that of Fe^{3+}. The buffer reaches its upper potential

$$E = E^{o}_{Fe^{3+}/Fe^{2+}} + 0.05916 \quad (23)$$

when the concentration of Fe^{2+} is 10× smaller than that of Fe^{3+}. The redox buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

Figure 9.37b shows the second step in our sketch. First, we superimpose a ladder diagram for Fe^{2+} on the *y*-axis, using its $E^{o}_{Fe^{3+}/Fe^{2+}}$ value of 0.767 V and including the buffer's range of potentials. Next, we add points representing the pH at 10% of the equivalence point volume (a potential of 0.708 V at 5.0 mL) and at 90% of the equivalence point volume (a potential of 0.826 V at 45.0 mL).

> *We used a similar approach when sketching the acid–base titration curve for the titration of acetic acid with NaOH.*

The third step in sketching our titration curve is to add two points after the equivalence point. Here the potential is controlled by a redox buffer of Ce^{3+} and Ce^{4+}. The redox buffer is at its lower limit of $E = E^{o}_{Ce^{4+}/Ce^{3+}} - 0.05916$ when the titrant reaches 110% of the equivalence point volume and the potential is $E^{o}_{Ce^{4+}/Ce^{3+}}$ when the volume of Ce^{4+} is $2 \times V_{eq}$.

Figure 9.37c shows the third step in our sketch. First, we add a ladder diagram for Ce^{4+}, including its buffer range, using its $E^{o}_{Ce^{4+}/Ce^{3+}}$ value of 1.70 V. Next, we add points representing the potential at 110% of V_{eq} (a value of 1.66 V at 55.0 mL) and at 200% of V_{eq} (a value of 1.70 V at 100.0 mL).

> *We used a similar approach when sketching the complexation titration curve for the titration of Mg^{2+} with EDTA.*

Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point's volume (Figure 9.37d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.37e). A comparison of our sketch to the exact titration curve (Figure 9.37f) shows that they are in close agreement.

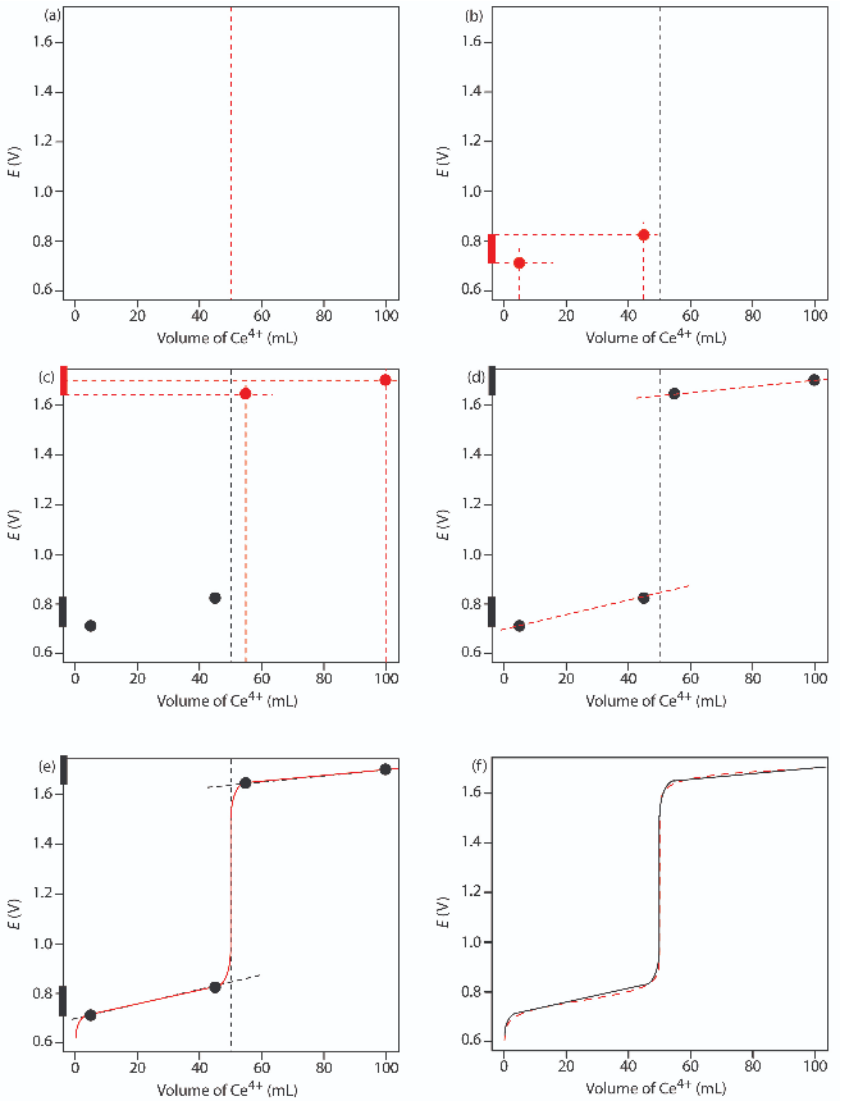

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Figure 9.37: *Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M $HClO_4$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.*

Exercise 2

Sketch the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{4+} with 0.100 M Tl^{+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}(aq) + Tl^{3+}(aq) \rightarrow Sn^{4+}(aq) + Tl^{+}(aq) \tag{24}$$

Compare your sketch to your calculated titration curve from Practice Exercise 9.17.

Click here to review your answer to this exercise.

9.4.2 Selecting and Evaluating the End point

A redox titration's equivalence point occurs when we react stoichiometrically equivalent amounts of titrand and titrant. As is the case with acid–base and complexation titrations, we estimate the equivalence point of a complexation titration using an experimental end point. A variety of methods are available for locating the end point, including indicators and sensors that respond to a change in the solution conditions.

Where is the Equivalence Point?

For an acid–base titration or a complexometric titration the equivalence point is almost identical to the inflection point on the steeping rising part of the titration curve. If you look back at Figure 9.7 and Figure 9.28, you will see that the inflection point is in the middle of this steep rise in the titration curve, which makes it relatively easy to find the equivalence point when you sketch these titration curves. We call this a **symmetric equivalence point**. If the stoichiometry of a redox titration is symmetric—one mole of titrant reacts with each mole of titrand—then the equivalence point is symmetric. If the titration reaction's stoichiometry is not 1:1, then the equivalence point is closer to the top or to bottom of the titration curve's sharp rise. In this case we have an **asymmetric equivalence point**.

Example 1

Derive a general equation for the equivalence point's potential when titrating Fe^{2+} with MnO_4^-.

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O \tag{25}$$

(We often use H^+ instead of H_3O^+ when writing a redox reaction.)

Solution

The half-reactions for Fe^{2+} and MnO_4^- are

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \tag{26}$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \tag{27}$$

for which the Nernst equations are

$$E = E^o_{Fe^{3+}/Fe^{2+}} - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \tag{28}$$

$$E = E^o_{MnO_4^-/Mn^{2+}} - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8} \tag{29}$$

Before adding these two equations together we must multiply the second equation by 5 so that we can combine the log terms; thus

$$6E = E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}} - 0.05916 \log \frac{[Fe^{2+}][Mn^{2+}]}{[Fe^{3+}][MnO_4^-][H^+]^8} \quad (30)$$

At the equivalence point we know that

$$[Fe^{2+}] = 5 \times [MnO_4^-] \quad (31)$$

$$[Fe^{3+}] = 5 \times [Mn^{2+}] \quad (32)$$

Substituting these equalities into the previous equation and rearranging gives us a general equation for the potential at the equivalence point.

$$6E_{eq} = E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}} - 0.05916 \log \frac{5[MnO_4^-][Mn^{2+}]}{5[Mn^{2+}][MnO_4^-][H^+]^8} \quad (33)$$

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}}}{6} - \frac{0.05916}{6} \log \frac{1}{[H^+]^8} \quad (34)$$

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}}}{6} + \frac{0.05916 \times 8}{6} \log[H^+] \quad (35)$$

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}}}{6} - 0.07888pH \quad (36)$$

Our equation for the equivalence point has two terms. The first term is a weighted average of the titrand's and the titrant's standard state potentials, in which the weighting factors are the number of electrons in their respective half-reactions. (Instead of standard state potentials, you can use formal potentials.) The second term shows that E_{eq} for this titration is pH-dependent. At a pH of 1 (in H_2SO_4), for example, the equivalence point has a potential of

$$E_{eq} = \frac{0.768 + 5 \times 1.51}{6} - 0.07888 \times 1 = 1.31 \text{ V} \quad (37)$$

Figure 9.38 shows a typical titration curve for titration of Fe^{2+} with MnO_4^-. Note that the titration's equivalence point is asymmetrical.

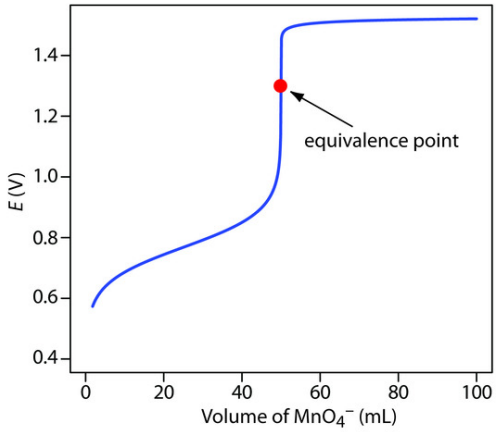


Figure 9.38: *Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.0200 M MnO_4^- at a fixed pH of 1 (using H_2SO_4). The equivalence point is shown by the red dot.*

Exercise 3

Derive a general equation for the equivalence point's potential for the titration of U^{4+} with Ce^{4+}. The unbalanced reaction is

$$Ce^{4+}(aq) + U^{4+}(aq) \rightarrow UO_2^{2+}(aq) + Ce^{3+}(aq) \quad (38)$$

What is the equivalence point's potential if the pH is 1?

Click here to review your answer to this exercise.

Finding the End point with an Indicator

Three types of indicators are used to signal a redox titration's end point. The oxidized and reduced forms of some titrants, such as MnO_4^-, have different colors. A solution of MnO_4^- is intensely purple. In an acidic solution, however, permanganate's reduced form, Mn^{2+}, is nearly colorless. When using MnO_4^- as a titrant, the titrand's solution remains colorless until the equivalence point. The first drop of excess MnO_4^- produces a permanent tinge of purple, signaling the end point.

Some indicators form a colored compound with a specific oxidized or reduced form of the titrant or the titrand. Starch, for example, forms a dark blue complex with I_3^-. We can use this distinct color to signal the presence of excess I_3^- as a titrant—a change in color from colorless to blue—or the completion of a reaction consuming I_3^- as the titrand—a change in color from blue to colorless. Another example of a specific indicator is thiocyanate, SCN^-, which forms a soluble red-colored complex of $Fe(SCN)^{2+}$ with Fe^{3+}.

The most important class of indicators are substances that do not participate in the redox titration, but whose oxidized and reduced forms differ in color. When we add a **redox indicator** to the titrand, the indicator imparts a color that depends on the solution's potential. As the solution's potential changes with the addition of titrant, the indicator changes oxidation state and changes color, signaling the end point.

To understand the relationship between potential and an indicator's color, consider its reduction half-reaction

$$\mathrm{In_{ox}} + ne^- \rightleftharpoons \mathrm{In_{red}} \tag{39}$$

where In_{ox} and In_{red} are, respectively, the indicator's oxidized and reduced forms.

> *For simplicity, In_{ox} and In_{red} are shown without specific charges. Because there is a change in oxidation state, In_{ox} and In_{red} cannot both be neutral.*

The Nernst equation for this half-reaction is

$$E = E^o_{\mathrm{In_{ox}/In_{red}}} - \frac{0.05916}{n} \log \frac{[\mathrm{In_{red}}]}{[\mathrm{In_{ox}}]} \tag{40}$$

As shown in Figure 9.39, if we assume that the indicator's color changes from that of In_{ox} to that of In_{red} when the ratio $[In_{red}]/[In_{ox}]$ changes from 0.1 to 10, then the end point occurs when the solution's potential is within the range

$$E = E^o_{\mathrm{In_{ox}/In_{red}}} \pm \frac{0.05916}{n} \tag{41}$$

> *This is the same approach we took in considering acid–base indicators and complexation indicators.*

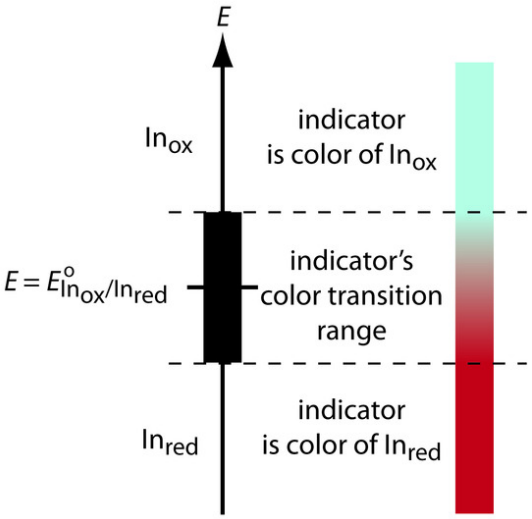


Figure 9.39 Diagram showing the relationship between E and an indicator's color. The ladder diagram defines potentials where In_{red} and In_{ox} are the predominate species. The indicator changes color when E is within the range

$$E = E^{o}_{Inox/Inred} \pm 0.05916/n$$

A partial list of redox indicators is shown in Table 9.16. Examples of appropriate and inappropriate indicators for the titration of Fe^{2+} with Ce^{4+} are shown in Figure 9.40.

Table 9.16 Selected Examples of Redox Indicators

Indicator	Color of In_{ox}	Color of In_{red}	$E^{o}In_{ox}/In_{red}$
indigo tetrasulfate	blue	colorless	0.36
methylene blue	blue	colorless	0.53
diphenylamine	violet	colorless	0.75
diphenylamine sulfonic acid	red-violet	colorless	0.85
tris(2,2´-bipyridine)iron	pale blue	red	1.120
ferroin	pale blue	red	1.147
tris(5-nitro-1,10-phenanthroline)iron	pale blue	red-violet	1.25

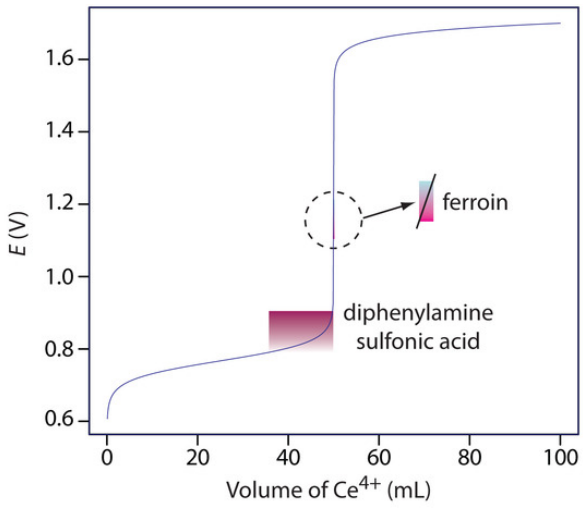


Figure 9.40: *Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The end point transitions for the indicators diphenylamine sulfonic acid and ferroin are superimposed on the titration curve. Because the transition for ferroin is too small to see on the scale of the x-axis—it requires only 1–2 drops of titrant—the color change is expanded to the right.*

Other Methods for Finding the End point

Another method for locating a redox titration's end point is a potentiometric titration in which we monitor the change in potential while adding the titrant to the titrand. The end point is found by visually examining the titration curve. The simplest experimental

design for a potentiometric titration consists of a Pt indicator electrode whose potential is governed by the titrand's or titrant's redox half-reaction, and a reference electrode that has a fixed potential. A further discussion of potentiometry is found in Chapter 11. Other methods for locating the titration's end point include thermometric titrations and spectrophotometric titrations.

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical redox titrimetric method. Although each method is unique, the following description of the determination of the total chlorine residual in water provides an instructive example of a typical procedure. The description here is based on Method 4500-Cl B as published in *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., American Public Health Association: Washington, D. C., 1998.

Representative Method 9.3: **Determination of Total Chlorine Residual**

Description of the Method

The chlorination of public water supplies produces several chlorine-containing species, the combined concentration of which is called the total chlorine residual. Chlorine may be present in a variety of states, including the free residual chlorine, consisting of Cl_2, HOCl and OCl^-, and the combined chlorine residual, consisting of NH_2Cl, $NHCl_2$, and NCl_3. The total chlorine residual is determined by using the oxidizing power of chlorine to convert I^- to I_3^-. The amount of I_3^- formed is then determined by titrating with $Na_2S_2O_3$ using starch as an indicator. Regardless of its form, the total chlorine residual is reported as if Cl_2 is the only source of chlorine, and is reported as mg Cl/L.

Procedure

Select a volume of sample requiring less than 20 mL of $Na_2S_2O_3$ to reach the end point. Using glacial acetic acid, acidify the sample to a pH of 3–4, and add about 1 gram of KI. Titrate with $Na_2S_2O_3$ until the yellow color of I_3^- begins to disappear. Add 1 mL of a starch indicator solution and continue titrating until the blue color of the starch–I_3^- complex disappears (Figure 9.41). Use a blank titration to correct the volume of titrant needed to reach the end point for reagent impurities.

Questions

1. Is this an example of a direct or an indirect analysis?

This is an indirect analysis because the chlorine-containing species do not react with the titrant. Instead, the total chlorine residual oxidizes I^- to I_3^-, and the amount of I_3^- is determined by titrating with $Na_2S_2O_3$.

2. Why does the procedure rely on an indirect analysis instead of directly titrating the chlorine-containing species using KI as a titrant?

Because the total chlorine residual consists of six different species, a titration with I^- does not have a single, well-defined equivalence point. By converting the chlorine residual to an equivalent amount of I_3^-, the indirect titration with $Na_2S_2O_3$ has a single, useful equivalence point.

Even if the total chlorine residual is from a single species, such as HOCl, a direct titration with KI is impractical. Because the product of the titration, I_3^-, imparts a yellow color, the titrand's color would change with each addition of titrant, making it difficult to find a suitable indicator.

3. Both oxidizing and reducing agents can interfere with this analysis. Explain the effect of each type of interferent has on the total chlorine residual.

An interferent that is an oxidizing agent converts additional I^- to I_3^-. Because this extra I_3^- requires an additional volume of $Na_2S_2O_3$ to reach the end point, we overestimate the total chlorine residual. If the interferent is a reducing agent, it reduces back to I^- some of the I_3^- produced by the reaction between the total chlorine residual and iodide. As a result. we underestimate the total chlorine residual.

Figure 9.41 Endpoint for the determination of the total chlorine residual. (a) Acidifying the sample and adding KI forms a brown solution of I_3^-. (b) Titrating with $Na_2S_2O_3$ converts I_3^- to I^- with the solution fading to a pale yellow color as we approach the end point. (c) Adding starch forms the deep purple starch–I_3^- complex. (d) As the titration continues, the end point is a sharp transition from a purple to a colorless solution. The change in color from (c) to (d) typically takes 1–2 drops of titrant.

9.4.3 Quantitative Applications

Although many quantitative applications of redox titrimetry have been replaced by other analytical methods, a few important applications continue to be relevant. In this section we review the general application of redox titrimetry with an emphasis on environmental, pharmaceutical, and industrial applications. We begin, however, with a brief discussion of selecting and characterizing redox titrants, and methods for controlling the titrand's oxidation state.

Adjusting the Titrand's Oxidation State

If a redox titration is to be used in a quantitative analysis, the titrand must initially be present in a single oxidation state. For example, iron can be determined by a redox titration in which Ce^{4+} oxidizes Fe^{2+} to Fe^{3+}. Depending on the sample and the method of sample preparation, iron may initially be present in both the +2 and +3 oxidation states. Before titrating, we must reduce any Fe^{3+} to Fe^{2+}. This type of pretreatment can be accomplished using an auxiliary reducing agent or oxidizing agent.

A metal that is easy to oxidize—such as Zn, Al, and Ag—can serve as an **auxiliary reducing agent**. The metal, as a coiled wire or powder, is added to the sample where it reduces the titrand. Because any unreacted auxiliary reducing agent will react with the titrant, it must be removed before beginning the titration. This can be accomplished by simply removing the coiled wire, or by filtering.

An alternative method for using an auxiliary reducing agent is to immobilize it in a column. To prepare a reduction column an aqueous slurry of the finally divided metal is packed in a glass tube equipped with a porous plug at the bottom. The sample is placed at the top of the column and moves through the column under the influence of gravity or vacuum suction. The length of the reduction column and the flow rate are selected to ensure the analyte's complete reduction.

Two common reduction columns are used. In the **Jones reductor** the column is filled with amalgamated zinc, Zn(Hg), prepared by briefly placing Zn granules in a solution of $HgCl_2$. Oxidation of zinc

$$\mathrm{Zn(Hg)}(s) \rightarrow \mathrm{Zn^{2+}}(aq) + \mathrm{Hg}(l) + 2e^- \tag{42}$$

provides the electrons for reducing the titrand. In the **Walden reductor** the column is filled with granular Ag metal. The solution containing the titrand is acidified with HCl and passed through the column where the oxidation of silver

$$\mathrm{Ag}(s) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{AgCl}(s) + e^- \tag{43}$$

provides the necessary electrons for reducing the titrand. Table 9.17 provides a summary of several applications of reduction columns.

Table 9.17 Examples of Reactions For Reducing a Titrand's Oxidation State Using a Reduction Column

Oxidized Titrand	Walden Reductor	Jones Reductor
Cr^{3+}	—	$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$
Cu^{2+}	$Cu^{2+}(aq) + e^- \rightarrow Cu^{+}(aq)$	$Cu^{2+}(aq) + 2e^- \rightarrow Cr(s)$
Fe^{3+}	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
TiO^{2+}	—	$TiO^{2+}(aq) + 2H^{+}(aq) + e^- \rightarrow Ti^{3+}(aq) + H_2O(l)$
MoO_2^{2+}	$MoO_2^{2+}(aq) + e^- \rightarrow MoO_2^{+}(aq)$	$MoO_2^{2+}(aq) + 4H^{+}(aq) + 3e^- \rightarrow Mo^{3+}(aq) + 2H_2O(l)$
VO_2^{+}	$VO_2^{+}(aq) + 2H^{+}(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$	$VO_2^{+}(aq) + 4H^{+}(aq) + 3e^- \rightarrow V^{2+}(aq) + 2H_2O(l)$

Several reagents are commonly used as **auxiliary oxidizing agents**, including ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, and hydrogen peroxide, H_2O_2. Peroxydisulfate is a powerful oxidizing agent

$$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq) \quad (44)$$

capable of oxidizing Mn^{2+} to MnO_4^-, Cr^{3+} to $Cr_2O_7^{2-}$, and Ce^{3+} to Ce^{4+}. Excess peroxydisulfate is easily destroyed by briefly boiling the solution. The reduction of hydrogen peroxide in acidic solution

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l) \quad (45)$$

provides another method for oxidizing a titrand. Excess H_2O_2 is destroyed by briefly boiling the solution.

Selecting and Standardizing a Titrant

If it is to be used quantitatively, the titrant's concentration must remain stable during the analysis. Because a titrant in a reduced state is susceptible to air oxidation, most redox titrations use an oxidizing agent as the titrant. There are several common oxidizing titrants, including MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_3^-. Which titrant is used often depends on how easy it is to oxidize the titrand. A titrand that is a weak reducing agent needs a strong oxidizing titrant if the titration reaction is to have a suitable end point.

The two strongest oxidizing titrants are MnO_4^- and Ce^{4+}, for which the reduction half-reactions are

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \quad (46)$$

$$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq) \quad (47)$$

Solutions of Ce4+ usually are prepared from the primary standard cerium ammonium nitrate, Ce(NO3)4•2NH4NO3, in 1 M H2SO4. When prepared using a reagent grade material, such as Ce(OH)4, the solution is standardized against a primary standard reducing agent such as Na2C2O4 or Fe2+ (prepared using iron wire) using ferroin as an indicator. Despite its availability as a primary standard and its ease of preparation, Ce4+ is not as frequently used as MnO4– because it is more expensive.

Note

The standardization reactions are

$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq) \quad (48)$$

$$2Ce^{4+}(aq) + H_2C_2O_4(aq) \rightarrow 2Ce^{3+}(aq) + 2CO_2(g) + 2H^+(aq) \quad (49)$$

Solutions of MnO_4^- are prepared from $KMnO_4$, which is not available as a primary standard. Aqueous solutions of permanganate are thermodynamically unstable due to its ability to oxidize water.

$$4\,MnO_4^-(aq) + 2H_2O(l) \rightleftharpoons 4MnO_2(s) + 3O_2(g) + 4OH^-(aq) \quad (50)$$

This reaction is catalyzed by the presence of MnO_2, Mn^{2+}, heat, light, and the presence of acids and bases. A moderately stable solution of permanganate can be prepared by boiling it for an hour and filtering through a sintered glass filter to remove any solid

MnO_2 that precipitates. Standardization is accomplished against a primary standard reducing agent such as $Na_2C_2O_4$ or Fe^{2+} (prepared using iron wire), with the pink color of excess MnO_4^- signaling the end point. A solution of MnO_4^- prepared in this fashion is stable for 1–2 weeks, although the standardization should be rechecked periodically.

Note

The standardization reactions are

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l) \quad (51)$$

$$2\,MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l) \quad (52)$$

Potassium dichromate is a relatively strong oxidizing agent whose principal advantages are its availability as a primary standard and the long term stability of its solutions. It is not, however, as strong an oxidizing agent as MnO_4^- or Ce^{4+}, which makes it less useful when the titrand is a weak reducing agent. Its reduction half-reaction is

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \quad (53)$$

Although a solution of $Cr_2O_7^{2-}$ is orange and a solution of Cr^{3+} is green, neither color is intense enough to serve as a useful indicator. Diphenylamine sulfonic acid, whose oxidized form is red-violet and reduced form is colorless, gives a very distinct end point signal with $Cr_2O_7^{2-}$.

Iodine is another important oxidizing titrant. Because it is a weaker oxidizing agent than MnO_4^-, Ce^{4+}, and $Cr_2O_7^{2-}$, it is useful only when the titrand is a stronger reducing agent. This apparent limitation, however, makes I_2 a more selective titrant for the analysis of a strong reducing agent in the presence of a weaker reducing agent. The reduction half-reaction for I_2 is

$$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq) \quad (54)$$

Because iodine is not very soluble in water, solutions are prepared by adding an excess of I^-. The complexation reaction

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \quad (55)$$

increases the solubility of I_2 by forming the more soluble triiodide ion, I_3^-. Even though iodine is present as I_3^- instead of I_2, the number of electrons in the reduction half-reaction is unaffected.

$$I_3^-(aq) + 2e^- \rightleftharpoons 3I^-(aq) \quad (56)$$

Solutions of I_3^- are normally standardized against $Na_2S_2O_3$ using starch as a specific indicator for I_3^-.

Note

The standardization reaction is

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + 2S_4O_6^{2-}(aq) \quad (57)$$

An oxidizing titrant such as MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_3^-, is used when the titrand is in a reduced state. If the titrand is in an oxidized state, we can first reduce it with an auxiliary reducing agent and then complete the titration using an oxidizing titrant. Alternatively, we can titrate it using a reducing titrant. Iodide is a relatively strong reducing agent that could serve as a reducing titrant except that a solution of I– is susceptible to the air-oxidation of I^- to I_3^-.

$$3I^-(aq) \rightleftharpoons I_3^-(aq) + 2e^- \quad (58)$$

Note

A freshly prepared solution of KI is clear, but after a few days it may show a faint yellow coloring due to the presence of I_3^-.

Instead, adding an excess of KI reduces the titrand, releasing a stoichiometric amount of I_3^-. The amount of I_3^- produced is then determined by a back titration using thiosulfate, $S_2O_3^{2-}$, as a reducing titrant.

$$2S_2O_3^{2-}(aq) \rightleftharpoons 2S_4O_6^{2-}(aq) + 2e^- \quad (59)$$

Solutions of $S_2O_3^{2-}$ are prepared using $Na_2S_2O_3 \cdot 5H_2O$, and must be standardized before use. Standardization is accomplished by dissolving a carefully weighed portion of the primary standard KIO_3 in an acidic solution containing an excess of KI. The reaction between IO_3^- and I^-

$$IO_3^-(aq) + 8I^-(aq) + 6H^+(aq) \rightarrow 3I_3^-(aq) + 3H_2O(l) \quad (60)$$

liberates a stoichiometric amount of I_3^-. By titrating this I_3^- with thiosulfate, using starch as a visual indicator, we can determine the concentration of $S_2O_3^{2-}$ in the titrant.

Note

The standardization titration is

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + 2S_4O_6^{2-}(aq) \quad (61)$$

which is the same reaction used to standardize solutions of I_3^-. This approach to standardizing solutions of $S_2O_3^{2-}$. is similar to the determination of the total chlorine residual outlined in Representative Method 9.3.

Although thiosulfate is one of the few reducing titrants that is not readily oxidized by contact with air, it is subject to a slow decomposition to bisulfite and elemental sulfur. If used over a period of several weeks, a solution of thiosulfate should be restandardized periodically. Several forms of bacteria are able to metabolize thiosulfate, which also can lead to a change in its concentration. This problem can be minimized by adding a preservative such as HgI_2 to the solution.

Another useful reducing titrant is ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in which iron is present in the +2 oxidation state. A solution of Fe^{2+} is susceptible to air-oxidation, but when prepared in 0.5 M H_2SO_4 it remains stable for as long as a month. Periodic restandardization with $K_2Cr_2O_7$ is advisable. The titrant can be used to directly titrate the titrand by oxidizing Fe^{2+} to Fe^{3+}. Alternatively, ferrous ammonium sulfate is added to the titrand in excess and the quantity of Fe^{3+} produced determined by back titrating with a standard solution of Ce^{4+} or $Cr_2O_7^{2-}$.

Inorganic Analysis

One of the most important applications of redox titrimetry is evaluating the chlorination of public water supplies. Representative Method 9.3, for example, describes an approach for determining the total chlorine residual by using the oxidizing power of chlorine to oxidize I^- to I_3^-. The amount of I_3^- is determined by back titrating with $S_2O_3^{2-}$.

The efficiency of chlorination depends on the form of the chlorinating species. There are two contributions to the total chlorine residual—the free chlorine residual and the combined chlorine residual. The free chlorine residual includes forms of chlorine that are available for disinfecting the water supply. Examples of species contributing to the free chlorine residual include Cl_2, HOCl and OCl^-. The combined chlorine residual includes those species in which chlorine is in its reduced form and, therefore, no longer capable of providing disinfection. Species contributing to the combined chlorine residual are NH_2Cl, $NHCl_2$ and NCl_3.

When a sample of iodide-free chlorinated water is mixed with an excess of the indicator *N*,*N*-diethyl-*p*-phenylenediamine (DPD), the free chlorine oxidizes a stoichiometric portion of DPD to its red-colored form. The oxidized DPD is then back titrated to its colorless form using ferrous ammonium sulfate as the titrant. The volume of titrant is proportional to the free residual chlorine.

Having determined the free chlorine residual in the water sample, a small amount of KI is added, catalyzing the reduction monochloramine, NH_2Cl, and oxidizing a portion of the DPD back to its red-colored form. Titrating the oxidized DPD with ferrous ammonium sulfate yields the amount of NH_2Cl in the sample. The amount of dichloramine and trichloramine are determined in a similar fashion.

The methods described above for determining the total, free, or combined chlorine residual also are used to establish a water supply's chlorine demand. Chlorine demand is defined as the quantity of chlorine needed to completely react with any substance that can be oxidized by chlorine, while also maintaining the desired chlorine residual. It is determined by adding progressively greater amounts of chlorine to a set of samples drawn from the water supply and determining the total, free, or combined chlorine residual.

Another important example of redox titrimetry, which finds applications in both public health and environmental analyses is the determination of dissolved oxygen. In natural waters, such as lakes and rivers, the level of dissolved O_2 is important for two reasons: it is the most readily available oxidant for the biological oxidation of inorganic and organic pollutants; and it is necessary

for the support of aquatic life. In a wastewater treatment plant dissolved O_2 is essential for the aerobic oxidation of waste materials. If the concentration of dissolved O_2 falls below a critical value, aerobic bacteria are replaced by anaerobic bacteria, and the oxidation of organic waste produces undesirable gases, such as CH_4 and H_2S.

One standard method for determining the dissolved O_2 content of natural waters and wastewaters is the Winkler method. A sample of water is collected without exposing it to the atmosphere, which might change the concentration of dissolved O_2. The sample is first treated with a solution of $MnSO_4$, and then with a solution of NaOH and KI. Under these alkaline conditions the dissolved oxygen oxidizes Mn^{2+} to MnO_2.

$$2Mn^{2+}(aq) + 4OH^-(aq) + O_2(g) \rightarrow 2MnO_2(s) + 2H_2O(l) \quad (62)$$

After the reaction is complete, the solution is acidified with H_2SO_4. Under the now acidic conditions I^- is oxidized to I_3^- by MnO_2.

$$MnO_2(s) + 3I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+} + I_3^-(aq) + 2H_2O(l) \quad (63)$$

The amount of I_3^- formed is determined by titrating with $S_2O_3^{2-}$ using starch as an indicator. The Winkler method is subject to a variety of interferences, and several modifications to the original procedure have been proposed. For example, NO_2^- interferes because it can reduce I_3^- to I^- under acidic conditions. This interference is eliminated by adding sodium azide, NaN_3, reducing NO_2^- to N_2. Other reducing agents, such as Fe^{2+}, are eliminated by pretreating the sample with $KMnO_4$, and destroying the excess permanganate with $K_2C_2O_4$.

Another important example of redox titrimetry is the determination of water in nonaqueous solvents. The titrant for this analysis is known as the Karl Fischer reagent and consists of a mixture of iodine, sulfur dioxide, pyridine, and methanol. Because the concentration of pyridine is sufficiently large, I_2 and SO_2 react with pyridine (py) to form the complexes py•I_2 and py•SO_2. When added to a sample containing water, I_2 is reduced to I^- and SO_2 is oxidized to SO_3.

$$py \bullet I_2 + py \bullet SO_2 + py + H_2O \rightarrow 2py \bullet HI + py \bullet SO_3 \quad (64)$$

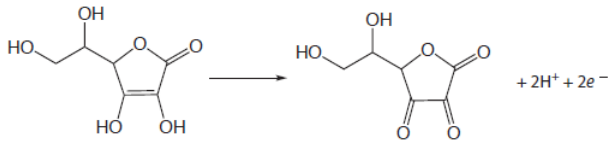
Methanol is included to prevent the further reaction of py•SO_3 with water. The titration's end point is signaled when the solution changes from the product's yellow color to the brown color of the Karl Fischer reagent.

Organic Analysis

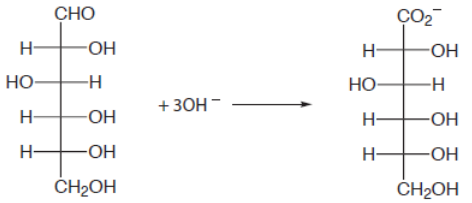
Redox titrimetry also is used for the analysis of organic analytes. One important example is the determination of the chemical oxygen demand (COD) of natural waters and wastewaters. The COD provides a measure of the quantity of oxygen necessary to completely oxidize all the organic matter in a sample to CO_2 and H_2O. Because no attempt is made to correct for organic matter that can not be decomposed biologically, or for slow decomposition kinetics, the COD always overestimates a sample's true oxygen demand. The determination of COD is particularly important in managing industrial wastewater treatment facilities where it is used to monitor the release of organic-rich wastes into municipal sewer systems or the environment.

A sample's COD is determined by refluxing it in the presence of excess $K_2Cr_2O_7$, which serves as the oxidizing agent. The solution is acidified with H_2SO_4 using Ag_2SO_4 to catalyze the oxidation of low molecular weight fatty acids. Mercuric sulfate, $HgSO_4$, is added to complex any chloride that is present, preventing the precipitation of the Ag^+ catalyst as AgCl. Under these conditions, the efficiency for oxidizing organic matter is 95–100%. After refluxing for two hours, the solution is cooled to room temperature and the excess $Cr_2O_7^{2-}$ is determined by back titrating using ferrous ammonium sulfate as the titrant and ferroin as the indicator. Because it is difficult to completely remove all traces of organic matter from the reagents, a blank titration must be performed. The difference in the amount of ferrous ammonium sulfate needed to titrate the sample and the blank is proportional to the COD.

Iodine has been used as an oxidizing titrant for a number of compounds of pharmaceutical interest. Earlier we noted that the reaction of $S_2O_3^{2-}$ with I_3^- produces the tetrathionate ion, $S_4O_6^{2-}$. The tetrathionate ion is actually a dimer consisting of two thiosulfate ions connected through a disulfide (–S–S–) linkage. In the same fashion, I_3^- can be used to titrate mercaptans of the general formula RSH, forming the dimer RSSR as a product. The amino acid cysteine also can be titrated with I_3^-. The product of this titration is cystine, which is a dimer of cysteine. Triiodide also can be used for the analysis of ascorbic acid (vitamin C) by oxidizing the enediol functional group to an alpha diketone



and for the analysis of reducing sugars, such as glucose, by oxidizing the aldehyde functional group to a carboxylate ion in a basic solution.



An organic compound containing a hydroxyl, a carbonyl, or an amine functional group adjacent to an hydoxyl or a carbonyl group can be oxidized using metaperiodate, IO_4^-, as an oxidizing titrant.

$$IO_4^-(aq) + H_2O(l) + 2e^- \rightleftharpoons IO_3^-(aq) + 2OH^-(aq) \quad (65)$$

A two-electron oxidation cleaves the C–C bond between the two functional groups, with hydroxyl groups being oxidized to aldehydes or ketones, carbonyl functional groups being oxidized to carboxylic acids, and amines being oxidized to an aldehyde and an amine (ammonia if a primary amine). The analysis is conducted by adding a known excess of IO_4^- to the solution containing the analyte, and allowing the oxidation to take place for approximately one hour at room temperature. When the oxidation is complete, an excess of KI is added, which converts any unreacted IO_4^- to IO_3^- and I_3^-.

$$IO_4^-(aq) + 3I^-(aq) + H_2O(l) \rightarrow IO_3^-(aq) + I_3^-(aq) + 2OH^-(aq) \quad (66)$$

The I_3^- is then determined by titrating with $S_2O_3^{2-}$ using starch as an indicator.

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. If you are unsure of the balanced reaction, you can deduce the stoichiometry by remembering that the electrons in a redox reaction must be conserved.

Example 9.11

The amount of Fe in a 0.4891-g sample of an ore was determined by titrating with $K_2Cr_2O_7$. After dissolving the sample in HCl, the iron was brought into the +2 oxidation state using a Jones reductor. Titration to the diphenylamine sulfonic acid end point required 36.92 mL of 0.02153 M $K_2Cr_2O_7$. Report the ore's iron content as %w/w Fe_2O_3.

(Although we can deduce the stoichiometry between the titrant and the titrand without balancing the titration reaction, the balanced reaction

$$K_2Cr_2O_7(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 2K^+(aq) + 6Fe^{3+}(aq) + 7H_2O(l) \quad (67)$$

does provide useful information. For example, the presence of H^+ reminds us that the reaction^fs feasibility is pH-dependent.)

Solution

Because we have not been provided with the titration reaction, let's use a conservation of electrons to deduce the stoichiometry. During the titration the analyte is oxidized from Fe^{2+} to Fe^{3+}, and the titrant is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}. Oxidizing Fe^{2+} to Fe^{3+} requires only a single electron. Reducing $Cr_2O_7^{2-}$, in which each chromium is in the +6 oxidation state, to Cr^{3+} requires three electrons per chromium, for a total of six electrons. A conservation of electrons for the titration, therefore, requires that each mole of $K_2Cr_2O_7$ reacts with six moles of Fe^{2+}.

The moles of $K_2Cr_2O_7$ used in reaching the end point is

$$(0.02153\ M\ K_2Cr_2O_7) \times (0.03692\ L\ K_2Cr_2O_7) = 7.949 \times 10^{-4}\ mol\ K_2Cr_2O_7 \quad (68)$$

which means that the sample contains

$$7.949 \times 10^{-4} \text{ mol } K_2Cr_2O_7 \times \frac{6 \text{ mol } Fe^{2+}}{\text{mol } K_2Cr_2O_7} = 4.769 \times 10^{-3} \text{ mol } Fe^{2+} \quad (69)$$

Thus, the %w/w Fe_2O_3 in the sample of ore is

$$4.769 \times 10^{-3} \text{ mol } Fe^{2+} \times \frac{1 \text{ mol } Fe_2O_3}{2 \text{ mol } Fe^{2+}} \times \frac{159.69 \text{ g } Fe_2O_3}{\text{mol } Fe_2O_3} = 0.3808 \text{ g } Fe_2O_3 \quad (70)$$

$$\frac{0.3808 \text{ g } Fe_2O_3}{0.4891 \text{ g sample}} \times 100 = 77.86\% \text{ w/w } Fe_2O_3 \quad (71)$$

Practice Exercise 9.20

The purity of a sample of sodium oxalate, $Na_2C_2O_4$, is determined by titrating with a standard solution of $KMnO_4$. If a 0.5116-g sample requires 35.62 mL of 0.0400 M $KMnO_4$ to reach the titration's end point, what is the %w/w $Na_2C_2O_4$ in the sample.

Click here to review your answer to this exercise.

As shown in the following two examples, we can easily extend this approach to an analysis that requires an indirect analysis or a back titration.

Example 9.12

A 25.00-mL sample of a liquid bleach was diluted to 1000 mL in a volumetric flask. A 25-mL portion of the diluted sample was transferred by pipet into an Erlenmeyer flask containing an excess of KI, reducing the OCl^- to Cl^-, and producing I_3^-. The liberated I_3^- was determined by titrating with 0.09892 M $Na_2S_2O_3$, requiring 8.96 mL to reach the starch indicator end point. Report the %w/v NaOCl in the sample of bleach.

Solution

To determine the stoichiometry between the analyte, NaOCl, and the titrant, $Na_2S_2O_3$, we need to consider both the reaction between OCl^- and I^-, and the titration of I_3^- with $Na_2S_2O_3$.

First, in reducing OCl^- to Cl^-, the oxidation state of chlorine changes from +1 to –1, requiring two electrons. The oxidation of three I^- to form I_3^- releases two electrons as the oxidation state of each iodine changes from –1 in I^- to –⅓ in I_3^-. A conservation of electrons, therefore, requires that each mole of OCl^- produces one mole of I_3^-.

Second, in the titration reaction, I_3^-. is reduced to I^- and $S_2O_3^{2-}$ is oxidized to $S_4O_6^{2-}$. Reducing I_3^- to $3I^-$ requires two elections as each iodine changes from an oxidation state of –⅓ to –1. In oxidizing $S_2O_3^{2-}$ to $S_4O_6^{2-}$, each sulfur changes its oxidation state from +2 to +2.5, releasing one electron for each $S_2O_3^{2-}$. A conservation of electrons, therefore, requires that each mole of I_3^- reacts with two moles of $S_2O_3^{2-}$.

Finally, because each mole of OCl^- produces one mole of I_3^-, and each mole of I_3^- reacts with two moles of $S_2O_3^{2-}$, we know that every mole of NaOCl in the sample ultimately results in the consumption of two moles of $Na_2S_2O_3$.

The balanced reactions for this analysis are:

$$OCl^-(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + Cl^-(aq) + H_2O(l) \quad (72)$$

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 3I^-(aq) \quad (73)$$

The moles of $Na_2S_2O_3$ used in reaching the titration's end point is

$$(0.09892 \text{ M } Na_2S_2O_3) \times (0.00896 \text{ L } Na_2S_2O_3) = 8.86 \times 10^{-4} \text{ mol } Na_2S_2O_3 \quad (74)$$

which means the sample contains

$$8.86 \times 10^{-4} \text{ mol } Na_2S_2O_3 \times \frac{1 \text{ mol NaOCl}}{2 \text{ mol } Na_2S_2O_3} \times \frac{74.44 \text{ g NaOCl}}{\text{mol NaOCl}} = 0.03299 \text{ g NaOCl} \quad (75)$$

Thus, the %w/v NaOCl in the diluted sample is

$$\frac{0.03299 \text{ g NaOCl}}{25.00 \text{ mL}} \times 100 = 0.132\% \text{ w/v NaOCl} \quad (76)$$

Because the bleach was diluted by a factor of 40 (25 mL to 1000 mL), the concentration of NaOCl in the bleach is 5.28% (w/v).

Example 9.13

The amount of ascorbic acid, $C_6H_8O_6$, in orange juice was determined by oxidizing the ascorbic acid to dehydroascorbic acid, $C_6H_6O_6$, with a known amount of I_3^-, and back titrating the excess I_3^- with $Na_2S_2O_3$. A 5.00-mL sample of filtered orange juice was treated with 50.00 mL of 0.01023 M I_3^-. After the oxidation was complete, 13.82 mL of 0.07203 M $Na_2S_2O_3$ was needed to reach the starch indicator end point. Report the concentration ascorbic acid in mg/100 mL.

Solution

For a back titration we need to determine the stoichiometry between I_3^- and the analyte, $C_6H_8O_6$, and between I_3^- and the titrant, $Na_2S_2O_3$. The later is easy because we know from Example 9.12 that each mole of I_3^- reacts with two moles of $Na_2S_2O_3$.

The balanced reactions for this analysis are:

$$C_6H_8O_6(aq) + I_3^-(aq) \rightarrow 3I^-(aq) + C_6H_6O_6(aq) + 2H^+(aq) \quad (77)$$

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 3I^-(aq) \quad (78)$$

In oxidizing ascorbic acid to dehydroascorbic acid, the oxidation state of carbon changes from +⅔ in $C_6H_8O_6$ to +1 in $C_6H_6O_6$. Each carbon releases ⅓ of an electron, or a total of two electrons per ascorbic acid. As we learned in Example 9.12, reducing I_3^- requires two electrons; thus, a conservation of electrons requires that each mole of ascorbic acid consumes one mole of I_3^-.

The total moles of I_3^- reacting with $C_6H_8O_6$ and with $Na_2S_2O_3$ is

$$(0.01023 \text{ M } {}_3I^-) \times (0.05000 \text{ L } {}_3I^-) = 5.115 \times 10^{-4} \text{ mol } {}_3I^- \quad (79)$$

The back titration consumes

$$0.01382 \text{ L } Na_2S_2O_3 \times \frac{0.07203 \text{ mol } Na_2S_2O_3}{\text{L } Na_2S_2O_3} \times \frac{1 \text{ mol } I_3^-}{2 \text{ mol } Na_2S_2O_3} = 4.977 \times 10^{-4} \text{ mol } {}_3I^- \quad (80)$$

Subtracting the moles of I_3^- reacting with $Na_2S_2O_3$ from the total moles of I_3^- gives the moles reacting with ascorbic acid.

$$5.115 \times 10^{-4} \text{ mol } {}_3I^- - 4.977 \times 10^{-4} \text{ mol } {}_3I^- = 1.38 \times 10^{-5} \text{ mol } {}_3I^- \quad (81)$$

The grams of ascorbic acid in the 5.00-mL sample of orange juice is

$$1.38 \times 10^{-5} \text{ mol } {}_3I^- \times \frac{1 \text{ mol } C_6H_8O_6}{\text{mol } I_3^-} \times \frac{176.13 \text{ g } C_6H_8O_6}{\text{mol } C_6H_8O_6} = 2.43 \times 10^{-3} \text{ g } C_6H_8O_6 \quad (82)$$

There are 2.43 mg of ascorbic acid in the 5.00-mL sample, or 48.6 mg per 100 mL of orange juice.

Practice Exercise 9.21

A quantitative analysis for ethanol, C_2H_6O, can be accomplished by a redox back titration. Ethanol is oxidized to acetic acid, $C_2H_4O_2$, using excess dichromate, $Cr_2O_7^{2-}$, which is reduced to Cr^{3+}. The excess dichromate is titrated with Fe^{2+}, giving Cr^{3+} and Fe^{3+} as products. In a typical analysis, a 5.00-mL sample of a brandy is diluted to 500 mL in a volumetric flask. A 10.00-mL sample is taken and the ethanol is removed by distillation and collected in 50.00 mL of an acidified solution of 0.0200 M $K_2Cr_2O_7$. A back titration of the unreacted $Cr_2O_7^{2-}$ requires 21.48 mL of 0.1014 M Fe^{2+}. Calculate the %w/v ethanol in the brandy.

Click here to review your answer to this exercise.

9.4.4 Evaluation of Redox Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a redox titration are similar to those described earlier in this chapter for acid–base or a complexation titration. As with acid–base titrations, we can extend a redox titration to the analysis of a mixture of analytes if there is a significant difference in their oxidation or reduction potentials. Figure 9.42 shows an example of

the titration curve for a mixture of Fe^{2+} and Sn^{2+} using Ce^{4+} as the titrant. A titration of a mixture of analytes is possible if their standard state potentials or formal potentials differ by at least 200 mV.

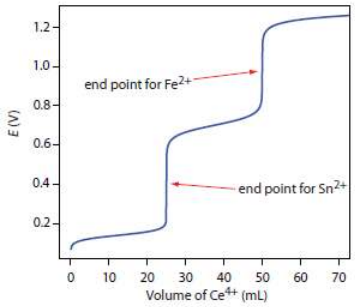


Figure 9.42 *Titration curve for the titration of 50.0 mL of 0.0125 M Sn^{2+} and 0.0250 M Fe^{2+} with 0.050 M Ce^{4+}. Both the titrand and the titrant are 1M in HCl.*

Contributors

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Titration of a Strong Acid With A Strong Base

Titration of a strong acid with a strong base is the simplest of the four types of titrations as it involves a strong acid and strong base that completely dissociate in water, thereby resulting in a strong acid-strong base neutralization reaction. This titration requires the use of a buret to dispense a strong base into a container of strong acid, or vice-versa, in order to determine the equivalence point.

Introduction

The purpose of a strong acid-strong base titration is to determine the concentration of the acidic solution by titrating it with a basic solution of known concentration, or vice-versa, until neutralization occurs. As both the acid and base are strong (high values of K_a and K_b), they will both fully dissociate, which means all the molecules of acid or base will completely separate into ions. At the equivalence point, equal amounts of H^+ and OH^- ions will combine to form H_2O, resulting in a pH of 7.0 (neutral). The pH at the equivalence point for this titration will always be 7.0, note that this is true only for titrations of strong acid with strong base. In addition, the anion (negative ion) created from the dissociation of the acid combines with the cation (positive ion) created from the dissociation of the base to create a **salt**. Therefore, the reaction between a strong acid and strong base will result in water and a salt.

Strong Acids and Bases

Table **1**

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
H_2SO_4	$Mg(OH)_2$
	$Ca(OH)_2$
	$Sr(OH)_2$
	Ba(OH

Table **1** lists common strong acids and strong bases, it is wise to memorize this table as this will be useful in solving titration problems. The acids and bases that are not listed in this table can be considered weak. Note that the strong bases consist of a hydroxide ion (OH^-) and an element from either the alkali or alkaline earth metals.

Strong Acid

An acid that is completely ionized in aqueous solution. This means when the strong acid is placed in a solution such as water, all of the strong acid will dissociate into its ions, as opposed to a weak acid. The general equation of the dissociation of a strong acid is:

$$HA\ (aq) \rightarrow H^+\ (aq) + A^-\ (aq) \tag{1}$$

The H represents hydrogen and the A represents the conjugate base (anion) of the acid.

Strong Base

A base that is completely ionized in aqueous solution. This means when the strong base is placed in a solution such as water, all of the strong base will dissociate into its ions. The general equation of the dissociation of a strong base is:

$$XOH\ (aq) \rightarrow X^+\ (aq) + OH^-\ (aq) \tag{2}$$

The OH represents hydroxide and the X represents the conjugate acid (cation) of the base.

Writing the reaction

The first step in writing an acid-base reaction is determining whether the acid and base involved are strong or weak as this will determine how the calculations are carried out. For reactions with strong acid and strong base, the net ionic equation will always be the same since the acid and base completely dissociate and the resulting salt also dissociates. This leaves the final product to simply be water, this is displayed in the following example involving hydrochloric acid (HCl) and sodium hydroxide (NaOH). From Table 1, you can see that HCl is a strong acid and NaOH is a strong base. Therefore, the reaction between HCl and NaOH is initially written out as follows:

$$HCl\ (aq) + NaOH\ (aq) \rightarrow H_2O\ (l) + NaCl\ (aq) \tag{3}$$

Since HCl and NaOH fully dissociate into their ion components, along with sodium chloride (NaCl), we can rewrite the equation as:

$$\mathbf{H^+}(aq) + \mathbf{Cl^-}(aq) + \mathbf{Na^+}(aq) + \mathbf{OH^-}(aq) \text{ --> } \mathbf{H_2O}(l) + \mathbf{Na^+}(aq) + \mathbf{Cl^-}(aq)$$

We can simplify this equation by writing the **net ionic equation** of this reaction by eliminating the reactants with state symbols that don't change, these reactants are known as spectator ions:

$$\mathbf{H^+}(aq) + \cancel{\mathbf{Cl^-}(aq)} + \cancel{\mathbf{Na^+}(aq)} + \mathbf{OH^-}(aq) \text{ --> } \mathbf{H_2O}(l) + \cancel{\mathbf{Na^+}(aq)} + \cancel{\mathbf{Cl^-}(aq)}$$

We are left with:

$$H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l) \tag{4}$$

The above equation describes the most important concept of a **strong acid/strong base** reaction, which is that a strong acid provides H^+ ions (more specifically hydronium ion H_3O^+) that combine with OH^- ions from a strong base to form water. One thing to note is that the **anion** of our acid HCl was $\mathbf{Cl^-}(aq)$, which combined with the **cation** of our base NaOH, $\mathbf{Na^+}(aq)$. This formed the salt NaCl(aq), which isn't shown in the net ionic equation since it dissociates. It is important, however, to remember that a strong acid/strong base reaction *does* form a salt. The net ionic equation for a strong acid-strong base reaction is always:

$$H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l) \tag{5}$$

Example 1

Write out the net ionic equations of the reactions:

a. HI and KOH
b. $H_2C_2O_4$ and NaOH

SOLUTION

From Table 1, you can see that HI and KOH are a strong acid and strong base, respectively. Therefore:

$$HI\ (aq) + KOH\ (aq) \rightarrow H_2O\ (l) + KI\ (aq) \tag{6}$$

$$\mathbf{H^+}(aq) + \mathbf{I^-}(aq) + \mathbf{K^+}(aq) + \mathbf{OH^-}(aq) \text{ --> } \mathbf{H_2O}(l) + \mathbf{K^+}(aq) + \mathbf{I^-}(aq)$$

$$\mathbf{H^+}(aq) + \cancel{\mathbf{I^-}(aq)} + \cancel{\mathbf{K^+}(aq)} + \mathbf{OH^-}(aq) \text{ --> } \mathbf{H_2O}(l) + \cancel{\mathbf{K^+}(aq)} + \cancel{\mathbf{I^-}(aq)}$$

$$\mathbf{H^+}(aq) + \mathbf{OH^-}(aq) \text{ --> } \mathbf{H_2O}(l) \text{ (Final Answer)}$$

Solution: NaOH is a strong base but H_2C_2O4 is a weak acid since it is not in the table. Therefore, this is a weak acid-strong base reaction which is explained under the link, titration of a weak acid with a strong base.

Titrating

Titration is a procedure for carrying out a chemical reaction between two solutions by the controlled addition from a buret of one solution into the other. A method, such as an indicator, must be used in a titration to locate the **equivalence point**. When titrating, acid can either be added to base or base can be added to acid, both will result in an equivalence point, which is the condition in which the reactants are in stoichiometric proportions. They consume each other, and neither reactant is in excess.

Equivalence Point

The equivalence point is the part of the titration when enough base has been added to the acid (or acid added to the base) that the concentration of $[H^+]$ in the solution equals the concentration of $[OH^-]$. Since $[H^+]$ = $[OH^-]$ at the equivalence point, they will combine to form the following equation:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O, .(l) \tag{7}$$

This reaction results in the production of water, which has a neutral pH of 7.0. The pH at the equivalence point is 7.0 because the solution only contains water and a salt that is neutral. Since neither H^+ nor OH^- molecules remain in the solution, we can conclude that at the equivalence point of a strong acid - strong base reaction, the pH is **always** equal to 7.0.

Further adding acid or base after reaching the equivalence point will lower or raise the pH, respectively.

Example 2

How many liters of 3.4 M HI will be required to reach the equivalence point with 2.1 L of 2.0 M KOH?

SOLUTION

Since we are given the molarity of the strong acid and strong base as well as the volume of the base, we are able to find the volume of the acid. The equation of the reaction is as follows:

$$HI(aq) + KOH(aq) \rightarrow H_2O\ (l) + KI\ (aq) \tag{8}$$

We see that the mole ratio necessary for HI to neutralize KOH is 1:1; therefore, we need the moles of HI to be equal to the KOH present in the solution.

To find the number of moles of KOH we multiply the molarity of KOH with the volume of KOH, notice how the liter unit cancels out:

2.0 mol KOH	2.1 ~~Liter~~	=	4.2 mol KOH
~~Liter~~			

As the moles of KOH = moles of HI at the equivalence point, we have 4.2 moles of HI.

To find the volume of the solution of HI, we use the molarity of HI (3.4 M) and the fact that we have 4.2 moles of HI:

3.4 mol HI	X	=	4.2 mol HI
Liter			

By dividing by 3.4 mol HI / L on both sides, we get:

X	=	4.2 ~~mol HI~~	=	**1.2 Liter**
		3.4 ~~mol HI~~ / Liter		

We are left with X = 1.2 L. The answer is **1.2 L** of 3.4 M HI required to reach the equivalence point with 2.1 L of 2.0 M KOH.

- Alternatively, as the required mole ratio of HI to KOH is 1:1, we can use the equation $\mathbf{M_1V_1 = M_2V_2}$ to solve the problem:

$(3.4\ M)(V_1) = (2.1\ L)(2.0\ M)$

$V_1 = (2.1\ L)(2.0\ \cancel{M}) / (3.4\ \cancel{M}) =$ **1.2**

Problems Involving pH

The following are examples of strong acid-strong base titration in which the pH and pOH are determined at specific points of the titration.

Example 3

What is the pH when 48.00 ml of 0.100 M NaOH solution have been added to 50.00 ml of 0.100 M HCl solution?

SOLUTION

Because it is a strong acid-base reaction, the reaction will be:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \quad (9)$$

The original number of moles of H^+ in the solution is:

$$50.00 \times 10^{-3}\text{L} \times 0.1\text{ M HCl} = .005\text{ moles}$$

The number of moles of OH^- added is:

$$48.00 \times 10^{-3}\text{L} \times 0.100\text{ M } OH^- = 0.0048\text{ moles}$$

Which results in:

$$0.005\text{-}0.0048 = .0002\text{ moles } H^+(aq)$$

The total volume of solution is 0.048L + 0.05L = 0.098L

$$[H^+] = (.0002/.098\text{L}) = 2.0 \times 10^{-3}$$

$$\text{pH} = 2.69$$

Example 4

What is the **pOH** when 5.0 L of a 0.45 M solution of sulfuric acid (H_2SO_4) is titrated with 2.3 L of a 1.2 M lithium hydroxide (LiOH) solution?

SOLUTION

To solve this problem we must first determine the moles of H^+ ions produced by the strong acid and the moles of OH^- ions produced by the strong base, respectively:

Acid:

0.45 ~~mol H_2SO_4~~	5.0 ~~Liter~~	2 mol H^+	=	**4.5 mol H^+**
~~Liter~~		1 ~~mol H_2SO_4~~		

(Since a single mole of H_2SO_4 produces two moles of H_2, we get the ratio of (2 mol H^+/ 1 mol H_2SO_4)

Base:

1.2 ~~mol LiOH~~	2.3 ~~Liter~~	1 mol OH^-	=	**2.8 mol OH^-**
~~Liter~~		1 ~~mol LiOH~~		

As the moles of H^+ are greater than the moles of OH^-, we must find the moles of excess H^+:

4.5 mol - 2.8 mol = **1.7 mol H^+** in excess.

Since pOH = -log[OH^-], we'll need to first convert the moles of H^+ in terms of molarity (concentration). Next, we'll need to determine the concentration of OH^- from the concentration of H^+.

Total volume:

2.3 L + 5.0 L = **7.3 L**

Using the total volume, we can calculate the molarity of H^+:

1.7 mol H^+	=	**0.23 M H^+**
7.3 L		

Next, with our molarity of H^+, we have two ways to determine the pOH:

1.

$$[H^+][OH^-] = 1 * 10^{-14}$$

$$[0.23][OH^-] = 1 * 10^{-14}$$

$$[OH^-] = 1 * 10^{-14} / 0.23 = \mathbf{4.35 * 10^{-14}}$$

$$pOH = -\log[OH^-] = -\log(4.35 * 10^{-14}) = \mathbf{13.4}$$

2.

$$pOH = 14 - pH$$

$$= 14 - (-\log[H^+])$$

$$= 14 + \log(0.23) = \mathbf{13.4}$$

The answer is 13.4 in both methods.

The Millimole for Problem Solving

In the examples above, the milliliters are converted to liters since moles are being used. To reduce the amount of unit conversions and complexity, a simpler method is to use the millimole as opposed to the mole since the amount of acid and base in the titration are usually thousandths of a mole. The millimole is one thousandth of a mole, therefore it will make calculations easier. Molarity will be expressed in millimoles to illustrate this principle:

Molarity = mol/L = mmol/mL

Steps for Problem Solving

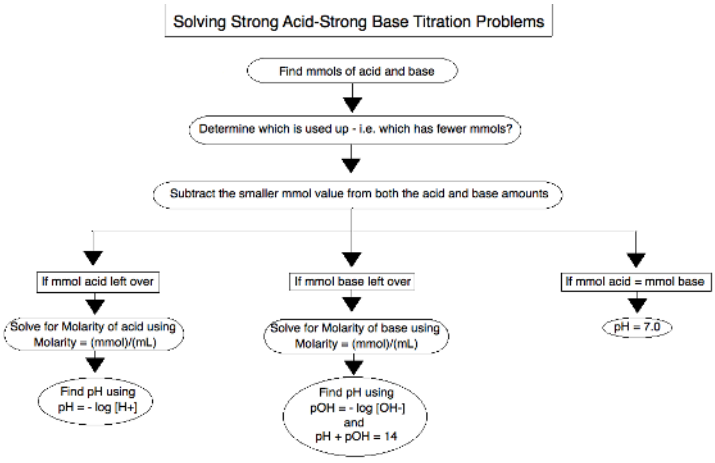


Figure 1: This figure displays the steps in simple terms to solving strong acid-strong base titration problems, refer to them when solving various strong acid-strong base problems. (created by Manpreet Kaur)-

Example 5

How many Liters of 3.4 M HNO_3 will be required to reach the equivalence point with 5.0 L of 3.0 M RbOH? What is the pH at the equivalence point?

SOLUTION

$$HNO_3\ (aq) + RbOH\ (aq) \rightarrow H_2O\ (l) + RbNO_3\ (aq)$$

$$= H^+\ (aq) + \cancel{NO_3^-\ (aq)} + \cancel{Rb^+\ (aq)} + OH^-\ (aq) \rightarrow H_2O\ (l) + \cancel{Rb^+\ (aq)} + \cancel{NO_3^-\ (aq)}$$

$$= \mathbf{H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l)}$$

$\mathbf{M_1V_1 = M_2V_2}$

$\mathbf{M_1}$ = 3.4 M

$\mathbf{V_1}$ = ?

$\mathbf{M_2}$ = 3.0 M

$\mathbf{V_2}$ = 5.0 L

(3.4 M) ($\mathbf{V_1}$) = (3.0 M)(5.0 L)

So,

V_1 = 4.4 L of HNO_3 required.

The pH at the equivalence point is 7.0 because this reaction involves a strong acid and strong base.

Only the salt $RbNO_3$ is left in the solution, resulting in a neutral pH.

Example 6:

Find the pH at the following points in the titration of 30 mL of 0.05 M $HClO_4$ with 0.1 M KOH.

A.) Before adding any KOH

SOLUTION

$pH = -\log[H^+]$

We know that initially there is 0.05 M $HClO_4$ and since no KOH has been added yet, the pH is simply:

$pH = -\log[0.05\ M]$

pH = 1.30

B.) When 5 mL of 0.1 M KOH is added

Solution

30 mL of 0.05 M $HClO_4$ = (30 mL)(0.05 M) = 1.5 mmol H^+

5 mL of 0.1 M KOH = (5 mL)(0.1 M) = 0.5 mmol OH^-

Write out the reaction between $HClO_4$ and KOH:

$HClO_4\ (aq) + KOH\ (aq) \rightarrow H_2O\ (l) + KClO_4$

$= H^+\ (aq) + \cancel{ClO_4^-\ (aq)} + \cancel{K^+\ (aq)} + OH^-\ (aq) \rightarrow H_2O\ (l) + \cancel{K^+\ (aq)} + \cancel{ClO_4^-\ (aq)}$

net ionic equation = $H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$

Based on this equation we can say that:

1 mol $HClO_4$ = 1 mol H^+

1 mol KOH = 1 mol OH^-

1 mol of H^+ reacts with **1 mol OH^-**

	$H^+ + OH^- \rightarrow H_2O$		
Inital	1.5 mmol	0.5 mmol	-
Change	-0.5 mmol	-0.5 mmol	-
Final	1 mmol	0 mmol	-

We subtract 0.5 mmol from both because the OH^- acts as the limiting reactant, leaving an excess of 1 mmol H^+.

Remember that:

Molarity = mmol/mL

We already have mmol, so to find mL, all we do is add the volume of $HClO_4$ and KOH:

Total Volume = mL $HClO_4$ + mL KOH = 30 mL + 5 mL = 35 mL

So,

Molarity of H^+ = (1 mmol)/(35 mL) = 0.029 M

pH = -log[H^+] = -log[0.029]

pH = 1.54

**** Notice the pH is increasing as base is added***

C.) When 15 mL of 0.1 M KOH is added

Solution

30 mL of 0.05 M $HClO_4$ = 1.5 mmol

15 mL of 0.1 M KOH = 1.5 mmol

	$H^+ + OH^- \rightarrow H_2O$		
Inital	1.5 mmol	1.5 mmol	-
Change	-1.5 mmol	-1.5 mmol	-
Final	0 mmol	0 mmol	-

Remember that when **[H^+] = [OH^-]**, this is the equivalence point.

We know that at the equivalence point for a strong acid-strong base titration, the pH = 7.0

So, ***pH = 7.0***

Example 7:

Determine the pH at the following points in the titration of 10 mL of 0.1 M HBr with 0.1 M CsOH when:

A.) When 8 mL CsOH is added

SOLUTION

mmol HBr = mmol H^+ = (10 mL)(0.1 M) = **1 mmol H^+**

mmol CsOH = mmol OH^- = (8 mL)(0.1 M) = **0.8 mmol OH^-**

H^+ (aq) + OH^- (aq) --> H_2O (l) *

***** *Remember, this will always be the net ionic equation for strong acid-strong base titrations.*

	$H^+ + OH^- \rightleftharpoons H_2O$		
Inital	1.0 mmol	0.8 mmol	-
Change	-0.8 mmol	-0.8 mmol	-
Final	0.2 mmol	0 mmol	-

We have 0.2 mmol H^+, so to solve for Molarity, we need the total volume.

Total Volume = 10 mL H^+ + 8 mL OH^- = 18 mL

Molarity = (0.2 mmol)/(18 mL) = 0.01 M

We know pH = -log[H^+] so,

pH = -log[0.01 M]

pH = 2.0

B.) When 10 mL CsOH is added

SOLUTION

mmol HBr = **1.0 mmol H^+**

mmol CsOH = (10 mL)(0.1 M) = **1.0 mmol OH^-**

Since **[H^+] = [OH^-]**, this is the equivalence point and thus,

pH = 7.0

C.) When 15 mL CsOH is added

SOLUTION

mmol HBr = **1.0 mmol H^+**

mmol CsOH = (15 mL)(0.1 M) = **1.5 mmol OH^-**

	$H^+ + OH^- \rightleftharpoons H_2O$		
Inital	1.0 mmol	1.5 mmol	-
Change	-1.0 mmol	-1.0 mmol	-
Final	0 mmol	.5 mmol	-

We have 0.5 mmol of OH^- so we can figure out molarity of OH^-, then find pOH and then use pOH to determine pH because:

pOH = 14 - pH

Total Volume = 10 mL H^+ + 15 mL OH^- = 25 mL

Molarity = (0.5 mmol)/(25 mL) = 0.02 M

Now,

pOH = -log[OH^-] = -log[0.02 M] = 1.70

pH = 14 - 1.70

pH = 12.30

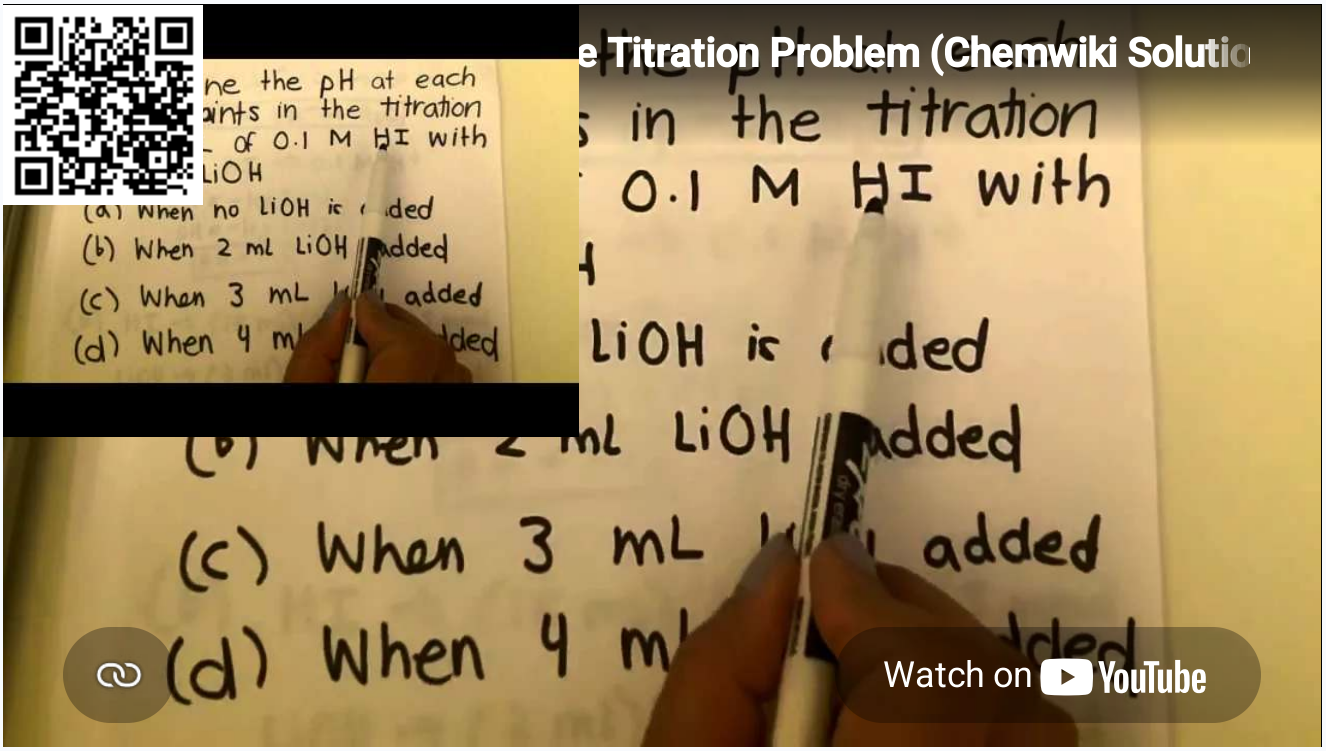
Example 9

Determine the pH at each of the following points in the titration of 15 mL of 0.1 M HI with 0.5 M LiOH

a. When no LiOH is added
b. When 2 mL LiOH added
c. When 3 mL LiOH added
d. When 4 mL LiOH added

SOLUTION

The solution to problem 4 is in video form and was created by Manpreet Kaur



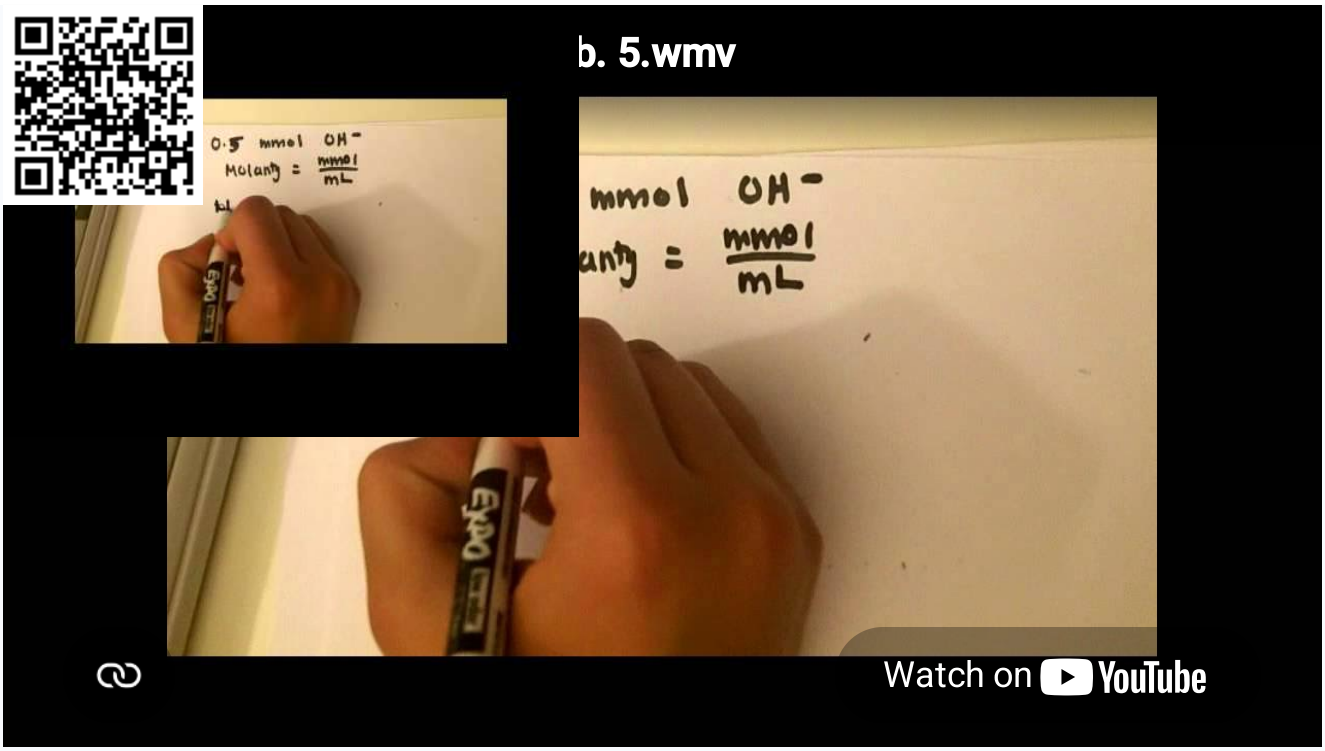
Example 10

Determine the pH at each of the following points in the titration of 10 mL of 0.05 M $Ba(OH)_2$ with 0.1 M HNO_3

a. When no HNO_3 is added
b. When 5 mL HNO_3 added
c. When 10 mL HNO_3 added
d. When 15 mL HNO_3 added

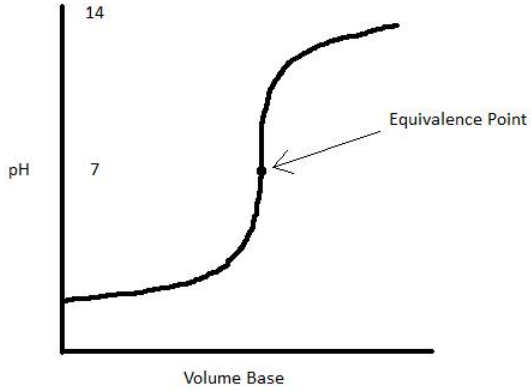
SOLUTION

The solution to problem 5 is in video form and was created by Manpreet Kaur



pH Curve of a Strong Acid - Strong Base Reaction

The pH curve diagram below represents the titration of a strong acid with a strong base:



As we add strong base to a strong acid, the pH increases slowly until we near the equivalence point, where the pH increases dramatically with a small increase in the volume of base added. This is due to the logarithmic nature of the pH system (pH = -log $[H^+]$). At the equivalence point, the pH is 7.0, as expected. Passing the equivalence point by adding more base initially increases the pH dramatically and eventually slopes off.

References

1. Kotz, et al. Chemistry and Chemical Reactivity. 7th edition. Belmont, California: Thomson Brooks/Cole, 2009.
2. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.

Outside Links

- http://www.youtube.com/watch?v=v7yRl48O7n8
- http://www.youtube.com/watch?v=KjBCe2SlJZc

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Titration of a Weak Acid with a Strong Base

A titration is a controlled chemical reaction between two different solutions.

Introduction

The titration of a weak acid with a strong base involves the direct transfer of protons from the weak acid to the hydoxide ion. The reaction of the weak acid, acetic acid, with a strong base, NaOH, can be seen below. In the reaction the acid and base react in a one to one ratio.

$$C_2H_4O_{2(aq)} + OH^-_{(aq)} \rightarrow C_2H_3O^-_{2(aq)} + H_2O_{(l)} \quad (1)$$

In this reaction a buret is used to administer one solution to another. The solution administered from the buret is called the titrant. The solution that the titrant is added to is called the analyte. In a titration of a Weak Acid with a Strong Base the titrant is a strong base and the analyte is a weak acid. In order to fully understand this type of titration the reaction, titration curve, and type of titration problems will be introduced.

Figure 1: *Titrations involve the addition of the titrant from the burret to the analyte. Figure is used with the permission of J.A. Freyre.*

The Titration Curve

The titration curve is a graph of the volume of titrant, or in our case the volume of strong base, plotted against the pH. There are several characteristics that are seen in all titration curves of a weak acid with a strong base. These characteristics are stated below.

1. The initial pH (before the addition of any strong base) is higher or less acidic than the titration of a strong acid
2. There is a sharp increase in pH at the beginning of the titration. This is because the anion of the weak acid becomes a common ion that reduces the ionization of the acid.
3. After the sharp increase at the beginning of the titration the curve only changes gradually. This is because the solution is acting as a buffer. This will continue until the base overcomes the buffers capacity.
4. In the middle of this gradually curve the half-neutralization occurs. At this point the concentration of weak acid is equal to the concentration of its conjugate base. Therefore the pH=pK_a. This point is called the half-neutralization because half of the acid has been neutralized.
5. At the equivalence point the pH is greater then 7 because all of the acid (HA) has been converted to its conjugate base (A-) by the addition of NaOH and now the equilibrium moves backwards towards HA and produces hydroxide, that is:

$$A^- + H_2O \rightleftharpoons AH + OH^- \quad (2)$$

6. The steep portion of the curve prior to the equivalence point is short. It usually only occurs until a pH of around 10.

The image of a titration curve of a weak acid with a strong base is seen below. All of the characteristics described above can be seen within it.

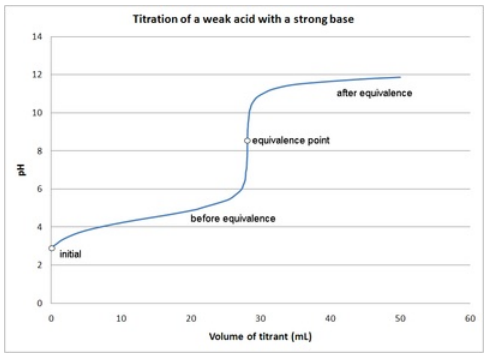

***Figure 2**: The titration of a weak acid with strong base. Figure is used with the permission of J.A. Freyre under the Creative Commons Attributions-Share Alike 2.5 Generic*

Weak Acid and Strong Base Titration Problems

When solving a titration problem with a weak acid and a strong base there are certain values that you want to attain. These include the initial pH, the pH after adding a small amount of base, the pH at the half-neutralization, the pH at the equivalence point, and finally the pH after adding excess base. This data will give sufficient information about the titration. Below is an example of this process.

Find the pH at each of the following points in the titration of 25 mL of 0.3 M HF with 0.3 M NaOH. The k_a value is 6.6 $\times 10^{-4}$

1. The initial pH
2. After adding 10 mL of 0.3 M NaOH
3. After adding 12.50 mL of 0.3 M NaOH
4. After adding 25 mL of 0.3 M NaOH
5. After adding 26 mL of 0.3 M NaOH

Example 1: Calculating the Initial pH

Finding the initial pH.

SOLUTION

Since HF is a weak acid, the use of an ICE table is required to find the pH. The question gives us the concentration of the HF.

$$HF + H_2O \rightleftharpoons H_3O^+ + F-$$

	HF	H_2O	H_3O^+	F^-
Initial	0.3 M	-	0 M	0 M
Change	- X	-	+ X	+X
Equilibrium	0.3 - X	-	X M	X M

Writing the information from the ICE Table in Equation form yields

$$6.6 \times 10^{-4} = \frac{x^2}{0.3 - x}$$

Manipulating the equation to get everything on one side yields

$$0 = x^2 + 6.6 \times 10^{-4}x - 1.98 \times 10^{-4}$$

Now this information is plugged into the quadratic formula to give

$$x = \frac{-6.6 \times 10^{-4} \pm \sqrt{(6.6 \times 10^{-4})^2 - 4(1)(-1.98 \times 10^{-4})}}{2}$$

The quadratic formula yields that x=0.013745 and x=-0.014405

However we can rule out x=-0.014405 because there cannot be negative concentrations. Therefore to get the pH we plug the concentration of H_3O^+ into the equation pH=-log(0.013745) and get **pH=1.86**

Example 2: After adding 10 mL of 0.3 M NaOH

Find the pH after the addition of 10 mL of 0.3 M NaOH.

SOLUTION

- The number of millimoles of HF to be neutralized is

$$(25\,mL)\left(\frac{0.3\,mmol\,HF}{1\,mL}\right) = 7.50 mmol HF$$

- The number of millimoles of OH^- that will be added within 10 mL is

$$(10\,mL)\left(\frac{0.3\,mmol\,OH^-}{1\,mL}\right) = 3\,mmol OH^-$$

To calculate the pH with this addition of base we must use an ICE Table

$$HF + H_2O \rightleftharpoons H_3O^+ + F-$$

	HF	H_2O	H_3O^+	F^-
Initial	7.5 mmol	0 mmol	-	0 mmol
Add	0 mmol	3 mmol	-	
Change	-3 mmol	-3 mmol	-	3 mmol
Equilibrium	4.5 mmol	0 mmol	-	3 mmol

However, this only gives us the millimoles. To get the concentration we must divide by the total volume. The total volume is the 25 mL original solution of HF plus the 10 mL of NaOH that was added. Therefore, the total volume is $25mL + 10mL = 35mL$

- Concentration of HF:

$$\frac{4.5\,mmol\,HF}{35\,mL} = 0.1287\ M \tag{3}$$

- Concentration of F^-:

$$\frac{3m\,molF^-}{35\,mL} = 0.0857\ M \tag{4}$$

Since an acid and its conjugate base are in equilibrium we can attempt to use the Henderson-hasselbalch equation. However, for this to work the reaction must follow certain rules. The ratio of the conjugate base and weak acid must be between 0.10 and 10. Also, both the ratio of the conjugate base and k_a value and the ratio of the acid and k_a value must exceed 100.

In this problem the Henderson-hasselbalch equation can be applied because the ratio of F- to HF is $\frac{0.0857}{0.1287} = 0.666$. This is between 0.10 and 10. The ratio of HF to k_a is $\frac{0.1287M}{6.6\times10^{-4}} = 195$ and the ratio of F^- to k_a is $\frac{0.0857M}{6.6\times10^{-4}} = 130$. These both exceed one hundred. Therefore, we continue by using the Henderson-hasselbalch equation.

$$pH = pk_a + \log\frac{[A^-]}{[HA]}$$

$$pH = -\log(6.6 \times 10^{-4}) + \log\frac{.0857}{.1287}$$

pH=3.00

Example 3: After adding 12.50 mL of 0.3 M NaOH

Find the pH after adding 12.50 mL of 0.3 M NaOH.

SOLUTION

The millimoles of OH^- added in 12.50 mL: $12.50mL * \frac{.3mmolOH^-}{mL} = 3.75mmolOH^-$

Once again we must use an ICE Table

	HF	H_2O	H_3O^+	F^-
Initial	7.5 mmol	0 mmol	-	0 mmol
Add	0 mmol	3.75 mmol	-	
Change	-3.75 mmol	-3.75 mmol	-	3.75 mmol
Equilibrium	3.75 mmol	0 mmol	-	3.75 mmol

To find the concentrations we must divide by the total volume. This is the initial volume of HF, 25 mL, and the addition of NaOH, 12.50 mL. Therefore the total volume is 25 mL + 12.50 mL = 37.50 mL

- Concentration of HF: $\frac{3.75mmolHF}{37.50mL} = 0.1M$
- Concentration of F^-: $\frac{3.75mmolF^-}{37.50mL} = 0.1M$

We have found the Half-neutralization point. We know this because the total amount of acid to be neutralized, 7.50mmol, has been reduced to half of its value, 3.75 mmol. At the half-neutralization point we can simplify the Henderson-Hasselbalch equation and use it. Since the amount of conjugate base and acid are equal, their ratio is one. We know that $log(1) = 0$ and therefore the ratio of conjugant base to acid will be zero as well. The equation at the half-neutralization point will be $pH = pk_a + log(1)$ which equals $pH = pk_a$

$$pH = -log(6.6 \times 10^{-4})$$

pH=3.18

Example 4: After adding 25 mL of 0.3 M NaOH

Find the pH after the addition of 25 mL of NaOH.

SOLUTION

- The millimoles of OH^- added in 25 mL:$25mL * \frac{.3mmolOH^-}{1mL} = 7.5mmolOH^-$

	HF	H_2O	H_3O^+	F^-
Initial	7.5 mmol	0 mmol	-	0 mmol
Add	0 mmol	+7.5 mmol	-	0 mmol
Change	-7.5 mmol	-7.5 mmol	-	7.5 mmol
Equilibrium	0 mmol	0 mmol	-	7.5 mmol

This is the equivalence point of the titration. We know this because the acid and base are both neutralized and neither is in excess. To find the concentrations we must divide by the total volume. This is the initial volume of HF, 25 mL, and the addition of NaOH, 25 mL. Therefore the total volume is 25 mL + 25 mL = 50 mL

Concentration of F^-:$\frac{7.5mmolF^-}{50mL} = 0.15M$

However, to get the pH at this point we must realize that F^- will hydrolyze. An ICE table for this reaction must be constructed

	HF	H_2O	H_3O^+	F^-
Initial	0.15 M	-	0 M	0 M
Change	- X	-	+ X	+X
Equilibrium	0.15 - X	-	X M	X M

In this reaction the F^- acts as a base. Therefore we must obtain the k_b value instead of the k_a value.

$$k_b = \frac{k_w}{k_a}$$

$$k_b = \frac{1.0 \times 10^{-14}}{6.6 \times 10^{-4}}$$

$$k_b = 1.515 \times 10^{-11}$$

Now that we have the k_b value, we can write the ICE table in equation the equation form

$$1.515 \times 10^{-11} \frac{x^2}{.15 - x}$$

Manipulating the equation to get everything on one side yields

$$0 = x^2 + 1.515 \times 10^{-11} x - 2.2727 \times 10^{-12}$$

Now this information is plugged into the quadratic formula to give

$$x = \frac{-1.515 \times 10^{-11} \pm \sqrt{(-1.515 \times 10^{-11})^2 - 4(1)(-2.2727 \times 10^{-12})}}{2}$$

The quadratic formula yields x=1.5075\times 10^{-6} and -1.5075\times 10^{-6} . However the negative value can be ruled out because concentrations cannot be zero.

Therefore to get the pOH we plug the concentration of OH^- into the equation pH=-log(1.5075\times 10^{-6}) and get pOH=5.82. To get the pH we minus the pOH from 14.

pH=14 - 5.82

pH= 8.18

Example 5: After adding 26 mL of 0.3 M NaOH

Find the pH after the addition of 26 mL of NaOH.

SOLUTION

The millimoles of OH^- added in the 26 mL: $26mL * \frac{.3mmolOH^{-1}}{1mL} = 7.8mmolOH^-$

This amount is greater then the moles of acid that is present. The 7.8 mmol OH^- neutralizes the 7.50 mmol HCl. To find how much OH^- will be in excess we subtract the amount of acid and hydroxide.

mmoles of hydroxide in excess: 7.8 mmol - 7.50 mmol= 0.3 mmol OH^-

To find the concentration of the OH^- we must divide by the total volume. This is the initial volume of HF, 25 mL, and the addition of NaOH, 26 mL. Therefore the total volume is 25 mL + 26 mL = 51 mL

The concentration of OH^- is $\frac{0.3mmolOH^-}{51mL} = 0.00588M$

pOH=-log(0.00588)=2.23

pH=14-2.23

pH=11.77

Example 6: Equivalence Point

When does the equivalence point of 15 mL of 0.15 M CH_3COOH titrated with 0.1 M NaOH occur?

SOLUTION

The equivalence point occurs when equal moles of acid react with equal moles of base.

The mmol CH_3COOH:

$$15mLCH_3COOH * \frac{.15mmolCH_3COOH}{1mL} = 2.25mmolCH_3COOH$$

We must find the amount of of mL of NaOH to give us the same mmols as CH_3COOH

$$2.25mmolCH_3COOH = 0.1MNaOH * XmLNaOH$$

X=22.5 mL

Therefore the equivalence point is after the addition of **22.5 mL** of NaOH

References

1. Levie, Robert De. Aqueous Acid-Base Equilibrium and Titrations. New York: Oxford University Press Inc. 1991
2. Petrucci, Ralph H. General Chemistry: Principles & Modern Application, 9th Edition. New Jersey: Pearson Prentice Hall. 2007.

Outside Links

1. http://www.youtube.com/watch?v=wgIXYvehTC4
2. http://www.youtube.com/watch?v=266wzpPXeXo

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Titration of a Weak Base with a Strong Acid

Data obtained through the process of titration can be used to compute the molarity and the correlated acidity of a solution at various times of the titration. The initial and final volumes of the analyte and titrant solutions, as well as the pH, or measure of acidity, are essential in calculating the total number of moles of analyte present. Once this information is determined, the molarity of the analyte, which was unknown before the titration, can then be computed, because its volume was measured beforehand. However, chemists are often interested in the data collected at various points during the titration as well, not just at the beginning and the end. These data can then be translated to points on a graph, resulting in an informational titration curve.

Introduction

Chemists are typically interested in calculating volume and acidity data for the following critical points: at the starting point before any titrant is added, at the midpoint, at a point before the equivalence point (excluding the initial condition), at the equivalence point, and past the equivalence point.

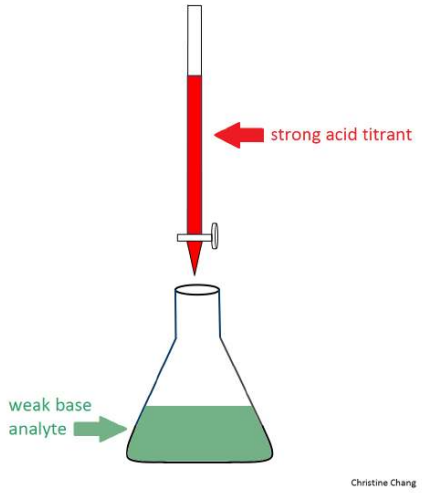

Figure **1**: Conventional setup of a lab titration. In this particular case, the weak base (colored in green), is being titrated by the strong acid (colored in red). In a typical titration, a few drops of indicator, such as phenolphthaelein, is added. The indicator causes the solution in the flask to undergo a color change that signifies the equivalence point has been reached. (CC BY 4.0; Christine Chang via LibreTexts)

Before titrant is added

Before the stopcock on the buret containing the strong acid is released, the analyte in the flask is completely unreacted. Calculating the pH of this initial solution allows chemists to analyze the changes in acidity, as well as the acidic strength of the titrant after the titration is complete. To calculate the pH, an ICE (Initial, Change, Equilibrium) table is used. When titrating weak bases, water is always a reactant in this initial step, and its conjugate base, hydroxide, in the products.

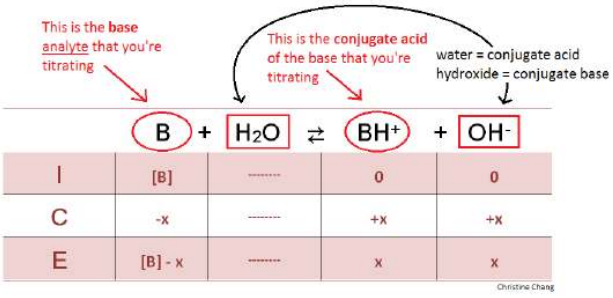

Figure **2**: ICE table at initial conditions. Drawing a chart like the one above is a useful step in calculating the concentration of hydroxide before any acid is added. The concentration can then be used to determine the starting pH. Since the quantity of water does not directly affect the reaction, its column is left blank. (CC BY 4.0; Christine Chang via LibreTexts)

At this point, there is no BH^+ or OH^- in the analyte solution—the molarities of these species are zero, as observed in the ICE table. Because the stopcock has not yet been released, there is no acid in the flask to react with the base and yield products BH^+ and OH^-. Once the strong acid is released into the flask, however, the BH^+ and OH^- begin to form.

The next step in determining the initial concentration of OH- is to use the information from the ICE table to set up an equilibrium expression with K_b. K_b is used in this case, instead of K_a, because the analyte being titrated is a base.

$$K_b = \frac{x^2}{[B] - x}$$

value of K_b should be given to you

$$K_b = \frac{x^2}{[B] - x}$$

Since K_b and [B] are given, the only variable left to solve for is x, which is equal to $[OH^-]$. This requires the quadratic equation:

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Once x is obtained, the pOH can be determined using the relation $pOH = -logx$. The pH can then be derived from the pOH using $pH = 14 - pOH$.

At the midpoint

The midpoint is when the **moles of strong acid added** = ½ **moles of base B** initially in the flask. In other words, at the midpoint, half the analyte has been titrated. Because the number of moles of the base is known (determined by measured volume multiplied by molarity), and the molarities of both the titrant and analyte are known, the volumes of acid and base at the midpoint can be calculated as follows:

$$L\ strong\ acid = \frac{mol\ strong\ acid\ added}{Molarity\ strong\ acid}$$

or in simpler terms:

$$\frac{1}{M} = \frac{L}{mol}, \text{ and } L = mol\frac{L}{mol}$$

Graphically, the midpoint is the first point at which the curve has zero slope, indicated in Figure 2.

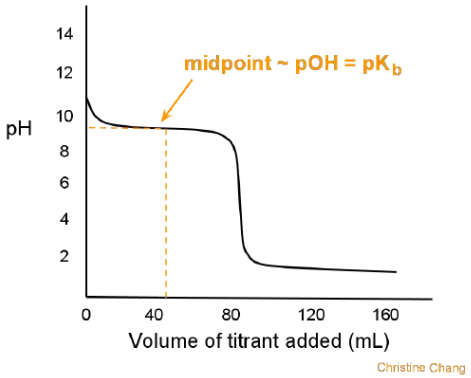

Figure **3**: Locating the midpoint on a titration curve. The midpoint is reached when enough titrant has been released to allow half the analyte to be neutralized. On the curve, that point is roughly the midpoint between the starting point and the equivalence point, or where the curve levels out. (CC BY 4.0; Christine Chang via LibreTexts)

Lastly, at the midpoint, pOH = pK_b. This makes it easy to calculate pH, because K_b is given.

Titrant added before the equivalence point

Chemists often calculate the acidity of the analyte at some point between the initial and the equivalence points to gauge the precise formation of the titration curve. Suppose 50 mL of 6 M strong acid is added to a base. Without looking at any graph, a chemist can determine whether or not he has passed the equivalence point.

The molarity of the acid is given, so the number of moles titrated can be calculated:
0.050 L × 6 mol/L = 0.3 moles of strong acid added thus far.

- If 0.3 < initial moles of base, the equivalence point has not yet been reached.
- If 0.3 = initial moles of base, the titration is at the equivalence point.
- If 0.3 > initial moles of base, the titration is past the equivalence point

If the equivalence point has not yet been reached, more acid is required. An ICE table is helpful in calculating the volume of B that has not been titrated at this point.

	B + H_2O ⇄		BH^+ +	OH^-
I	moles B	-------	0	0
C	-0.3 mol	-------	+0.3 mol	+0.3 mol
E	moles B – 0.3	-------	0.3 mol	0.3 mol

Christine Chang

Figure 4: ICE table before equivalence point is reached. The reaction for the ICE table for the titration before the equivalence point is the same as the reaction at the initial point. Instead of subtracting a variable x from the reactant B, the moles of strong acid titrated is subtracted.

Notice that this time the variable x is not used, because the number of moles of titrant added is already known. Also note that the units are consistent across all values used in the ICE table. In an ICE table, either moles must be used for everything, or molarity for everything. Any inconsistency in units will result in incorrect values. The green ICE table above uses moles (the red ICE table in Step 1 used molarity).

Because there is no variable in the ICE table before the equivalence point, the Henderson-Hasselbalch equation can be directly applied to to find pOH.

$$pOH = pK_b + log\frac{[BH^+]}{[B]}$$

Because the solution being titrated is a weak base, the pOH form of the Henderson Hasselbalch equation is used. If the analyte was an acid, however, this alternate form would have been used:

$$pH = pK_a + log\frac{[A^-]}{[HA]}$$

The two should not be confused. The latter formula would likely be used in the titration of a weak acid with a strong base. If moles were used in the ICE table, as in the table above, the ***values must be converted to molarities*** before being inserted into the Henderson Hasselbalch equation. When converting to molarity, compute as follows:

$$Molarity\ BH^+ = \frac{moles\ BH^+}{V_{titrant\ added} + V_{analyte}}$$

The same must be done for base B. Do not forget the volume of titrant added in the denominator (liters of solution).

At the equivalence point

The equivalence point is defined as the point where the moles of strong acid added = initial moles of base B in solution. Graphically, the equivalence point is where the curve is most vertical.

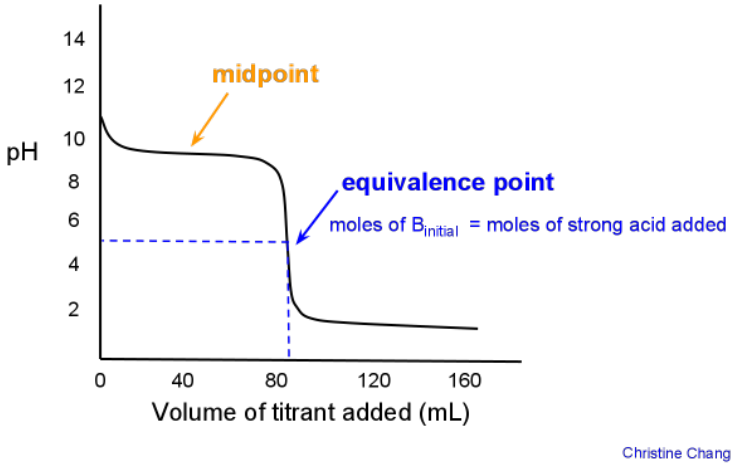

Figure 5: Comparing equivalence point with midpoint. It is apparent by studying a graph that the equivalence point is distinctly different from the midpoint. On the curve, the equivalence point is located where the graph is most steep. There is a fast and abrupt change of pH around this point, which can be observed by the color change the takes place during titration.

At the equivalence point, an ICE table is required to determine volume and acidity. At this point in the titration, however, the reaction is flipped. This is because the base B has been fully titrated, which means adding more titrant will not yield the same products. The reaction goes backwards.

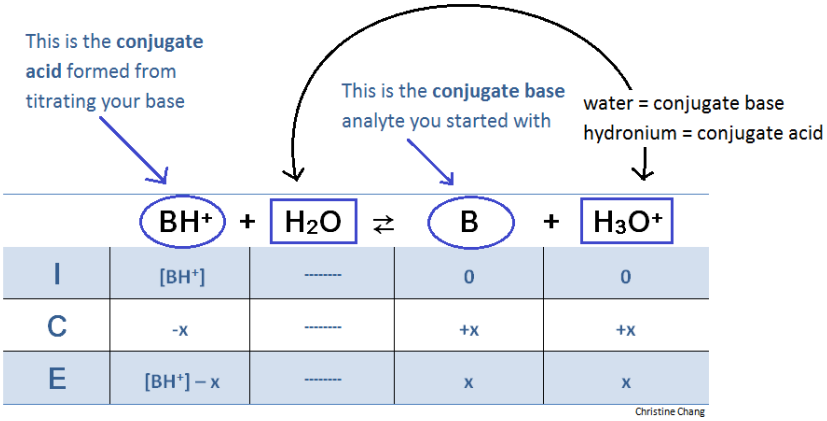

Figure 6: ICE table for reaction at equivalence point. The reaction at the equivalence point essentially goes backwards because all the base available to be titrated has been titrated. Think of the titration as an escalator. Once the highest level, or "equivalence point," is reached, the only option is to take a U-turn and go back down the other escalator lane.

At the equivalence point, there is no more of base B. Hence, “reactant” is now considered the BH^+ that formed from titrating B with strong acid. When calculating $[BH^+]$, do not forget to divide number of moles by the volume of base analyte PLUS **TITRANT added**.

Because the neutralization of the starting base is complete, the solution becomes increasingly acidic from this point on (as more acidic titrant is added. This is indicated by the hydronium in the product. Using an analogy, the titration can be thought of as a rising escalator. Once a person reaches the very top, or "equivalence point," he or she can only head back down in the opposite direciton. Likewise, at the equivalence point, the fully reacted reaction takes a "U-turn"—the former product becomes the reactant, and vice versa. Similar to step one, calculating the molarity of the products entails setting up an equilibrium expression with K_a (not K_b this time, because hydronium, which is acidic, is being produced instead of hydroxide, which is basic). Hint: K_b is given, and $K_w = 1.0 \times 10^{-14}$

$$K_a = \frac{K_w}{K_b}$$

Past the Equivalence Point

Suppose 100 mL of the 6 M strong acid titrant, which comes out to 0.6 moles, is added. If that number is greater than the number of moles of base B, the titration is past the equivalence point. To find the pH, first simply find the moles of *excess* H_3O^+. The excess can be calculated by subtracting initial moles of analyte B from moles of acidic titrant added, assuming a one-to-one stoichiometric ratio. Once the number of moles of excess H_3O^+ is determined, $[H_3O^+]$ can be calculated.

$$[\mathrm{H_3O^+}] = \frac{moles\ excess\ H_3O^+}{V_{titrant\ added} + V_{analyte}}$$

The denominator ($V_{titrant\ added} + V_{analyte}$) is the total volume of the solution in the flask.

Once the $[H_3O^+]$ is determined, pH can be calculated with the knowledge that $pH = -\log[\mathrm{H_3O^+}]$.

Example 1

You are given 90 mL of 0.6 M of the weak base $\mathrm{NH_3}$ ($K_b = 1.8 \times 10^{-5}$), and 1 M of the strong acid titrant HCl.

a. What is the pH before any acid is added?
b. What volume of acid (in mL) is needed to reach the equivalence (stoichiometric) point?
c. What volume of acid (in mL) is needed to reach the halfway point where pH = pK_a?
d. What is the pH after 50 mL of acid is added?
e. What is the pH at the equivalence (stoichiometric) point?
f. What is the pH after 60 mL of acid is added?

Solution

First, calculate the number of moles of base (analyte) present initially.

$$0.090\ L\ base \times \frac{0.6\ mol\ base}{L\ base\ solution} = 0.054\ mol\ base$$

a) An ICE table helps determine the molarity of OH^-.

	NH_3	H_2O	$\rightleftharpoons$	NH_4^+	OH^-
Initial	0.6 M	-		0	0
Change	-x	-		+x	+x
Equilibrium	0.6 - x	-		x	x

$$1.8 \times 10^{-5} = \frac{x^2}{0.6 - x}$$

$$(1.08 \times 10^{-5}) - (1.8 \times 10^{-5})x - x^2 = 0$$

$$x = \frac{1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(-1)(1.08 \times 10^{-5})}}{2(-1)}$$

$$= \frac{1.8 \times 10^{-5} \pm 6.57 \times 10^{-3}}{-2}$$

The two solutions are thus $[\mathrm{OH^-}] = -3.29 \times 10^{-3}$ and $[\mathrm{OH^-}] = 3.28 \times 10^{-3}\ M\ OH^-$. The first one is meaningless, so from the second value we can calculate the pOH and pH:

$$pOH = -\log(3.28 \times 10^{-3}) = 2.5$$

$$pH = 14 - pOH = 14 - 2.5 = 11.5$$

b) At the equivalence point, the number of moles of HCl added is equal to the initial number of moles of NH_3, because the analyte is completely neutralized.

$$0.054\ mol\ HCl \times \frac{1\ L\ HCl}{mol\ HCl} = 0.054\ L\ HCl,\ or\ 54\ mL\ HCl$$

c) At the midpoint, pOH = pK_b.

$$-\log(1.8 \times 10^{-5}) = 4.74\ pOH$$

$$pH = 14 - pOH = 14 - 4.74 = 9.26\ pH$$

At the midpoint, the number of moles of HCl added equals half the initial number of moles of NH_3. In other words, the number of moles of HCl added at the midpoint is half of the number of moles of HCl added by the equivalence point. Hence:

$$\frac{1}{2}(0.054\ L\ HCl\ added\ at\ equivalence\ point) = 0.027\ moles\ HCl\ at\ midpoint$$

$$\text{Volume of acid needed} = 0.027\ mol\ HCl \times \frac{1\ L}{1\ mol\ HCl} = 0.027\ L\ HCl = 27\ mL\ HCl$$

d) First, find the moles of HCl in 50 mL of HCl.

$$0.05\ L\ HCl \times \frac{mol\ HCl}{L\ HCl} = 0.05\ mol\ HCl$$

	NH_3	H_2O	$\rightleftharpoons$	NH_4^+	OH^-
Initial	0.054 mol	-		0	0
Change	-0.050 mol	-		+0.050 mol	+0.050 mol
Equilibrium	0.004 mol	-		0.050 mol	0.050 mol

Because 50 mL of acid have been added, and we started out with 90 mL of analyte, there are a total of 140 mL of analyte solution at this point. Hence, the molarity of NH_3 is the following:

$$\frac{0.004\ mol\ NH_3}{0.140\ L\ solution\ in\ flask} = 0.0286M$$

The molarity of NH_4^+ is:

$$\frac{0.050\ mol\ NH_4^+}{0.140\ L\ solution\ in\ flask} = 0.357M$$

Now we can use the Henderson-Hasselbalch approximation:

$$pOH = pK_b + log\frac{NH_4^+}{NH_3}$$

$$pOH = 4.74 + log\frac{0.357}{0.0286} = 5.84\ pOH$$

$$pH = 14 - pOH = 14 - 4.84 = 8.16$$

e) To find the pH at the equivalence point, first calculate the molarity of the NH_4^+ in the flask at this point.

$$\frac{0.054\ mol\ NH_4^+}{0.140\ L\ analyte\ solution} = 0.375M\ NH_4^+$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

	NH_4^+	H_2O	$\rightleftharpoons$	NH_3	H_3O^+
Initial	0.375	--		0	0
Change	-x	--		+x	+x
Equilibrium	0.375 -x	--		x	x

$$5.56 \times 10^{-10} = \frac{x^2}{0.375 + x}$$

$$2.09 \times 10^{-10} + (5.56 \times 10^{-10})x - x^2 = 0$$

We can use the quadratic equation to solve for x:

$$x = \frac{-5.56 \times 10^{-10} \pm \sqrt{(5.56 \times 10^{-10})^2 - 4(-1)(2.09 \times 10^{-10})}}{2(-1)}$$

$$= \frac{-5.56 \times 10^{-10} \pm 2.89 \times 10^{-5}}{-2} = -1.45 \times 10^{-5},\ 1.45 \times 10^{-5}\ M\ H_3O^+$$

$$pH = -log(1.45 \times 10^{-5}) = 4.84\ pH$$

f) First, find the moles of HCl in 60 mL of HCl.

$$0.06\ L \times \frac{mol\ HCl}{L\ HCl} = 0.06\ mol\ OH^-$$

Find the excess amount of HCl, or the amount added after neutralization has occurred.

0.054 moles of HCl reacted with the NH_3 to neutralize it.

$$excess\ HCl = 0.06 - 0.054 = 0.006\ mol\ HCl$$

Now we need to find the molarity of HCl in the flask at this point. We started out with 90 mL of NH_3 analyte in the flask, and added 60 mL. That gives a total of 150 mL, or 0.150 L of solution in the flask.

$$MOLARITY_{HCl\ in\ flask} = \frac{0.006\ mol}{0.150\ L\ solution} = 0.04\ M\ HCl$$

Because HCl dissociates into H_3O^+, equate [HCl] to [H_3O^+]. Now we have the information to determine pH.

$$pH = -log(0.04) = 1.4\ pH$$

Example 2

One titrates 100 ml of 1.00 M sodium chlorate(NaClO) with 1.00M HCl. What is the pH after you add 50 ml of acid? K_b for ClO^- = 3.6×10^{-7}.

Solution

Two main steps

1. Do the stoichiometry to find how much base has been absorbed by the acid.
2. Figure out the equilibrium concentrations of each species by doing an equilibrium problem.

Reaction of weak base and strong acid.

$$H^+(aq) + ClO^-(aq) \longrightarrow HClO(aq)$$

1. Start with 100 ml(1.00 M) = 0.100 moles of ClO^-.

2. If you add 50ml(1.00 M) = 0.05 moles of HCl to the base, the reaction in the previous step will consume all of the H^+, leaving 0.100 - 0.050 = 0.050 moles of ClO^-.
3. Because we added 50 ml of acid to 100 ml of base, we have a solution volume of 150 ml.
4. The concentration of ClO^- after adding the base is $[ClO^-]$ = 0.050 moles/0.150 L = 0.333 M.
5. 0.050 moles of HClO also forms, thus the concentration of HClO is also 0.333 M.
6. The solution above is a buffer of the weak acid HClO and the conjugate base ClO^-.
7. Now we can solve for the pH of a buffer by using the Henderson-Hasselbalch approximation.

Titration of a Weak Base with a Strong Acid is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Kelly Cox & Christine Chang.

Titration of a Weak Polyprotic Acid

An Arrhenius acid donates a proton (H^+), so a polyprotic acid donates protons. However, a polyprotic acid differs from a monoprotic acid because it has more than one acidic H^+, so it has the ability to donate multiple protons. As a *weak* polyprotic acid, it does not completely dissociate. Here are some examples of weak polyprotic acids:

- A triprotic acid: H_3PO_4
- A diprotic acid: H_2CO_3
- A diprotic acid: H_2SO_3

Acid Dissociation Constant

As an acid, a polyprotic acids have a very small acid dissociation constant (K_a), which measures the strength of the acid. K_a corresponds to the reaction of a weak acid with water and can be used to determine the pH of a solution. In the figure below, water serves as the base because it accepts a proton, H^+, from the phosphoric acid to become a hydronium ion. Phosphoric acid becomes a conjugate base because it loses a proton.

Figure **1**: This reaction shows the dissociation of a weak acid. (CC BY; Heather Yee via LibreTexts)

The acid dissociation constant can be attained by the following equation:

$$K_a = \frac{\text{Concentration of Products}}{\text{Concentration of Reactants}}$$

or even by acid dissociation constant at a logarithmic scale, also known as pK_a:

$$pK_a = -\log_{10} K_a \tag{1}$$

The equation can be manipulated into

$$K_a = 10^{-pK_a} \tag{2}$$

pK_a also be used to determine the pH of a solution given the concentrations of the conjugate base and undissociated acid. The equation is as follows:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{3}$$

with A^- is the conjugate base and HA is the undissociated acid.

There are as many acid ionization constants as there are acidic protons. For example, the ionization steps for phosphoric acid with ionization constants are

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \tag{4}$$

with

$$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 6.9 \times 10^{-3} \tag{5}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \tag{6}$$

with

$$K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8} \tag{7}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} \tag{8}$$

with

$$K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13} \tag{9}$$

Note that the acid dissociation constant of the first proton, indicated by K_{a1}, is the largest of all the successive acid dissociation constants. Acid dissociation constants, along with information from a titration, give the information needed to determine the pH of the solution.

Titration

The purpose of titration is to find the concentration of an unknown solution by adding a known volume of a solution with a known concentration to the unknown concentration of a solution. After finding the concentration of this unknown solution, one can find the pH of the solution, given information about the acid dissociation constant(s). Figure **2** below shows the typical lab titration setup prior to adding any titrant to the analyte.

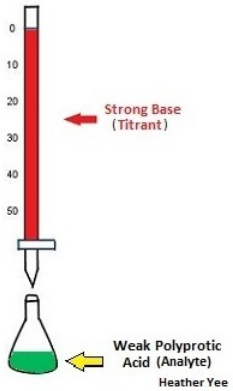

Figure **2**: Setup of a titration experiment. Like other titrations, this includes both an analyte and a titrant. The weak polyprotic acid (analyte) is in green and is titrated with teh strong base (the titrant) in red. (CC BY; Heather Yee via LibreTexts)

When an acid is titrated, there is an equivalence, or stoichiometric, point, which is when the moles of the strong base added equal of the moles of weak acid present. However, when a weak polyprotic acid is titrated, there are *multiple* equivalence points because the equivalence point will occur when an H^+ is dissociated. Therefore, the number of equivalence points depends on the number of H^+ atoms that can be removed from the molecule. Note that when the weak polyprotic acid dissociates, the proton (H^+) combines with H_2O to form H_3O^+.

The midpoint, also indicated in the figure, is when the number of moles of strong base added equals half of the moles of the weak acid that are present. For this reason, the midpoint is half of the equivalence point. Notice that there are as many midpoints as there are equivalence points. At the midpoint, pH equals the value of pKa because there is 50:50 mixture of the weak acid and the strong base. To quantify this, the Henderson-Hasselbalch Approximation can be used:

$$pH = pK_a + log\frac{[A^-]}{[HA]} \tag{10}$$

Since the solution is a 50/50 mixture, then the concentrations of both A- and HA are equal. Therefore, $\frac{[A^-]}{[HA]} = 1$. Plugging it back into the original equation, you get $pH = pK_a + log(1)$. Since $log(1) = 0$, the equation becomes $pH = pK_a$.

Titration

This next example shows what occurs when titrating the weak polyprotic acid H_3A with a strong base, like LiOH and NaOH. Since there are 3 acidic protons in this example, there is expected to be three equivalence points. (Note: This is disregarding the base used in the titration which would change your products depending upon the base used)

$$H_3A + H_2O \rightleftharpoons H_3O^+ + H_2A^- \tag{11}$$

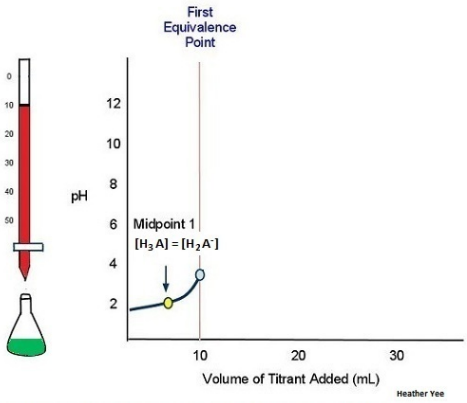

Figure 3: Titration of a weak Polyprotic acid. Adding 10 ml of the titrant was required to reach the first equivalance point. (CC BY; Heather Yee via LibreTexts)

As illustrated above in Figure 3, adding 10 mL of the titrant to the weak polyprotic acid is need to reach the first equivalence point.

$$H_2A^- + H_2O \rightleftharpoons H_3O^+ + HA^{2-} \tag{12}$$

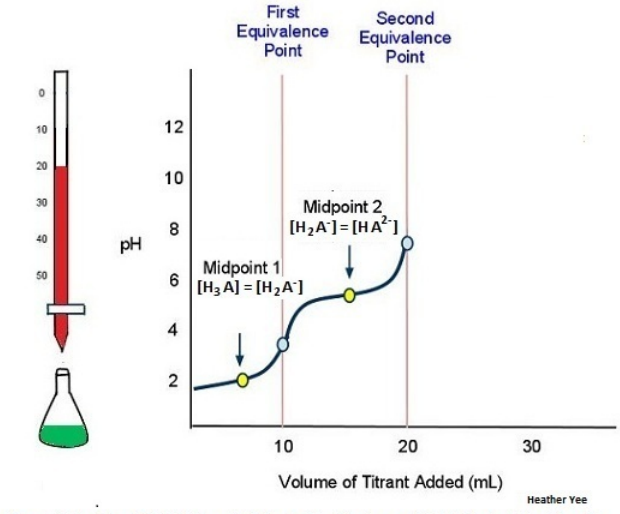

Figure 3.2 Titration of a Weak Polyprotic Acid. Another 10 mL, or a total of 20 mL, of the titrant is added to the weak polyprotic acid to reach the second equivalence point. Image created by Heather Yee.

Figure 4: Titration of a Weak Polyprotic Acid. Another 10 mL, or a total of 20 mL, of the titrant is added to the weak polyprotic acid to reach the second equivalence point. (CC BY; Heather Yee via LibreTexts)

Figure 4 illustrates that adding another 10 mL (total of 20 mL) to the weak polyprotic acid solution will allow for another H^+ to dissociate. Another equivalence points also means yet another midpoint.

$$HA^{2-} + H_2O \rightleftharpoons H_3O^+ + A^{3-} \tag{13}$$

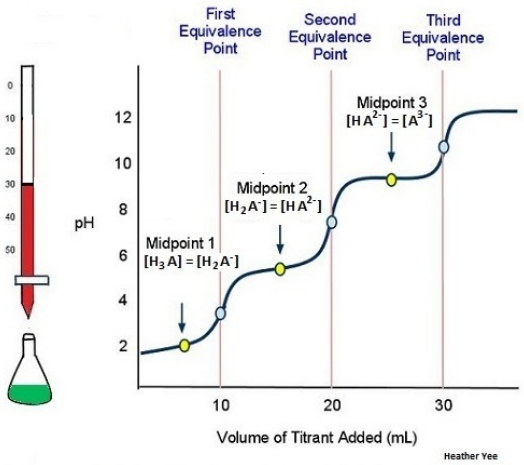

Figure 5: Titration of a weak polyprotic acid. The final equivalence popint is attained by adding another 10 ml, or a total of 30 ml of titrant to the weak polyprotic acid. (CC BY; Heather Yee via LibreTexts)

In Figure 5, the titration is finally complete because there are three equivalence points, with the third being attained by adding yet another 10 mL (total of 30 ml) of the titrant.

Attributes of a Weak Polyprotic Acid Titration Curve

The following example below, we can conclude that the graph of a weak polyprotic acid will show not one (as the graph of a weak acid with a strong base titration graph would look), but multiple equivalence points.

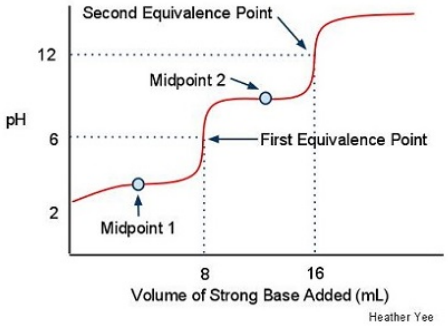

Figure 6: Titration curve of a weak diprotic acid. This figure shows the basic features of a titration curve of a weak polyprotic acid. (CC BY; Heather Yee via LibreTexts)

- The curve starts at a higher pH than a titration curve of a strong base
- There is a steep climb in pH before the first midpoint
- Gradual increase of pH until past the midpoint.
- Right before the equivalence point there is a sharp increase in pH
- pH steadies itself around the midpoint because the solutions at this point in the curve are buffer solutions, which means that adding small increments of a strong base will only barely change the pH
- Increase in pH near the equivalence point

Problems

1. Suppose you titrate the weak polyprotic acid H_2CO_3 with a strong base, how many equivalence points and midpoints would result?
2. How does pH relate to pK_a at any point on the titration curve?
3. Out of all the acid dissociation constants for the dissociation of the protons for a weak polyprotic acid, which is the largest?
4. Given that $K_{a1} = 5.9 \times 10^{-3}$ and $K_{a2} = 6.0 \times 10^{-6}$, calculate the pH after titrating 70 mL of 0.10 M H_2SO_3 with 50 mL of 0.10 M KOH.
5. Consider the titration of 30 mL of 0.10 M H_2CO_3 with 50 mL of 0.10 LiOH. What would the final pH be if $K_{a1} = 6.0 \times 10^{-3}$ and $K_{a2} = 5.9 \times 10^{-7}$?

Solutions

1. Two equivalence points and two midpoints would result.
2. pH relates to pKa in the equation $pH = pK_a + \log \frac{[A^-]}{[HA]}$ for any point on the titration curve except at the midpoint. At the midpoint $pH = pK_a$
3. The acid dissociation constant of the first proton is the largest out of the successive protons.
4. The number of moles of H_2SO_3 and KOH are

$$mol\ H_2SO_3 = Molarity * Volume = 0.10M * 0.07L = 0.007$$

$$mol\ KOH = Molarity * Volume = 0.10M * .05L = 0.005$$

After this titration, 0.002 mol H_2SO_3 remain and 0.005 mol HSO_3^- form.

$$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$$

$$K_{a1} = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]} = 5.9 \times 10^{-3}$$

$$[H_3O^+] = 2.36 \times 10^{-3}$$

$$pH = -log[H_30^+] = -log(2.36 \times 10^{-3}) = 2.63$$

5. The number of moles of H_2SO_3 and LiOH are

$$mol\ H_2CO_3 = Molarity * Volume = 0.10M \times 0.03L = 0.003$$

$$mol\ LiOH = Molarity * Volume = 0.10M * .05L = 0.005 \quad (14)$$

After this titration, 0.001 mol HCO_3^- remain and 0.002 mol CO_3^{2-} form.

$$HCO_3^{-1} + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$

$$K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^{-1}]} = 5.9 \times 10^{-7}$$

$$[H_3O^+] = 2.95 \times 10^{-7}$$

$$pH = -log[H_30^+] = -log(2.95 \times 10^{-7}) = 6.53$$

References

1. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.
2. Barnum, Dennis W.; Predicting Acid-Base Titration Curves without Calculations. *Journal of Chemical Education* **1999**, *76* (7), 938.
3. Hamann, S. D.; Titration behavior of monoprotic and diprotic acids. *Journal of Chemical Education* **1970**, *47* (9), 658.

Contributors

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Use of a Volumetric Pipet

In this course you will use three types of precision calibrated glassware: burets, pipets and flasks. This type of calibrated glassware is usually referred to as volumetric glassware. This precision glassware is capable of measurements of volume that are good to four significant digits and is consequently expensive. You should be careful in handling this type of equipment so that breakage losses are minimized. Be particularly careful with the tips of pipets and burets.

The only volumetric glassware in your lockers are 50, 100 and 250 mL volumetric flasks. These are characterized by long slender necks with a graduation mark on them. Volumetric pipets are stored in drawers on the west wall of the lab and the burets are kept in a cabinet on the wall near the door to the weighing room. Any other glassware in your locker with graduation marks is not volumetric. Such equipment is machine-made and not individually calibrated. It can be used for less accurate measurements but should never be used when high, analytical accuracy is required. It takes some practice to use volumetric glassware properly and before you begin using such equipment you should inspect the pieces of glassware you plan to use, washing them in the Alconox solution provided if necessary, followed by rinsing first in tap water and then three or four rinses with distilled water. It is usually not necessary to dry volumetric ware. As for reading volumetric ware, take advantage of the Web links which illustrate the proper use of a buret and the proper use of a pipet

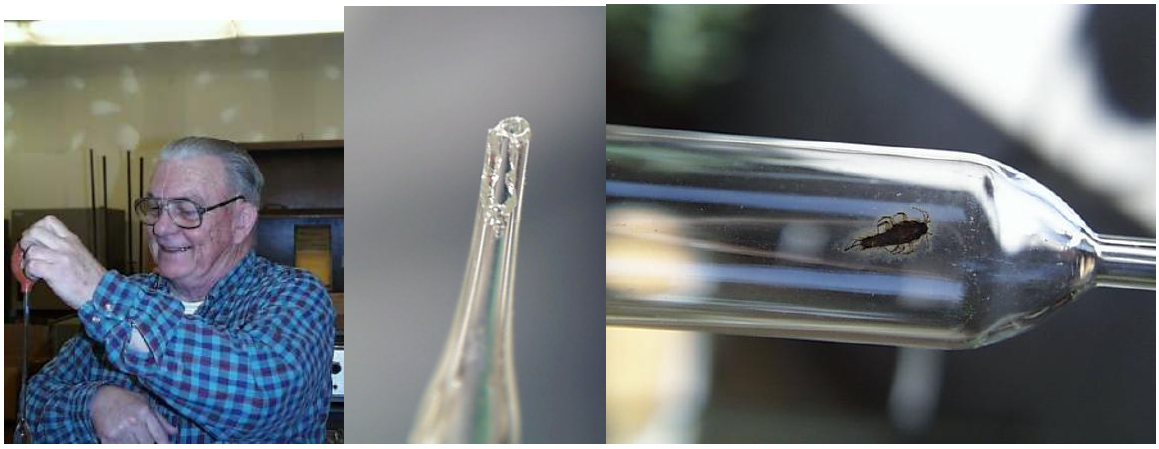
You must never expose any volumetric glassware to sources of heat since such exposure will adversely affect the calibration. Thus, you must never dry any volumetric glassware in a drying oven.

It is important that the volumetric glassware be completely clean before you use it. It must drain in such a manner that a smooth film of solution adheres to the inside, there must be no beading or droplet formation on the inside walls of the vessel. If you observe such droplets, wash the glassware with small amounts of warm Alconox solution. If necessary use a brush. If Alconox treatments do not suffice, it may be necessary to clean the glassware using other methods. Contact your lab instructor if you feel that this is required.

Volumetric pipets and burets that have recently been cleaned will not be dry on the inside. Before you use such wet glassware it must be rinsed with small portions of the solution to be measured. If you don't know how this is done consult your instructor.

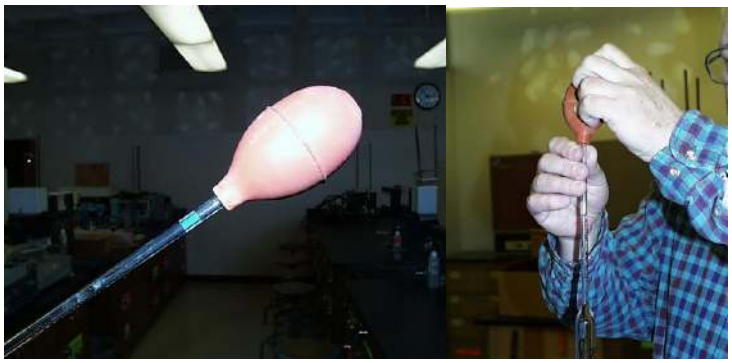
Discussion

The volumetric analysis exercises will make use of a 25 mL volumetric pipet. Dr. Reilly, always willing to lend a hand, is going to be our demonstrator on the proper use of a volumetric pipet. Our pipets are kept in the drawers at the west end of lab. Pick out a 25 mL pipet and practice a few times with distilled water before using it to draw in any reagent.



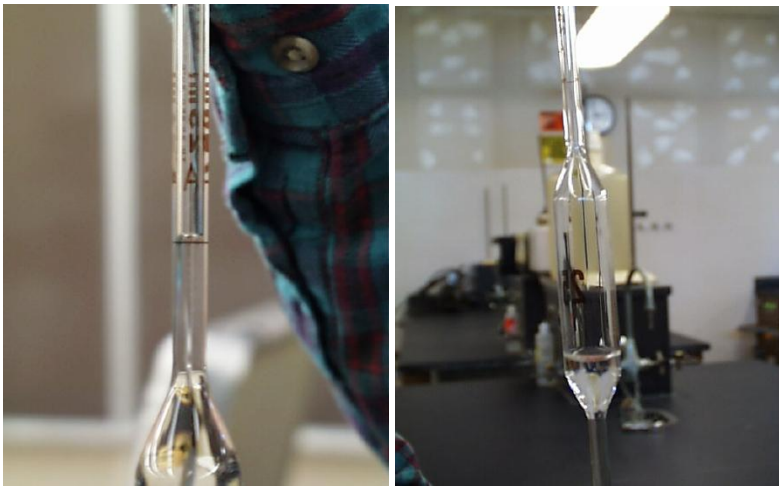
It is always a good idea to examine each pipet you take from the drawer because occasionally you will find a stowaway who got in and couldn't get out. Here's one that got stuck a long time ago, maybe even before Proposition 13. We wouldn't know how old he is without first doing some C-14 dating on him (far right). You ought also to examine the tip for breakage. Many breaks are trivial. That is they show minor chipping around the edge of the tip, but here's one (near right) in which the entire wall has fractured at one

point. You can just barely see the intact nozzle, but the pipet is unusable because the liquid path has been compromised. Better discard this one.

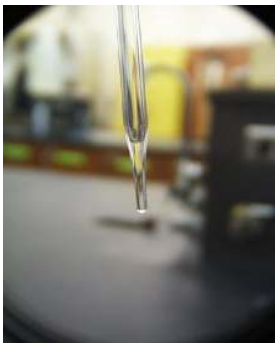


You're going to use one of two kinds of suction devices to fill the pipet. If your suction device is a rubber bulb, it ought NOT to be placed so that it is attached to the mouth of the pipet.

It ought instead to be pressed so that the hole of the bulb makes an air-tight seal against the mouth of the pipet. Note here that Dr. Reilly has squeezed the bulb before he pressed it against the mouth of the pipet. The tip of the pipet can then be placed in the solution which is to be drawn up and the bulb slowly released. This method requires a little practice but in the final analysis may be considerably more practical and satisfying than the use of the high-tech bulb Dr. Reilly will show you next.



You must exercise care not to allow the tip of the pipet to break the surface of the liquid while you are drawing in the solution or the sudden decrease in viscosity at the tip will cause a large amount of liquid to contaminate the inside of your rubber bulb because of the entry of air pushing the liquid up beyond the mouth of the pipet. Draw up the solution until the meniscus is several centimeters above the calibration line, then quickly put your finger over the open hole of the pipet.



Making sure that your line of sight is perpendicular to the length of the pipet, allow a tiny amount of air in so that the meniscus drops to the calibration mark, as Dr. Reilly is showing at the right.

When the bottom of the meniscus coincides with the calibration mark, your pipet contains a precisely measured volume, as in the image at the left.

The pipet can then be removed from your reagent solution, transferred to the receiving flask and allowed to drain.

A volumetric pipet should not be "blown out" to eject all liquid at the tip because volumetric pipets are calibrated in a manner that takes into account the solution which remains at the tip due to surface tension.

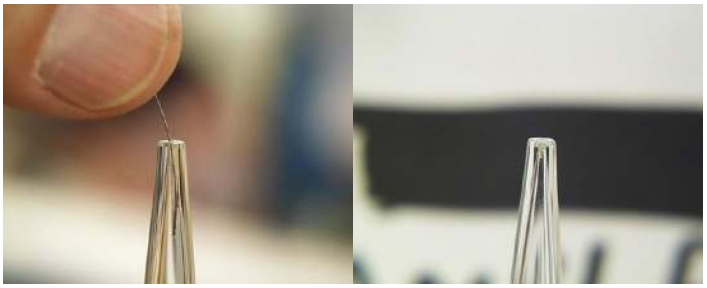
The "high-tech"pipet bulb is an Eppendorf bulb. It can be placed firmly on the mouth of the pipet.

At the side of the Eppendorf is a protruding lever attached to a slide. Pull it down to create a vacuum inside the bulb.

Use your thumb to push the two way valve up when you are ready to draw your solution into the pipet, as shown at the left, but make sure the nozzle of your pipet remains below the surface of the solution (right) so that you don't suck air into your pipet causing lots of solution to pass into the filter in the bulb area which will require disassembly, drying out and replacement of parts.


When a sufficient amount of the solution has been drawn in so that the meniscus is above the calibration mark, use your thumb to slide the two-way valve down, as shown at the left. Do it gently so that the meniscus drops slowly to the calibration mark. Then you can transfer the solution in the pipet to the receiving flask and push the two-way valve lever down to empty the pipet. The nozzle of the pipet can be kept in the open air for the transfer, as shown at the right.


Finally, pipettes and burettes accumulate inert solid material which must be removed from time to time. Here at the left is the nozzle of a burette which has material which will not pass through. You may have to use a wire, available on the lower ledge of the burette case, to clean out this material. It is best to do it with the petcock valve removed so that when you do a reverse wash after poking it free, the material can be washed out at the point of the valve instead of at the other end of the burette cylinder.



To illustrate that sometimes things just don't work out as we wish, look at the piece of solid material lodged in the nozzle of the pipette on the left. Usually, poking the material with a piece of wire breaks it up so that it flows freely out the nozzle, but in this case the material won't be broken (right photo).

Water from a wash bottle was squirted in the upper neck of the pipette to wash the material out through the nozzle, but it wouldn't budge. The only solution here is to do a normal filling of the pipette with distilled water and then a reverse drain through the upper neck so as to wash the particle out the other end.

Contributor

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Vacuum Equipment

Vacuum equipment is used to generate, maintain, and manipulate pressures below that of the ambient atmosphere. Many common lab procedures require vacuum conditions, such as inert gas purging, cannulation, and solvent evaporation. Vacuum equipment often requires special care to maintain.

Quality

Higher quality vacuum contains less matter, and therefore a lower pressure. A commonly used convention is:

- Low vac: 760 torr - 25 torr
- Medium vac: 25 - 10^{-3} torr
- High vac: 10^{-3} - 10^{-9} torr
- Ultra high vac: 10^{-9} - 10^{-12} torr

Pumps

- **Diaphragm:** Diaphragm pumps use a flexible diaphragm and a set of check valves to produce pumping pressure and typically produce low to medium vac. They are often resistant to solvent and mildly corrosive vapors, making them useful for rotary evaporators, but their inability to produce high vacuum limits their utility. Diaphragm pumps often do not require oil.
- **Rotary Vane:** Rotary vane pumps use rotating sets of circular vanes in an elliptical cavity to create pumping pressure, and can achieve medium to high vacuum. If your pump requires oil changes, it is likely a rotary vane pump. Though they can achieve higher vacuum than diaphragm pumps, they are easily damaged by solvent or corrosive vapors. Steps must be taken to prevent harmful vapors from reaching this type of pump such as the implementation of a cold trap as contamination can significantly reduce a pump's efficiency and lifetime.
- **Diffusion**: Diffusion pumps have no moving mechanical parts; instead they use a high speed vapor jet to direct gases toward the exhaust. This type of pump can achieve high to ultra high vacuum, but can not discharge directly to the atmosphere and must use a secondary pump to maintain low pressure at the outlet. Diffusion pumps can also introduce oil vapors into the vacuum chamber.
- **Turbomolecular**: Turbomolecular pumps use sets of spinning blades to accelerate gases. They can achieve medium to ultra high vacuum. Higher vacuum requires faster rotational rates, so turbomolecular pumps must also be treated with care to avoid introducing particles or corrosive vapors. Some types of turbomolecular pump also require a secondary pump at the outlet.

Schlenk Lines

A Schlenk line, often referred to as a vacuum manifold, is composed of a vacuum line connected by several valves to an inert gas line and a port. The valve position connects the port to either the vacuum line or the inert gas line. The inert gas line often has an oil-filled bubbler at its outlet to prevent atmospheric contamination.

McLeod Gauge

A McLeod Gauge is an instrument for measuring pressure in high-vacuum systems. It is filled (typically) with mercury. When pressure is not being measured, the gauge should be held in the "evacuating" position; the mercury rests in a chamber connected to two capillary tubes, which should be (just past) horizontal. To make a measurement, the gauge should be connected the line and opened to vacuum. Pressure should be allowed to equilibrate for a couple of minutes. Then the gauge should be rotated so that the capillaries are vertical (the "measuring" position); the mercury should flow from the chamber into the capillaries. One of these capillaries is open to the rest of the system, while the other is closed. The difference between the levels of the mercury when these are vertical gives the pressure of the system (the instrument should have its own scale, which should be zeroed to the level of mercury in the open capillary). For accurate measurements, the rotation from evacuating to measuring positions should be slow, to prevent discontinuities in the mercury.

Before disconnecting the gauge, it should be returned to the evacuating position and returned, slowly, to atmospheric pressure. Disconnecting the system while it is still under vacuum can cause splattering of mercury, potentially out of the gauge. Returning it to atmospheric pressure while it is in the measuring position can cause mercury to get stuck in the closed capillary.

Safety

Care should be used to avoid venting harmful vapors into the lab atmosphere. Pump exhaust should be either vented into a fume hood, or fitted with an appropriate scrubber or filter. When broken, evacuated glassware shatters and violently implodes, sending fragments flying at high velocity. Inspect your glassware for cracks and flaws before applying vacuum.

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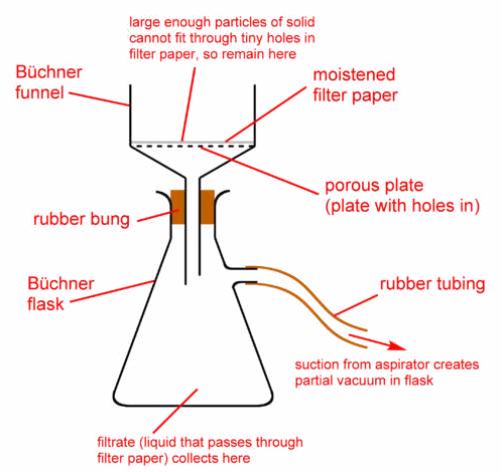
Vacuum Filtration

Suction filtration is a chemistry laboratory technique which allows for a greater rate of filtration. Whereas in normal filtration gravity provides the force which draws the liquid through the filter paper, in suction filtration a pressure gradient performs this function. This has the advantage of offering a variable rate depending on the strength of the pump being used to extract air from the Büchner flask. Care must be taken not to use such a strong vacuum that the filter paper rips (in which case all the solid will be lost back into the solvent) or in extreme cases the glass flask breaks. Suction filtration is used in recrystallisation experiments.



Contributors

- Wikipedia

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