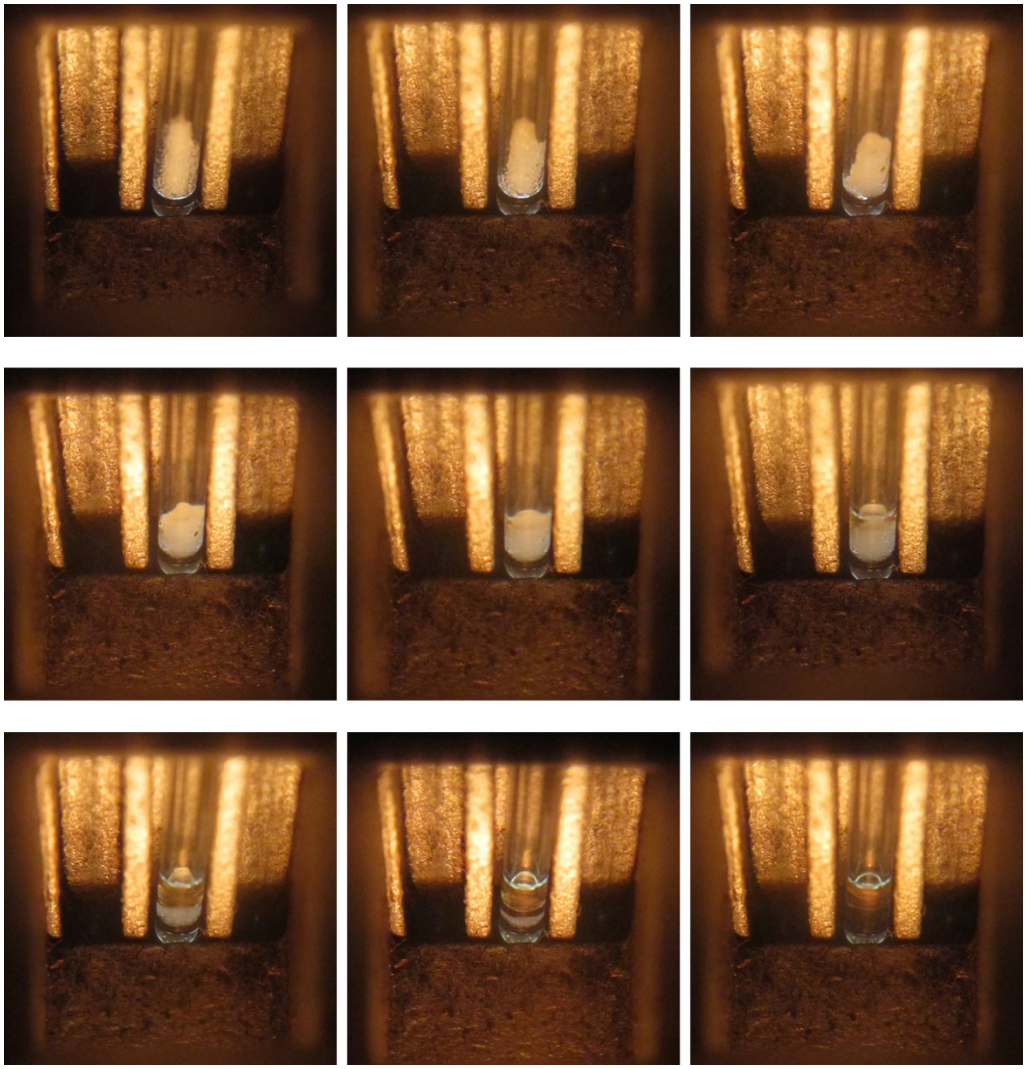
CHAPTER 6

MISCELLANEOUS TECHNIQUES



Time-lapse melting of para-bromobenzoic acid in a melting point apparatus.

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6.1 MELTING POINT

6.1.A OVERVIEW OF MELTING POINT

Measurement of a solid compound's melting point is a standard practice in the organic chemistry laboratory. The melting point is the temperature where the solid-liquid phase change occurs. In some reference books it is listed as a single value (*e.g.* 98 ˚C), but in chemical catalogs it is more often listed as a range of values (*e.g.* 96-98 ˚C). The melting "point" is therefore more of a melting "range," and in part, reflects how melting points are experimentally determined.

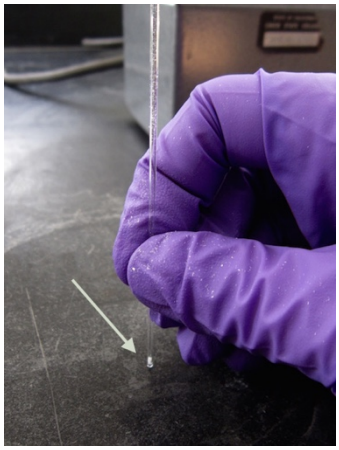


Figure 6.1: White solid (indicated with an arrow) in a capillary tube.

A melting point is determined by loading a small amount of sample into a capillary tube (Figure 6.1), and then slowly heating the sample. Figure 6.2 shows a close-up view of a sample inside a melting point apparatus, where the sample is slowly heated through contact with hot vertical metal blocks on either side of the capillary tube. The sample is kept small in this technique to ensure adequate heat transfer between the metal and sample.

The first value recorded for the melting range is with the very first appearance of liquid. As this temperature is approached, the solid may begin to glisten (Figure 6.2b), and the temperature is recorded with the first hint of liquid movement (a droplet) inside the tube (Figure 6.2c). The second value recorded for the melting range is with the melting of the entire sample, which occurs when all areas of opaque solid have turned into a transparent liquid (Figure 6.2h).

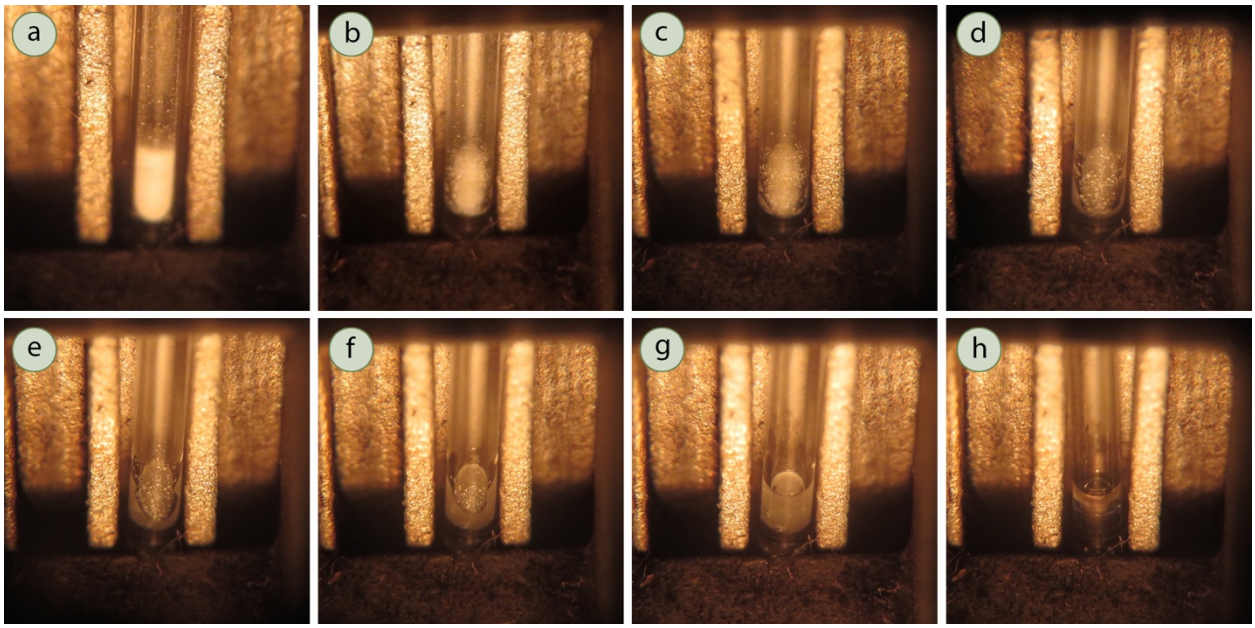


Figure 6.2: Time-lapse melting of benzoic acid: a) Well below the melting point, b) "Glistening" of the solid, c) First liquid droplet is seen (the temperature is recorded as the lower value of the melting range), d-g) Melting, h) Sample is completely melted (the temperature is recorded as the upper value of the melting range).

6.1.B USES OF MELTING POINT

There are several reasons to determine a compound's melting point: it is useful in supporting the identification of a compound, as well as serving as a rough guide to the relative purity of the sample.

6.1.B.1 IDENTIFICATION

As a compound's melting point is a physical *constant*, it can be used to support the identity of an unknown solid. The melting point can be looked up in a reference book (this value would then be called the "**literature melting point**"), and compared to the experimental melting point. For example, the literature melting point of ferrocene, is 172-174 ˚C.[1] The author found the melting point of a ferrocene sample (Figure 6.3) to be 176-178 ˚C,[2] and there is good agreement between these two values.

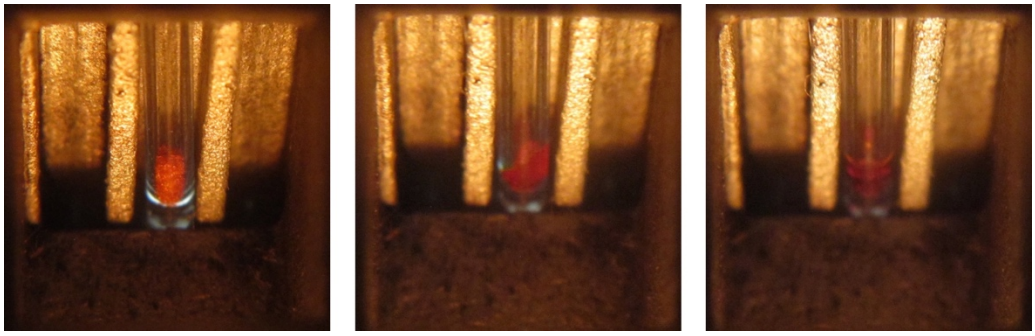
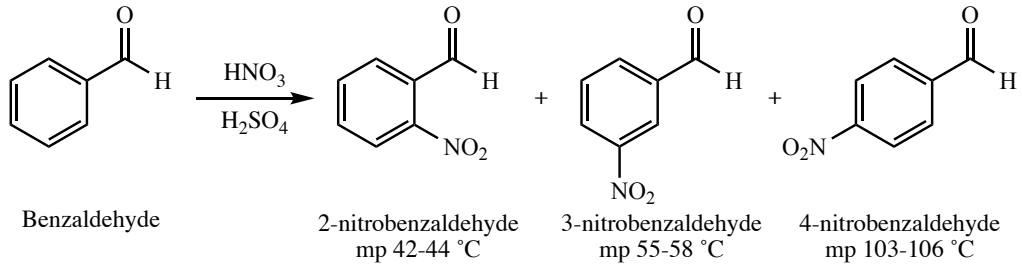


Figure 6.3: Melting of ferrocene inside a melting point apparatus.

Care must be taken to refrain from jumping to conclusions about the identity of a compound based *solely* on a melting point. Millions of solid organic compounds exist, and most have melting points below 250 ˚C. It is not uncommon for two different compounds to have coincidentally similar or identical melting points. Therefore, a melting point should be used as simply one piece of data to *support* the identification of an unknown.

Although coincidentally similar melting points are not unheard of, when used in the context of assessing the product of a chemical reaction, melting points can be a powerful identification tool. For example, three possible products of the nitration of benzaldehyde are 2, 3, or 4-nitrobenzaldehyde (Figure 6.4). Since these products have very different melting points, the melting point of the resulting solid (if pure) could be used to strongly suggest which product was formed.



Benzaldehyde

2-nitrobenzaldehyde
mp 42-44 ˚C

3-nitrobenzaldehyde
mp 55-58 ˚C

4-nitrobenzaldehyde
mp 103-106 ˚C

Figure 6.4: Nitration of benzaldehyde.[1]

[1] Melting points are from the Aldrich Chemical Catalog.

[2] As determined using a MelTemp melting point apparatus. The temperature values are uncorrected.

6.1.B.2 ASSESSING PURITY

A second reason to determine a compound's melting point is for a rough measure of purity. In general, **impurities lower and broaden the melting range.**

For example, the melting points of samples of benzoic acid contaminated with known quantities of acetanilide are summarized in Table 6.1. As the quantity of impurity increased, melting began at a lower temperature, and the breadth of the melting range increased.

Mol % Benzoic Acid	Mol % Acetanilide	Melting Point (˚C)
100%	0%	120 - 122
95%	5%	114 - 121
90%	10%	109 - 120
85%	15%	105 - 117
80%	20%	94 - 116

Table 6.1: Melting points of benzoic acid / acetanilide mixtures (taken with a MelTemp apparatus).

Figure 6.5 shows the time-lapse melting of three samples side by side in a melting point apparatus: pure benzoic acid (left), benzoic acid with 10 mol% acetanilide impurity (middle), and benzoic acid with 20 mol% acetanilide impurity (right). As the samples are heated, the sample with the greatest impurity (on the right) melts first. Interestingly, both of the impure samples complete melting before the pure sample (on the left) begins to melt.

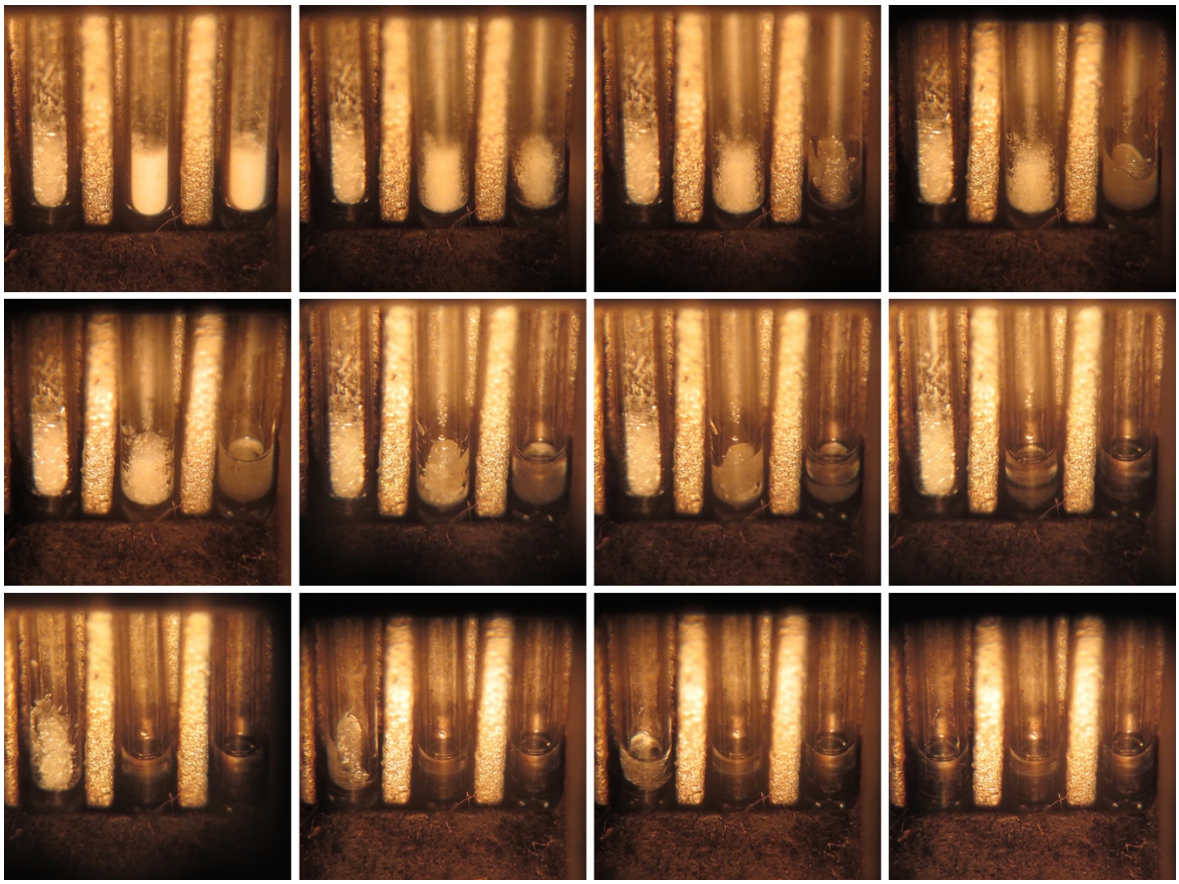


Figure 6.5: Time-lapse melting of three samples side by side in a melting point apparatus. Pure benzoic acid (left), benzoic acid with 10 mol% acetanilide (middle), benzoic acid with 20 mol% acetanilide (right).

A solid's melting point may be so reduced by impurity that it becomes a liquid at room temperature. For example, when piperonal (melting point of 35-39 ˚C) is mixed with resorcinol (melting point of 109-112 ˚C) in a 4:1 ratio by mass,[3] the mixture become slushy and eventually melts at room temperature (Figure 6.6). This sort of behavior is not uncommon for solids whose melting points are only marginally higher than room temperature.

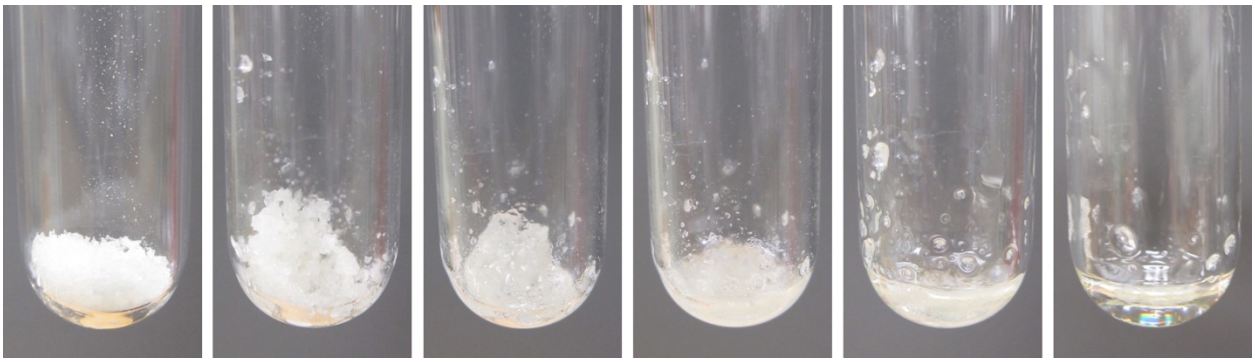


Figure 6.6: Time-lapse melting of a mixture of piperonal and resorcinol at room temperature (both are white solids when pure). Note: no heat is applied in the process. The mixture eventually melts as a result of its depressed melting point.

[3] As published in Di Pippo, A.G., *J. Chem. Ed*, **1965**, 42(5), p A413.

6.1.C MELTING POINT THEORY

6.1.C.1 MELTING POINT DIAGRAMS

The typical behavior of an impure solid containing two components is summarized by the general phase diagram in Figure 6.7a. The furthest left side of the graph represents a sample that is pure compound "A," while the furthest right side of the graph represents a sample of pure compound "B." The lines mark the solid-liquid transition temperature (melting points). The melting point decreases the further the composition is from purity, toward the middle of the graph. In many mixtures, the minimum melting temperature for a mixture occurs at a certain composition of components, and is called the **eutectic point** (Figure 6.7a). Some systems do not have any eutectic points and some have multiple eutectic points.

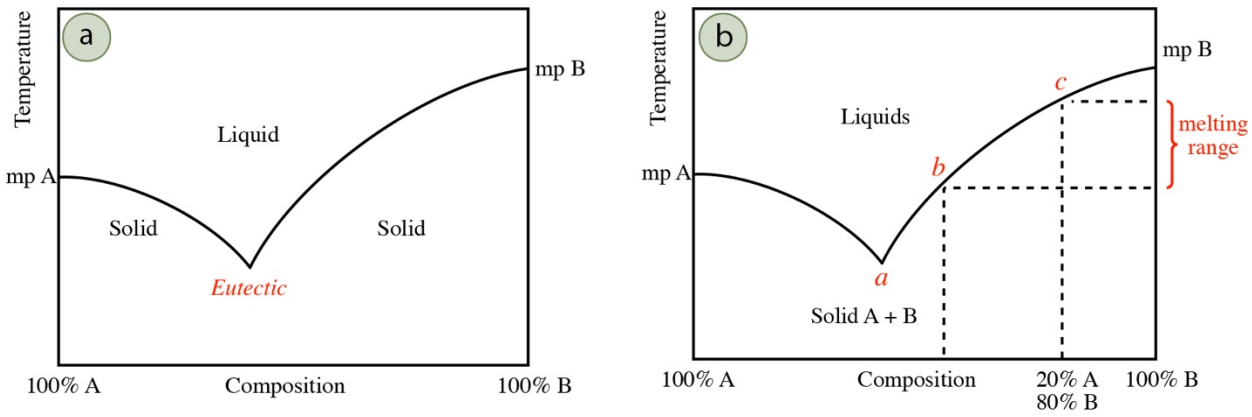


Figure 6.7: a) Generic phase diagram of a two-component system (A+B), b) Same diagram with additional markings.

An impure solid is typically heterogeneous on the microscopic level, with pure regions of each component distributed through the bulk solid much like granite. When an impure solid is warmed, microscopic melting first occurs in a pure region by the component with the lower melting point (compound A in Figure 6.7a). This microscopic melting is not visible to the eye.

The preliminary melting of compound A in Figure 6.7a forms tiny pools of liquid that begin to dissolve compound B from the bulk solid. As compound B is dissolved into the melt (causing it to become more impure), the freezing point of this mixture is depressed. Compound B will continue to dissolve in the melt, until it reaches the eutectic composition (point *a* in Figure 6.7b), and the system will continue to melt at this composition until the entirety of the minor component (the impurity) is dissolved. Once the minor component is completely dissolved, further melting continues of the bulk component. This increases the purity of the melt, so the melting temperature increases somewhat. The system follows the melting line in Figure 6.7b either to the left or right of the eutectic temperature (depending on which side of the eutectic point is started), adjusting its melting temperature as the bulk component increases its concentration in the melt. This continues until the entire sample is melted.

Although microscopic melting begins at the eutectic temperature, the first value of the melting range (when a droplet of liquid is seen with the eye) is not necessarily recorded at this temperature. A droplet of liquid is not seen until approximately 10-20% of the sample has melted. Depending on the quantity of impurity, the system may have progressed far from the eutectic temperature (perhaps to point *b* in Figure 6.7b) before liquid becomes visible to the eye. The final value of the melting range is at the highest the melting point of the pure solid, but is often lower, reflecting the depressed melting point of the bulk solid. For example, a solid that is 20% compound A and 80% compound B would have a final melting temperature of point *c*

in Figure 6.7b. The recorded melting range for this system would be at the maximum between temperatures *a* and *c*, but if the first droplet is seen at point *b*, the recorded melting range would be between temperatures *b* and *c*.

6.1.C.2 IMPURITIES EFFECT ON THE MELTING POINT

A melting point is a useful indicator of purity as there is a general lowering and broadening of the melting range as impurities increase. In this section is described the theory behind the phenomenon of melting point depression (which is identical to freezing point depression since freezing and melting are the same processes in reverse) and why an impure sample has a broad melting range.

6.1.C.2.A MELTING POINT DEPRESSION (LOWERING THE M.P.)

Melting of a pure solid occurs at a higher temperature than melting of an impure solid, a concept called **melting point depression**. The melting point is the temperature where the solid and liquid phases are in equilibrium with each other, and the change in free energy (ΔG°) for the process (solid $\rightleftharpoons$ liquid) is zero. ΔG° is dependent on both the changes in enthalpy (ΔH°) and entropy (ΔS°) during the process (see versions of the Gibbs free energy equation in Figure 6.8b), but the changes in enthalpy are similar when melting a pure and impure solid as similar intermolecular forces are broken. Melting point depression is the result of different changes in entropy when melting a pure and impure solid.

As solids are restricted in atomic motion, there is little difference in entropy between a pure and impure solid. However, there is a more significant difference in entropy between a pure and impure liquid, and an impure liquid has greater disorder and greater entropy. **Melting of an impure solid into an impure liquid therefore has a larger change in entropy** than melting a pure solid into a pure liquid (Figure 6.8a). A larger change in entropy **corresponds to a lower melting temperature**. This can be rationalized either mathematically or conceptually. A mathematical description is in Figure 6.8b: as ΔS° is the denominator in the final equation, a larger ΔS° corresponds to a smaller $T_{melting}$. A conceptual approach is to consider that melting occurs when the enthalpy (ΔH°) and entropy components ($T\Delta S^\circ$) are equal in magnitude (when $\Delta G^\circ = 0$). A larger ΔS° means that a smaller temperature will be required to "match" the enthalpy component.

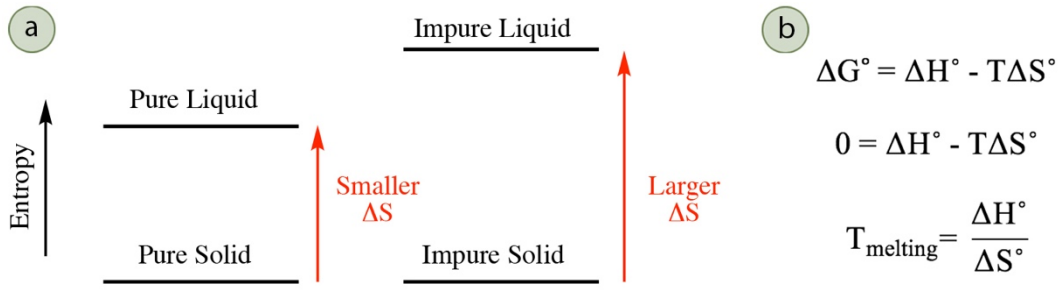


Figure 6.8: a) Entropy changes for melting of a pure and impure solid, b) Rearranged Gibbs free energy equation for melting.

6.1.C.2.B BROADENING OF THE MELTING POINT

The breadth of an experimentally determined melting point can often be correlated to the purity of the solid. Although all samples start melting at the eutectic temperature, the first droplet of liquid is not seen until approximately 10-20% of the sample has microscopically melted. As the melting temperature does not rise above the eutectic temperature until the entirety of the impurity has melted, the quantity of impurity will determine how far the system will have progressed along the melting point line in the phase diagram before reaching the visible minimum of 10-20% of solid.

For example, if a solid has a minor amount of impurity, the impurity will quickly melt at the eutectic temperature (point *a* in Figure 6.9a), and the melting temperature will increase, following the melting point line in the phase diagram. When 10-20% of solid has melted and a droplet is visible, the system may have progressed far from the eutectic composition (perhaps to begin visibly melting at point *b* in Figure 6.9a). The solid will continue melting until perhaps point *c* in Figure 6.9a, to give a relatively narrow melting range (between points *b* and *c*). If instead the solid has a significant amount of impurity, it may take melting of nearly 10% of the solid to fully dissolve the impurity, which means the melting temperature may not have progressed far from the eutectic temperature when a droplet becomes visible. A more impure solid may first visibly melt at perhaps point *d* in Figure 6.9b, to give a broader melting range (between points *d* and *e*).

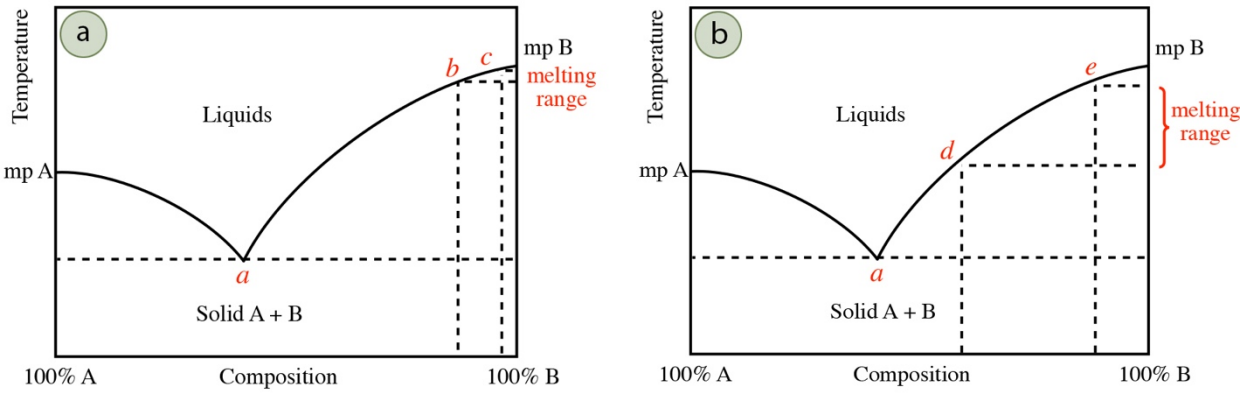


Figure 6.9: Melting point diagrams showing the melting range for: a) Fairly pure sample, b) More impure sample.

It is for these reasons that a low melting range (< 2 ˚C) is associated with purity, although it is also possible that the solid's composition could be coincidentally near a eutectic point. If the eutectic composition is, for example, 40% A / 60% B, and the solid's composition is 45% A / 55 % B, nearly all of the impure solid will melt before the melting temperature will change from the eutectic temperature in the phase diagram. Therefore, mixtures with compositions near the eutectic composition also give a sharp melting range, even though they may be far from pure.

Whether a system is in fact pure, or sharply melting because it is at the eutectic composition, can be proven by performing a mixed melting point.

6.1.D STEP-BY-STEP PROCEDURES

There are a variety of methods by which a sample's melting point can be measured, with the newest being electrical probes (*e.g.* Vernier MeltStation). Presented in this section are traditional methods that use an electrical melting point apparatus and Thiele tube. Both methods use capillary samples that are prepared in the same manner.

6.1.D.1 SAMPLE PREPARATION

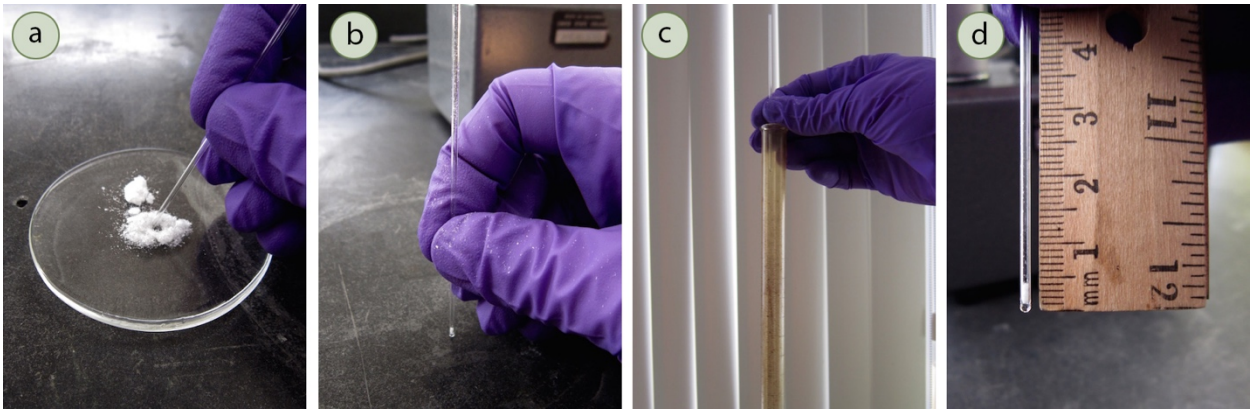


Figure 6.10: a) Depositing sample into the open end of a capillary tube, b) Inverting and tapping the tube on the benchtop, c) Dropping the sample through a long tube, d) Correct height of sample in the tube.

1. Obtain a glass capillary melting point tube, which has one end sealed and the other end open. Jab the open end of the tube into a pile of the solid to be analyzed (Figure 6.10a). The solid must be dry or the results will be affected as solvent can act as an impurity and affect the melting range. If the solid is granular, pulverize the solid somewhat before packing.

2. Invert the capillary tube and gently tap the tube on the benchtop to cause the solid to fall to the closed end (Figure 6.10b). Then, drop the capillary tube closed side down several times through a long narrow tube (glass tube or cut PVC pipe, Figure 6.10 c). The capillary tube will bounce as it hits the benchtop, and pack the solid into the bottom of the tube. Failure to pack the solid well may cause it to shrink when heating, which can cause confusion as to the correct melting temperature.

3. If needed, repeat the previous steps to load sample until it is a height of **2-3 mm** in the tube (when packed, Figure 6.10d). It is important that the sample be no higher than 3 mm or the melting range will be artificially broad.

6.1.D.2 MELTING POINT APPARATUS

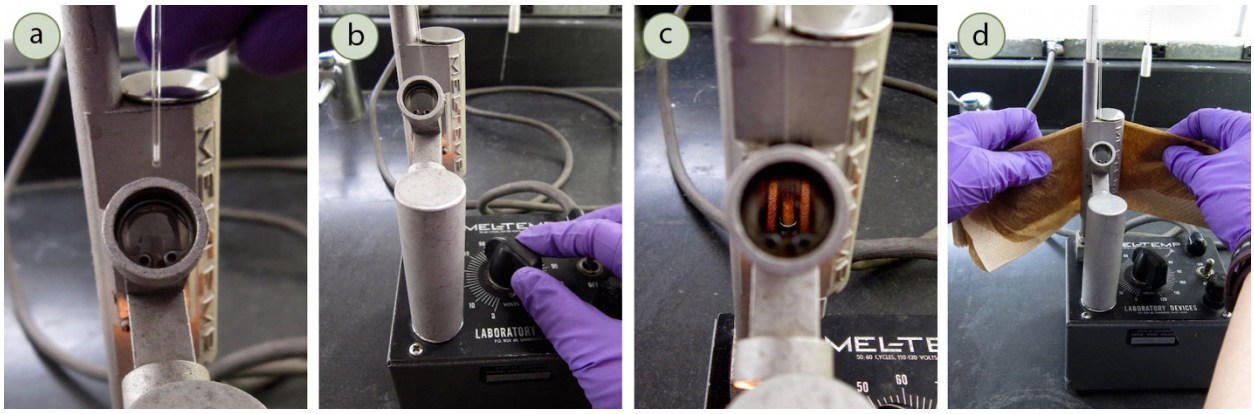


Figure 6.11: a) Insertion of capillary sample into the melting point apparatus, b) Adjustment of the heating rate, c) Monitoring of the sample through the viewfinder, d) Cooling down the apparatus.

1. Insert the capillary tube containing the sample into a slot behind the viewfinder of a melting point apparatus (Figure 6.11a). There are usually three slots in each apparatus, and multiple melting points can be taken simultaneously after gaining experience with the technique.

2. Turn on the apparatus and adjust the setting to an appropriate heating rate (Figure 6.11b). The rate of heating is often experimental and should be adjusted by careful monitoring of the thermometer on the apparatus.

3. Look through the viewfinder (Figure 6.11c) to see a magnified view of the sample in the apparatus, which should be illuminated.

4. If the expected melting point of the compound is known, heat at a medium rate to 20 ˚C below the expected melting point, then slow the rate of heating such that the temperature increases no more than **1 ˚C every 30 seconds** (*i.e.,* very slowly).

   The temperature must be incremental as the melting point is approached so the system can reach equilibrium, making the thermometer temperature an accurate gauge of the solid's true temperature.

5. If the expected melting point of the compound is NOT known, heat the sample at a medium rate the entire time and determine an approximate melting point. Repeat the process with a fresh sample after allowing the apparatus to cool and use the recommendations in prompt 4 to perform a more careful assessment of the melting point.

   A fresh sample is necessary for a second melting point trial; even if the first sample solidifies after cooling it should not be used again. Differences in crystal structure between the original solid and the previously melted solid could lead to different melting ranges.

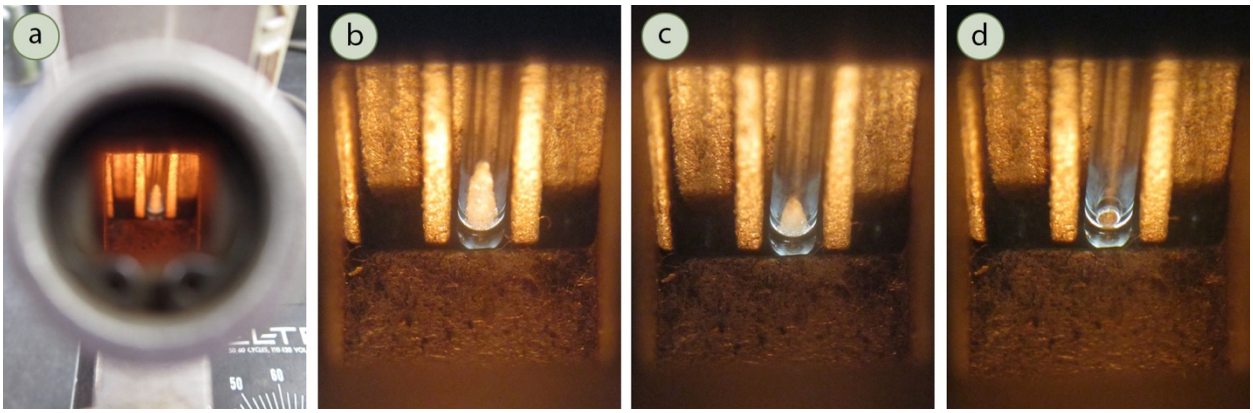


Figure 6.12: a) Monitoring the sample by looking through the viewfinder, b) Initial melting of a sample, c) Midway, d) Mostly melted sample.

6. The solid may be approaching its melting point if the solid is seen pulling away from the walls of the tube to form a cone of solid (Figure 6.12b), which is called "**sintering**." Melting will normally occur within a few degrees of this point. The solid may also shrink or compact before melting.

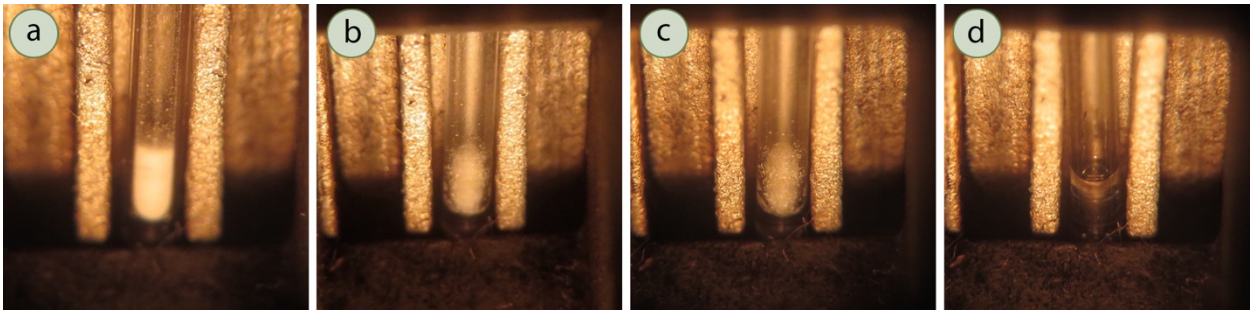


Figure 6.13: Melting of benzoic acid: a) Well below the melting point, b) Glistening, c) First liquid droplet seen, d) Sample is completely melted. Additional pictures for the melting of this sample can be seen in Figure 6.2.

7. Record the first temperature of the melting range with the appearance of the first visible drop of liquid. At first it may seem as if the sides of the solid glisten (Figure 6.13b), and the temperature should be recorded when a droplet is seen on the side or bottom of the tube (a hint of movement will be noticed in the tube, Figure 6.13c).

   Record the temperature reading to the nearest degree. Although some thermometers may read to greater precision, the imperfect heat transfer between the metal block and sample leaves the error larger than 0.1 ˚C.

8. Record the second temperature of the melting range when the entire sample has just melted (Figure 6.13d), which occurs when all portions of the opaque solid have turned to a transparent liquid.

9. The following unusual situations may occur in the process:

   a. The sample may begin to darken, which indicates decomposition is occurring before the sample is melting. Take note of the decomposition temperature, as it is sometimes as reliable a reference point as a compound's melting point. Use the letter "d" after a melting point to indicate decomposition (*e.g.* 251 ˚C d).

b. The sample may sublime instead of melting. Sublimation may be noticed by a ring of solid above where the sample is heated. Take note of this behavior in your lab notebook.

10. If another melting point trial is to be performed directly after the first, the metal block should be rapidly cooled to at least 20 ˚C below the next melting point by touching it with wet paper towels (Figure 6.11d) or cooling it with a jet of air.

Figure 6.14: Organic chemistry students determine the melting point of samples.

6.1.D.3 THIELE TUBE METHOD

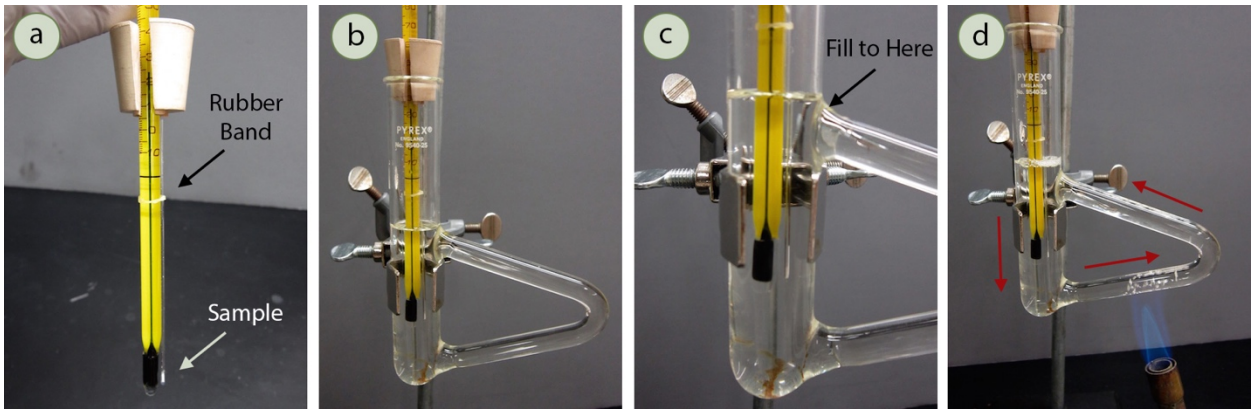


Figure 6.15: a) Capillary sample attached to a thermometer with a small rubber band, b) Placement of the sample in the Thiele tube, c) Correct location of the sample, with an arrow indicating the minimal height of mineral oil in the tube, d) Heating the Thiele tube with a burner, and arrows showing the oil current.

1. Obtain a Thiele tube and clamp it to a ring stand or latticework (Figure 6.15b). The tube is normally filled with clear mineral oil, but it may have darkened from oxidation or spilled compounds. If the oil is quite dark, it should be replaced. The oil should be filled to at least 1 cm higher than the top triangular arm (an appropriate oil level is pointed to in Figure 6.15c), and if too low the oil will not circulate as needed (Figure 6.15d).

2. Insert a thermometer into a one-holed rubber stopper with a slit down one side. Attach the capillary sample to the thermometer with a tiny rubber band (as indicated in Figure 6.15a). These tiny rubber bands are often made by cutting pieces of small rubber tubing.

3. Position the capillary tube so that the solid sample is lined up with the middle of the thermometer bulb (Figure 6.15a).

4. Place the rubber stopper and thermometer assembly into the Thiele tube, adjusting the height so that the sample is midway inside the tube (Figure 6.15c). The rubber band should be adjusted so it is not submerged in the mineral oil, keeping in mind that the oil may expand somewhat during heating. The thermometer should not touch the sides of the glass, and if it does it should be clamped in such a way that it no longer touches.

5. Heat the apparatus gently on the side arm of the Thiele tube with a microburner if available or Bunsen burner using a back and forth motion (Figure 6.15d). As the oil warms and becomes less dense, it will rise and travel up the triangular portion of the tube. The cooler, denser oil will sink, thereby creating an oil current as shown in Figure 6.15d. This method is an excellent way to indirectly and slowly heat the sample.

6. Although bubbles should not be seen in the Thiele tube as it warms, they commonly are seen if the tube is used for other purposes (bubbles are seen in Figure 6.15d). For example, Thiele tubes can be used for boiling point determinations, and on occasion a sample falls into the oil and contaminates it. If the oil is not subsequently changed, the sample may boil when heated in the tube. If bubbles are seen upon heating a Thiele tube, the entire setup should be conducted in the fume hood.

7. If the expected melting point of the compound is known, heat at a medium rate to 20 ˚C below the expected melting point, then slow the rate of heating such that the temperature increases no more than **1 ˚C every 30 seconds** (*i.e.,* very slowly).

   The temperature must be incremental as the melting point is approached so the system can reach equilibrium, making the thermometer temperature an accurate gauge of the solid's true temperature.

8. If the expected melting point of the compound is NOT known, heat the sample at a medium rate the entire time and determine an approximate melting point. Repeat the process with a fresh sample after allowing the oil to cool to at least 20 ˚C below the previous melting point, and use the recommendations in prompt 7 to perform a more careful assessment of the melting point.

   A fresh sample is necessary for a second melting point trial; even if the first sample solidifies after cooling it should not be used again. Differences in crystal structure between the original solid and the previously melted solid could lead to different melting ranges.

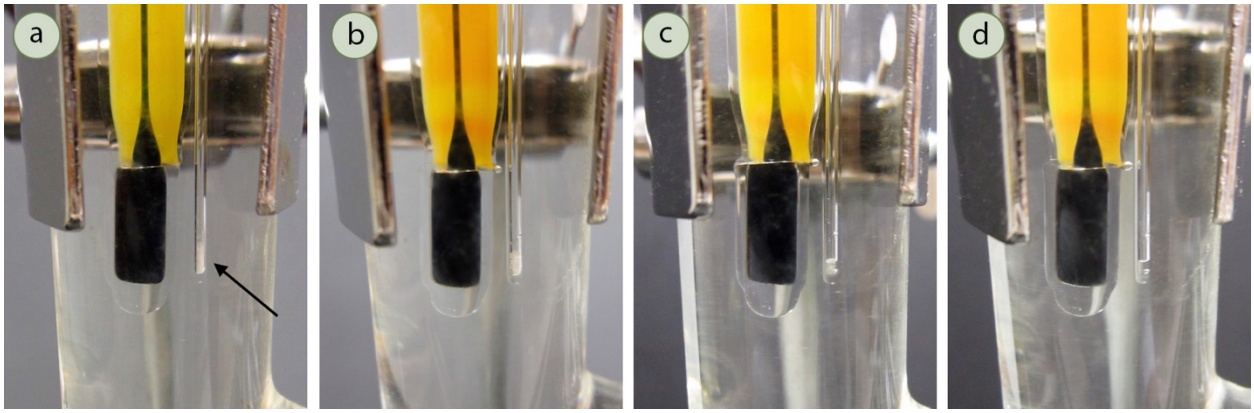


Figure 6.16: a) Solid sample inside a Thiele Tube, as indicated with an arrow, b) Initial melting of the sample, c) Midway, d) Melted sample.

9. Record the first temperature of the melting range with the appearance of the first visible drop of liquid. At first it may seem as if the sides of the solid glisten (Figure 6.13b), and the temperature should be recorded when a droplet is seen on the side or bottom of the tube (a hint of movement will be noticed in the tube, Figure 6.16b).

   Record the temperature reading to the nearest degree. Although some thermometers may read to greater precision, the imperfect heat transfer between the oil and sample leaves the error larger than 0.1 ˚C.

10. Record the second temperature of the melting range when the entire sample has just melted (Figure 6.16d), which occurs when all portions of the opaque solid have turned to a transparent liquid.

11. Take note if darkening or sublimation occur.

12. If another melting point trial is to be performed directly after the first, be sure to allow the oil to cool to at least 20 ˚C below the next melting point beforehand.

13. Cleanup note: drops of mineral oil on the benchtop do not easily wipe away, but can be cleaned by a paper towel soaked with either window cleaner or hexanes.

6.1.D.4 MELTING POINT SUMMARY

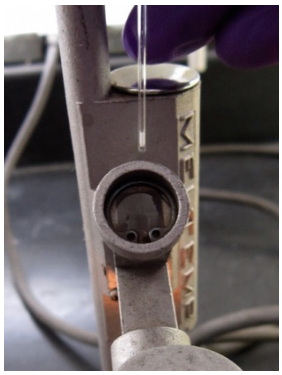
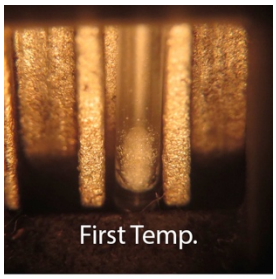
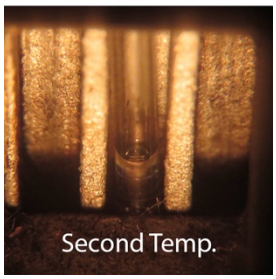
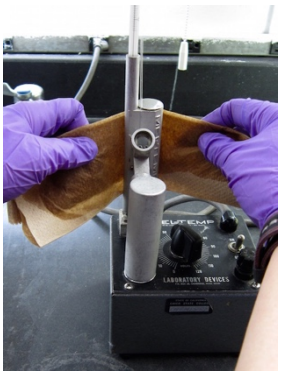
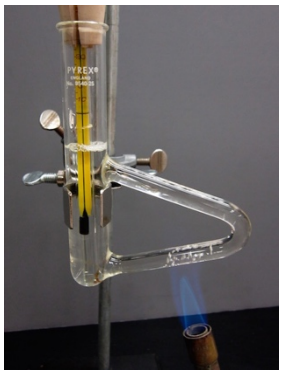
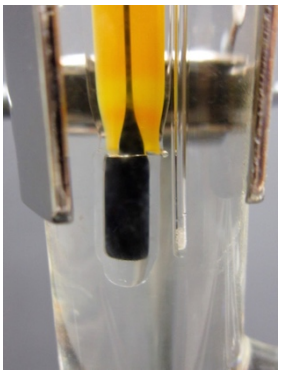
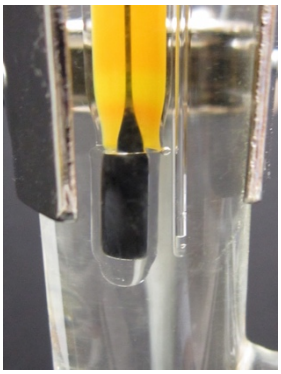
		 	
Load the sample by jabbing the open end of a capillary tube into a pile of the sample. With closed end down, drop the tube down a long hollow tube so that it hits the benchtop and packs the sample into the closed end of the tube. Load the sample to a height of **2-3 mm**.	Place the sample into a slot in the MelTemp. Turn the dial to begin heating. Heat at a medium rate to 20 ˚C below the expected melting point. Then heat *very slowly* (**1 ˚C every 30 seconds**).	Record the temperature where the first droplet of liquid is seen (there is movement in the tube). Record the second temperature when the entire sample liquefies (the entire sample changes from opaque to transparent). Record a melting range, *e.g.* 120-122 ˚C.	If another melting point trial is to be performed, cool the metal block to at least 20 ˚C below the next melting point, by wiping it with a wet paper towel or cooling with a jet of air.
Thiele Tube Variation: Attach the sample to a thermometer with a tiny rubber band, positioning the sample flush with the bottom of the thermometer. Insert the sample into a Thiele tube, so that the sample is near the middle of the tube.			

Table 6.2: Procedural summary for obtaining a melting point.

6.1.E MIXED MELTING POINTS

As previously discussed, there are a large number of compounds that have coincidentally identical melting points. Therefore, caution should be used in identifying a compound based solely on matching the literature melting point. However, mixed melting points offer an ability to almost certainly identify an unknown compound.

Imagine that the nitration of benzaldehyde (Figure 6.17), produces a solid that is determined to have a melting point of 54-57 ˚C. This solid would be assumed to be 3-nitrobenzaldehyde due to the proximity of the experimental melting point to the literature melting point.

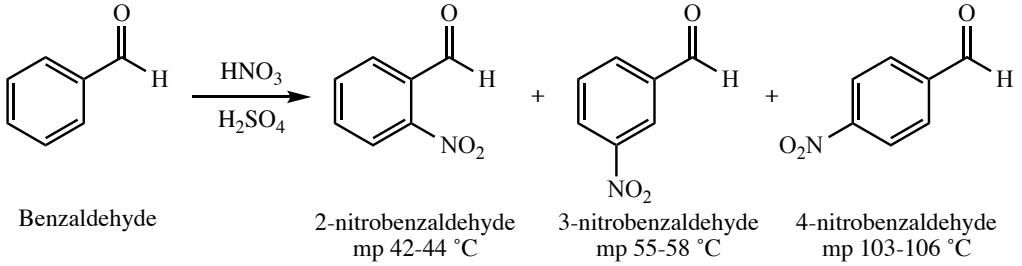


Figure 6.17: Nitration of benzaldehyde. The melting point data is from the Aldrich Chemical Catalog.

Although the product likely is as identified, if a pure sample of 3-nitrobenzaldehyde is available, there is a possibility of more strongly identifying the product. A **mixed melting point** can be taken, by measuring the melting point of a sample composed of roughly equal volumes of the unknown product and of known 3-nitrobenzaldehyde (ground together well with a mortar and pestle, as in Figure 6.18a). If the product is indeed 3-nitrobenzaldehyde, then this "mixture" would not be a mixture at all. Its melting point would be sharp and around the literature range of 55-58 ˚C. If this result occurs, the two samples are almost certainly the same compound. If the product however is not 3-nitrobenzaldehyde, then this "mixture" would truly be very impure (50% of each component), and the resulting melting point would have a much lowered and broadened range.

Figure 6.18: a) Mortar and pestle in front of sample, b) A student prepares a sample for a mixed melting point.

6.2 BOILING POINT

6.2.A OVERVIEW OF BOILING POINT

The boiling point of a compound is the temperature where the liquid-gas phase change occurs. In more technical terms, it is when a liquid's vapor pressure equals its applied pressure (typically the atmospheric pressure). Boiling points are very sensitive to changes in applied pressure, so all boiling points should be reported along with the measured pressure. A compound's "normal boiling point" refers to its boiling point at a pressure of 760 mmHg.

A compound's boiling point is a physical constant just like melting point, and so can be used to support the identification of a compound. Unlike melting points however, boiling points are not generally used as a gauge of purity. Impure liquids do boil over a range of temperatures (similar to how melting points have breadth), but the temperature span does not correlate well to purity. Thus, measurement of a compound's boiling point is mainly used to support its identification.

An experimental boiling point is often compared to the literature boiling point, which are typically reported for 1 atmosphere of pressure. If a boiling point is determined at any pressure significantly different than 1 atmosphere, the pressure should be corrected. A general rule of thumb is that for pressures within 10% of one atmosphere, a 10 mmHg drop in pressure will account for a 0.3 - 0.5 ˚C drop in boiling point.[4] Another rule of thumb is that for every halving of pressure, the boiling point drops by about 10 ˚C.

6.2.B STEP-BY-STEP PROCEDURES

There are a variety of methods by which a sample's boiling point can be determined, including distillation, reflux and by using a Thiele tube. The most straight-forward method uses a Thiele tube, and has the advantage of using less than 0.5 mL of material.

6.2.B.1 DISTILLATION METHOD

There are simpler methods than a distillation to measure a compound's boiling point, and it is recommended to explore other options (*e.g.* Thiele tube) if this is the only goal. However, if materials are limited, or if a purification is planned anyhow, a distillation can be used to determine a compound's boiling point. The distillation technique is discussed in great detail in Chapter 5.

A simple distillation should suffice for most situations (Figure 6.19), and at least 5 mL of sample should be used in the distilling flask along with a few boiling stones or stir bar. As the bulk of the material distills, the highest temperature noted on the thermometer corresponds to the boiling point. A major source of error with this method is recording too low a temperature, before hot vapors fully immerse the thermometer bulb.[5] Be sure to monitor the thermometer periodically, especially when the distillation is active. Record the barometric pressure along with the boiling point.

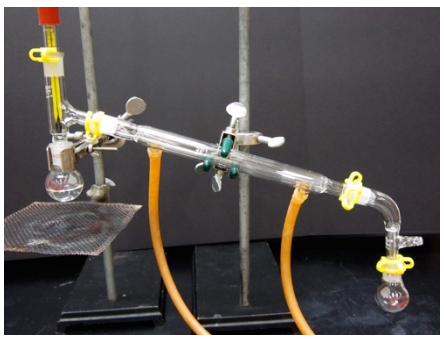


Figure 6.19: Simple distillation.

[4] This generality is based on tables in the *Handbook of Chemistry and Physics*, CRC Press, 84th edition, **2003-2004**, 15-19.

[5] The author found the boiling point of ethanol to be 76 ˚C (765 mmHg) with distillation (literature boiling point is 78 ˚C).

6.2.B.2 REFLUX METHOD

A reflux setup can also be used to determine a compound's boiling point. **Reflux** is when a liquid is actively boiling and condensing, with the condensed liquid returning to the original flask. It is analogous to a distillation setup, with the main difference being the vertical placement of the condenser.

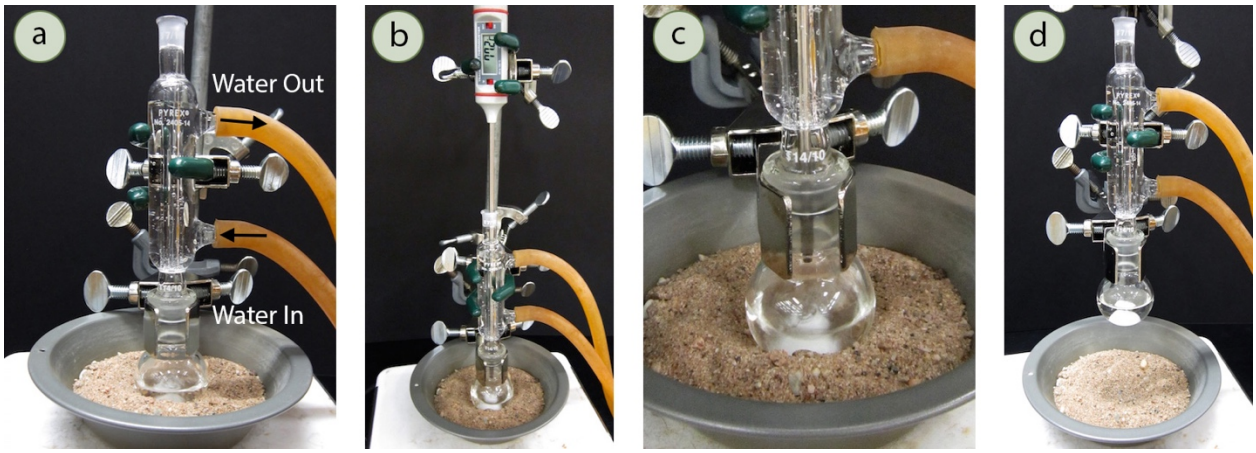


Figure 6.20: a) Reflux setup, b) Insertion of digital thermometer into condenser, c) Position of thermometer, d) Cooling the setup.

If materials are available, the best reflux setup for this application is shown in Figure 6.20b and uses a microscale condenser and digital thermometer. The setup uses 5 mL of liquid, and a few boiling stones or stir bar. The condenser is attached to the round bottomed flask, with the lower water hose connected to the water spigot and the upper water hose draining to the sink. It is important to check that the joint connecting the flask and condenser is securely fastened. The liquid is brought to a boil on a sand bath, and the thermometer is placed low into the apparatus (Figure 6.20c) such that the bottom inch is between the boiling liquid and the bottom of the condenser. In this position, the thermometer can accurately measure the hot vapors and the temperature will stabilize at the compound's boiling point[6]. Record the barometric pressure along with the boiling point.

Although it might seem prudent to plunge the thermometer directly into the boiling liquid, it is possible the liquid may be superheated, or hotter than its boiling point. After determining the boiling point, the flask should be raised from the sand bath (Figure 6.20d) to cool, and condenser kept running until the flask is only warm to the touch. At this point the setup can be dismantled.

If a microscale condenser is not available, an alternative reflux method can also be used as shown in Figure 6.21. Roughly 5 mL of sample is placed in a medium test tube (18 × 150 mm) with thermometer clamped inside so it does not touch the sides of the glass. The apparatus is carefully heated on a sand bath such that reflux happens controllably and vapors do not escape from the tube. The temperature during reflux will eventually stabilize (this takes some time), and the highest temperature noted corresponds to the compound's boiling point.[6] The boiling points measured with this method may have significant error if the boiling point is very low or high (< 70 ˚C or > 150 ˚C) as low boiling compounds boil away too easily and high boiling compounds tend to cool too easily.

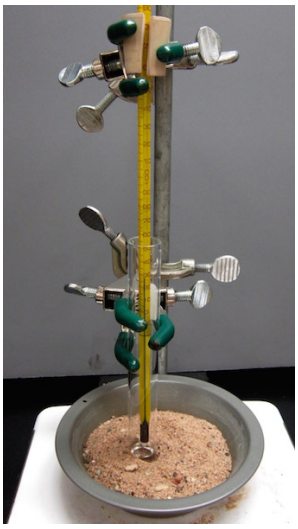


Figure 6.21: Reflux apparatus using a sand bath and test tube.

[6] The author found the boiling point of ethanol (literature boiling point of 78 ˚C) to be 77.2 ˚C with the microscale condenser setup and 76 ˚C with the test tube reflux setup (765 mmHg). Note: Different thermometers were used with each method.

6.2.B.3 THIELE TUBE METHOD

6.2.B.3.A THIELE TUBE THEORY

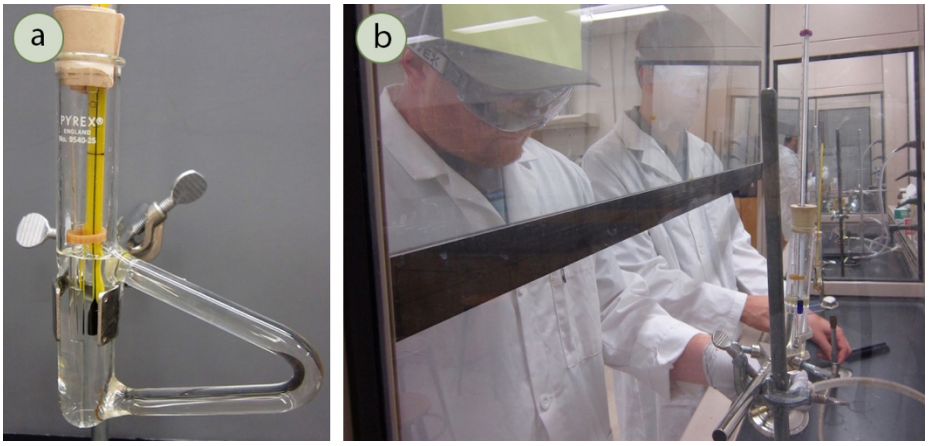


Figure 6.22: a) Thiele tube apparatus, b) Students perform the boiling point technique in the hood.

The Thiele Tube method is one of the simplest methods to determine a compound's boiling point, and has the advantage of using small amounts of material (less than 0.5 mL of sample). The sample is placed in a small tube along with an inverted capillary tube. The setup is attached to a thermometer (Figure 6.23a) and heated inside a Thiele tube (Figure 6.22a) to slightly higher than the compound's boiling point (which is evidenced by a continuous stream of bubbles emerging from the capillary tube). The tube is then allowed to cool, and the moment liquid is drawn into the capillary tube, the temperature is the compound's boiling point.

This method utilizes the definition of boiling point: the temperature where the compound's vapor pressure equals the applied (atmospheric) pressure. The inverted capillary tube acts as a reservoir to trap the compound's vapors. As the apparatus is heated, the air initially trapped in the capillary tube expands and causes bubbles to emerge from the tube (Figure 6.23b). With further heating, the compound's vapors eventually displace all of the trapped air, which is why heat is applied until there is a continuous stream of bubbles.

When the apparatus is cooled, eventually the pressure inside the capillary tube (due solely to the compound's vapors) will match the atmospheric pressure, at which point the bubbles will slow and liquid will be drawn into the tube. The temperature where this begins is the compound's boiling point (Figure 6.23d).

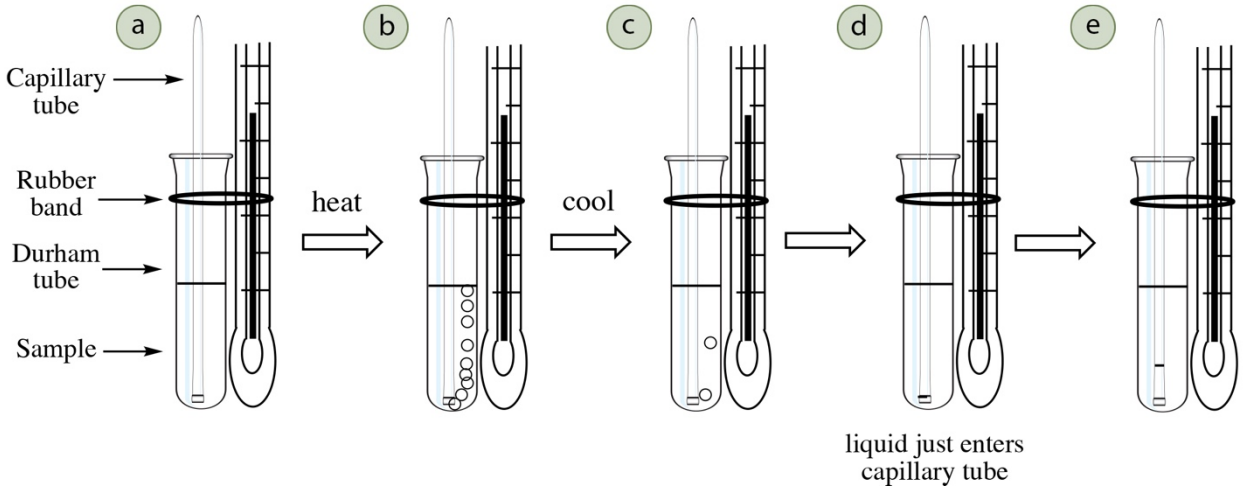


Figure 6.23: Boiling point determination: a) Initial setup, b) After heating past the boiling point, c) Cooling, d) Liquid just enters the capillary tube (temperature is the boiling point), e) Liquid is inside the capillary tube (temperature is lower than the boiling point).

6.2.B.3.B THIELE TUBE PROCEDURE

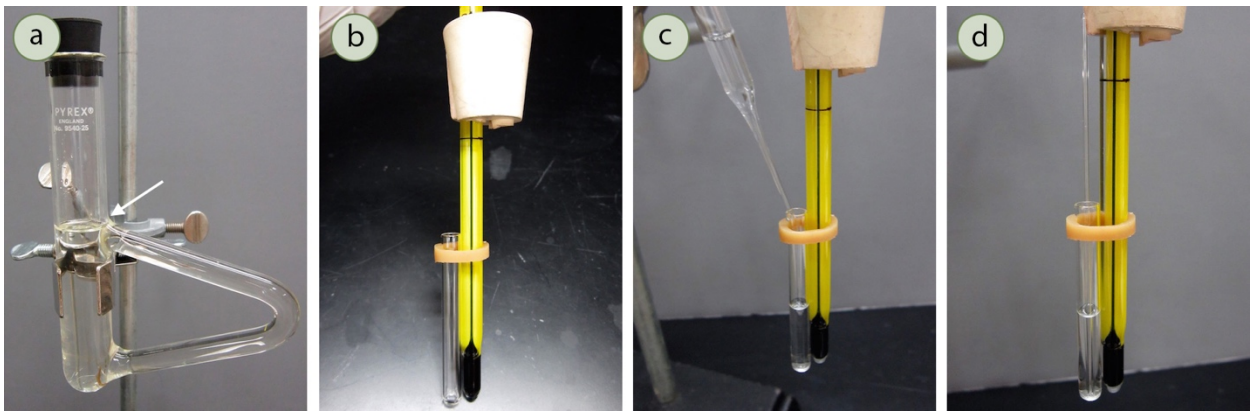


Figure 6.24: a) Thiele tube, with arrow indicating the minimum height of oil, b) Tube attached to the thermometer with a rubber band, c) Addition of sample, d) Insertion of the capillary tube.

1. Obtain a Thiele tube and clamp it to a ring stand in the fume hood (Figure 6.24a). The tube is normally filled with clear mineral oil, but it may have darkened from oxidation or spilled compounds. If the oil is quite dark, it should be replaced. The oil should be filled to at least 1 cm higher than the top triangular arm (an appropriate oil level is indicated in Figure 6.24a), and if too low the oil will not circulate as needed (Figure 6.25c).

2. Insert a thermometer into a one-holed rubber stopper with a slit down one side. Attach a small glass vial ("Durham tube," or 6 × 50 mm culture tube) to the thermometer with a small rubber band (Figure 6.24b). The bottom of the vial should be flush with the bottom of the thermometer.

3. Fill the vial about half-full with sample, which will require between 0.25 – 0.5 mL of sample (Figure 6.24c).

4. Insert a capillary tube into the sample (the same type that is used for melting points), open end down and sealed end up (Figure 6.24d).

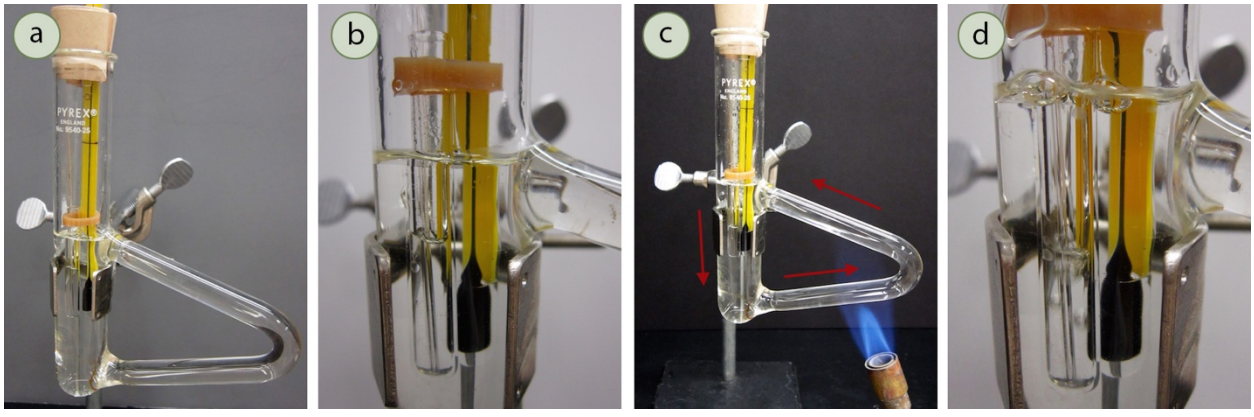


Figure 6.25: a) Insertion of the assembly into the Thiele tube, b) Rubber band is above the oil, c) Heating, d) Vigorous bubbling of sample.

5. Place the rubber stopper and thermometer assembly into the Thiele tube, adjusting the height so that the sample is midway (if possible) inside the tube (Figure 6.25a). The rubber band should be higher than the top of the mineral oil (Figure 6.25b), keeping in mind that the oil may expand somewhat during heating. The thermometer should not touch the sides of the glass, and if it does it should be clamped in such a way that it no longer touches.

6. Heat the oil gently on the side arm of the Thiele tube with a microburner if available, or Bunsen burner using a back and forth motion (Figure 6.25c). As the oil warms and becomes less dense, it will rise and travel up the triangular portion of the tube. The cooler, denser oil will sink, thereby creating a current as shown in Figure 6.25c. This method is an excellent way to indirectly and slowly heat the sample.

7. Although bubbles should not be seen in the Thiele tube as it warms, they commonly are seen if the tube had been used previously for boiling point determinations. In this method, the rubber band occasionally breaks causing the sample to fall into the oil and contaminate it. If the oil is not subsequently changed, the sample may boil when heated in the tube. It is okay to continue heating a Thiele tube if bubbles are seen.

8. Studies of this method[7] have determined that it is best to **heat the oil gently and in a continual manner**, as stopping and starting have caused the results to suffer.

9. Continue heating until a vigorous stream of bubbles emerges from the tip of the capillary tube (Figure 6.25d), such that individual bubbles can barely be distinguished. The purpose of this step is to expunge the air originally present in the capillary tube and replace it with the sample's vapor. Do not heat so vigorously that the entire sample boils away. When bubbles are vigorously emerging from the capillary tube, the vapor pressure inside the tube is greater than the atmospheric pressure (the oil is at a higher temperature than the boiling point).

10. Turn off the burner and allow the apparatus to cool. The bubbles will slow and eventually stop. At some point the vapor pressure inside the capillary tube will equal the atmospheric pressure and liquid will be drawn into the tube. The boiling point should be recorded as the temperature when liquid *just* begins to enter the capillary tube (Figure 6.26b).

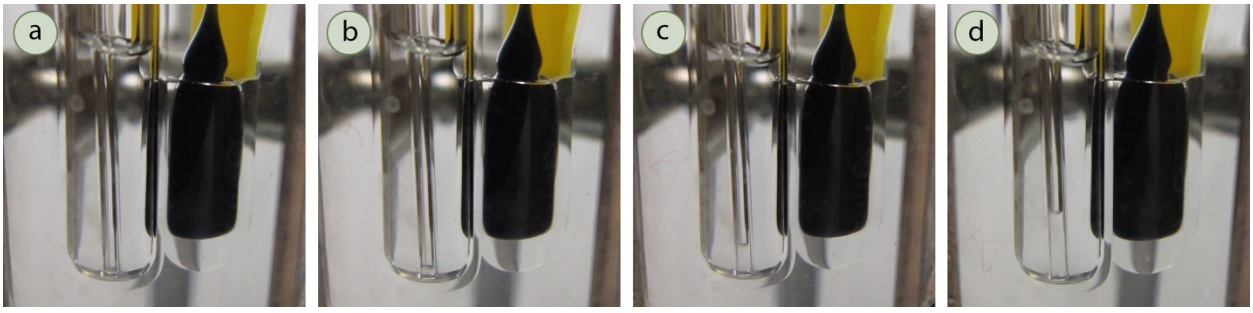


Figure 6.26: Time-lapse entry of liquid into the capillary tube. The boiling point should be recorded as the temperature at b).

11. Record the atmospheric pressure along with the boiling point.

[7] Blank, E.W., *Ind. Eng. Chem. Anal. Ed.*, **1933**, 5(1), p 74-75.

6.2.B.3.C THIELE TUBE SUMMARY

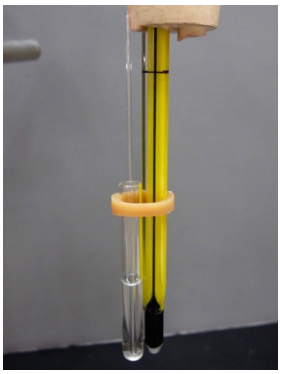
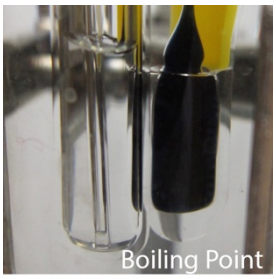
			 
Fill a small tube about half-full with sample and insert a capillary tube, closed end up. Attach the tube to a thermometer with a small rubber band.	Insert the sample into a Thiele tube, so that the sample is near the middle of the oil. Heat the arm of the Thiele tube with a burner, gently and continuously.	Heat until a vigorous stream of bubbles emerges from the capillary tube, such that individual drops can be barely distinguished.	Remove the heat and allow the oil to cool. The boiling point is the temperature when the oil just begins to enter the capillary tube.

Table 6.3: Procedural summary for obtaining a boiling point.

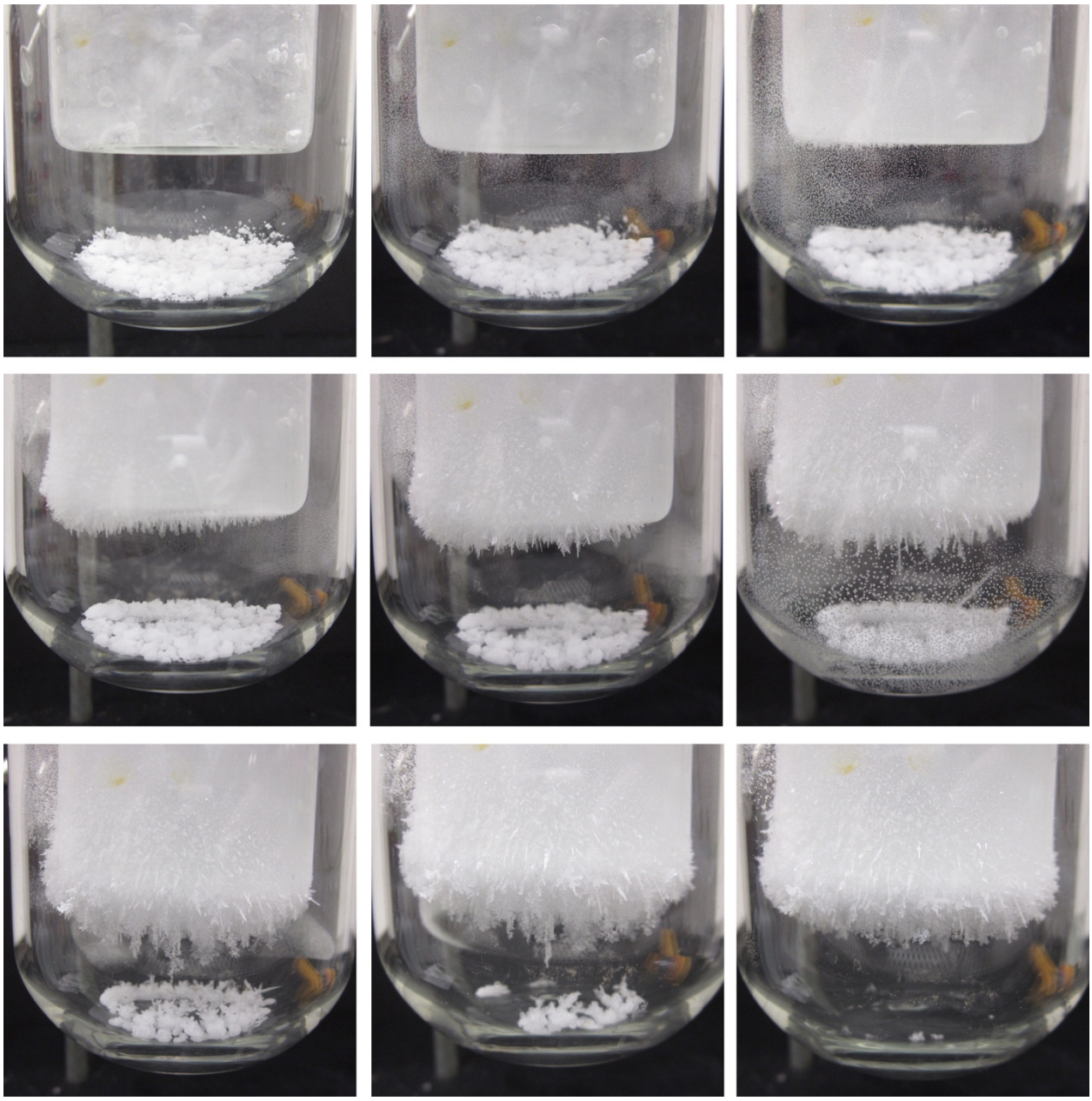


Figure 6.27: Time-lapse large scale sublimation of camphor.

6.3.A OVERVIEW OF SUBLIMATION

Some compounds are capable of sublimation, which is the direct phase change from solid to gas. Solid carbon dioxide is an example of a substance that sublimes readily at atmospheric pressure, as a chunk of dry ice will not melt, but will seem to "disappear" as it turns directly into carbon dioxide gas. Sublimation is an analogous process to boiling, as it occurs when a compound's vapor pressure equals its applied pressure (often the atmospheric pressure). The difference is that sublimation involves a *solid's* vapor pressure instead of a liquid's. Most solids do not have an appreciable vapor pressure at easily accessible temperatures, and for this reason the ability to sublime is uncommon. Compounds that are capable of sublimation tend to be those with weak intermolecular forces in the solid state. These include compounds with symmetrical or spherical structures. Examples of compounds that can be sublimed are in Figure 6.28.

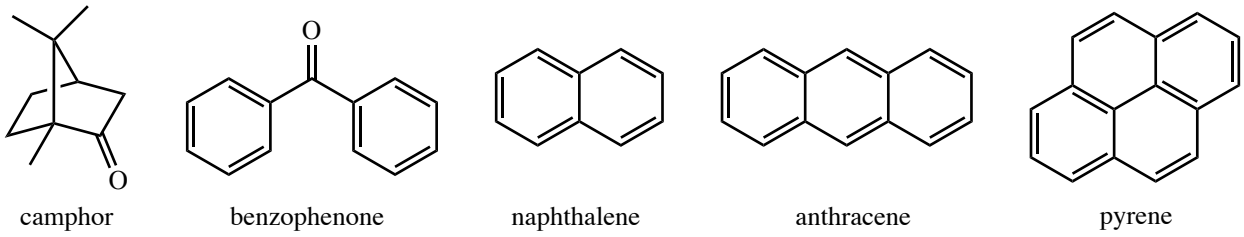


Figure 6.28: Compounds that can be vacuum sublimed.[8]

As relatively few solids are capable of sublimation, the process can be an excellent purification method when a volatile solid is contaminated with non-volatile impurities. The impure solid is heated in the bottom of a vessel in close proximity to a cold surface, called a "**cold finger**" (Figure 6.29). As the volatile solid sublimes, it is deposited on the surface of the cold finger (where it can later be recovered), and is thus separated from the non-volatile substance left in the vessel. Sublimation is an example of a "green chemistry" technique, as no solvents are used and no waste is generated. The process, however, is not particularly efficient at separating volatile solids from one another.

Of the solids with appreciable vapor pressures at room temperature, many still require rather high temperatures to actively sublime (when their vapor pressure equals the atmospheric pressure of nearly 760 mmHg). If these solids are heated to their sublimation points under atmospheric pressure, some will char and decompose during the process. For this reason, it is very common to perform sublimation under a reduced pressure (vacuum sublimation). Analogous to vacuum distillation in which liquid boils when its vapor pressure equals the reduced pressure in the apparatus, in vacuum sublimation solid sublimes when its vapor pressure equals the reduced pressure in the apparatus. In vacuum distillation, reducing the pressure allows for liquids to boil at a lower temperature. Similarly, reducing the pressure in vacuum sublimation allows for solids to sublime at a lower temperature, one which avoids decomposition.

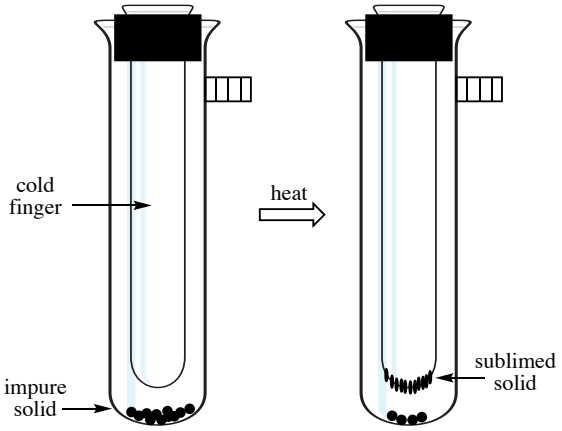


Figure 6.29: Diagram of the sublimation process.

[8] As reported in D.D. Perrin, W.L.F. Armarego, *Purification of Organic Chemicals*, Pergamon Press, 3rd edition, **1988**.

6.3.B STEP-BY-STEP PROCEDURES

6.3.B.1 UNDER ATMOSPHERIC PRESSURE

The sublimation pictured in this section shows purification of 0.29 g of ferrocene, which grew in long needles on the bottom and top of the petri dishes (90% recovery).

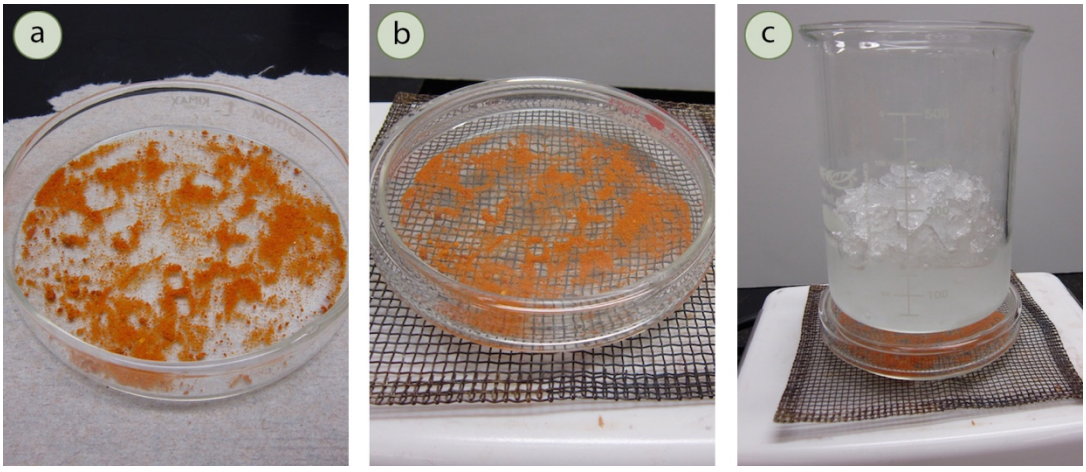


Figure 6.30: a) Ferrocene before sublimation, b) Sample with top petri dish in place, and on a wire mesh on a hotplate, c) Petri dishes with cold beaker.

1. Spread the crude, dry solid to be sublimed in a thin layer on a "bottom" petri dish (Figure 6.30a). If chunky, first crush with a mortar and pestle. Determine the empty mass of the top petri dish.

   It is important that the solid to be purified is dry: if the sample is wet with solvent, condensation may form on the top petri dish during the sublimation. In the beginning stages of the sublimation, small amounts of condensation can be wiped off the top petri dish with a paper towel. However, too much condensation may wash crystals off from the top dish.

2. Cover the bottom petri dish with the top dish and set atop a wire mesh on a hotplate in the fume hood (Figure 6.30b) set to the appropriate temperature (depending on the sublimation point of the compound of interest, perhaps medium low). The wire mesh helps dissipate the heat evenly to the dish and minimizes charring.

3. Place a large 600 mL beaker filled with ice water atop the petri dish (Figure 6.30c).

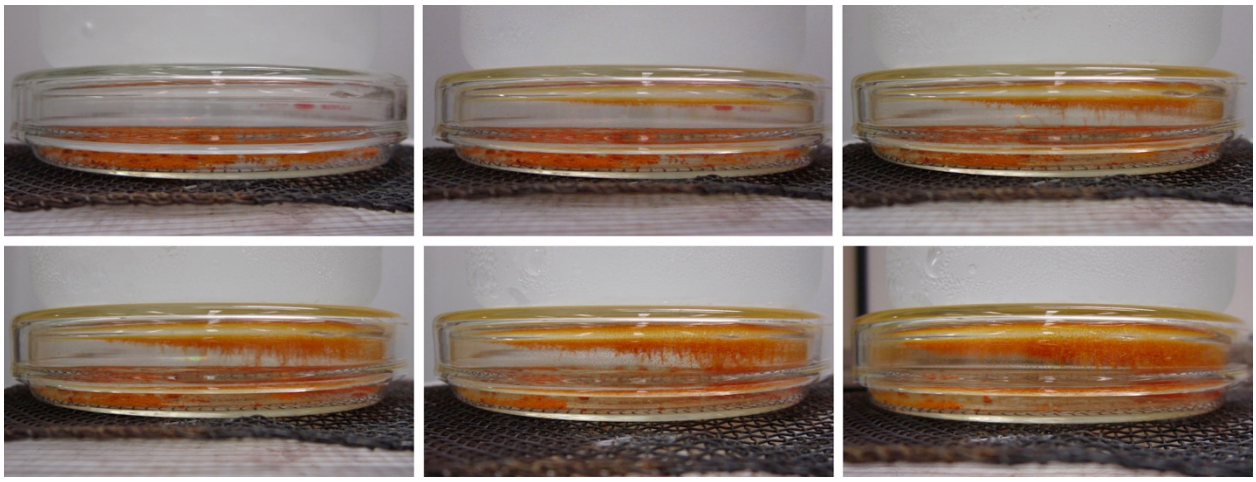


Figure 6.31: Time-lapse sublimation of ferrocene from the bottom petri dish onto the top petri dish.

4. Over time the sample will sublime and collect on the upper petri dish (Figure 6.31). Monitor the sublimation as compounds may char during the process (if it starts to blacken, turn down the heat). Continue the sublimation until it appears as if little (or no) solid remains on the bottom petri dish. It is very common for crystals to also grow along the sides of the bottom dish.

5. ***Delicately*** remove the petri dishes from the hotplate using cotton gloves (Figure 6.32a) or a silicone hot hand protector. Jostling the dishes will cause sublimed crystals to fall from the top petri dish.

   Safety note: Allow the two dishes to cool intact on a ceramic tile in the fume hood (Figure 6.32b). Do not remove the top petri dish right away or noxious fumes may escape.

6. The crystals on the top petri dish are purified and should be retained (and their mass determined). Sometimes material on the bottom dish may also be saved if it appears crystalline (signifying it underwent a sublimation process) and doesn't appear contaminated with char (Figure 6.32c).

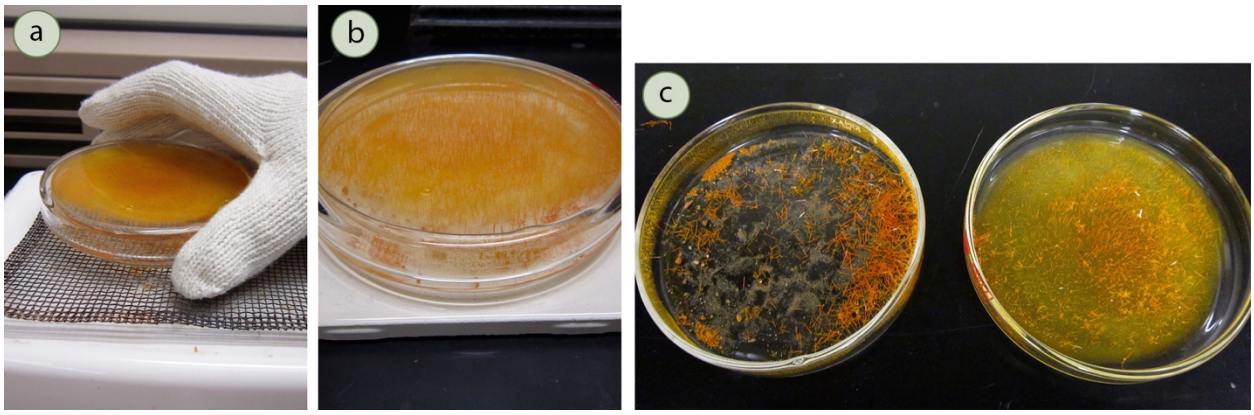


Figure 6.32: a) Removal of the sublimation apparatus from the hotplate, b) Cooling on a ceramic tile, c) Separated petri dishes: bottom dish (left), top dish (right).

6.3.B.2 UNDER REDUCED PRESSURE (VACUUM SUBLIMATION)

The sublimation in this section shows purification of camphor on two scales: 2.28 g (large scale, 77% recovery), and roughly 0.2 g (small scale).

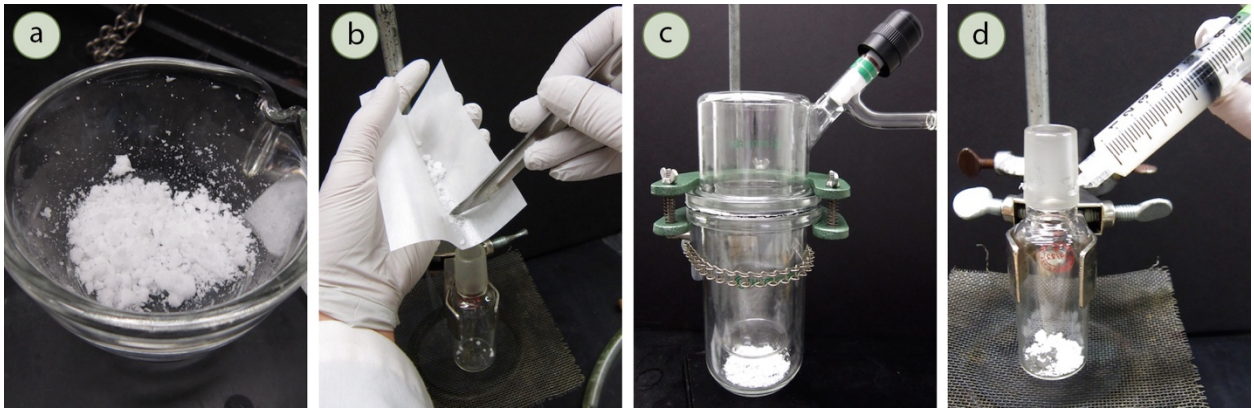


Figure 6.33: a) Camphor ground in a mortar, b) Adding camphor to a small scale sublimator, c) Large scale sublimator with camphor in the bottom, d) Greasing the ground glass joint.

1. If the solid to be sublimed is chunky, first crush with a mortar and pestle (Figure 6.33a). Then place the crude, dry solid in the bottom of the sublimation apparatus (Figure 6.33b).

   It is important that the solid is dry: if the sample is wet with solvent, condensation may form on the cold finger during the sublimation. Too much condensation may wash crystals off the cold finger.

2. Secure the apparatus to a ring stand or latticework (Figures 6.33 c+d). For small scales, support the apparatus with a platform (Figure 6.33d). A large scale sublimator is shown in Figure 6.33c.

3. Lightly grease the joint that connects the two pieces of sublimation glassware. Grease can be easily applied with a syringe full of grease. If using ground glass, lightly grease the joint near the end that will not be in contact with the sample (Figure 6.33d).

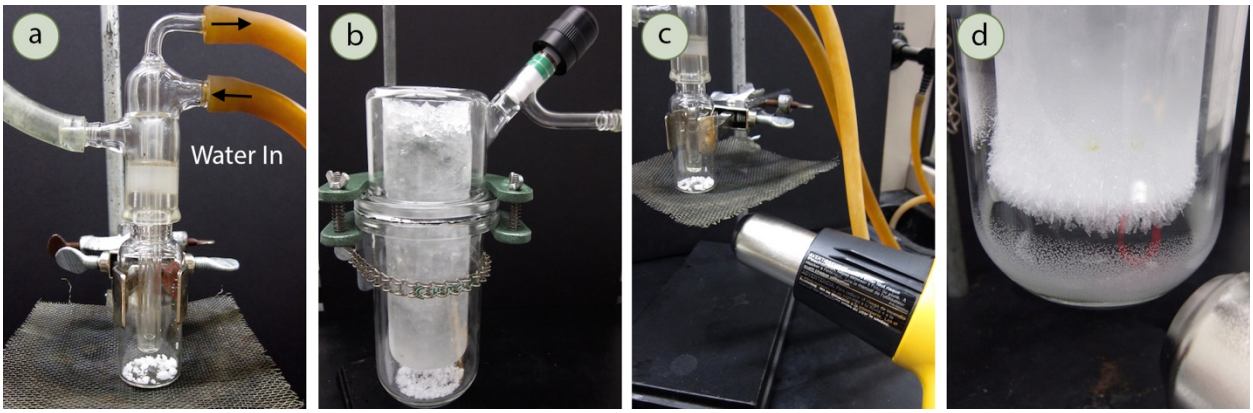


Figure 6.34: a) Small scale sublimation apparatus greased appropriately, b) Large scale sublimation apparatus with the cold finger filled with ice water, c) Heating the apparatus with a heat gun, d) Solid deposits on the outside of the glassware.

4. Insert the top piece of the sublimation apparatus (cold finger), and twist the two pieces of glassware together to spread the grease in the joint. When using ground glass, the grease should cause the bottom half of the joint to become transparent all the way around (Figure 6.34a). If the entire joint becomes transparent, too much grease has been used and some should be wiped off.

5. Use thick-walled rubber tubing (clear hose in Figure 6.34a) to connect the apparatus to a vacuum source (vacuum line or water aspirator). Apply the vacuum. The setup should not hiss or there is a leak in the system.

6. Prepare the cold finger:

    a. If the cold finger has a condenser, connect water hoses such that the lower arm connects to the water spigot and the upper arm drains to the sink (tan hoses in Figure 6.34a). Begin circulating water through the condenser.

    b. If the cold finger is an empty tube, fill the cold finger to the brim with ice, then pour in enough water to fill the finger about three-quarters of the way (Figure 6.34b). In some cases, the cold finger could be filled with dry ice and acetone.

    c. It is proper technique to apply the vacuum *before* cooling the finger to prevent water condensation from forming, which could wash crystals off the cold finger.

7. Heat the solid with a heat gun (Figure 6.34c) or Bunsen burner, beginning slowly with a back and forth motion and low heat. It is not recommended to use a sand bath or heating mantle for sublimation, as heating is often too slow and can only direct heat to the bottom of the apparatus, not the sides. Increase the rate of heating if the sublimation does not begin within a few minutes.

8. Over a short amount of time, solid should begin to deposit on the cold finger. It will undoubtedly also deposit on the outsides of the glassware (Figure 6.34d). Solid can be coaxed away from the outside of the glassware and toward the cold finger by waving the heat gun or burner periodically up the sides of the glass.

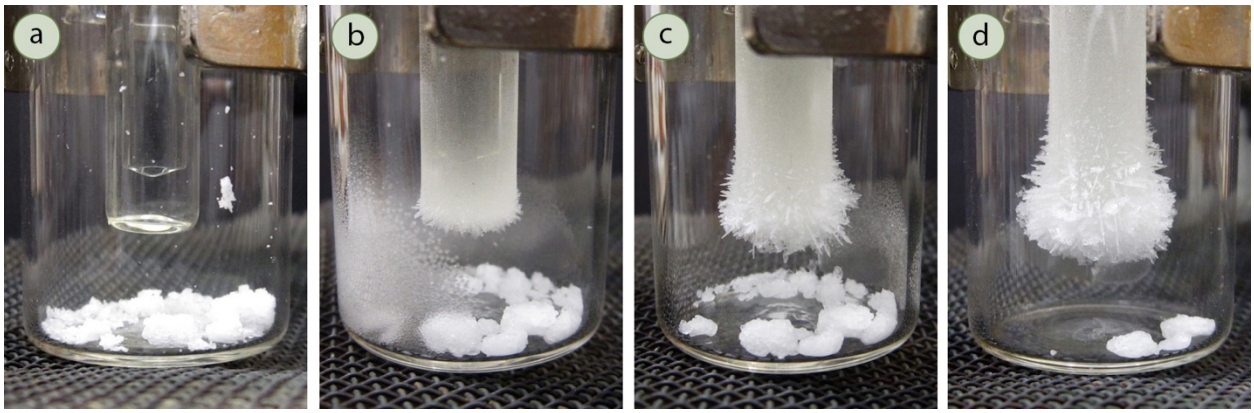


Figure 6.35: Time-lapse sublimation of camphor (small scale).

9. Continue the sublimation until all of the volatile substance is transferred from the bottom piece of glassware to the cold finger (Figure 6.35). If the compound begins to darken, decrease the rate of heating to prevent decomposition.

10. Remove the coolant from the cold finger:

    a. If a condenser was used, turn off the circulating water and remove the water hoses from the apparatus (carefully, without making a large mess).

    b. If an ice water coolant was used, scoop out the ice if possible, and remove the water by pipette (or for large scales with a turkey baster, Figure 6.36a).

11. Allow the system to come to room temperature.

12. *Delicately* reinstate air pressure to the apparatus (Figure 6.36b), noting that an abrupt opening of the system will cause air to violently enter the apparatus and will likely cause crystals to dislodge from the cold finger.

13. Delicately remove the emptied cold finger from the apparatus, and scrape the sublimed crystals onto a watch glass (Figure 6.36c). Alternatively, rinse the crystals from the cold finger with solvent through a funnel and into a round bottomed flask (Figure 6.36d), to later remove the solvent using a rotary evaporator.

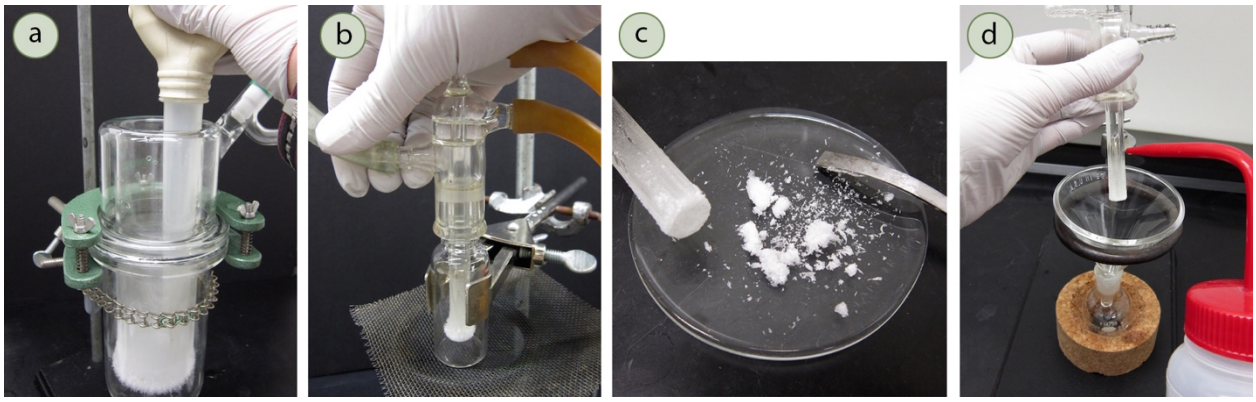


Figure 6.36: a) Removing ice water from the cold finger using a turkey baster, b) Releasing the pressure after the sublimation, c) Scraping the crystals from the cold finger, d) Rinsing the cold finger into a round bottomed flask for later evaporation.

6.3.B.3 VACUUM SUBLIMATION SUMMARY

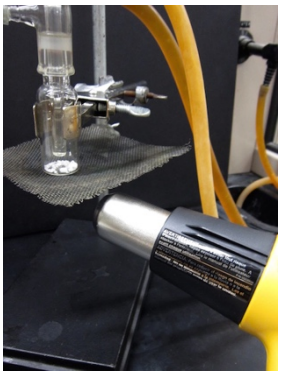
			
Place the sample to be sublimed in the bottom of the sublimation apparatus. Lightly grease all joints. Use thick walled tubing to attach to the vacuum arm, and apply the vacuum. The setup should not hiss or there is a leak.	Fill the cold finger, or run water through the condenser. Be sure to apply the vacuum first, then coolant. If cooled before the vacuum, condensation may occur on the cold finger. Wave a heat gun or Bunsen burner on the apparatus to heat the sample.	Sublimation should begin within a few minutes. Coax solid deposited on the side of the glassware toward the cold finger by waving the heat gun / burner on the sides of the glass.	When the sublimation is complete: Remove the coolant. Allow the apparatus to come to room temperature. Delicately reinstate the air pressure, noting that an abrupt opening of the vessel will cause air to knock crystals off the cold finger. Remove the cold finger.

Table 6.4: Procedural summary for vacuum sublimation.

6.4 CHEMICAL TESTS

6.4.A OVERVIEW OF CHEMICAL TESTS

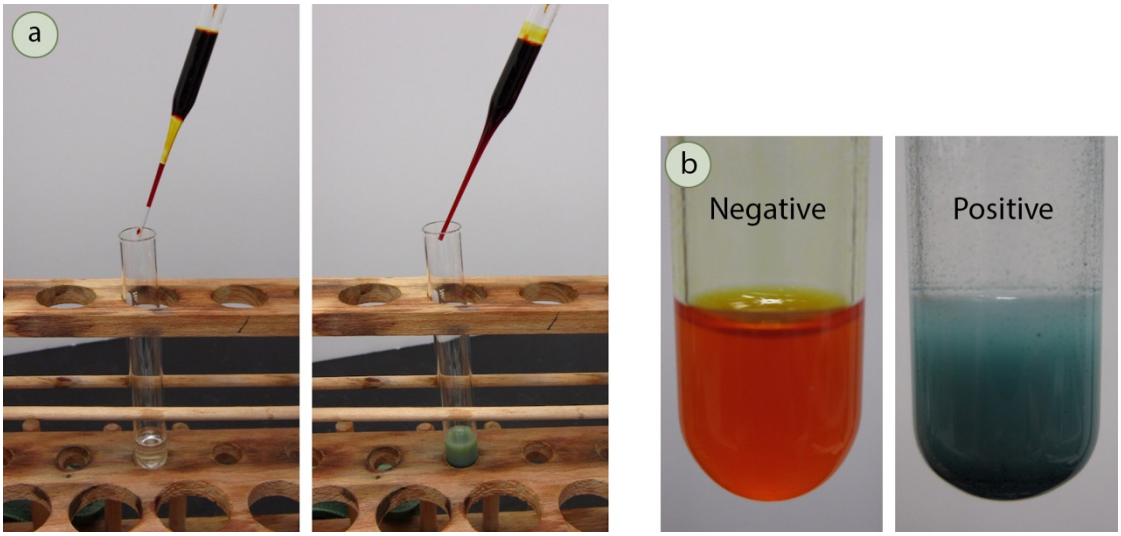


Figure 6.37: a) Addition of orange chromic acid reagent to a solution of 2-butanol in acetone (before and after), b) Negative and positive results for the chromic acid test.

Before spectroscopic analysis (IR, NMR) became commonplace in the organic chemistry lab, chemical tests were heavily relied upon to support compound identification. A **chemical test** is typically a fast reaction performed in a test tube that gives a dramatic visual clue (a color change, precipitate, or gas formation) as evidence for a chemical reaction. For example, addition of an orange chromic acid reagent to some compounds causes the chromium reagent to change to a blue-green color (Figure 6.37a). This is considered a "positive" test result, and in this case indicates the presence of a functional group that can be oxidized (alcohol or aldehyde). A negative test result is retention of the original color of the reagent, in this case the orange color (Figure 6.37b).

Performing chemical tests is commonly done in the teaching lab. Although the tests work well in general, when using a chemical test to support identification of a structure, caution should be used in interpretation of the results. For example, aldehydes are stated to give a positive result in the bromine test, which is when the compound turns the orange bromine solution clear. Figure 6.38 shows the reaction of two aldehydes with the bromine test: one gives a positive result (the left tube), and one gives a negative result (the right tube). Variation in chemical structure can sometimes interfere with "typical" results, leading to both false positives and false negatives. It is for this reason that spectroscopic methods are often more reliable in structure determination than chemical tests. Nonetheless, the ease of administration makes chemical tests preferable in certain applications, for example in roadside drug testing by police officers, and in environmental and chemical laboratories.

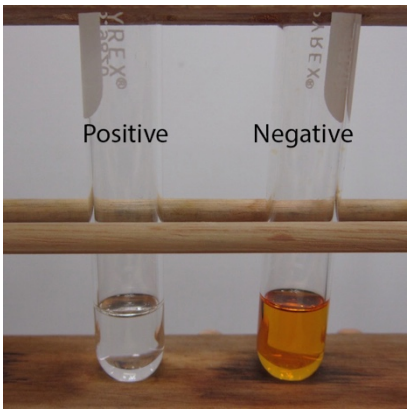


Figure 6.38: Results of two aldehydes in the bromine test (left tube is isobutyraldehyde and right tube is benzaldehyde).

6.4.B FLOWCHARTS

In some teaching labs, a combination of spectroscopy and chemical tests are used in determination of an unknown. If available, an infrared spectrometer (Figure 6.39) is very useful in determining possible functional groups present in an unknown. The following flowcharts summarize key signals present in an IR spectrum, and chemical tests that can be used to support or narrow down structural identification.

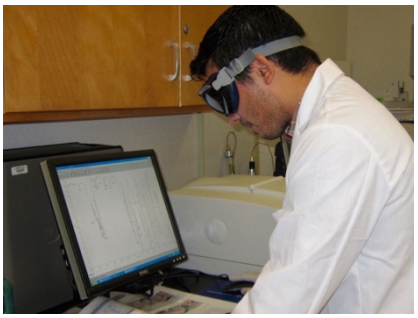


Figure 6.39: Student using an Infrared spectrometer.

1. O-H Bond

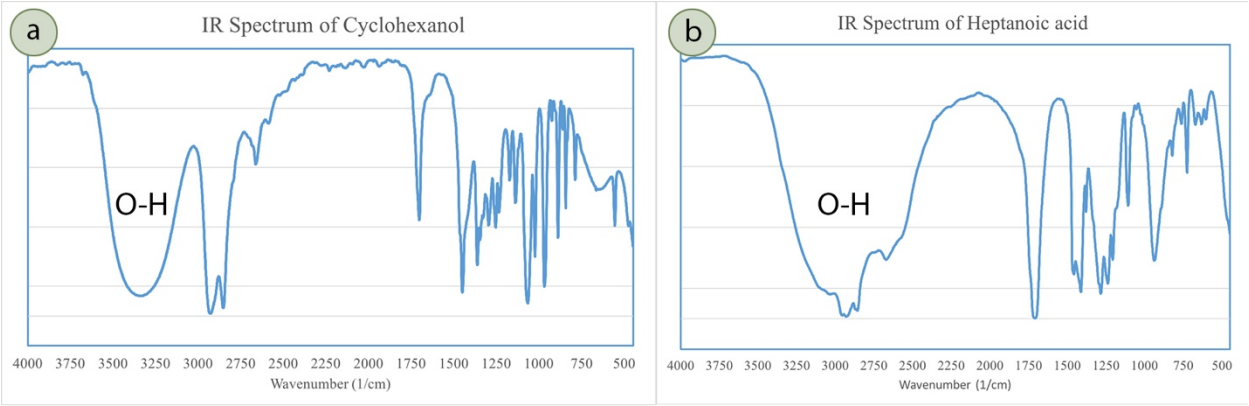


Figure 6.40: IR spectra of: a) cyclohexanol (alcohol), b) heptanoic acid (carboxylic acid).

An O-H bond strongly absorbs infrared radiation over a broad range of wavenumbers (2400-3400 cm^{-1}), and has a characteristic shape in IR spectra. The specific range of absorption can be used to identify whether the O-H is part of an alcohol or carboxylic acid functional group: a broad absorption centering around **3300 cm^{-1}** corresponds to an alcoholic O-H bond (Figure 6.40a), while a broader absorption centering around **3000 cm^{-1}** corresponds to a carboxylic acid O-H bond (Figure 6.40b).

Chemical tests (pH and bicarbonate tests) can be done to support the identification of a carboxylic acid. Specific structural features of alcohols (1˚, 2˚, or 3˚) can be determined using a variety of chemical tests, as summarized by the flowchart in Figure 6.41.

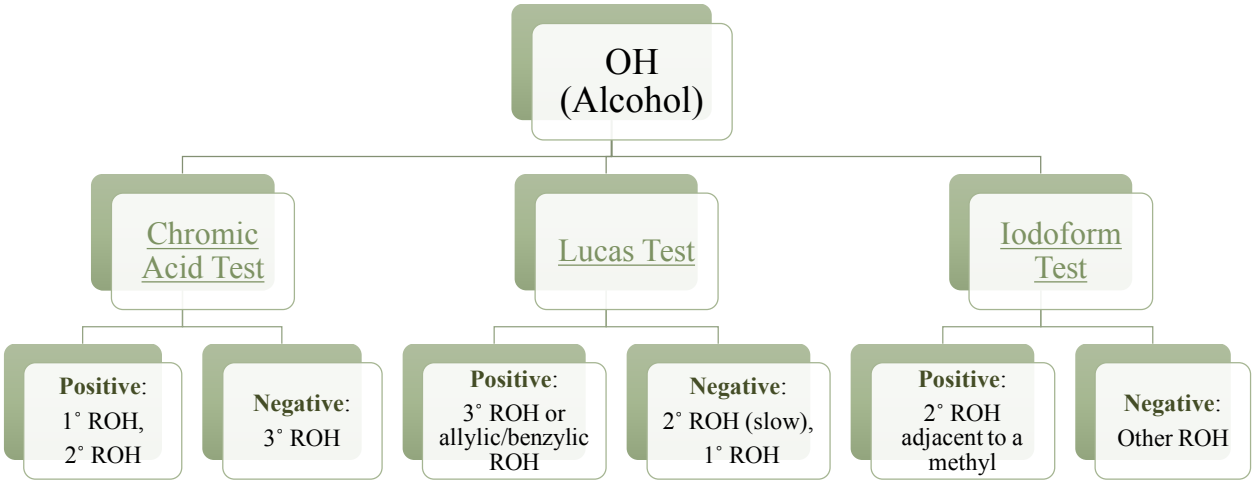


Figure 6.41: Flowchart summarizing chemical tests that support identification of an alcohol.

2. Carbonyl, C=O Bond

The carbonyl bond absorbs infrared radiation very strongly and sharply in the **1700 cm^{-1}** region (Figure 6.42). The specific wavenumber (1715 cm^{-1} or 1735 cm^{-1} for example) often correlates well to a specific functional group (aldehyde, ketone, ester, amide, or carboxylic acid), but it is not uncommon for compounds to absorb outside of their "expected" range. Chemical tests can be useful in narrowing down the specific functional group once a carbonyl bond is identified in an IR spectrum, as summarized by the flowchart in Figure 6.43.

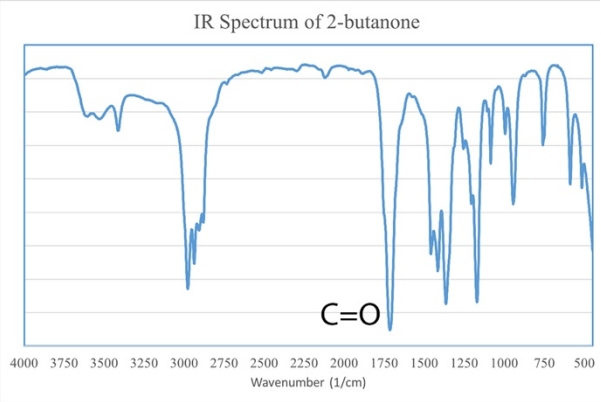


Figure 6.42: IR spectrum of 2-butanone.

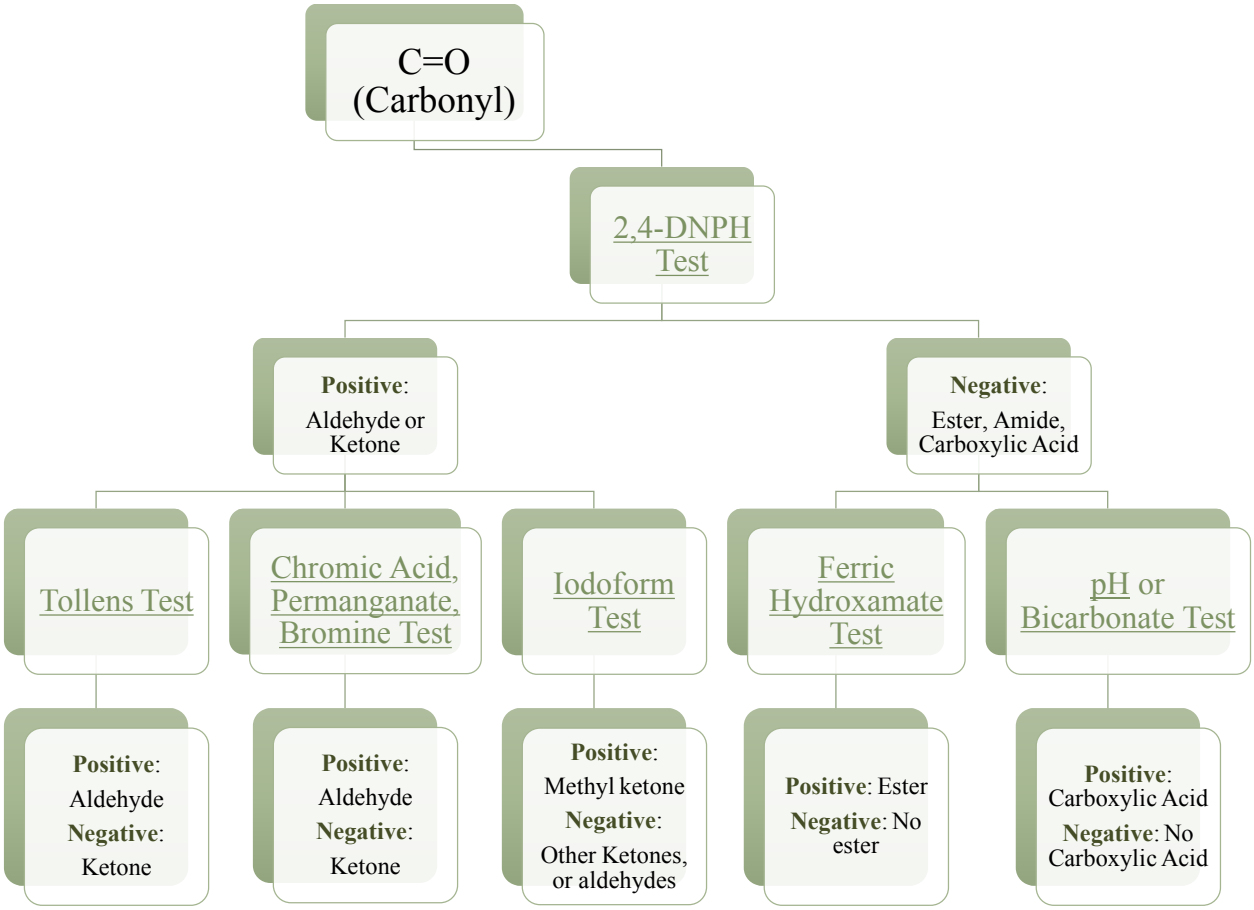


Figure 6.43: Flowchart summarizing chemical tests that support identification of a carbonyl compound.

3. Unsaturated Hydrocarbons (Alkenes, Alkynes, Aromatics)

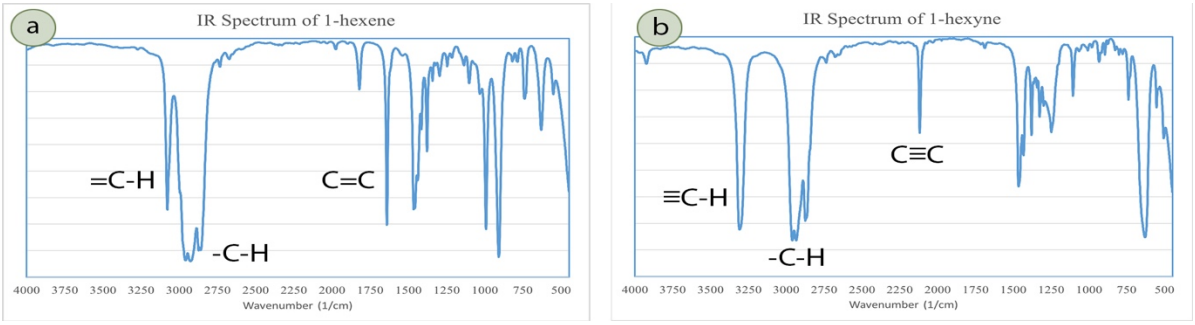


Figure 6.44: IR spectra of: a) 1-hexene (alkene), b) 1-hexyne (alkyne).

Unsaturated compounds have the following characteristic signals in their IR spectrum:

Alkenes / Aromatics (Figure 6.44a):

- C-H stretch involving sp^2 hybridized carbon atom: medium strength signal **slightly above 3000 cm^{-1}**, normally appearing as a shoulder on the C-H block of signals around 3000 cm^{-1}.
- C=C stretch: medium strength signals in the **1480-1680 cm^{-1}** region.

Alkynes (Figure 6.44b):

- C-H stretch involving sp hybridized carbon atom (terminal alkynes only): strong, sharp signal around **3300 cm^{-1}**. This signal is in the same region as an O-H signal, but is much sharper.
- C≡C triple bond stretch: **around 2100 cm^{-1}**, where few other signals occur. The signal is often weak, and may be absent if the compound is mostly symmetric about the triple bond.

Verification of the presence of an alkene or alkyne can be accomplished with the Permanganate and Bromine tests. Aromatic groups give no reaction in these tests.

4. Alkyl Halide

Presence of an alkyl halide is not obvious from an IR spectrum, as the C-X signals occur in the "fingerprint region" (< 1500 cm^{-1}) and near the lower limit of the IR spectrum (C-Cl stretches occur at **550-850 cm^{-1}** while C-Br stretches occur at **515-690 cm^{-1}**). However, several chemical tests can be used to verify the presence of halogens, the most reliable being the Beilstein test. Two other tests can be used to infer structural features (1°, 2°, 3°), as shown by the flowchart in Figure 6.45.

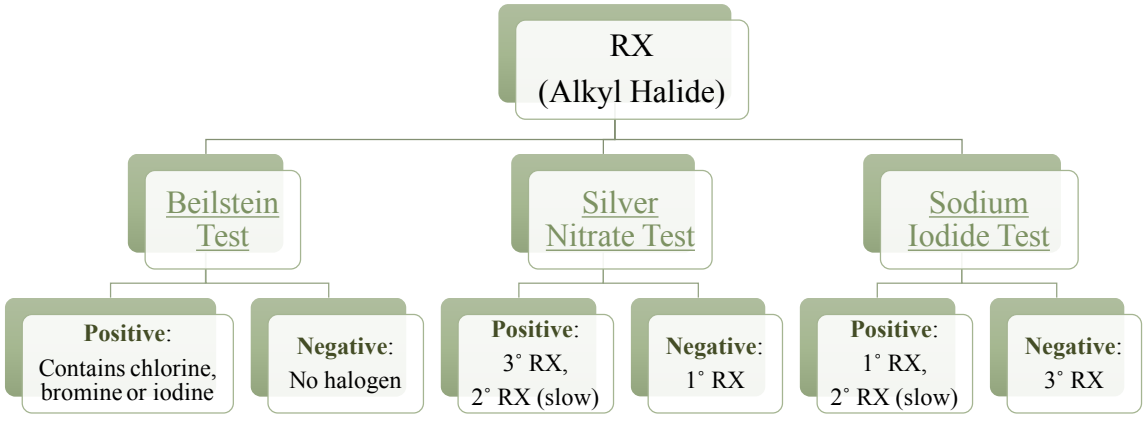
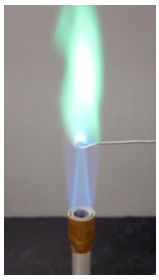
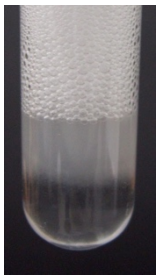
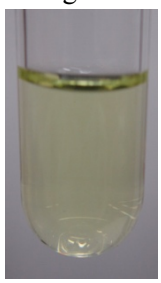
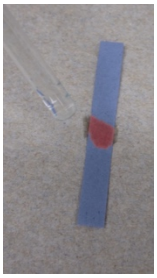


Figure 6.45: Flowchart summarizing chemical tests that support identification of a halogenated compound.

6.4.C CHEMICAL TEST SUMMARY

To follow is a visual summary of the various chemical tests. Procedures and details are provided for each in the following section.

Beilstein Test		**Benedict's Test**		**Bicarbonate Test**	
Positive	Negative	Positive	Negative	Positive	Negative
					
Chlorine, bromine or iodine compounds	Many groups	Reducing Carbohydrates (contain hemiacetal)	Non-reducing Carbohydrates (contain acetal) + many groups	Carboxylic Acids	Many groups
Bromine Test		**Chromic Acid (Jones) Test**		**2,4-DNPH (Brady's) Test**	
Positive	Negative	Positive	Negative	Positive	Negative
					
Alkenes, alkynes, aldehydes	Aromatics + many groups	1˚ and 2˚ alcohols, aldehydes	3˚ alcohols + many groups	Aldehydes, ketones	Esters + many groups
Ferric Hydroxamate Test		**Iodoform Test**		**Lucas Test**	
Positive	Negative	Positive	Negative	Positive	Negative
					
Esters	Aldehydes, Ketones + Many groups	Methyl ketones and 2˚ alcohols adjacent to a methyl group	Many groups	3˚ alcohols, allylic/benzylic alcohols, some 2˚ alcohols	1˚ alcohols + many groups

Permanganate (Baeyer) Test		pH Test		Phenol Test	
Positive	Negative	Positive	Negative	Positive	Negative
					
Alkenes, alkynes, some alcohols + aldehydes	Aromatics + Many groups	Carboxylic acids, sulfonic acids	Many groups	Phenols	Many groups

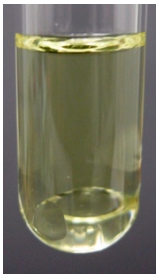
Silver Nitrate Test		Sodium Iodide (Finkelstein) Test		Tollens Test	
Positive	Negative	Positive	Negative	Positive	Negative
					
3˚ alkyl halides, allylic/benzylic RX, some 2˚ alkyl halides	1˚ alkyl halides + many groups	1˚ alkyl halides, allylic/benzylic RX, some 2˚ alkyl halides	3˚ alkyl halides + Many groups	Aldehydes	Ketones, esters + many groups

Table 6.5: Chemical tests summary.

6.4.D INDIVIDUAL TESTS

6.4.D.1 BEILSTEIN TEST

The Beilstein Test confirms the presence of a halogen in solution, although it does not distinguish between chlorine, bromine, or iodine. A copper wire is dipped into the halogen-containing solution and thrust into a flame. The copper oxide on the wire reacts with the organic halide to produce a copper-halide compound that gives a blue-green color to the flame.

Procedure: In the fume hood, clean a looped copper wire by thrusting it into the tip of the blue cone of a Bunsen burner flame until it glows (Figure 6.46a). Be sure to "burn off" any residual liquid on the wire (make sure any green flames from previous tests are gone before you begin).

Allow the copper to cool to room temperature, then dip it into a test tube containing 5-10 drops of your sample, coating it as much as possible (Figure 6.46b). If the sample is a solid, adhere some of the solid to the copper wire by first wetting the wire with distilled water then touching it to the solid.

Immediately plunge the wire with sample into the blue cone of the flame. A positive result is a green flame, although it might be short-lived and faint (it may be easier to see if the fume hood light is turned off). A negative result is the absence of this green color (Figures 6.46 c+d).

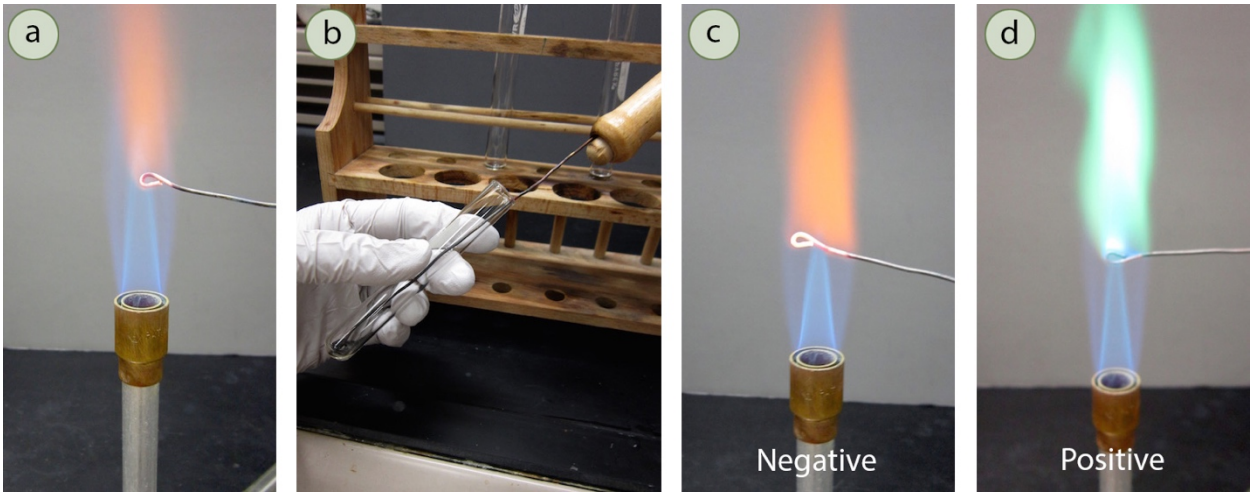


Figure 6.46: a) Cleaning copper wire in a flame, b) Dipping copper wire into the reagent, c) Negative result (hexanes), d) Positive result (1-chlorobutane).

6.4.D.2 BENEDICT'S TEST

The Benedict's test can verify the presence of reducing carbohydrates: compounds that have hemiacetals in their structures and are therefore in equilibrium with the free carbonyl form (aldehyde or α-hydroxyketone). The carbonyl forms are oxidized by the Cu^{2+} in the Benedict's reagent (which complexes with citrate ions to prevent the precipitation of $Cu(OH)_2$ and $CuCO_3$). An insoluble Cu_2O is the inorganic product of this reaction, which usually has a red-brown color (Figure 6.47). Carbohydrates with only acetal linkages are non-reducing sugars and give a negative result with this test.

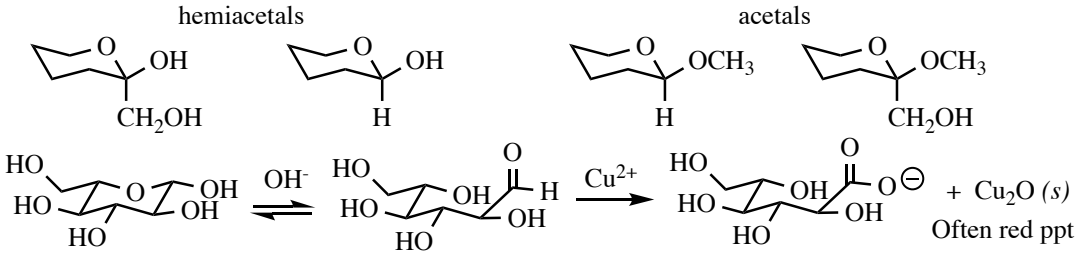


Figure 6.47: Structure of hemiacetal and acetals, along with the reaction of a hemiacetal with the Benedict's reagent.

Procedure: Dissolve 10-30 mg of solid or 3 drops liquid sample in a minimal amount of water (0.5 mL) in a small test tube (13 × 100 mm). Add 2 mL of Benedict's reagent.[9] Warm the blue solution in a boiling water bath for 2 minutes (Figure 6.48a). A positive result is the formation of a reddish-brown solution or precipitate after some time, while a negative result is retention of the blue color (Figures 6.48 c+d).

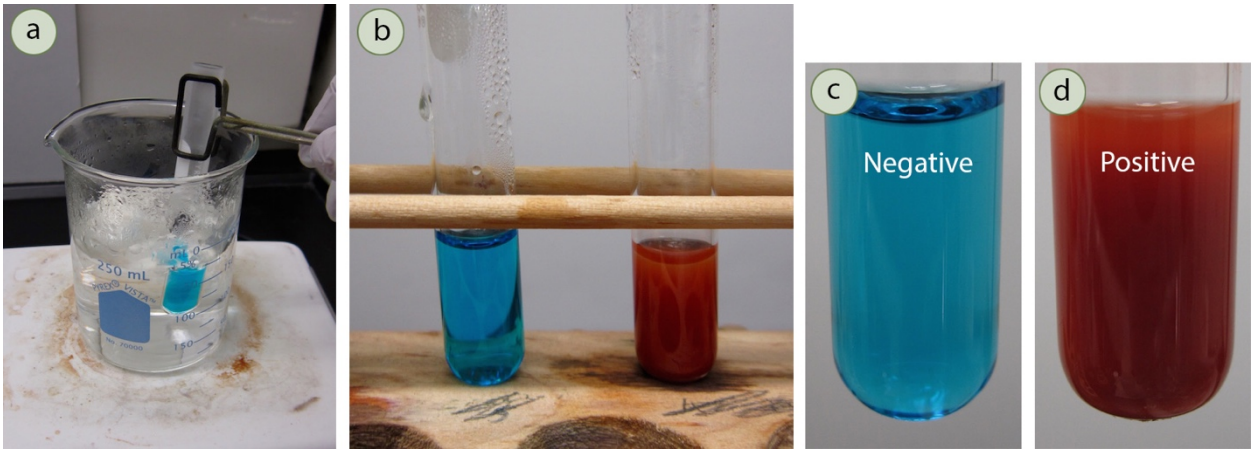


Figure 6.48: a) Heating the Benedict's solution in a boiling water bath, b) Benedict's test results: left tube is sucrose (negative), right tube is glucose (positive), c) Negative result, d) Positive result.

[9] The Benedict's reagent is prepared as follows, as published by the Flinn Scientific catalog: 173 g of hydrated sodium citrate and 100 g of anhydrous sodium carbonate is added to 800 mL of distilled water with heating. The mixture is filtered, then combined with a solution of 17.3 g copper(II) sulfate pentahydrate dissolved in 100 mL distilled water. The combined solutions are diluted to 1L.

Conjugated aldehydes are unreactive in the Benedict's test, and the author found many non-conjugated aldehydes to also be unreactive. Formation of colloids seem to prevent the formation of the red precipitate (Figure 6.49 shows the appearance of propionaldehyde in the hot water bath, forming a cloudy colloid).

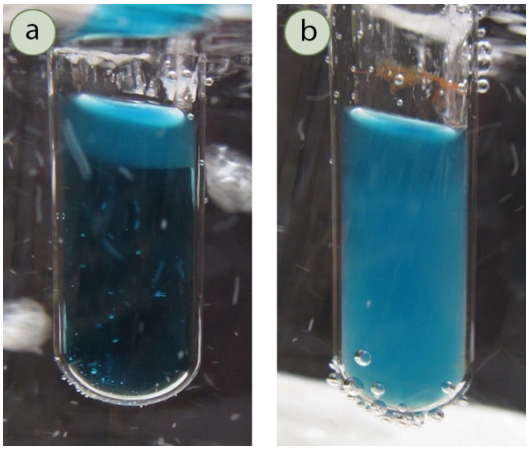


Figure 6.49: Reaction of propionaldehyde in the Benedict's test: a) In the beginning, colloid formation on the surface, b) After time. Notice orange solid on the test tube rim, indicating a reaction is possible when exposed to the atmosphere.

The reaction may only work for compounds that are water soluble (like carbohydrates), as the reaction seems to initiate at the surface (Figure 6.50), and the author found aldehydes that formed an insoluble layer on the surface to be unreactive.

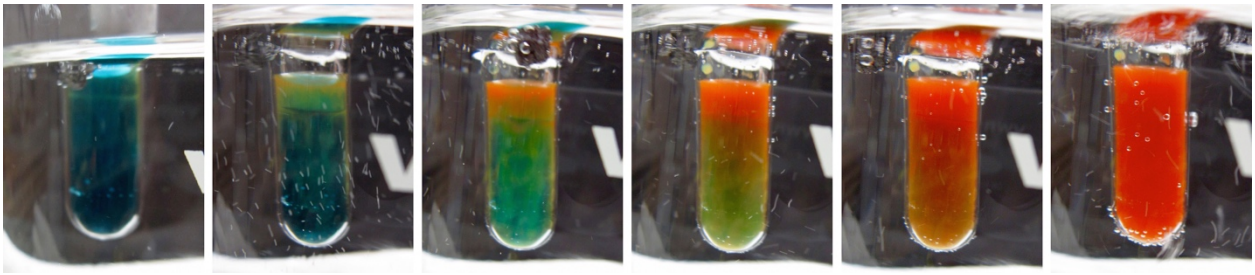


Figure 6.50: Time-lapse reaction progress of the Benedict's reagent reacting with glucose.

The Benedict's test is related to the **Fehling's test**, which uses different ligands on the copper oxidizing species. The Fehling's reagent uses a Cu^{2+} ion complexed with two tartrate ions.

6.4.D.3 BICARBONATE TEST

Carboxylic acids and sulfonic acids can react with sodium bicarbonate ($NaHCO_3$) to produce carbon dioxide and water (Figure 6.51). Other mainstream functional groups (most phenols and alcohols) are not acidic enough to produce a gas with bicarbonate.

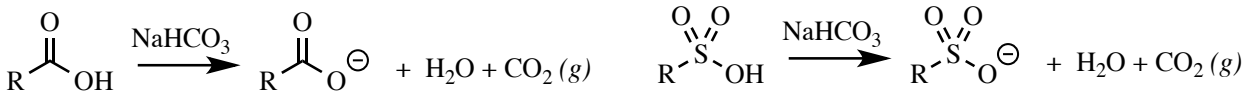


Figure 6.51: Reaction of carboxylic and sulfonic acids with bicarbonate ion.

Procedure: Add 2 mL of 5% $NaHCO_3$ *(aq)* into a test tube and add 5 drops or 50 mg of your sample. Mix the solution by agitating the test tube. A positive test for carboxylic acids is the formation of bubbles or frothing (Figure 6.52).

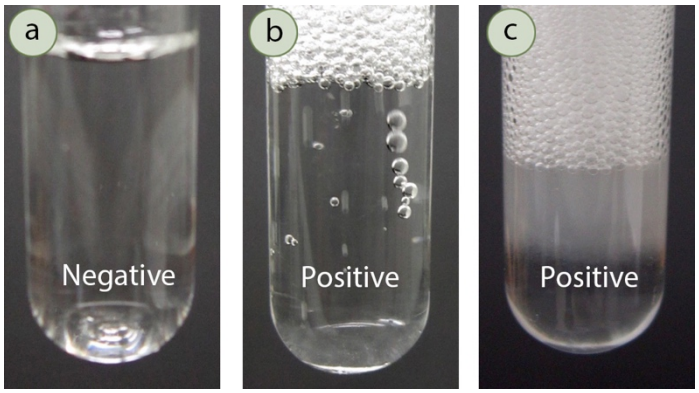


Figure 6.52: a) Negative result (acetone), b) Positive result (lactic acid), c) Positive result (octanoic acid).

6.4.D.4 BROMINE TEST

A solution of bromine in CH_2Cl_2 is a test for unsaturation (alkenes and alkynes) and in some cases the ability to be oxidized (aldehydes). The bromine solution is orange and upon reaction the solution turns colorless due to the consumption of bromine. Bromine reacts with alkenes and alkynes through addition reactions and with aldehydes through oxidation (Figure 6.53). It gives no reaction with aromatics, making this a good test to distinguish alkenes from aromatics.

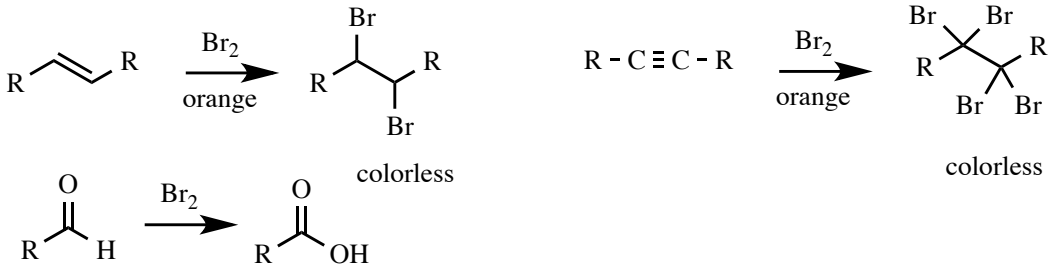


Figure 6.53: Reaction of an alkene, alkyne, and aldehyde with bromine.

Procedure: Dissolve 4 drops or 50 mg of sample in 1 mL of dichloromethane (CH_2Cl_2) or 1,2-dimethoxyethane. Add 2 drops of the orange 5% Br_2 in CH_2Cl_2 solution to the test tube and observe. A positive result is the immediate disappearance of the orange color to produce a clear or slightly yellow solution (Figure 6.54). A negative result is the retention of the orange color. An aldehyde may require a small amount of time to decolorize the solution and produce a positive result (approximately 1 min, Figure 6.55) and conjugated aldehydes are unreactive (Figure 6.55).

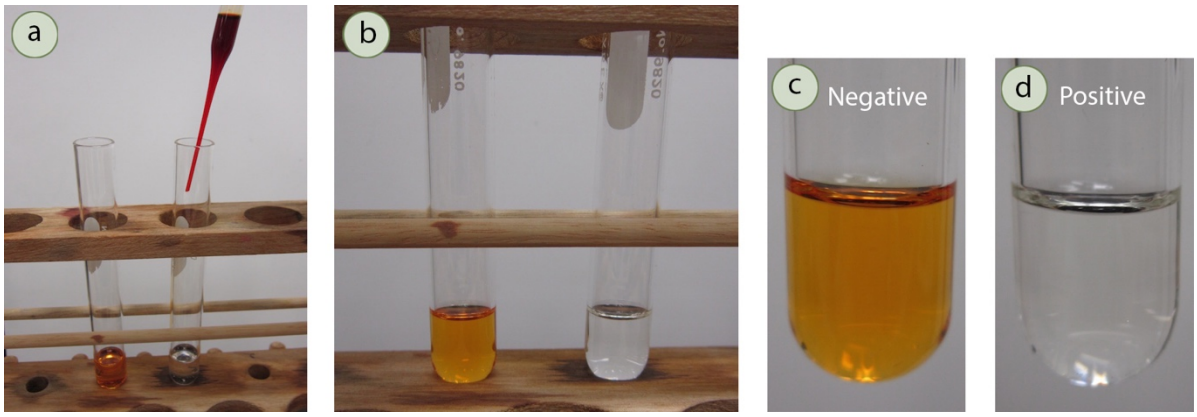


Figure 6.54: a) Addition of the bromine solution (orange liquid) to a test tube, b) Bromine results: hexanes (left tube), 1-hexene (right tube), c) Negative result, d) Positive result.

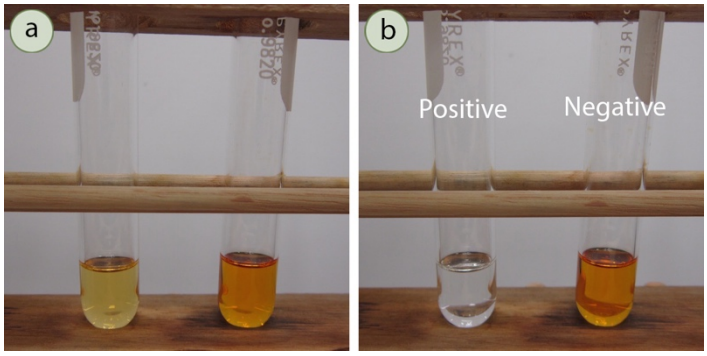
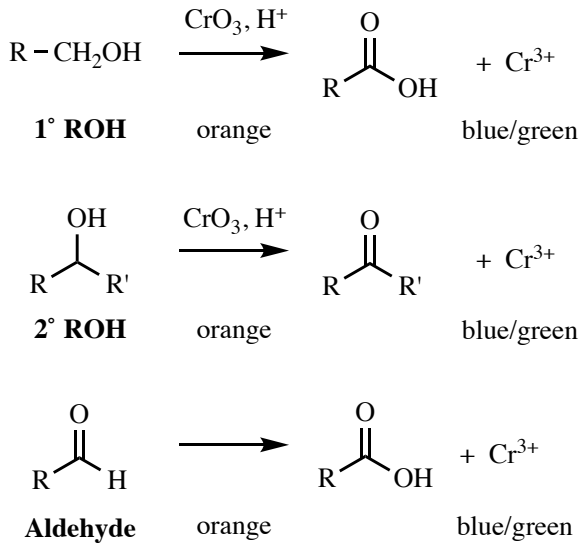


Figure 6.55: Bromine results for isobutyraldehyde (left tube) and benzaldehyde, a conjugated aldehyde (right tube): a) Immediately after addition of the bromine reagent, b) After 1 minute.

6.4.D.5 CHROMIC ACID (JONES) TEST

A solution of CrO_3 in H_2SO_4 is a test for polar functional groups that can be oxidized, which includes aldehydes, 1˚ alcohols, and 2˚ alcohols (Figure 6.57). 3˚ alcohols give a negative result with this test (Figure 6.56). The orange Cr^{6+} reagent converts to a blue-green Cr^{3+} species, which often precipitates in acetone.



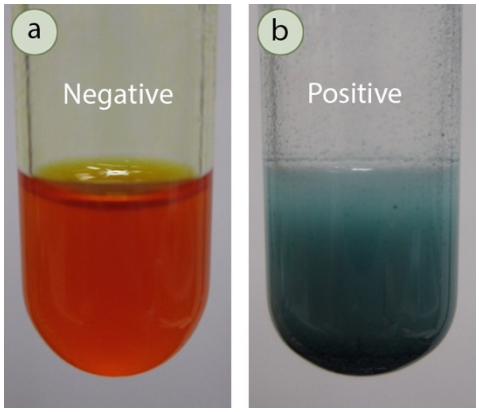


Figure 6.56: Negative (a) and positive (b) results for the chromic acid test.

Figure 6.57: Reaction of a primary alcohol, secondary alcohol, and aldehyde with the chromic acid reagent.

Procedure: Place 1 mL of acetone in a small test tube (13 × 100 mm) and add 2 drops or 20 mg of your sample. While wearing gloves, add 2 drops of the orange chromic acid reagent[10] (**safety note:** the reagent is highly toxic!) and mix by agitating. A positive result is a blue-green color or dark precipitate, while a negative result is a yellow-orange solution or precipitate with no dark-colored precipitate (Figure 6.58).

Water works better than acetone to rinse chromium reagents into the waste beaker, although some time needs to be allowed for dissolution of the Cr^{3+} species.

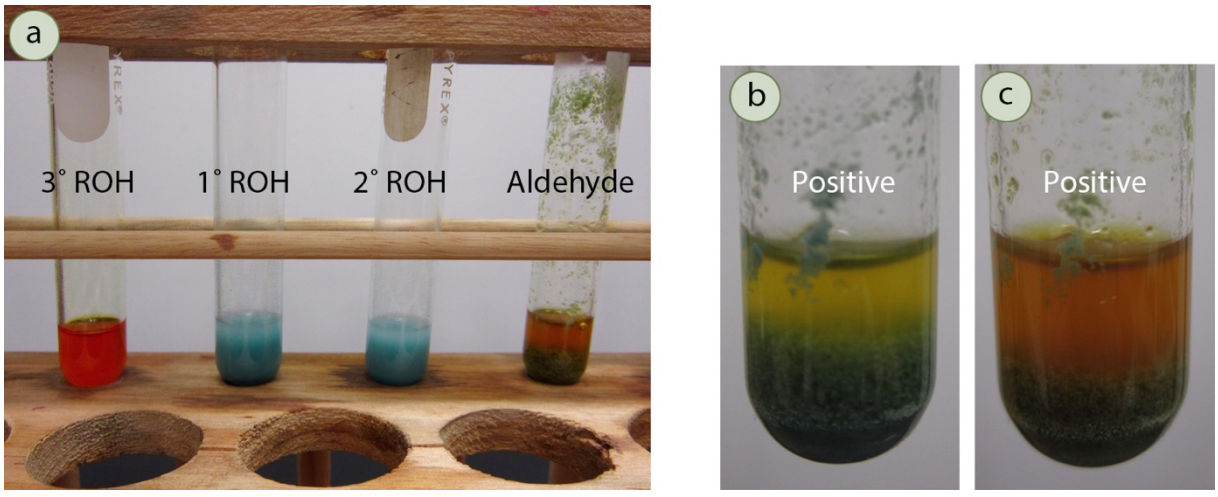


Figure 6.58: a) Chromic acid results (left to right): *t*-butanol (3˚, negative), 1-propanol (1˚, positive), 2-propanol (2˚, positive), benzaldehyde (positive), b) Immediate reaction of benzaldehyde, c) Benzaldehyde reaction after 1 minute.

[10] The chromic acid reagent is prepared as follows: 25.0 g of chromium(VI) oxide is added to 25 mL concentrated sulfuric acid, which is then added in portions to 75 mL of water. The reagent has a very long shelf life (10^+ years).

6.4.D.6 2,4-DNPH (BRADY'S) TEST

A solution of 2,4-dinitrophenylhydrazine (2,4-DNPH) in ethanol is a test for aldehydes or ketones (Figure 6.59). Most aldehydes or ketones will react with the orange reagent to give a red, orange, or yellow precipitate. Esters and other carbonyl compounds are generally not reactive enough to give a positive result for this test.

The color of the precipitate may give evidence for the amount of conjugation present in the original carbonyl: an orange precipitate forms for non-conjugated carbonyls (Figure 6.60c shows the result for 2-butanone), and a red precipitate forms for conjugated carbonyls (Figure 6.60d shows the result for cinnamaldehyde).

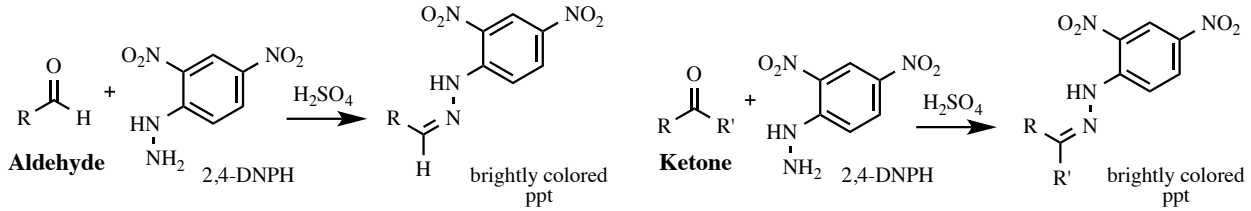


Figure 6.59: Reaction of an aldehyde and ketone with 2,4-DNPH.

Procedure: Add 3 drops of sample to a small test tube (13 × 100 mm), or dissolve 10 mg of solid sample in a minimal amount of ethanol in the test tube. While wearing gloves, add about 1 mL of the orange 2,4-DNPH reagent[11] (**safety note:** the reagent is highly toxic!) and mix the test tube by agitating.

A positive result is the immediate formation of a large amount of brightly colored precipitate (red, orange, or yellow). A negative result is the absence of this precipitate and a transparent yellow-orange solution (Figure 6.60).

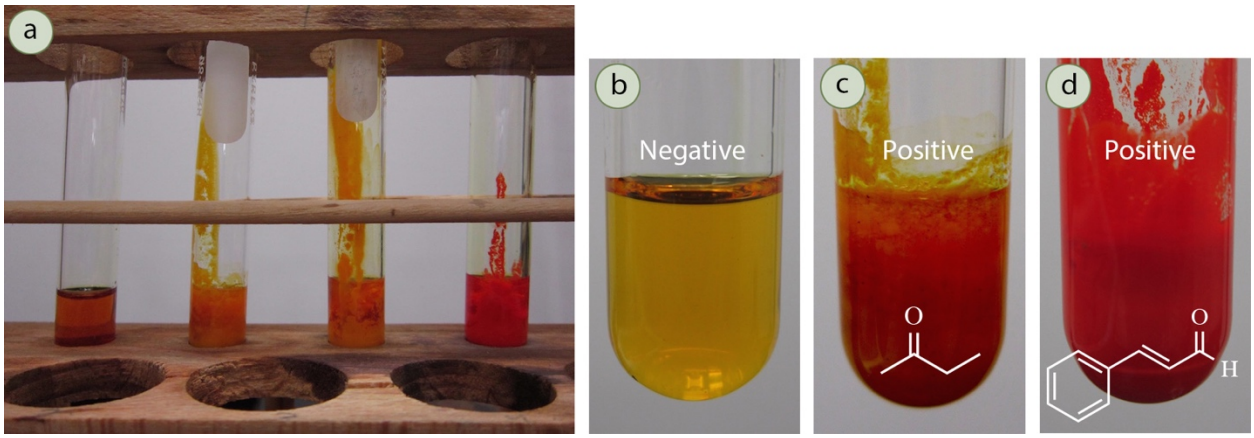


Figure 6.60: a) 2,4-DNPH results for (left to right) ethyl acetate (negative), 2-butanone (positive), benzaldehyde (positive), cinnamaldehyde (positive), b) Negative result, c) Positive result from a non-conjugated carbonyl, d) Positive result from a conjugated carbonyl.

[11] Preparation of the 2,4-DNPH reagent, as published in B. Ruekberg, *J. Chem. Ed*, **2005**, 82(9), p. A1310, is as follows: To a dry 125 mL Erlenmeyer flask is added 3 g 2,4-dinitrophenylhydrazine, 20 mL water and 70 mL of 95% ethanol. The solution is cooled in an ice bath with stirring, and when at 10 ˚C, 15 mL of concentrated sulfuric acid is added slowly in portions. If the temperature exceeds 20 ˚C during the addition, the solution should be allowed to cool to 10 ˚C before continuing. The solution is then warmed to 60 ˚C with stirring, and if solids remain, they are filtered. Finally, the solution is cooled.

6.4.D.7 FERRIC HYDROXAMATE TEST

The ferric hydroxamate procedure is a probe for the ester functional group. Esters heated with hydroxylamine produce hydroxamic acids, which form intense, colored complexes (often dark maroon) with Fe^{3+}. A possible structure of these complexes is shown in Figure 6.61. This test is related to the phenol test, and as in that test, compounds with high enolic character can give a colored complex with Fe^{3+}. Therefore, a preliminary test is performed to see if the carbonyl compound being tested produces enough enol to form a colored complex with Fe^{3+}, which would lead to a false positive result.

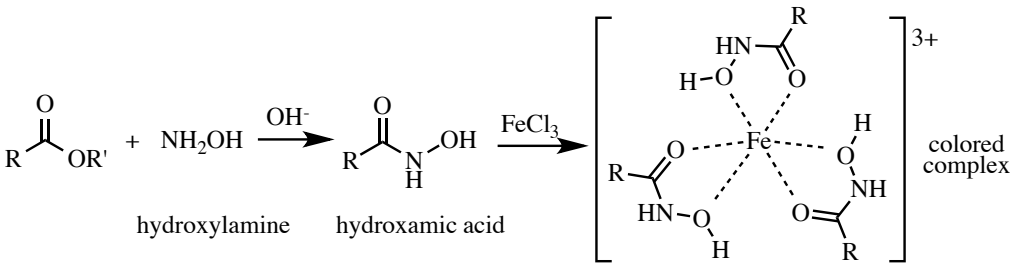


Figure 6.61: Reaction of ester with hydroxamic acid.

Procedure: Perform a preliminary test to be sure that this test will not give a false positive. Add the following to a small test tube (13 × 100 mm): 1 mL ethanol, 2 drops or 20 mg of your sample, 1 mL of 1 *M* HCl *(aq),* and 2 drops of 5% $FeCl_3$ *(aq)* solution. If the solution is clear or yellow (the color of the $FeCl_3$, Figure 6.62a), this test will work and not produce a false positive (continue on). If a definite color other than yellow appears, this test will not work for your sample, as it forms a colored complex with Fe^{3+} even without hydroxylamine.

Into a clean *medium sized* test tube (18 × 150 mm), add 1 mL of 0.5 *M* aqueous hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), 0.5 mL of 6 *M* NaOH *(aq),* and 5 drops or 50 mg of sample. Heat the mixture in a boiling water bath for about 3 minutes (the volume will reduce by about half, Figure 6.62b).

Quickly cool the solution by immersing it in a tap water bath, then add 2 mL of 1 *M* HCl *(aq).* If the solution becomes cloudy, add enough ethanol to clarify it. Then add 6-10 drops of a yellow 5% $FeCl_3$ *(aq)* solution. Vigorously mix the tube.

A positive result is a *deep* burgundy, umber, or magenta color (red/brown) while a negative result is any other color (Figures 6.62 c+d). Note: use water to rinse out the test tubes, and if a red result won't easily clean up, add a few drops of 6 *M* HCl.

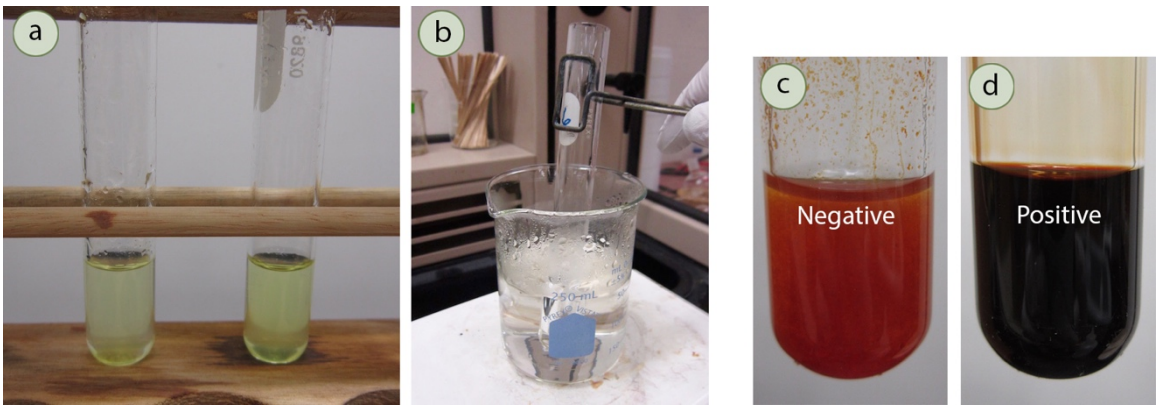


Figure 6.62: a) Preliminary procedure to be sure the test will not give a false positive, b) Heating the solution, c) Negative result (2-pentanone), d) Positive result (ethyl acetate).

6.4.D.8 IODOFORM TEST

A solution of iodine (I_2) and iodide (I^-) in NaOH can be used to test for methyl ketones or 2˚ alcohols adjacent to a methyl group. This is a very specific test that will give a positive result (formation of a canary yellow precipitate) only for compounds with the structure $RCH(OH)CH_3$ or $RC{=}OCH_3$ (Figure 6.63). It does not work for all alcohols or ketones, and does not work well for water-insoluble compounds.

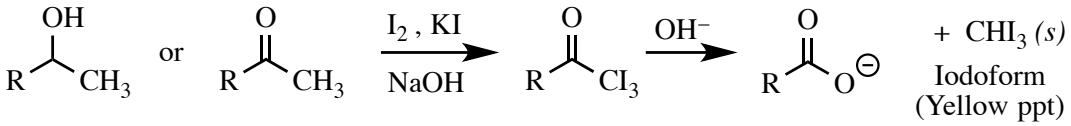


Figure 6.63: Reaction of secondary alcohol or methyl ketone with the iodoform reagent.

Procedure: Add 10 drops sample to a small test tube (13 × 100 mm) or 0.10 g sample dissolved in the minimal amount of 1,2-dimethoxyethane followed by 1 mL of 10% NaOH *(aq)*. Next add 10 drops of the dark brown iodoform reagent[12] (I_2 / KI solution) and vigorously mix the test tube by agitating.

A positive result is a cloudy yellow solution, or a yellow precipitate. A negative result is a clear, yellow, or orange solution with no precipitate (Figure 6.64).

If the sample is not water soluble, a small organic layer separate from the solution may be seen (it will likely be on top). This layer may become dark yellow or brown from dissolving the iodine. Vigorously mix the tube to encourage a reaction, but if the darkened organic layer remains and no precipitate forms, this is still a negative result (Figure 6.64d).

Note: a false positive result may occur if the test tube was cleaned with acetone before use, and residual acetone remained in the tube.

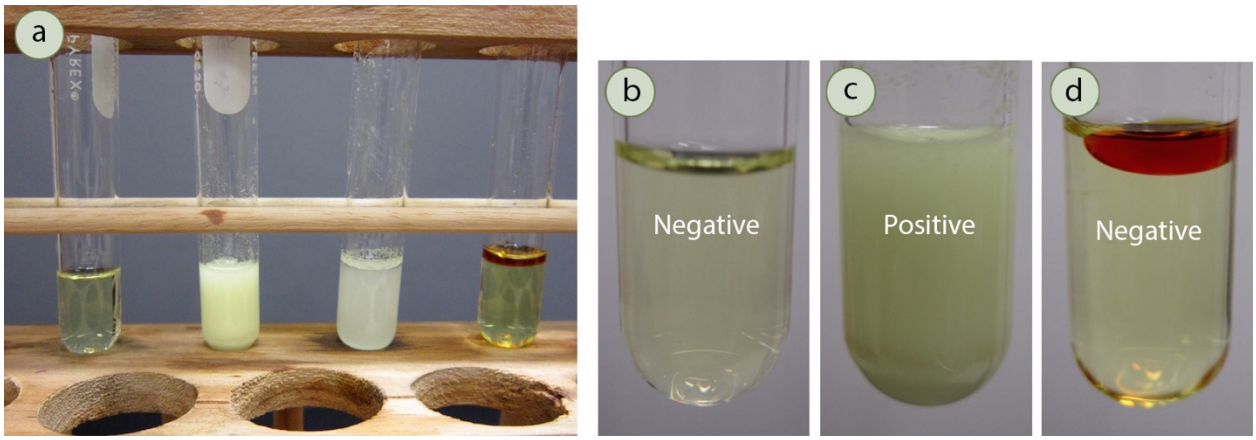


Figure 6.64: a) Iodoform results (left to right): 1-propanol, 2-propanol, acetone, 1-octanol, b) Negative result, c) Positive result, d) Negative result when the sample is insoluble in the reagent.

[12] Preparation of the iodoform reagent is as follows: 10 g KI and 5 g I_2 is dissolved in 100 mL water.

6.4.D.9 LUCAS TEST

The Lucas Reagent (concentrated HCl and $ZnCl_2$) is a test for some alcohols. Alcohols can react through an S_N1 mechanism to produce alkyl halides that are insoluble in the aqueous solution and appear as a white precipitate or cloudiness. The test cannot be used for water-insoluble alcohols (generally > 5 carbon atoms), as they may produce a cloudiness or second layer regardless if any reaction occurred or not.

$$2^{\circ} \text{ or } 3^{\circ} \text{ ROH} + \text{HCl} / ZnCl_2 \rightarrow \text{RCl } (s)$$

As the mechanism is S_N1, a 3˚ alcohol should react immediately, a 2˚ alcohol should react more slowly (perhaps in 5 minutes if at all) and 1˚ alcohols often don't react at all. Benzylic alcohols (Ph-C-OH), allylic alcohols (C=C-C-OH) and propargylic alcohols (C≡C-C-OH) often give immediate results just like 3˚ alcohols.

Procedure: Place 2 mL of the Lucas reagent[13] (**safety note:** the reagent is highly acidic and corrosive!) into a small test tube (13 × 100 mm). Add 10 drops of sample, and mix by agitating the test tube.

A positive result is a white cloudiness within 5 minutes or a new organic layer (RCl) formation on the top.[14] A negative result is the absence of any cloudiness or only one layer (Figure 6.65).

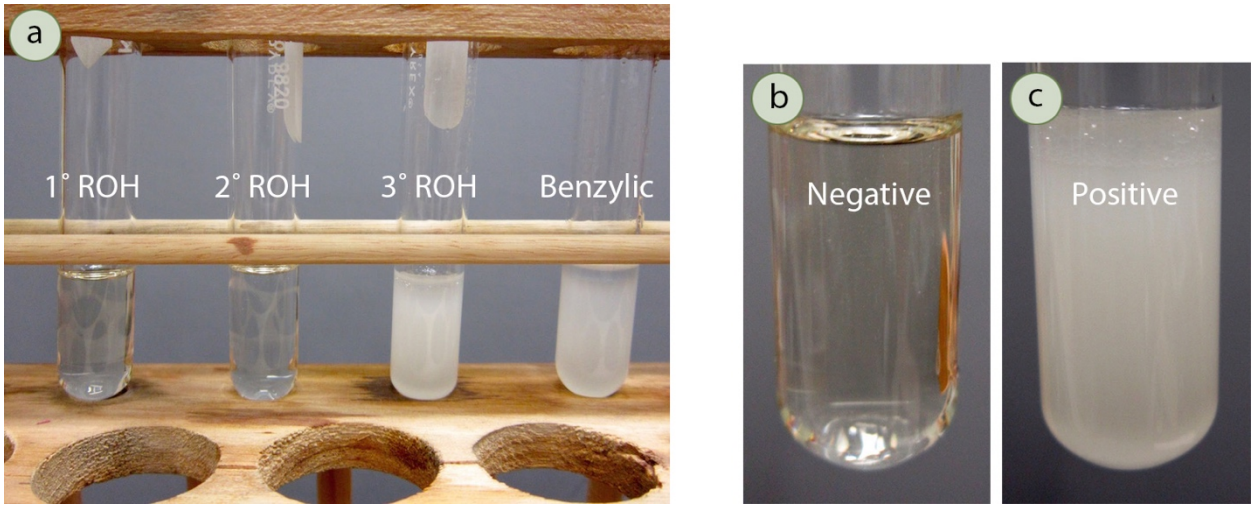


Figure 6.65: a) Lucas test results (left to right): 1-propanol (1˚, negative), 2-propanol (2˚, negative), *t*-butanol (3˚, positive), benzyl alcohol (benzylic, positive), b) Negative result, c) Positive result.

[13] Preparation of the Lucas reagent is as follows: 160 g of fresh anhydrous $ZnCl_2$ is dissolved in 100 mL of cold concentrated HCl.

[14] Although chlorinated organics are typically denser than water, the Lucas reagent has a high quantity of solute, and chlorinated compounds tend to be less dense than the reagent.

6.4.D.10 PERMANGANATE (BAEYER) TEST

A potassium permanganate ($KMnO_4$) solution is a test for unsaturation (alkenes and alkynes) or functional groups that can be oxidized (aldehydes and some alcohols, Figure 6.66). The permanganate ion (MnO_4^-) is a deep purple color, and upon reduction converts to a brown precipitate (MnO_2). Permanganate cannot react with aromatics, so is a good test to discern between alkenes and aromatics. A positive reaction with alcohols is not always dependable (a negative result is seen with benzyl alcohol in Figure 6.67).

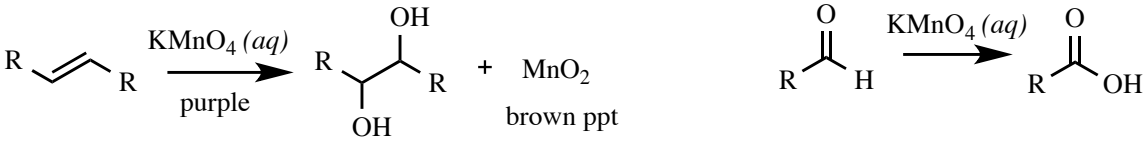


Figure 6.66: Reaction of an alkene and aldehyde with permanganate ion.

Procedure: Dissolve 4 drops or 40 mg of sample in 1 mL of ethanol (or 1,2-dimethoxyethane) in a small test tube (13 × 100 mm). While wearing gloves, add 3 drops of the deep purple 1% $KMnO_4$ *(aq)* solution to the test tube (**safety note:** reagent is corrosive and will stain skin brown!). Mix the test tube with agitation, and allow it to sit for 1 minute. A positive result is the appearance of a brown color or precipitate. A negative result is a deep purple color with no precipitate (unreacted $KMnO_4$, Figure 6.67).

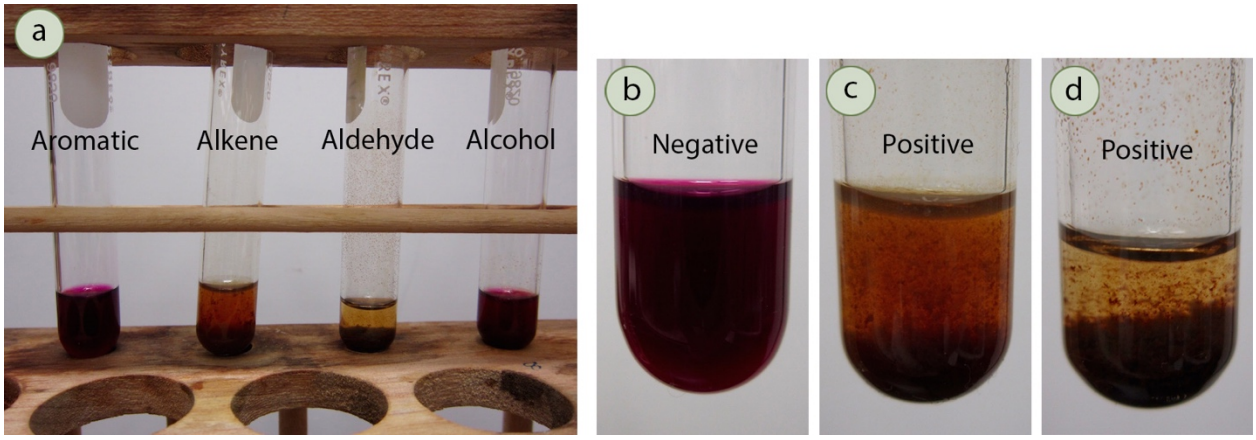


Figure 6.67: a) Baeyer test results for (left to right) ethyl benzene (negative), 1-hexene (positive), isobutyraldehyde (positive), benzyl alcohol (mostly negative), b) Negative result, c+d) Positive results.

6.4.D.11 pH TEST

Carboxylic acids and sulfonic acids produce acidic aqueous solutions (Figure 6.68a), which can be confirmed by turning blue litmus paper pink. The paper changes color (Figure 6.68c) as the indicator molecules react in the lowered pH and form a structure that has a different color.

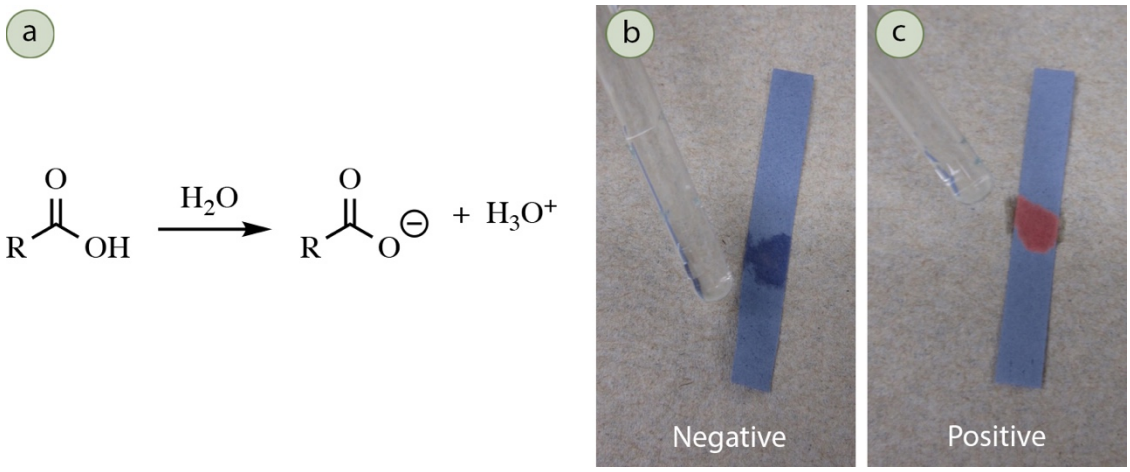


Figure 6.68: a) Reaction of carboxylic acid with water to produce a slightly acidic solution, b) Results of a negative pH test, c) Results of a positive pH test.

Procedure: Dissolve 3 drops or 30 mg of sample in 1 mL of water. Dip a glass stirring rod into the solution and touch the rod to blue litmus paper. A positive result is a pink or red color on the litmus paper (Figure 6.68c). If the sample doesn't dissolve in water, instead dissolve the same amount of unknown in 1 mL of ethanol. Add enough water to make the solution barely cloudy. Then add a few drops of ethanol to turn the solution clear again, and test with the litmus paper.

6.4.D.12 PHENOL TEST

A ferric chloride solution is a test for phenols, as they form intensely colored complexes with Fe^{3+} (often dark blue). The actual structure of these complexes is debated,[15] but may be of the general form in Figure 6.69. Some carbonyl compounds with high enol content can give false positives with this test.

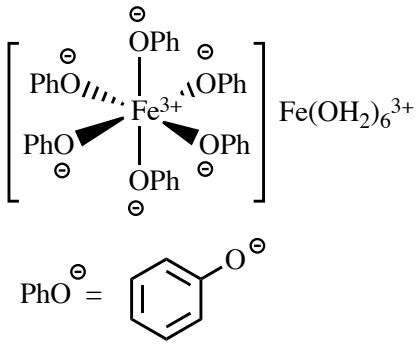


Figure 6.69: Proposed structure of color complex of Fe^{3+} with phenol.

Procedure: Place 1 mL water in a small test tube (13 × 100 mm) along with either 3 drops or 30 mg of sample. Add 3 drops of the yellow 5% $FeCl_3$*(aq)* solution, and mix by agitating.

A positive result is an intense blue, purple, red, or green color while a negative result is a yellow color (the original color of the $FeCl_3$ solution, Figure 6.70).

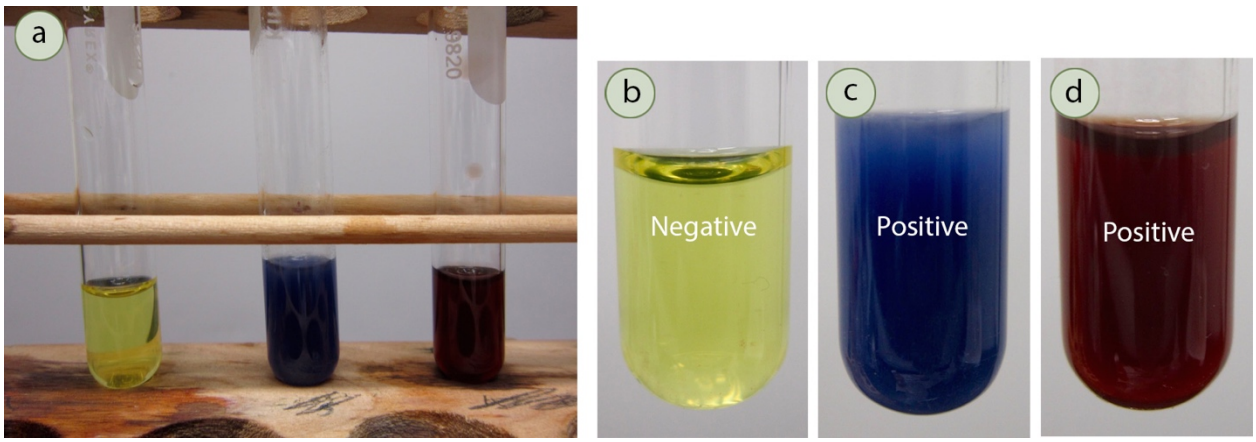


Figure 6.70: a) Phenol test results (left to right) lactic acid (negative), *p*-cresol (positive), pyrogallol (positive), b) Negative result, c) Positive result (typical color), d) Positive result (less common color, by pyrogallol, a bidentate ligand).

[15] See *Nature*, 24 June **1950**, 165, 1012.

6.4.D.13 SILVER NITRATE TEST

A dilute solution of silver nitrate in ethanol is a test for some alkyl halides. Silver has a high affinity for halogens (forms strong AgX ionic bonds), and so encourages an S_N1 mechanism. For this reason, 3˚ alkyl halides react faster than 2˚ alkyl halides (which may or may not react, even with heating), and 1˚ alkyl halides or aromatic halides give no reaction. Benzylic ($PhCH_2X$) and allylic ($CH_2=CHCH_2X$) alkyl halides will also give a fast reaction. A positive test result is the formation of the insoluble AgX (Figure 6.71). AgCl and AgBr are white solids, while AgI is a yellow solid.

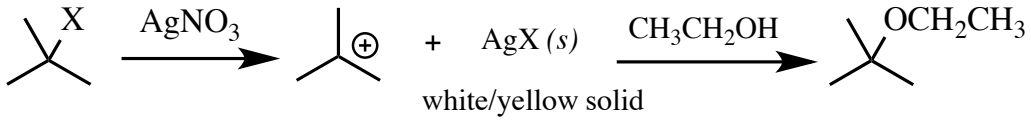


Figure 6.71: Reaction of alkyl halides with the silver nitrate solution.

Procedure: In a small test tube (13 × 100 mm), add 2 mL of 1% $AgNO_3$ in ethanol solution. Add 4 drops of liquid sample or 40 mg of solid dissolved in the minimal amount of ethanol. Mix the test tube by agitating. Some compounds will have an initial insolubility when first mixed, but the solid often dissolves with swirling. A positive result is a sustaining white or yellow cloudiness. If cloudiness does not occur within 5 minutes, heat the tube in a 100 ˚C water bath for 1 minute (Figure 6.72b). Absence of cloudiness even at 100 ˚C is a negative result (Figures 6.72 + 6.73).

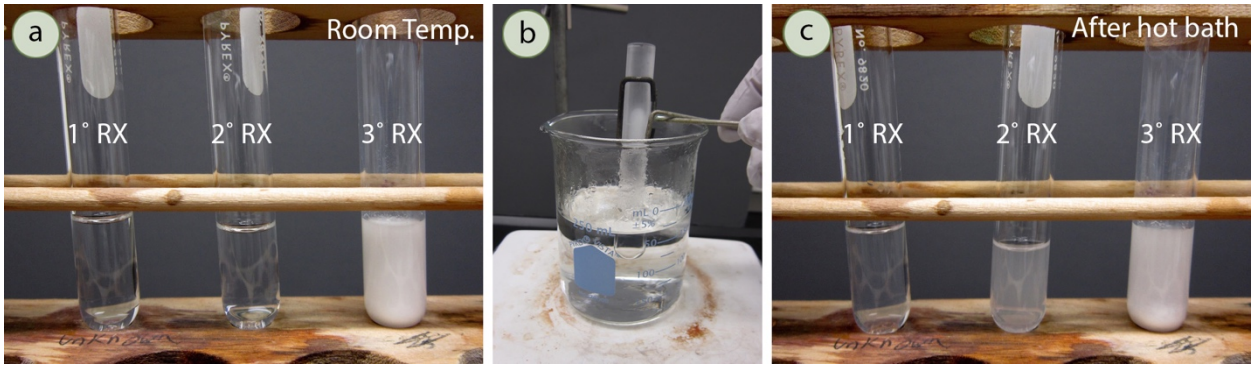


Figure 6.72: a) Silver nitrate results at room temperature, (left to right) 1-chlorobutane (1˚, negative), 2-chlorobutane (2˚, negative), 2-chloro-2-methylpropane (3˚, positive), b) Boiling water bath, c) Results after boiling water, middle tube is faintly cloudy (2˚, positive).

For reactions that produce an intense precipitate, the solution may also turn blue litmus paper pink (Figures 6.73 c+d). An analysis of the reaction mechanism can explain the source of this acidity.

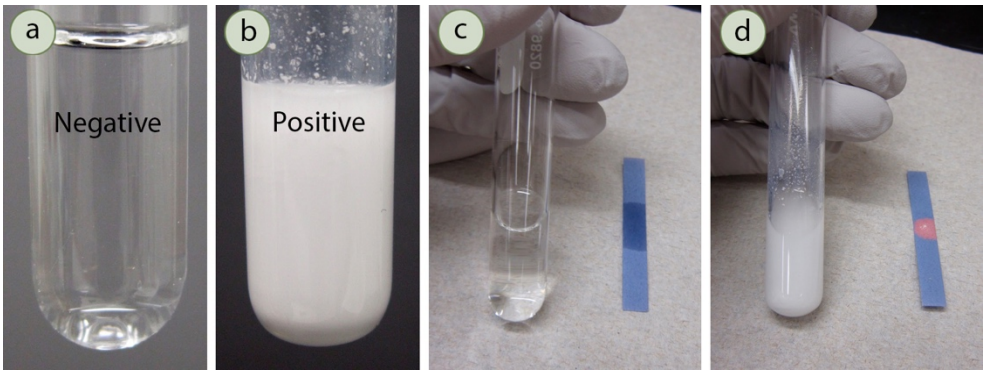


Figure 6.73: a) Negative result, b) Positive result, c) Litmus test on a negative $AgNO_3$ test, d) Litmus test (acidic) on a positive $AgNO_3$ test.

6.4.D.14 SODIUM IODIDE (FINKELSTEIN) TEST

A solution of sodium iodide in acetone is a test for some alkyl chlorides and bromides. The mechanism is largely S_N2, so 1˚ alkyl halides react faster than 2˚ alkyl halides, and 3˚ alkyl halides generally give no reaction. The reaction is driven by the precipitation of the NaCl or NaBr in the acetone solvent. Therefore, a positive test result is the appearance of a white cloudiness (NaX solid).

$$CH_3CH_2X + NaI\ (acetone) \rightarrow \underset{\text{white solid}}{CH_3CH_2I + NaX\ (s)} \quad (X = Cl, Br)$$

Procedure: In a small test tube (13 × 100 mm), add 2 mL of 15% NaI in acetone solution.[16] Add 4 drops of liquid sample or 40 mg of solid dissolved in the minimal amount of ethanol. Mix the test tube by agitating.

A positive result is a sustaining white cloudiness. If cloudiness does not occur within 5 min, heat the tube in a 50 ˚C water bath for 1 minute. Absence of cloudiness even at 50 ˚C is a negative reaction (Figure 6.74 + 6.75).

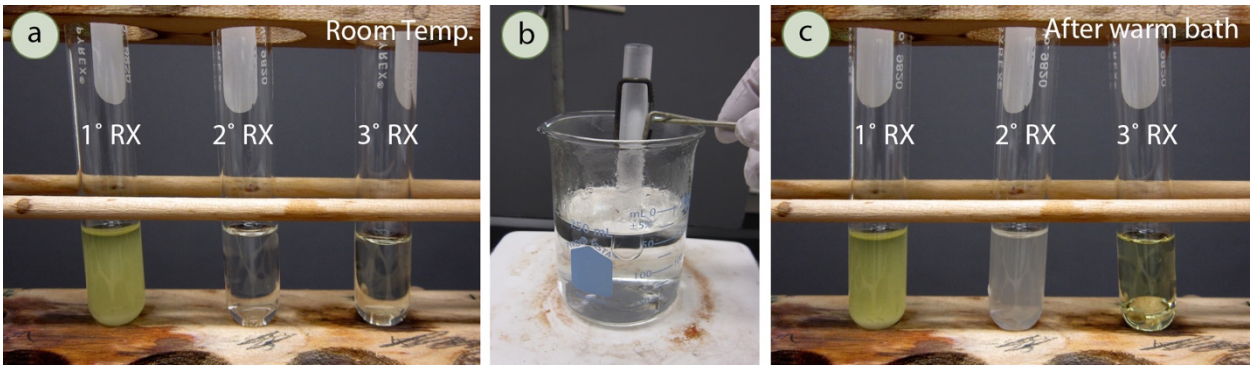


Figure 6.74: Sodium iodide results at room temperature, (left to right) 1-chlorobutane (1˚, positive), 2-chlorobutane (2˚, negative), 2-chloro-2-methylpropane (3˚, negative), b) Heating in a warm water bath, using a thermometer to monitor the temperature, c) Results after the warm water bath water, resulting in the clouding of the middle tube (2˚, positive).

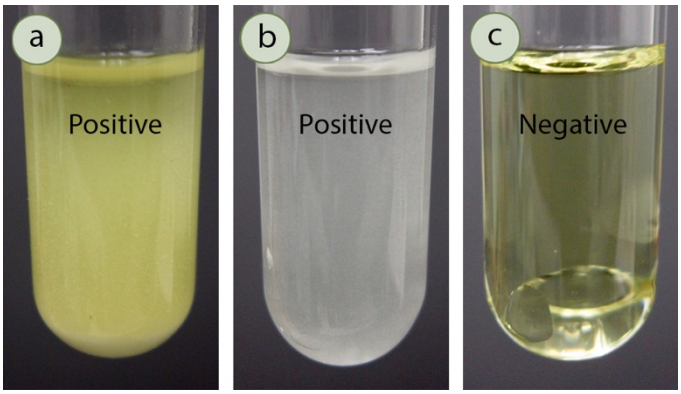


Figure 6.75: a) Positive result (1˚ alkyl halide), b) Positive result after heating in a 50 ˚C water bath (2˚), c) Negative result (3˚).

[16] This solution often has a yellow tint to it.

6.4.D.15 TOLLENS TEST

The Tollens reagent ($Ag(NH_3)_2^+$) is a mild oxidizing agent that can oxidize aldehydes, but not alcohols or other carbonyl compounds. A positive test result is the formation of elemental silver (Figure 6.76), which precipitates out as a "silver mirror" on the test tube, or as a black colloidal precipitate.

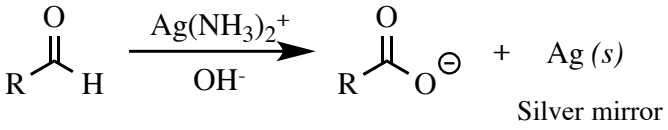


Figure 6.76: Reaction of an aldehyde with the Tollens reagent.

Procedure: While wearing gloves, mix 1 mL of 5% $AgNO_3$ *(aq)* (**safety note:** toxic!) with 1 mL of 10% NaOH *(aq)* in a medium-sized test tube (18 × 150 mm). A dark precipitate of silver oxide will form (Figure 6.77b). Add dropwise enough 10% NH_4OH *(aq)* to just dissolve the precipitate (note some time should be allowed in between additions). This solution is now the Tollens reagent $Ag(NH_3)_2^+$ (Figure 6.77c).

Dissolve 3 drops or 30 mg of sample in a few drops of diethyl ether (omit solvent if compound is water soluble). Add this solution to the 2-3 mL of previously prepared Tollens reagent. Mix the test tubes by agitating. A positive result is a silver mirror on the edges of the test tube, or formation of a black precipitate. A negative result is a clear solution (Figures 6.77d + 6.78).

Clean-up: The reagent may form a very explosive substance (silver fulminate) over time, so the test should be immediately cleaned up. Acidify the solution with 5% HCl *(aq),* then dispose in a waste beaker. A silver mirror can be removed from the glassware by adding a small amount of 6 *M* HNO_3 *(aq)*.

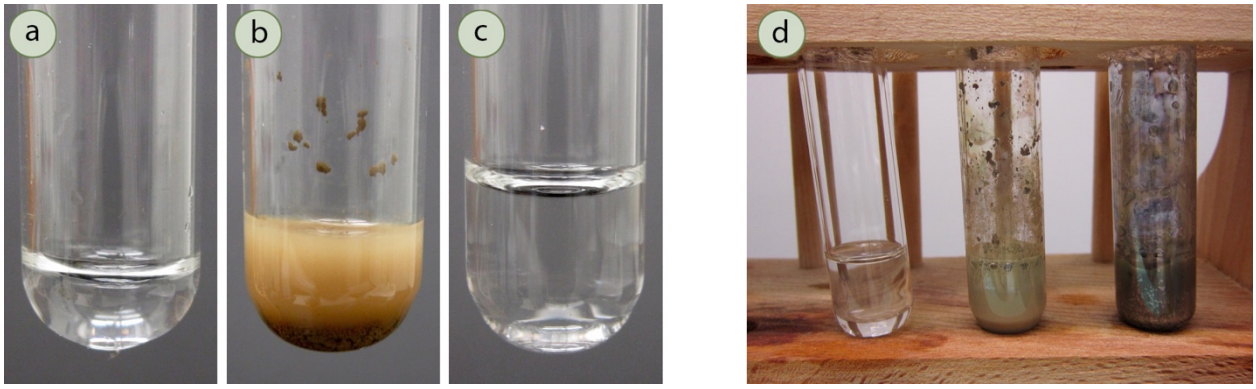


Figure 6.77: a) Silver nitrate solution, b) Ag_2O precipitate formed after addition of NaOH, c) Clarified solution after the addition of ammonium hydroxide, d) Tollens test results: (left to right) 2-pentanone (negative), isobutyraldehyde, benzaldehyde (positive).

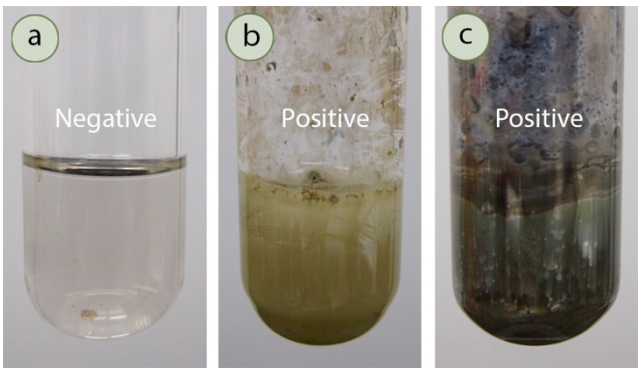


Figure 6.78: a) Negative result, b+c) Positive results.