# Experiment 3
## Preparation of *tert*-Butyl Chloride

The purpose of this experiment is to prepare *tert*-butyl chloride (2-chloro-2-methylpropane) from *tert*-butyl alcohol (*tert*-butanol) using an acid catalyzed substitution reaction. (Note: the correct IUPAC name for this compound is 2-methyl-2-propanol).

We will also use a separatory funnel, the use and purpose of a drying agent and the technique of distillation. The reaction is shown in Figure 3.1



**Figure 3.1** Preparation of *t*-Butyl Chloride
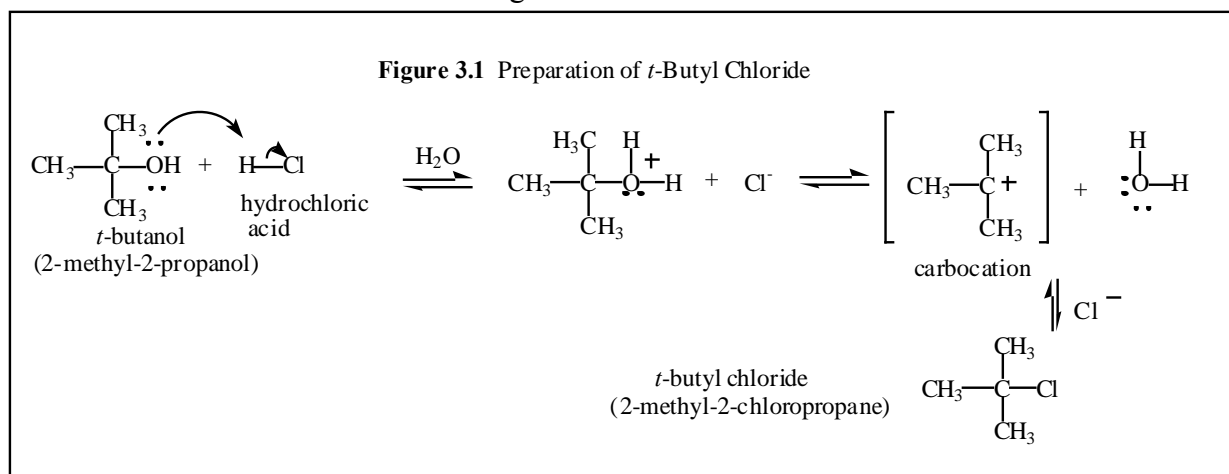
The first step of the overall reaction is an acid-base reaction between the *t*-butanol and the hydrochloric acid. The *t*-butanol is a weak base and the hydrochloric acid is a strong acid. The alcoholic oxygen becomes fully protonated and so the equilibrium lies far to the right. In the second step we have the slow loss of water to form a carbocation intermediate. This species is very reactive and is immediately attacked by the chloride ion liberated in the first step to form the final product. This is an example of an $S_N1$ reaction (Substitution Nucleophilic Unimolecular).
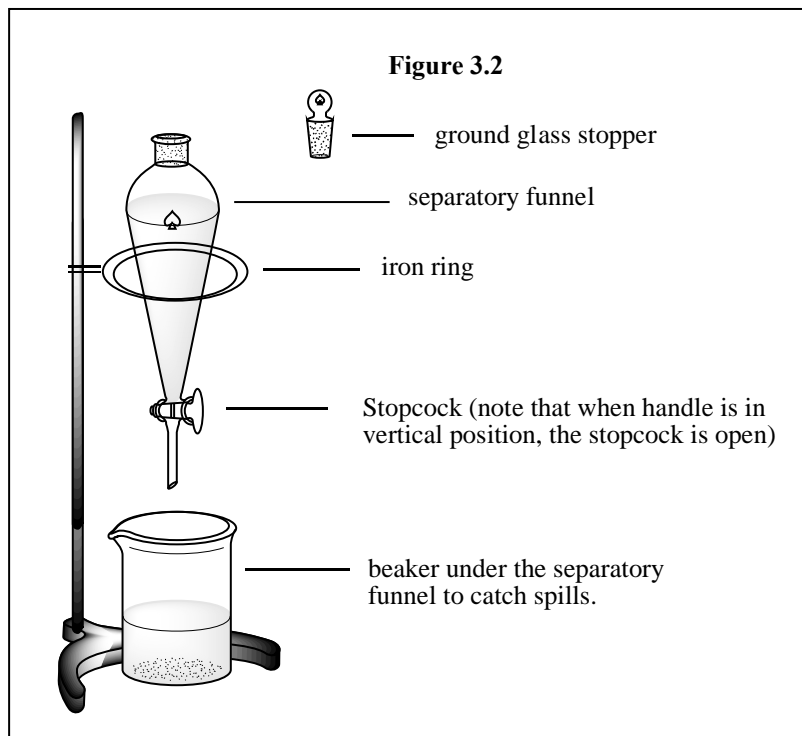
## Physical Constants

| Compound | Mol. Wt (g/mol) | Density (g/mL) | b.p. (°C) | m.p. (°C) |
|---|---|---|---|---|
| 2-Methyl-2-propanol | 74.12 | 0.775 | 83 | 25 – 26 |
| 2-Chloro-2-methylpropane | 92.57 | 0.85 | 51 – 52 | -25 |
| Hydrochloric acid | 37% soln in $H_2O$ | 1.18 | | |

## Proper Use of the Separatory Funnel

Set up the separatory funnel as shown in Figure 3.2. Use a small iron ring stand to hold the funnel. You can also use a metal clamp attached to the top neck of the separatory funnel but the iron ring is more convenient. **ALWAYS KEEP A BEAKER UNDERNEATH THE SEPARATORY FUNNEL TO CATCH ANY SPILLS.** When the handle of the stopcock is parallel to the separatory funnel (see shown in Fig. 3.2), the stopcock is in the open position. When the handle is perpendicular to the length of the funnel it is closed.

With the stopcock in the closed position, pour in your solution into the top of the funnel. Place a very small amount (just a tiny dab) of stopcock grease on the ground glass stopper. Insert the glass stopper. Hold the funnel in one hand by grasping the top around the glass stopper. Lift it from the iron ring and **SLOWLY** invert the funnel, holding it with your other hand. When it is now upside down, the glass stopper should be in the

palm of one hand, holding it securely.  **IMMEDIATELY VENT** the funnel by opening the stopcock and pointing the end of the funnel **AWAY** from your lab neighbor.  **CAUTION**: always vent the



**Figure 3.2**

ground glass stopper

separatory funnel

iron ring

Stopcock (note that when handle is in vertical position, the stopcock is open)

beaker under the separatory funnel to catch spills.

separatory funnel immediately when you invert it.  Pressure can build up and the contents of the funnel can shoot out uncontrollably.

Once you have vented the separatory funnel, close the stopcock and shake it **GENTLY AT FIRST** 2-3 times.  Then VENT the funnel again.  Now you can shake it more vigorously several times.  Then vent it again. You may hear the sound of escaping gases when you open the stopcock to vent.  Once this subsides then it is safe to shake the separatory funnel vigorously for 2-3 minutes.  It is very important to shake the funnel very thoroughly to ensure intimate mixing of the two layers.

When you have finished shaking, replace the separatory funnel back in the iron ring and **REMOVE THE GLASS STOPPER** before draining off the bottom layer.  Otherwise you will create a vacuum inside the separatory funnel and it will not drain.

Note that if there are two layers in a separatory funnel it is because the two liquids contained in the funnel are not soluble in each other.  In most of our experiments, including the one today, we have a relatively non-polar organic layer – usually containing the product that we want to isolate – and a polar aqueous layer. The more dense layer is on the bottom.  In many cases, this is the water layer (recall that oil floats on the surface of water), but not always!!  Be careful.  When using the separatory funnel, **ALWAYS SAVE BOTH LAYERS** until you are sure that you have isolated the correct layer.  Never throw anything away until you are finished with your experiment.  To test which layer is which – organic or aqueous – simply add a little water to the layer that you think is the aqueous layer.  If you see only one layer then you were correct in thinking that this was the aqueous layer.

**Experimental Procedure**

Place 35 mL of concentrated hydrochloric acid in a small beaker (100 mL) or small Erlenmeyer flask (50 mL) and cool for five minutes in an ice bath. Add 12.0 mL of *t*-butanol slowly with pipette to the concentrated HCl in the **open** beaker or Erlenmeyer flask. Swirl the solution with a glass stirring rod or metal spatula to mix the t-butanol and the hydrochloric acid thoroughly. Pour the mixture into your separatory funnel and allow to stand with the stopper off for **20 minutes**. Swirl the mixture occasionally. You will gradually see two layers forming. (What are they?)

**Work-up:**
After twenty minutes drain off the bottom layer. This is the aqueous layer. It is waste, but be sure to save it until you have finished with the experiment.

Add 10 mL tap water to the separatory funnel and shake again several times to mix the two layers. Again separate the aqueous layer and set it aside. (You can save this with the first aqueous layer.)

Add 10 mL 5% sodium bicarbonate solution to the separatory funnel. Be careful here. The sodium bicarbonate is a weak base. The purpose for adding this is to neutralize any hydrochloric acid that may be remaining. When it reacts with the hydrochloric acid, carbon dioxide gas is given off. Pressure can build up very quickly in a closed separatory funnel and your solution will shoot out of the funnel (just like when you shake up a can of soda). The reaction is shown in Figure 3.3.



**Figure 3.3** Formation of Carbon dioxide From Sodium Bicarbonate
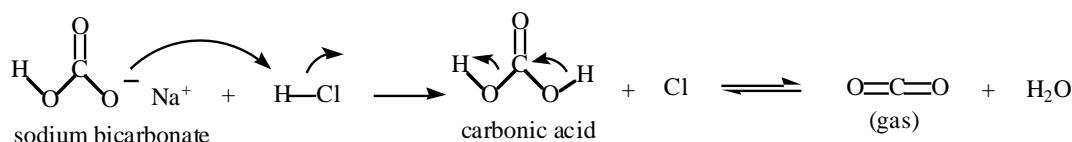
**CAUTION: PRESSURE BUILD-UP!**
Be sure to swirl the separatory funnel and mix the bicarbonate layer and the organic layer with a glass stirring rod before you begin to shake the funnel. Do not put the stopper in the funnel until you see that all visible bubbling of the carbon dioxide has ceased. When you first invert the separatory funnel, vent immediately to release the pressure. Then shake gently at first, vent, etc.

Drain the sodium bicarbonate layer into a separate container (save this as always).

Add 10 mL tap water and shake one more time. Drain off this layer and save.

Prepare a clean, dry 25 mL Erlenmeyer flask. Cover the bottom sparsely with calcium chloride drying agent. Do not use too much drying agent since some of your compound will adhere to the drying agent and be lost. Pour the contents of the separatory funnel (it now contains your product) from the top opening into the Erlenmeyer with the drying agent. Stopper the flask with a cork and let stand for 10-15 minutes while you set up the apparatus for distillation (see Figure 3.6 and discussion below).

When you have your apparatus set-up, remove the thermometer and thermometer adapter and decant your product into the distilling flask using your long-stemmed funnel. If you are careful you can pour all of the liquid into the flask without also pouring any of the drying agent. You can also use a tiny piece of cotton (about the size of the end of your little finger) as a plug in your long-stemmed funnel to catch any drying agent.

**Be sure to add 2-3 boiling chips to the distilling flask. (refer to Appendix 3.3)**
Before you begin your distillation, have your instructor check your set-up. The rheostat is an auto-transformer and the numbers on the rheostat correspond to volts. The correct setting depends on the size of the

flask and the size of the heating mantle and the desired reaction temperature.  In this case a setting of 35-45 Volts should be sufficient.  If your product does not boil you can slowly increase the rheostat setting.

Distill your product collecting the fraction that boils between 49 – 52°C.  Any material that boils before 49°C is not what you want and any material that boils above 52°C is also not the correct material.  Watch the thermometer carefully, collecting only material in the specified boiling range.

Pour your product into a clean, weighed vial, record the weight of the contents and submit this to your Teaching Assistant.  Calculate your percent yield and turn this in on your Organic Yield Report Sheet.
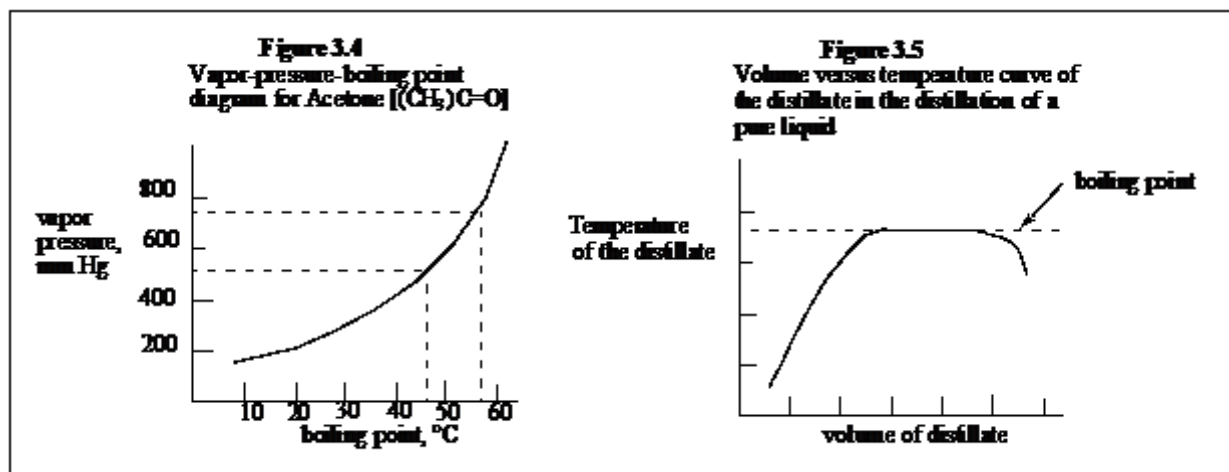
## Appendix 3.1  Distillation
## Theory and Background:

Distillation is the separation of liquids by vaporization and condensation of the vapor back to the liquid phase.  It is an excellent and convenient way to purify liquids.  The liquid to be purified is put into the distilling flask which is heated to the boiling point of the liquid.  The vapors then rise up to the thermometer at the top of the three-way adapter which has a sidearm attached to the cold condensing column.  When the hot vapors hit the cold condensing column they condense back to liquid and are collected in the receiving flask.

The boiling point of a liquid is defined as the temperature at which its vapor pressure equals the atmospheric pressure.  It is characterized by vigorous bubbling of the liquid as it vaporizes.  The actual temperature of a boiling liquid is sometimes higher than the boiling point of the compound due to superheating, which is ameliorated by the use of boiling chips.
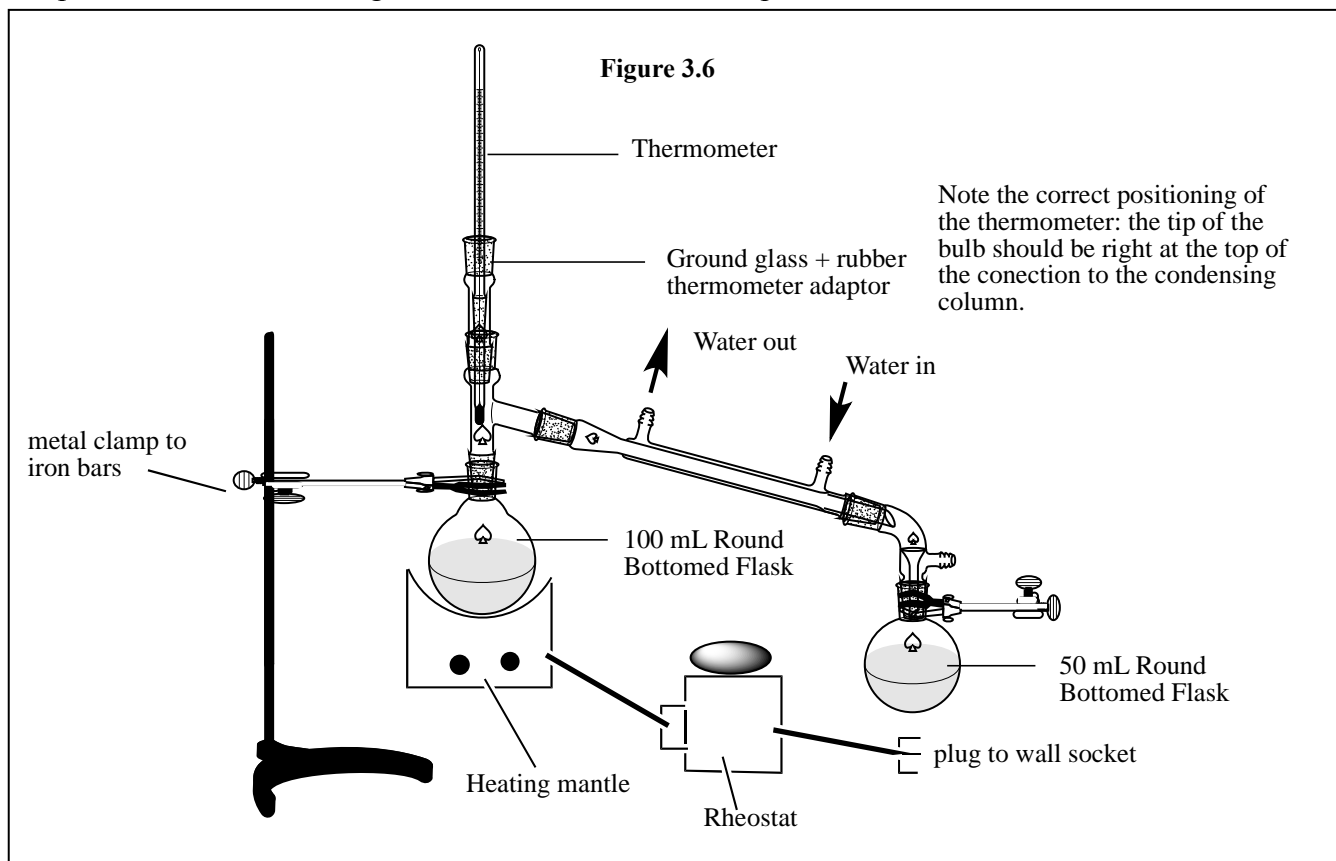
The boiling point is a function of the atmospheric pressure.  As we lower the atmospheric pressure we also lower the boiling point.  This relationship is shown in Fig 3.4 for acetone.  At 760 mm Hg (atmospheric pressure) the boiling point of acetone is 56.2 °C, but at 500 mm Hg it is only about 45 °C.



Figure 3.4
Vapor-pressure-boiling point diagram for Acetone [(CH$_3$)$_2$C=O]

Figure 3.5
Volume versus temperature curve of the distillate in the distillation of a pure liquid

When a reasonably pure liquid is distilled, the observed temperature rises rapidly to the boiling point (see Figure 3.5).  Once the distillation apparatus has reached thermal equilibrium, the boiling point remains relatively constant, not changing more than 1-2 ° during the distillation.  When there is a significant drop in temperature, it is a good signal that the desired compound has all distilled.  But be careful here.  Very often the temperature can drop as the distillation proceeds because the volume of distillate decreases as you get toward the end.  Usually you need to increase the heat in order to drive all of the distillate up the column.

## General Procedure for Set-up of Distillation Apparatus

The set-up of the apparatus for distillation is shown in Figure 3.6. You really need to use only two metal clamps. Those with three fingers are best. Follow these steps:

**Figure 3.6**

Thermometer

Ground glass + rubber thermometer adaptor

Note the correct positioning of the thermometer: the tip of the bulb should be right at the top of the conection to the condensing column.

Water out

Water in

metal clamp to iron bars

100 mL Round Bottomed Flask

50 mL Round Bottomed Flask

plug to wall socket

Heating mantle

Rheostat

1. First set up the heating mantle on the iron ring at a convenient height (12-16 inches) above the bench top. Make sure it is the correct size for the flask. Attach it to one of the vertical bars on the lab bench.
2. Then clamp the distilling flask securely in the heating mantle so that the flask is touching the bottom of the heating mantle. **Be sure to add your boiling chips!**
3. Add the three-way adapter. You do not need a clamp for this, since it is positioned vertically.
4. Attach the condensing column to the three-way adapter, using one of the blue plastic clamps to secure the joint. Note that the smaller ring of the plastic clamp fits over the inner tube of the three-way adapter and the larger ring of the clamp fits over the outer tube (the larger tube) of the condenser. The plastic clamp spans the joint connection.
5. Attach the vacuum adapter to the end of the condensing column using a second blue plastic clamp. Attach your water hoses so that the hose providing the water-in is connected to the lower end of the condenser. The water should always flow "up-hill". This provides better cooling. Only a slow flow of water is required. You should see just a trickle of water coming out of the exit tubing.
6. Attach the receiving flask to the end of the vacuum adapter using a burette clamp. Attach the metal clamp to a vertical bar on the bench top.
7. First put the red neoprene adapter over the ground glass thermometer adapter and then carefully slide the thermometer through the hole in the rubber adapter leaving a small portion of the thermometer sticking out. Attach the thermometer adapter and thermometer to the three-way adapter so that the ground glass portions are joined together. Adjust the height of the thermometer so that the bulb of the thermometer is just at or below the

level of the sidearm.  Correct positioning of the thermometer is critical to getting accurate measurements of the boiling point.

8.  Plug-in the heating mantle into the rheostat and plug the rheostat into the outlet.  Have your instructor or Teaching Assistant check your set-up before finally turning on the rheostat.  Note that the exact setting on the rheostat varies with the size of the flask, the size of the heating mantle and the boiling point of the solvent used in the particular experiment.  Check with your instructor as to the proper setting.

   Do not heat your distilling flask too quickly.  The proper rate of distillation is about one drop of distillate every 2-3 seconds.


## Appendix 3.2 Drying Agents

   Often, when we prepare a liquid sample it is still contaminated with small amounts of water or other impurities, especially when we have used the separatory funnel in the work-up.  A good way to remove the contaminating water is to add a drying agent.  We will use two drying agents in this course, calcium chloride and magnesium sulfate.

**Calcium chloride**:  This is a very effective drying agent and has a high capacity for water but it reacts rather slowly.  It usually takes 10 -15 minutes to react with all of the water in the sample.  It is available in pellet form and so the liquid is easily decanted from the drying agent.  It has a major limitation, however.  Calcium chloride is a good Lewis acid and so also binds strongly to alcohols, amines, phenols and to other polar functional groups.  For this reason it should be used mainly with hydrocarbons and with alkyl halides.  When it reacts with water it tends to form large clumps.  Be sure that there are still a few loose pellets still present to ensure that enough drying agent has been added.  But do not add too much drying agent or you will lose some of your compound.  A good rule of thumb is to add enough drying agent to just cover the bottom of the container.  Choose a container so that is will be about 1/3-1/2 full when it contains your product.  Always close the container (usually a 25 or 50 ml Erlenmeyer flask) after you have added your drying agent.

   As with all drying agents, you must close the bulk container of the drying agent tightly after you remove your material.  Otherwise, the drying agent will lose is potency by absorbing water from the humid atmosphere.  For calcium chloride, the reaction with water is as follows:


**Anhydrous magnesium sulfate**:  This usually reacts faster than calcium chloride and is safer to use with a wide variety of organic compounds (though still not with alcohols).  This is a fluffy white powder that has a high surface area and settles slowly to the bottom of an organic solution.  When it reacts with water it tends to form clumps at the bottom of the flask.  Add a small amount of magnesium sulfate and swirl.  If all of the material has formed clumps, then more drying agent needs to be added until some fluffy material remains.  Again, do not use too much since it will bind other polar molecules besides just water and also  be sure to stopper the bulk container.


## Appendix 3.3  Boiling Stones or Boiling Chips

   Boiling stones are small porous stones of calcium carbonate (marble) or silicon carbide that contain trapped air.  When the chips are heated in a solvent, they release tiny air bubbles which ensure even boiling.  When all the air has been released, the stone's pores provide cavities where bubbles of solvent vapor can form.  Without boiling chips, part of the solvent may become superheated and boil in sudden and often violent bursts.  This is called bumping.  It can be dangerous and can result in the loss of some of your product.  Sometimes the bumping can be so violent as to cause the stopper or thermometer to explode from the flask and spew boiling solvent and product over your bench.

You generally need only two or three boiling chips to prevent bumping. **Never add boiling chips to a hot solution**. If a solution is at or near the boiling point, then the addition of boiling stones will cause the flask to boil up suddenly and most likely some of the boiling liquid will escape uncontrollably from the flask.

Boiling stones will maintain their function for a long period of boiling but once they are used and cooled, the pores of the stones become filled with solvent and lose their ability to release small bubbles. Therefore, if the solution is cooled and reheated, **fresh boiling stones should be added.**

## Appendix 3.4: Percent Yield Calculation

Percent yield is defined as:

Percent yield = (actual yield/theoretical yield) x 100.

The actual yield is the number in grams of the product that you actually isolate at the end of the experiment.

The theoretical yield is the number of moles of the limiting reagent times the molecular weight of the product. The limiting reagent is defined as the reagent that is present in the smallest number of equivalents used in the reaction. It is almost always the organic starting material and the number of equivalents is simply the number of moles used divided by the stoichiometric coefficient.

Sample Calculation. For the reaction shown in Figure 3.4, two equivalents of methanol



**Figure 3.7**

terephthalic acid

dimethyl terephthalate
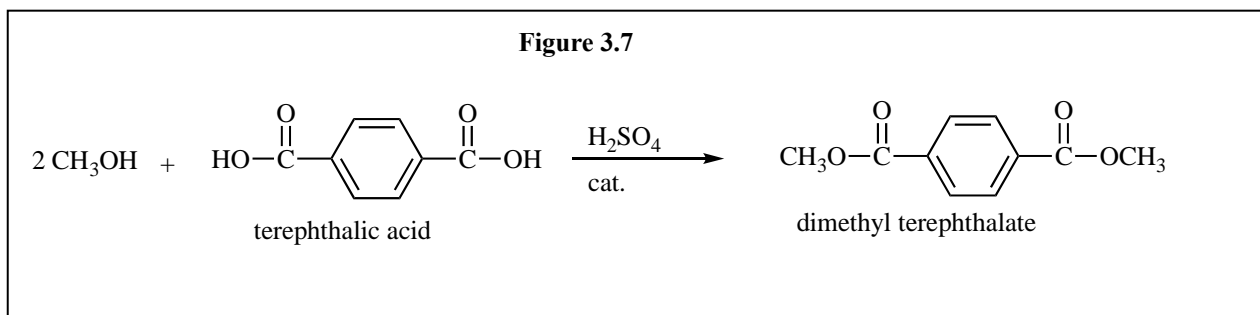
react with one equivalent of terephthalic acid to give one equivalent of dimethyl terephthalate. So, for every mole of terephthalic acid consumed, two moles of methanol are also used up. The catalyst, $H_2SO_4$, is not consumed in the reaction and therefore it does not have to be considered when determining the limiting reagent. To find the number of equivalents, simply divide the number of moles by the stoichiometric coefficient.

For example, if we do a reaction in which we start with 1.0 g of terephthalic acid and use 5 mL of methanol and 3 drops of sulfuric acid and isolate 0.65 g. of product, the table of reagents that summarizes the information is given below.

### Physical Constants

| Compound | Mol. Wt (g/mol) | Amt used | Density (g/mL) | Wt used(g) | Moles used | Equiv. used |
|---|---|---|---|---|---|---|
| Terephthalic acid | 166.14 | 1.0 g | solid | 1.0 | 0.00602 | 0.00602 |
| Methanol | 32.04 | 5 mL | 0.7914 | 3.96 | 0.124 | 0.0620 |
| Sulfuric acid | 98.08 | 3 drops | 1.84 | 0.2 | Not used up | Not used up |

The smallest number of reaction equivalents is 0.00602 for terephthalic acid.  It is therefore the limiting reagent.

Therefore:  theoretical yield = moles limiting reagent x molecular weight of product
= 0.00602 mol x 194.19 g/mol = 1.17 g

Therefore, the Percent yield = (0.65 g/1.17 g) x 100 = 56%.

Another way to calculate the percent yield is to divide moles of product by moles of limiting reagent used.

Moles Product = (0.65 g)/ (194.19 g/mol) = 0.00347 mol
Therefore, % yield = (0.00347 mol/0.00602 mol) x 100 = 56%