# Distillation of Alcohol

- To learn about the separation of substances.
- To learn about the separation technique of distillation.
- To learn how to characterize a substance using its density.
- To learn about fermentation.

In this laboratory exercise, we will distill a ferment to boost its Alcohol content. For the present case, our ferment will be a sample of a commercially produced wine of about 10-12% Alcohol and the resulting distillate will be a crude form of brandy. We will characterize the resulting Brandy by its density, its combustibility and its boiling point. The density measurement will allow us to determine the Volume Percentage Alcohol in the Brandy, which will in turn allow us to determine its Proof. The simple distillation process we will employ typically produces a Brandy of approximately 120-140 Proof.

Alcohols are important industrially and commercially. Principally important commercial alcohols include Methanol, Ethanol, Isopropanol and Ethylene Glycol. Ethanol, or Ethyl Alcohol, is used as a solvent, fuel additive, and in lotions, tinctures and medicines. It is probably most familiar as the alcohol of alcoholic beverages and is referred to generically as Alcohol, Common Alcohol or Grain Alcohol. For this last purpose, Ethanol (CH_3CH_2OH; or EtOH for short) is produced by fermentation of sugars. Fermentation alone does not produce beverages with an Alcohol content greater than 12 to 15% because the fermenting yeast is destroyed at high Alcohol concentrations. To produce beverages of higher Alcohol content the aqueous ferment must be distilled.

The fermentation of carbohydrates into Alcohol is one of the oldest known chemical processes. Fermentation can be represented as:

$$Sugar \longrightarrow Alcohol + Carbon\ Dioxide \qquad (Eq.\ 1)$$
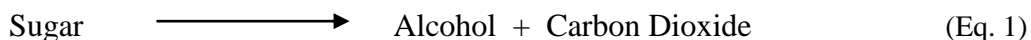
The reaction is catalyzed by yeast enzymes called zymases. A balanced chemical reaction for this process, assuming the sugar is Table Sugar or Sucrose, is:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 4\ CH_3CH_2OH + 4\ CO_2 \qquad (Eq.\ 2)$$
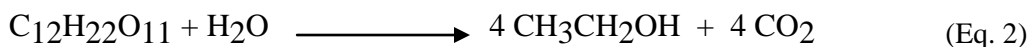
The fermentation process is started by mixing a source of sugar, water and yeast and allowing the yeast to act in an oxygen free environment. This anaerobic environment forces the yeast to shut down the "burning" of sugar and allows them to instead ferment Alcohol.
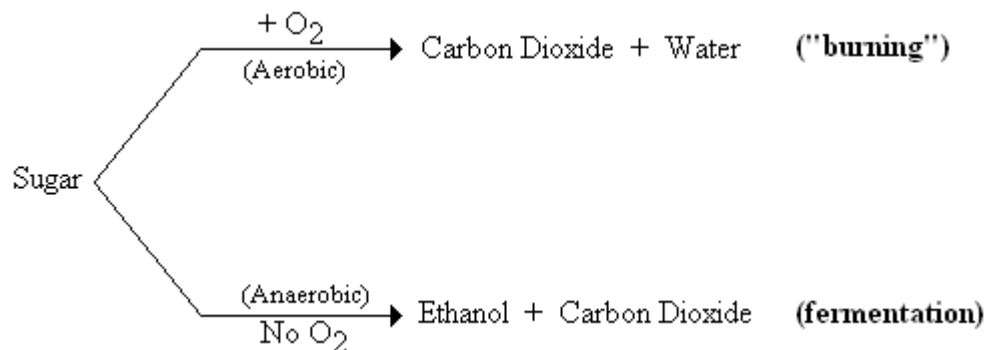
Commercially, fermentation is the first step in the production of wine, beer, mead and cider.

The Alcohol produced by this fermentation process can be concentrated from the aqueous solution in which the fermentation takes place by distillation.

Distillation is a separation process for a mixture of liquids or oils. It relies on differences in the boiling points of the component liquids to be separated. The mixture to be separated is added to a Distilling Pot where it is heated to the boiling point. Lower boiling components will preferentially vaporize first. The resulting vapor passes into a Distilling Head and then into a

Condensor. Within the Condensor the vapor is cooled and it liquifies. The resulting liquid is then collected in a Receiving Flask. Initially, low boiling components are collected in the Receiving Flask. As the distillation proceeds, these components are depleted from the Distilling Pot and higher boiling components begin to distill over. Switching out the Receiving Flask at the appropriate point allows for the separation of the component liquids of the mixture.

The particular type of distillation we will be employing in this laboratory is known as Simple Distillation. Simple distillation works particularly well on mixtures of two liquids which have a very large boiling point difference. The lower boiling component distills off first and can be collected. The higher boiling component then follows. A downside of simple distillation is that the purity of the distillate is rarely 100%. This is because the distillation vapor is only enriched in the lower boiling component. Some of the higher boiling component will be present as well. So the condensed distillate will be a mixture enriched in the lower boiling component, but still containing some of the higher boiling component. To make matters worse, as the distillation proceeds, the liquid in the distilling pot will have a greater, and greater percentage of higher boiling component. Hence, the distillate, over time, will wind-up containing more, and more of the higher boiling component.
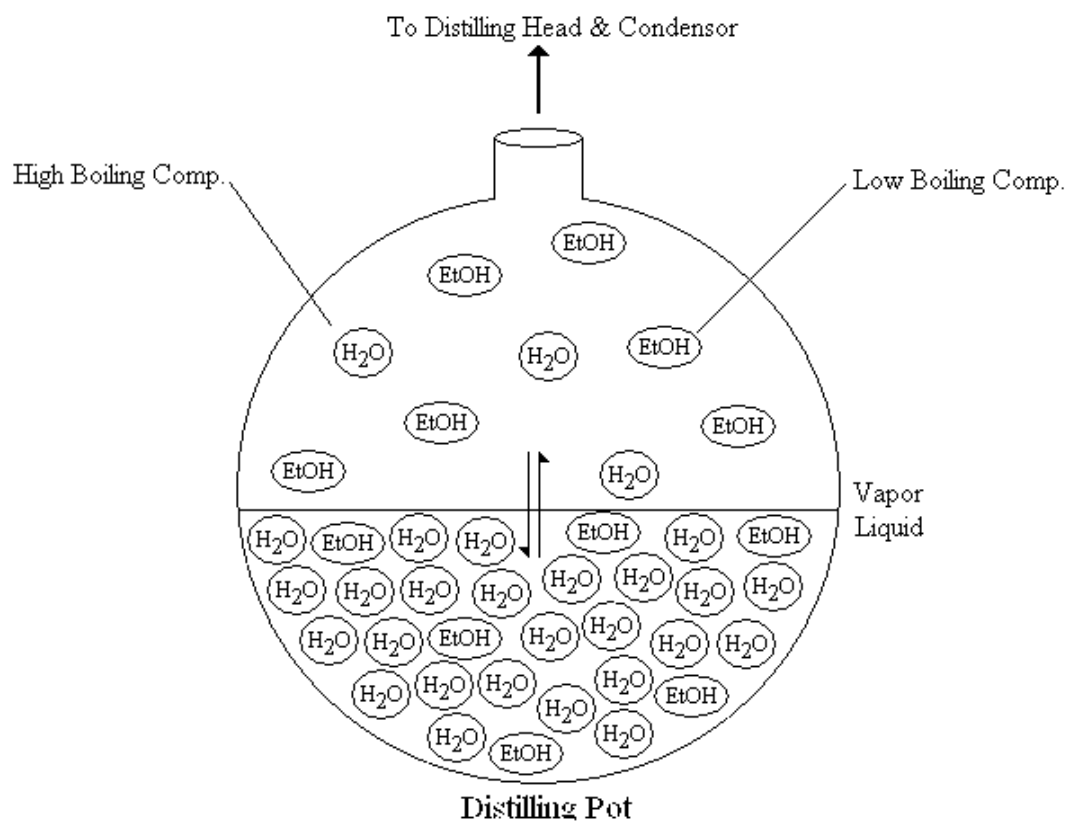
Mixtures of a large number of similarly boiling liquids can be separated by a technique called Fractional Distillation. In fractional distillation, a fractionating column allows the vapor arising from the distillation pot to be repeatedly recondensed and revaporized. After a number of these recondensation/revaporization steps, the lower boiling component will be relatively free of any higher boiling components. This allows for a more thorough separation of the liquids. This

method of distillation is employed to separate the hydrocarbon components of Crude Oil as a part of the Refining process.

Medium Heavy Crude Oil

Gasoline
(Key Hydrocarbon Component of Crude Oil)

Distillation of Alcohol from an Alcohol/Water ferment is the second major step in producing Liquor. The source of the fermentation sugar helps define the type of liquor to be produced.

Liquor	Sugar Source
Brandy	Grapes, Apple, Pear
Whisky	Barley, Rye, Wheat, Corn
Gin	Grapes, Sugar Beets, Sugarcane
Vodka	Potato, Grain
Rum	Molasses
Tequila	Agave

Whisky Still
https://en.wikipedia.org/wiki/Distilled_beverage

19th Century Bourbon
By Gettysburg National Military Park, GETT 31373 -http://www.cr.nps.gov/museum/treasures /html/B/gett31373.htm, Public Domain, https://commons.wikimedia.org/w/index.php?curid=336178

Ethyl Alcohol has a boiling point of 78.5^{o}C and that of Water is 100°C. Hence, initially a simple distillation will be relatively efficient in enriching Alcohol. But, because the simple distillation process is not 100 % efficient, we will have to determine the Alcohol content of our distillate. This can be done by measuring its density, which as we have seen previously depends heavily on the composition of the system. The density of a substance, be it a pure substance or a mixture, is given by:

$$density = \frac{mass}{volume}$$ (Eq. 3)

We can compare our distillate's density with tabulated values of the density of known mixtures of Alcohol and Water to determine its Alcohol content; typically reported as the Volume Percentage Alcohol.

Most manufacturers of liquor report the Alcohol content by its Proof. In the US system, the Proof is double the Vol. Percentage Alcohol:

$$Proof = 2 \text{ x Volume Percentage}$$ (Eq. 4)

Historically, the term Proof derives from a method of measuring the Alcohol content of liquors which "proved" they were not diluted. If gunpowder mixed with liquor would still ignite after the Alcohol burnt off, then the Alcohol was not considered to be diluted. The minimum Vol. Percentage Alcohol required for ignition is 57%; which, historically, was assigned a value of 100 degrees Proof. Levels of Alcohol in liquor are still measured by Proof, for tax purposes, but the scale is different in different countries.

In addition to the distillate's density, we will also test the quality of our distillate by combustion. Mixtures high in Alcohol content will readily combust, producing a light blue color flame. Those that are high in water content will not combust at all.

Finally, noting the boiling temperature of our distillate also gives us a qualitative feel for its composition. The closer the boiling temperature is to 100°C, the boiling point of Water, the less Alcohol it contains.

We will distill a *Carlo Rossi* red wine of Alcohol content 10-12%, collecting the distillate in fractions of about 15 mL each. We will measure the density of the first fraction only, which we expect to be the most enriched in Alcohol, to determine its Alcohol content or Proof. This, and subsequent fractions, will also be tested for combustibility. And, the temperature at which each distillate is collected will be noted; a final qualitative measure of the composition of the distillate.

<u>Pre-Lab Safety Questions</u>

1.   Do a short internet search for an NFPA 704 Fire Diamond for Ethanol. What is the Degree of Hazard for Ethanol's flammability? What does this rating mean?

2.   What is the definition of the flashpoint for a substance? Specifically, what is the flashpoint for pure Ethanol?

3.   Why are Steam burns more damaging than those of boiling Water?

Procedure

Our distillation apparatuses have been used over the years for distilling a number of different organic compounds, some of which are toxic. Under no circumstances should you drink the Alcohol produced by this distillation. The product is not a beverage quality Alcohol.

1.   Obtain a distillation apparatus as pictured below. Use a small Bunsen burner flame as the heat source. Be sure the distillation apparatus is thoroughly clean. Use a 500 mL Round-Bottom flask as a distilling pot. Use a 25 mL Round-Bottom flask as a receiver.
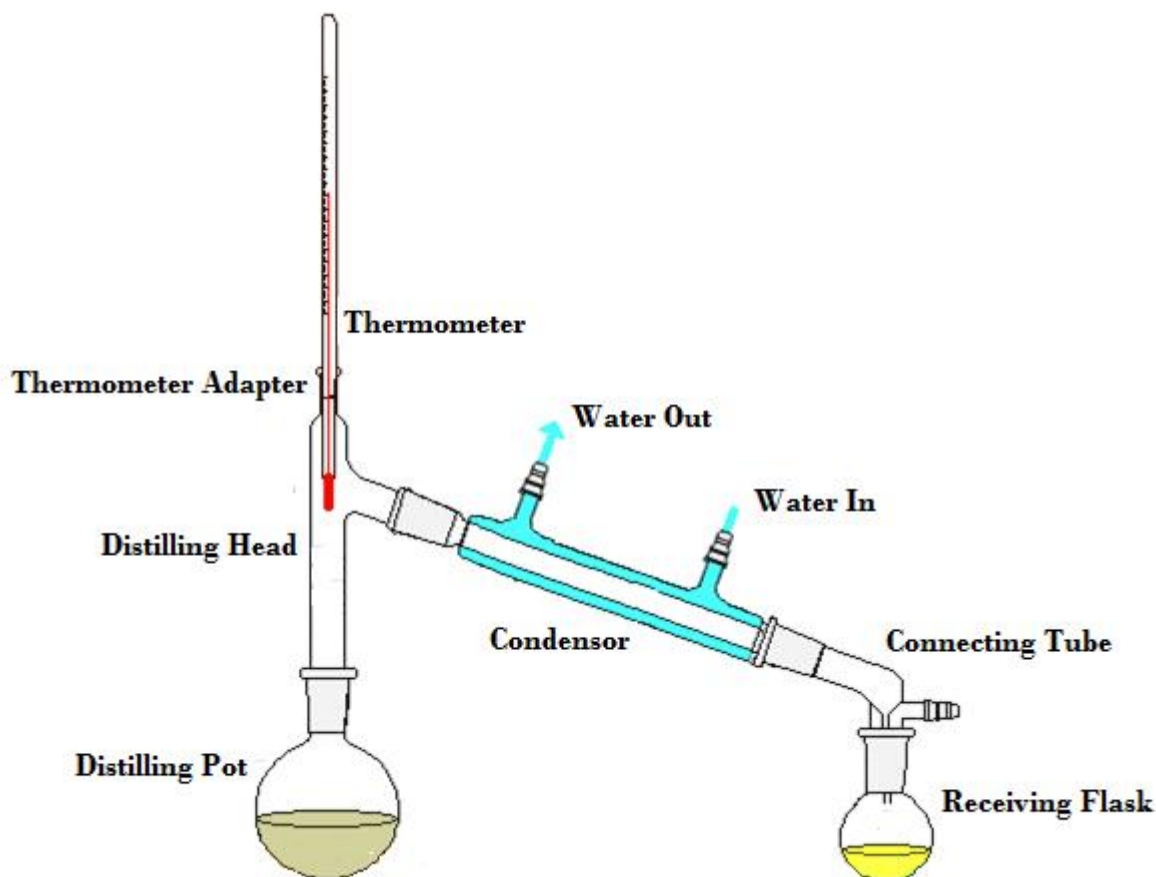
http://en.wikipedia.org/wiki/File:Simple_distillation_apparatus.svg

2.   Obtain a sample of wine from your laboratory instructor. Your instructor will add the wine directly to your 500 mL distilling flask. The flask should be ¼ to ½ full. **(You are not allowed to obtain this sample yourself.)**

3.   Add a few boiling chips to the ferment. Set-up the distillation apparatus. (You must have your apparatus inspected by your lab instructor.) **Now, heat slowly to maintain a steady distillation rate.**

4.   Collect <u>four</u> distillate fractions, of about 15 mL each. Note the temperature <u>range</u>, the beginning and ending temperature, over which each distillate is collected. As each fraction is collected, place the distillate into a large, stoppered test tube.

5.   Determine the density of the distillate (Only done for the first fraction.):

      a)   Pre-weigh a 25 mL Erlenmeyer flask with stopper.

      b)   Using a volumetric pipet, transfer 5 mL of distillate into the 25 mL Erlenmeyer flask.

      c)   Weigh the flask plus distillate.

      Determine the density of the first distillate fraction.

6.   Place approximately half a milliliter of each distillate fraction onto a watch glass. Try lighting it with a match. Note the color and quality of the flame.

7.   **You may want to determine the Proof of your fraction #1 distillate before you leave the lab. Tabulated density data for aqueous Alcohol solutions is available below; see step 4 of the Data Analysis. A crude computer program to carry-out a Lagrange Interpolation of this data is available on the laptop computers in the laboratory.**

Data Analysis

1. Calculate the Density of Fraction #1 of the Distillate.

2. Comment on the Combustibility of each Fraction of the Distillate.

3. Comment of the Boiling Point of each Fraction of the Distillate.

4. Use the data below to determine the Percentage by Volume Alcohol content for Fraction #1 of the Distillate. Interpolate as needed. Report this result.

% by Volume	Density [g/ml]
0.00	0.99908
5.00	0.99190
10.00	0.98569
15.00	0.98024
20.00	0.97518
25.00	0.97008
30.00	0.96452
35.00	0.95821
40.00	0.95097
45.00	0.94277
50.00	0.9335
55.00	0.9235
60.00	0.9128
65.00	0.9013
70.00	0.8892
75.00	0.8765
80.00	0.8631
85.00	0.8488
90.00	0.8331
95.00	0.8153
100.00	0.7932

5. Determine the Proof of Fraction #1 of the Distillate. **You must do this using a Lagrange Interpolation method on a subset of this data set.** A crude program to do this will be available on the computers in the Lavender Lounge.

Post Lab Questions

1. The boiling points of heptane and octane, two components of petroleum, are $98.42^{\circ}C$ and $125.66^{\circ}C$ respectively. Would Simple Distillation be an effective method for <u>completely</u> separating a mixture of these two hydrocarbons? Explain.

2. Would it be worth our time to calibrate the 5 mL pipette we used in Procedure step 5 (c) when measuring the density of our first distillate fraction? Explain.

3. What is the highest proof to which an aqueous Alcohol solution be boosted to using distillation? (You may need to use external sources.)

4. What is the boiling point of the alcohol Methanol? How is Methanol typically removed from Moonshine?

Appendix - Interpolation

Interpolation is a method whereby a new data point is generated from a set of data points that are already tabulated. How do we best perform an interpolation? We will illustrate two methods for interpolating tabulated data in the following examples.

Suppose we have a series of solutions of Fuming Sulfuric Acid, Sulfuric Acid (H_2SO_4) infused with Sulfur Trioxide (SO_3), for which the density has been measured.
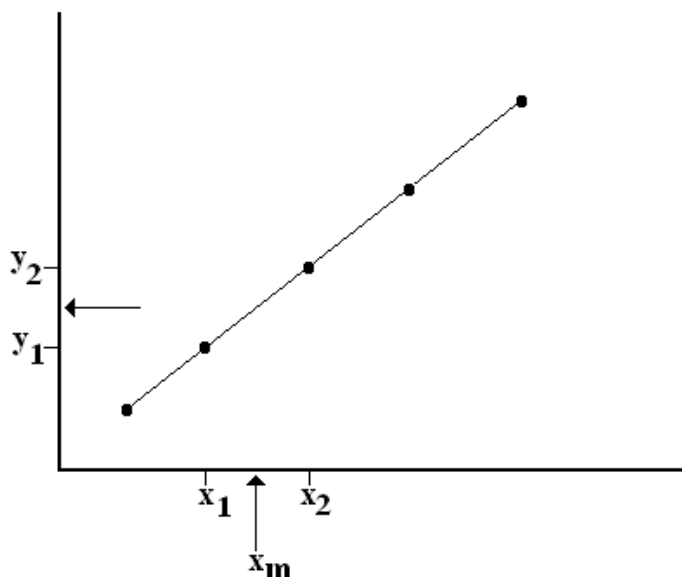
Fuming Sulfuric Acid

% H_2SO_4	Density [g/mL]
100	1.839
95	1.862
90	1.880
85	1.899
80	1.915
75	1.934
70	1.952

Now suppose we have measured the density of a Fuming Sulfuric Acid solution whose composition is not known. Take this measurement to be 1.887 g/mL. From the tabulated results we can see the composition of the mixture is between 85 and 90% Sulfuric Acid. Interpolation will allow us to hone in on a prediction of the composition that is more accurate by generating a new data point between these two compositions.

If the data is perfectly linear, interpolation is particularly easy. A simple plot of this data shows it to indeed be linear.
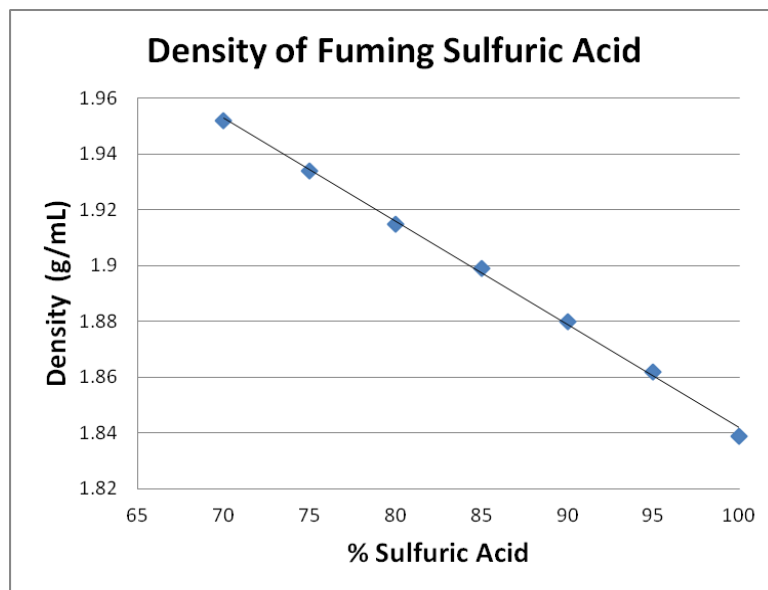
Linear interpolation can be illustrated rather easily:

We simply determine how much the slope of the line moves us from y_1 up the y-axis over an increment of $(x_m - x_1)$. Then, the new data point y_m, based on our measurement x_m, can be determined via:

$$y_m \;\; = \;\; y_1 \; + \; [(y_2 - y_1)/(x_2 - x_1)] \, (x_m - x_1)$$

For our Fuming Sulfuring Acid example, we have:

$$y_m \;\; = \;\; 90 \; + \; [(85 - 90)/(1.899 - 1.880)] \, (1.887 - 1.880) \;\; = \;\; 88.15$$

Unfortunately, much data exhibits significant curvature. In this case a polynomial fit to the data might be more appropriate. And, more than two tabulated data points will be required for the interpolation. Afterall, n data points are required to define a polynomial of degree $n - 1$.

Consider the density of Water as a function of temperature:

Temp. ($^\circ$C)	Density (g/mL)
0	0.99987
10	0.99973
20	0.99823
30	0.99567
40	0.99224
50	0.98807
60	0.98324
70	0.97781
80	0.97183
90	0.96534
100	0.95838

A quick plot of this data illustrates its curvature. This is particularly true at lower temperatures.
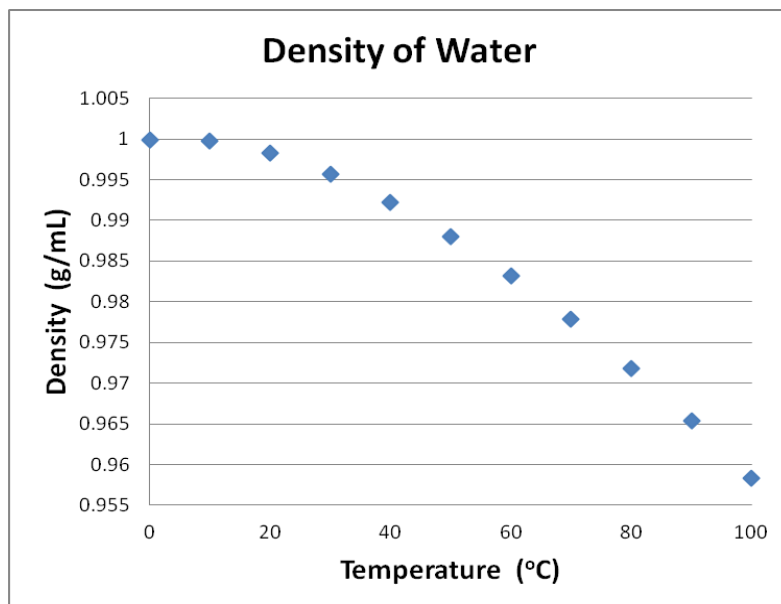
So, if we attempt to use a linear interpolation scheme to determine the density of Water at say 15°C from the Tabulated densities at 10°C and 20°C, we obtain the following result:

$$y_m \quad = \quad 0.99973 \ + \ [(0.99823 - 0.99973)/(20\text{-}10)] \ (15 \text{ - } 10) \quad = \quad 0.99868 \text{ g/mL}$$

Experimentally, the density of Water at 15°C is found to be 0.99913 g/mL. The interpolated value is in error by 0.045%.

Another interpolation method, that of Lagrange, takes into account changes in the slope between neighboring pairs of points and therefore accounts for, to some degree, curvature in the data. Using this method, and data at 10°C, 20°C and 30°C, results in a better interpolated result of 0.99898 g/mL. The error has now been reduced to 0.015%. The interpolation method of Lagrange is encoded in a number of software packages. A simple DOS program encoding this algorithm is available on the computer in the Lavender Lounge of Jones Hall.