Another important property of solutions is the viscosity. Viscosity can be defined as the resistance to change form. The units of measure are dynes per second per cm or mass per unit volume per unit time (g cm^-1 s^-1) or poises. The viscosity of a liquid “η” that will flow through a tube of length “l”, radius “r”, with a difference of pressure at both ends of “p” and a volume per second of “V” can be found using:

\[
\eta = \frac{\pi p r^2 m}{8 l V} = \frac{m}{8 l t}
\]

The “m” is the mass in grams, “l” the length of the tube in cm, and “t” the time it takes to empty the tube in seconds. The kinematic viscosity is the ratio of the viscosity to the density in units of “stokes”. The Viscosity of water at 0°C is 1.798 centipoises. Viscosity is inversely proportional to temperature, or increases at lower temperatures. For example, water at –9.3°C is 2.549 centipoises.

**Rheology.** “Rheo” comes from the Greek word meaning “to flow.” Thus, rheology is the study of flow. Fluids are either Newtonian or non-Newtonian. Newtonian fluids are pure homogenous fluids whose viscosity does not change with shear rate or speed of stirring (the rate one surface passes over another). Water at room temperature would be considered essentially a Newtonian fluid. Non-Newtonian fluids have different apparent viscosities at different shear rates. They usually characterize heterogeneous solutions and suspensions. Non-Newtonian fluids can be further classified by how they deviate from Newtonian solutions.

Solutions that are more viscous when the initial shear or stirring begins and then increase viscosity with shear rate like Newtonian solutions are said to be “thixotropic”. Some examples include suspensions of paper pulp or pigments. The opposite of pseudoplastic solutions are “dilatant” solutions that are less viscous when the shear begins and then increase viscosity with shear like Newtonian liquids. Some examples of dilatant solutions include quick sand, beach sand, and starch and mica suspensions. Solutions that become more viscous when the shear or stirring ends are said to be “thixotropic”.

Thixotropic solutions describe butter, orange juice concentrate, honey, mayonnaise, drilling...
mud, paints, and inks. The opposite, solutions that become less viscous when the shear ends are called “rheopectic”. Bentonite clay, vanadium pentoxide solutions and aqueous suspensions of gypsum are of this type. Usually pseudoplastic solutions are thixotropic. Conversely dilatant solutions are usually rheopectic.

Sugar Solutions. Solutions of common table sugar (sucrose) are pseudoplastic thixotropic solutions that have a high resistance to initial shear with decreasing resistance as stirring continues (said to be going from a “gel” to a “sol” condition). Upon shear termination the viscosity is restored (said to be going from a “sol” to a “gel”). Thus shear rate, status of the shear (beginning, middle or end), as well as concentration and temperature characterize the viscosity of sugar solutions. Density is also dependent on concentration as is the ability of a solution to refract or bend light. Therefore, viscosity, density, and refraction can all be used to determine the concentration of a solution, especially a sugar solution. The density (g/mL) of sucrose solutions has been related to the concentration using the Kimball equation:

\[ D = 0.524484 e^{(B+330.872)/170435} \]

“B” is the Brix or w/w % sucrose (named after the German mathematician Adolf Ferdinand Wenceslaus Brix, 1798-1870). The value “e” is the exponential value of 2.7183. This equation was found using a least squares regression analysis of laboratory data. Solving for “B” we get:

\[ B = 412.84 \sqrt{\ln(D/0.524484)} - 330.872 \]

Notice that the natural log function (ln) is used instead of the base 10 log function. Thus, a measure of the density can give us the w/w % sucrose or Brix.

Refraction. When light travels from a medium at one density into another medium of another density it bends. This is called refraction. However, the angle at which it bends depends on the densities of the two mediums. There exists an ideal angle that light takes when it goes from a medium of low density, such as an aqueous solution of sucrose, to a
medium of higher density, such as glass. It takes the ideal angle to reach a certain point in the fastest possible time. It is said that light has a NOSE for or KNOWS the ideal angle to take to minimize the time from going from one point in the less dense medium to a point in the denser medium.

The angle of refraction can be used to determine the concentration of a solute such as sugar. As the concentration of sugar increases, the angle of refraction changes, the density of the glass prism being constant. Most refractometers give an index of refraction by reading a shadow defined by the degree of bending of the light. Some refractometers have a built in Brix scale. The index of refraction can be converted to Brix using a table from the *Handbook of Chemistry and Physics* published by Chemical Rubber Company (CRC). Using the index, this table can be located and used to convert the index of refraction to % sucrose or Brix. The temperature also affects the Brix reading using a refractometer. To make a correction to the Brix for temperature the following equation, again arrived at through a double nested least squares analysis.

\[
\text{Cor}T = B^2 (+1.425 \times 10^{-4} - 8.605 \times 10^{-6} T + 7.138 \times 10^{-8} T^2) + \\
B (-2.009 \times 10^{-2} + 1.378 \times 10^{-3} T - 1.857 \times 10^{-5} T^2) + \\
(-7.788 \times 10^{-1} + 1.700 \times 10^{-2} T + 1.100 \times 10^{-3} T^2)
\]

The “T” value is the centigrade temperature of the solution. This factor is added to the Brix to give a temperature corrected value.

In this experiment you are going to measure the refractive index to determine the concentration of sugar or Brix, correct for temperature and compare it to the results of a density measurement and a viscosity measurement. You will also apply the method of least squares to determine a relationship between viscosity and the Brix.

**Linear Least Squares Regression Analysis.** Regression analysis is the relating of empirical data to a mathematical relationship. One way to do this is to determine the average deviance from a known mathematical equation and vary the parameters of the equation in order to minimize this difference. Differential calculus is used to minimize this difference. When applying this method to a linear
equation \((y = mx + b)\) and to our experiment, the “x” value becomes the viscosity (V) and the “y” value becomes the Brix (B) or concentration (or \(B = mV + b\)). The slope (m) and y-intercept (b) can be found for the line of best fit to the laboratory data using summations as follows.

\[
m = \frac{n \sum VB - (\sum V \sum B)}{n \sum V^2 - (\sum V)^2} \quad b = \frac{\sum V^2 \sum B - \sum V \sum VB}{n \sum V^2 - (\sum V)^2}
\]

Here “n” is the number of viscosity-Brix data pairs that are used in the analysis. The “goodness of fit” can be determined using the following.

\[
R^2 = \frac{n \sum VB - (\sum V \sum B)}{\sqrt{n \sum V^2 - (\sum V)^2} \sqrt{n \sum B^2 - (\sum B)^2}}
\]

The closer \(R^2\) (correlation coefficient) comes to one, the better the fit or the better the linear equation will be able to predict the Brix from viscosity data.

**General Least Squares Analyses.** The software accompanying this text can be used to determine the least square parameters for 19 equations. You select 1 and ENTER to enter a new set of data. Enter the Brix value, followed by comma, then the viscosity and ENTER. Continue until you have entered your data. When you are through, enter “M,” and then ENTER. Options 2-4 allow you to view, correct, or add to your data. Option 5 will calculate the \(R^2\) values for the 19 equations. Using the \(R^2\) values, the program selects the curve of best fit and gives you the constants at the bottom. You can use option 6 so find the calculated constants for any of the other equations. Some equations have a good correlation coefficient and are easier to use than the best equation determined by the program. You can use option 7 to insert an “X” value and calculate the “Y” value using the equation selected in option 6. Option 8 and 9 allow you to save the data in a file,
Analysis of Variance. The Analysis of Variance (ANOVA) is a statistical method of determining if a series of values are significantly different. ANOVA uses an F-distribution where a significant variance is said to occur if the test statistic (F value) falls within the 95% critical value. In other words, if the data exist within 95% of the standard normal frequency distribution, a significant difference can be assumed. If such is the case, it is said that the variance is significant at the 0.05 level (1.00 - .95). For example, suppose that you had 3 Students that were performing Brix measurements. You may notice that there seems to be a difference in readings but you are not sure if there is a significant difference and why that difference is occurring. In order to find out, you can have all 3 students analyze each of 10 samples of sucrose solutions. The answers that you receive will probably have some differences. Are these differences due to the student or perhaps the samples of sugar? Are these differences significant? This can be determined using an analysis of variance. An analysis of variance tests what is called the "null" hypothesis or the hypothesis that no difference exists. The limits of the "null" hypothesis are expressed in terms of probability limits or levels. If there is a certain probability that the differences can lie outside a certain range, then the difference is considered statistically significant. As mentioned previously, a common probability of 5% (0.05) is used as the critical value to determine the acceptance or rejection of the "null" hypothesis. The best way to illustrate the use of an analysis of variance is by using an example. Suppose the three students that measure the Brix on 3 samples of sucrose collect the null data:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Student A</th>
<th>Student B</th>
<th>Student C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>61.2</td>
<td>61.4</td>
<td>60.8</td>
</tr>
<tr>
<td>Sample 2</td>
<td>61.3</td>
<td>61.0</td>
<td>60.9</td>
</tr>
<tr>
<td>Sample 3</td>
<td>60.9</td>
<td>61.2</td>
<td>60.9</td>
</tr>
</tbody>
</table>
We will try to determine if there is a significant difference between the results from each student or if one student significantly varies from another. First, we can simplify our calculations by subtracting 60.0 from each of the numbers above to give:

<table>
<thead>
<tr>
<th></th>
<th>Student A</th>
<th>Student B</th>
<th>Student C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE 1</td>
<td>1.2</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td>SAMPLE 2</td>
<td>1.3</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>SAMPLE 3</td>
<td>0.9</td>
<td>1.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Then the following procedure can be used.

1. Sum each column, square the sum, add the squares and divide by the number of items in each column. For example:

\[
\frac{(1.2+1.3+0.9)^2 + (1.4+1.0+1.2)^2 + (0.8+0.9+0.9)^2}{3} = 10.43
\]

2. Square each number and add. For example:

\[
(1.2)^2 + (1.3)^2 + (0.9)^2 + (1.4)^2 + (1.0)^2 + (1.2)^2 + (0.8)^2 + (0.9)^2 + (0.9)^2 = 10.60
\]

3. Sum all the items, square, and divide by the total number of items. For example:

\[
\frac{(1.2 + 1.3 + 0.9 + 1.4 + 1.0 + 1.2 + 0.8 + 0.9 + 0.9)^2}{9} = 10.24
\]

4. Subtract the results in (3) from the results in (1). For example:

\[
(1) - (3) = 10.43 - 10.24 = 0.19
\]

5. Subtract the results in (3) from (2). For example:

\[
(2) - (3) = 10.60 - 10.24 = 0.36
\]

6. Subtract the results in (4) from those in (5). For example:

\[
(5) - (4) = 0.36 - 0.19 = 0.17
\]
With this information we can now construct an analysis of variance table. The sum of squares for the columns is found from step 4 above. The sum of squares for the residual error is found from step 6 above. The degrees of freedom (df) for the columns is found by taking the number of columns (c) and subtracting 1 or c-1. The degrees of freedom for the residual error is found from c(r-1) where "r" is the number of rows or Brix tests per student. The mean square is found by dividing the sum of the squares by the degrees of freedom. The variance ratio can then be found by dividing the mean square of the columns by the mean square of the residual error. For example:

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>Variance Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>columns</td>
<td>0.19</td>
<td>2</td>
<td>0.10</td>
<td>3.33</td>
</tr>
<tr>
<td>residual</td>
<td>0.17</td>
<td>6</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

The variance ratio can then be compared to the table below where $V_1$ equals the degrees of freedom for the columns and $V_2$ equals the degrees freedom of the residual.

<table>
<thead>
<tr>
<th>$V_2$</th>
<th>$V_1=1$</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>161</td>
<td>200</td>
<td>216</td>
<td>225</td>
<td>230</td>
<td>234</td>
<td>237</td>
<td>239</td>
<td>241</td>
<td>242</td>
</tr>
<tr>
<td>2</td>
<td>18.5</td>
<td>19.0</td>
<td>19.2</td>
<td>19.2</td>
<td>19.3</td>
<td>19.3</td>
<td>19.4</td>
<td>19.4</td>
<td>19.4</td>
<td>19.4</td>
</tr>
<tr>
<td>3</td>
<td>10.1</td>
<td>9.55</td>
<td>9.28</td>
<td>9.12</td>
<td>9.01</td>
<td>8.94</td>
<td>8.89</td>
<td>8.85</td>
<td>8.81</td>
<td>8.79</td>
</tr>
<tr>
<td>4</td>
<td>7.71</td>
<td>6.94</td>
<td>6.59</td>
<td>6.39</td>
<td>6.26</td>
<td>6.16</td>
<td>6.09</td>
<td>6.04</td>
<td>6.00</td>
<td>5.96</td>
</tr>
<tr>
<td>5</td>
<td>6.61</td>
<td>5.79</td>
<td>5.41</td>
<td>5.19</td>
<td>5.05</td>
<td>4.95</td>
<td>4.88</td>
<td>4.82</td>
<td>4.77</td>
<td>4.47</td>
</tr>
<tr>
<td>6</td>
<td>5.99</td>
<td>5.14</td>
<td>4.76</td>
<td>4.53</td>
<td>4.39</td>
<td>4.28</td>
<td>4.21</td>
<td>4.15</td>
<td>4.10</td>
<td>4.06</td>
</tr>
<tr>
<td>7</td>
<td>5.59</td>
<td>4.47</td>
<td>4.35</td>
<td>4.12</td>
<td>3.97</td>
<td>3.87</td>
<td>3.79</td>
<td>3.73</td>
<td>3.68</td>
<td>3.64</td>
</tr>
<tr>
<td>8</td>
<td>5.32</td>
<td>4.46</td>
<td>4.07</td>
<td>3.84</td>
<td>3.69</td>
<td>3.58</td>
<td>3.50</td>
<td>3.44</td>
<td>3.39</td>
<td>3.35</td>
</tr>
<tr>
<td>9</td>
<td>5.12</td>
<td>4.26</td>
<td>3.86</td>
<td>3.63</td>
<td>3.48</td>
<td>3.37</td>
<td>3.29</td>
<td>3.23</td>
<td>3.18</td>
<td>3.14</td>
</tr>
<tr>
<td>10</td>
<td>4.96</td>
<td>4.10</td>
<td>3.71</td>
<td>3.48</td>
<td>3.33</td>
<td>3.22</td>
<td>3.14</td>
<td>3.07</td>
<td>3.02</td>
<td>2.98</td>
</tr>
</tbody>
</table>

At the 0.05 probability level the variance ratio must exceed 5.14 in order for a significant difference to occur between the lab students. Since 3.33 is less than 5.14 we fail to reject the null hypothesis which means there is no significant difference between the lab students from a statistical point of view. That is not to say that the lab students are
performing Brix measurements with sufficient accuracy. It only means that statistically they are all performing equally at the 5% level.

**Procedure**

**Part 1  Refractive Index**

1. Prepare 4 solutions of sugar by adding 2.5g, 5.0g, 10g, and 20g of sugar to 4 beakers, each containing 50 mL of water. A fifth beaker should contain just water. This will give you solutions with 0 Brix, 5 Brix, 10 Brix, 20 Brix, and 40 Brix.

2. Put a few drops of each solution and the unknown on the refractometer prism. Close the top cover and observe the shadow through the eyepiece. The shadow changes with the angle of refraction. Adjust the shadow to the center of the cross hairs or read it directly on the refractive index or Brix scale. Record the refractive index from the refractometer and look up the corresponding % sugar in the *Handbook of Chemistry and Physics* (CRC). Also, record the temperature of each solution. Use the temperature correction equation to adjust the Brix values.

**Part 2  Viscosity and Density Measurements**

1. Obtain a 80-100 cm length of glass tubing that has been fire polished at both ends.

2. Using a pipette bulb, withdraw the sugar solution as close to the top as you can. Seal the top of the tube with your forefinger. Measure the length of the sugar solution in the tube. Repeat this and subsequent steps for all 5 solutions and the unknown.

3. Weigh the beaker containing the solution from which you withdrew the solution and record.
4. Hold the tube vertically over the beaker and release the sugar solution back into the beaker timing how long it takes to do so in seconds.

5. Measure the inner radius of the tube and use $\pi r^2 l$ to determine the volume of the solution. Reweigh the beaker and subtract to get the weight of the solution used in the tube. Divide the weight by the calculated volume to get the density (g/mL). Use the Kimball Equation to determine the Brix from the density.

5. Calculate the viscosity using the equation given in the discussion.

6. Heat one of your sucrose solutions to 50°C and repeat the refractive index, density and viscosity measurement. Remember to apply a temperature correction to the Brix from the refractive index measurement.

Part 3  Statistical Analyses

1. Use the average Brix values for each solution with the corresponding viscosity measurements to determine a line of best fit (for a linear equation). You can use the equations in the discussion or the statistical software accompanying the text. Using the linear regression and the measured viscosity of the unknown, calculate the Brix of the unknown.

2. Use the statistical software to determine the equation of best fit and use this equation to calculate the predicted Brix of the unknown. Compare this value with that found using a linear regression in step 1.

3. Compare to the calculated Brix of the unknown found from the density measurement and the refractometer measurement and that found from step 2 above. Perform an Analysis of Variance to see if there is a statistically significant difference between the values. You can use the method described in the discussion or the statistical software.
1. Using the data above determine the Brix from the refractive index and the Brix from density. Then determine the viscosity using the formula given in the discussion. Complete the chart. Show all your calculations.

2. Determine the line of best fit for the viscosity (y-value) vs. the average Brix value of the density and refractometer measurements. Calculate the correlation coefficient. Show all calculations.
3. Determine if the Brix values from the three measurements in the last set of data are significantly different using Analysis of Variance. Use the equations in the discussion and not the statistical software. Show all of your work.

4. If the second refractometer reading was carried out at 30.2°C, what would be the correction to the Brix and the final Brix value? Show work.
### Lab Report for Unit 12

Unit 12  Viscosity of Solutions

**Part 1: Refractive Index**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ref. Index</th>
<th>Uncor. Brix</th>
<th>Temp.</th>
<th>Correction</th>
<th>Corrected Brix</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unknown</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Show calculations:
### Part 2  Viscosity and Density Measurements

<table>
<thead>
<tr>
<th>Solution</th>
<th>Mass</th>
<th>Tube Length</th>
<th>Volume</th>
<th>Density</th>
<th>Time</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unknown</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Show calculations:
Part 3: Statistical Analyses

Average Brix (x) Viscosity (y)

Linear Regression Equation and Correlation Coefficient:

Equation of Best Fit and Correlation Coefficient:

Analysis of Variance Table and Conclusion:
Unit 12 Solutions and Viscosity