Note: Read your assignment first. Not all sections below are relevant to all assignments.

**SYSTEM OVERVIEW**

The Permeameter apparatus consists of five horizontal fixed beds and one vertical fluidized bed. Bed 1 (the top horizontal bed) is housed in a stainless-steel reactor, which can be used for reaction engineering experiments requiring higher-temperature conditions. It is currently used for the acid-catalyzed sucrose inversion reaction. Beds 2-5 are contained in horizontal glass columns. There is also a vertical bed which can be fluidized. The properties of the columns and the packed beds are given in Tables 1, 2, and 3 respectively. If you are unfamiliar with the fluid mechanics of packed and fluidized beds, you should consult a fluid mechanics textbook or your unit operations textbook[1].

<table>
<thead>
<tr>
<th>Table 1. Column Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Glass - Length</strong></td>
</tr>
<tr>
<td><strong>Glass - Inner diameter</strong></td>
</tr>
<tr>
<td><strong>Maximum operating pressure</strong></td>
</tr>
<tr>
<td><strong>Steel – Length</strong></td>
</tr>
<tr>
<td><strong>Steel - Diameter</strong></td>
</tr>
</tbody>
</table>
The apparatus is set up for water, air, and an organic-phase feed to the beds. Water can be fed from the city water supply via a pressure regulator set at 40 – 45 psig. Note the location of the shut-off valve at the inlet, which should be closed only if an uncontrolled leak in the system develops. Water enters the system through an automatic control valve for flow rate control, an orifice/differential pressure (d/p) transmitter for flow rate measurement, and a tracer sampling loop (usually 10 mL volume) for the injection of pulse tracers. The water feed then splits, allowing flow to the five horizontal fixed beds and the vertical fluidized bed. Air enters the system through a regulator and can also flow to either the horizontal or the vertical beds. There is both a manual valve and a check valve on the air line to the unit.
Flow is directed through any single bed by manually opening the upstream and downstream valves to that bed, except for horizontal bed #5, which has an automatic valve downstream that must be operated from the computer. The effluent from the fixed beds flows through an on-line spectrometer, and exits to a drain valve. The effluent from the vertical fluidized bed flows through a separator which has two exits, one to the drain and the other to the TCD detector/dry test meter.

Two devices prevent exceeding the pressure rating of the glass beds. The first is the pressure regulator for the inlet water feed. The second is a pressure relief valve set to release at 20 psig. Note that although the feed pressure is higher than the relief valve setting, the inlet water pressure is reduced considerably by flow through the control valve and orifice. Despite these safety precautions, it is advisable to prevent pressure spikes from occurring in the beds, the most common cause of which is opening the upstream valve to a bed without having the corresponding downstream valve open. When shutting off flow to a bed, make sure the water flow is shut off, or another bed has been opened, and close the upstream valve first. This practice prevents high pressures from getting sealed in the columns.

Important system variables are as follows:

1. Volumetric flow rate into the system, measured by reading pressure drop across a 0.109” orifice in a ½” schedule-40 pipe (water) or by a turbine meter (air).

2. Pressure drop across a bed, which is measured by d/p transmitters located (a) above the five horizontal beds and (b) alongside the vertical bed. Pressure drop is shown on the computer interface in units of inches of water.

3. Ultraviolet (UV) and visible (VIS) absorbance in the outlet stream from the beds, are detected by a flow-through spectrometer. The signal is displayed and acquired using the Ocean Optics software program, SpectraSuite, explained on page 4 below.

4. A thermal conductivity detector (TCD) in one of the parallel outlet streams from the vertical bed. The signal is displayed on the Experion schematic, along with the flow rates and pressure drops.

## BASIC OPERATION OF THE PERMEAMETER EXPERIMENT FROM THE PKS SCHEMATIC

Basic operation of the Permeameter horizontal beds for pressure drop measurements is outlined in the next subsections.

## UNDERSTANDING EXPERION PKS CONTROL SYSTEM TERMINOLOGY

In Experion, each process variable is represented by an entity called a Control Module (CM). Each CM is a collection of Function Blocks (FB). And each FB consists of many values called parameters. Within a CM (and sometimes between CM’s), the FB’s are “wired” together in various ways to monitor and control the process. Desired values of many parameters may be entered via the computer keyboard. The purpose of the next few paragraphs is to explain how to use Experion to run this equipment.
Access to the Honeywell Experion DCS application is through a virtual machine using VMware Horizon View software. After logging into one of the computers in the UO Control Room, among the icons on the desktop shown is the **VMware Horizon View Client** icon. Double-clicking this icon should bring up the following popup with the `che-view.lsu.edu` icon showing. If that icon does not appear, then click **New Server**; complete the requested information to add it. The following should show:

Double-click the `che-view.lsu.edu` icon. If an additional login menu appears, login using your LSU ID and password. At this point the following view should appear:
Virtual machines are available for the microscope in the UO Analytical Lab (shown as Microscope) and for access to the Honeywell DCS (shown as Uolab). Double-click the Uolab icon. A splash screen for the virtual machine should appear with an OK button. Click OK. The VMware software should start up a virtual machine and show you the desktop of that machine.

Open the Honeywell Station software either by double-clicking the Station icon if visible or by navigating using the following pathway:

Start>All Programs>Honeywell Experion PKS>Client Software>Station

If login credentials are proper, the Station program will appear and – exercise patience here – the following default splash screen within it:

The Honeywell login process is now complete.

**INITIATING WATER FLOW**

Flow through the system is controlled using a combination of automatic and manual valves in the system. Automatic valves are operated using the Experion interface. Familiarize yourself with the valves that can be controlled through the interface, and with their physical location.

1. From the **Unit** item on the menu, select Perm. The Perm P&ID schematic will appear. This schematic is much like a Process and Instrumentation Diagram (P&ID). All important data are collected into an Excel spreadsheet (see below for detailed operating instructions).

2. Open the inlet and exit valves to the bed being tested (all are manual valves except the exit valve for bed #5 – D501).

3. Open the water supply solenoid (left click D531 to bring up the device control faceplate, and then left click the “Open” radio button on the right side of the faceplate).
4. Open the water flow rate control valve (left click F531 to bring up the controller faceplate, enter an OP of 20-30% to start water flowing through the bed). Raise flow rate as necessary to reach assigned targets.

5. Monitor differential pressure across the beds (see P502 at the top of the schematic), trying to keep it below the maximum readout of 250 inches water. For some beds this is impossible, and the Bourdon pressure gauge must be used instead.

6. After a while, confirm that water is flowing to the drain.

7. Open the bypass valve on the differential pressure gauge to purge air from the pressure lines. Re-close this valve after a minute or two.

8. Switch F531 to AUTO and adjust the setpoint (it’s in ml/min) until the desired flow rate is achieved.

**SHUTTING DOWN SYSTEM**

1. Close the water flow rate control valve (left click F531 to bring up the controller faceplate, left click the SP field and enter 0.0, left click the MD dropdown list box and select MAN, left click the OP field and enter -6.9).

2. Close the water supply solenoid valve (left click D531 to bring up the device control faceplate, left click the “Closed” radio button on the right side of the faceplate).

3. Close the block and/or solenoid valves on the bed that was used.

**USING THE EXCEL DATA COLLECTOR**

On the Desktop, look for a folder named

**Excel Spreadsheets**

Within that folder, open the folder named

**snr**

and double click on **PermRecorder.xls**. The workbook will open with a **Start** button, the experiment name, a collection frequency drop-down menu box, and a **Stop** button on the top line.

Click on the **Start** button, and the workbook will start collecting the relevant data at a collection frequency chosen from the dropdown menu. When you are ready to save the data, press the **Stop** button, cut/paste the data into another instance of Excel, and then save this second instance wherever you need it. Note that while data are being collected, if you should do anything in that instance of Excel other than scrolling around to look at the data, the collector may stop and you will have to restart the data collection. Note: Ocean Optics data are not collected by the Experion System. See instructions below.
Effluent tracers are measured by UV or VIS spectroscopy. An online and offline analyzer probe (Ocean Optics UV dip probe) is provided for this purpose. This probe must be handled with care. Nothing (no solid object, especially) should ever enter the liquid cavity of the probe except the process fluid or distilled water for cleaning. The probe should never be placed on a dirty surface. The probe is normally mounted in the effluent flow line. However, it can be removed as shown by the instructor to make batch readings for calibration or other purposes.

**Be sure to turn off the lamps at the end of a lab period, to prolong their life.**

The Ocean Optics spectrometer itself resides in a module (connected to the PC through a USB port) near the experiment. Fiber-optic cables transmit the radiation from the DT-1000 source to the dip probe and the detected signal to the PC.

To perform a calibration and then a tracer experiment, use the following procedure.

1. Power up the spectrometer equipment.
   
   To do this, first be sure that the Silex Technology USB hub / network connector is powered up and the rocker power switch at the rear of the Ocean Optics spectrometer is in the **ON** or **1** position. Then, press both the **UV Start** and **Visible Start** buttons on the front of the spectrometer. These two buttons turn on the specific light sources.

2. Ensure that USB communication from the Permeameter spectrometer is enabled.

   To do this, locate the **SX Virtual Link** icon on the desktop, as shown in Figure 1. Double-click that icon to begin connection to the UV-Vis detector. Doing so will display the main application window for the **SX Server Link** application, as shown in Figure 2. This display should show two Ocean Optics USB 2000 devices, one for the Permeameter and one for the Crystallizer. If the desired instrument does not appear on this display, disconnect and reconnect the power to the Silex Technology field USB hub. After the hub completes its self-test cycle, these two devices should appear on this display. If not, contact your Instructor or the Lab Coordinator (Patrick Doring).

   [03/06/16: One possible explanation for a failure of the two Ocean Optics USB 2000 device icons to appear upon opening the SX Virtual Link is that the network address is in error. To check this (and to set it correctly if it is in error), click on the **Options** button (the small wrench icon) and under the **Search for device servers** tab, make sure that the only address there is: **10 20 149 98**. If this is not the address, then **Add** this address and **Delete** any others. Click **Apply** and **OK** and then the Ocean Optics USB 2000 device icons should appear.]
Section: Performing a Tracer Test – Water Flow

Figure 1. Locating the SX Virtual Link application icon.

Figure 2. SX Virtual Link main application screen.
With the SX Virtual Link application window still open, select the desired Ocean Optics device by double-clicking on **Permeameter**. “Available” should change to **You are Connected** (Fig. 3).

![SX Virtual Link window](image)

*Figure 3. SX Virtual Link application showing Connected Permeameter USB device.*

At the end of use on any lab day, disconnect the SX Virtual Link USB connection by clicking the rightmost of the two round buttons on the bottom of the window.

**Please be sure to perform this disconnect operation as no other computer will be able to connect to the Permeameter spectrometer until your connection is closed!**

3. Open the SpectraSuite application to **Scope** Mode.

The SpectraSuite® icon should appear on the desktop. If it does not, there are two other possible ways to start the program up: 1) Click Start -> All Programs -> Ocean Optics -> SpectraSuite, or 2) go to the following directory path to start this application: \C:\Program Files\Ocean Optics\SpectraSuite\spectrasuite\bin\ and start the SpectraSuite application file by double-clicking the icon there. For detailed reference information on the SpectraSuite application, locate and have available the SpectraSuite© Spectrometer Operating Software- Installation and Operating Manual at the imbedded link here, or in your folder, or at [www.oceanoptics.com](http://www.oceanoptics.com). On the website, select Technical, then Operating Instructions, then Software Operation. The instructions apply to our USB 2000 model.

Opening the SpectraSuite application displays a screen like the one shown in Figure 4.
4. On the top menu bar, change the **Integration Time** to 250 ms, the **Scans to Average** to 2, and the **Boxcar Width** to 2 (unless otherwise instructed). Check the boxes for **Strobe/Lamp Enable**, **Electric Dark Correction**, and **Stray Light Correction**. No other boxes should be checked or parameters changed on the top menu bar.

5. Prepare **Dark Spectrum** and **Reference Spectrum** files.

The spectrometer – in order to give you meaningful results from your work – will require the generation of a **Dark Spectrum** file and a **Reference Spectrum** file.

a) Immerse the probe into a test tube filled with DI water. Be sure that the probe mirror/cap is completely secured to the probe. A partially secured mirror/cap (i.e., not completely screwed on) will negatively affect your readings.

b) To create a **Dark Spectrum** file, unplug the probe from the light source (white box). Your graph should nearly trace the x-axis. When the probe has no light source and the detector has no light reaching it, the spectrum generated is called a **Dark Spectrum**. To save your newly created **Dark Spectrum**, click on the grey light bulb button (labeled **Store Dark Spectrum**). You can also save this spectrum through File -> Store -> Store Dark Spectrum.

c) To create a **Reference Spectrum** file, plug the probe connection back into the light source. Some peaks should appear on the graph in SpectraSuite. To save this **Reference Spectrum**, click on the yellow light bulb button (labeled **Store Reference Spectrum**). You can also save this spectrum through File -> Store -> Store Reference Spectrum.
d) Both of these saved files – the dark and reference spectra – will serve as reference points throughout the calibration process. It may be possible to use these saved files over and over again, without having to generate them every time you wish to use the spectrometer – which is why you saved them as files in the first place. However, there’s nothing wrong with regenerating them each day that you use the spectrometer.

e) If ANY settings are ever changed (e.g., Integration Time, etc.), both the Dark Spectrum and Reference Spectrum must be generated again.

6. Create a set of suitable calibration standards. These can be made from fluorescing dyes (a visible spectrum tracer) or from reagent potassium iodide solution (a near UV tracer). The Instructor will specify. The discussion below assumes fluorescent dyes.

a) Reasonable calibration requires a minimum of four standard samples – you may decide to make up more to reduce uncertainty or to deal with nonlinearity (if this is evident). A fifth standard is deionized (DI) water.

b) The concentration of the pre-made standards – both red and yellow-green fluorescent dyes – is 250 ppm; dilution will be required.

c) One reasonable series of low-level calibration standard concentrations, for either dye, might be 1, 2, 3 and 4 ppmw.

| The actual standards concentrations are not so critical. However, none of them should result in a spectrometer absorbance reading greater than 1. |

Using 250 ppm pre-made standard, make a 25 ppm working standard by adding 450 mL of DI water to 50 mL of the pre-made standard in a 500 mL volumetric flask.

To prepare the low-level calibration standards, make further dilutions with DI in 25 mL volumetric flasks, employing the following equations to determine the final solution volume and thus the amount of DI water to add:

\[ V_{\text{working-standard-to-add}} \cdot C_{\text{working-standard-to-add}} = V_{\text{desired-low-level-solution}} \cdot C_{\text{desired-low-level-solution}} \] \hspace{1cm} (1.1)

For example, to create a 25 mL low-level calibration standard at 2 ppm from a 25 ppm yellow-green fluorescent dye working standard, we’d see that:

\[ V_{\text{working-standard-to-add}} \cdot 25 \text{ ppm} = 25 \text{ mL} \cdot 2 \text{ ppm} \]

\[ V_{\text{working-standard-to-add}} = 2 \text{ mL} \] \hspace{1cm} (1.2)

So, to make up this low-level calibration standard – a 2 ppm standard – use 2 mL of the more concentrated working standard and 23 mL of DI water.

7. Run your low-level calibration standards on the Permeameter spectrometer.

a) Pour your standards into aluminum foil-covered test tubes. One tube should contain only DI water and one each for the low-level standards prepared. Be sure to have each tube labeled appropriately.
b) When the Dark and Reference Files have been stored on SpectraSuite, click on the Absorbance button (blue “A” located immediately above the graph). Prior to beginning, a good rule of thumb is to start with the lowest concentration (water itself) and finish with the highest concentration.

c) With the probe in the water test tube, click on the “Strip Chart” button (far right button on uppermost menu bar, icon is a graph with a red and green line on it). You should be in the Single Wavelength setting. For red, use 550nm, while 486nm works best for yellow-green. Use the arrow keys next to the values to select your wavelengths; if you try to simply type in your wavelengths, it will not save and refer to the defaults.

d) When you click Accept, a new graph will appear and the program will plot your data. When the line reaches the end of the screen, click the Save button (button with disc on it, directly above the graph). In the popup window, highlight the settings for the plotline (there should be only one line listed). Create a folder in the desktop to save this data and data for the remaining standard samples. Once you have your location selected, click Save. You must then click **Save** in the Save Trend window in addition to the normal Save procedure or the data will not save.

e) This completes the analysis for the first point. Repeat steps 3-5 for the subsequent standard samples.

f) To retrieve your data, open the desktop folder you created. Open the specific file with WordPad. Copy and paste the absorbance data into an Excel file. Create a calibration curve of concentration verses average absorbance.

8. Perform tracer tests in the Permeameter using dye standards.

   a) Ensure that the manual inlet and outlet valves corresponding to your bed of interest are open.

   b) Insert the spectrometer probe into the sample point. Unscrew the cap and then extend the plunger. Ensure that you are using the metal collar located within the sample point cap (including the O-ring) on the probe itself so that a water-tight seal can be achieved. Carefully guide the probe into the sample point.

Open the water supply valve on Station by clicking on D531.

   c) Begin to flow water into the unit: Click on F531 (water flow rate control valve). Enter an OP valve of 20-30% to start water flowing into the unit.

   d) Monitor the differential pressure (d/p transmitter) using P502 (top of the schematic, units = inches of water). The span of the d/p is 250 inches of water. For higher ΔP’s, the Bourdon pressure gauge must be used instead.

   e) Visually confirm that water is flowing to the drain. Also confirm that no water is flowing out of the probe sample point.
f) Purge air from the pressure lines by opening the bypass valve on the d/p transmitter. Close the valve after 1-2 minutes.

g) Change F531 from “MAN” to “AUTO.” Adjust the setpoint until the assigned flowrate (in mL/min) is achieved.

h) Verify that the UV/Vis software is loaded and ready to read and the spectrometer is online.

i) When water begins flowing through the unit, your Absorbance profile should match up to the profile of the probe in the test tube of water.

j) Prep for sample injection: Click on D504 and change the status from “Running” to “Charging.” This will allow you to load your sample into the injection valve.

k) Detach the syringe from the unit. Draw approx. 15 mL, attach the loaded syringe back onto the unit, and inject the contents into the sample loop. DO NOT detach the syringe after injection while in “Charging” mode, as most of your sample will drain out of the loop.

l) Prepare a Strip Chart to track the passage of your sample across the spectrometer probe. Use the same protocol for prepping a Strip Chart as you did for the Calibration.

m) Once the Strip Chart is ready and a plot is being drawn on the chart (should be a horizontal line at or close to 0), change the status of D504 from “Charging” to “Running.” Your sample is now introduced into the unit.

n) When your sample has been recorded, you can save your data using the same protocol for saving data for calibration points. Make note of the clock time when your sample begins and ends; when moving your data to Excel, you will not need all of the zero-absorbance points.

o) Clean out the injection chamber: Change the status of D504 from “Running” to “Charging.” Detach and load the syringe with water, then inject the water into the chamber. Do this at least twice. Change the D504 status to “Running” and let the unit water flow for 5 minutes.

p) Flush the unit lines: The dyes used for this experiment can stain and potentially skew future results if not flushed out. To ensure that trace remnants of the dye do not coat the walls of the piping, set the flow rate to 2500 mL/min (or as high as possible) and let flow for 10-15 minutes.

q) When done injecting tracers, click on F531 and change the status from “AUTO” to “MAN.” Set the OP to -6%. Click on D531 and change the status from “Open” to “Closed.”
r) When water has stopped flowing, carefully remove the probe from the sample point and place back into the water-filled test tube. Place the collar and O-ring back into the nut, put the plunger back in its starting position, and re-attach the nut.

s) Turn off the light source, each light individually and then the main on/off switch.

t) Log off of Honeywell Station and SpectraSuite. Be sure to disconnect from the USB2000 on SX Virtual Link before logging off entirely.

**SPECTROPHOTOMETER TROUBLESHOOTING TIPS**

Successful operation of the spectrometer requires careful attention to detail; and even then, some problems inevitably occur and troubleshooting skills are called upon. Follow the guidance given below to both avoid and correct problems that may occur.

1) Daily standard checks must be made prior to operation of the unit. Use one of your previous standards at the same conditions as before. The spectrum should not vary more than 0.05 Å (10 nm) from before. The absorbance should not vary by more than ±15% from before. If you cannot reproduce the previous readings, then something is "WRONG" and you must correct before you can successfully use the unit. See below, and possibly consult with your Instructor.

2) The following are possible problems:

   a) The probe mirror is coated with something other than the standard. Inspect it carefully and clean the glass with a soft cloth. Wash it thoroughly with DI water, shake off any excess water and insert the probe in your sample again with some stirring.

   b) The lamp has failed and its raw signal intensity is < 1000 in the Scope mode.

   c) The optical fiber connecting the probe to the USB 2000 unit is broken or frayed.

   d) Your sample has become turbid due to contamination or other reason.

   e) The USB connection has failed and needs to be reinitialized. (See the earlier section in this manual on using the SX Virtual Link application to reconnect).

   f) See the Lab Coordinator for a replacement probe if no other problem can be found.

3) Never let the PC go into standby or hibernation mode as the USB communication will be lost when this occurs. To correct, go to START then CONTROL PANEL then POWER OPTIONS. “System Standby” and “System Hibernate” should be set to “Never”.

4) Ensure that you have entered the “Path” to your references in the SpectraSuite directory. Be sure the reference file is not set to “Read Only.” You must take and store a dark and solvent reference in the Scope mode before switching to the Absorbance mode to run a sample. New references must be taken after any change to settings such as integration time, averages, boxcars, and cursor (wavelength) setting.
5) Obtaining an unusual spectrum can be the result of detector saturation. This can be caused when you have to select too high an integration time due to a dirty sample window. Try cleaning the probe, and restarting the software. Restarting the software has solved problems which arose for no known reason.

6) A “ragged” spectrum can be caused by the following:

   a) A loose connection. Check to see that all connections are hand tight.

   b) A damaged probe mirror or blue cable. These cables contain optic fibers which can fail if twisted too much or otherwise abused.

   c) Probe mirrors are delicate and can be broken by dropping the probe or letting it hit the metal reactor or piping. The mirrors can be crushed by inserting the probe too deeply into the outlet line when continuously sampling.

   d) The spectrometer is “sensitive” to very small quantities of impurities. When removing the probe from a sample tube, be sure to clean it thoroughly before inserting it anywhere else for an absorbance reading or calibration. When in doubt, re-clean all test tubes and the probe thoroughly.

**REACTIVE (PARTITIONING) TRACERS**

Some assignments may require you to use a reactive (adsorbing) tracer. Almost all reactive tracers are more soluble in the organic than the water phase. So in order to determine the equilibrium K in a batch experiment (use test tubes) it’s better to use an excess of water (why?). There is no need to determine a calibration curve for the tracer in the organic phase (why?). Sometimes impurities from the organic phase cause aberrant absorbance readings for the tracer when the organic/water phases are present in equilibrium. If you find this to be the case, decant some of the water phase into a new test tube and heat it to drive off these impurities, and then determine its absorbance.

**INITIATING TWO PHASE FLOW TO HORIZONTAL BEDS**

If two phase flow operations are needed as part of an experimental program, follow the directions below to achieve two phase flow.

1. Be sure that F531 and D531 (water to fixed beds) are closed. Be sure that the inlet and exit valves to the desired bed are open.

2. Be sure D511 (drain from fluid bed) is open. Be sure the manual valve for air to fixed beds is closed.

3. Slowly open air regulator to establish an air flow (< 5 psig at first).

4. Open the manual valve for the air to the fixed beds.

6. Set water flow controller at desired setpoint and open F531. Check pressure drop – is it too high? Adjust controller setpoint as necessary in all subsequent steps.

7. Open D502 to gas-liquid separator; be sure BV12 to fluid bed is closed and BV13 to drain is open.

8. Close D501 so that all flow goes to gas-liquid separator.

9. Confirm that water is exiting to drain. You may want to close BV13 for a period of time to build up a liquid head in the gas-liquid separator.

10. Adjust air flow as desired using the pressure regulator and the dry test meter on the gas exit line. You can close BV13 for short periods of time to get a correct gas flow reading on the dry test meter.

11. Disconnect the dry test meter if you see water exiting from the gas exit line!

12. When shutting down, shut off water (F531 and D531) first.

**USING THE POLARIMETER – SUCROSE INVERSION REACTION**

Polarimetry measures the extent to which a substance interacts with plane polarized light (light which consists of waves that vibrate only in one plane). It can rotate the polarized light to the left, to the right, or not at all. If it rotates polarized light to the left or to the right, it is “optically active”. If a compound does not have a chiral center, it will not rotate polarized light. The number of degrees and the direction of rotation are measured to give the observed rotation. In the literature and handbooks, the observed rotation is corrected for the length of the cell used and the solution concentration, using the following equation:

\[
[a]_{lt} = \frac{([a]_{obs})(l \times c)}{(1)}
\]

Where: \( a \) = specific rotation (degrees) (literature value), \( l \) = path length (dm), and \( c \) = concentration (g/mL).

Comparing the corrected observed rotation to literature values can aid in the identification of an unknown compound. However, if the compounds are known, it is more common to prepare calibration standards of the unknowns and correlate the observed rotation to concentration.

The WXG-4 polarimeter is located in Room 159. Turn on the sodium lamp (remember to turn it off when you leave). It takes approximately 5 to 10 min to warm up – should see yellow light. Check the zero position of the dial. At zero, you should see a uniform dark field (no dark/light fringes). Add the solution to one of the clean tubes. Note that you must stick with the same tube for both calibrations and measurements (why?). Use DI water to clean tubes. Place the tube in the polarimeter, with the bulb near the eyepiece and facing up to remove any trapped air from the line of sight, and then close the cover. If the solution rotates polarized light, you should see dark/light fringes through the lens. Rotate dial until the fringes disappear, and you again see the uniform dark field. Read the rotation angle through the magnifying glass, also using the vernier
scale. The dial divisions are 1 degree each, the vernier divisions 0.05 degrees. You may have to adjust the focus by rotating the black dial just below the eyepiece.

We have sucrose, glucose and fructose available to prepare calibration solutions for the polarimeter. The Instructor will tell you if it needs to be calibrated, or will provide a calibration.

**USING THE REACTOR (BED 1) FOR SUCROSE KINETICS STUDIES**

The sucrose inversion reaction is:

\[
\text{sucrose} \rightarrow \text{glucose (dextrose)} + \text{fructose}
\]  

(2)

This is an acid-catalyzed reaction and the catalyst (AM-15) is a common industrial solid acid catalyst of the sulfonic acid type – the sulfonic acid groups are attached to a poly (styrene-co-divinylbenzene) backbone. Catalyst properties are: size – 20-40 mesh; weight = 223 g; water content = 30 wt. %; apparent (bulk) density = 1010 kg/m³; acid site concentration = 4.6 mmol acid groups/g dry weight; surface area = 50 m²/g; macroporosity (macropore volume/total volume of cat.) = 0.34; average macroapore size = 80 nm.

The catalyst can be activated by passing 0.25 M sulfuric acid over it. About 2 L of acid should do the trick, followed by ~200 mL of DI water. The acid protons will exchange for whatever other ions are attached to the sulfonic acid anions. This is called “regenerating” the catalyst.

The reaction kinetics are usually found to be first order in sucrose concentration and first order in concentration of catalyst sites. So for a non-deactivating or slowly deactivating catalyst this reaction can be approximated as simple first order. Of course, like most acid catalysts, some deactivation will take place over time. Lifshutz and Dranoff report a second-order rate constant of ~0.014 g dry cat./(mmol acid sites-min) for a similar catalyst at 60°C, with an activation energy of 77 kJ/mol[2]. Gilliland et al. report ~0.020 g dry cat./(mmol acid sites-min) with an activation energy of 84 kJ/mol, again for a similar catalyst at these conditions[3].

A typical temperature for the reaction is 60°C. You should see reasonable conversions in the range of 80 to 100 mL/min of a 20 wt. % sucrose (in DI water) feed. You MUST use DI water for the feed. When preparing the sucrose solution, add it slowly to some water, while stirring, at room T. Use both a magnetic stirrer and a paddle.

The temperature controller, T505, should be using the following tuning parameters for operation in the 80 to 100 mL/min range near 60°C: \(K_c = 0.34 \%OP/%PV\), \(T_i = 21\) min, \(T_d = 5\) min. Use T5AVG for the control thermocouple unless instructed otherwise. Implementing control with the specifications just given should allow the unit to move from ambient to 60°C in roughly 45 to 60 minutes and control within 3 to 4°C of the set point, using this average sensor reading (computed from T503 and T502) for temperature control.

When starting the heater up, first place the T505 set point (SP) to near (say 10°C below) the process value. Then place the controller in AUTO. When the reactor T first crosses the set point, move the set point to the desired final temperature. There may be a temperature profile across
the catalyst section, as can be seen by examining thermocouples T502 and T503. Consider this in experimental design and data analysis.

Do not conduct runs in excess of 60°C without the express authorization of your instructor. Additionally, recognize these issues: a) liquid flow must be present at all times in the bed once heat has been applied, and b) if process water from F531 is used to supply flow at any point with heat on, the flow rate indicated on the flow controller may not be correct – so, a bucket and stopwatch flow check should be initiated to ensure that adequate flow is being used.

The biggest problem in controlling $T$ is keeping the flow rate constant. Try setting the peristaltic pump to constant output and controlling flow with the manual rotameter valve. Fairly consistent attention to this is necessary.-

Samples of the reaction products should be collected at the drain in test tubes or sample bottles. Do **not** use the online spectrometer probe when running the sucrose inversion reaction or regenerating the catalyst (why?). Also, do not collect samples until at least two bed residence times have passed (why?).

**SHUT DOWN PROCEDURE FOR KINETICS STUDIES**

T505, Bed #1 Temperature Control in Station, must be set to zero (0) temperature on MANUAL (-6.90 % OP) before you leave the lab. Serious damage to the catalyst and bed can occur if the temperature exceeds 100°C.

Station is programmed to cut off the heaters if the bed temperature reaches 90°C. The computer is also programmed to shut off the heaters if the pressure drop, as measured by the d/p cell, falls below 1 in. H₂O column pressure, indicating no water is flowing. See your instructor if this pressure drop limit needs to be set higher for the 80 ml/min flow during the sucrose reaction.

**USING THE REACTOR (BED 1) FOR PROCESS CONTROL STUDIES**

A variety of process control studies can be carried out using the Permeameter Bed 1 subsystem. One can attempt to control process temperature by adjusting the heat input to the bed or by adjusting the liquid flow through the bed.

To control temperature using the heater output is referred to as **Standard mode**. Bed 1 exit temperature (T501) is used to sense the temperature of the exiting liquid stream; Bed 1 start-of-catalyst bed temperature (T503) and end-of-catalyst-bed temperature (T502) can be used to sense the temperature within the bed. Between-the-heaters temperature is measured by T504. The average of T503 and T502 is computed at T5AVG. Any of these couples (and the T5AVG) may be used as the control couple for the T505 temperature controller. Notice that in Standard mode, the left-most selector button reads **Cascade** – to indicate that clicking this selector button will switch the display and control scheme to Cascade mode. In Standard mode, temperature controller T505 senses the appropriate temperature (depending on which thermocouple has
been selected) and automatically adjusts the heat input to the reactor by adjusting the electrical current to the heater elements.

To control temperature using the liquid flow rate is referred to as **Cascade mode**. In Cascade mode (see Figure 2), any of the four Bed 1 thermocouples can be used to control the temperature (just as in Standard mode) while the T531 controller manipulates the F531 secondary controller. Notice that in Cascade mode, the left-most selector button reads **Standard** – to indicate that clicking this selector button will switch the display and control scheme to Standard mode. In Cascade mode, the temperature controller T531 senses the appropriate temperature (depending on which thermocouple has been selected) and adjusts the heat load on the reactor by adjusting the set point of the main water flow rate to the reactor using a typical cascade control configuration. A constant heater output is supplied by adjusting the output of the T505 controller in MANUAL mode.

Suitable tuning parameters must be in place in all controllers to allow for proper temperature control of Bed 1 using the control strategy of choice. The Honeywell system has been configured to cut off the heater elements if the exiting bed temperature reaches 90°C or if the flow rate of water is so low that the Bed 1 pressure drop falls below 1 in. H₂O column pressure.
SHUT DOWN PROCEDURE FOR CONTROL STUDIES

Use the following steps to ensure that the Permeameter is left in a suitably safe mode after conducting Bed 1 control studies:

- Place the unit display into the Standard mode.
- Change the set point of T505 to 0°C.
- Place controller T505 in MANUAL mode and set its output to -6.9%.
- If the heater has been on and the bed temperature is elevated, raise the water flow rate (F531) to 2000 cc/min and wait till the temperature of the exiting stream is less than 30°C.
- Place controller F531 in MANUAL mode and set its output to -6.9%.

Serious damage to the catalyst and bed can occur if the temperature exceeds 100°C.

INITIATING AIR FLOW TO VERTICAL (FLUIDIZED) BED AND GAS TRACER INJECTION

Use the same Steps 1 through 3 as that for introducing two phase flow.

4. Close D511 (drain from fluid bed) and BV13 from the separator to the drain.
5. Confirm that air is exiting from the line near the gas cylinders.
6. Monitor differential pressure across the bed (see the “Fluid Bed del(P)” graphic).
7. Open the rotameters to the “Sample” and “Reference” sides of the TCD detector to near their maximum values (2.0). They should be kept equal to one another.

8. Turn on power to TCD detector; using the “Zero” knob, zero the signal. Check for zero on the computer also. It doesn’t have to be exactly zero, just near zero and stable.

9. The inert tracer for the gas phase experiments is CO$_2$. It must be syringe-injected using a LARGE syringe with a 25-ga. needle. Turn the CO$_2$ cylinder on and adjust regulator pressure until you reach ~5 psig at the sample point. Keeping some pressure on a syringe, insert it into the sample point, and allow it to fill. Then, after noting the time, inject the sample at the injection point below the fluidized bed.

10. Note the need to periodically check for leaks at the sample and injection points and replace septa as necessary. You can use Snoop to check for leaks.
REFERENCES

