UNIVERSITY OF MINNESOTA DULUTH
DEPARTMENT OF CHEMICAL ENGINEERING
ChE 3211-4211

ABSORPTION OF CARBON DIOXIDE INTO WATER

OBJECTIVE

The objective of this experiment is to determine the equilibrium line, the height and number of liquid transfer units, and overall mass transfer coefficient in the removal of CO_2 from a gas stream. Henry's Constant for CO_2 can also be calculated from the data gathered in this experiment.

INTRODUCTION

The apparatus consists of a cylindrical column or tower with a gas inlet and a distribution space at the bottom; a liquid inlet and distribution space at the top; gas and liquid outlets at the top and bottom respectively; and a supported mass of tower packing, known as raschig rings.

REFERENCES

McCabe, W. L., Smith, J. C., Marriott, P., "Unit Operations of Chemical Engineering", 4th Edition, McGraw-Hill, 1985

Washburn, E. W., Editor, "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology", McGraw-Hill Book Company, Inc., New York, N.Y.

Treybal, Robert E., "Mass-Transfer Operations", McGraw-Hill Book Company, Inc., New York, N.Y., 1980

EQUIPMENT

1. Gas absorption column
2. 50 mL buret and buret clamp
3. 50 mL graduated cylinder
4. Stopwatch
5. 1-50 mL pipet (if needed)
6. 125 mL erlenmeyer flasks
7. Thermometer
8. 2-L pop bottle
9. 3 or 5 gallon bucket
10. Clamp stand
11. Elbows with short piece of plastic tubing

12. 1-1 L graduated cylinder

CHEMICALS/MATERIALS

1. Phenolphthalein indicator solution.
2. 0.0500 M sodium hydroxide solution.
3. Carbon dioxide gas.
4. Tap water at a temperature of 20-22°C.
5. 1.0 M sodium hydroxide

EXPERIMENTAL PROCEDURE

A schematic diagram of the gas absorption column is shown in Figure 1. The inside diameter of the column is 3-1/8" (8 cm) and the dimensions of the Raschig rings are OD 1.0 cm, ID 0.8 cm, L 1.0 cm.

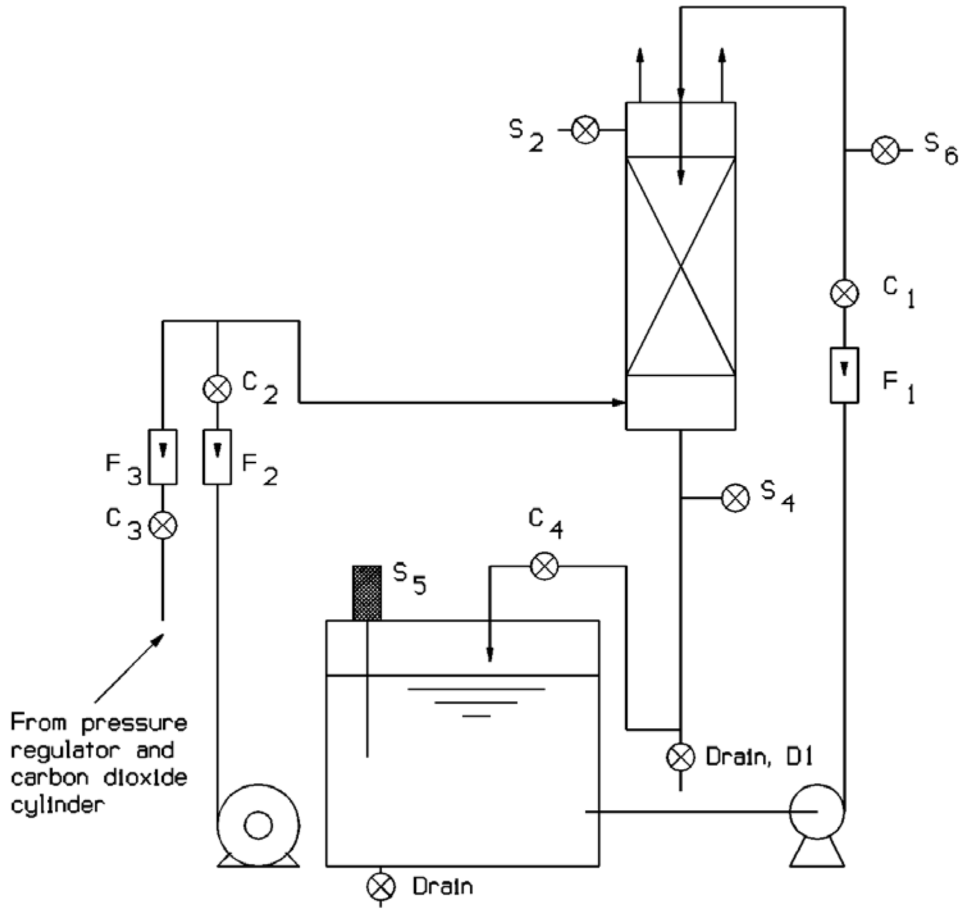

Figure 1. Gas Absorption Column System

The experimental procedure is split into three separate parts. In part 1, you will calibrate the flow meter used to deliver CO_2 by measuring the volume fraction of CO_2 in a flowing mixture of air and CO_2. In part 2, you will first bring water to equilibrium with an airstream containing CO_2. After equilibrium is reached, you will follow the desorption of CO_2 into normal laboratory air. In part 3, you will study the absorption of CO_2 by water in a column in a common operating mode. Follow the procedures below.

Part 1. Calibration of Gas Flow Meters and the Measurement of CO_2 in the Gas Phase

Calibration of the CO_2 flow meter

1. Fully open the main valve on the CO_2 tank carefully. Slowly adjust the regulator on the cylinder to give a gauge reading of about 20 psi. The valve $\mathbf{C_3}$ on the flow meter $\mathbf{F_3}$ is then used to deliver CO_2 at the metered flow rate.

2. Disconnect the CO_2-delivery line on the downstream side of $\mathbf{F_3}$ at the plastic coupling (this coupling is on the tubing at the back of the apparatus). Find the section of tubing with a right angle connector attached to it with another short piece of tubing connected to the connector in the box containing the 2 liter pop bottle. Connect this section of tubing to this coupling (connect to the coupling on the section of tubing coming from the meter).

3. Fill the bucket with water to within a few inches of the top. Place the tripod in the bucket; the top of the tripod should be just immersed.

4. A 2-L pop bottle is used the calibrate the flow rate of CO_2. First determine the volume of the pop bottle by measuring the mass and temperature of water required to fill the bottle.

5. Fill the 2-L pop bottle with water and cap loosely. Invert the bottle and place the top under the water in the bucket using the tripod and clamp stand to support the bottle. When in position uncap the bottle.

6. Adjust the CO_2 flow to 2 L/min. Place the tubing with the right angle connector you attached in Step 2 under the water and insert the end of the tubing into the bottle so that its end is well away from the neck of the bottle, then insert the tube into the neck of the bottle. As you insert the tube into the neck of the bottle, your partner should start the stopwatch. Record the time required for the CO_2 to displace the water and fill the bottle with CO_2. You should check the setting of the flow meter as the bottle is filling with gas. If it has changed you will have to redo the calibration or use the value read from the meter.

7. Repeat the calibration for settings of 3, 4 and 5 L/min. Redo the calibration for one of the settings.

Measurement of the Volume Fraction of CO_2 in the Gas Stream

1. Familiarize yourself with the analysis system for CO_2 in the gas stream; this is described in Appendix A. The Lab Coordinator or Faculty Instructor will show you how it works. (The absorption globes should already be filled with 1.0 M NaOH.) It is important for you to understand the operation of the three-way stopcocks; diagrams

are attached to the wall behind the apparatus and in Appendix A.

2. What are the safety precautions that must be taken when working with high pressure gas cylinders?

3. Try out the analysis system by measuring the volume fraction of CO_2 in the ambient air. What do you expect the volume fraction to be? Are the results reasonable?

4. Insure the compressed air line is connected to the unit and the valve on the air line is open (next to the unit). Adjust the air flow rate through the flow meter to 20 L/min using the control valve $\mathbf{C_2}$. The air flow tends to drift so it is important to monitor it periodically.

5. Reconnect the CO_2 line to the flow meter at the rear of the experiment panel. Adjust the CO_2 flow to 2 L/min.

6. Collect a sample of gas from the top of the column, valve $\mathbf{S_2}$, and determine the volume fraction of CO_2 in it. Repeat the measurement with a new gas sample.

7. You should continue to measure the volume fraction of CO_2 in gas samples from the top of the column for CO_2 flow rates of 3, 4 & 5 L/min with the air flow set at 20 L/min throughout.

With these volume fractions and the calibrated CO_2-flow rate, you can calibrate the air flow setting of 20 L/min.

Part 2a: Bringing water to equilibrium with CO_2 and analysis of CO_2 in water

1. Close the drain valve under the liquid reservoir tank, the control valve, $\mathbf{C_4}$, and the column drain valve, $\mathbf{D_1}$. Fill the liquid reservoir tank at the base of the column three-quarters full with water from the tap. Use the white bucket with the volume marking on the outside. Use hot water to bring the temperature within room temperature range (20-22°C). Record the volume and temperature of water. Place the cover on the tank. Collect a sample and determine its initial CO_2 concentration following the directions in the Analysis Procedure (Appendix B).

2. Open control valve $\mathbf{C_4}$. With gas flow control valves $\mathbf{C_2}$ and $\mathbf{C_3}$ closed, start the liquid pump, open valve $\mathbf{C_1}$ a couple turns for 15-30 s to expel air from the pump, then adjust the water flow through the column to 6 L/min on flowmeter $\mathbf{F_1}$ by adjusting flow control valve $\mathbf{C_1}$.

3. Adjust the air flow rate through flowmeter $\mathbf{F_2}$ to 20 L/min using control valve $\mathbf{C_2}$. **NOTE:** Monitor and readjust the air flow rate during the experiment as it has a tendency to drift. Note any readjustments on your data sheets.

4. Carefully open the main valve on the carbon dioxide cylinder all the way. Slowly adjust the pressure regulating valve on the carbon dioxide regulator to give a gauge reading of approximately 20 psi. Adjust valve $\mathbf{C_3}$ to give a CO_2 flow rate on the flowmeter $\mathbf{F_3}$ corresponding to the flow rate you have been assigned by your faculty instructor, 2 through 5 L/min. Insure that the liquid seal at the base of the absorption column is maintained by adjustment of control valve $\mathbf{C_4}$ if necessary.

5. After 10 min of operation, take 50 mL samples at appropriate intervals from $\mathbf{S_6}$ until the dissolved CO_2 values are constant. Analyze the samples following the directions in the Analysis Procedure (Appendix B). Once the levels of dissolved CO_2 appear to be constant, take a couple samples from $\mathbf{S_4}$ to confirm that equilibrium has been reached.

6. Measure the volume fraction of CO_2 in the air leaving the column (from $\mathbf{S_2}$) once the dissolved CO_2 levels are constant.

Part 2b: Desorption of CO_2 into laboratory air

1. Once the CO_2 values from step 5 are constant, shut off the CO_2 flow at the flowmeter (valve $\mathbf{C_3}$), decrease the liquid flow rate to 1.5 L/min, open the drain valve, $\mathbf{D_1}$, under the column, and close the control valve, $\mathbf{C_4}$. Adjust the drain valve, $\mathbf{D_1}$, under the column to maintain a liquid level above sample tap, $\mathbf{S_4}$. Immediately take samples as quickly (e.g. 1 minute intervals) as possible from $\mathbf{S_4}$ and $\mathbf{S_6}$. Analyze the samples following the directions in the Analysis Procedure (Appendix B).

Part 3: Absorption of CO_2 by H_2O in a common column mode

1. Close the drain valve under the liquid reservoir tank, the control valve, $\mathbf{C_4}$, and the column drain valve, $\mathbf{D_1}$. Fill the liquid reservoir tank at the base of the column full with tap water. Use hot water to bring the temperature in the range of 20-22°C. Fill one 5-gallon carboy with water at the same time as you fill the reservoir tank so the temperature of this water will be approximately the same as the water in the reservoir tank in case you need to add additional water to finish the experiment. Record the temperature of the water. Collect a sample and determine its CO_2 concentration following the directions in the Analysis Procedure (Appendix B).

2. Open the control valve, $\mathbf{C_4}$. With gas flow control valves $\mathbf{C_2}$ and $\mathbf{C_3}$ closed, start the liquid pump. Open valve $\mathbf{C_1}$ a couple turns for 15-30 seconds to expel air from the pump, then adjust the water flow to 1.5 L/min, open the column drain valve, $\mathbf{D_1}$, and close control valve $\mathbf{C_4}$. Use the column drain valve, $\mathbf{D_1}$, to maintain a liquid water

height below the air/CO_2 inlet but above the sampling valve $\mathbf{S_4}$. It is much easier to maintain a liquid level if sample valve $\mathbf{S_4}$ is left open. A bucket can be placed under the sample tubing to collect the water.

3. Adjust the air flow rate through flowmeter $\mathbf{F_2}$ to a value of 20 L/min using control valve $\mathbf{C_2}$. **NOTE:** Monitor and readjust the air flow rate during the experiment as it has a tendency to drift. Note any readjustments on your data sheets.

4. Carefully open the main valve on the carbon dioxide cylinder all the way. Slowly adjust the pressure regulating valve on the carbon dioxide regulator to give a gauge reading of approximately 20 psi. Adjust valve $\mathbf{C_3}$ to give a CO_2 flow rate on the flowmeter $\mathbf{F_3}$ corresponding to the flow rate you have been assigned by your faculty instructor, 2 through 5 L/min.

5. As soon as the CO_2 is turned on, take 50 mL samples from $\mathbf{S_4}$ at 30 second intervals during the first two minutes. Increase the interval between samples to one minute for the next five minutes. The interval can then be increased to five minutes until the concentration reaches a steady state. Analyze the samples following the directions in the Analysis procedure (Appendix B).

6. Analyze a gas sample from $\mathbf{S_2}$ once steady state is reached.

Note: Steps 2, 3, and 4 should be done as quickly as possible or the flow rates pre-set, the reservoir again filled with water and the experiment started. This will insure that you have enough water to complete the experiment.

SAFETY NOTES

1. Before starting the experiment, review the Material Safety Data Sheets (MSDS) on NaOH. The sheets can be found in the MSDS notebook located in the laboratory.

2. Personal protective equipment shall include goggles. Disposable nitrile gloves should be worn when handling NaOH solutions.

3. Check the safety requirements you need to be aware of when using high pressure gas cylinders.

4. A small amount of NaOH spilled on the outside of glassware can cause the glassware to be extremely slippery when wet. Be careful.

WASTE DISPOSAL PROCEDURES

All wastes from this experiment can be put into the sewer system without causing any problems. When disposing of wastes into the sewer system, please run additional water from the tap at the same time.

12/09

Appendix A

Use of Gas Analysis Equipment

In the following procedure three-way stopcocks are used in sampling the gas stream. The operation of the three-way stopcock is shown in Figure 2.

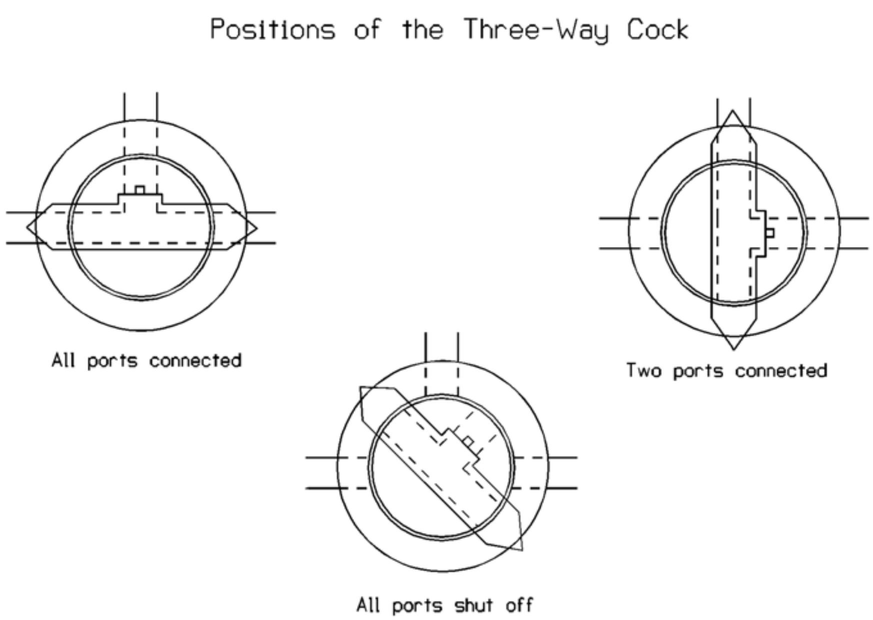

Figure 2. Three-way stopcock positions

PROCEDURE

1. Fill the two globes of the absorption analysis equipment on the left of the panel with 1.0 M NaOH solution if it has not already been done. Use a small funnel and tubing. **NOTE: Wear safety gloves and goggles.** Adjust the level in the globes to the "0" mark on the sight tube, by draining liquid through valve $\mathbf{C}_v$ into a flask (See A in Figure 3.). This will normally have been done for you. Ask the Lab Services Coordinator to add more NaOH if necessary to bring the level to zero on the measuring tube scale.

2. After 15 minutes or so of steady operation, take samples of gas from sample point S_2. Analyze these samples as given in the instructions listed below.

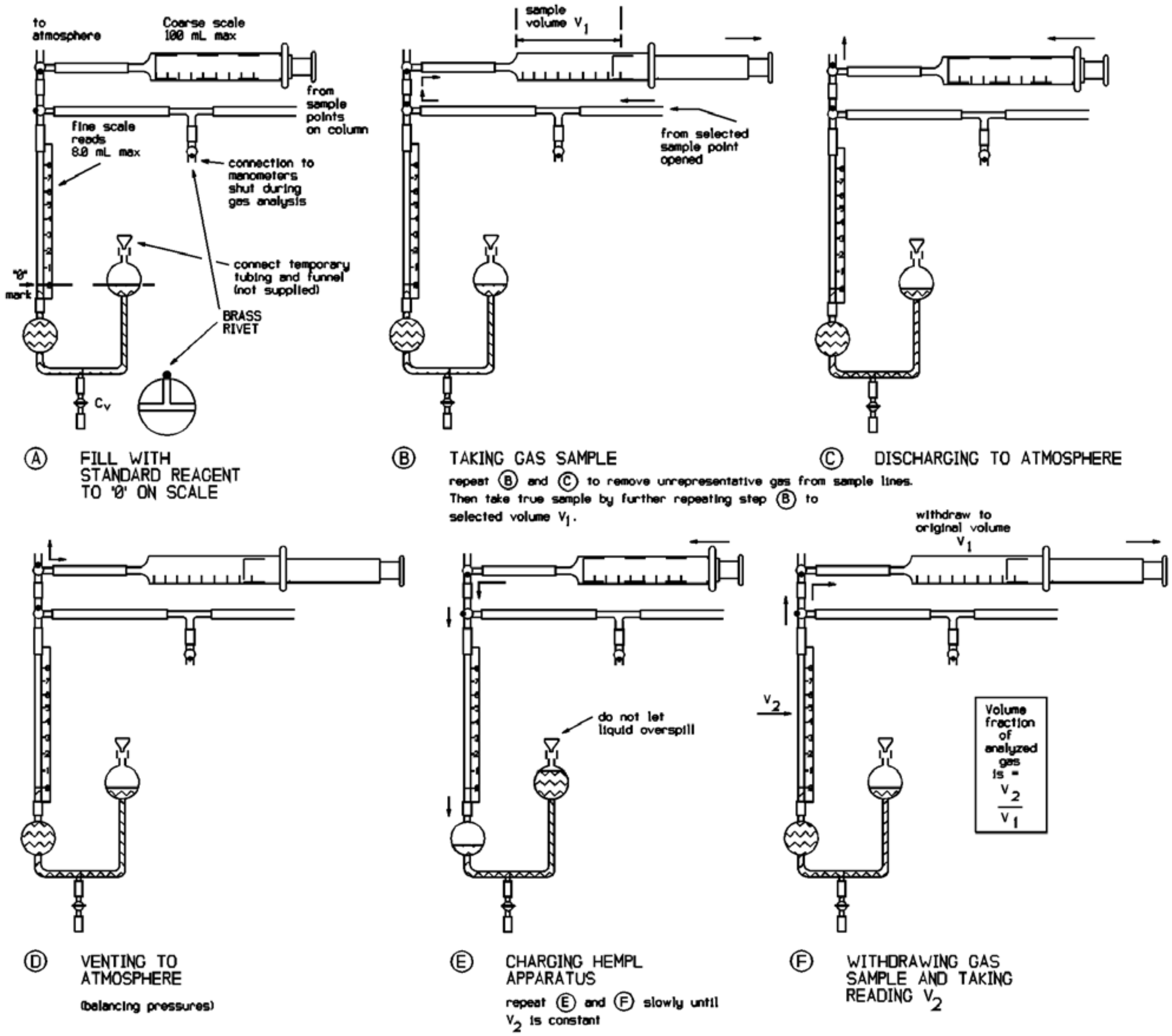

Figure 3. Hempl apparatus for gas analysis

3. Pull the piston of the syringe out to the stop. Take a squirt bottle of deionized water and wet the piston of the syringe. This insures there is a water seal so the gas pulled into the syringe can not leak out to the atmosphere around the syringe piston. This may have to be done several times during the experiment since the water on the piston does evaporate.

4. Flush the sample lines by repeated sucking from the line using the syringe and expelling the contents of the syringe to the atmosphere. Note that the volume of the cylinder is about 100 mL. Estimate the volume of the tubing leading to the syringe. How do you estimate this volume and how many times will you need to purge the line (Steps B & C)?

5. With the absorption globe isolated and the vent to atmosphere closed, fill the syringe from the selected line by drawing the syringe piston out slowly (Step B). Note volume taken into the syringe V_1, which should be approximately 20 mL for this particular experiment See **WARNING** note below). Wait at least two min to allow the gas to come to the temperature of the syringe.

6. Isolate the syringe from the column and the absorption globe and vent the syringe to atmospheric pressure. Close after about 10 seconds. (Step D).

7. Connect the syringe to the absorption globe. The liquid level should not change. If it does change, briefly open to atmosphere again.

8. Wait until the level in the indicator tube is on zero showing that the pressure in the cylinder is atmospheric.

9. <u>Slowly</u> close the piston to empty the gas in the syringe into the absorption globe. <u>Slowly</u> draw the piston out again (Steps E and F). Why would you want to do this step slowly?

   Note the level in the indicator tube.

   Repeat steps E and F until no significant change in level occurs. Read the indicator tube marking - V_2. This represents the volume of the gas sampled.

WARNING: If the concentration of CO_2 in the gas sampled is greater than 8%, it is possible to suck liquid into the cylinder. This will ruin your experiment and takes time to correct. Under these circumstances, do not pull the piston out to the end of its travel. Stop it at a particular mark, e.g. V_1 = 20 on the coarse scale, and read the fine scale.

Appendix B

ANALYSIS PROCEDURE FOR CO_2 IN WATER

1. The sodium hydroxide used in the experiment is standardized using the acidimetric standard (potassium hydrogen phthalate) available on the bench (a minimum of three titrations). It should be standardized each day.

2. Collect 50 mL with a graduated cylinder from the inlet to the column $\mathbf{S_6}$ or the liquid outflow point $\mathbf{S_4}$ depending on the sample point specified in the experimental procedure. If needed, collect a sample from the reservoir tank. **NOTE:** Purge the sample line before collecting sample. The sample should be collected with the sample tube below the liquid level in the graduated cylinder.

3. Place the sample in a 125 mL erlenmeyer flask.

4. Add 3-5 drops of phenolphthalein indicator solution. If the sample turns red immediately, no free CO_2 is present. If the sample remains colorless, swirl the flask and titrate with standard NaOH solution. The end point is reached when a definite pink color persists for about 30 seconds - record volume V_B of the NaOH added.

5. The amount of free CO_2 in the water sample is calculated from:

$$\text{gram mole / liter of free } CO_2 = \frac{V_B \times (\text{Conc. Base})}{\text{mL of Sample}} = C_d$$

C_{di} = Concentration at inlet (corresponds to conditions at the top of the tower, $\mathbf{S_6}$).

C_{do} = Concentration at outlet (corresponds to conditions at the bottom of the tower, $\mathbf{S_4}$).

Note: Solubility of CO_2 in water is a strong function of temperature and pH.

Department of Chemical Engineering

Stockroom Checkout slip

Absorption of Carbon Dioxide into water   ChE 4211

Name: __________________________   Date: ________________________

(print name)

Lab No.: Lab 1 Tuesday 12:00 - 4:50 PM   Lab 2: Thursday 12:00 - 4:50 PM

Lab No.: Lab 3 Tuesday and Thursday morning (9:30 - 11:50 AM)

(circle one)

Equipment	Out	In	Equipment	Out	In
2 - 50 mL grad cylinder			Stopwatch		
12 - 125 mL E-flask			Digital Thermometer		
5 mL transfer pipet			2 - 250 mL beaker		
Pipet bulb					

Name: _____________________________

(Signature)