

GAS ABSORPTION EXPERIMENT

Objectives:

The educational objectives of this experiment are many; a few of the most obvious are to review mass transfer for two-phase systems, and to gain experience with a gas-absorption column and several auxiliary instruments for analysis. The student will use an infrared gas analyzer, manometers, wet test meter, gas cylinder with regulator and heater, do extensive volumetric analysis and standardization, and use numerous manuals and material data safety sheets. Because of the time-intensive nature of the assignment, the student will get experience efficient experimental design, time management and division of work. The nominal objective for the student is to characterize the performance of a packed-bed absorption column, and to compare these observations with analyses or empirical information recorded in the literature.

Cautions:

Study the Material Safety Data Sheets (MSDS's). Know the chemicals you are handling. You will be using caustic solutions (NaOH) that can cause severe chemical burns, and high-pressure gas cylinders. Use disposable gloves and goggles to handle caustic and for cleaning spills. Always wear safety glasses, and supplement these with goggles or face shield when handling solutions. Gas cylinders should always be securely strapped.

Do not proceed with different phases of the experiment until you understand how each piece of apparatus works. Do not be afraid to ask for help, for this experiment is rather complex and requires attention to detail to get good results.

When starting up the system, always use low initial air and water velocities. Be sure the recycle valve to the sump pump is always at least partially open to prevent buildup of liquid and flooding. An extension has been added to the top of the column to help prevent spillage of caustic.

The gas cylinder regulator handle should be "loose" (easy to turn) before opening the tank. See safety instructions in the auxiliary section notebook. Open the tank valve slowly. Remember to plug in the gas heater 5 minutes before turning on the gas. Turn off the gas at the end of the day, or else you will not be able to operate during the next lab period!! Relieve the spring pressure on the regulator diaphragm by backing out the regulator handle to its original "loose" position.

Calibrations:

1. Volumetric Solutions – See separate section.
2. Infrared Meter – Check with pure air and the available 8% CO₂/air mixture. Normally the meter does not require any adjustment.

3. Gas Flow – A wet test meter (maximum flow 13 liter/minute) is available. See auxiliary manual for use to check air and CO₂ flows.
4. Solution Flow – This is rather difficult to check. Normally, water is pumped into a drum and weighed.
5. pH Meter – A pH meter is not needed, but students sometimes want to do a quick check on pH of a solution. pH 7 and pH 4 buffers are available for two-point calibration. Due to CO₂ pickup from the atmosphere, the pH 10 buffer is accurate only if fresh.

Procedure:

Make an initial run with distilled water, using 37.5 L water in the sump tank. Turn on the heater and then the air, using low initial flows. Turn the CO₂ heater on for five minutes before using. Set air 20-40 L/min and Liquid 1.5-6 L/min. Set CO₂ to no more than 10% of the air flow rate. Run the system for at least 5 min before sampling.

Analyze inlet and outlet gases and take 250-mL samples from the tank and bottom of the column. The manometers can be used for measuring pressure drops across the two parts of the column. The gases are analyzed by the infrared analyzer. The liquids are analyzed by the procedures included in this handout. Also see appropriate manuals. Do not get liquid into the infrared analyzer. *Do* ask for help if you have any uncertainty about these procedures.

Because water has very low affinity for CO₂, you may have trouble measuring the amount of CO₂ transferred. Thus, use the water runs mostly to learn (under safe non-alkaline conditions) the operation and behavior of the column, master the use of the CO₂ meter, examine pressure drops at a few flow rates, and find conditions that cause flooding. Plot water flow vs. air flow where flooding is observed and use this graph to plan your experiments.

Now add 300 g NaOH pellets to 37.5 L water in the tank and stir with a plastic paddle to effect solution. Caution – do not let the pellets clump in the bottom or you can waste an hour trying to dissolve them! Start the mechanical stirrer before running.

Make several runs with NaOH. Include different liquid and gas flow rates so that the effect of these variables on the mass transfer can be determined. Note that $K_g a$ may also depend on CO₂ fraction in the gas and NaOH concentration in the liquid.

Sample input, output gases, and liquid from the tank and bottom of the column. A center port is also available for gas analysis. Titrate samples taken at different times and check the carbon balance to establish steady state.

If time permits make comparison runs with water to compare the effect of chemical reaction on the mass transfer coefficient. Also, a more dilute concentration of NaOH might be tried. Consider the effects of the build up of carbonate in the recycled solution.

At the end of the experiment, turn off the valve to the CO₂ tank, open the regulator valve, and unplug the heater. After neutralization, the solution tank can be emptied into the floor drain through the spigot on the bottom after attaching a suitable length Tygon tubing. Rinse a few times to remove caustic and clean up all caustic spills on the apparatus and floor.

Report:

Calculate mass balances and mass-transfer coefficients for all runs. Correlate the mass-transfer coefficients with gas and liquid flow rates. Derive an empirical process model for the column's performance, and compare your results with those found in the literature. From your findings, decide which phase is the controlling resistance to mass transfer and suggest methods for improving the column's performance.

References:

J. H. Perry, Ed., *Chemical Engineer's Handbook*, 5th or 6th ed., p. 14.2 - 14.40, McGraw-Hill Publishing Co., New York, NY, 1973.

W. L. McCabe and J. C. Smith, *Unit Operations of Chemical Engineering*, 4th ed., p. 617-631, McGraw-Hill Publishing Co., New York, NY., 1985.

See the Appendices for theory, standardization, and gas and liquid analysis procedures.

An auxiliary manual is available containing information on the infrared analyzer, wet test meter, carbon dioxide chemistry, gas apparatus, and Material Safety Data Sheets.

Theory:

In a gas absorption column, a component of the gas stream is absorbed into the liquid stream. The absorption may be purely physical, or it may involve solution of the gas into the liquid followed by chemical reaction.

The rate of mass transfer is governed by stream flow rates, interfacial contact area, component diffusivities, temperature, pressure, and concentration. They are all represented in the equation:

$$Z_T = \int_{y_o}^{y_i} \frac{d(Gy)}{K_g a A (y - y^*)} \quad (1)$$

where

- y_o = outlet gas mole fraction
- y_i = inlet gas mole fraction
- y = bulk gas mole fraction
- y^* = mole fraction of gas in equilibrium with the liquid at any point in the column
- G = molar flow rate of gas, mol/s
- Z_T = column height, m
- $K_g a$ = overall mass-transfer coefficient based on gas phase, mol/m³-s-mol fraction
- A = cross sectional area of the column, m²

For dilute gases in an otherwise inert gas stream, the above equation can be simplified to the expression:

$$\frac{Z_T A K_g a}{G} = \int_{y_o}^{y_i} \frac{dy}{y - y^*} \quad (2)$$

The driving force on the right hand side of the equation can be estimated from the partial pressures in the gas stream. Therefore, for transfer of a particular component of a gas stream:

$$N = K_g a A Z_T (\log - \text{mean driving force}) \quad (3)$$

where

- N = gram moles component absorbed/s

Assuming ideal gas behavior in the vapor phase, the mass-transfer coefficient can be found from:

$$K_g a = \frac{PN}{AZ_T} \left(\frac{\ln(P_i / P_o)}{(P_i - P_o)} \right) \quad (4)$$

where

- P_i = partial pressure of absorbing component in inlet stream, atm
- P_o = partial pressure of absorbing component in outlet stream, atm
- P = total pressure in the column, atm

Review the many assumptions in going from Eq.1, which is a simplified definition of K_a , and Eq.4. Design your experimental conditions to maintain the validity of these assumptions.

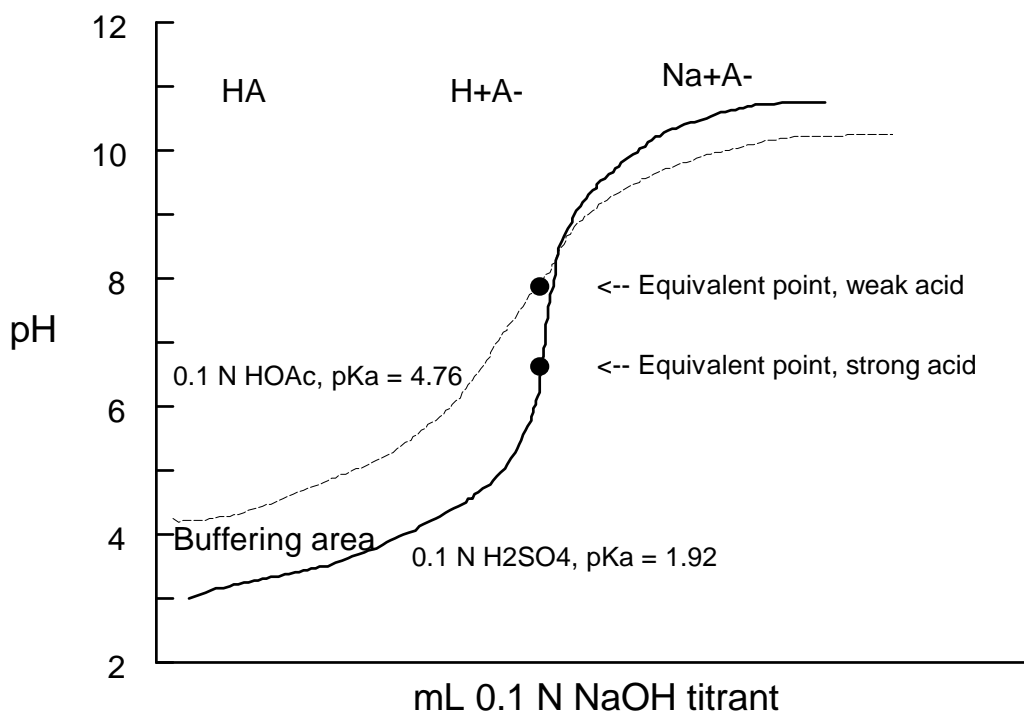
Analysis of Gas Samples for CO₂ Content:

A direct-reading infrared analyzer for CO₂ analysis has been installed. Read the auxiliary manual on this apparatus. Be careful not to draw liquid into the analyzer when taking samples. A 8% CO₂ mixture is available for calibration. Lab air should produce a reading of less than 1%.

Standardization of Acids and Bases:

Standardization is required to obtain the exact concentration of the titrant. It is accomplished by comparing to a solution of known (exact) concentration or by titrating a primary standard (dried solid accurately weighed).

A titration follows a curve with equivalence points depending on the nature of the material.



The equivalence point (end point) is where the moles of reactant (in this case an acid) equals the moles of titrant added. Depending on the pK_a the end point pH differs for various acids and bases. For volumetric solutions the number of milli equivalents (meq.) is:

$$(V, \text{ mL}) \times \left(N, \frac{\text{equivalents}}{\text{liter}} \right) = \text{meq.}$$

For solids: meq. = (mg of sample/molecular weight) (equivalents/mole)

To determine when the end point is reached, either an indicator that changes color at the right pH or a pH meter is used. Refer to prior work or the literature to determine the nature of the end point. Running your own full titration curve is one way of determining the end point (see above figure).

Examples:

1. To prepare 0.1 N NaOH weigh 4.00 g NaOH and dissolve in 1 L of distilled water. Titrate an accurately weighed portion (approx. 0.4 g) of dried Potassium Biphthalate to phenolphthalein end point (pink). Normally three titrations are averaged. (1 mL = 20.42 mg)

2. To prepare one liter of 0.1 N HCl from concentrated HCl at ~11.6 N.

$$11.6 \times V = 0.1 \times 1000 \quad V = 8.62 \text{ mL}$$

Add 9 mL concentrated HCl to 1 L distilled water.

Reagent grade Na_2CO_3 is dried 270 °C for 1 h, and desiccated 30 min. Weigh accurately approximately 150 mg of the Na_2CO_3 and titrate with the unknown HCl to clear phenolphthalein end point.

3. Given 0.1 N NaOH factor 1.013 to standardize \approx 0.1 N HCl.

Take 20.00 mL by pipette of NaOH solution, fill burette with HCl and titrate to phenolphthalein end point.

$$20.00 \times 0.1 \times 1.013 = V_{\text{HCl}} \times N_{\text{HCl}}$$

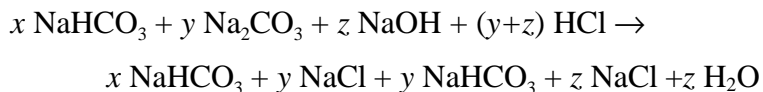
Alternately add 20.00 mL HCl and titrate with NaOH.

$$20 \times N_{\text{HCl}} = 0.1013 \times V_{\text{NaOH}}$$

Titration of Liquid Samples for Carbonate and Bicarbonate Content

This section serves as a supplement to the procedure in the Manual.

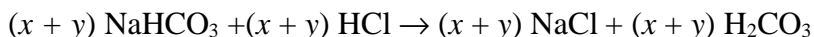
Examine the graph of carbonate species vs. pH. Follow the procedure in the Instruction Manual to titrate a 10-mL aliquot against standardized 0.1 N HCl to the phenolphthalein end point of pH 8.2 (clear color). The volume (titer) is T_1 mL of HCl solution. (Note that “ T ” refers to the volume of titer, which is the difference between the before and after burette readings.) The titration accomplishes the following reaction:



Note that either x or z will be very small at the beginning, depending on the starting pH. At the ending pH of 8.2, the predominant species is bicarbonate, HCO_3^- (refer to the attached graph). Carbonates concentration of the sample is $x + y$ moles/L, but $T_1 \propto y + z$.

To determine the bicarbonate now present, add Methyl Orange or Methyl Red indicator and continue to titrate with 0.1N HCl to a Red end point (pH = 3.1 for methyl orange or 4.2 for methyl red; a methyl orange end point should take only a very small amount more titrant than methyl red since the titration end point should be rather rapid below pH 5).

The conversion now is:



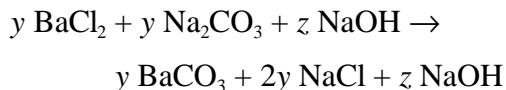
The total titer to the Red end point is T_2 . Note that below pH 5 the dominant species is H_2CO_3 .

The titer corresponding to total carbonates (as titrated bicarbonate and total CO_2 absorbed) would be $T_2 - T_1$, since $T_2 \propto (x + y) + (y + z)$ and $T_1 \propto (y + z)$, so

$$(T_2 - T_1) \propto x + y = \text{concentration of carbon in the liquid phase,}$$

which is proportional to the amount of CO_2 absorbed. The attached drawing shows these titrations.

At high pH, one can determine the excess NaOH in the sample. To do this, a second 10-mL aliquot is treated with a 5% solution of BaCl_2 in slight (~10%) molar excess to precipitate out carbonate (virtually no bicarbonate will be present):



Then, titrating to pH 8.2 end point (phenolphthalein) with HCl gives:



For this titration:

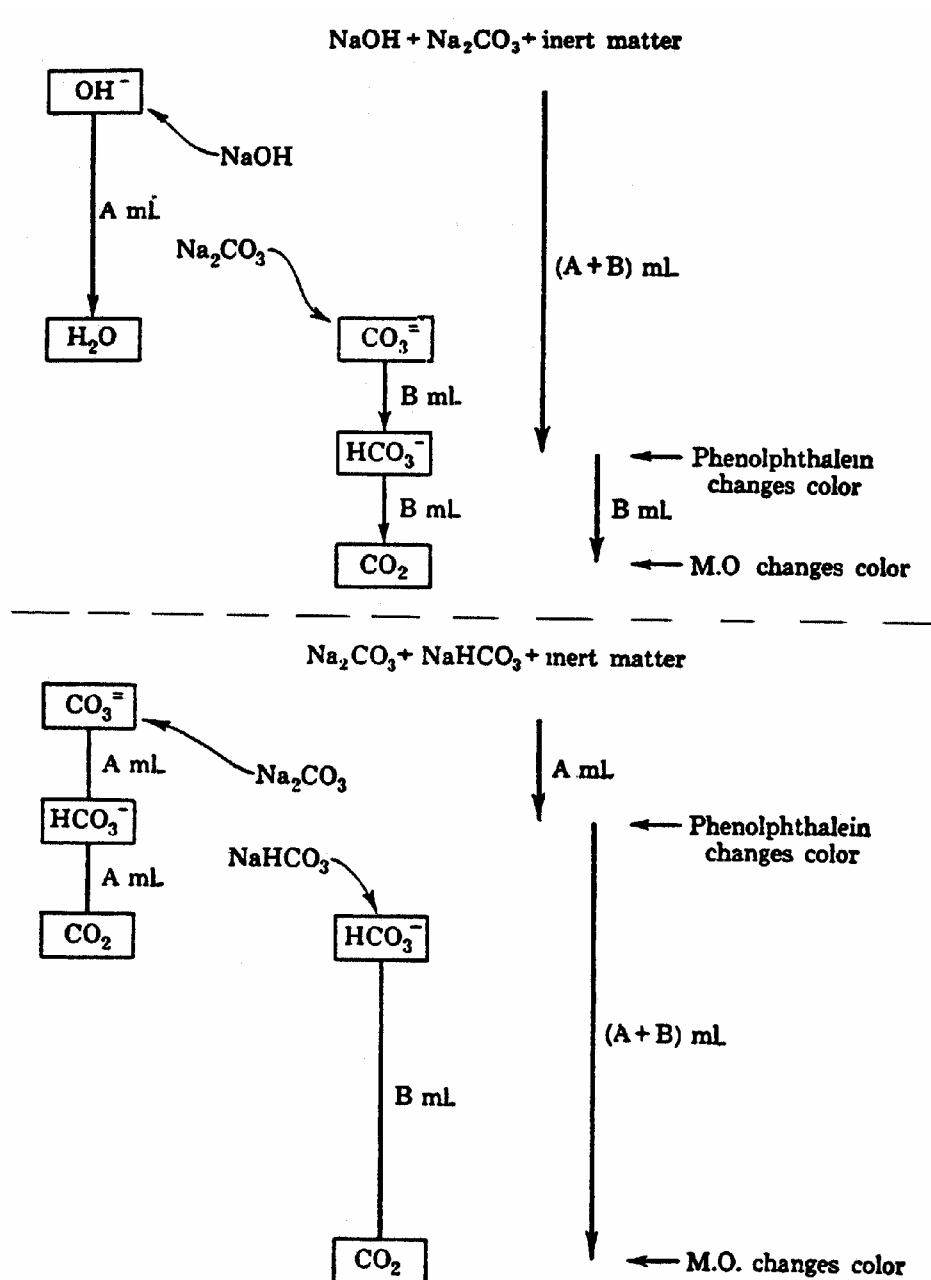
$$T_3 \propto (z) \text{ and} \\ T_1 \propto (y + z), \text{ from first set of titrations gives} \\ T_1 - T_3 \propto (y + z) - (z) = y = \text{concentration of carbonate in sample.}$$

The two titrations for carbon should agree; i.e., $(T_2 - T_1) = (T_1 - T_3)$. Alternatively, if the original concentration of NaOH is known gravimetrically, this information can be combined with T_3 to give the amount of carbonate.

The proportionality between the titer and concentration in the liquid sample employs the normality of the titrating liquid N , and the volume of the sample V_s , e.g,

$$x + y = \frac{(T_2 - T_1, \text{ mL})(N, \text{ mol/L})}{V_s, \text{ mL}} \quad (= \text{ mol/L})$$

To help explain the titration, a schematic from *Quantitative Chemical Analysis*, L. F. Hamilton and S. G. Simpson, Macmillan, New York, 1958, p. 187 is reproduced below. The top drawing is the situation at high pH, the lower at lower pH. The columns with the boxes track the original amounts of each species present during the titration. Regardless of pH, the amount of CO_2 released is always proportional to the difference between the Methyl Orange (M.O.) and the Phenolphthalein end points: B in the upper drawing and A + B in the lower.



The drawing below shows schematically the equilibrium in the NaOH/CO₂ system. The OH⁻ anion dominates at very high pH, but is not shown. Note that while all species are always present due to the equilibrium, the concentrations of all but two are normally very low.

