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CBE 140A: Gas and Liquid Diffusion

1 Introduction

The importance of mass transfer, and more specifically diffusion, cannot be overstated for certain chemical engineering unit operations: a heterogeneous catalyst supported on a porous support will have little utility if the rate of reaction is limited by the diffusion of reactants to the catalyst's active sites. The efficiency of a membrane-based separations is determined by relative diffusion rates, comparing the component to be extracted with its contaminants—applications include water purification via reverse osmosis, dialysis, and a cardiopulmonary bypass machine. In all these cases, characterization of diffusivity is critical to determining feasibility. This experiment will introduce how this physical property might be determined.

2 Objective

The primary goals of this experiment are twofold: determine the diffusivity of acetone vapor in air for a range of temperatures; and estimate the diffusivity of ionic salts (for example, sodium chloride) in water for several salt concentrations.

3 Theory

To determine the diffusivity of acetone vapor, liquid acetone is placed in a thin glass capillary tube, whose top is exposed to an air current. (An illustration is provided in the experimental apparatus section.) The velocity of the air is sufficiently low to ensure the gaseous phase in the capillary above the acetone is stagnant. The diffusivity can be determined for this geometry using the well-known Winkelmann method, which is described in many mass transfer textbooks. Assuming binary, one-dimensional diffusion of acetone and air, Fick's first law tells us:

$$N_A = J_A + x_A \sum N_i = -D \frac{dx_A}{dz} + x_A \sum N_i \quad (1)$$

where N and J are the total and diffusional molar fluxes, respectively, in units of moles per time per area, D is the diffusivity to be determined, x is the mole fraction, and z is the vertical position in the capillary. The subscript denotes the component of interest, acetone, and the summation is over all components.

Consider the initial length between the capillary opening and the acetone meniscus, L_0 . As time passes and acetone evaporates, L will increase, but given the experimental conditions, only the difference $L - L_0$ can be measured with sufficient accuracy and precision. The special consideration for this derivation is determining the diffusivity from this difference in liquid level height. As the derivation is rather involved and is available in textbooks elsewhere, we will proceed to its result:

$$\frac{t}{L - L_0} = \left(\frac{\rho_L C_{LM}}{2MDC_A C_T} \right) (L - L_0) + \left(\frac{\rho_L C_{LM}}{MDC_A C_T} \right) L_0 \quad (2)$$

where t = elapsed time,

$L - L_0$ = difference in liquid level height at time t ,

ρ_L = liquid density,

C_{LM} = the log-mean molar concentration of air across the capillary,

M = acetone molecular weight,

D = diffusivity of acetone vapor in air,

C_A = molar concentration of acetone vapor at the meniscus, and

C_T = total gaseous molar concentration.

To determine the diffusivity, the left-hand side of Equation 2 must be plotted as a function of the drop in liquid level, $L - L_0$. Upon estimation of the slope, the diffusivity can then be calculated.

The effect of temperature on diffusivity of gases has many models of differing levels of empiricism, based on the gas properties and the system temperature and pressure. The simplest model is the Fuller-Schettler-Giddings correlation. A summary of correlations are provided in Table 5-10 of [1].

Considering the diffusion of a concentrated salt solution into deionized liquid water, particularly through stagnant water in thin capillaries, we can again start from Fick's first law. In this case, there is equimolar conterdiffusion, negating the summation term.

$$N_A = J_A = -D \frac{dC_A}{dz} \quad (3)$$

Evaluating the mass balance for the water reservoir into which the salt is diffusing,

$$N_A = \frac{V}{A_C} \frac{dC_{\text{bulk}}}{dt} \quad (4)$$

Where V is the volume of deionized water, A_C is the cross-sectional area available for diffusion, and C_{bulk} is the concentration of salt in the bulk of the deionized water phase. For this apparatus, the area results from 121 (denoted N) cylindrical capillaries of identical diameter (d) and length (L). Setting equations 3 and 4 equal to each other, the diffusivity can be determined by evaluating the derivative with respect to position at its initial condition and the time derivative found empirically through regression. This results in the following, where $C_{A,0}$ represents the intial concentration of the salt solution:

$$D = -\frac{4VL}{\pi d^2 N C_{A,0}} \frac{dC_{\text{bulk}}}{dt} \quad (5)$$

To predict the diffusivity of various dilute salts in water at different temperatures, the Nernst-Haskell equation is commonly used, although others are tailored for other experimental conditions. It can be found in many mass transfer textbooks, such as [2, 24] and [1, 5-57].

Salt concentration will be observed indirectly through measurement of conductivity (denoted by κ , with units of $\Omega^{-1}m^{-1}$). Pure water has nearly zero conductivity, but as the concentration of an electrolyte in solution is increased, a linear relationship is expected:

$$\kappa = C_M C_A \quad (6)$$

Where C_A is the salt concentration in units of molarity and C_M is a proportionality constant which can be determined empirically.

4 Experimental Apparatus

In Figure 1, the gas diffusion apparatus is illustrated. A water bath (5) is heated to maintain a steady temperature through the controller (1) and heater power switch (2). The temperature can be observed with a submerged thermometer (4). The acetone is visible in a T-shaped glass capillary held in place by a tightened nut at the top of the water enclosure (6). Air flows through tubing across the capillary top and is supplied from a fan controlled by its power switch (3). The liquid level of the acetone in the capillary can be observed in two ways, both illustrated as (7): in front of the apparatus there is an optical microscope on a vertically-traveling Vernier height gauge. Care must be taken not to alter the angle of this microscope, as this reduces the reliability of future data taken. The liquid level can also be observed with a digital microscope, whose display can be recorded using software on the connected computer. Using the digital microscope requires height calibration, for example through the use of adhesive measuring tape on the side of the capillary—through this approach, the change in liquid level height can be deducted from distances measured on digital graphics during data analysis.

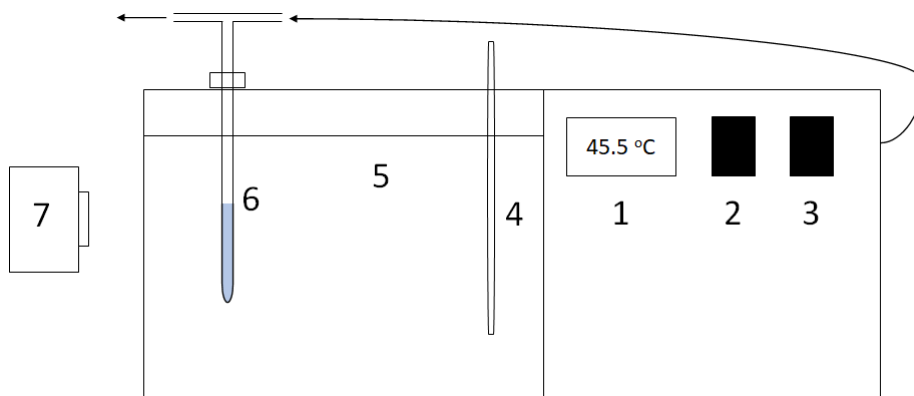


Figure 1: Experiment 5: Gas diffusion apparatus.

Figure 2 below illustrates the liquid diffusion apparatus. A cylindrical reservoir of deionized water (1), agitated by a magnetic stir bar (4) is placed on a stir plate with stirring control knob (5). A J-shaped tube is filled with a salt solution up to the capillary plate (3) consisting of 121 cylindrical capillaries, each 4.5 mm long and a diameter of 1 mm. (Insert B shows an overhead view of the capillary plate, although not to scale and without all 121 holes shown.) The J-tube should be carefully lowered into the deionized water, so as to not preemptively mix the two solutions prior to the experiment, until the top of the capillary plate is roughly 5 mm below the surface of the deionized water. At that height, it can be secured in place by tightening the nut on top of the reservoir. A Vernier conductivity probe (6) allows instantaneous measurement and recording of the bulk water's conductivity over time through connected software.

5 Safety

The major hazards associated with this experiment are the following: The stir plate, powered from an electrical outlet, introduces the risk of injury from electric shock. Avoid by ensuring the power cord is not touched when in operation. The heating element and hot water produced by this apparatus introduces the risk of scalds and burns. Mitigate by not touching hot surfaces without proper PPE. Through accumulation of biological contaminants in the water, there is a risk

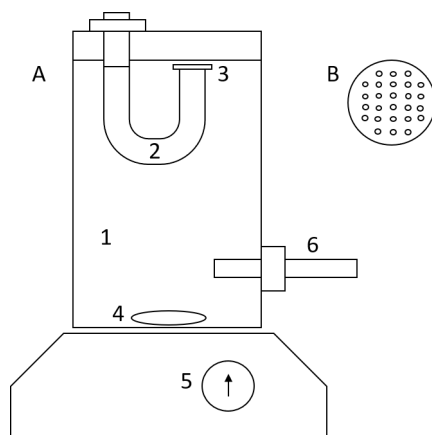


Figure 2: Experiment 5: Liquid diffusion apparatus.

of infection. Contact the instructional staff if you believe the equipment needs cleaned or replaced. If water splashes out of the apparatus, there are risks to clothing damage, slips, and falls. Avoid this by carefully considering the impact of opening or closing of valves prior to acting, and clean spills immediately if they do occur. This list is only a starting point and not intended to be fully comprehensive—please keep the safety of yourself and others in mind throughout the laboratory sessions.

6 Experimental Procedure

To study the diffusion of acetone vapor, begin by setting a set-point water temperature to 40 °C. While it is reaching equilibrium, rinse the T-tube with water. If needed, it can also be washed with a detergent. In either case, use a syringe or pipette to direct liquid into the bottom of the capillary. If air pockets obstruct flow, gently tap the tube with a finger. After rinsing, turn over the capillary and shake until no liquid remains. The capillary can now be charged with acetone. Record the initial height of acetone from the capillary top, which should be approximately 35 mm.

When the water bath has reached its set point temperature, submerge the T-tube in the bath and secure in place with the nut—do not over-tighten as the glass might crack. Ensure the meniscus height aligns with the microscopes chosen for use. Connect the air tubing to the T-tube. Record the change in liquid height as a function of elapsed time, using either digital microscope video or pictures, and/or through use of the Vernier scale optical microscope. Continue collecting data for four hours to complete a single trial.

Additional trials can be conducted at other temperatures and for other solvents. To avoid boiling, do not set the temperature above 50 °C for acetone.

Once the gas diffusion experiment is underway, the liquid diffusion experiment can begin. Clean, rinse, and fill the reservoir with 1.00 L deionized water. Place a clean stir bar in the water and set the reservoir on a stir plate. Prepare a 1 L of 1 M NaCl solution by mixing 58.44 g of NaCl into 1 L of deionized water. Prepare several 50 mL standard solutions of NaCl in beakers from this stock solution: 0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 M solutions are recommended. Rinse and dry the tip of the conductivity probe to remove residual salts. Starting with the lowest concentration salt and increasing, measure the conductivity of the standard solutions. Rinse and dry the probe between measurements. This will provide the basis for determining the salt concentration later. Reassemble the conductivity probe into the water reservoir after thoroughly rinsing.

Secure the empty, clean J-shaped tube to the lid and set on top the reservoir. Ensure the height of the capillary plate is about 5 mm below the water level. Once the J-tube is at the appropriate height, fill with 1.0 M NaCl solution until it reaches the capillary plate. Remove air bubbles by adding additional solution with a syringe or pipette. Carefully lower into the water reservoir, being careful not to disturb the solutions. Begin data collection in the Vernier software program to record the bulk water conductivity and time elapsed. Continue data collection for about thirty minutes.

Additional trials can be conducted at varying concentrations of NaCl, as well as for other salts like KCl, CaCl₂, etc.

7 Data Analysis

Plot the change in acetone liquid level height as a function of time. Subsequently, graph $t \cdot (L - L_0)^{-1}$ vs. $(L - L_0)$. Determine the slope of this line, and calculate the diffusivity of acetone vapor from the slope, as described in the theory section. Comment on the plotted data shape, compare to their expected shape, and describe why they differ, if substantial. Display the effect of temperature and component on diffusivity. Do these results agree with predicted trends? If not, why, and what evidence is there that supports these claims?

First, determine C_M , the proportionality constant between conductivity and salt molarity, using the data collected on standard solutions. Using the conductivity data obtained, plot the salt concentration in the bulk water as a function of time. Analyze the initial slope of this plot, where the initial conditions are still more likely to be valid. With the calculated slope, use Equation 5 to estimate the diffusivity of NaCl. Comment on the shape of the calibration curve and the plot of salt concentration as a function of time. Are these similar to your expectations, and if not, what might explain the difference? What was the effect of salt type and salt concentration on diffusivity? Does this agree with expected results? If not, is there evidence supporting why there is disagreement?

References

- [1] Don W. Green, editor. *Perry's chemical engineers' handbook*. McGraw-Hill, eighth edition, 2008.
- [2] Stanley Middleman. *An introduction to mass and heat transfer*. John Wiley and Sons, Inc., 09 1998.