

Diffusivity in Gases Experiment

ver 5.10b

A number of experimental techniques have been developed for the measurement of the diffusivity in gases. Both steady-state and unsteady-state methods are used. However, an accurate determination of the diffusivity demands a careful analysis of the experimental method involved. To demonstrate some of the problems encountered when making diffusivity measurements, an unsteady-state procedure will be used to determine the diffusivity in a binary system. The results and method will be analyzed in some detail.

THEORY

A convenient and classical method for determining the diffusivity in binary, gaseous systems is to measure the time necessary to produce a concentration change when two different gases of equal volumes are allowed to diffuse into each other after an initial separation at a flat interface. It is necessary that the two gaseous species be ideal to the extent that there be no pressure change upon mixing when isothermal conditions prevail if this method is to function satisfactorily. For cylindrical chambers where the interface is normal to their longitudinal axes, the diffusion takes place in one dimension only. The differential mass-balance for either of the two molecular species in the system is given by

$$c \frac{\partial X_A}{\partial t} = - \frac{\partial N_{Az}}{\partial z} \quad (1)$$

where:

c = total molar density of the system

N_{Az} = molar flux of a species 'A' along the z -axis

t = time

X_A = mole fraction of species 'A'

In this particular situation equimolar counterdiffusion occurs in stationary coordinates. Applying Fick's First Law of diffusion, it reduces to

$$N_{Az} = -cD_{ab} \frac{\partial X_A}{\partial z} \quad (2)$$

where D_{ab} is the mass diffusivity for the binary system based on concentration driving forces. When the total molar density c and mass diffusivity D_{ab} are independent of the composition of species B, combination of equations (1) and (2) gives

$$D_{ab} \frac{\partial^2 X_A}{\partial z^2} = \frac{\partial X_A}{\partial t} \quad (3)$$

The boundary conditions for this differential equation, determined by the apparatus, are

$$\left. \frac{\partial X_A}{\partial z} \right|_{z=-L} = 0 \quad (4)$$

$$\left. \frac{\partial X_A}{\partial z} \right|_{z=L} = 0 \quad (5)$$

where L is the length of each diffusion cell.

The initial value condition, determined by experimental procedure, is

$$X_A(z)|_{t=0} = \begin{cases} 1 & -L < z < 0 \\ 0 & 0 < z < L \end{cases} \quad (6)$$

A solution to equation (3) with conditions (4-6) is

$$X_A(z, t) = \frac{1}{2} + \sum_{n=1}^{\infty} \frac{\text{Sin}(\lambda_n L)}{\lambda_n L} \text{Cos}(\lambda_n z) e^{-\lambda_n^2 D_{ab} t} \quad (7)$$

with the eigenvalues $\lambda_n = n\pi/2L$.

Instead of measuring the concentration at a particular point in the system as a function of time, the diffusion process may be stopped at any particular time and the average concentration in each cell determined. The average concentration of molecular species 'A' in each cell is

$$\overline{X_A(t)} = \frac{\int_A^B X_A(z, t) dz}{\int_A^B dz} = \frac{1}{2} \pm \frac{4}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} e^{-\left(\frac{(2k+1)\pi}{2L}\right)^2 D_{ab} t} \quad (8)$$

where the '+' sign refers to the lower diffusion cell and the '-' sign refers to the upper diffusion cell.

The infinite series in equation (8) must be truncated in some way in order to develop an analytical or numerical expression for the diffusivity. If the series is truncated to the first term a direct analytical solution for the diffusivity can be made

$$\overline{X_A(t)} = \frac{1}{2} \pm \frac{4}{\pi^2} e^{-\left(\frac{\pi}{2L}\right)^2 D_{ab} t} \rightarrow D_{ab} = \frac{4L^2}{\pi^2 t} \text{Ln} \left(\frac{\pm 4}{\pi^2 (\overline{X_A(t)} - 1/2)} \right) \quad (9)$$

The use of this equation must be validated by comparison of the first term to subsequent terms. If subsequent terms are negligible compared to the first term then equation (9) is usable.

The average concentrations in the diffusion cells can be determined in many ways. One of the simplest and fastest methods is a gravimetric scheme whereby one of the two gases being investigated is preferentially reacted with and/or absorbed on solid materials and a change in weight is used to determine the amount of gas in the binary mixture.

PROCEDURE

Before conducting this experiment, you should understand and become familiar with the operation of the equipment (Note that the diffusion cells are constructed of glass and are therefore to be handled with care). Experience has shown that the following procedure is successful in producing reasonable experimental values. This procedure is not, however, the only method which is valid. At each step of this or any procedure, you must ask yourself 'Why this step? What purpose does this step hold?'

Before starting, familiarize yourself with the regulator valves (Figure 1) and the diffusion cells (Figure 2).

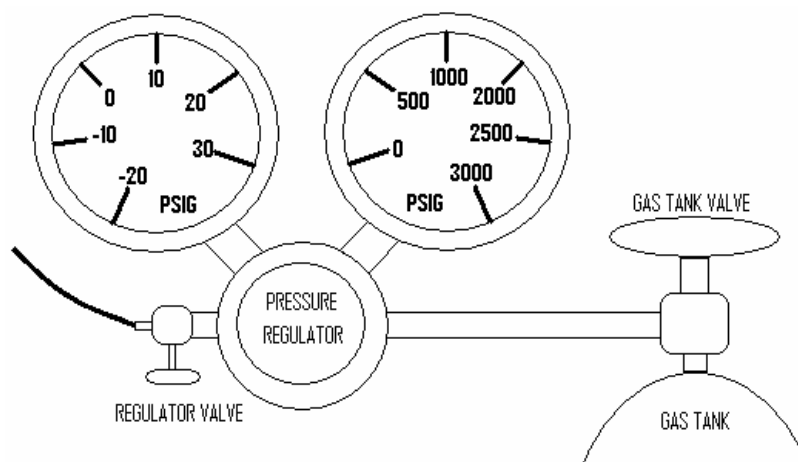


Figure 2: Gas Tank Regulator

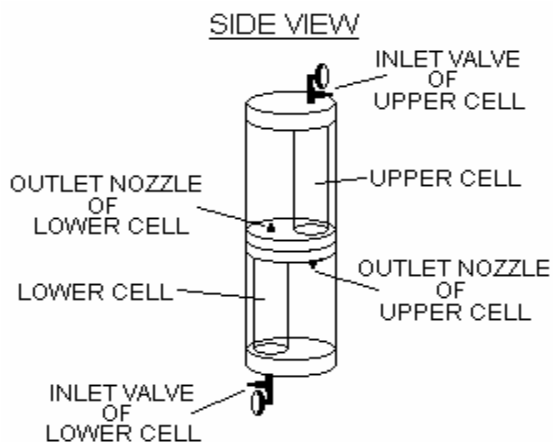


Figure 1: Loschmidt Diffusion Apparatus

At this point it should be noted how to manipulate a valve. A valve is closed by turning the valve disk clockwise until it stops. A valve is opened by turning the disk handle counterclockwise until desired. A valve must be opened sufficiently to avoid throttling in the valve. In this experiment two turns is sufficient because the airflow is small. In other situations, however, this would be inadequate. Therefore, it is good practice to always open a valve completely, then back half of a turn. This technique should be practiced in this experiment.

The suggested procedure is as follows:

1. Rotate the diffusion cells to their loading positions. Each cell will be aligned with its outlet nozzle and the cells will be situated 120° to each other (Figure 3).

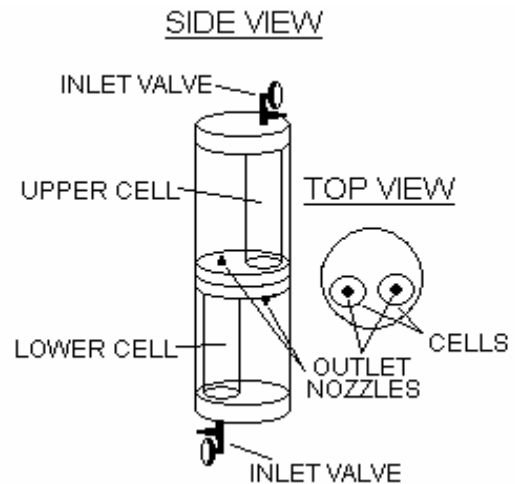


Figure 3: Loading Position

2. Open both inlet valves.
3. Remove the caps from the outlet nozzles, if necessary.
4. Connect the gray tubing to the inlet valve of the lower cell and the black tubing to the inlet valve of the upper cell (Figure 4).

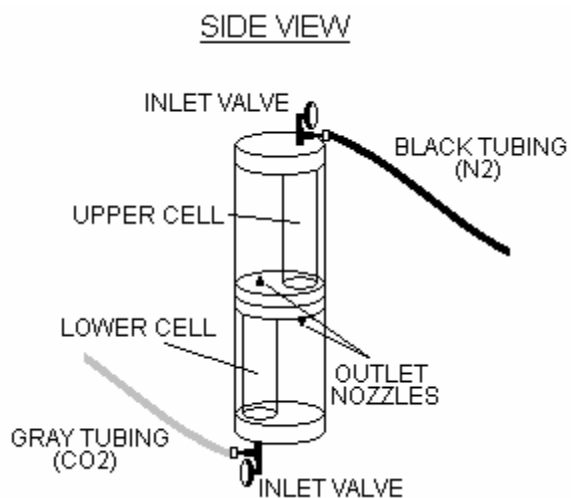


Figure 4: Flushing Connections

5. Open the nitrogen gas tank valve.
6. Turn the nitrogen pressure regulator 10 turns counterclockwise.
7. Open the nitrogen regulator valve

8. Turn the nitrogen pressure regulator clockwise until the reading on the nitrogen rotameter reads between one and two SCFH (Figure 5).

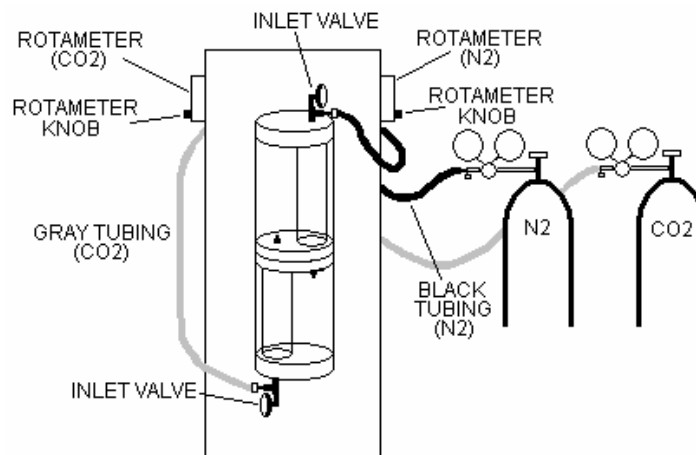


Figure 5: Rotameter Locations

9. Use the nitrogen rotameter knob to adjust the flow rate to 1.0 SCFH. Counterclockwise turning increases the flow rate while clockwise turning decreases the flow rate. The left pressure gauge on the nitrogen regulator should show less than 1 psig.
10. Repeat steps 5-9 to adjust the CO₂ flow rate.
11. Allow the gases to flow through the cells for 5 minutes.
12. In quick succession perform the following steps
 - a. Close both inlet valves.
 - b. Rotate the cells into neutral position (Figure 6).
 - c. Close both regulator valves.

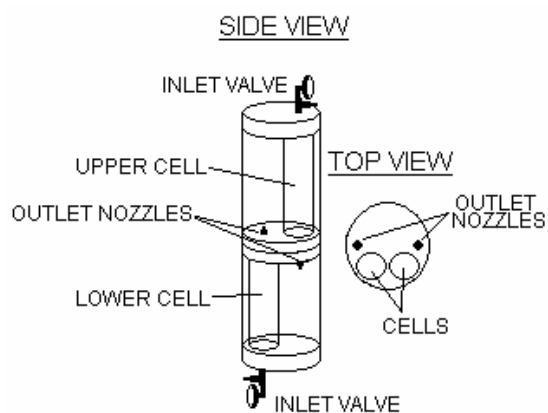


Figure 6: Neutral Position

13. Rotate the cells in a smooth, slow fashion into diffusing position (Figure 7). Do this with as little shaking or jarring as possible. This rotation should be accomplished in about 2 seconds. No more, no less.

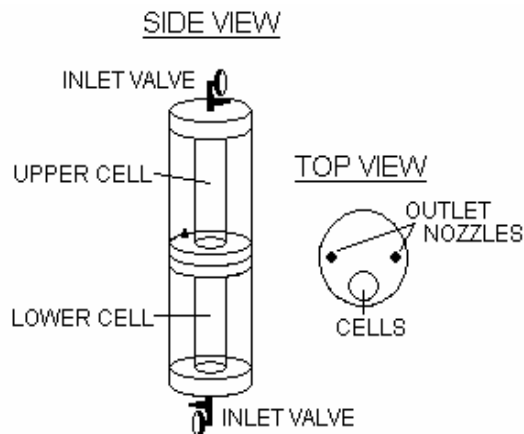


Figure 7: Diffusing Position

14. Immediately start the stopwatch. Allow diffusion to occur for at least 15 minutes. During this time prepare an absorption tube, if necessary. Directions on how to prepare absorption tubes are included in the next section.
15. A minute before stopping diffusion weigh a prepared absorption tube on the analytical balance. Record the initial mass in a lab notebook! Clamp the absorption tube to the post located next to the apparatus. The soda lime section of the tube should be lower than the Drierite™ end. The vertical center of the absorption tube should be level with the inlet valve of the lower cell (Figure 8).

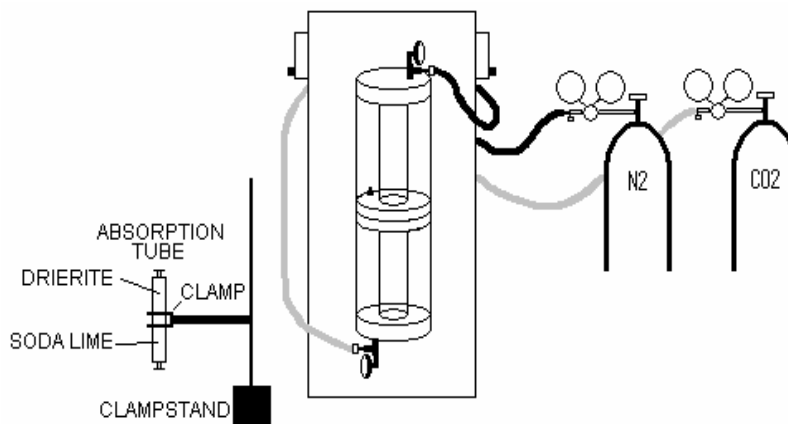


Figure 8: Absorption Tube Orientation

16. At the chosen time, rotate the cells out of diffusing position into neutral position and stop the stopwatch. Record this time in a lab notebook!
17. Remove the gray tubing from the inlet valve of the lower cell. Remove both end caps from the absorption tube. Attach the clear plastic end of the transfer tubing to the soda lime end so that flushed gas will flow upward through the tube reacting first with soda lime before contacting the Drierite™. Connect the other end of the transfer tubing to the inlet valve of the lower cell. Remove the cap from the outlet nozzle of the lower cell if not already done so. Remove the black tubing from the inlet valve of the upper cell.
18. Cover the outlet nozzle of the upper cell with a nozzle cap.
19. Adjust the flow of nitrogen gas using steps 6-9 with the following changes:
 - a. Step 8: Turn the nitrogen pressure regulator clockwise until the rotameter indicates a gas flow of 0.5 SCFH.
 - b. Step 9: Adjust gas flow using the rotameter knob to a flow rate of 0.25 SCFH.
20. Close the nitrogen regulator valve.
21. Connect the black tubing to the outlet nozzle of the lower cell.

22. Rotate the cells into loading position (Figure 9).

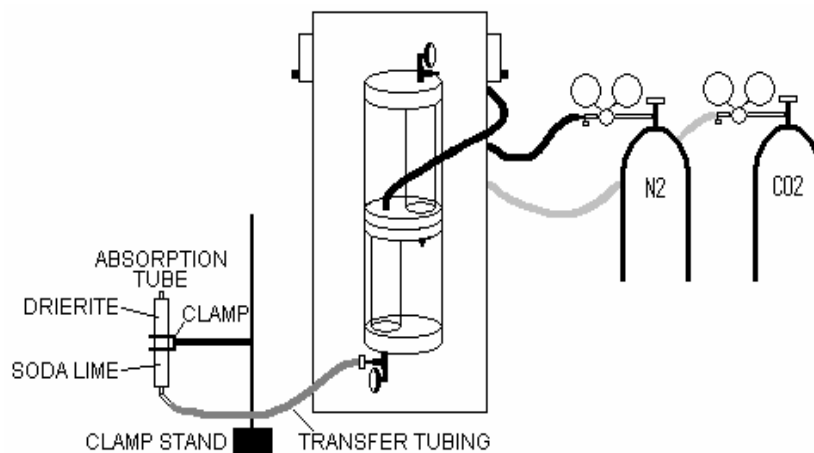


Figure 9: Flushing of the Lower Cell

23. Slowly open the nitrogen regulator valve.

24. Check the nitrogen rotameter. Adjust the gas flow rate to maintain 0.25 SCFH.

25. Allow the nitrogen to flow for 120 seconds exactly.

26. Remove the clear end of the transfer tubing from the absorption tube. Immediately replace the end caps. Close the nitrogen regulator valve.

27. Weigh the absorption tube. Record this mass in a lab notebook!

28. Rotate the cells into neutral position.

29. Clamp the absorption tube to the stand. The soda lime end should be on bottom, as before. The vertical center of the absorption tube should be level with the outlet nozzle of the upper cell. Remove both end caps from the absorption tube. Attach the clear end of the transfer tubing to the soda lime end of the absorption tube and the other end to the outlet nozzle of the upper cell.

30. Rotate the cells into loading position (Figure 10).

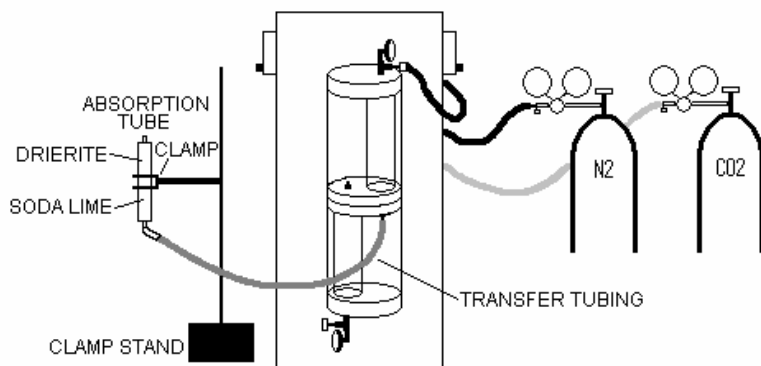


Figure 10: Flushing of the Upper Cell

31. Open the inlet valve of the upper cell.

32. Repeat Steps 25-29 in order to flush the upper cell.

33. Close the nitrogen regulator valve.

SHUTDOWN

Shutdown is straightforward. Simply ensure the following items are done.

- Clean out all unused absorption tubes and place waste in the waste container. Leave the counter clean! A sponge to clean and a paper towel to dry are appropriate means.
- Close the regulator valves and open the inlet valves.
- Remove both nozzle caps and remove all tubing from the diffusion cells.
- Rotate the cells into loading position and leave the apparatus in a vertical position.
- In an emergency situation, close both gas tanks before leaving.

PREPARATION OF ABSORPTION TUBES

The absorbent used to capture flushed CO₂ is soda lime. The measured mass of the tube initially and after each cell flushing provides the relative amounts of carbon dioxide absorbed from the cells. The assumptions that 100% of the carbon dioxide present in the cells is absorbed, or that the percentage absorbed are equal for both cells may or may not be valid. In the course of data analysis and drafting of reports the assumptions used in order to reach conclusions must be stated and explained. Responses to the following questions should be clear in your mind. Research into the properties of the chemicals used may be necessary.

- What is soda lime?
- What is the chemical reaction(s) involved when soda lime absorbs CO₂?
- What does Drierite do? Why is it included in this experiment?
- What assumption is nearly valid when Drierite is used properly? Why?
- In mathematical terms, how are the experimental data and calculated molar fractions of the two cells connected?

The proper preparation of an absorption tube is as follows:

1. Each tube consists of a long, hollow tube, two end pieces, and two end caps. Clean each piece with a paper towel. DO NOT blow into the tube in order to clean out residue.
2. Fill each end piece with glass wool. Place an end cap on each end piece.
3. Place an end piece on one end of the tube.
4. Using a funnel, slowly spoon soda lime into an upright tube (the end with the attached end piece is on bottom and the open end is on top) until 75% of the inner volume is filled. Do not hold it too close to your body, especially your face; the pouring action creates a fine dust which is corrosive to skin and mucous membranes.
5. Gently push glass wool into the tube above the soda lime.
6. In a manner similar to step 4, pour Drierite™ into the tube until the remaining 20% of the tube volume is occupied. DO NOT leave the bottles of soda lime and Drierite™ uncapped.
7. Place the other end piece onto the open end.
8. Gently brush off the tube with a paper towel to remove any dust.
9. Place any waste into the waste container and replace the cap immediately. Soda lime is a hazardous waste once destined for disposal.

Proper experimental procedure includes the careful handling of the absorption tube. All reasonable means to ensure that all change in absorption tube mass is due only to carbon dioxide absorption should be taken. It should not be handled by bare hands. Gloves or paper towels are acceptable means of tube handling. Careful weighing of the tube is essential; a difference of 0.1mg can be the difference between reasonable and unreasonable values. The tube should be weighed on the analytical balance, with the door on the balance closed. The weighing should occur immediately before and after flushing.