Diffusivity in Gases Experiment

ver 3.04

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 in when making diffusivity measurements, an unsteady-state procedure will be used to determine the diffusivity in a binary system and 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 chambers formed from cylinders and where the interface is normal to their 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

$$c\left(\frac{\partial x_A}{\partial t}\right) = -\frac{\partial N_{Az}}{dz} \quad (1)$$

where:

c = total molar density of the solution
N_{Az} = molar flux of a species 'A' along the z-axis
t = time
x_A = mole fraction of species 'A'
z = linear distance on z-axis

In this particular situation equimolal counterdiffusion exists and Fick's first law of diffusion 1, based on stationary coordinates, reduces to

$$N_{Az} = -c\mathrm{D}_{AB}\left(\frac{dx_A}{dz}\right) \quad (2)$$

where D_{AB} is the mass diffusivity for the binary system based on concentration driving forces.

When the total molar density and mass diffusivity are independent of composition 2, combination of Eqns. 1 and 2 gives

$$\frac{\partial x_A}{\partial t} = D_{AB}\left(\frac{\partial^2 x_A}{\partial z^2}\right) \quad (3)$$

The boundary conditions for this differential equation, as determined by the conditions of operation, are

$$\frac{\partial x_A}{\partial z} = 0 \text{ at } z = -L \text{ for all } t \quad (4)$$

$$\frac{\partial x_A}{\partial z} = 0 \text{ at } z = +L \text{ for all } t$$

$$x_A = 1.0 \text{ at } -L \le z < 0 \text{ for all } t \le 0$$

$$x_A = 0 \text{ at } 0 < z \le +L \text{ for all } t \le 0$$

where L is the length of each diffusion chamber. A solution to Eqn. 3 is

$$x_A = \frac{1}{2} + \frac{2}{\pi}\sum_{n=0}^{\infty}\frac{\sin\left[(2n+1)\left(\frac{\pi}{2}\right)\left(\frac{z}{L}\right)\right]}{(2n+1)} \exp\left[-(2n+1)^2\left(\frac{\pi}{2L}\right)^2 D_{AB}t\right] \quad (5)$$

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 chamber determined. The average concentration of molecular species 'A', $x_{Z,avg}$, in each chamber is then given by

$$x_{A,avg} = \frac{\int_{-L}^{0} x_A\,dz}{\int_{-L}^{0} dz} \quad \text{and} \quad x_{A,avg} = \frac{\int_{0}^{+L} x_A\,dz}{\int_{0}^{+L} dz} \quad (6)$$

Evaluation of Eqn. 6 with the aid of Eqn. 5 gives

$$x_{A,avg} = \frac{1}{2} \pm \frac{4}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)} \exp\left[-(2n+1)^2\left(\frac{\pi}{2L}\right)^2 D_{AB}t\right]$$

where the + sign refers to the lower diffusion chamber
and the - sign refers to the upper diffusion chamber

When the argument $\left(\frac{\pi}{2L}\right)^2 \mathrm{D}_{AB} t$, in Eqn. 7 becomes greater than about 0.7, all the remaining terms in the series become negligible in relation to the first term. Therefore, a direct solution for the diffusivity can be made

$$\mathrm{D}_{AB} = \frac{4L^2}{\pi^2 t} \ln\left[\frac{\pm 4}{\pi^2 \left(x_{A,avg} - \frac{1}{2}\right)}\right] \quad (8)$$

The average concentrations in the diffusion chambers can be determined in many ways. One of the simplest and fastest methods is 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.

Apparatus

The apparatus consists of

1. modified Loschmidt, shear-type, diffusion cell[4];
2. two flow meters (a dry meter with a flow-rate such as a rotameter);
3. stop clock;
4. barometer;
5. thermometer;
6. two U-shaped drying-tubes equipped with glass stoppers;
7. pure, dry gases whose diffusivities are to be determined;
8. solid reacting and/or absorbing material(s) in granular form;
9. analytical balance.

The design and construction details of a diffusion cell are shown in Fig. 1. A typical entire apparatus is shown in Fig. 2.

Procedure

1. Understand and become familiar with the operation of the equipment. (Note that the diffusion chambers proper are constructed of glass and are therefore to be handled with care.)
2. Rotate the diffusion chambers to their loading positions (here the chambers are oriented at 180° from each other).
3. Open the valves at the top and bottom of the diffusion cell and introduce the two gases for the binary system under investigation each into a separate chamber. (If both gases are less dense than air, feed them into the tops of the diffusion chambers; if both gases are more dense than air, then feed them into the bottoms of the diffusion chamber; if one gas is more dense than air and the other is less dense than air, then feed the former into the bottom of one chamber and the latter into the top of the other chamber.) Charge the gases into the diffusion chambers at a rate from 300 to 500 cc/min for 2 to 5 minutes.

4. When each of the chambers is charged, turn off the flow of gas and close the valves at the ends of the diffusion cell. Orient the diffusion cell so that the more dense of the two gases is located in the lower chamber.
5. Rotate, at a constant and slow (but not to slow) angular velocity, the diffusion chambers until they are exactly in line with each other. Start measuring the time of diffusion at the moment when the chambers are in line with each other.
6. Allow the diffusion to take place for at least 20 minutes or more. Then stop the diffusion by rotating the chambers back to their loading positions. Stop measuring the time of diffusion at the moment when the chambers begin rotating.
7. Load the drying tubes with the granular material(s) which will preferentially absorb and/or react with one of the two gases in the system being studied.
8. Weigh the loaded drying tubes.
9. Attach one loaded drying tube to each diffusion chamber and flush the chambers out with the inert gas. Flush the chambers at a rate of about 300 cc/min for 2 to 5 minutes. (If the inert gas is the less dense gas, attach drying tubes to the bottoms of the chambers; if the inert gas is the more dense gas, attach the drying tubes to the tops of the chambers.)
10. Weigh the drying tubes after the diffusion chambers have been completely flushed out by the inert gas.

Suggested Experimental Work

1. Determine the mass diffusivity for the binary system composed of carbon dioxide and nitrogen, oxygen, methane, argon or Freon-12™. (For these systems the amount of carbon dioxide in a diffusion chamber can be determined by passing the gaseous mixture through a bed of Ascarite™ followed by calcium chloride in about a 4:1 volume-ratio respectively.)
2. Measure the mass diffusivity for the system composed of carbon dioxide and dry air or a mixture of helium and nitrogen. (The amount of carbon dioxide can be determined by the same scheme as given above.)

Suggested Data Record

1. Diffusion-Cell Particulars
    a. diameter and length
    b. hold-up volumes outside the diffusion chambers
2. Diffusion Measurements
    a. system components
    b. time duration of diffusion
3. Composition Measurements
    a. weight of drying tube and preferential adsorption and/or reaction-bed before contacting with the contents of the diffusion chamber
    b. weight of drying tube and preferential adsorption and/or reaction-bed after contacting with the contents of the diffusion chamber

Suggested Report Items

1. Tabulate the measured diffusivities as a function of the time allowed for diffusion to take place in the diffusion cell.
2. Tabulate the diffusivities obtained by other investigators for the systems studied in this experiment.[5]
3. Tabulate the mass diffusivities for the binary systems studied in this experiment as calculated from available, recommended relationships.[6]

Suggested Calculations

1. Calculate the mass diffusivities from the experimental data obtained in this experiment with the aid of Eqn. 8.
2. Adjust the experimentally determined diffusivities from the conditions of measurement to 25°C and 1 atm pressure.
3. Calculate the mass diffusivities for the binary systems studied in this experiment from available, recommended relationships.[7]
4. Calculate the theoretical inventory of the various gaseous species in the diffusion cell and compare this inventory with the results obtained by the analysis technique used in this experiment.

Suggested Discussion Questions

1. Does the analytical solution given in Eqn. 5 satisfy the differential equation represented in Eqn. 3? Prove.
2. Are the boundary conditions given in Eqn. 4 satisfied by the conditions of this experiment? Discuss fully.
3. Develop Eqn. 7 from Eqns. 5 and 6.
4. For what types of gaseous systems and what conditions of temperature and pressure is the experimental technique, which was used in this experiment, applicable?

   (Hint: Consider the restrictions connected with the development of Eqn. 3. Also note that for the equation of state given by $V = V(z, p, T)$, where:
   P = absolute pressure
   T = absolute temperature
   V = volume
   z = compressibility factor,

   the pressure in the system will remain constant for isothermal conditions if 'z' is independent of composition.

5. Why was the more dense of the two gases, in the binary systems which were studied, located in the bottom chamber of the diffusion cell?
6. In this experiment the diffusion process was allowed to take place when the diffusion cell was in a vertical position. Discuss the feasibility of operating the diffusion cell in a horizontal position.

7. The diffusion measurements were carried out under isothermal conditions at room temperature. How much will the diffusivity vary for a 1°C change in temperature? Why, then, is it desirable to control the temperature of the system being investigated within ±0.01°C or narrower limits? I.e., why is the temperature control so critical?
8. Derive the differential massñbalance given by Eqn. 1.
9. Discuss the significance of the diffusivity measurements when air or a mixture of helium and nitrogen is used as one of the diffusing components. Is such a reported diffusivity meaningful? Discuss.
10. Discuss the end effects which exist at the interface between the two diffusion chambers as a result of the shearing action which takes place when the cell is opened and closed. Sketch the flow patterns which occur at the shear interface.
11. Discuss quantitatively the absorption and/or reaction scheme used in the gravimetric determination of the composition of the binary mixture in the diffusion chambers. Present the chemical equations which describe any chemical reactions which are involved in this determination.
12. Why is it important that the gases used in this experiment be perfectly dry?
13. Discuss the experimental errors encountered in this experiment. Substantiate your arguments with calculations.
14. Estimate the possible error in the measured diffusivity due to the errors in the measurements of time, cell length and average concentration.
15. By what other methods might the average concentrations inside the diffusion chambers be measured? Discuss the accuracy and convenience of these proposed methods.
16. When the dimensionless time, $\left(\frac{\pi}{2L}\right)^2 D_{AB} t$, is equal to 0.7, how much error is incurred by using Eqn. 8 instead of Eqn. 7 to calculate the value of the mass diffusivity?
17. Compare Eqns. 5 and 7 and determine for what values of $\frac{z}{L}$ the point concentration is equal to the average concentration in the diffusion chamber. For what conditions is the value of $\frac{z}{L}$ constant?

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[1] Bird, R.B., Stewart, W.E. and Lightfoot, E.N., îTransport Phenomena.ì John Wiley and Sons, Inc., New York (1960), pp.502504.

[2] Bird, R.B., Stewart, W.E. and Lightfoot, E.N., op. cit., pp.504508.

[3] Bird, R.B., Theory of Diffusion, contribution to îAdvances in Chemical Engineering.ì Vol. 1, T.B. Drew and J.W. Hoopes, Jr., editors, Academic Press Inc., New York (1956), pp.155-239.

[4] Loschmidt, , Akademie der Wissenschaften in Wien, Setzungsberichte, 61, 367-3--, and 62, 468-4-- (1870).

[5] Bird, R.B., Stewart, W.E. and Lightfoot, E.N., op. cit., Table 16.2-2, p. 503.

[6] Perry, J.H., editor, îChemical Engineersí Handbook,ì 3rd edition, McGraw-Hill Book Company, Inc., New York (1950), Table 11, p. 539.

[7] Bird, R.B., Stewart, W.E. and Lightfoot, E.N., op. cit., pp.504513; see especially Eqns. 16.3-1 and 16.4-12.