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

$$c\frac{\partial X_A}{\partial t} = -\frac{\partial N_{Az}}{\partial z} \tag{1}$$

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 equimolal counterdiffusion occurs in stationary coordinates. Applying Fick's First Law of diffusion, it reduces to

$$N_{Az} = -cD_{ab}\frac{\partial X_A}{\partial z} \tag{2}$$

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

$$D_{ab}\frac{\partial^2 X_A}{\partial z^2} = \frac{\partial X_A}{\partial t} \tag{3}$$

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

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

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

where L is the length of each diffusion cell.

The initial value condition, determined by experimental procedure, is

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

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

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

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

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

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

$$\overline{X_A(t)} = \frac{1}{2} \pm \frac{4}{\pi^2} e^{-\left(\frac{\pi}{2L}\right)^2 D_{ab} t} \rightarrow D_{ab} = \frac{4L^2}{\pi^2 t} Ln\left(\frac{\pm 4}{\pi^2 \left(\overline{X_A(t)} - {}^1\!/_2\right)}\right) \tag{9}$$

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.