Diffusion Coefficient Measurement of Diiodomethane in Air by a Natural Convection Method

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The diffusion coefficient of diiodomethane in air has been measured using a natural convection method. The diffusion coefficient at 25 °C and 760 mmHg was found to be $(6.0 \pm 0.5) \times 10^{-6}$ m²/s.

Introduction

Gaseous diffusion coefficients can be measured using several methods, most of which are appropriate only for liquids having appreciable vapor pressures. The method employed in this study for determination of the diffusion coefficient of diiodomethane, CH_2I_2, is particularly suitable for liquids of low vapor pressure and high molecular weight.

The method is based on mass transfer from a vertical plate under the influence of laminar natural convection flow which occurs due to a density differential within the fluid. This density differential is a result of the mass transfer from the vertical plate surface.

The essence of the natural convection technique employed in this study is to coat a plate with a silicone polymer and then to swell the polymer coating with diiodomethane. Transfer of CH_2I_2 vapor from the surface of the silicone polymer coating to the working gas stream, in this case, air, can be recorded as a weight loss by having the coated plate suspended from a balance. As the diiodomethane vapor density is higher than air, natural convection flow becomes established and mass transfer occurs under the influence of laminar natural convection. By the use of accepted mass transfer correlations for this type of flow, the diffusion coefficient can then be evaluated.

Theory

Mass transfer due to laminar natural convection from a vertical plate is given by (3)

$$Sh = 0.666 Ra^{1/4} \qquad (1)$$

where Sh is the average Sherwood number, Ra is the Rayleigh number and they are given by

$$Sh = kL/D \qquad (2)$$

and

$$Ra = \left(\frac{\rho_\infty g (\rho_s - \rho_\infty) L^3}{\mu^2} \right) \left(\frac{\mu}{\rho_\infty D} \right) \qquad (3)$$

where k is the mass transfer coefficient, L is the plate length, ρ_s is the gas density at the surface of the polymer coating, and ρ_∞ is the ambient air density. k is defined by

$$F = k(\rho_s - \rho_\infty) WL \qquad (4)$$

where F is the rate of mass transfer and W is the plate width. Combining eq 1–4 leads to

$$1.7194 \left[\frac{\mu F^4}{g (\rho_s - \rho_\infty)^5 W^4} \right]^{1/3} = LD \qquad (5)$$

Assuming that D is inversely proportional to P and directly proportional to $T^{1.75}$, then eq 5 becomes

$$48.41 \left[\frac{\mu F^4}{g (\rho_s - \rho_\infty)^5 W^4} \right]^{1/3} \frac{P}{T^{1.75}} = LD_{STP} \qquad (6)$$

where D_{STP} is the diffusion coefficient at 25 °C and 760 mmHg.

Assuming ideal gas law and assuming that the partial vapor pressure of CH_2I_2 at the surface of the polymer coating is that of the vapor pressure of diiodomethane, then $(\rho_s - \rho_\infty)$ can be evaluated. The slope of variation of the plate weight with time provides F. Using different plate lengths, a linear plot of the left-hand side of eq 6 against L gives a straight line the slope of which provides the diffusion coefficient at standard temperature and pressure. This straight line should pass through the origin.

Experimental Procedure

Glass plates of various lengths (0.15–0.35 m) and 0.0611 m wide were coated on one side with silicone rubber (RTV-615 silicone rubber manufactured by General Electric, Waterford, N.Y.), and this polymer coating was cured according to the manufacturer's instructions. The silicone polymer coating thickness was about 10^{-3} m. Silicone rubber films were swelled with CH_2I_2 by immersing the glass plates, on which the silicone rubber is coated, in a CH_2I_2 bath for a period of 24 h to ensure that the equilibrium state was reached. This equilibrium state is considered to have been reached when no further increase in the weight of the polymer coating occurs with immersion time. Once the equilibrium swelling state is reached, the plate was taken from the diiodomethane bath and dried with lint-free tissue paper. The plate was suspended from the arm of a slightly modified balance in a large enclosure. The balance rested on a large concrete block and the experiments were conducted in a constant-temperature room. The arrangement is shown in Figure 1. The weight loss due to the transfer of CH_2I_2 from the polymer coating was continuously monitored by reading off the indicated weight as given by the balance without the need to disturb the suspended plate. After completion of the experimental run, the plate was reimmersed in the CH_2I_2 bath for a period of at least 3 h before it was reused. At least two runs were made for each plate.

Discussion of Results

A typical plot of the variation of the plate weight with time is shown in Figure 2. The zero time is arbitrarily chosen and usually readings were obtained 2 min after suspension of the plate. This is to ensure that all external air distrubances have died out and steady-state natural convection is established. It can be observed that initially the rate of mass transfer is constant and it decreases with time for $t > 200$ s. During this initial constant rate period it can be assumed that the polymer coating offers no resistance to mass transfer and as the plate was swollen to equilibrium it is possible to assume that at equilibrium the vapor pressure at the coating surface is that of the diiodomethane vapor pressure (2).

A plot using eq 6 is given in Figure 3. The evaluated diffusion coefficient for CH_2I_2 was found to be $(6.0 \pm 0.5) \times 10^{-6}$ m²/s. The vapor pressure of CH_2I_2 was taken from Dreisbach (1). As in most runs the pressure was about 700 mmHg and the
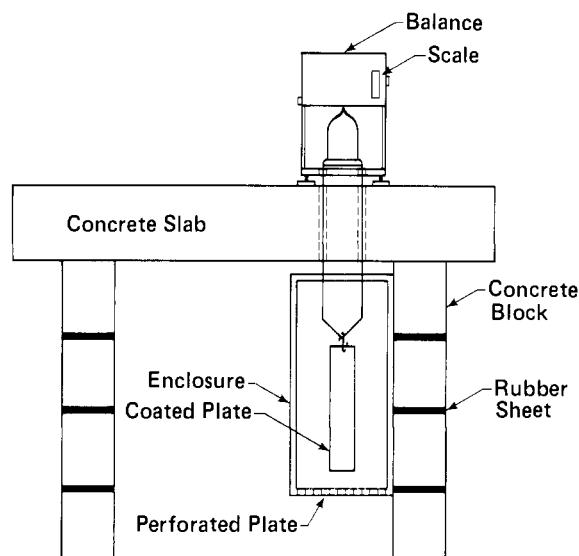
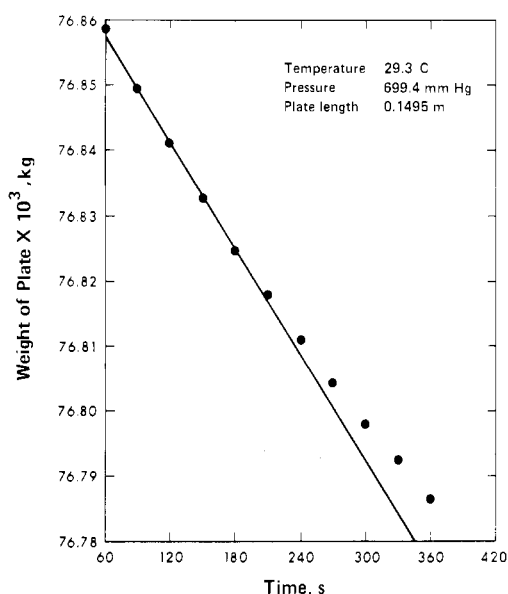**Figure 1.** Physical arrangement.

Figure 2. Weight loss of polymer coating with time.

temperature 29.3 °C; little error was introduced in converting the diffusion coefficient to standard conditions to allow for eq 6 to be plotted.

The Wilke–Lee correlation used in the manner proposed by Reid et al. (*4*) gave a diffusion coefficient of 8.1×10^{-6} m²/s. The agreement between our experimental and the predicted value is within 35%.

Concluding Remarks

The natural convection method described was found to be useful in the determination of diffusion coefficient of a high molecular weight liquid having a low vapor pressure (1 mmHg
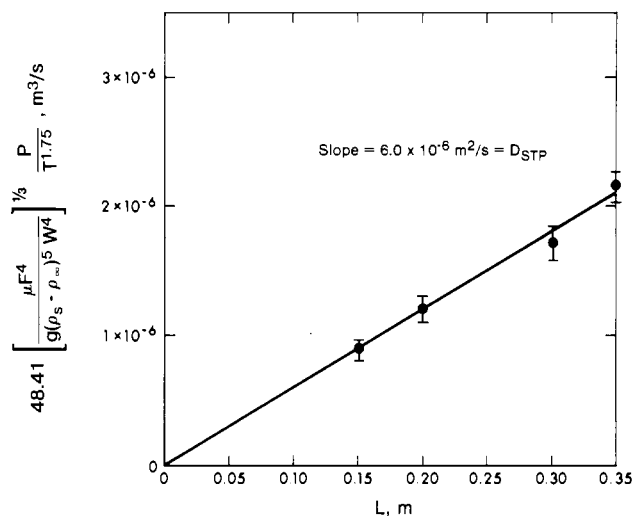
Figure 3. Determination of D_{STP} using eq 6.

at 20 °C) since for such a liquid the more standard techniques, for example, the Stefan cell method become inappropriate. Although the error in the determination is relatively high, the method is fast and does not require special equipment.

Glossary

D	diffusion coefficient, m²/s
F	mass flux, kg/s
g	acceleration of gravity = 9.8 m/s²
k	overall mass-transfer coefficient, m/s
L	plate length, m
P	pressure, mmHg
Ra	Rayleigh number, dimensionless
Sh	Sherwood number, dimensionless
T	absolute temperature, K
W	plate width, m

Greek

μ	air viscosity, kg/(m s)
ρ	gas density, kg/m³

Subscripts

s	at the polymer surface
STP	evaluated at 25 °C and 760 mmHg
∞	ambient conditions

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