# Measurement of Diffusivity in a High-Viscosity Liquid

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Measurement of diffusivities in low-viscosity liquids (for example, water, benzene, ethanol) has been accomplished by use of the diaphragm cell developed by Northrop and McBain (*4, 5, 6*). The conventional procedure and mathematical description is given by Gilliland (*3*). In that method, a linear gradient of concentration is established across the diaphragm before the measurement is started, and the subsequent change of concentration is related to diffusivity. The method is limited to systems of low viscosity. With high-viscosity liquids it would take months to establish the linear gradient across the porous diaphragm, after which months would elapse before there would be an accurately measurable change in the reservoirs.

Rapid determination of diffusivities in high-viscosity liquids had not been demonstrated heretofore, and the objective of this investigation was to develop such a technique. The liquid chosen was glycerol and the solute was sodium chloride. An operating temperature of 32 ± 0.5°C. was low enough to keep the viscosity at 580 centipoises. The solute was tagged with the isotope sodium-22.

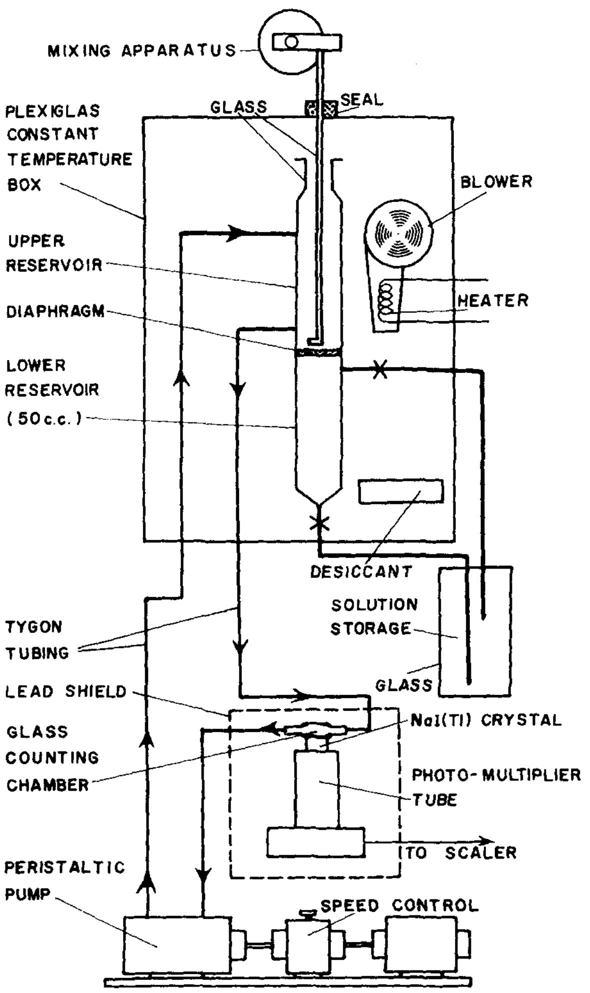

Fig. 1. Experimental setup.

The transient profile in the diaphragm, which is predicted by the solution of the appropriate equations, results in a flux that was monitored using a scintillation detector and an electronic scaler. The diffusivity of this high-viscosity system can be measured in a matter of hours with this technique.

## DESCRIPTION OF APPARATUS

A schematic diagram of the experimental setup appears in Figure 1. The general nature of the setup is a diaphragm cell with side arms from which liquid is drawn out, circulated through the counting chamber, and returned to the cell. The cell is a Pyrex fine frit with a porosity of 4 to 5$\mu$. The total volume of the circulation system including the upper reservoir is 250 cc.

The mixing apparatus, in conjunction with the circulation of the liquid, rapidly disperses the solute throughout the system as it enters the upper reservoir. The paddle on the mixing rod, which turns at about 1 rev./sec., is placed as close to the diaphragm as possible. This prevents a concentration buildup in a stagnant layer above the diaphragm.

The counting chamber (about 20 cc.) is streamlined to prevent stagnant liquid pockets from being formed. The disk shape of the glass chamber results in a good geometric efficiency for a maximum counting rate. A lead shield houses the counting chamber to lower the background count and thus increase the sensitivity of tracer detection.

A thermostatically controlled heater and a continuously operating fan maintained the constant-temperature plexiglas box at 32 ± 0.5°C. A desiccant was placed in the box, and all penetrations were sealed. The peristaltic pump is of the pulsating positive displacement type with capacities from 0.5 to 250 cc./min.

A scintillation counter was used. This consisted of a 1.25-in. thallium-activated sodium iodide crystal, a photomultiplier tube, preamplifier, an amplifier, single-channel analyzer and a scaler. The analyzer threshold was set high enough to suppress noise yet low enough to record the gammas following the decay of sodium-22. A second, shielded scintillation unit was used to continually monitor the background while the main counter was measuring concentration buildup.

## PROPERTIES OF TRACER SOLUTION

The selection of the sodium-22 isotope in the form of sodium chloride was based on its hard gamma emission, known diffusivity in water, ability to dissociate completely in glycerol at a concentration of $1.25 \times 10^{-4}$ normal, and a long half-life (2.7 yr.).

## PROCEDURE

For standardization, the prepared aqueous solution is pumped into the lower reservoir until it contacts and rises into the diaphragm. Bubbles are removed from under the diaphragm through the side arm. All tubing and the counting chamber in the circulation system are initially filled with distilled water. Water is then added to the upper reservoir to bring the total of the circulation system to 250 cc. Circulation and mixing are started immediately.

The glycerine run is similar. When filling the lower reservoir, care must be used to get as little as possible of the glycerol solution through the diaphragm into the upper reservoir.

After each run, the counting chamber is filled with solution from the lower reservoir of the diaphragm cell.

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Since the geometry is identical, the ratio of the counting rate of the upper to that of the lower reservoir is equal to the ratio of the concentrations.

## THEORETICAL ANALYSIS

To determine the diffusion rate, the concentration profile through the diaphragm must be derived. Bird (*1*), for example, develops the equation

$$\partial c/\partial t = D\, \partial^2 c/\partial x^2 \qquad (1)$$

known as Fick's Law which is limited to dilute solutions, constant diffusivity, and no convection. These conditions are met in the experimental work as follows:

1. The solutions used are less than $10^{-3}$ normal.
2. The experiment is run at constant temperature. There are no ionic association problems at these concentrations.
3. A diaphragm with small pores which prevents convection is used.

The solution for a semi-infinite medium (the diaphragm may be considered as such, at least as long as $Dt/L^2 < 0.3$) whose boundary conditions are

$$c(x, 0) = c' \quad x > 0 \qquad (2)$$

$$c(0, t) = 0 \quad t > 0 \qquad (3)$$

is given in Carslaw and Jaeger (2) as

$$c = c' \operatorname{erf}\,(x/2\sqrt{Dt}) \qquad (4)$$

The concentration buildup in the upper reservoir is

$$c_2 - c_1 = (+\,DA/V) \int_{t_1}^{t_2} (\partial c/\partial x)_{x=0}\, dt \qquad (5a)$$

$$c_2 - c_1 = \frac{2\,A\,c'\sqrt{D}}{\sqrt{\pi}\;V}\,(\sqrt{t_2} - \sqrt{t_1}) \qquad (5b)$$

This form of the equation makes it possible to discount solute that might be pulled into the upper reservoir initially. The selection of $t_1$ depends on the length of time it takes to distribute the initial solute throughout the circulation system. (In this investigation a value of $t_1$ equal to 1 hr. was chosen).

In the standardization run, which employs an aqueous system, the steady state profile forms rapidly. The following equation may be used for that condition:

$$dc/dt = (DA/V)\, dc/dx \qquad (6)$$

Although solute was diffusing through the diaphragm, the resulting change in the linear gradient was minute for the 18 hr. the experiment ran. The maximum error owing to this change is 0.2%. Hence, $A$ may be solved for accurately.

The counting rate is directly proportional to the solute concentration. Only relative concentration data of the upper and lower reservoir is required in any of these calculations; therefore, the relative counting rate serves.

## EXPERIMENTAL RESULTS

In the standardization runs, the gradient changes negligibly. The concentration ($c'$) of the bottom chamber is measured in each run. Therefore, $dc/dx$ (at any time) is equal to $(c' - 0)/L$ (at time $= 0$). Using the measured data and the diffusivity of sodium chloride in water (correcting for temperature by assuming $D\mu/T$ is constant), Equation (6) can be employed to calculate the effective area ($A$). The results of the area calculations for two runs are 0.3006 and 0.2949 sq. cm.

The results of a glycerol run are given in Figure 2 where $(c_2 - c_1)$ is plotted against $(\sqrt{t_2} - \sqrt{t_1})$. The slope of the resulting line, as determined by the least squares method, is set equal to

$$\frac{2\,A\,c'}{\sqrt{\pi}\;V}\sqrt{D}$$

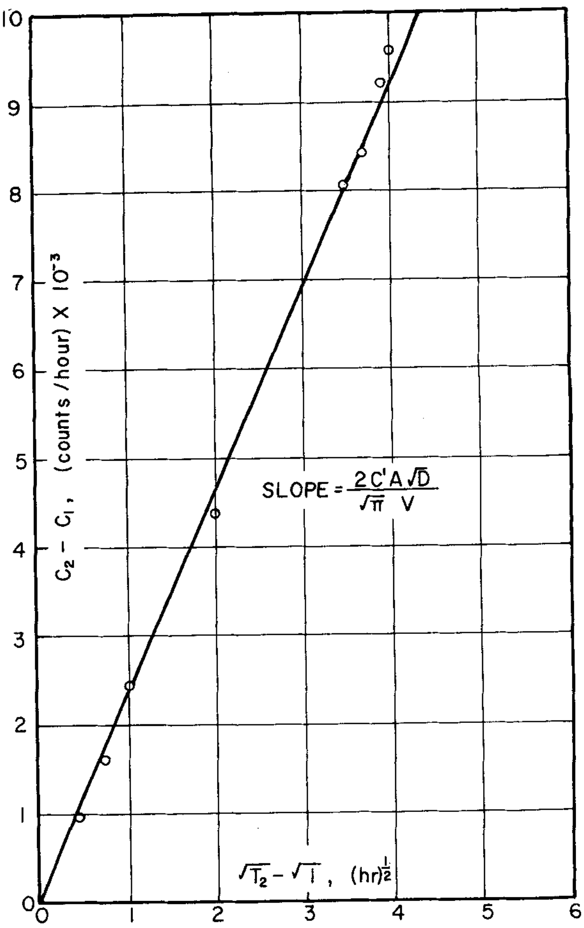

Fig. 2. Sodium chloride in glycerol at 32°C.

When $A$ has been determined by the standardization runs, since all other quantities are known, the diffusivity may be easily calculated, and the results for two runs are $(18.83 \pm 0.38) \times 10^{-8}$ and $(17.88 \pm 0.36) \times 10^{-8}$ sq. cm./sec. (These values are considerably larger than the value $2.6 \times 10^{-8}$ sq. cm./sec. which is obtained by correcting the diffusivity in water to that in glycerol through the Stokes-Einstein relation $D\mu/T =$ constant.)

The experimental-error estimates can be attributed in part to the counting equipment. (In well-behaved counting equipment the error is the square root of the counts.) Another, and principal, source results from the temperature fluctuations in the box (± 0.5°C.), and in the part of the circulation system (outside box) exposed to room temperature. The viscosity varies 32 centipoises/°C. at these temperatures.

## SUMMARY

A rapid method of measuring molecular diffusivities in viscous systems, based on monitoring a radioactive tracer during the transient phase of operation of a diaphragm cell, was developed and used to measure the diffusivity of sodium chloride in glycerol at 32°C. as $18.36 \pm 0.36 \times 10^{-8}$ sq. cm./sec. The experimentally determined diffusivity is considerably larger than the value indicated by the Stokes-Einstein equation. The ease of the method should stimulate further applications to other viscous systems which may lead to a better understanding of the liquid state.

## ACKNOWLEDGMENT

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## NOTATION

$A$ = effective area, sq. cm.
$c$ = concentration, counts/time, or moles/cc.
$c'$ = concentration in lower reservoir, counts/time, or moles/cc.
$c_1$ = concentration in upper reservoir at time = $t_1$, counts/time, or moles/cc.
$c_2$ = concentration in upper reservoir at time = $t_2$, counts/time, or moles/cc.
$D$ = diffusivity, sq. cm./sec.
$L$ = thickness of diaphragm, cm.
$t, t_1, t_2$ = time, hours
$V$ = volume of upper reservoir and circulation system, cc.
$x$ = distance to any point in the diaphragm
$\mu$ = viscosity, centipoise

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# Fluid Flow and Convective-Radiative Energy Transfer in a Parallel-Plate Channel Under Free-Molecule Conditions

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**The flow of a highly rarefied gas in a parallel-plate channel and the transfer of heat owing to simultaneous thermal radiation and free-molecule convection has been investigated analytically. The analysis is facilitated by analogies which exist between the processes. The mass throughflow has been determined as a function of the temperatures and pressures of the system and of the channel dimensions. The heat transfer analysis is first carried out in general and then specialized to the boundary conditions of uniform wall temperature, uniform wall heat flux, and the adiabatic wall. It was found that at temperature levels corresponding to room temperature and above, the results for the combined convective-radiative transport differed little from those for a purely radiative transport.**

This paper is concerned with the fluid flow and heat transfer characteristics of a highly-rarefied gas passing through a parallel-plate channel. The density level of the gas is such that collisions among molecules of the gas are much less probable than are collisions between the gas molecules and the bounding walls. This is called the *regime of free-molecule flow*. The very low gas density is effective in decreasing the convective energy transport, and as a consequence any complete analysis of the heat transfer must include the interchange of thermal radiation between the walls of the channel. Such an analysis including simultaneous convection and radiation is presented here. The relative importance of the two transport mechanisms will be carefully investigated.

The fluid-flow analysis will lead to a relationship between the mass flux through the channel and the pressures and temperatures at the inlet and exit. From the energy transport analysis, a relationship between wall temperature and wall heat transfer will be derived. The flow problem for the parallel-plate channel has been previously studied by DeMarcus (*1*) with a variational method. Comparison of his results with those of this analysis will be made later. Within the knowledge of the authors, the heat transfer problem for the parallel-plate channel has not been previously studied with or without radiation. It is the heat transfer problem which forms the larger part of this study.

The analysis to be reported here is facilitated by an analogy between the transport of mass and energy in a rarefied gas on one hand and the transport of thermal radiation on the other hand. This analogy is described in a general manner by Eckert (*2*). The specific application of the analogy to the free-molecule flow situation has been made in reference 3. There, consideration was given to flow and convective-energy transport (without radiation) in a circular tube. To assist in a concise presentation here, reference will be made to this prior work whenever possible.

A schematic diagram of the flow system is presented in Figure 1. The channel is of length $L$ and of height $h$. The coordinate $x$ measures the distance from the entrance. The channel connects two reservoirs which are of sufficient size so that thermal equilibrium exists within each. The left-hand reservoir has pressure and temperature $p_1$ and