THE DETERMINATION OF
DIFFUSION COEFFICIENTS OF MODERATELY SOLUBLE GASES
IN LIQUIDS

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A rapid method of determining the diffusion coefficients of sparingly soluble gases in liquids with an accuracy of about 1% is described. The technique consists of measuring the rate of absorption of the gas in a laminar jet of the liquid, and by maintaining a constant liquid flow rate the entry and end effects are reduced to minimum significance.

Diffusion coefficients of carbon dioxide in water over a range of temperatures from 18.5°C to 75.1°C, and of nitrous oxide in water and glycerol-water solutions at 20°C are determined. Where comparison is possible the results compare favourably with those of previous workers using other methods.

The jet has also been used to determine values of \( c_s \sqrt{D} \) for the carbon dioxide - monoethanolamine system over a range of amine concentrations from 0.988 to 4.738 moles/litre and an attempt has been made to estimate the "physical" solubility \( c_s^* \) and the diffusion coefficient \( D \) from these values.

A new interferometric method utilizing birefringence for determining gaseous diffusion coefficients directly from the gas to the liquid phase is introduced. This has the important advantage of a truly stagnant liquid surface, and a knowledge of gas solubilities is not required. The determination of the diffusion coefficient of carbon dioxide in water at 20°C is described, and suggestions are made for improving the apparatus and for its application in a modified form to other spheres of gas-liquid mass-transfer.
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The determination of diffusion coefficients of sparingly soluble gases such as carbon dioxide and nitrous oxide in liquids is a problem of considerable technical interest, since the prediction of mass transfer rates and investigations into the mechanism of mass transfer require accurate values of these coefficients.

Before the following discussion on the measurement of diffusion coefficients it is necessary to discuss briefly the process of molecular diffusion and the physical laws governing diffusion.

Molecular diffusion can be defined as the process by which matter is transferred from one part of a single-phase system to another as a result of random motion of the molecules. The transfer of heat by conduction is also due to random molecular motion and the analogy between heat conduction and diffusion was first recognised by BERTHOLLET. In 1855 FICK applied FOURIER'S mathematical treatment of heat conduction to diffusion processes by replacing FOURIER'S temperature gradient with a concentration gradient, and formulated the relationships known as FICK'S Laws of Diffusion. Assuming that the mass transferred in a steady-state system is proportional to the temperature gradient a relationship of the form
is obtained, where

\[ F = -(\text{constant}) \frac{dc}{dx} \]

is obtained, where

- \( F \) = Flow of matter across a reference plane perpendicular to the direction of flow (mass/unit area, time)
- \( c \) = Concentration of matter at any point \( x \)
- \( x \) = Distance between reference plane and the point of maximum potential

Replacing the constant of proportionality by \( D \), the diffusion coefficient;

\[ F = -D \frac{dc}{dx} \]

which is FICK'S First Law of Diffusion. This has a negative sign due to the fact that diffusion occurs in a direction opposite to that of increasing concentration.

In diffusion systems involving liquids and solids the steady state is not rapidly attained and its rate of establishment is also of practical interest. Here it is necessary to eliminate the dependent variable \( F \), which can be done by means of a mass balance between planes at \( x \) and \( (x + dx) \). See for example CRANK,\textsuperscript{16} p.3); this gives rise to FICK'S Second Law
As seen below, it is often preferable to deal with systems in the unsteady state where the Second Law applies. In order to obtain a value of the diffusion coefficient $D$ from these systems it is necessary to solve the differential equation for boundary conditions appropriate to the experimental conditions chosen. Under some conditions $D$ is not constant and the integrated form of the equation which assumes constancy cannot be applied; it is therefore necessary to choose conditions where any variation in $D$ is small enough to be ignored.

There are three main methods by which diffusion coefficients can be measured. Briefly, these are as follows:

(a) The Sintered Cell Method

Here the gas in solution diffuses across a sintered disc into a solution of lower concentration; the diffusion coefficient can be estimated from analyses of the upper and lower solutions. This method has the disadvantages that first, accurate analysis of solutions containing small quantities of gases is a tedious and difficult procedure, and second, the cell must be calibrated with a liquid of known diffusivity having approximately the same viscosity as the liquid under test. It will be appreciated that this method is of extremely limited application, except in the case of water and a few common organic solvents.
(b) Unsteady State Methods

The transfer of gas across an interface between two solutions of different concentrations or between a gas and liquid can be measured by chemical analysis, conductivity measurements, or by optical means. Here there is the difficulty of forming a sharp interface between solutions of very similar density, and the relatively long times involved in measurement give rise to the danger of convection currents. This however is capable of more general application than the sintered cell method, and an investigation based on optical measurements involving birefringence in polarized light is currently under way.

(c) Measurements of Mass Transfer

Under certain circumstances it is possible to express the rate of absorption of a gas by a liquid in terms of interfacial area, contact time, viscosity of the liquid, diffusion coefficient and solubility of the gas in the liquid, and in cases where reaction occurs between the dissolved gas and the liquid, the reaction velocity constant. The value of the diffusion coefficient can be obtained from these quantities provided enough is known about the hydrodynamic properties of the system to enable an accurate evaluation of their effect on the absorption rate.

Types of Apparatus

In the past several types of apparatus have been designed to expose a known area of liquid surface to a gas for a definite time. HIGBIE in 1935 in an investigation into interfacial
equilibrium, applied the penetration theory of VON WROBLEWSKI to a system where bubbles of known dimensions could be contacted with liquids for a known time; but his apparatus proved unsatisfactory due to the complicated flow regime at the surface of the bubble. In the case of falling drops of liquid the flow pattern within the drop is difficult to analyse with sufficient accuracy. Wetted-wall columns provide somewhat more predictable fluid dynamics and have been used for diffusivity measurements, but end effects and a tendency towards rippling are a disadvantage. DANCKWERTS and KENNEDY used a rotating drum as a support for a liquid film but this equipment failed to produce results substantiating the now widely accepted theory of immediate interfacial equilibrium. Diffusion coefficients determined by DAVIDSON and CULLEN using a wetted-sphere absorber compared satisfactorily with values obtained by previous workers using other methods; but exposure times with the equipment are long (0.2 to 1.0 seconds) giving rise to a possibility of convection currents, calculations involve a trial and error procedure, and there is the inherently undesirable necessity of varying the liquid flow rate in order to obtain a result.

Over the last ten years many investigations into gas-liquid mass transfer have been carried out using a jet in which the liquid is in laminar flow; and while earlier workers found some evidence of interfacial resistance, later work indicates that this was due
to defects in apparatus and secondary effects such as boundary layers and surface contamination, and that the laminar jet provides a convenient and accurate means of investigating gas-liquid absorption.

Since unsteady-state mass transfer such as occurs in an absorbing jet is dependent on the diffusivity of the gas in the liquid, it appeared that this might provide an original and efficient method of determining diffusion coefficients with a reasonable degree of accuracy while also being applicable to a wide range of gases and liquids.

The absorption of a gas by a liquid may be influenced by physicochemical or hydrodynamic factors, of which the former (rate of reaction between solute and liquid-phase reactant, interfacial resistance to transfer, diffusion coefficients, gas solubility) are of interest to the chemical engineer. If investigations are carried out in a system in which the hydrodynamic and mechanical factors (interfacial area, fluid dynamics, viscosity, density) can be assessed, accurate information on the physicochemical factors can be obtained. Laminar liquid jets possess several attractive advantages over other types of apparatus for fundamental studies of gas absorption. First, the fluid dynamics of the system can be analysed; and since there is little or no rippling of the surface and end effects can be reduced to insignificance, the interfacial area can be readily determined by direct measurement. Second, it has been shown by HIGBIE that contact
times in industrial absorbers are very short and a particular feature of the laminar jet is the very short exposure times that can be obtained, i.e. from 0.0005 to 0.1 seconds.

With these points in mind, this investigation was undertaken primarily to investigate the application of the laminar jet apparatus for the determination of diffusion coefficients of moderately soluble gases in liquids, but results obtained in the course of the work have led to a study of several related phenomena including an estimation of diffusion coefficients and 'physical' solubility of gases in chemically reacting systems, mass-transfer coefficients, and the effect of temperature, concentration and viscosity on diffusion coefficients in specific systems.
1. **DESIGN AND OPERATION OF LAMINAR JET APPARATUS**

(a) **General Layout of Apparatus.** (See Plates I and II)

The aim of the system is to pass a laminar jet of liquid through an atmosphere of the gas under test in such a way that all parts of the jet surface can be exposed to the gas for a definite period of time; and to determine the rate of absorption of gas. Entrance and end effects should be reduced to minimum significance.

Photographs of the equipment are shown in Plates I and II, and a flow sheet of the equipment is shown in Fig. 1. Liquid from a supply tank fitted with an air-tight cover was pumped by a reduced-speed stainless steel gear-pump through a needle valve system allowing recirculation of part of the flow and a constant stream for feed sampling if required. Flow to the jet was metered by a rotameter fitted with a needle-valve and passed through glass heating coils in a temperature control bath to the absorption chamber which could be submerged in a glass constant-temperature tank. Liquid from the jet was caught in a receiver in the bottom of the absorption chamber and passed to a constant-level device the height of which could be adjusted by a screw mechanism, and thence to a disposal tank.

Gas from a cylinder fitted with a pressure regulator and needle-valve could be passed dry or presaturated via a rotameter or soap-film meter through temperature control baths to the absorption chamber. Incorporated in the line was a device by which the pressure of the gas to the absorption
FIGURE 1. FLOW DIAGRAM OF LAMINAR JET APPARATUS
chamber could be maintained at atmospheric pressure provided an excess of gas was passed through the saturators. Provision was made for venting the absorption chamber to the atmosphere.

(b) Production of Jet and Design of Nozzle.

The method in which the jet is produced is of primary importance, and in the past jets have been produced in a variety of ways. Early workers using cone-shaped nozzles or precision-bore capillary tubes (such as DIRKEN and MOOK for surface tension studies) obtained jets which were not laminar and therefore obviously unsuitable in this application. The first published work in which the question of jet formation was stressed was that of CULLEN and DAVIDSON in 1956 who used a nozzle in which the curved portion of a cross-section through the orifice had the same shape as the initial part of the free streamline as given by SOUTHWELL; at the outlet the convergence of the streamlines is very small and a good approach to laminar flow was obtained. SCRIVEN and PIGFORD used a nozzle in which the profile of the converging section was made to approach the quadrant of an ellipse, and again a good jet was obtained. Shaped orifices such as these have the disadvantage of being difficult to construct accurately in small sizes.

TOOR produced jets from a square-edged accurately round hole in a thin (0.01cm.) orifice plate. These were shown to be satisfactory in performance, and investigations using dye-studies in a large-scale model indicated steady rectilinear flow in the jet; there is also the added advantage of relative ease of construction and it
was decided to adopt the square-edged orifice for this investigation.

The nozzle used is shown in Fig. 2. The orifice plate consisted of a disc of hard-rolled 10% rhodium-platinum alloy, half an inch in diameter and 0.0102 cm. thick. Holes were produced by a drilling and lapping technique at the National Physical Laboratory at Teddington; the diameter of the hole used in this work was determined microscopically and found to be 0.0823 cm. The stainless-steel orifice holder was screwed onto the end of a one-centimetre. 1 D. x 60 cm. long stainless steel approach tube, in which the liquid flow was always laminar. Ten orifice-plates were examined under a microscope and the one that appeared best chosen for this work.

(c) Jet Receiver

The jet receiver (Fig. 3) was of the type used by SCRIVEN and PIGFORD and was made from a 20 mm. length of 1 mm. I.D. selected capillary tube joined to a standard taper male joint member which fitted into a carefully aligned female tapered joint blown into the bottom of the absorption chamber and was held by a stainless-steel spring clip.

(d) Absorption Chamber Assembly (Fig. 4 and Plate II)

The 1 cm. I.D. x 60 cm. stainless steel approach tube passed through a brass cover plate used to seal the top of the glass absorption chamber. The flanged open top of the chamber was ground flat and the lower surface of the cover plate was polished so that a gas-tight seal allowing sliding movement
FIGURE 2. DETAIL OF ORIFICE PLATE HOLDER ASSEMBLY

1.0 mm
Upper End of Receiver
Ground to this Shape

20 mm Length of Selected Capillary Tubing

6.0 mm

FIGURE 3. SECTION THROUGH RECEIVER

1 cm. O.D. St.Stl.
Approach Tube

Orifice Plate, \( \frac{1}{2} \)-in. Diam x 0.0102 cm.
thick 10% Rhodium-Platinum Alloy

Orifice Plate Holder

These Flanges Held by Stainless Spring Clip

Bottom of Absorption Chamber
Assembly and Support of Absorption Chamber

- Externally Threaded S.S. Approach Tube
- Traversing Mechanism
- Brass Locking Nuts Threaded on Approach Tube
- Pressure Nut
- Rubber Gasket
- Brass Cover Plate
- Upper Rubber-Lined Clamp for Absorption Chamber
- Gas Exit
- Glass Absorption Chamber
- Nozzle Assembly
- Tangential Gas Entry
- Lower Clamp
- Centre-Line of Receiver
- Drain
PLATE 2. ABSORPTION CHAMBER AND TRAVERSING MECHANISM
was possible by lubricating the mating surfaces with silicone grease. The absorption chamber, a glass vessel 5 cm. diameter and 25 cm. in length was provided with gas entry and outlet tubes at the bottom and top respectively, a drain port at the bottom, and a female tapered joint to hold the receiver; and was held securely by rubber-lined clamps to a rigid vertical support which also held a traverse mechanism by which the liquid jet could be accurately aligned with the receiver. Jet length could be adjusted by means of threaded brass collars which clamped the externally threaded approach tube to the support plate of the traverse mechanism. When the jet length was set the brass cover plate could be tightened against the absorption chamber by means of a third collar.

The vertical support, equipped with levelling screws, hung from an overhead beam which was supported by a vertical 4 -in. steel -section. This was bolted to a 42 - in. square by 8 - in. concrete base resting on a vibration-damping mounting. In this way a minimum of vibration was transmitted to the jet.

For measurements at temperatures above 25°C, the absorption chamber was completely submerged in a glass constant-temperature tank, water from which could be pumped to a glass jacket around the approach tube.

\( (e) \) Temperature and Pressure Measurement and Control

Liquid temperatures were determined by inserting thermometers in pockets at the entry to the approach tube and in the line between the receiver and overflow device as near
as possible to the receiver. Gas temperatures were measured by passing the gas through vacuum flasks fitted with thermometers. All temperatures could be measured to 0.05°C and it was found that the temperature of liquid entering and leaving the absorption chamber and of the absorption chamber water bath could be kept within a 0.1°C range for temperatures up to 45°C, and 0.2°C range for temperatures from 45°C to 75°C.

Gas pressures at the soap-bubble meter and in the absorption chamber were measured by water U-tube manometers.

The whole apparatus was erected in a constant-temperature room which could be held at any temperature between 18.0°C and 25.0°C with a variation of less than ±0.5°C, by means of a forced-convection electric heater actuated by a contact thermometer placed near the apparatus. Fans provided extra air circulation, and the heating was kept on during each series of runs.

(f) Measurement of Absorption Rates

It is possible to determine the amount of gas absorbed by chemical analysis of the outflowing stream, and while fairly satisfactory methods exist for more common systems such as carbon dioxide-water \(^1,7\) the analytical method in general had the following disadvantages:

1. There is a chance of contamination or gas desorption during sampling.

2. At short jet lengths and high temperatures where the
amount of gas absorbed is small, inaccuracies in analysis of the dilute solutions may materially affect the results.

3. It is tedious and inconvenient to perform a large number of chemical analyses, more especially so since elaborate precautions are necessary when dealing with low concentrations.

4. Satisfactory methods of analysis may not be available for other than the most common systems.

The method of semi-continuous analysis by means of a precalibrated conductivity cell as described by EMLERT and PIGFORD may be suitable for some applications but the temperature dependence of liquid conductivities require accurate (± 0.05°C) temperature control of the sampled streams, and in investigations covering a range of temperatures this would require considerable extra equipment. Also, calibration of the cell for any system is subject to the above analytical difficulties.

A simple and accurate method is the direct measurement of the gas absorbed by means of a soap-film meter. A constant-pressure supply of gas is connected to the absorption chamber via a soap-film meter, and the gas flowing to the chamber is determined by measuring the time required for the absorption of a definite volume of gas by means of a stopwatch. This eliminates the inconvenience of a large number of analyses and is the method chosen for this investigation. Gas entrained by the jet will introduce an error and it is important to ensure proper operations at all times.
The room-temperature control equipment was switched on twenty-four hours before runs were commenced and kept on until a series of runs was finished. Constant-temperature baths were switched on six hours before runs commenced.

Filtered water from the mains supply was passed to the main storage tank through a permixt Deminrolit de-ionizing unit which produced water containing less than 0.1 ppm. of dissolved carbon dioxide, and the water could be de-aerated by closing the tank and applying a vacuum. If solutions were required instead of pure water they were made up by adding the required amount of solute to the tank and mixing by recirculation for two hours.

In the case of the runs at 25.0°C considerable adjustment was necessary before the required temperatures could be attained, but in later runs exact temperatures were not required and measurements were made when temperatures of liquid to jet, liquid from receiver, and gas to absorber were constant and within 0.1°C for runs up to 45°C and 0.2°C for runs at higher temperatures. It was found that the required temperature constancy could be obtained after about 40 minutes operation.

With the outflow line almost closed, the jet was aligned with the receiver by setting the required flow rate through the rotameter and manipulating the traverse mechanism until the overflowing liquid formed a pear-shaped film about the
receiver (Fig. 5a). Upon opening the outflow line the jet entrains a large amount of gas as in Fig. 5b. By partially closing the outflow line the liquid in the capillary reaches a level near the top of the receiver and final adjustment is made by raising the constant-level overflow device until the liquid level is at the top of the receiver. At this point there is neither entrainment of gas nor liquid spillover and the jet is satisfactorily adjusted as in Fig. 5c.

Next the absorption chamber is purged with pure gas by opening clip A, closing B (Fig. 1) and setting a flow rate of about 25 cc/min through the gas rotameter. The apparatus is left in this state until all temperatures are constant at the required value.

Before taking the first reading the gas is directed through the bubble flowmeter for five minutes. The gas vent from the absorption chamber is then closed (clip A), clip B simultaneously opened, and the time required for a known volume of gas to be absorbed measured by a stopwatch reading to 0.1 seconds. Times were measured at ten-minute intervals until they became approximately constant.

The maximum length of jet that could be used was found to be about 15 cm. and stability increased at shorter lengths. In general, four or five jet lengths between 2 and 10 cm. were used for each determination, jet length being measured by a cathetometer to an accuracy of 0.005 cm. Flow rate was kept
FIGURE 5  OPERATION OF JET RECEIVER

FIGURE 6  TYPES OF ABSORPTION CURVES
constant by frequent checks of the rotameter during each run, and was determined periodically by timing the discharge of a known volume.
2. THEORETICAL ASPECTS OF THE MEASUREMENT OF DIFFUSION COEFFICIENTS BY THE LAMINAR JET APPARATUS - PHYSICAL ABSORPTION

(a) Theory of Physical Absorption of a Pure Gas by Laminar Liquid Jets

The early film theory of LEWIS and WHITMAN\(^{13}\) postulated that resistance to mass transfer at a gas-liquid interface was the sum of two separate resistances, one concentrated in the stagnant gas film adjacent to the interface, and the other in a stagnant liquid film adjacent to the interface; transfer taking place by molecular diffusion across these stagnant films. The use of a pure gas in absorption experiments eliminates the gas-film resistance and the rate of absorption depends only on conditions in the liquid phase.

Under certain conditions absorption rates into laminar jets can be interpreted in terms of the penetration theory of unsteady state diffusion into a stagnant liquid. Originally derived in one form by VON WROBLEWSKI in 1878, special cases of this theory were treated mathematically by STEFAN\(^{24}\), and TAMMAN and JESSEN\(^{22}\); but the modern general application to moving surfaces is due to HIGBIE, who applied the theory to short exposure times in his bubble absorber\(^1\).

There are four basic assumptions made in the derivation of the penetration theory. These are discussed below in the context of the laminar jet.

1. Each element of liquid surface is assumed to be exposed to the gas for the same length of time, and to absorb gas
during this time at the same changing rate as though it were a stagnant layer of infinite depth. This requires that the jet surface has constant velocity, is in rod-like flow, and that the depth of penetration of the absorbed molecules is small compared with the total jet diameter. NIJSING\textsuperscript{14} has shown that this last condition is fulfilled when
\[
4D\tau \ll \frac{d^2}{2}
\]
For diffusion coefficients of the order of $10^{-5}$ cm\textsuperscript{2}/sec. and exposure times of less than $20 \times 20^{-3}$ seconds it is obvious that this will hold for all jet diameters of practical interest.

2. The surface of each element of area is saturated with gas at the instant of exposure and remains saturated throughout the period of absorption, i.e. there is immediate interfacial equilibrium.
The truth of this assumption has been the subject of a number of investigations. The earlier work of HIGBIE\textsuperscript{1} and subsequently that of MATSUYAMA\textsuperscript{2}, DANCKWERTS and KENNEDY\textsuperscript{3}, EMMERT and PIGFORD\textsuperscript{21}, and EDWARDS\textsuperscript{17}, indicated the presence of an interfacial resistance in the carbon dioxide-water system; but later work with laminar jets by CULLEN and DAVIDSON\textsuperscript{5}, NIJSING\textsuperscript{14}, TOOR\textsuperscript{10}, and SCRIVEN and PIGFORD,\textsuperscript{7,15} indicates that this apparent resistance could be explained by contamination and hydrodynamic entry and end effects, and in general they conclude that any resistance which may exist is negligible. Immediate equilibrium obviously
cannot be obtained in theory since the number of gas molecules condensing on the liquid surface is limited by considerations of the kinetic theory of gases, a fact pointed out by ELGIN\textsuperscript{12} in 1935; but it has been shown\textsuperscript{7} that the time required for surface to be saturated even with a fairly soluble gas is many orders of magnitude less than the rate at which it can be removed by diffusion into the liquid bulk. In view of this practical and theoretical evidence the assumption of interfacial equilibrium appears justified.

3. The effect of diffusion of dissolved gas in the direction of liquid flow is negligible. It has been shown mathematically by PEACEMAN\textsuperscript{21} that this is theoretically a valid assumption.

4. The diffusivity of the dissolved gas is constant and heat effects can be neglected. This is a necessary working hypothesis, and is probably true for moderately soluble gases.

\textbf{Mathematical Derivation of Formulae}

Dissolved gas diffuses through unit area of the liquid in accordance with FICK'S second law of diffusion

\[ D, \frac{d^2 c}{dx^2} = \frac{dc}{dt} \quad (1) \]

with the boundary condition

\[ c = c^* \text{, } x = 0, \text{ t } 0 \quad (2) \]

(since the liquid surface is saturated with gas at contact), and the initial condition

\[ c = C_0 \text{, } x > 0, \text{ t } = 0 \quad (3) \]

If the initial concentration of gas in the liquid is zero at contact, \( C_0 = 0 \) and (3) becomes

\[ c = 0, \text{ } x > 0, \text{ t } = 0 \quad (4) \]
A solution of equation (1) with boundary conditions (2) and (4) is given by CRANK\textsuperscript{16} and CARSLAW and JAEGER\textsuperscript{31},

\[ c = c^* \text{erfc} \, \frac{x}{2\sqrt{D}t} \]  

(5)

The instantaneous rate of absorption \( N' \) is given by

\[ N' = -D \frac{dc}{dx} \quad x = 0 \]  

(6)

By expanding (5) in a series form, differentiating with respect to \( x \) and substituting in (6)

\[ N' = -D \frac{2}{\sqrt{\pi}} (-c^*) \frac{1}{2\sqrt{D}t} \]  

(7)

\[ N = \frac{1}{t} \int_0^t N' \, dt \]

Substituting for \( N' \) as given by (7)

\[ N = \frac{1}{t} \int_0^t c^* \sqrt{D/\pi} \, t \]  

(8)

(8) is a rate equation. The amount of gas absorbed per unit area after time \( t \) is given by

\[ Q = (\text{average rate of absorption}) \times \text{time of exposure} \]

\[ = N \times t \]

\[ = 2c^* \sqrt{D/\pi} \times t \]

\[ Q = 2c^* \sqrt{D/t} \]  

(9)

Equation (9) can be adapted for convenient application to readings obtained from the laminar jet apparatus as follows:

If fresh surface is produced by the jet at the rate of \( A \text{ cm}^2/\text{sec.} \) and is removed after \( t \) seconds, \( \phi \), the overall rate of absorption in \( \text{gm.moles/sec.} \) is given by
\[ \phi = (\text{rate of production of surface}) \times (\text{Amount of gas absorbed per unit area after exposure of } t \text{ seconds}) \]
\[ = A \times 2c^* \sqrt{(Dt/\pi)} \quad (10) \]

For a laminar jet \( d \) cm. in diameter, \( h \) cm. in length, and having a surface velocity of \( v \) cm/sec. for a liquid flow rate of \( L \) cm\(^3\)/sec.,

\[ A = \pi d^2 v \]
\[ t = h/v \]
\[ v = 4L/\pi d^2 \]

and substituting in (10)

\[ \phi = 4c^* \sqrt{D/Lh} \quad (11) \]

It should be noted that (11) is derived on the assumption that the surface velocity of the jet is the same as the mean velocity of the whole jet.

If any four of the five quantities in (11) are known, the fifth can be calculated. This is the basis for the determination of diffusion coefficients by this method since the value of \( c^* \) can be measured or found in the literature and \( \phi, L, \text{ and } h \) can be measured experimentally. For any system at one definite temperature and pressure, if the liquid flow rate \( L \) is kept constant and the jet length varied, (11) is the equation of a straight line when \( \phi \) is plotted against corresponding values of \( \sqrt{h} \). The gradient of this line is given by

\[ \frac{\phi}{\sqrt{h}} = 4c^* \sqrt{D/L} \]
and D, the diffusion coefficient by

\[ \sqrt{D} = \frac{1}{4c^3 \nu L} \cdot \frac{\phi}{\sqrt{h}} \]

(b) Hydrodynamic Considerations of Laminar Jets

While it is not the purpose of this work to examine in detail the hydrodynamic characteristic of jets, the theory developed above makes the assumption of rod-like flow in the jet, and it is necessary to consider the effect of conditions actually existing on the calculated rate of absorption and on the calculation of diffusion coefficients.

When a liquid leaves any orifice the liquid surface must initially have zero velocity since it was in contact with a fixed wall, and there must be a finite distance travelled before the surface can be accelerated to its final velocity by the bulk of the jet. The assumption of rod-like flow assumes instantaneous acceleration.

Examining an absorbing jet empirically, it appears that deviations from theoretical behaviour could be effected by two main and opposing factors; namely, the slow-moving or stagnant boundary layer near the nozzle which tends to reduce absorption by decreasing the 'fresh' surface of the jet, and the end effect at the receiver where there will be extra absorption at the pool surface and possibly some gas entrainment. The standing waves at the lower end of the jet reported by some observers would also tend to reduce absorption. At constant flow rate in a perfect jet with no end effects, a plot of gas
absorbed against the square root of the jet length is a straight line passing through the origin in accordance with the equation derived above.

\[ \phi = 4c^* \sqrt{D_i L h} \]  \hspace{1cm} (11)

having a gradient of

\[ \frac{\phi}{\sqrt{h}} = 4c^* \sqrt{D_i L} \]

as shown by line A in Fig.6, (page 26)

If there is a constant end effect at the receiver the results will take the form of line B where B is parallel to A but does not pass through the origin; this type of result was reported by Nijsingh\(^9\),\(^14\) who attributed it to entrainment. When there is little or no entrainment effect the absorption will follow line C (Scriven and Pigford\(^7\)) where the effect of the boundary layer is shown up to point 'a'. After this point is passed this is a constant effect independent of jet length and C will be parallel to A. For a well-operated jet with minimum receiver end effects the absorption line would be expected to lie somewhere between A and C, being of the same general shape as C.

The significant conclusion to be drawn is this: if a single jet is operated at a constant flow rate it appears reasonable to assume that the overall end effects will be constant and independent of jet length, and their actual magnitude will not affect the accuracy of D which depends solely on the gradient of the \( \phi - \sqrt{h} \) plot. This is an important point in favour of this jet technique for the
measurement of diffusion coefficients since it is not necessary to alter the flow characteristics in order to vary contact times as is done by CULLEN and DAVIDSON in the wetted-sphere absorber and would be necessary in the rotating-drum apparatus of DANCKWERTS and KENNEDY and in wetted-wall columns.

When the laminar jet is used for the absolute measurement of absorption rates or verification of theories of absorption an estimation of the boundary-layer effect must be made. The various mathematical analyses published by DAVIDSON, PIGFORD, TOOR, and NIJSING can be briefly summarised thus:

The formation of a boundary layer at an orifice and its subsequent dissipation in the jet are analogous to the formation and dissipation of the boundary layer in the wake of an infinitely thin flat plate oriented parallel to the direction of flow. The symmetry line in the wake of the plate corresponds to the surface of the jet, and the solution for the mid-point of the wake gives an approximate description of the surface velocity of the jet, which can be determined from Goldstein's solution for the wake behind a plate. Various investigators, have applied mathematical analyses based on measurements of jet diameter and the above analogy to their experimental results on absorption by jets; but the experimental rates are nearer those predicted by the 'plug-flow' equation (11) than those making allowances for calculated boundary-layer effects, and it has been concluded that the boundary layer does
in fact accelerate to final jet velocity at a considerably faster rate than theoretically predicted.

The accelerating effect of the force of gravity will result in a downstream contraction of the jet, but for fast-moving jets (300 - 500 cm/sec) the reduction is negligible, i.e. of the order of 1% or less.
3. **THE ABSORPTION OF CARBON DIOXIDE IN WATER. EXPERIMENTAL RESULTS AND INTERPRETATION OF DATA.**

This section deals with the physical absorption of carbon dioxide in water at temperatures between 18.5°C and 75.1°C. First, data on the absorption rates of CO₂ into water at 25°C have been used to investigate hydrodynamic conditions in the jet and to demonstrate the adequacy of the theory derived above.

(a) **Investigation of Hydrodynamic Conditions**

It has been shown the rate of absorption of a pure gas by a laminar jet in rod-like flow is given by

\[ \phi = 4c^*D_L T \]  \hspace{1cm} (11)

As discussed above, deviations from the theoretically assumed rod-like flow will occur to a greater or lesser extent due to imperfections in the jet apparatus, and as a test for hydrodynamic suitability equation (11) will be applied to experimental results under conditions where \( L \), the flow rate is kept constant; \( c^* \), the equilibrium saturation of the gas at the interface, and \( D \), the diffusion coefficient are accurately known. The system chosen for this was the absorption of carbon dioxide at atmospheric pressure in water at 25.0°C.

The absorption of carbon dioxide in water cannot be theoretically regarded as totally physical absorption since there is a reaction between dissolved CO₂ and water forming carbonic acid

\[ CO_2 + H_2O \xrightarrow{\varphi} H_2CO_3 \]
which dissociates instantaneously thus

\[ \text{H}_2\text{CO}_3 \overset{\text{\textendash}}{=} \text{H}^+ + \text{HCO}_3^- \]

K_b, the equilibrium constant for the first reaction is
given by

\[ K_b = \frac{(\text{H}_2\text{CO}_3)}{(\text{CO}_2)} = 3.4 \times 10^{-3} \text{ at } 25^\circ\text{C} \]

i.e. only 0.3\% of the total dissolved CO_2 will have reacted
to form carbonic acid, and for the purposes of this
investigation the absorption can safely be regarded as
physical.

The experimental conditions were as follows:

- Diameter of orifice = 0.0823 cm.
- Water Flow Rate = 2.50 cm³/sec
- Jet Lengths = 2.28 to 14.04 cm.
- Exposure Times = 4.95 x 10⁻³ to 29.9 x 10⁻³ sec.
- Nominal Run Temp. = 25.0°C
- Room Temperature = 18.5°C
- Atmospheric Pressure = 747 mm Hg.
- Feed Gas = 99.9\% pure CO_2, dry.

(i) Equilibrium Saturation Concentration of CO_2, c^

It has been shown 7, 10 that even when the feed gas to the
absorption chamber is dry, that the gas immediately adjacent
to the jet surface is very nearly saturated and the proper
partial pressure of gas used in calculating absorption rates
is equal to the total pressure less the vapour pressure of
water at the temperature of the experiment.
Thus, Total pressure $= 747$ mm.
Vapour pressure of water at 25.0°C $= 23.8$ mm.
Partial pressure of CO$_2$ $= 723.2$ mm.

Henry's Law Constant at 25.0°C
(I.C.T. vol. 3, p.260)

Mole fraction of CO$_2$ in solution

\[ \frac{0.98 \times 10^3}{1.64 \times 10^3} = 0.000597 \]

Moles of CO$_2$ per cm$^3$ of water

\[ \frac{0.000597 \times 1}{1-0.000597} = 18.02 \]

\[ c^* = 3.31 \times 10^{-5} \text{gm.mols/cm}^3 \]

(ii) Diffusion Coefficient of CO$_2$ in water

Values for the diffusivity of CO$_2$ in water appear in the International Critical Tables and in a number of studies on absorption$^{1,2,5,7,8}$. A comprehensive summary of these is given by SCRIVEN and PIGFORD$^7$ and their value of $1.97 \times 10^{-5}$ cm$^2$/sec. will be adopted for this work.

The value of $\frac{\mu D t}{d^2}$ at the longest exposure time of $29.9 \times 10^{-3}$ sec. and a diffusivity of $1.97 \times 10^{-5}$ cm$^2$/sec is $3.7 \times 10^{-6}$ which satisfies the limit on jet diameter mentioned earlier, i.e. $\frac{\mu D t}{d^2} \ll 1$.

For the CO$_2$ – water system at 25.0°C and 747 mm. pressure accurate values can now be substituted for $c^*$, D, and L in equation (11)
\[ \phi = 4 \pi c^2 \sqrt{D \frac{L}{h}} \] (11)

\[ \phi = 4 \times (3.31 \times 10^{-5} \times \sqrt{1.97 \times 10^{-5}} \times \sqrt{2.50} \times \sqrt{h} ) \]

\[ \phi = 0.93 \times 10^{-6} \sqrt{h} \text{ mm-moles/sec} \] (12)

The theoretical absorption rate for any jet length can now be calculated from (12) and compared with the experimental results.

(iii) Experimental Results at 25.0°C

Two sets of runs were made at 25.0°C and 747 mm. pressure with jet lengths varying from 2.28 cm. to 14.04 cm. and a constant liquid flow rate of 2.50 cm³/sec, giving exposure times of 4.95 \times 10^{-3} \text{ sec.} to 29.9 \times 10^{-3} \text{ sec.} Experimental procedure was as described in Section 1 (g), and a specimen set of experimental readings is given below:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
<td>18.5°C</td>
</tr>
<tr>
<td>Run Temperature</td>
<td>25.0°C</td>
</tr>
<tr>
<td>Jet Length</td>
<td>6.98 cm</td>
</tr>
<tr>
<td>Atmospheric Pressure</td>
<td>746.9 mm. Hg</td>
</tr>
<tr>
<td>Liquid Temp. at Jet Entry</td>
<td>25.0°C</td>
</tr>
<tr>
<td>Liquid Temp. at Jet Exit</td>
<td>25.0°C</td>
</tr>
<tr>
<td>Absorber Bath Temperature</td>
<td>25.05°C</td>
</tr>
<tr>
<td>Flow Rate Check: Time to fill 1- litre flask</td>
<td></td>
</tr>
<tr>
<td>Start of run</td>
<td>400.9</td>
</tr>
<tr>
<td>End of run</td>
<td>401.3</td>
</tr>
<tr>
<td>Average</td>
<td>401.1</td>
</tr>
</tbody>
</table>

Time taken to absorb 7.0 cc. of carbon dioxide

<table>
<thead>
<tr>
<th>At time</th>
<th>0 min.</th>
<th>= (109.2 sec) rejected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 min.</td>
<td>= (116.2 sec) rejected</td>
</tr>
<tr>
<td></td>
<td>20 min.</td>
<td>= 118.9 sec</td>
</tr>
<tr>
<td></td>
<td>30 min.</td>
<td>= 118.3 sec</td>
</tr>
<tr>
<td></td>
<td>40 min.</td>
<td>= 118.7 sec</td>
</tr>
<tr>
<td></td>
<td>50 min.</td>
<td>= 118.1 sec</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>= 118.5 sec</td>
</tr>
</tbody>
</table>
Ambient temp. at bubble meter 18.5°C
Gas temp. to meter 18.5°C
Gas temp. from meter 18.5°C
Gas pressure at meter Atmospheric + $\frac{1}{2}$ H$_2$O
Gas pressure in absorption chamber Atmospheric + 0" H$_2$O

(iv) Calculation of Absorption Rate

The absorption rate at this jet length is calculated as follows:

Time to absorb 7.0 cc = 118.5 sec (18.5°C, 747 mm.Hg)

Absorption Rate = \[
\frac{7}{118.5} \times \frac{273}{291.5} \times \frac{747}{760} \text{ cc/sec at N.T.P.}
\]

= 0.0542 cc/sec at N.T.P.

= \frac{0.0542}{22.412} \text{ gm-moles/sec.}

= 2.42 x 10^{-6} \text{ gm-moles/sec.}

The absorption rates for CO$_2$ into water at 25.0°C at nine jet lengths are compared with the theoretical rates for a perfect jet calculated from Equation (12) in Table 1. Absorption rates are plotted versus the square root of the jet length in Fig. 7.
Fig. 7. Absorption of CO₂ in water jet formed by 0.0823 cm. diam. orifice at 25°C, 723 mm pp.

Absorption rate \( \phi \) = \( \frac{\text{molecules CO}_2}{\text{sec} \times 10^6} \)

Theoretical line

\( \phi = 0.92 \sqrt{h} \)

Experimental line

\( \phi = 0.92 \sqrt{h} \)
### Table 1. Theoretical and Experimental Rates of Absorption

<table>
<thead>
<tr>
<th>Jet Length (h cm)</th>
<th>1/h</th>
<th>( \phi_{th} ) moles/sec of ( CO_2 ) x ( 10^{-6} )</th>
<th>( CO_2 ) Abs. by Jet cc/sec at N.T.P. x ( 10^{-6} )</th>
<th>( \phi_{exp} ) moles/sec of ( CO_2 ) x ( 10^{-6} )</th>
<th>( \phi_{th} - \phi_{exp} ) moles/sec of ( CO_2 ) x ( 10^{-6} )</th>
<th>( \phi_{th} - \phi_{exp} ) x 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.28</td>
<td>1.51</td>
<td>1.40</td>
<td>0.0302</td>
<td>1.35</td>
<td>0.05</td>
<td>3.5</td>
</tr>
<tr>
<td>2.52</td>
<td>1.58</td>
<td>1.48</td>
<td>0.0325</td>
<td>1.44</td>
<td>0.04</td>
<td>2.5</td>
</tr>
<tr>
<td>4.47</td>
<td>2.12</td>
<td>1.97</td>
<td>0.0428</td>
<td>1.91</td>
<td>0.06</td>
<td>3.0</td>
</tr>
<tr>
<td>4.93</td>
<td>2.22</td>
<td>2.06</td>
<td>0.0441</td>
<td>1.97</td>
<td>0.09</td>
<td>5.3</td>
</tr>
<tr>
<td>6.98</td>
<td>2.64</td>
<td>2.45</td>
<td>0.0542</td>
<td>2.42</td>
<td>0.03</td>
<td>1.2</td>
</tr>
<tr>
<td>7.30</td>
<td>2.70</td>
<td>2.51</td>
<td>0.0550</td>
<td>2.45</td>
<td>0.06</td>
<td>2.5</td>
</tr>
<tr>
<td>10.05</td>
<td>3.17</td>
<td>2.94</td>
<td>0.0646</td>
<td>2.89</td>
<td>0.05</td>
<td>1.7</td>
</tr>
<tr>
<td>10.65</td>
<td>3.27</td>
<td>3.04</td>
<td>0.0660</td>
<td>2.96</td>
<td>0.08</td>
<td>2.5</td>
</tr>
<tr>
<td>14.04</td>
<td>3.74</td>
<td>3.48</td>
<td>0.0765</td>
<td>3.41</td>
<td>0.07</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*From Table 2*

### (v) Conclusions

The difference between calculated and observed absorption rates (Table 1) appear to indicate that the boundary layer effect reduces absorption by about 3% at the shorter lengths and 2% at greater lengths. Within the limits of accuracy the reduction can be regarded as constant over the range of jet lengths tested, i.e. the total end and entry effect do not depend on jet length.
Mathematical analyses based on the analogy between conditions in the jet and the wake behind a flat plate indicate that the effect of the boundary layer should be to reduce absorption rates by from 18% at very short (2 cm.) lengths to 5% at 10 to 15 cm. However, results obtained in practice are usually only 1% to 4% below theoretical due presumably to faster acceleration of the boundary layer than calculated.

On the $\phi$ vs. $\sqrt{h}$ plot (Fig.7.) the best line through the experimental points has a gradient of 0.92 which is approximately 1% less than the theoretical value for $\phi/\sqrt{h}$ of 0.93 (Equation 12). The position of the theoretical line indicates a small reduction in absorption.

It can be concluded from these results that under the experimental conditions described here, namely a flow rate of 2.50 cm/sec and jet lengths of 2.28 cm. to 14.04 cm:

(a) From hydrodynamical aspects, the jet apparatus is satisfactory and can be expected to produce measurements of diffusion coefficients not more than about 1% in error.

(b) Assumptions made in deriving Equation (11) are justified and the theory is adequate.

(c) Absolute measurements of absorption rates should be less than 3% in error.

It should be noted that the concept of using a constant flow rate providing constant end effects enables greater accuracy in determining diffusion coefficients than hitherto
available from other absorption measurements.

(b) **Determination of Diffusion Coefficients of Carbon Dioxide in Water.**

It has been shown that the rate of absorption of carbon dioxide by a laminar jet can be expressed thus

$$\phi = 4c^* \sqrt{D \frac{L}{h}}$$

(11)

By arranging (11)

$$\frac{\phi}{\sqrt{h}} = \frac{1}{4c^* \sqrt{L}}$$

(13)

The flow rate $L$ can be fixed, the saturation concentration $c^*$ can be determined from the literature over a range of temperatures, and the value of $\phi/\sqrt{h}$ can be obtained experimentally as the gradient of a plot of absorption rate versus the square root of the jet length; the diffusion coefficient can then be obtained by squaring equation (13).

The results of tests carried out over a range of temperatures from 18.5°C to 75.1°C and jet lengths of 2.28, 4.93, 7.30, and 10.65 cm are shown in Table 2; absorption rates are plotted against the square root of the jet lengths in Figure 8. A specimen calculation of the diffusion coefficient at 45.2°C is given below:

From Fig. 8

$$\frac{\phi}{\sqrt{h}} = 0.68 \times 10^{-6}$$

$L$, liquid flow rate = 2.50 cm²/sec.

$$\frac{\sigma}{L} = 1.58$$

V.P. of water at 45.2°C = 72.6mm
<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>18.5</th>
<th>25.0</th>
<th>34.7</th>
<th>45.2</th>
<th>54.9</th>
<th>65.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of absorption</td>
<td>cc/sec</td>
<td>moles/sec</td>
<td>cc/sec</td>
<td>moles/sec</td>
<td>cc/sec</td>
<td>moles/sec</td>
</tr>
<tr>
<td>Jet Length ( \frac{m}{h} ) cm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.28</td>
<td>1.51</td>
<td>0.0329</td>
<td>1.47</td>
<td>0.0302</td>
<td>1.35</td>
<td>0.0257</td>
</tr>
<tr>
<td>4.93</td>
<td>2.22</td>
<td>0.0497</td>
<td>2.15</td>
<td>0.0441</td>
<td>1.97</td>
<td>0.0385</td>
</tr>
<tr>
<td>7.30</td>
<td>2.70</td>
<td>0.0603</td>
<td>2.69</td>
<td>0.0550</td>
<td>2.45</td>
<td>0.0464</td>
</tr>
<tr>
<td>10.65</td>
<td>3.27</td>
<td>0.0725</td>
<td>3.24</td>
<td>0.0661</td>
<td>2.96</td>
<td>0.0570</td>
</tr>
<tr>
<td>( \frac{\phi}{m} ), gm-moles/sec</td>
<td>0.99</td>
<td>0.92</td>
<td>0.78</td>
<td>0.68</td>
<td>0.57</td>
<td>0.47</td>
</tr>
<tr>
<td>( \frac{\delta}{m} ), ( \frac{\phi}{m} ) ( \times 10^6 ) ((cm)^3 \times 10^6) from Fig. 8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* at N.T.P.  ** \( \times 10^6 \)

Table 2. Absorption of \( CO_2 \) in Laminar Jet, 747 mm Hg Total Pressure
Figure 8: Absorption of CO₂ in water jets. Flow rate = 2.50 cc/sec, P.P. of gas = 723 mm.

Absorption rate = cm² moles CO₂/sec x 10⁶
Total pressure = 747 mm
P. press. of CO₂ = 674.4 mm

\(c^*\) at 45.2°C, 674.4 mm = 1.94 x 10⁻⁵ gm-moles/cc.

\[ \sqrt{D} = \frac{\phi}{\sqrt{h}} \cdot \frac{1}{4c^*\sqrt{D}} \]

\[ = \left(0.68 \times 10^{-6}\right) \times \frac{1}{4 \times (1.94 \times 10^{-5}) \times 1.58} \]

\[ = 5.50 \times 10^{-3} \]

\[ D = 3.03 \times 10^{-5} \text{ cm}^2/\text{sec} \]

The evaluation of D at other temperatures is shown in Table 3.

(c) Discussion of Results

It appears from Table 3 that the temperature dependence of carbon dioxide diffusion coefficients in water can be
<table>
<thead>
<tr>
<th>Temp,°C</th>
<th>c eq, sol of CO₂ in water (gm-moles/cc x 10^5)</th>
<th>L=2.50 cc/sec</th>
<th>1/vLc₀</th>
<th>1/vHc₀</th>
<th>φ x 10⁶</th>
<th>√D = φ x 10³/4H L</th>
<th>Diff. Coeff. D x 10⁵</th>
<th>Visc. μ cp</th>
<th>T Abs. Temp.</th>
<th>DₓT x 10²</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.5</td>
<td>3.86</td>
<td>2.46</td>
<td>4.06</td>
<td>0.99</td>
<td>4.05</td>
<td>1.65</td>
<td>1.043</td>
<td>291.6</td>
<td>5.87</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>3.31</td>
<td>2.09</td>
<td>4.78</td>
<td>0.92</td>
<td>4.41</td>
<td>1.95</td>
<td>0.894</td>
<td>298.1</td>
<td>5.85</td>
<td></td>
</tr>
<tr>
<td>34.7</td>
<td>2.52</td>
<td>1.59</td>
<td>6.29</td>
<td>0.78</td>
<td>4.91</td>
<td>2.41</td>
<td>0.729</td>
<td>307.8</td>
<td>5.72</td>
<td></td>
</tr>
<tr>
<td>45.2</td>
<td>1.94</td>
<td>1.23</td>
<td>8.12</td>
<td>0.68</td>
<td>5.50</td>
<td>3.03</td>
<td>0.598</td>
<td>318.3</td>
<td>5.69</td>
<td></td>
</tr>
<tr>
<td>54.9</td>
<td>1.50</td>
<td>0.95</td>
<td>10.51</td>
<td>0.57</td>
<td>5.98</td>
<td>3.68</td>
<td>0.506</td>
<td>328.0</td>
<td>5.58</td>
<td></td>
</tr>
<tr>
<td>65.0</td>
<td>1.12</td>
<td>0.71</td>
<td>14.10</td>
<td>0.47</td>
<td>6.62</td>
<td>4.40</td>
<td>0.436</td>
<td>333.1</td>
<td>5.68</td>
<td></td>
</tr>
<tr>
<td>75.1</td>
<td>0.78</td>
<td>0.49</td>
<td>20.40</td>
<td>0.36</td>
<td>7.35</td>
<td>5.40</td>
<td>0.380</td>
<td>348.2</td>
<td>5.87</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Calculation of Diffusion Coefficients for CO₂ in Water and Evaluation of DₓT
described by the Nernst-Einstein relationship \( \frac{D_D}{T} = \text{constant} \)

where \( \mu \) is the liquid viscosity and \( T \) is the absolute temperature. Values of the Nernst-Einstein constant calculated in Table 3 vary between \( 5.58 \times 10^{-2} \) and \( 5.87 \times 10^{-2} \) which is within \( 2\% \) of the mean value of \( 5.72 \times 10^{-2} \), viscosities being expressed in terms of centipoises and diffusivities in cm\(^2\)/sec. The experimental values show no trend to increase or decrease with increasing temperature.

An interesting point arising from this is that if it can be accepted that the diffusivities obtained in this investigation can be fully described by the above relationship, then the diffusion coefficient of carbon dioxide in water appears to be independent of its concentration, at least over the temperature range of \( 18.5^\circ C \) to \( 75.1^\circ C \), since the concentration varies from \( 3.96 \times 10^{-5} \text{ gm-moles/cc at } 18.5^\circ C \) to \( 0.78 \times 10^{-5} \text{ gm-moles/cc at } 75.1^\circ C \) - a variation of \( 500\% \). A plot of diffusion coefficient versus temperature is shown in Fig. 9.

Comparison with Results of Other Investigators

The results of five other investigators are compared with those obtained here in Table 4. For purposes of comparison all results up to \( 45.2^\circ C \) are plotted on temperature-diffusion coefficient graph (Fig. 10). The agreement is close in all
FIGURE 9. DIFFUSION COEFFICIENTS OF CO$_2$ IN WATER AS A FUNCTION OF TEMPERATURE.
FIGURE 10. DIFFUSIVITY OF CO₂. COMPARISON WITH RESULTS OF OTHER INVESTIGATORS.
Table 4. Summary of Diffusion coefficients and $\frac{Du}{T}$ values for CO$_2$ - water at different Temperatures.

 cases, although HUFNER'S results appear to be generally higher and the results of CULLEN and DAVIDSON generally lower. The average values of $\frac{Du}{T}$ obtained from the results of other investigators agree very well (within 3%) with the values determined in this work, again with the exception of HUFNER. KRAMERS' value of $5.8 \times 10^{-2}$ is very slightly higher while the other results are somewhat

<table>
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<th>Investigators</th>
<th>Method</th>
<th>Temp $^\circ$C</th>
<th>Diff. Coeff. $D$ cm/sec $\times 10^5$</th>
<th>Vis. Coeff. $\mu$ cp</th>
<th>$\frac{Du}{T}$ $\times 10^2$</th>
<th>Average $\frac{Du}{T}$ $\times 10^2$</th>
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<td>2.08</td>
<td>0.801</td>
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<td>Cullen and Davidson (6)</td>
<td>Wetted-sphere absorber</td>
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lower, but these discrepancies can be explained by experimental error, and the comparative evidence indicates that the laminar jet technique described here is a suitable and accurate method of determining diffusion coefficients over a wide range of temperatures.
4. **THE DETERMINATION OF DIFFUSION COEFFICIENTS OF NITROUS OXIDE IN WATER AND AQUEOUS SOLUTIONS OF GLYCEROL AT 20°C.**

(a) **Experimental Results and Calculation of Diffusion Coefficients**

Rates of absorption of nitrous oxide into laminar jets of water and glycerol-water solutions up to 22.7% at 20°C and 753 mm. Hg. total pressure were determined as described in the previous section. The diffusion coefficient can be determined from the relationship

\[ \sqrt{D} = \frac{\phi}{\sqrt{H}} \cdot \frac{1}{4c^* \sqrt{L}} \]

(i) **Determination of Solution Strengths**

Solutions were made up with the purest available commercial glycerol and de-ionized water, and strengths determined by measuring the densities at 20°C. From a tabulation by BOSART and SNODDY (Ref. 1, p. 191), the percentage of glycerol in a solution can be determined from the density of the solution.

(ii) **Determination of \( c^* \), equilibrium gas solubility**

Information on the solubility of nitrous oxide in water appears in PERRY, and SEIDELL. At 20°C, I.C.T. (Vol. 3, p. 259) gives a value of the Henry's Law Coefficient of \( 1.98 \times 10^3 \), and from this the solubility at a partial pressure of 729.2 mm Hg can be determined

\[ c^* = 2.68 \times 10^{-5} \text{ moles/cc} \]

The solubility in glycerol-water solutions are obtained from the results of HENKEL (SEIDELL, 3rd Ed. p. 1140).
Values for $c^*$ up to 15.82% glycerol are plotted in Figure A1, and solubilities at the concentration used here obtained from the curve (extrapolated where necessary).

The gas used was 99.5% pure unsaturated nitrous oxide, liquid flow rate was kept constant for each run, and as before the rate of absorption determined by timing the absorption of a known quantity with a soap-film meter. Room temperature was kept at $20^\circ \pm 0.2^\circ$C, and jet lengths measured with a cathetometer.

$\phi$, the rate of absorption of gas in moles/sec was calculated at each jet length $h$, and the value of $\frac{\phi}{h}$ determined from the gradient of the $\phi - \frac{1}{h}$ plot (Figure 11). Corresponding values of $c^*$ and $L$ were increased in Equation 13 and the diffusion coefficients calculated (Table 5).

(b) Discussion of Results

Diffusion coefficients are plotted against solution concentrations in Figure 12.

The value of the coefficient in water at 20.0°C determined here is $1.92 \times 10^{-5}$ cm$^2$/sec. Few results are available for comparison, but HUFNER'S value of $1.74 \times 10^{-5}$ cm$^2$/sec (I.C.T. vol 5, p. 63 is about 9.5% lower; and the result of CULLIN and DAVIDSON ($1.87 \times 10^{-5}$ cm$^2$/sec) 2.4% lower. This tends to confirm the latter result (for which an accuracy of 5% is obtained) and it appears that HUFNER'S result must be low.
**Figure 11. Absorption Rates of N₂O in Water and Glycerol Solutions at 20°C, 753 mm Hg.**
<table>
<thead>
<tr>
<th>Density (gm/cc)</th>
<th>% Glycerol</th>
<th>Liquid Flow Rate (cc/sec)</th>
<th>Eq. Sol. c^8 mols/cc x 10^5</th>
<th>Jet length (h cm)</th>
<th>( \sqrt{h} )</th>
<th>cc/sec N(_2)O Abs at 20(^{\circ})C, 753 mm Hg</th>
<th>( \phi ) mols/sec N(_2)O Abs</th>
<th>( \phi \times 10^6 ) ( \sqrt{h} ) From Eqn.11</th>
<th>( \sqrt{D} ) x 10(^3)</th>
<th>Diffusion Coefficient ( D ), cm(^2)/sec x 10(^5)</th>
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Table 5. Calculation of Diffusion Coefficients for N\(_2\)O in Water and Solutions of Glycerol.
<table>
<thead>
<tr>
<th>Density (gm/cc)</th>
<th>% Glycerol</th>
<th>Liquid Flow Rate (cc/sec)</th>
<th>Eq. Sol. c^2 mols/cc x 10^5</th>
<th>Jet Length (cm)</th>
<th>√h</th>
<th>cc/sec N_2O Abs. at 20°C 753mm</th>
<th>N_2O Abs. x 10^6</th>
<th>h x 10^6</th>
<th>√D From Eqn(13) x 10^3</th>
<th>Diffusion Coefficient D, cm^2/sec x 10^5</th>
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Table 5 (contd) Calculation of Diffusion Coefficients for N_2O in Solutions of Glycerol
From the Stokes-Einstein relationship

\[
\frac{D_u}{T} = \text{Constant}
\]

it might be expected that the product \(D_u\) for glycerol solutions would be constant at a constant temperature.

The viscosities in the experimental range covered here were determined at 20.0°C; and are presented in Figure A2, Appendix I. Table 6 shows a tendency for \(D_u\) to increase with viscosity, suggesting that a relationship of the form

\[
D_u^m = \text{Constant}
\]

might fit the experimental data better. From a plot of log \(D\) versus log \(\mu\) (Figure 12a) a

<table>
<thead>
<tr>
<th>Solution % Glycerol</th>
<th>(\mu) cp</th>
<th>Diffusion Coeff. (D\ x 10^5\ cm^2/sec)</th>
<th>(D_u x 10^5)</th>
<th>(0.94 \mu)</th>
<th>(D_u 0.94\ x 10^5)</th>
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Table 6. Investigation of Viscosity - Diffusion Coefficient Relationship

value of 0.94 was obtained for the exponent of viscosity. The value of \(D_u^{0.94}\) in Table 6 show no tendency to increase with viscosity, and all values lie within 1.1% of the mean value of 1.93 \(x 10^{-5}\).
FIGURE 12A. PLOT OF LOG (VIScosity) VERSUS LOG $D_{N_2O}$ FOR GLYCEROL-WATER SOLUTIONS AT 20°C.
5. EVALUATION OF THE LAMINAR JET TECHNIQUE

A most important feature of unsteady state methods for the determination of diffusion coefficients from absorption measurements is the requirement that the interfacial area must be accurately known. Uncertainties arise due to entrance and exit effects and rippling of the liquid surface, and since it is desirable to base a result under a given set of conditions of temperature, pressure, etc., on more than one reading, the necessary change in flow conditions gives rise to a change in the above effects. This work has proposed a technique in which exposure time can be altered over a considerable range without altering the entrance and exit effects since the liquid flow rate is kept constant, and by using the gradient of the absorption curve rather than individual values of absorption, values of diffusion coefficient are derived from a change in absorption rate rather than absolute point rates of absorption. Other absorption methods use the total gas absorbed as a basis for their calculations and it is necessary to accurately assess the end effects and flow characteristics, usually in rather complex circumstances.

Other advantages include:

(i) The effect of convection is minimised due to the very short exposure times which can be varied between 0.0005 sec. and 0.05 sec. With no other apparatus is this extreme flexibility in exposure time so easily obtained, and only with the rotating drum of DANCKWERTZ and KENNEDY^3 can exposure times
as low as 0.008 secs. be approached.

(ii) Since the timing of a soap film is used to determine absorption rates, errors due to sampling and analysis are not introduced.

(iii) The method is absolute, requiring only a knowledge of the solubility of the gas in the absorbing liquid and has general application to all sparingly soluble gases. In cases where gas solubilities are not well established it may be necessary to determine them experimentally. The method is impracticable when gas solubility is high due to heat effects at the interface.

(iv) The apparatus is simple to construct and operate, although great care must be taken in the construction of the orifice plate for the production of the jet since it is essential that the hole is accurately round and square-edged. The size of the absorption chamber makes accurate temperature control possible and permits measurements at high temperatures.

(v) Provided the apparatus is well constructed, diffusion coefficients can be determined to an accuracy of about 1% assuming the value for $c^*$, the equilibrium solubility of the gas is correct. However, it should be noted that since the diffusion coefficient is calculated from the product $c^*\sqrt{D}$, any error in $c^*$ will produce the square of the error in the value of the diffusion coefficient.
6. ABSORPTION WITH CHEMICAL REACTION IN LAMINAR LIQUID JETS

The foregoing section has shown that it is possible to regard the laminar jet apparatus as one capable of exposing a stagnant liquid surface to a gas for very short periods of time. The hydrodynamic properties of the system introduce no difficulties, and as will be shown below a value of the product \( \frac{c^* D}{c^*} \) for a system in which chemical reaction is occurring can be easily obtained. From this product it should be possible to obtain fairly accurate estimates of the equilibrium solubility \( c^* \) and the diffusion coefficient in a reacting system.

The system shown for investigation was monoethanolamine - water at 25°C. Since 1930 monoethanol-amine solutions have been extensively used for the absorption of carbon dioxide, and it was felt that further information on the system would be a useful contribution. Also, published work on the reaction mechanism exists enabling calculation of the reaction velocity constant which is required in determining the value of \( \frac{c^* D}{c^*} \). Since amine concentrations of up to 30% are commonly met with in industry, solutions varying in strength from one-to five-molar will be examined.

Since the laminar jet provides an easily measured mass-transfer area, it is also possible to determine accurate mass-transfer coefficients.
(a) The theory of Absorption by Diffusion and Simultaneous Chemical Reaction

As in the case of physical absorption, the absorption of a gas by a moving jet of liquid with which it reacts can be theoretically interpreted in terms of unsteady state transfer into a stagnant liquid provided hydrodynamic conditions in the jet are such that there is no movement of the liquid surface relative to the bulk, at least for the depth of penetration of the absorbed molecules.

The recent applications of VON WROBLEWSKI'S Penetration Theory due to HIGBIE¹ and DANCKWERTS¹⁷ assume that after some period of time the interface is renewed by fresh liquid and gas. Since in this work it is intended to use pure gases, it is unnecessary to consider the effect of the gas film and the discussion relates to conditions on the liquid side only.

Elements of saturated liquid leave the interface and penetrate towards the bulk of the liquid; the times of renewal of these elements of surface can be assumed equal as in the HIGBIE concept, or to follow a statistical distribution according to DANCKWERTS.

DANCKWERTS²⁹ has developed a mathematical treatment for the case of absorption of a gas into a semi-infinite liquid medium with which it undergoes a first-order or pseudo first-order chemical reaction, and where the following conditions apply.
1. The liquid surface is continuously saturated with the solute gas.

2. Effects of convection can be neglected. For very short exposure times this is a valid assumption.

3. The solute gas has limited solubility in the liquid.

4. The diffusion of unreacted solute through the medium obeys FICK'S law of ideal diffusion.

5. At exposure, the concentration of the solute in the bulk of the liquid is zero.

Let k be the velocity constant of the first-order reaction between the solute and medium.

The rate at which a weight of solute Q crosses unit area of a plane at a distance x below the surface is given by FICK'S Law

\[
\frac{dQ}{dt} = -D \frac{dc}{dx} \quad (14)
\]

The rate at which chemical reaction destroys the solute (per unit volume) is \( kc \).

Consider an element of unit area between the planes \( x \) and \( (x + dx) \). The volume of the element is then \( dx \), and the following changes in its content of solute occur in time \( dt \)

\[
\text{Diffusing in:} \quad -D \frac{dc}{dx} \cdot dt
\]

\[
\text{Diffusing out:} \quad -\left\{ D \cdot dt \left( \frac{dc}{dx} + \frac{d^2c}{dx^2} \cdot dx \right) \right\}
\]

\[
\text{Reacting:} \quad -kc \cdot dx \cdot dt
\]

Net increase of solute = \[
\frac{-D \cdot dc}{dx} \cdot dt + D \cdot dt \left( \frac{dc}{dx} + \frac{d^2c}{dx^2} \cdot dx \right) - kc \cdot dx \cdot dt
\]
If this increase of solute is equivalent to an increase in concentration of \( dc \ \text{gm-moles/cc} \), i.e. \( dc.\text{dx} \ \text{gm-mole} \) in the element of volume under consideration, then

\[
\frac{dc}{dx} = \frac{d^2c}{dx^2} - kc
\]

The differential equation (15) with these boundary conditions is identical in form to that obtained for the problem of heat conduction along a thin rod which loses heat from its periphery at a rate proportional to its temperature. The solution of this equation is given by CARSLAW and JAEGER\(^{31}\) and is

\[
\frac{c}{c^*} = \exp(-x\sqrt{k/D}) \ \text{erfc} \left( \frac{x}{2\sqrt{D}} \right) - \sqrt{kt} \\
+ \exp(x\sqrt{k/D}) \ \text{erfc} \left( \frac{x}{2\sqrt{D}} \right) + \sqrt{kt}
\]

where \( \text{erfc} \ Z = 1 \ -\ \text{erf} Z = 1 - \frac{2}{\sqrt{\pi}} \left( \int_0^Z e^{-y^2} \ \text{dy} \right) \)

If (16) is differentiated with respect to \( x \), and setting \( x = 0 \) for the liquid surface
\[
\frac{dc}{dx} \bigg|_{x=0} = -c^* \sqrt{\frac{k}{D}} \left( \text{erf} \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right)
\]

From (14) rate of absorption at the surface is

\[
\frac{dQ}{dt} = -D \frac{dc}{dx} \bigg|_{x=0}
\]

and substituting from equation (16)

\[
\frac{dQ}{dt} = -D \cdot -c^* \sqrt{\frac{k}{D}} \left( \text{erf} \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right)
= c^* \sqrt{Dk} \left( \text{erf} \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right)
\]

(17)

Integrating, the quantity \( Q \) absorbed in time \( t \) is

\[
Q = c^* \sqrt{\frac{D}{k}} \left\{ \left( kt + \frac{1}{2} \right) \text{erf} \sqrt{kt} + \sqrt{\frac{kt}{\pi}} e^{-kt} \right\}
\]

(18)

Rearranging to obtain a dimensionless quantity,

\[
\frac{Q}{c^* \sqrt{\frac{k}{D}}} = \left\{ \left( kt + \frac{1}{2} \right) \text{erf} \sqrt{kt} + \sqrt{\frac{kt}{\pi}} e^{-kt} \right\}
\]

(18a)

For a range of values of \( kt \), corresponding values of the dimensionless quantity \( \frac{Q}{c^* \sqrt{\frac{k}{D}}} \) can be calculated, and a plot of \( kt \) against \( \frac{Q}{c^* \sqrt{\frac{k}{D}}} \) gives a curve which has an asymptote the equation of which is

\[
\frac{Q}{c^* \sqrt{\frac{k}{D}}} = \left( kt + \frac{1}{2} \right)
\]

(19)

\[
Q = c^* \sqrt{Dk} \left( t + \frac{1}{2k} \right)
\]

(20)

Equation (20) follows directly from equation (18) since at large values of \( kt \), \( \text{erf} \sqrt{kt} \) is approximately equal to unity, \( e^{-kt} \) becomes negligibly small.

The error introduced by using the approximate solution (20) instead of the exact solution is

\[
\% \text{ Error} = \frac{\text{Approximate } Q - \text{Exact } Q}{\text{Exact } Q} \times 100
\]
\[
= (kt + K) \left\{ \frac{\text{erf} \sqrt{kt} + \sqrt{kt/\pi} \cdot e^{kt}}{(kt + K)^2} \right\} \times 100
\]

The percentage error is calculated for a number of values of \(kt\) in Table 7. From this it can be seen that the error involved in using the approximate solution is less than 1.9% for values of \(kt\) greater than 4.

<table>
<thead>
<tr>
<th>#t</th>
<th>((kt + K))</th>
<th>(\sqrt{kt})</th>
<th>(\text{erf} \sqrt{kt})</th>
<th>(\sqrt{(kt/\pi)})</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.500</td>
<td>1.000</td>
<td>0.84270</td>
<td>0.20710</td>
<td>1.90</td>
</tr>
<tr>
<td>2</td>
<td>2.500</td>
<td>1.414</td>
<td>0.95236</td>
<td>0.10817</td>
<td>0.48</td>
</tr>
<tr>
<td>4</td>
<td>4.500</td>
<td>2.000</td>
<td>0.99532</td>
<td>0.02102</td>
<td>0.09</td>
</tr>
<tr>
<td>8</td>
<td>8.500</td>
<td>2.828</td>
<td>0.99993</td>
<td>0.00049</td>
<td>0.006</td>
</tr>
<tr>
<td>16</td>
<td>16.500</td>
<td>4.000</td>
<td>0.99999</td>
<td>2.5 x 10^{-7}</td>
<td>negligible</td>
</tr>
</tbody>
</table>

Table 7. Calculation of Error introduced by the Use of the Approximate Solution of the Absorption Equation

In the experiments on absorption of carbon dioxide by aqueous monoethanolamine solutions described in this work, the reaction velocity constants varied from 6,578 sec^{-1} to 36,465 sec^{-1} and the exposure times from 3.48 to 17.60 milliseconds. The minimum value of \(kt\) therefore is \(3.48 \times 10^{-3} \times 6,578 = 22.9\), and the error involved in using the approximate solution equation (20) is negligible.

Application of Theory to Laminar Jet Apparatus

\(Q\), the amount of gas absorbed per unit area at any time \(t\) is given by

\[
Q = c^* \sqrt{Dk} \left( t + \frac{1}{2k} \right)
\]

(20)

\(N\), the average rate of absorption per unit area over the period \(t\) is given by

\[
N = \frac{Q}{t} = c^* \sqrt{Dk} \left( 1 + \frac{1}{2kt} \right) \text{gm-moles/sec}
\]
For a jet length $h$ and diameter $d$,

Interfacial area $= \pi dh$

and the average rate of absorption into the jet is

$$N \times \text{area} = c^{\infty}(Dk) \cdot \pi dh \cdot (1 + \frac{1}{2kt}) \text{gm-moles/sec}$$

$$= \phi$$

$$\phi = c^{\infty}(Dk) \cdot \pi dh \cdot (1 + \frac{1}{2kt}) \text{gm-moles/sec} \quad (21)$$

If liquid passes through the orifice at a constant flow rate $L \text{ cm}^3/\text{sec}$, the time of exposure $t$ is given by

$$t = \frac{\pi d^2 h}{4L} \text{ sec}$$

and substituting for $t$ in equation (21)

$$\phi = c^{\infty}(Dk) \pi dh + c^{\infty}(D/k) \cdot \frac{2L}{d} \quad (22)$$

At constant flow rate and jet diameter and otherwise constant conditions, a plot of absorption rate $\phi$ versus jet length $h$ will be a straight line with gradient

$$\frac{\phi}{h} = c^{\infty}(Dk) \pi d, \quad (23)$$

Using the technique described earlier $\phi$, the rate of absorption can be determined at various jet lengths and the value of $\frac{\phi}{h}$ obtained from a plot of $\phi$ against $h$. Since, from (23)

$$c^{\infty}/D = \frac{\phi}{h} \cdot \frac{1}{\pi dh/k} \quad (24)$$

if $k$ is also known, a value of the product $c^{\infty}/D$ can be easily obtained.
Considerations Regarding Practical Application of Unsteady-State Absorption Theory

In practice, the theory developed above will often be applied to systems where the absorbed gas does not react with the liquid medium in toto, but rather with a component B in solution in the liquid, and it is necessary to briefly examine the effect of this.

(1) Depletion of Liquid-Phase Reactant

Since the highest concentration of absorbed gas A exists at the interface, the rate of reaction here is greatest. The depletion of B due to reaction starts at the interface, and after a certain time the concentration of B will drop to zero, and the rate of reaction being no longer proportional to the concentration of A assumptions made in the derivation of the theory will no longer be valid. VAN DE VUSSE has developed an expression for the "depletion time" i.e. the time after which the concentration of reactant B at the interface is zero. At the larger values of kt encountered in this investigation his expression simplifies to

\[
\frac{B_0 + A_i}{A_i} = \frac{2\sqrt{kt}}{\pi}
\]

where \(A_i\) is the concentration of component A at the interface, and \(B_0\) is the initial concentration of the liquid-phase reactant.

Rearranging equation (25)

\[
t_d = \frac{\pi}{4} \cdot \frac{1}{k} \left( \frac{B_0}{A_i} + 1 \right)^2
\]

and using as a first approximation \(A_i = \) equilibrium solubility of carbon dioxide in water, it is possible to calculate depletion
-73-

times for conditions encountered in this investigation.

(1) For lowest value of \( B_0 \)

\[
B_0 = 0.948 \text{ moles/litre monoethanolamine}
\]
\[
k = 6,578 \text{ sec}^{-1}
\]
\[
A_i = 3.30 \times 10^{-2} \text{ moles/litre carbon dioxide}
\]
\[
\tau_d = \frac{\pi}{4} \cdot \frac{1}{6,578} \cdot \left( \frac{0.948}{0.034} + 1 \right)^2
\]
\[
\tau_d = 0.095 \text{ sec}
\]

(ii) For highest value of \( B_0 \)

\[
B_0 = 4.661 \text{ moles/litre}
\]
\[
k = 36,465 \text{ sec}^{-1}
\]
\[
A_i = 3.39 \times 10^{-5}
\]
\[
\tau_d = \frac{\pi}{4} \cdot \frac{1}{36,465} \cdot \left( \frac{4.661}{0.034} + 1 \right)^2
\]
\[
\tau_d = 0.465 \text{ sec}
\]

Experimental exposure times varied between 0.0035 sec and 0.0176 sec, well below the depletion times calculated above and it is concluded that in this respect the theory may be applied as derived.

(2) Reaction-Rate Velocity Constants

In most cases met with in practice the controlling reaction between the absorbed gas and the liquid reactant is not strictly first-Order but of the type

\[
\text{Dissolved Gas} + \text{Liquid Reactant} \rightarrow \text{Products}
\]

A          B            X
which is a second-order reaction. However, in the case of a moderately soluble gas being absorbed by a relatively concentrated solution under conditions where the exposure time is very short compared with the depletion time mentioned above, then the concentration of B will always be greatly in excess of A.

If in the above reaction a, b, and x are the concentrations of dissolved gas, reactant, and product after time t, the rate of reaction is given by

\[
\frac{dx}{dt} = k'(a-x)(b-x)
\]

where \(k'\) is the second-order reaction velocity constant having the units of litres/gm-mole/sec. When \(b\) is much greater than \(a\), the maximum value of \(x\) is \(a\), so that \(b\) is much greater than \(x\), and \((b-x)\) is approximately constant and equal to \(b\). Under these conditions the rate equation now becomes

\[
\frac{dx}{dt} = k'b(a-x)
\]

and since \(b\) can be regarded as constant, this is the rate equation of a pseudo-unimolecular reaction in which \(k'b\) is equivalent to a first-order reaction velocity constant.

In the context of equations (18) and (20) and their derivation, \(k\) is defined thus

\[
kc = \text{rate at which chemical reaction destroys solute}, c
\]

being the concentration of solute. This definition will be used as the basis in the determination of the correct values of \(k\) to be substituted in equations (23) and (24). For a second-order reaction having a second-order velocity constant \(k'\)
\[ k'_{\text{r}} = k'B \quad \text{(units sec}^{-1}\text{)} \]

For a third-order reaction

\[(A) + (B) + (C) \quad \longrightarrow \quad \text{Products} \]

with a third-order velocity constant \(k''\)

\[ k_2 = k'' \quad (B)(C) \quad \text{(units sec}^{-1}\text{)} \]

and if the dissolved gas is removed by simultaneous second and third-order reactions the overall first-order constant will be the sum of two pseudo-first-order constants thus:

\[ k_{\text{overall}} = k_1 + k_2 = k'(B) + k''(B)(C) \]
(a) Mechanics of the Reaction

This discussion will be limited mainly to the reaction mechanisms of interest here, i.e. those near the beginning of the absorption period when complete chemical equilibrium is not attained and the monoethanolamine concentration is greatly in excess of the concentration of carbon dioxide. Amine concentrations are expressed in moles of total amine, and were determined by titration with standard hydrochloric acid using bromocresol green indicator.

The structural formula of monoethanolamine

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{O} - & \quad \text{C} - \text{C} - \text{N} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

shows the presence of two functional groups, the hydroxy (-OH⁻) and the amino (-NH₂), both of which may contribute to the overall reaction between a solution of the amine and carbon dioxide.

When monoethanolamine is dissolved in water its solution shows an alkaline reaction since its basic strength is greater than the acidic strength of its conjugate acid, the monoethanolammonium ion. The basic dissociation, which has been studied by PATES and PINCHING⁴⁹ is given by
Thus a solution of monoethanolamine contains free amine, monoethanolammonium ions, and hydroxyl ions, and the concentration of hydroxyl is a measure of the amount of free amine that has been converted by the reaction (R1) into monoethanolammonium ion. BATES and PINCHING\textsuperscript{39} have determined the value of the dissociation constant $K_b$ for reaction (R1), and from this it is possible to calculate the actual amounts of free amine and hydroxyl ion in a solution of the amine, since this instantaneous reaction is the only source of hydroxyl ion.

If the activity coefficients of the reacting species can be taken as unity, the equilibrium constant of (R1) is given by\textsuperscript{39}

$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2^+][\text{H}_2\text{O}]} = 3.18 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

Taking as an example a solution in which the total amine concentration is 2.036 moles/litre,

Concentration of $\text{H}_2\text{O} = 48.8$ moles/litre,

since this is much larger than other concentrations it can be regarded as constant and

$$\frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2^+]} = 3.18 \times 48.8 \times 10^{-5}$$

Let $B_o = \text{Concentration of undissociated amine}$

Thus $[\text{OH}^-] = [\text{RNH}_3^+]$ (B)

and $\frac{(\text{OH}^-)^2}{(B_o - [\text{OH}^-])} = 1.55 \times 10^{-3}$
Cross-multiplying and rearranging

\[
(\text{OH}^-)^2 + (1.55 \times 10^{-3}) \ (\text{OH}^-) - (1.55 \times 10^{-3}) (\text{BO}) = 0
\]

\[
(\text{BO}) = 2.036 \ \text{moles/litre} \quad \text{and solving the equation}
\]

\[
(\text{OH}^-) = 0.554 \ \text{gm-ions/litre}
\]

Therefore \((\text{BO}) = 1.981 \ \text{moles/litre}\)

The concentrations of free amine and hydroxyl ion in the solutions used in this investigation are shown below

<table>
<thead>
<tr>
<th>B₀ \text{ Total Amine moles/litre}</th>
<th>\text{RNH₂} \text{ Free Amine in Solution moles/litre}</th>
<th>\text{OH}^- \text{ Concentration of Hydroxyl Ion moles/litre}</th>
<th>% of Total Amine Dissociated in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.988</td>
<td>0.948</td>
<td>0.0396</td>
<td>4.01</td>
</tr>
<tr>
<td>2.036</td>
<td>1.981</td>
<td>0.0554</td>
<td>2.72</td>
</tr>
<tr>
<td>2.878</td>
<td>2.814</td>
<td>0.0642</td>
<td>2.23</td>
</tr>
<tr>
<td>3.938</td>
<td>3.866</td>
<td>0.0721</td>
<td>1.86</td>
</tr>
<tr>
<td>4.738</td>
<td>4.661</td>
<td>0.0767</td>
<td>1.62</td>
</tr>
</tbody>
</table>

Table 8. Concentrations of Free Amine and OH⁻ ion in solutions of various strengths at 25.0°C.

The mechanism of the overall reaction between aqueous amine solutions and carbon dioxide has been studied by several investigators\(^{12,20,32,38}\) and it appears that there are four main reactions by which carbon dioxide is chemically consumed.

1. Reaction between dissolved carbon dioxide and water forming hydrogen and bicarbonate ions

\[
\begin{align*}
\text{H₂O} + \text{CO}_2 & \rightleftharpoons \Delta \text{H₂CO}_3 \\
\text{H₂CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- 
\end{align*}
\] (R2) (R2a)
Reaction (R2) is very slow, having a velocity constant of 0.0257 litres/mole·sec at 25°C according to PINSENT, PEARSON and ROUGHTON, and is followed by instantaneous dissociation of the carbonic acid. The overall reaction is too slow to have any effect on the rate of absorption under the conditions considered here and will not be taken into account.

(2) The direct attack of molecules of dissolved carbon dioxide on the amino group of the amine forming monoethanolamine carbamate

\[ \text{RNH}_2 + \text{CO}_2 \rightleftharpoons \text{RNH}_2\text{CO}_2 \]  

(R3)

This reaction has been studied extensively by JENSEN, JORGENSEN and FAURHOLT who found a reaction velocity constant of 3.190 litres/mole·sec at 18°C, (5.400 litres/mole·sec at 25°C). In the view of JENSEN due to the large concentration of undissociated amine present this reaction would be expected to be of primary importance in determining the overall reaction rate.

(3) Hydroxyl ions formed by reaction (R1) will react with free amine to form an alkylate ion

\[ \text{RNH}_2 + \text{OH}^- \rightleftharpoons \text{O} \cdot \text{CH}_2 \cdot \text{NH}_2 + \text{H}_2\text{O} \]  

(R4a)

which reacts with carbon dioxide to form an ester of carbonic acid.

\[ \text{CO}_2 + \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \rightleftharpoons \text{OCOCOCH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \]  

(R4b)

The rate of this reaction has not been studied specifically for the carbon-dioxide-monoethanolamine system, but the analogous reaction for diethanolamine has been studied by JORGENSEN who found a velocity constant of \(3 \times 10^4\) (Litres)
/(mole)$^2$. sec at 25.0°C, expressed as a third-order constant in terms of amine, carbon dioxide, and hydroxyl ion concentration. This is based on the assumption that reaction (R4a) reaches equilibrium instantaneously.

(4) Reaction between carbon dioxide and hydroxyl ion

$$\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \quad (R5)$$

followed by the instantaneous reaction

$$\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (R5a)$$

Reaction (R5) has been studied by PINSENT, PEARSON and ROUGHTON who found the velocity constant to be 8,300 litre/mole.sec. at 25.0°C.

It should be stressed that the carbamate formed in reaction (R3) is not chemically an equilibrium product since an appreciable amount of carbonate will be formed after a time, and finally an equilibrium will be established where both carbamate and carbonate are present, the equilibrium being governed by the equation

$$\text{H}_2\text{O} + \text{RNHCOO}^- \rightleftharpoons \text{RNH}_2 + \text{HCO}_3^- \quad (R6)$$

The equilibrium constant for this reaction

$$K_{eq} = \frac{(\text{RNH}_2)(\text{HCO}_3^-)}{(\text{RNHCOO}^-)}$$

has a value of $10^{-1.71}$ according to JENSEN and FAURHOLT. In the presence of excess amine, however, the carbonate reaction (R3) will proceed at a rate independent of (R6) and can be regarded as pseudo-unimolecular.
Calculation of the Reaction Velocity Constant for the Overall Reaction

From the foregoing it appears that the rate of absorption of carbon dioxide into a laminar jet of aqueous monoethanolamine will be governed by the three simultaneous reactions:

\[
RNH_2 + CO_2 \rightleftharpoons RNH_2CO_2 \quad (R3)
\]

(velocity constant \(k_1 = 5,400 \text{ litres/mole.sec. at } 25^\circ\text{C}\))

\[
OH^- + CO_2 \rightleftharpoons HCO_3^- \quad (R5)
\]

(velocity constant \(k_2 = 8,300 \text{ litres/mole.sec. at } 25^\circ\text{C}\))

\[
RNH_2 + OH^- + CO_2 \rightleftharpoons -\text{COOCH}_2\cdot\text{CH}_2\cdot\text{NH}_2 + H_2O \quad (R4)
\]

(velocity constant \(k_3 = 3 \times 10^4 \text{ litres}^2\text{/mole}^2\text{.sec. at } 25^\circ\text{C}\))

The rates at which carbon dioxide is consumed by each of these reactions are

Reaction (R3) \(k_1 \cdot (RNH_2) \cdot (CO_2) = k_1\' \cdot (CO_2)\)

(R5) \(k_2 \cdot (OH^-) \cdot (CO_2) = k_2\' \cdot (CO_2)\)

(R4) \(k_3 \cdot (RNH_2) \cdot (OH^-) \cdot (CO_2) = k_3\' \cdot (CO_2)\)

and \(k\) the overall first-order reaction velocity constant is

\(k = k_1' + k_2' + k_3'\)

so that the rate at which chemical reaction destroys the solute is \(k(CO_2)\) as required by the theory.

From the concentrations of free amine and hydroxyl ion in Table 8 it is possible to calculate the value of \(k\) at the concentrations used in these experiments; and also the relative proportions of carbon dioxide involved in reactions (R3), (R4) and (R5) since if
\[ W_1 = \text{wt. of CO}_2 \text{ involved in reaction (R3)} \]
\[ W_2 = \ldots \ldots \ldots \ldots \ldots \ldots \ (R5) \]
\[ W_3 = \ldots \ldots \ldots \ldots \ldots \ldots \ (R4) \]

\[ \frac{W_1}{W_1+W_2+W_3} = \frac{k_1}{k_1 + k_2 + k_3} \]
similarly for \( W_2 \) and \( W_3 \). It should be noted that these pseudo-unimolecular velocity constants strictly apply to the initial rate of reaction only, but in view of the short exposure times and relatively high concentrations of amine the error involved is unlikely to be significant.

A specimen set of calculations are presented below for a total amine concentration of 2.036 moles/litre; the results for all other concentrations are summarized in Table 9.

For 2.036 molar amine solutions

Free amine concentration  = 1.981  = (RNH\textsubscript{2})

Hydroxyl ion concentration  = 0.0554  = (OH\textsuperscript{-})

\[ k'_1 = k_1(RNH_2) = 5,400 \times 1.981 = 10,700 \text{ sec}^{-1} \]
\[ k'_2 = k_2(OH^-) = 8,300 \times 0.0554 = 465 \text{ sec}^{-1} \]
\[ k'_3 = k_3(OH^-)(RNH_2) = 3 \times 10^4 \times 0.0554 \times 1.981 = 3,920 \text{ sec}^{-1} \]

\[ k = k'_1 + k'_2 + k'_3 \]
\[ = 14,455 \text{ sec}^{-1} \]

\[ W_1(\%) = \frac{k'_1}{k} \times 100 \]
\[ = \frac{10,700 \times 100}{14,455} \]
\[ = 74.0\% \]
<table>
<thead>
<tr>
<th>Conc. of Total Amine moles/litre</th>
<th>Pseudo 1st-order velocity constants, sec⁻¹</th>
<th>Overall 1st ord vel. const. k sec⁻¹</th>
<th>% of CO₂ consumed by reaction R3, R5, R4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.988</td>
<td></td>
<td>6.578</td>
<td>81.1 78.0 5.1 16.9</td>
</tr>
<tr>
<td>2.036</td>
<td></td>
<td>14.455</td>
<td>120.2 74.0 3.2 22.8</td>
</tr>
<tr>
<td>2.878</td>
<td></td>
<td>21.160</td>
<td>145.5 71.8 2.5 25.7</td>
</tr>
<tr>
<td>3.938</td>
<td></td>
<td>29.881</td>
<td>172.9 70.0 2.0 28.0</td>
</tr>
<tr>
<td>4.738</td>
<td></td>
<td>36.465</td>
<td>190.9 68.8 1.8 29.4</td>
</tr>
</tbody>
</table>

Table 9. Calculations of Overall Reaction Velocity Constant k, √k, and Percentages of Carbon Dioxide involved in Reactions (R3), (R4) and (R5)
As a check on the values of $k$ in Table 9, reference was made to a paper by ASTARITA$^{12}$ who expresses the initial reaction rate $r$ by the equation

$$r = (4150 + 270B_o^\frac{1}{2} + 980B_o^\frac{1}{2}) (B_o) (C_O^2)$$

at 21.5°C where $B_o = \text{initial concentration of amine}$. Calculated values of $(4150 + 270B_o^\frac{1}{2} + 980B_o^\frac{1}{2}) (B_o)$ corrected to 25.0°C are presented in Table 10, and may be compared with the values for $k$ in Table 9.

<table>
<thead>
<tr>
<th>Concentration of Total Amine (Moles/litre)</th>
<th>$k$ (this work) sec$^{-1}$</th>
<th>$\frac{4150 + 270B_o^\frac{1}{2} + 980B_o^\frac{1}{2}}{sec^{-1}} (B_o)$</th>
<th>Diff. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.988</td>
<td>6,578</td>
<td>6,900</td>
<td>4.6</td>
</tr>
<tr>
<td>2.036</td>
<td>14,455</td>
<td>15,100</td>
<td>4.0</td>
</tr>
<tr>
<td>2.878</td>
<td>21,160</td>
<td>22,200</td>
<td>4.6</td>
</tr>
<tr>
<td>3.938</td>
<td>29,881</td>
<td>31,600</td>
<td>5.5</td>
</tr>
<tr>
<td>4.738</td>
<td>36,465</td>
<td>39,000</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table 10. Values of Velocity Constant $k$ compared with corresponding values from Equation of Astarita$^{12}$.

Agreement between the values is quite good, although ASTARITA'S values average approximately 5% higher than the values calculated for this work. Since there is no explanation of how his rate is arrived at it is not possible to comment on the difference.
CHEMICAL ABSORPTION - EXPERIMENTAL RESULTS AND INTERPRETATION OF DATA

(a) Determination of $c^w/D$ values

It has been shown earlier that the rate of absorption of a gas by a laminar jet under conditions where the gas reacts with a component of the liquid phase is given by

$$
\phi = c^w(Dk) \cdot \pi dh + c^w(D/k) \cdot \frac{2L}{d}
$$

(22)

At constant flow rate and jet diameter a plot of absorption rate $\phi$ versus jet length will give a straight line of gradient

$$
\frac{\phi}{h} = c^w(Dk) \pi d
$$

(23)

Rearranging

$$
c^w/D = \frac{\phi}{h} \cdot \frac{1}{\pi d/k}
$$

(24)

Thus if the absorption rate at various jet lengths is measured and $k$ the reaction velocity constant for the reaction is known, a value of the product $c^w/D$ may be obtained from equation (24).

Experiments were carried out in a constant-temperature room controlled at $25 \pm 0.2^\circ C$, and water-baths were held at this temperature. Solutions of approximately the required concentration over the range one to five moles were made up by adding de-ionized water to re-distilled monoethanolamine in the air-tight feed storage tank, the actual concentrations being determined by acidimetric titration. The laminar jet apparatus was as described for the experiments on physical absorption,
with a jet diameter of $8.20 \times 10^{-2}$ cm, and jet lengths between 1.90 and 8.55 cm. Flow rate through the orifice was kept constant at about $2.50$ cm$^3$/sec and was accurately determined at each concentration run by timing the discharge of one litre. Rates of absorption were determined by means of bubble flowmeter and jet lengths measured with a cathetometer to 0.005 cm.

The re-distilled monoethanolamine which was supplied by The Distillers Company Limited, boiled over a range of $0.8^\circ$C and was estimated to be 99.9% pure by acidimetric titration using bromocresol green indicator.

Viscosities of amine and carbamate solutions were determined by means of an NPL-calibrated Stokes viscometer in a water-bath at $25.0^\circ$C. Carbamate solutions were prepared by bubbling air containing 10% CO$_2$ through the corresponding amine solution held at constant temperature in a water-bath.

A specimen calculation for 0.988 molar amine solution is given below:

<table>
<thead>
<tr>
<th>Solution</th>
<th>0.988 moles/litre total amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
<td>25 $^\circ$C</td>
</tr>
<tr>
<td>Atmospheric Pressure</td>
<td>751 mm Hg</td>
</tr>
<tr>
<td>Jet Diameter</td>
<td>$8.20 \times 10^{-2}$ cm</td>
</tr>
<tr>
<td>Liquid Flow Rate</td>
<td>$2.64$ cm$^3$/sec</td>
</tr>
<tr>
<td>Solution moles/litre Amine</td>
<td>Jet Length cm.</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>2.036</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td>4.71</td>
</tr>
<tr>
<td></td>
<td>5.59</td>
</tr>
<tr>
<td></td>
<td>6.49</td>
</tr>
<tr>
<td></td>
<td>8.05</td>
</tr>
<tr>
<td>2.878</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>4.76</td>
</tr>
<tr>
<td></td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>7.06</td>
</tr>
<tr>
<td></td>
<td>8.55</td>
</tr>
<tr>
<td>3.938</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>3.01</td>
</tr>
<tr>
<td></td>
<td>4.41</td>
</tr>
<tr>
<td></td>
<td>5.52</td>
</tr>
<tr>
<td></td>
<td>6.75</td>
</tr>
<tr>
<td></td>
<td>8.03</td>
</tr>
<tr>
<td>4.738</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>4.44</td>
</tr>
<tr>
<td></td>
<td>5.92</td>
</tr>
<tr>
<td></td>
<td>7.16</td>
</tr>
</tbody>
</table>

Table 11 Experimental Results - Absorption of Carbon Dioxide in monoethanolamine Solutions at 25°C
Jet length, Time to absorb 7cc of CO₂ and 25°C, 751 mm Absorption Rate of CO₂

<table>
<thead>
<tr>
<th>Jet length, h cm</th>
<th>Time to absorb 7cc of CO₂ and 25°C, 751 mm</th>
<th>Absorption Rate of CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.48</td>
<td>43.5</td>
<td>0.161, 0.65 x 10⁻⁵</td>
</tr>
<tr>
<td>3.56</td>
<td>31.4</td>
<td>0.223, 0.90</td>
</tr>
<tr>
<td>5.01</td>
<td>20.5</td>
<td>0.342, 1.38</td>
</tr>
<tr>
<td>6.00</td>
<td>25.8 (10 cc)</td>
<td>0.387, 1.56</td>
</tr>
<tr>
<td>6.93</td>
<td>22.7</td>
<td>0.441, 1.78</td>
</tr>
<tr>
<td>8.55</td>
<td>18.4</td>
<td>0.543, 2.19</td>
</tr>
</tbody>
</table>

The absorption rate $\phi$ is plotted against the jet length $h$ in Figure 13.

Gradient of $\phi$ - $h$ line $= \frac{\phi}{h} = 2.56 \times 10^{-6}$

From equation (24)

$$c^{\infty/D} = \frac{\phi}{h} \cdot \frac{1}{\pi d/k}$$

From Table 9, $\sqrt{k} = 81.1$ sec⁻¹ for 0.988 molar amine

$$c^{\infty/D} = 2.56 \times 10^{-6} \times \frac{1}{81.1} \times 8.20 \times 10^{-2} \times 81.1$$

$$= 12.25 \times 10^{-8}$$

Experimental results for other concentrations of amine are presented in Table 11, and plots of $\phi$ versus $h$ in Figures 14, 15, and 16.

Calculated values of $c^{\infty/D}$ appear in Table 12.

<table>
<thead>
<tr>
<th>Solution moles/litre amine</th>
<th>$\phi \times 10^{-6}$ from graph</th>
<th>$\sqrt{k}$ from Table 9</th>
<th>$c^{\infty/D} \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.988</td>
<td>2.56</td>
<td>81.1</td>
<td>12.25</td>
</tr>
<tr>
<td>2.036</td>
<td>3.18</td>
<td>120.2</td>
<td>10.25</td>
</tr>
<tr>
<td>2.878</td>
<td>3.38</td>
<td>145.5</td>
<td>9.06</td>
</tr>
<tr>
<td>3.938</td>
<td>3.44</td>
<td>172.9</td>
<td>7.75</td>
</tr>
<tr>
<td>4.738</td>
<td>3.34</td>
<td>190.9</td>
<td>6.80</td>
</tr>
</tbody>
</table>

Table 12. Evaluation of Product $c^{\infty/D}$ for CO₂ - Monoethanolamine at 25.0°C
FIGURE 13. ABSORPTION RATES IN MONOETHANOLAMINE SOLUTIONS.
FIGURE 15. ABSORPTION RATES IN 3.92-MOLAR MONOETHANOLAMINE SOLUTIONS.
FIGURE 16. ABSORPTION RATES IN 4.78-MOLAR MONOETHANOLAMINE SOLUTIONS.

Absorption Rate, cm. moles CO₂/sec. x 10⁻⁵
(b) Discussion of Results

(i) The Significance of 'Physical' Solubilities in Chemical Reacting Systems

The estimation of rates of absorption of a gas by a liquid with which it undergoes chemical reaction involves a knowledge of the quantity $c^\ast$, the concentration of "physically" dissolved gas in equilibrium with the liquid and the partial pressure of the gas above it. While it is possible in various ways to obtain the value of the product $c^\ast N/D$, at present it appears that there is no method available for the direct determination of either $c^\ast$ or $D$ and these are usually estimated indirectly or by empirical methods.

It is necessary to examine the mechanism of interfacial transfer accompanied by chemical reaction in order to obtain a clearer picture of the physical significance of $c^\ast$; the mathematical significance is that its value gives a measure of the number of molecules of gas available for chemical reaction. In general, the rate of gas absorption is controlled by one of the following types of mechanism:

(1) The dissolved gas ionizes and then reacts with one or more components of the liquid medium.

(2) Undissociated molecules of dissolved gas react with ions present in solution.

(3) Molecules of dissolved gas react with non-ionized molecules in the solution.
The following discussion relates specifically to the third case but can also be applied to the other two. Provided the reagent in the liquid medium is not markedly surface-active it can be assumed that a freshly-formed surface of the solution will consist of molecules of reagent and molecules of water approximately in proportion to their molar concentrations. On exposure, gas molecules condense on the surface at a rapid rate which can be predicted by the Kinetic Theory, saturating the surface almost instantaneously; and a condensing molecule can either strike water in which it will dissolve, or strike a reagent molecule with which it will react. If it can be assumed that the rate of reaction between molecules in contact is instantaneous, then it is possible to regard the liquid surface as a solution containing physically dissolved gas and reaction product where the concentration of the former will depend on the salting-out effect of the reaction product plus any other ions present, and the concentration of the latter on the original concentration of the liquid reagent. The required value of \( c^* \) therefore will be the solubility of the gas in a solution of the reaction product of the controlling reaction. This 'product layer' may be extremely thin - possibly one or two molecules in depth and at the start of absorption will have no holding capacity in the context of mass transfer, but its existence would mean that the significant viscosity for purposes of mass transfer would be that of a solution of the product rather than that of the unreacted absorbing solution. In many cases there is no
significant difference between these viscosities, but solutions of monoethanolamine carbamate are considerably more viscous than solutions of unreacted monoethanolamine.

The values of $c^2D$ obtained above will be used to investigate certain aspects of this theory.

(ii) Estimation of Diffusion Coefficients

The usual procedure for the estimation of gas diffusion coefficients in solutions is to use the diffusivity of the gas in water and to correct for the viscosity of the solution and if necessary the temperature by means of the Stokes-Einstein relationship

$$\frac{D_H}{T} = \text{Constant}$$

This presupposes that diffusivity is dependent on viscosity and temperature and independent of any other effects of the liquid medium or chemical reaction. In the absence of further information these assumptions will be applied here.

Solutions varying in concentration from 1 to 5 moles were prepared and analysed for total amine by acidimetric titration. Corresponding "carbamate" solutions were made from these by passing air containing 10% of CO$_2$ through the amine solutions held at 25.0°C in a water-bath. Viscosities at 25.0°C were measured by means of an NPL-calibrated viscometer in the usual way, and densities of all solutions were determined. Diffusivities were calculated by the Stokes-Einstein relationship using the data
Diffusivity of Carbon Dioxide in water $^7 = 1.97 \times 10^{-5}$ cm/sec at 25°C.

Viscosity of Water (41) = 0.8937 cp at 25°C.

Then, $D' = 1.97 \times 10^{-5} \times \frac{0.8937}{\mu'}$

where $D'$ is the diffusion coefficient in a medium of viscosity $\mu'$.

Results are presented in Table 13 and diffusivities plotted versus total amine concentration in Figure 17, from which values corresponding to amine concentrations used in the absorption experiments can be obtained.

<table>
<thead>
<tr>
<th>Conc. of Amine moles/litre</th>
<th>Amine Solutions</th>
<th>Carbamate Sols.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density gm/ml</td>
<td>Viscosity cp</td>
</tr>
<tr>
<td>1.024</td>
<td>1.001</td>
<td>1.08</td>
</tr>
<tr>
<td>2.012</td>
<td>1.002</td>
<td>1.30</td>
</tr>
<tr>
<td>2.981</td>
<td>1.003</td>
<td>1.58</td>
</tr>
<tr>
<td>3.973</td>
<td>1.004</td>
<td>1.95</td>
</tr>
<tr>
<td>4.989</td>
<td>1.005</td>
<td>2.45</td>
</tr>
</tbody>
</table>

Table 13. Densities, Viscosities and Diffusion Coefficients of Aqueous Monoethanolamine and 'Carbamate' Solutions.
FIGURE 17. DIFFUSION COEFFICIENTS IN AMINE AND CARBAMATE SOLUTIONS
Values of \( c^* \) are calculated using diffusivity values from Figure 17 and values of the product \( c^* \sqrt{D} \) from Table 12. Results are presented in Table 14.

<table>
<thead>
<tr>
<th>Conc. of Amine ml/litre</th>
<th>( c^* \sqrt{D} c \times 10^8 ) (Tab. 12)</th>
<th>Using Amine Diff.</th>
<th>Using Carbamate Solns.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D ) cm(^2)/sec ( \times 10^3 )</td>
<td>( \sqrt{D} ) cm(^2)/sec ( \times 10^3 )</td>
<td>( c^* ) gm moles/cm(^3) ( \times 10^5 )</td>
</tr>
<tr>
<td>0.988</td>
<td>12.25</td>
<td>1.65</td>
<td>4.06</td>
</tr>
<tr>
<td>2.036</td>
<td>10.25</td>
<td>1.34</td>
<td>3.66</td>
</tr>
<tr>
<td>2.678</td>
<td>0.96</td>
<td>1.13</td>
<td>3.36</td>
</tr>
<tr>
<td>3.938</td>
<td>7.75</td>
<td>0.91</td>
<td>3.02</td>
</tr>
<tr>
<td>4.738</td>
<td>6.80</td>
<td>0.76</td>
<td>2.76</td>
</tr>
</tbody>
</table>

**Table 14. Calculations of \( c^* \), the Equilibrium Physical Solubility of Carbon Dioxide in Monoethanolamine Solutions**

The effect of a dissolved substance on the solubility of a gas in its solution can be expressed in the form

\[
\log \frac{c^*}{c^*_{w}} = -ml
\]  

(25)

where \( c^*_{w} \) represents the solubility in water, \( m \) is a constant for the system, and \( I \) the ionic strength of the solution.

Table 15 gives the values of \( \log c^*_{w} \) (corrected to 760 mm p.p. of CO\(_2\)) and the ionic strengths of the amine solutions. A plot of \( \log \frac{c^*}{c^*_{w}} \) versus ionic strength is shown in Figure 18 for values of \( c^* \) calculated on a basis of amine viscosity and 'carbamate' viscosity.
FIGURE 13. PLOT OF $\log \frac{c^*}{c_W^*} \times 10^2$ VERSUS IONIC STRENGTHS OF AMINE SOLUTIONS
Table 15. Ionic Strength and log $\frac{c^*}{c^*_w}$ for Amine Solutions

Figure 18 shows that the log $\frac{c^*}{c^*_w}$ vs I plot for c* calculated on a product viscosity basis is a straight line; whereas if c* is calculated on the basis of original amine viscosity the plot is a definite curve. While this cannot be taken as proof of the 'product viscosity' theory it is at least a strong point in its favour, and diffusion coefficients here will be calculated on this basis. From the Figure the gradient of the log $\frac{c^*}{c^*_w}$ vs I plot has a value of -1.11, and c*, the physical solubility of carbon dioxide in monoethanolamine solutions can be expressed by

$$\log \frac{c^*}{c^*_w} = 1.11 I$$

for monoethanolamine solutions in the range one to five molar, and CO₂ partial pressures of 760 mm. The extended line does not pass through the origin as demanded by equation (25) in fact it indicates a solubility for carbon dioxide of $3.59 \times 10^{-5}$ gm.moles/sec at 25°C compared with the actual value of $3.39 \times 10^{-5}$ gm.moles/cc; it is assumed that this is due to experimental error.
(iii) Rate of Mass Transfer

Mass transfer rates are usually related to driving force in accordance with the relation

\[
N_A = k_L (c^* - c_0)
\]  

(26)

where

- \(N_A\) = Average absorption rate (moles/sec \cdot cm²)
- \(k_L\) = Average liquid-side mass transfer coefficient (cm/sec)
- \(c^*\) = Equilibrium concentration of gas in bulk of liquid (moles/cm³)

In the system under consideration \(C_0\) is zero and (26) becomes

\[
N_A = k_L c^*
\]

from which

\[
k_L = \frac{N_A}{c^*}
\]  

(27)

Since the true value of \(c^*\) is often difficult to obtain in practice the equilibrium solubility of the gas in water is often used in determining the value of the mass transfer coefficient. Denoting this solubility by \(c^*_w\)

\[
k'_{L} = \frac{N_A}{c^*_w}
\]  

(28)

Values of the mass transfer coefficient can be determined from the absorption measurements carried out above as follows:

The plots of \(\phi\) (the absorption rate in moles/sec) versus jet length \(h\) give a value of \(\frac{\phi}{h}\) which is a measure of the absorption rate per unit length of jet. Since

Jet diameter = 8.2 x 10^{-2} cm
Mass transfer area per unit length of jet
\[ = \pi \times 8.2 \times 10^{-2} \times 1 \text{ cm}^2 \]
\[ = 0.258 \text{ cm}^2/\text{cm} \]
and \( N_A \) the average absorption rate given by
\[ N_A = \frac{\phi}{h} - 0.258 \text{ moles/sec}\cdot \text{cm}^2 \]
(29)

Using this relationship and the values of \( \frac{\phi}{h} \) from Table 12, values of \( k_L \), and \( k'_L \) have been calculated in Table 16 for various strengths of amine solutions, and a plot of mass transfer coefficients versus solution strengths is shown in Figure 19.

<table>
<thead>
<tr>
<th>Solution Strength (moles/litre)</th>
<th>( \frac{\phi}{h} \times 10^6 ) (Table 12)</th>
<th>( N_A \times 10^6 ) ml/sec/cm² (Eqn. 29)</th>
<th>( c^* \times 10^5 ) ml/cm³ (Table 14)</th>
<th>( k_L ) cm/sec</th>
<th>( c^* \times 10^5 ) ml/cm³</th>
<th>( k'_L ) cm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.988</td>
<td>2.56</td>
<td>9.93</td>
<td>3.14</td>
<td>0.316</td>
<td>3.24</td>
<td>0.297</td>
</tr>
<tr>
<td>2.036</td>
<td>3.18</td>
<td>12.30</td>
<td>3.00</td>
<td>0.410</td>
<td></td>
<td>0.368</td>
</tr>
<tr>
<td>2.878</td>
<td>3.38</td>
<td>13.10</td>
<td>2.94</td>
<td>0.446</td>
<td></td>
<td>0.392</td>
</tr>
<tr>
<td>3.938</td>
<td>3.44</td>
<td>13.33</td>
<td>2.89</td>
<td>0.461</td>
<td></td>
<td>0.399</td>
</tr>
<tr>
<td>4.738</td>
<td>3.34</td>
<td>12.95</td>
<td>2.84</td>
<td>0.456</td>
<td></td>
<td>0.388</td>
</tr>
</tbody>
</table>

Table 16. Calculation of \( k_L \) and \( k'_L \) for \( \text{CO}_2 \) - Monoethanolamine at 25.0°C and 727 mm p.p.

Figure 19 shows that maximum values of the mass transfer coefficient occur when the concentration of monoethanolamine is approximately 4-molar, i.e. about 24%. It has been stated\(^45\) that the choice of amine concentration for commercial plants is quite arbitrary and is usually based on operating experience, but surveys by FEAGAN\(^45\) and REED and WOOD\(^46\) indicate that concentration of 15-20% is typical and values as low as 10%...
FIGURE 19. LIQUID-SIDE MASS-TRANSFER COEFFICIENTS FOR CO₂-MONOETHANOLAMINE 
at 25°C & 727 mm. pp. CO₂

\[ k_\text{L} \]

Amorphous Concentration, Moles/Litre.
and as high as 30% are not unusual. CRYDER and MAHONEY in their work on diethanolamine found that the overall mass transfer coefficient increased with concentration up to about 3-Normal and then decreased above this due to viscosity. Although this work indicates that a 4-Normal solution will give a maximum mass transfer coefficient, it appears that corrosion increases with increasing concentration, and the recommended strength of 15% has probably been arrived at with this in mind.

Comparison with Results of other Investigators.

The results obtained in this investigation are not strictly comparable with other work on the absorption of carbon dioxide by aqueous monoethanolamine solutions since the exposure times are shorter and the range of concentrations wider than those encountered in similar investigations by EMMERT and PIGFORD and ASTARITA (see Table 17)

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Apparatus</th>
<th>Exposure Times sec. x 10^3</th>
<th>Range of Concentrations moles/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emmert and Pigford (20)</td>
<td>Short Wetted-Wall Column</td>
<td>60 - 200</td>
<td>0.1, 0.5, 1.0, 2.0</td>
</tr>
<tr>
<td>Astarita (12)</td>
<td>Liquid Jet</td>
<td>20 - 72</td>
<td>0.25, 0.50, 1.0</td>
</tr>
<tr>
<td>Astarita (12)</td>
<td>Disk Column</td>
<td>17 to 78</td>
<td>0.25, 0.50, 1.0</td>
</tr>
<tr>
<td>This work</td>
<td>Liquid Jet</td>
<td>3.5 to 18</td>
<td>0.988 to 4.738</td>
</tr>
</tbody>
</table>

Table 17. Comparison of Conditions for this and similar investigations

The exposure times used by these workers are of the order of the depletion time, and thus their results cannot be interpreted by equation (22)
\[ \phi = c^* \sqrt{(Dk) \pi dh} + c^* \sqrt{D/k} \cdot \frac{2L}{d} \]  \hspace{1cm} (22)

since a pseudo first-order reaction between gas and solvent cannot be assumed, and the mass transfer coefficient will vary with time.

It has been shown\(^{13}\) that for a rapid second order reaction of the form

\[ A + nB \rightarrow C \]

the ratio of the film coefficients with reaction to that without reaction is approximately given by

\[ \frac{k_L}{k^0_L} = \sqrt{(D_A D_B)} \left( \frac{1 + D_B}{D_A} \cdot \frac{Bo}{nc^2} \right) \]  \hspace{1cm} (30)

and these investigators have expressed their results in terms of equation (30). Their results show the effect of amine concentration on the ratio \( k_L / k^0_L \) empirically, thus

\[ \frac{k_L}{k^0_L} = 0.077 \frac{B_o}{c^6_n} + 10.8 B_o + 4.2 \]  \hspace{1cm} (Emmert and Pigford)\(^{20}\)

\[ \frac{k_L}{k^0_L} = 3.78 + 12.5 B_o \pm 1.80 \]  \hspace{1cm} (Astarita, jet)\(^{12}\)

As these authors state, these empirical relationships apply only to the conditions of their experiments; since they imply that mass transfer coefficients will increase with increasing amine concentration, which is not the case with monoethanolamine concentrations above 4 - Molar.
Using equation (30) EMMEERT and PIGFORD have calculated values for $c^*$, the physical equilibrium saturation concentration of carbon dioxide in monoethanolamine solutions and found values approximately three times the solubility in water. This is unlikely to be the case and the values for $c^*$ obtained from this work are more realistic.
SUMMARY AND CONCLUSIONS

A preliminary survey of methods previously available for the determination of gaseous diffusion coefficients in liquids showed that there was room for a more accurate and more convenient method. This work proposes the application of the recently developed laminar jet apparatus to this field and operation of the apparatus so that the significance of entry and end effects is reduced to a minimum, since it was noticed that a range of contact times could be obtained without altering the flow characteristics of the system.

The laminar jet apparatus designed and built by the author embodies the best features of six jets described in the literature over the past seven years. It is simple to construct and operate and is capable of investigations over a wide range of temperatures. The original concept of ensuring constant entry and end effects by maintaining a constant flow rate enables the significance of these effects to be minimised.

Constructional adequacy and suitability of mathematical theory was demonstrated by measuring absorption rates of carbon dioxide into water at 25.0°C and one atmosphere total pressure. Under these conditions where the equilibrium solubility $c_0$ and the diffusion coefficient are accurately known, the experimental rate of absorption was less than 3% below the calculated rate. The gradient of the (absorption rate) versus (square root of the jet length) line which is the basis of the determination of diffusion coefficients by this method was only
1% less than the theoretical value.

The apparatus was used to determine diffusion coefficients of carbon dioxide in water over a range of temperatures from 18.5°C to 75.1°C. The results agreed with the \( \frac{D_u}{T} = \text{constant (Stokes-Einstein) relationship to within } \pm 2\% \), and if it is accepted that the diffusivities can be described by this relationship, it follows that the diffusion coefficient is independent of concentration since the latter varies 500% in this range. Comparison of results with those of five other investigators show good agreement.

Diffusion coefficients of nitrous oxide in water and solutions of glycerol up to 22.7% glycerol were also determined at 20.0°C. The value of \( 1.92 \times 10^{-5} \text{ cm}^2/\text{sec} \) for the diffusion coefficient of nitrous oxide in water at 20.0°C is 2% higher than CULLEN and DAVIDSON'S value of \( 1.87 \times 10^{-5} \text{ cm}^2/\text{sec} \) for which an accuracy of 5% is claimed; and 9.5% higher than HUFNER'S value of \( 1.74 \times 10^{-5} \text{ cm}^2/\text{sec} \) reported in 1875. In view of the supporting evidence of CULLEN and DAVIDSON'S result, HUFNER'S value may be assumed to be low.

The relationship between the diffusion coefficient in solutions of glycerol and the viscosity can be expressed in the form \( D_u^{0.94} = \text{Constant} \). Values obtained in this investigation conform to this relationship to within \( \pm 1.1\% \).
The apparatus was also used in an attempt to estimate diffusion coefficients in the chemically reacting system carbon dioxide-monoethanolamine over a range of amine concentrations from 0.988 to 4.738 moles/litre. The theory of absorption with reaction into laminar jets is developed from Danckwert's treatment of the penetration theory, and diffusion coefficients calculated on a basis of product viscosity rather than the usual solution viscosity basis produce values of the 'physical' equilibrium solubility $c^*$ which appear reasonable and conform to the relationship

$$\log \frac{c^*}{c^*_w} = 1.11 I$$

where $I$ is the ionic strength of the solution. The depletion of liquid-phase reactant at the interface is also examined.

The mechanism of the reaction between carbon dioxide and aqueous solutions of monoethanolamine is discussed and the pseudo first-order reaction velocity constant calculated. It is shown that the carbamate reaction

$$RNH_2 + CO_2 \rightarrow RNH_2CO_2$$

is of primary importance, and that between 68.8% and 78.0% of the total carbon dioxide is consumed by this reaction. The reaction velocity constants are approximately 5% lower than those calculated by ASTARITA\textsuperscript{12} for solutions up to 1.0 moles/litre concentration.
Two liquid-film mass-transfer coefficients have been determined from the experimental results; one is the true coefficient calculated on the basis of the physical solubility of carbon dioxide in monoethanolamine solutions, the other on the usual basis of the gas solubility in water. On a plot of transfer coefficients versus amine concentration a maximum value is obtained at a concentration of approximately 4 moles/litre or 24% amine. A similar maximum was observed at 3 moles/litre by CRYDER and MALONEY in their investigations into diethanolamine. The results obtained here cannot be easily compared with similar investigations of EMMERT and PIGFORD and ASTRIRITA since the exposure times here are shorter and the range of concentrations greater. These authors however express their results in a form which implies that the ratio of the chemical transfer coefficient to that of the physical transfer coefficient increases with amine concentration, which, in the light of information obtained here will be true only up to concentrations of less than 4-molar.

Accuracy of Results.

In the case of physical absorption with the laminar jet it appears that the product $c^2/D$ can be obtained with an accuracy of about 1%. In calculating the diffusion coefficient, a value for gas solubility $c^*$ is required, and an error in this will produce the square of the error in $D$. In the case of chemical absorption, the accuracy of the $c^2/D$ is subject to the accuracy of $k$, the reaction velocity constant, and furthermore
the accuracy of $D$ will depend on $c^*$. 

**Suggestions for Further Work on Diffusion with the Laminar Jet Apparatus**

With the establishment of the apparatus as an accurate method of determining diffusion coefficients, there are many systems to which it could be applied. (1) The effect of adding various percentages of an inert to the gas phase should be examined. (2) The effect on gas diffusivity of various inerts, soluble, colloidal or in the form of a suspension in the absorbing liquid could also be of interest. (3) Application to a wide range of gases and liquids would enable an analysis of the relationships between diffusion coefficient, liquid viscosity, and temperature to be made.
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INTRODUCTION

The most convenient existing methods for the determination of diffusion coefficients of gases in liquids which involve measurements of mass-transfer rates under unsteady-state conditions suffer from the inherent disadvantage of requiring flowing systems. While the laminar-jet apparatus described above has been shown to provide an accurate means of determining diffusion coefficients, the presence of entry and end effects and slight deviations from ideality in flow are undesirable. Furthermore, the accuracy is strongly dependent on the degree of accuracy with which the gas equilibrium concentration $c^*$ can be determined.

Heat effects due to solution at the interface also present a problem, since although the rate of dissipation of heat by conduction into the liquid bulk is rapid, it is probably of the same order as the contact times met with in absorption apparatus. In the case of moderately soluble gases the overall effect will be slight, but in the case of more soluble gases this may not be the case.

Absorption of a gas into a completely stagnant liquid would eliminate the disadvantages of a flowing system, and if the absorption period was of the order of 5 - 60 minutes major heat effects would disappear before measurements were commenced. (In the case of the absorption of carbon dioxide into water at atmospheric pressure, HARVEY and SMITH concluded that heat effects at the interface died out about 5 seconds after
admission of the gas). In the optical method developed here a knowledge of the gas saturation concentration is not required for calculation of diffusion coefficients.

The determination of diffusion coefficients by an examination of concentration distributions and concentration gradients across a liquid-liquid interface by optical methods is well known; the most interesting basic methods are due to LAMM and GOUY. The latter has recently been examined by THOMAS and FURZER who programmed a computer for counting the interference fringes, but both methods are unsuitable for application to the extremely dilute solutions that would be met with here. A recent method using birefringence interferences introduced by INGELSTAM and later developed by BRYNGDAHL has the advantage of being applicable to extremely dilute solutions. In spite of the recent advances in diffusion-cell design the difficulty of forming a sharp interface between a liquid and a solution of a moderately soluble gas is obvious, and it was decided here to attempt to determine diffusion coefficients of gases in liquids by applying the shearing interferometer to a system containing a gas-liquid interface.

As will be discussed later, refinements in experimental techniques and an extension of the mathematical theory allow determinations to be carried out with great accuracy, but the primary purpose of this investigation is to establish the feasibility of determining diffusion coefficients in this manner.
DESCRIPTION OF APPARATUS

(a) General Layout

In principle the optical system is similar to that described by BRYNGDAHL, the general layout is shown in Fig. 20 and Plate 3. All components were mounted on a 3-metre triangular section steel optical bench equipped with levelling screws, resting on a supporting bench consisting of two 10 ft. long 5-inch I-sections bolted to three concrete pillars. The whole assembly weighing 1200 lb was separated from the floor by rubber blocks; thus damping out vibrations which could be transmitted to the apparatus through the floor. Experiments were carried out in the constant-temperature room described earlier.

Illumination was provided by a 125 W mercury-vapour lamp operated in a horizontal position. The discharge from the lamp was focussed by a 3-inch diameter condenser of about 8 cm focal length onto a horizontal Hilger adjustable slit with an opening of about 75 μ through infra-red and green filters.

The equal lenses \( L_1 \) and \( L_2 \) were corrected for chromatic and spherical aberrations and were 102 mm diameter, having a focal length of 500 mm. The lens \( L_2 \) was a two-element collimating lens 20 mm in diameter and with a focal length of 75 mm. By means of these lenses parallel light from the horizontal slit was focussed through the diffusion cell placed between \( L_1 \) and \( L_2 \), through the Savart
FIGURE 20. ARRANGEMENT OF OPTICAL COMPONENTS, PLAN VIEW.
PLATE 3. LAYOUT OF OPTICAL SYSTEM
plate S, the cell plane being imaged at M. With this system the optical magnification at M is 0.150.

A polaroid disc \( P_1 \) with its axis of polarization horizontal was inserted between the lens \( L_3 \) and the Savart plate, and another \( P_2 \) with a vertical axis of polarization between the Savart plate and the image plane \( M, L_3 \), the Savart plate and the polaroid discs were mounted in a single unit with a device by which the Savart plate could be tilted a small amount about its horizontal axis.

(b) The Savart Plate

This consisted of two quartz crystal plates with 25 mm sides and 10 mm in thickness, cemented together in such a way that a vertical displacement \( b \) is introduced between the wavefronts in the x-direction. For a Savart plate adjusted perpendicular to the optic axis the displacement \( b \) is given by

\[
b = e\sqrt{2} \cdot \frac{n_e^2 \cdot n_e^2}{n_e^2 + n_o^2}
\]

where \( e \) = thickness of each part of the double plate,

\( n_e, n_o \) = principal refractive indices.

The plate used here was supplied by Bernhard Halle Nachfolger, Hubertusstrasse 11, Berlin, Germany, and had \( e = 10 \text{ mm}, \) and \( b = 84.2 \mu \).

If the optical magnification of the system is \( G \), the real distance at the object is not \( b \), but \( b_1 \), where

\[
b_1 = \frac{b}{G}
\]
Diffusion Cells

Two cells were used in this work. For the purpose of verifying the optical equipment the diffusion coefficient of sucrose in water was measured and for this a flowing-junction cell of the type designed by Svensson was used. In his investigation into types of cell BRYNGDAHL found that this design produced the most ideal diffusion boundary with very small zero-time corrections. The cell used here was constructed by FURZER and is illustrated with ancillary equipment in Plate 4. Details of construction and operation may be found in References 52 and 53.

The cell used for the determination of diffusion coefficients direct from the gas to the liquid phase is shown in Plate 5 and Figure 21. The four walls of the cell were constructed of good quality optical glass (flat to an accuracy of 1/50,000 of an inch), and the cell was fitted with a cover ground flat to enable a gas-tight seal to be obtained with the use of silicone grease. Dimensions were 10 cm long x 8 cm wide and 8 cm high and cell lengths of 10 cm or 8 cm could be obtained by turning the cell through 90°. Gas from a constant-pressure source could be admitted through an inlet in the cover plate which also carried a baffle to prevent disturbance of the liquid surface. By opening the entry and exit cocks simultaneously gas was admitted at the start of each run.
FIGURE 21. OPTICAL CELL FOR GAS-LIQUID SYSTEMS.

- Excess Gas Vent to Atmosphere
- Constant-Pressure Gas Supply
- Rubber Bung
- Gas Entry Cock
- Baffle Plate
- Liquid Level
- Glass Cover Plate
- Optical Glass Cell Wall
PLATE 5. GAS-LIQUID OPTICAL CELL
Photographic Registration

In order to photograph the interference fringes at regular intervals a 35-mm Robot Recorder camera which automatically advances the film was used in conjunction with a Robot Time Control Set II, which enabled exposures to be made at any required rate while diffusion proceeded. The back of the camera was removable and could be replaced by a magnifying ground glass screen for purposes of focussing. Ilford or Kodak Tri-X film was used with a two-second exposure, developer was Ilford Microphen fine grain.

THEORY AND DERIVATION OF FORMULAE

In this section the theoretical treatment will first be applied to diffusion occurring across an interface in a liquid-liquid system. Formulae will then be developed for gas-liquid systems.

(a) Liquid - Liquid Diffusion Systems

It is assumed that diffusion proceeds across the interface in accordance with FICK'S Law.

\[ \frac{dc}{dt} = D \frac{d^2c}{dx^2} \tag{1} \]

(1) can be solved for the boundary conditions

\[ c = c^\ast, \quad x < 0 \]
\[ c = 0, \quad x > 0, \quad t = 0 \]

which exist when a column of pure solvent rests on a column of solution giving (See for example CRANK) \[ c = c^\ast \text{ erf} \frac{x}{\sqrt{4Dt}} \tag{31} \]

To give the concentration gradient (31) can be differentiated with respect to \( x \)
For dilute solutions the refractive index \( n \) is proportional to \( c \), and if \( n_0 \) corresponds to \( c^* \):

\[
\begin{align*}
    n_s &= n_0 + c^* \frac{dn}{dc} \\
    \frac{dn}{dc} &= n_s - n_0 = \Delta n \\
    c^* &= \Delta n \cdot \frac{dc}{dn}
\end{align*}
\]

Substituting in equation (32)

\[
\frac{dc}{dx} + \frac{dn}{dc} = \frac{\Delta n}{2\sqrt{DT}} e^{-(x^2/4DT)}
\]

\[
\frac{dn}{dx} = \frac{\Delta n}{2\sqrt{7DT}} e^{-(x^2/4DT)}
\]

Equation (34) giving the refractive index gradient in the diffusion cell.

It is not intended to give here a detailed description of the optical principles involved in determining \( D \) from (34), but the following discussion is necessary to explain the mathematical derivation of the formulae. Further details may be obtained from the Handbuch der Physik\(^{49}\) and from papers by INGELSTAM\(^{55,56}\) and BRYNGDAHL\(^{57,58,59,60,61}\).

When a plane wave front passes through a cell containing a diffusing boundary it is distorted in accordance with the variation of concentration within the solution. The wave
front gives the representation of the optical paths \( Z \), which vary with \( x \), the space coordinate in the direction of diffusion, with the time \( t \), and with the refractive index \( n \) at the plane \( x \). Since the optical path length through a liquid is the physical path length multiplied by the refractive index, the relationship between \( Z \), \( n \), \( x \), and \( t \) can be expressed thus

\[
Z(x, t) = n(x, t) \times \text{(cell length)} \tag{35}
\]

The gradient of the curve represented by (35) may be found by differentiating with respect to \( x \)

\[
\frac{dZ}{dx} = \frac{d}{dx} n(x, t) \tag{36}
\]

and the right-hand-side of (36) is given by (34),

\[
\frac{dZ}{dx} = \frac{\Delta n}{2} \cdot \frac{1}{\sqrt{(\pi Dt)}} \cdot e^{-\left(\frac{x^2}{4Dt}\right)} \tag{35}
\]

As diffusion proceeds, the curve given by (35) tends towards a straight line. If it were possible to follow one constant value of \( \frac{dZ}{dx} \) by its corresponding values of \( x \) and \( t \), then (35) could be written

\[
\frac{\Delta n}{2\sqrt{\pi Dt}} \cdot (t)^{-\frac{1}{2}} \cdot e^{-\left(\frac{x^2}{4Dt}\right)} = \text{Constant}
\]

\[
(t)^{-\frac{1}{2}} \cdot e^{-\left(\frac{x^2}{4Dt}\right)} = c
\]

taking logarithms

\[
-\frac{1}{2} \ln t - \frac{x^2}{4Dt} = \ln c
\]

\[
\frac{x^2}{4Dt} = \ln c - \frac{1}{2} \ln t
\]

multiplying by \( 16D \)

\[
\left(\frac{2x}{t}\right)^2 = (2\ln c - \ln t) 8D \tag{36}
\]

The grouping on the left-hand-side of equation (36) is chosen because from a photograph of the liquid-liquid fringe
pattern, it is easier to measure the distance $2x$ between corresponding fringes on either side of the interface than the distance $x$ between a fringe and the interface. From equation (36) it can be seen that a graph of $(2x)^2$ versus $\ln t$ gives a straight line with gradient of $-8 \, \text{D}$. The shearing interferometer provides a convenient means of following a constant value of the optical path gradient through the corresponding values of $x$ and $t$.

If the distorted wave front described above is polarized and passed through a Savart plate in parallel light, the front is split into two equally strong, perpendicularly polarized fronts separated from each other by a distance $\lambda x$ which is equal to $b$, the shear induced by the Savart plate. The introduction of another polarizer with its axis perpendicular to the first causes the fronts to interfere, resulting in an interference pattern of fringes which can be photographed.

The principle of fringe formation is illustrated in Figure 22a. The left-hand column shows the relationship between the refractive index and the height in the diffusion cell in the double image formed by the Savart plate, the full line indicating one image and the broken line the other. The middle column shows the path difference $\Delta Z$ between the two displaced images, this is proportional to the refractive index gradient. When the path difference is $0, \lambda, 2\lambda$, etc. dark fringes are formed as shown in the right hand column.

Figure 22b shows the situation when the diffusion curve
FIGURE 22. PRINCIPLE OF FRINGE FORMATION
has straightened to an extent where the path difference is less than one wave length and no fringes are formed. By tilting the Savart plate, a constant path difference \( w \) is introduced and a fringe pair is formed as in Figure 22 c. Due to this it is possible to form fringes when the path difference is very small and the method is applicable to very dilute solutions.

An interference fringe appears when the path difference \( \Delta Z \) between two rays emerging from the Savart plate at the same point, but originating at a distance \( b \) apart satisfies the relationship

\[
\Delta Z = \frac{m \lambda}{2}
\]

(37)

where \( m = 0, 2, 4, 6, \) etc. for perpendicular polarizers, i.e. \( \Delta Z = 0, \lambda, 2\lambda, \) etc., dark fringes are formed. Each dark fringe in the interference pattern, therefore, corresponds to one value of \( \Delta Z \), and also to one value of \( \frac{\Delta Z}{b} \) since \( b \) is constant. If the space coordinate \( x \) corresponding to one fringe is followed with time, this is equivalent to following a constant value of \( \frac{\Delta Z}{b} \).

If

\[
\frac{\Delta Z}{b} = \frac{\Delta Z}{\Delta x} = \frac{\Delta Z}{dx}
\]

then the value of \( \frac{\Delta Z}{dx} \) is given by equation (35) and since it is constant, \( D \) can be obtained from equation (36).

**Application of Theory to Experimental Results**

There are two points which must be examined before equation (36) can be applied to experimental results. It is necessary to calculate the difference between the gradient \( \frac{\Delta Z}{b} \) which is measured, and \( \frac{\Delta Z}{dx} \) which is required; furthermore, since
for practical reasons it is difficult to determine exactly when diffusion begins, a constant zero-time correction \( \Delta t \) must be added to the measured time \( t \).

Before shearing, any point on the wave front a distance \( x \) from the interface and corresponding to an optical path length \( Z(x) \) has a gradient \( \frac{dZ}{dx} \). After shearing, two points corresponding to the original one are formed a vertical distance \( \Delta x \) apart, where

\[
\Delta x = (x + b/2) - (x - b/2) = b
\]

(38)

since the two new wave fronts are respectively \( +b/2 \) and \(-b/2\) above and below their original positions.

Their corresponding optical path lengths are now

\[
Z(x + b/2) \text{ and } Z(x - b/2)
\]

and the path difference introduced, \( \Delta Z \), is given by

\[
\Delta Z = Z(x + b/2) - Z(x - b/2)
\]

The gradient is given by

\[
\frac{\Delta Z}{\Delta x} = \frac{dZ}{dx} \left( 1 + \frac{1}{2} \cdot \frac{b^2}{2Dt} \cdot \frac{x^2 - 2Dt}{2Dt} \right)
\]

(39)

Equation (39) can be expanded as a series by Taylor's Theorem, from which

\[
\frac{\Delta Z}{b} = \frac{dZ}{dx} \left( 1 + \frac{1}{2} \cdot \frac{b^4}{4D^2 t^2} \cdot \frac{x^4 - 12x^2 Dt + 12D^2 t^2}{4D^2 t^2} + \ldots \right)
\]

(40)

Details of the expansion can be found in Appendix II (a).

Replacing \( t \) by \( (t + \Delta t) \) in Equation (35)

\[
\frac{dZ}{dx} = \frac{\Delta p}{2} \cdot \frac{1}{\sqrt{D(t + \Delta t)}} \cdot e^{-x^2/4D(t + \Delta t)}
\]

(41)
Substituting for \( \frac{\partial z}{\partial x} \) in Equation (40), since \( \frac{\Delta z}{b} \) is a constant (= m), and neglecting terms involving \( t \) of higher than the first order

\[
m = \frac{\Delta n}{2} \cdot \frac{1}{\sqrt{2\pi D(t+\Delta t)}} \cdot \left( 1 + \frac{b^2}{48Dt} \cdot \frac{x^2-2Dt}{2Dt} \right) e^{-x^2/4D(t+\Delta t)} (42)
\]

or

\[
x^2/4D(t+\Delta t) e = \frac{\Delta n}{2m} \cdot \frac{1}{\sqrt{2\pi D(t+\Delta t)}} \cdot \left( 1 + \frac{b^2}{48Dt} \cdot \frac{x^2-Dt}{2Dt} \right) (43)
\]

Taking logarithms,

\[
\frac{x^2}{4D(t+\Delta t)} = \ln \frac{\Delta n}{2m\sqrt{\pi D(t+\Delta t)}} + \ln \left( 1 + \frac{b^2}{48Dt} \cdot \frac{x^2-2Dt}{2Dt} \right) (44)
\]

and since \( \ln (1+a) = a \)

\[
\frac{x^2}{4D(t+\Delta t)} = \ln \frac{\Delta n}{2m\sqrt{\pi D(t+\Delta t)}} + \frac{b^2}{48Dt} \cdot \frac{x^2-2Dt}{2Dt} (45)
\]

Rearranging

\[
\frac{(2x)^2}{t+\Delta t} = 8D \ln \frac{\Delta n}{4m^2\pi Dt_o} - 8D \ln \left( \frac{t+\Delta t}{t_o} \right) + \frac{b^2}{48Dt} \cdot \frac{x^2-Dt}{2Dt} (46)
\]

\[
\frac{(2x)^2}{t+\Delta t} = C - 8D \ln \frac{t+\Delta t}{t_o} + \frac{b^2}{48Dt} \cdot \frac{x^2-2Dt}{2Dt} (47)
\]

where \( t_o \) is a constant time value corresponding to the maximum value of \( x \). A step-by-step derivation of equation (47) from equation (43) is given in Appendix II (b).

For small values of \( \Delta t \), (47) can be written

\[
\frac{(2x)^2}{t} = C - 8D \ln \frac{t}{t_o} + \frac{1}{t} \left( \frac{2x}{t} - 8D \right) \left( \frac{2b^2}{48D} + \Delta t \right) (48)
\]

Substituting \( P = (2x)^2/t \) and \( S = \ln \frac{t}{t_o} \)

\[
P = C - 8D \cdot S + P - 8D \cdot \left( \frac{b^2}{24D} + \Delta t \right) (49)
\]
A plot of P versus S will be linear or approximately linear
(i) For small values of Δt
(ii) For large values of t
(iii) When P = 8D

For conditions (iii), if \( \frac{(2x)^2}{t} = 8D \)
\[ x = \pm \sqrt{2Dt} \]
this condition is satisfied at the inflexion points of the concentration curve. INGELSTAM \(^{56, 57}\) has shown that the effect of the correction term is negligible if
\[ b_1 = \frac{b}{G} < \frac{3\sqrt{2}Dt}{\Gamma_1} \]  \( (50) \)
\[ \text{i.e., if} \quad t > \frac{b_1^2}{18D} \]  \( (51) \)

In the apparatus used here:
\[ b = 84.2 \times 10^{-4} \text{ cm} \]
\[ G = 0.150 \]
\[ b_1 = 56.0 \times 10^{-3} \text{ cm} \]

For values of D of the order of \( 5 \times 10^{-6} \text{ cm}^2/\text{sec} \),
\[ t > \frac{56.0 \times 56.0 \times 10^{-6}}{18 \times 5 \times 10^{-6}} \text{ sec} \]
\[ t > 35 \text{ sec} \]

Thus for diffusion times greater than 35 seconds equation \((49)\) approximates to
\[ \frac{(2x)^2}{t} = C - 8D \ln \frac{t}{t_0} \]
or
\[ \frac{(2x)^2}{t} = C' - 8D \ln t \]  \( (52) \)
and the gradient of a plot of \( \frac{(2x)^2}{t} \) versus \( \ln t \) is a straight line with gradient equal to \(-8D\).
Diffusion proceeds from the interface in accordance with FICK'S Law
\[
\frac{dc}{dt} = D \frac{d^2c}{dx^2} \tag{1}
\]
Assuming that the interface is instantaneously saturated upon exposure to the gas
\[
c = c^* \text{ for } x = 0, \ t > 0 \tag{53}
\]
and the initial gas concentration in the bulk of the liquid is zero
\[
c = 0 \text{ for } x > 0, \ t = 0 \tag{54}
\]
Equation (1) can be solved for boundary conditions (53) and (54) giving
\[
c(x, t) = c^* e^{-\frac{x^2}{4Dt}} \text{erfc} \left(\frac{x}{2\sqrt{D}t}\right) \tag{55}
\]
(cf. CRANK\cite{16})

Differentiating (55) with respect to \(x\)
\[
\frac{dc}{dx} = \frac{c^*}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \tag{56}
\]
Assuming as before that the refractive index \(n\) is proportional to the concentration and \(\Delta n = \) the difference in refractive index between the saturated solution and the solvent, it can be shown that
\[
\frac{dn}{dx} = \frac{\Delta n}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \tag{57}
\]
See Equations (32) to (34) in preceding section.
Since the optical path length \(Z\) is equal to the cell length multiplied by the refractive index
\[
Z(x,t) = n(x,t) \times (\text{cell length}) \tag{35}
\]
it follows that

\[ \frac{dZ}{dx} = \frac{\Delta n}{\sqrt{(\pi Dt)}} e^{-(x^2/4Dt)} \quad (58) \]

For a constant value of \( \frac{dZ}{dx} \), (58) can be written

\[ \Delta n = \frac{1}{\sqrt{(\pi Dt)}} e^{-x^2/4Dt} \quad \text{Constant} \]

\[ e^{-x^2/4Dt} = Ct^{-\frac{1}{4}} \]

Taking logarithms

\[ \frac{x^2}{4Dt} = \ln C - \frac{1}{4} \ln t \]

\[ \frac{x^2}{t} = 4D \ln C - 2D \ln t \quad (59) \]

From equation (59) a plot of \( \frac{x^2}{t} \) versus \( \ln t \) is a straight line having a gradient of \(-2D\).

The shearing interferometer provides a means of following a constant value of \( \frac{\Delta Z}{b} \) with corresponding values of \( x \) and \( t \), and before applying equation (59) to the results it is necessary to determine the extent of the required correction due to the use of \( \frac{\Delta Z}{b} \) instead of \( \frac{dZ}{dx} \).

Expanding \( \frac{\Delta Z}{b} = \frac{Z(x + b/2) - Z(x - b/2)}{b} \) as a Taylor Series it can be shown that (compare Equation 40)

\[ \frac{\Delta Z}{b} = \frac{dZ}{dx} \left( 1 + \frac{1}{2.3} \cdot \frac{b^2}{2Dt} \cdot \frac{x^2 - 2Dt}{2Dt} \right) \quad (60) \]

(Terms involving \( t \) of higher than the first order having been neglected)
Equation (58) defines \( \frac{dZ}{dx} \) as

\[
\frac{dZ}{dx} = \frac{\Delta n}{\sqrt{\pi Dt}} e^{-x^2/4Dt}
\]

For experimental application a positive increment \( t, \) the zero-time-correction must be added to \( t, \) the measured time

\[
\frac{dZ}{dx} = \frac{\Delta n}{\sqrt{\pi D(t+\Delta t)}} e^{-x^2/4D(t+\Delta t)}
\]

(61)

Substituting this value for \( \frac{dZ}{dx} \) in equation (60)

where \( \frac{dZ}{b} \) has a constant value \( m \)

\[
m = \frac{\Delta n}{\sqrt{\pi D(t+\Delta t)}} \left\{ 1 + \frac{b^2}{4\delta D} \cdot \frac{x^2-2Dt}{2Dt} \right\} e^{-x^2/4D(t+\Delta t)}
\]

Rearranging

\[
x^2/\pi \tau(t+\Delta t) e^{-x^2/4D(t+\Delta t)} = \frac{\Delta n}{m\sqrt{\pi D(t+\Delta t)}} \left\{ 1 + \frac{b^2}{4\delta D} \cdot \frac{x^2-2Dt}{2Dt} \right\}
\]

Taking logarithms, since \( \ln(1+a) = a \) for small \( a \)

\[
\frac{x^2}{4\delta D(t+\Delta t)} = \ln \frac{\Delta n}{m\sqrt{\pi D(t+\Delta t)}} + \frac{b^2}{4\delta D} \cdot \frac{x^2-2Dt}{2Dt}
\]

Rearranging

\[
\frac{x^2}{t} = C - 2D \ln t + \frac{1}{t} \left( \frac{x^2 - 2D}{t} \right) \left( \frac{b^2}{24D} + \Delta t \right)
\]

(62)

A plot of \( \frac{x^2}{t} \) versus \( \ln t \) is a straight line with a gradient of \(-2D\) if \( \frac{x^2}{t} = 2D, \) and for large values of \( t. \) INGELSTAM 56, 57 has shown that the correction term in (62) is negligible when

\[
t > \frac{b^2}{18D}
\]

(51)

For values of \( D \) of the order of \( 2 \times 10^{-5} \, \text{cm}^2/\text{sec.} \)

\[
t > \frac{(56.0)^2 \times 10^{-6}}{2 \times 18 \times 10^{-5}}
\]
It should be noted that even when the correction term cannot be neglected the diffusion coefficient is accurately given by the gradient of the $\frac{x^2}{t} - \ln t$ plot when $\frac{x^2}{t} = 2D$.

For the present, we shall use the approximation

$$\frac{x^2}{t} = C' - 2D \ln t$$

(63)

for the calculation of diffusion coefficients.
EXPERIMENTAL RESULTS AND DISCUSSION OF RESULTS

(a) The Diffusion Coefficient of Sucrose in Water at 25.0°C

As a check on the apparatus and method it was decided to measure the diffusion coefficient of sucrose in water at 25.0°C, since the true value is well established. A solution containing 0.0691% by weight of sucrose was prepared and an interface between the solution and water formed in the flowing-junction cell described earlier. Interference fringes were photographed 30 seconds after diffusion commenced and thereafter at intervals of 150 seconds. Exposure time was 2.5 seconds; Kodak Tri-X film was used, developer was Ilford Microphen with a tank development time of 11 minutes.

The photographs of fringes were examined under an 80-power microscope, and the distance between corresponding fringes measured by means of a micrometer eye piece. A typical fringe pattern (enlarged) is shown on Plate 6, and distances between the fringes on Table 18.
Figure 6. PHOTOGRAPHS OF INTERFERENCE FRINGES

Above: Sucrose / Water (0.0691% at 25.0°C)
Below: CO₂ / Water (25.0°C)
Table 18. Distance between corresponding fringes and calculation of \((2x)^2/t\) for a 0.0691\% Sucrose solution.

From Equation (36)

\[
\frac{(2x)^2}{t} = 16D \ln C - 8D \ln t
\]  

(36)

it can be seen that a plot of \((2x)^2/t\) versus \(\ln t\) is a straight line with a gradient of \(-8D\).

The values of \((2x)^2/t\) are plotted versus \(\ln t\) in Figure 23.

Gradient = \(0.930 \times 10^{-6} = 8D\)

\[D = 0.116 \times 10^{-6} \text{ cm}^2/\text{sec.}\]

The measured \(x\) - values refer to the photographic plate and in order to relate them to the cell, it is necessary to multiply by the magnification factor. From the focal lengths of the lenses in the system the magnification factor should be \(50/7.5 = 6.67\), but as a check an image of 6.00 cm was photographed and found to give an object on the photographic plate of 0.895 cm. Hence the magnification factor \(G = 6.00/0.895 = 6.70\)
FIGURE 23. \( \ln t \) vs \( \frac{(2x)^2}{t} \times 10^6 \) for 0.0691% Sucrose / water at 25.0°C.
Since D obtained from measurements on the photographic plate involves the square of x,

\[ D_{\text{cell}} = D_{\text{plate}} \times G^{2} \]

\[ = 0.116 \times 10^{-6} \times (6.70)^{2} \]

\[ = 0.116 \times 10^{-6} \times 44.90 \]

\[ = 5.21 \times 10^{-6} \text{ cm}^{2}/\text{sec} \]

This is less than 0.2% less than the value of 5.22 x 10^{-6} cm^{2}/sec from the literature, which indicates the accuracy of this method. No zero-time correction has been applied since this appears to be unnecessary for this type of liquid cell; BRYNGDAHL\(^5\) having shown that this is of the order of 3 or 4 seconds.
In the determination of diffusion coefficients of gases in water the optical arrangement was unchanged, but the flowing-junction cell was replaced by the glass cell described earlier and illustrated in Figure 21 and Plate 5. This cell proved to be remarkably efficient in use, and the baffle arrangement permitted a high rate of gas flow without disturbing the liquid surface; this enables the start of diffusion to be taken as the time when gas is admitted to the cell.

Experimental procedure was the same as for liquid-liquid diffusion, with the exception that Ilford HP3 film was used, and exposures were more frequent. A typical fringe pattern is shown on Plate 6, and the distance between fringes presented in Table 19.

For the calculation of the diffusion coefficient from Equation (63),
\[ \frac{x^2}{t} = C^1 - 2D \ln t \]
values of \( \frac{x^2}{t} \) are plotted against \( \ln t \) in Figure 24.
FIGURE 24. In t vs \( \frac{k^2}{t} \) for CO₂ / water at 25.0°C.
Table 19. Distance between fringe and interface and calculation of $x^2/t$ for CO$_2$ water at 25.0°C.

<table>
<thead>
<tr>
<th>$t$ Time (sec)</th>
<th>$x \times 10^2$ Distance Fringe to Interface (cm)</th>
<th>$x^2 \times 10^4$ (cm$^2$)</th>
<th>$\frac{x^2}{t} \times 10^6$ cm$^2$/sec.</th>
<th>$\ln t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>2.5</td>
<td>6.25</td>
<td>4.62</td>
<td>4.91</td>
</tr>
<tr>
<td>260</td>
<td>2.5</td>
<td>6.25</td>
<td>2.40</td>
<td>5.56</td>
</tr>
<tr>
<td>385</td>
<td>2.75</td>
<td>7.60</td>
<td>1.97</td>
<td>5.95</td>
</tr>
<tr>
<td>570</td>
<td>3.0</td>
<td>9.00</td>
<td>1.58</td>
<td>6.35</td>
</tr>
<tr>
<td>815</td>
<td>3.25</td>
<td>10.5</td>
<td>1.29</td>
<td>6.70</td>
</tr>
<tr>
<td>1120</td>
<td>3.5</td>
<td>12.2</td>
<td>1.09</td>
<td>7.02</td>
</tr>
<tr>
<td>1485</td>
<td>3.5</td>
<td>12.2</td>
<td>0.82</td>
<td>7.30</td>
</tr>
<tr>
<td>1850</td>
<td>3.5</td>
<td>12.2</td>
<td>0.66</td>
<td>7.52</td>
</tr>
</tbody>
</table>

From Figure 24,

Gradient = $0.84 \times 10^{-6} = 2$ D plate

D plate = $0.42 \times 10^{-6}$ cm$^2$/sec

Magnification Factor $G = 6.00/0.875 = 6.85$

$G^2 = 47.0$

D cell = D plate x $G^2$

= $0.42 \times 10^{-6}$ x 47.0

= $1.975 \times 10^{-5}$ cm$^2$/sec
(c) Discussion of Results

The foregoing section has shown the extreme accuracy of which this method is capable, and for moderately soluble gases it appears to be superior to existing methods for the determination of diffusion coefficients.

The value of $1.975 \times 10^{-5}$ cm²/sec for the diffusion coefficient of carbon dioxide in water at 25.0°C is about 0.25% higher than the value of $1.970 \times 10^{-5}$ cm²/sec given by PIGFORD. The difference between these values is insignificant.

In its present form the apparatus has the disadvantage of producing a relatively small image of the cell. This can be overcome by incorporating a lens after the Savart plate to enlarge the image at the photographic plate.
SHEARING INTERFEROMETER - CONCLUSIONS
AND DISCUSSION

(a) Evaluation of the Interferometer Technique

It has been seen that existing methods for the determination of diffusion coefficients of gases in liquids suffer from three disadvantages,

(i) Unsteady-state theory derived for stagnant liquid surfaces is applied to non-stagnant systems.

(ii) A value of the gas saturation concentration is required.

(iii) Heat effects at the surface may affect the results.

The work reported here has shown that the shearing interferometer provides a means of determining diffusion coefficients under experimental conditions where a perfect interface of stagnant liquid is exposed to the gas, a value for gas solubility is not required, and the major heat effects are dissipated before measurements are commenced. Added to this are the advantages of great accuracy since one measurement only is required, and the fact that determinations can be carried out with very small quantities of gas and liquid.

The main disadvantage of the method is due to the fact that a solution of gas is formed above the liquid into which it diffuses, giving rise to a danger of convection. The effect however should be slight since the difference in densities is small.

There is also the problem of the meniscus formed at the
walls of the optical cell, and it is recommended that the
effect of treating the walls with a lyophobic substance be
investigated.

(b) Suggestions For Further Work

Further work with the interferometer should consist of
improving the apparatus and experimental techniques outlined
above, as well as an investigation into possible applications
to other fields of mass-transfer.

(1) Development of Present Method

(i) Improvement of Optical Cell.

It is felt that a sliding cell of the type illustrated
in Figure 25 would be ideal. This design would allow filling
with liquid under an inert atmosphere, and simple and rapid
exposure to the test gas. Refinements such as an accurate
temperature sensing device and a contact for starting the
camera could be included and the whole submerged in a constant
temperature bath.

(ii) Methods of Determining 'x' values from Photographs

Several methods of determining fringe displacements from
photographs of the interference pattern are discussed by
BRYNGDAHL. Of these, the method of producing a photogram,
constructing the medians of the curves, and measuring the
distance between them is tedious, but will produce the most
accurate results.

(iii) Improved Methods of Calculation

Although the value of the zero-time-correction \( \Delta t \) is
FIGURE 25. PROPOSED DESIGN OF SLIDING CELL FOR GAS-LIQUID ABSORPTION
small in gas-liquid experiments, it might prove interesting to compare values of $D$ accurately determined from Equation (62)

$$\frac{x^2}{t} = C' - 2D \ln t + \frac{1}{t} \left( \frac{x^2}{t} - 2D \right) \left(\frac{b^2}{24D} + \Delta t\right)$$  (62)

with those obtained from the approximate solution (63)

$$\frac{x^2}{t} = C' - 2D \ln t$$

(62) could be solved by computer techniques by a trial-and-error procedure since the "most correct" value of $t$ will give a constant value of $D$ for all values of $x$ and $t$. Methods outlined for the determination of $\Delta t$ by BRYNGDAHL\textsuperscript{57} are tedious.

(2) Further Application of the Shearing Interferometer

(i) Modification Enabling Direct Plot of Refractive Index Gradient.

A recent paper by BRYNGDAHL and LJUNGGREN\textsuperscript{62} describes a modification to the shearing interferometer which enables the refractive index gradient in the diffusion cell to be photographed directly. The modification is shown in Figure 26 and consists of focusing the image from the Savart plate in the existing equipment through a second Savart plate and polarizer onto a photographic plate.

The significance of this is that it is no longer necessary to assume the form of the refractive index gradient, and it would enable investigations into the effect of heat of solution at the interface.

(ii) Application to Systems involving Chemical Reaction
FIGURE 26. MODIFICATION OF INTERFEROMETER TO ENABLE DIRECT REGISTRATION OF REFRACTIVE INDEX GRADIENTS.
An investigation is currently under way into the application of the shearing interferometer to systems where the gas reacts with a component of the liquid phase. In this it is hoped to include photographs of the refractive index gradient.
APPENDIX I

1. Solubility of Nitrous Oxide in Solutions of Glycerol at 20.0°C (Seidell, 3rd Ed. p. 1140)

2. Viscosities of Glycerol-Water Solutions up to 22.7% at 20.0°C.
Figure A2. $c^*$ versus % Glycerol, from Seidell, 3rd Edition, p 1140.
FIGURE A2. VISCOSITY OF GLYCEROL SOLUTIONS
APPENDIX II

DETAILS OF DERIVATION OF MATHEMATICAL FORMULAE FOR THEORY OF SHEARING INTERFEROMETER

(a) Taylor Theorem Expansion of $\frac{\Delta z}{b}$

(b) Stepwise derivation of Equation (47) from Equation (43)
Taylor Series Expansion of Equation (39)

\[
\frac{\Delta Z}{\Delta x} \bigg|_{x = b} = \frac{2(x + b/2) - 2(x - b/2)}{b}
\]

(39)

Taylor's expansion

\[
2(x + hx) = 2(x) + \frac{h}{1!} 2'(x) + \frac{h^2}{2!} 2''(x) + \frac{h^3}{3!} 2'''(x) + \frac{h^4}{4!} 2''''(x) + \ldots
\]

So

\[
\frac{2(x + b/2)}{2} = 2(x) + \frac{b}{2!} 2'(x) + \frac{(b)^2}{2} 2''(x) + \frac{(b)^3}{3!} 2'''(x) + \frac{(b)^4}{4!} 2''''(x) + \ldots
\]

and

\[
z\left(x - \frac{b}{2}\right) = 2(x) + \frac{(b)}{2} 2'(x) + \frac{(-b)^2}{2} 2''(x) + \ldots
\]

Consequently

\[
\frac{\Delta Z}{\Delta x} \bigg|_{x = b} = \frac{1}{b} b2'(x) + \frac{2(b)^3}{3!} 2'''(x) + \frac{2(b)^5}{5!} 2''''(x) + \ldots
\]

Now

\[
z'(x) = \frac{dn}{dx} = A e^{-x^2/B} \quad \text{where} \quad A = \frac{n}{2\sqrt{\pi Dt}} \quad B = 4Dt
\]

\[
z''(x) = A \left(-\frac{2x}{B}\right) e^{-x^2/B} = -\frac{2x}{B} z'(x) \quad 2'''(x) = \left(-\frac{2}{B}\right) z'(x) + \ldots
\]

where

\[
\begin{align*}
\left(-\frac{2x}{B}\right) \left(-\frac{2x}{B}\right) 2'(x) &= \frac{2}{B^2} 2'(x) 2x^2-B \\
z^{iv}(x) &= z''(x) \frac{2}{B^2} 2x^2-B + 2'(x) \frac{2}{B^2} 4x^4 \\
&= \frac{2z'(x)}{B^3} - 2x(2x^2-B) + 4xB = \frac{2z'(x)}{B^3} 6xB - 4x^3
\end{align*}
\]

and

\[
z^v(x) = \frac{2z''(x)}{B^3} 6xB - 4x^3 + \frac{2z'(x)}{B^3} 6B - 12x^2
\]
\[
\begin{align*}
&= \frac{42'(x)}{B^3} (2x - (3xB - 2x^3) + 3B - 6x^2 \\
&= \frac{42'(x)}{B^4} 4x^4 - 12x^2B + 3B^2 \\
\end{align*}
\]

Substituting in (i)

\[
\frac{dn}{dx} = 2' + \left( \frac{B}{2} \right)^2 2'' + \left( \frac{B}{2} \right)^3 2''' + \frac{1}{2} \left( \frac{B}{2} \right)^4 2'''
\]

\[
= 2'(x) + \left( \frac{B}{2} \right)^2 2'(x) - B + \left( \frac{B}{2} \right)^3 2' + \frac{1}{2} \left( \frac{B}{2} \right)^4 2''
\]

\[
= 2'(x)(1 + \left( \frac{B}{2} \right)^2 2'(x) - B + \left( \frac{B}{2} \right)^3 2') + \frac{1}{2} \left( \frac{B}{2} \right)^4 2''
\]

Substituting for \( B = 4 \)

\[
= 2'(x) \left( 1 + \frac{1}{2^3} \right) \frac{2b^2}{B^2} (2x^2 - B) + \frac{1}{2^4} \frac{4b^4}{B^4} (4x^4 - 12x^2B + 3B^2) + \ldots
\]

\[
\frac{\Delta Z}{b} = \frac{dn}{dx} \left( 1 + \frac{1}{2^3} \right) \frac{b^2}{2D} \left( \frac{x^2 - 2Dt}{2Dt} \right) + \frac{1}{2^4} \frac{4b^4}{4D^2t^2} \left( \frac{x^4 - 12x^2Dt + 12D^2t^2}{4D^2t^2} \right) + \ldots
\]
(b) Details of steps from Equation (43) to Equation (47)

\[
\exp \left( \frac{x^2}{4D(t + \Delta t)} \right) = \frac{\Delta n}{2m\sqrt{\pi D}(t + \Delta t)} \left( 1 + \frac{b^2}{48Dt} \right) \frac{x^2 - 2Dt}{2Dt} \tag{43}
\]

Taking logs

\[
\frac{x^2}{4D(t + \Delta t)} = \ln \frac{\Delta n}{2m\sqrt{\pi D}(t + \Delta t)} + \ln \left( 1 + \frac{b^2}{48Dt} \right) \frac{x^2 - 2Dt}{2Dt}
\]

\[
(2x)^2 = 16D \left( \ln \frac{\Delta n}{2m\sqrt{\pi D}(t + \Delta t)} + \ln \left( 1 + \frac{b^2}{48Dt} \right) \frac{x^2 - 2Dt}{2Dt} \right)
\]

\[
= 16D \ln \frac{\Delta n}{2m\sqrt{\pi D}(t + \Delta t)} + \frac{b^2}{3Dt} \frac{x^2 - 2Dt}{2Dt}
\]

since \( \ln (1 + a) = a \)

\[
= 16D \ln \frac{\Delta n}{2m} \left( \pi D \left( t + \Delta t \right) \right) + \frac{b^2}{3Dt} \frac{x^2 - 2Dt}{2Dt}
\]

\[
= 8D \ln \frac{\Delta^2 n}{(2m)^2 \pi D} \left( t + \Delta t \right)^{-1} + \frac{b^2}{3Dt} \frac{x^2 - 2Dt}{2Dt}
\]

\[
(2x)^2 = C - 8D \ln \frac{t + \Delta t}{t_0} + \frac{b^2}{3Dt} \frac{x^2 - 2Dt}{2Dt} \tag{47}
\]
NOTATION

\[ A = \text{Rate of production of fresh surface by jet} \quad \text{cm/sec} \]

\[ A_1 = \text{Concentration of solute gas in physical solution at interface} \quad \text{gm-moles/cm}^3 \]

\[ a = \text{Cell thickness} \quad \text{cm} \]

\[ B_0 = \text{Initial concentration of liquid-phase reactant} \quad \text{gm-moles/cm}^3 \]

\[ b = \text{Shear produced by Savart Plate} \quad \text{cm} \]

\[ b_1 = \text{Real shear distance at Object} \quad \text{cm} \]

\[ c = \text{Point concentration of diffusing solute} \quad \text{gm-moles/cm}^3 \]

\[ c^* = \text{Equilibrium saturation concentration of solute gas in liquid phase} \quad \text{gm-moles/cm}^3 \]

\[ c_0 = \text{Initial concentration of solute gas in bulk liquid} \quad \text{gm-moles/cm}^3 \]

\[ D = \text{Diffusion coefficient} \quad \text{cm}^2/\text{sec} \]

\[ d = \text{Diameter of liquid jet} \quad \text{cm} \]

\[ e = \text{Thickness of each part of Savart Plate} \quad \text{cm} \]

\[ f = \text{Focal length of lens} \quad \text{cm} \]

\[ G = \text{Magnification Factor of Imaging System} \quad \text{cm} \]

\[ I = \text{Ionic strength of amine solution} \quad \text{gm-ions/litre} \]

\[ K_b = \text{Equilibrium constant} \]

\[ k_L = \text{Liquid-side mass transfer coefficient} \quad \text{cm/sec} \]

\[ k_L^0 = \text{Mass-transfer coefficient for system without chemical reaction} \quad \text{cm/sec} \]

\[ k = \text{Reaction velocity constant of first-order or pseudo first-order reaction} \quad \text{sec}^{-1} \]

\[ k' = \text{Velocity constant of second-order reaction} \quad \text{Litres/gm-moles/sec} \]

\[ L = \text{Liquid flow rate through jet orifice} \quad \text{cm}^3/\text{sec} \]

\[ h = \text{Length of laminar jet} \quad \text{cm} \]
m = Constant \[ \text{cm} \]

N = Average rate of absorption over period of \[ \text{gm-moles/cm}^2 \text{ sec.} \]

N' = Instantaneous rate of absorption at time \( t \) \[ \text{gm-moles/cm}^2 \text{ sec.} \]

n = Refractive Index

n = Number of moles of moles of gas reacting with one mole of liquid reactant

Q = Amount of solute crossing unit area of any liquid plane parallel to interface after exposure of \( t \) seconds \[ \text{moles} \]

T = Absolute Temperature \[ ^\circ R \]

t = Time \[ \text{sec.} \]

t_d = Depletion time \[ \text{sec.} \]

v = Velocity of liquid jet \[ \text{cm/sec.} \]

x = Linear coordinate in direction of diffusion \[ \text{cm} \]

Z = Optical Path Length

\( \mu \) = Absolute viscosity \[ \text{centipoises} \]

\( \phi \) = Rate of absorption of gas into liquid jet \[ \text{gm-moles/sec} \]

\( \lambda' \) = Wave length of light in Optical System

\( \Delta Z \) = Optical path difference between two points on sheared Gaussian Curve.
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