LIQUID DIFFUSION OF NON-ELECTROLYTES[1]

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Received January 20, 1956

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[1] This project was supported by the Office of Ordnance Research of the U. S. Army and the National Science Foundation.

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I. INTRODUCTION

Theoretical and practical interest in liquid diffusion has been maintained for over a century. Since the diffusion process is one of the aspects of liquid behavior which must be described by a satisfactory liquid-state theory, observed diffusion rates have been useful in both formulating and testing such theories. The practical utilization of rates of liquid diffusion has also increased recently, as more fundamental consideration is being given to various mass-transfer processes where liquid diffusion is one of the rate-controlling factors.

This review is intended to be a convenient source of reference material for those engaged in research on liquid diffusion as well as a general source of information of diffusion phenomena for those engaged in the applied aspects of diffusional processes.

II. DIFFUSION CONCEPTS

A. BASIC MECHANISM OF DIFFUSION

Because diffusivities are necessarily reported in terms of experimental observations on a somewhat arbitrary basis, it is worthwhile to review in some detail an elementary picture of the diffusion process and the development of the basic diffusion equations. In the usual sense, diffusion of mass refers to the dissipation of a concentration gradient by molecular transfer with no overall mass flow caused by external forces. To visualize the reasons for this observed motion, consider the behavior of a solute molecule in a given solution. The energy possessed by the molecules in the liquid state causes a solute molecule to collide constantly with solvent molecules and in more concentrated solutions also with other solute molecules. These collisions keep the solute molecule in a state of random motion, each individual collision moving it without regard for any concentration gradient that may be present. While it is possible to calculate the mean distance which a molecule would travel in a given time interval, there is no way of predicting its actual path. A plot of probable position with time would be a series of concentric circles about its initial position.

This basic motion is reconciled with observed net transport when a concentration gradient exists, by the following analysis. Consider two thin adjacent slices of solution, in which the concentration of A and of B is slightly greater in the lower slice. The concentration gradient will be assumed unidirectional, so the lateral concentration in the slices will be uniform. Neglecting for the moment any effects which the difference in concentration might have on the frequency with which a molecule moves, it follows that the same fraction of A molecules originally in the lower slice will move to the upper as will move from the upper to the lower. Since there were more A molecules in the lower slice originally, a net transport of A molecules from the lower to the upper slice results. This observed net motion ordinarily represents only a small fraction of the total molecules which moved across the reference boundary between the slices, but in general it is this net transport which is of practical concern.

In actual solutions the simplified argument presented above must be modified. If A and B are identical molecules in a binary solution, the rates of random motion across a fixed volume section are probably equal and opposite. In general the molecules are not identical and the random motion of one type of molecule is greater than that of the other. This results in a hydrostatic pressure building up in regions of the solution contributing least to the volume rate of transfer. This pressure gradient is relieved by a mass flow of A and B together which is superimposed on the statistical flow.

The basic motion of the molecules is further complicated in non-ideal solutions by force fields which cause the motions to become not strictly random. If solute molecules could find themselves in a less favorable force environment in more dilute solution, for example, they might experience a real force toward the direction of high concentration and actually have a velocity component opposing the statistical flow.

In view of the apparent statistical behavior inherent in the diffusion process, it should be possible to relate the unordered molecular motion to diffusion flow. The first successful attempt was made by Einstein (27) in his discussion of Brownian motion in the following manner.

Considering the motion along the x-direction only, plus and minus displacements are probably equal and smaller displacements are more probable than large ones. It can be shown that the probability of a horizontal displacement having a value between x and $x + \mathrm{d}x$ is:

$$P = \frac{1}{\sqrt{2\pi\Delta_l^2}} \exp\left(-x^2/2\Delta_l^2\right) \mathrm{d}x \tag{1}$$

where Δ_l^2 is the mean of the squares of the average linear displacement.

Δ_l is simply related to a diffusion coefficient, D_s, defined as the number of molecules passing a unit cross-section in unit time when the concentration gradient is unity:

$$D_s = \tfrac{1}{2}(\Delta_l^2)/t \tag{2}$$

If diffusion now occurs across a plane in a horizontal tube with concentrations C_1 and C_2 on each side of the plane, then in a time t only those particles closer than the mean displacement will pass through the plane. The number of particles passing through the plane will be $\frac{1}{2}(\Delta_l)(C_2 - C_1)$. From the above definition of D_s equation 1 becomes:

$$P = \frac{1}{\sqrt{4\pi D_s t}} \exp\left(-x^2/4D_s t\right) dx \tag{3}$$

Practical utilization of this equation is restricted to the case where an amount of solute, S, is initially contained in a differential volume at $x = 0$ and $t = 0$. The concentration distribution of solute at time t is then given by the right-hand side of equation 3 when it is multiplied by S. Even then there is no general method of predicting the average linear displacement, so the coefficient D_s must be determined by other means, usually experimentally. When one considers the more general case with an initial solute distribution, the difficulty of evaluating average displacements with changing solution environment becomes enormous.

1. Fick's first law

Although the statistical approach gives better physical insight into the nature of diffusion, the first successful mathematical formulation of diffusion rates is due to Fick (33), who deduced forces in the diffusion process analogous to those in heat flow. He observed that for a given temperature and pressure the rate of transfer appeared to be proportional only to the concentration gradient. He thereby established the simple relation, now well known as Fick's first law, which for unidirectional diffusion flow may be written:

$$J = -D(\partial C/\partial x) \tag{4}$$

where J is the rate of material transfer per unit area and $\partial C/\partial x$ is the concentration gradient. The diffusion coefficient, D, is presumed to be a constant for a given system, and the minus sign indicates that the flow is opposite in sense to the direction of the concentration gradient.

Since diffusion of both components of a binary system requires that the flow of one be balanced by an opposite flow of the other, an equation can be written for each component. In general only one equation is used to describe diffusion in a binary system under a given set of conditions, implying that the diffusion coefficient is the same for each component. The diffusion coefficients, however, are identical only when the volumes of A and B do not change in the diffusion process. This can be shown as follows. Let the diffusion equation for each substance be written:

$$J_{\mathrm{A}} = -D_{\mathrm{A}}(\partial C_{\mathrm{A}}/\partial x) \tag{5}$$

$$J_{\mathrm{B}} = -D_{\mathrm{B}}(\partial C_{\mathrm{B}}/\partial x) \tag{6}$$

and let V_{A} and V_{B} be equal to the constant volumes of the unit amounts used to define the concentrations of A and B. Where changes in volume with concentration can be neglected, V_{A} and V_{B} will be the partial molar volumes. The volume transfer of A per unit time across a unit cross-section is then $-D_{\mathrm{A}}V_{\mathrm{A}}(\partial C_{\mathrm{A}}/\partial x)$, and that of B is $-D_{\mathrm{B}}V_{\mathrm{B}}(\partial C_{\mathrm{B}}/\partial x)$. With a constant volume system there is no net transfer of volume across a reference section, so:

$$D_A V_A(\partial C_A/\partial x) + D_B V_B(\partial C_B/\partial x) = 0 \tag{7}$$

The volume of A per unit overall volume of solution is $V_A C_A$ and that of B is $V_B C_B$. With only A and B present:

$$V_A C_A = V_B C_B = 1 \tag{8}$$

Differentiating this expression results in the following:

$$V_A(\partial C_A/\partial x) + V_B(\partial C_B/\partial x) = 0 \tag{9}$$

For equations 7 and 9 to be true, it follows that $D_A \equiv D_B$ or else V_A and/or $V_B = 0$. If V_A or V_B cannot be considered constant, then D_A need not equal D_B. For the usual organic systems D_A will generally be considered always equal to D_B and the coefficient measured and discussed will be the one common to both substances, designated as the mutual diffusion coefficient, D_{AB}.

The basic diffusion law may be generalized in the case of diffusion in several directions by setting it down as

$$\vec{J} = -D \operatorname{grad} C = -D\nabla C \tag{10}$$

Ordinarily diffusion in one direction only is considered. Most practical applications of diffusivity values are for cases where this is essentially true, and experimental determinations of diffusivity values for other than unidirectional flow would be very difficult.

Inspection of the basic diffusion law in equation 10 shows that the units of D must be in terms of L^2t^{-1}. As long as the units used to express the quantity of material are the same in J and C, such units do not affect the numerical value of D. Ordinarily length is designated in centimeters and time in seconds, so D is expressed in terms of cm.^{2}/sec., although some data are reported in units of cm.^{2}/day and engineering literature often uses the units of ft.^{2}/hr.

2. Fick's second law

For mathematical analysis of diffusion experiments it is convenient to transform Fick's basic diffusion law into a form known as Fick's second law. By combining the basic equation 10 with the requirement of a continuity of mass over a differential volume element of unit cross-section the following expression for Fick's second law is obtained:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{11}$$

where D is considered to be independent of concentration. In the more general case where D is a function of C, the law is of the form:

$$\frac{\partial C}{\partial t} = \operatorname{div}(D \operatorname{grad} C) = \nabla\cdot(D\nabla C) \tag{12}$$

3. *Hydrodynamic derivation of Fick's law*

It has since been shown that the basic diffusion law can be developed from theoretical hydrodynamics in the following manner (*cf.* Glasstone (40)) when osmotic pressure is considered the driving force for diffusion. In dilute solution the force on a single solute particle may be expressed as:

$$\vec{f} = -(m/C) \text{ grad } P \tag{13}$$

where C is the concentration, m is the mass of the particle, and P is the osmotic pressure. Since $P = (CRT/mN)$, where N is Avogadro's number, equation 13 may be written in the following form:

$$\vec{f} = -(RT/N)[(\text{grad } C)/C] \tag{14}$$

In steady motion where each particle may be assumed to have a constant velocity $\vec{v}$, this velocity $\vec{v} = B\vec{f}$, where B is a "mobility" factor dependent on the size and shape of the particle and the viscosity of the suspending medium. Substituting the above value for $\vec{f}$:

$$\vec{v} = -(RT/N)(B)[(\text{grad } C)/C] \tag{15}$$

Designating the flow as $\vec{J}$:

$$\vec{J} = C\vec{v} = (R - T/N)(B)(\text{grad } C) = -D \text{ grad } C \tag{16}$$

where D is set equal to $(RT/N)(B)$.

When the flow resistance $(1/B)$ is set equal to that obtained from Stokes' law, $6\pi\eta r$, equation 16 becomes the familiar Stokes–Einstein equation.

B. TYPES OF MUTUAL DIFFUSION COEFFICIENTS

Although Babbitt (5) has recently discussed the development of various diffusion equations utilizing a basic hydrodynamic pressure gradient driving force, it is currently agreed by most investigators that the fundamental driving force in diffusion phenomena is one of chemical potential or activity derived from chemical potential. A number of authors appear to have introduced the chemical potential intuitively, but choosing the proper fluxes and forces for the diffusion phenomenon and applying thermodynamics of irreversible processes show that the driving force is chemical potential. Further evidence for the validity of using chemical potential is that the variation of the diffusion coefficient with molar composition is more linear in a number of cases when an activity gradient is used in place of the concentration gradient (26, 96).

The presence of a concentration gradient term in Fick's law merely serves to define the numerical value of the diffusion coefficient and does not detract from the validity of practical applications. Troubles do arise, however, when reported experimental observations in terms of the Fick diffusion coefficient are related to other properties of the system because of the definition of the coefficient for a point condition only.

Assuming for the moment constant volume conditions during an experiment and neglecting self-diffusion, diffusion coefficients may still be classified broadly into: (*1*) differential coefficients, which represent conditions when diffusion occurs between two solutions of only differential concentration differences, and (*2*) integral coefficients, which satisfy the diffusion equation for the case where diffusion occurs between two solutions of significant concentration difference and in which ordinarily a significant change in concentration difference occurs during the diffusion process. Since most experimental diffusion measurements have been made where both a concentration difference and a change in concentration difference were observed during the experiment, most reported coefficients are really integral in the strictest sense. It is the differential coefficient, however, which has theoretical interest, since it is the one which should be most easily predicted from theories of the liquid state. Moreover, it is most useful in comparing data of different investigators, as a true differential coefficient leaves no uncertainty in the environmental description.

It is not possible, in general, to measure differential diffusion coefficients rigorously; consequently their measurement is approached by making the concentration gradients small and assuming that the measured coefficient is a differential coefficient for the mean of the two starting concentrations used. This is usually a valid assumption and in many cases yields a value within the experimental error of the measurements, but it should be emphasized that except where the diffusivity–composition relation is linear, it is only a coincidence in most cases if the integral coefficient is the true differential coefficient for the average of the concentrations.

The manner of determining the exact concentration value for which the integral coefficient is equal to that of the differential coefficient depends both on the variation of the differential coefficient with concentration and on the method of calculation used in conjunction with the experimental observations. Gordon (42) has described a method for relating the two types of coefficients when measurements are made with diaphragm cells, and Hammond and Stokes (51) have used such methods to convert measured integral coefficients into differential coefficients for the ethanol–water system. Stokes (110) has also discussed the problem of relating integral and differential coefficients when diffusion occurs from an initially sharp boundary between two columns of liquid and diffusion is not allowed to reach the ends of the cell.

The usual methods of obtaining diffusion coefficients for systems of organic liquids are such that the coefficients for each component may be assumed equal. It is possible, however, to define other reference states for diffusion measurements than the usual boundary across which no volume change occurs, and this concept has been discussed extensively by Hartley and Crank (52). In general, if a reference section is based on other than constant volume on a side, it may be necessary to use a modified scale of length in order that the form of the basic diffusion equation will not be changed. In particular, one might use a section which has a fixed total mass on each side or one with a fixed amount of one component. Although these notions do not find ready application in the study of ordinary liquid diffusion, they are useful in considering such special cases as diffusion through membranes, absorption in sheets of material, and diffusion of one component through another restrained within a membrane permeable only to the diffusing substance. Other diffusion coefficients have been defined, particularly for gaseous systems. Relationships among several types of coefficients have been discussed recently by Opfell and Sage (92), but in liquid diffusion the Fick coefficient has been used almost exclusively. For these reasons these special reference planes and other defined coefficients will not be considered further here.

C. SELF-DIFFUSION COEFFICIENTS

Although the phenomenon was no doubt considered by many early investigators, only recently has it become convenient to measure the self-diffusion coefficients of substances in the liquid state either as pure materials or as components of mixtures. This coefficient is unlike those previously discussed in that its measurement does not require the existence of any overall chemical concentration gradient, thus giving the nearest approach possible today to observing the magnitudes of actual molecular motion in a gross sense. The method involves observing the net translational motion of a given amount of a substance labelled with a known isotope of one of the constituent elements in an otherwise chemically uniform mixture. Ordinarily the technique is to use an isotope with a different mass than that normally present, or else to utilize a radioactive isotope whereby the progress of diffusion can be conveniently followed by appropriate radioactivity measurements. It is noted that the disturbing influences of concentration gradients and volume changes during an experiment have been eliminated with this type of measurement, with the result that the random motion of the molecules should be strictly that caused by the established uniform molecular environment. The behavior of the labelled compounds is no doubt slightly different from that of the natural isotope, since radioactive molecules have slightly different masses and emit small amounts of energy. It has generally been presumed that these differences are slight and that the resulting observations yield a value interpretable in terms of true random molecular motion. Some recent work of Longsworth (81) has indicated, however, a small but definite influence of concentration when deuterium oxide was used to measure the self-diffusion rates of water.

The self-diffusion coefficient is calculated from experimental observations in the usual manner by observing the change in concentration gradient with time and distance of the tagged molecules in a given experimental environment. Since the overall concentration is uniform, the diffusion equations developed from the form of Fick's law shown in equation 12 may be safely used with an invariant value for D for given overall composition. While this calculation does not immediately give the number of molecules changing position in the solution, it is a measure of the extent of random motion of the tagged molecules in the given environment.

At first glance this type of experiment might appear to yield a true differential diffusion coefficient, but it has been recently shown that significant differences exist between mutual diffusion and self-diffusion coefficients for the same average solution composition (58, 104, 127).

III. Mathematical Solutions of Basic Diffusion Equations

In order to perform quantitative diffusion experiments and report the observations in terms of the classic diffusion coefficient, D, it is necessary to convert the basic diffusion laws into forms such that the terms other than D can be related to measurable quantities. Most of the useful solutions to the basic diffusion equations have been developed either by previous workers in the field of diffusion or by analogy to the related equations for heat flow. The solutions are available in a number of references, although particular mention may be made of the books by Barrer (7), Carslaw and Jaeger (15), and Jost (60). Since detailed development of these solutions appears unnecessary here, this presentation will be confined to a brief summary of the most useful solutions of Fick's first and second laws for unidirectional diffusion, designated as the x-direction, followed by a brief discussion of the mathematical relations between differential and integral diffusion coefficients.

A. SOLUTIONS OF FICK'S FIRST LAW

Although restricted to rather few types of experimental methods, calculations by use of Fick's first law are simply made. If it is possible to measure the diffusion flux in a given system with a known concentration gradient for the given flux, the value for D is immediately calculable, for:

$$D = -J/(\partial C/\partial x) \tag{17}$$

It is possible to integrate the above equation if D is assumed constant and the concentration is a linear function of distance. The most useful application is with diaphragm cells, where diffusion takes place across a diaphragm between two solutions of uniform concentrations C' and C''. For this case the following equation can be derived:

$$\ln \frac{(C' - C'')_f}{(C' - C'')_i} = -\left[\left(\frac{1}{V'} + \frac{1}{V''}\right)\frac{A}{l}\right]Dt \tag{18}$$

where C' and C'' are uniform concentrations on each side of the diaphragm, f and i refer to the final and initial states respectively, V' and V'' are the volumes of solution on each side of the diaphragm, A is the effective path area for diffusion across the diaphragm, and l is the effective path length across the diaphragm.

The quantity β is often evaluated, where:

$$\beta = [(1/V') + (1/V'')](A/l) \tag{19}$$

Since A/l must be determined by calibration, the use of the same volumes during the calibration and the later experiments allows a constant value to be used for β for a given cell. Occasionally β changes with the age of the cell, owing to diaphragm wear.

B. SOLUTIONS OF FICK'S SECOND LAW WITH D A CONSTANT

Although D is almost invariably concentration-dependent, many experimental methods can be utilized over sufficiently small concentration ranges that D can be considered constant. In addition, many methods will yield a value for D equal to the true differential coefficient for the mean of the concentrations used if D can be assumed a linear function of concentration over the range under study.

The solutions of the equation

$$(\partial C/\partial t) = D(\partial^2 C/\partial x^2) \tag{20}$$

to be presented were originally developed by Fourier series analysis. Solutions will be given for a number of geometric possibilities useful in diffusion studies along with a brief mention of some of the common experimental techniques utilizing the given solutions.

1. Infinite cylinder

Boundary conditions:

Uniform cylinder cross-section and infinite length:

$$C = C_0' \text{ at a height of } x < 0 \text{ at } t = 0$$

$$C = C_0'' \text{ at a height of } x > 0 \text{ at } t = 0$$

Concentration distribution at time t:

$$C = C_0'' + \frac{(C_0' - C_0'')}{2}\left[1 - \operatorname{erf}\,(x/2\sqrt{Dt})\right] \tag{21}$$

where erf (x) is Gauss' error function (*cf.* 15).

Concentration gradient distribution at time t:

$$\frac{\partial C}{\partial x} = \frac{C_0' - C_0''}{2\sqrt{\pi D t}} \exp\,(-x^2/4Dt) \tag{22}$$

If the refractive index is linearly related to concentration and n'' and n' are the refractive indices for solutions of concentrations C_0'' and C_0', respectively, several useful equations relating the diffusion coefficient to refractive indices follow immediately.

Refractive index gradient distribution at time t:

$$(\partial n/\partial x) = [(n' - n'')/2\sqrt{\pi D t}]\,\exp\,(-x^2/4Dt) \tag{23}$$

Maximum gradient of refractive index at time t, located at $x = 0$:

$$(\partial n/\partial x) = (\partial n/\partial x)_{\max} = (n'' - n')/2\sqrt{\pi D t} \tag{24}$$

Applications: These are probably the most used of all solutions to Fick's laws, as the boundary conditions are fulfilled practically by allowing diffusion to proceed for such a time that the concentrations at the ends of the cell remain unchanged, a situation often designated as free diffusion. Most experiments today using optical techniques meet the above conditions and the calculations are based on either equation 23 or equation 24.

2. Semi-infinite cylinder

Boundary conditions:

Uniform cross-section with infinite length in positive x-direction:

$$C = C_0' \text{ for } 0 < x < h \text{ at } t = 0$$
$$C = C_0'' \text{ for } h < x < \infty \text{ at } t = 0$$

Concentration distribution at time t:

$$C = C_0'' + \left[\frac{C_0' - C_0''}{2}\right]\left[\operatorname{erf}\left(\frac{h - x}{2\sqrt{Dt}}\right) + \operatorname{erf}\left(\frac{h + x}{2\sqrt{Dt}}\right)\right] \tag{25}$$

Applications: Although the semi-infinite length requirement can be met experimentally by simply insuring that diffusion does not reach the presumed infinite end of the cell, the method has no advantages over the infinite cylinder case and is rarely utilized.

3. Semi-infinite cylinder with solute originally in a differential volume

Boundary conditions:

Uniform cross-section with infinite length in positive x-direction: $C = 0$ over all x except that an amount S of material is contained at $x = 0$ at the time $t = 0$.

Concentration distribution at time t:

$$C = (S/\sqrt{\pi Dt}) \exp(-x^2/4Dt) \tag{26}$$

Applications: Although the boundary conditions can never be met precisely, the use of radioactive isotopes increases analytical sensitivity to the point where the solute can be initially contained in approximately a differential volume.

4. Finite cylinder

Boundary conditions for the general case:

Length l with uniform cross-section:

$$C = C_0' \text{ at } 0 < x < h \text{ at } t = 0$$
$$C = 0 \text{ at } h < x \leqq l \text{ at } t = 0$$

Concentration distribution at time t:

$$C = A + \sum_{n=1}^{\infty} B_n \left[\exp(-1)\,\frac{n\pi}{l}^{2} Dt\right]\left[\cos\left(\frac{n\pi x}{l}\right)\right] \tag{27}$$

where A and B_n are constants which must be evaluated for the special case under consideration.

Boundary conditions for the case where the cylinder originally contains half solution and half solvent:

Length l with uniform cross-section:

$$C = C_0' \text{ at } 0 < x < l/2 \text{ at } t = 0$$
$$C = 0 \text{ at } l/2 < x < l \text{ at } t = 0$$

Concentration distribution at time t:

$$C = \frac{C_0'}{2} + \frac{C_0'}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} [1 - (-1)^n] \left[\cos \frac{n\pi x}{l} \right] \left[\exp (-1) \left(\frac{n\pi}{l} \right)^2 Dt \right] (-1)^{(n-1)/2} \tag{28}$$

Applications: This equation was used with earlier measurements in which the average concentration in each half of the diffusion cell was determined at the end of an experiment. It is currently useful with radioactive tracer techniques where it is possible to measure the radioactivity from a thin segment of a diffusion cell.

Boundary conditions for the case where the bottom fourth of the cell initially contains solution and the other portion contains solvent:

Length l with uniform cross-section:

$$C = C_0' \text{ for } 0 < x < h \text{ at } t = 0$$

$$C = 0 \text{ for } h < x \leqq l \text{ at } t = 0$$

$$h = \tfrac{1}{4} l$$

Concentration distribution at time t:

$$C = C_0' \left[\frac{1}{4} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \left(\frac{n\pi}{4} \right) \cos \left(\frac{n\pi x}{l} \right) \exp \left[(-1) \left(\frac{n\pi}{l} \right)^2 Dt \right] \right] \tag{29}$$

Applications: Calculations of the layer analysis techniques used by many early investigators were based on the above equation. Although the calculations are laborious, they were simplified by the tables of Stefan (108) and Kawalki (62) for certain of the functions in the above equation.

Boundary conditions for a cylinder closed at one end with the concentration maintained zero at the open end:

Length l with uniform cross-section:

$$C = C_0' \text{ for } 0 < x \leqq l \text{ at } t = 0$$

$$C = 0 \text{ for } x > l \text{ at all } t$$

Average concentration of material left in the cylinder at time t:

$$C_{\text{avg}} = \frac{8C_0'}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp [-(2n + 1)^2 \pi^2 Dt/4l^2] \tag{30}$$

Applications: Capillary-cell experiments are ordinarily calculated by this equation. In the usual experiment only two or three terms need to be evaluated.

C. SOLUTIONS OF FICK'S SECOND LAW WITH D A VARIABLE

1. Boltzmann method

Although more difficult mathematically it is possible to directly calculate values for the diffusion coefficient as a function of concentration over the range of concentrations in the diffusing zone. The classical solution of the equation:

$$\frac{\partial C}{\partial t} = D(C) \frac{\partial^2 C}{\partial x^2} + \mathrm{d}\, \frac{D(C)}{\mathrm{d}C} \left(\frac{\partial C}{\partial x} \right)^2 \tag{31}$$

was presented by Boltzmann (8) for the case of an infinite cylinder, and this solution has been discussed in detail by many later authors.

Boundary conditions:

Infinite cylinder of uniform cross-section:

$$C = C'_0 \text{ for } x < 0 \text{ at } t = 0$$

$$C = 0 \text{ for } x > 0 \text{ at } t = 0$$

Diffusion coefficient at concentration C at time t:

$$D = \left(\frac{1}{2t}\right)\left(\frac{\mathrm{d}x}{\mathrm{d}C}\right)\int_{C}^{C'_0} x\,\mathrm{d}C \tag{32}$$

The equation is evaluated by plotting C as a function of x and determining $\mathrm{d}x/\mathrm{d}C$ and the integral of $x(\mathrm{d}C)$ between the limits of C and C'_0 from this plot.

Applications: Although used by a number of earlier investigators to evaluate free diffusion experiments, this method has the disadvantage of requiring both integration and determination of slope by graphical methods which often introduce serious errors. For this reason it is little used today.

D. RELATIONSHIP BETWEEN DIFFERENTIAL AND INTEGRAL DIFFUSION COEFFICIENTS

Although it is experimentally possible in general to measure only integral diffusion coefficients, it is desirable at times to convert the measured integral coefficients into differential coefficients. The latter are more useful in that they represent point conditions and can be immediately used to compare data among investigators, whereas integral coefficients obtained by different experimental methods can be compared only qualitatively. The two coefficients are related rather simply mathematically. The differential coefficient by definition is expressed as:

$$D = -J/(\partial C/\partial x) \tag{33}$$

and the integral coefficient, $\bar{D}$, is equal to:

$$\bar{D} = -J(x' - x'')/(C' - C'') \tag{34}$$

For diffusion between concentrations C' and C'' it follows that:

$$\bar{D} = \frac{1}{(C' - C'')}\int_{C'}^{C''} D\,\mathrm{d}C \tag{35}$$

This relationship is particularly useful in work with diaphragm cells, and the conversion of such coefficients has been discussed in considerable detail by Gordon (42). Cases of free diffusion have been discussed by Kraus (69) and by Stokes (110). An important conclusion in both the above cases is that when the differential diffusion coefficient can be considered a linear function of concentration over the range under study, the observed integral coefficient is equal in value to the true differential coefficient for the mean of the two initial concentrations.

IV. EXPERIMENTAL TECHNIQUES FOR MEASURING LIQUID-DIFFUSION COEFFICIENTS

The great variety of experimental methods used to measure diffusion coefficients is evidence that considerable ingenuity and effort have been spent in devising equipment in which the variables of concentration, distance, and time can be observed in such a manner during a diffusion process that the diffusion coefficient, D, can be calculated from one of the various mathematical forms of the basic diffusion equations. Many of the techniques once used have been supplanted by those which are capable of either greater accuracy or a combination of simplicity and considerable accuracy. The most precise techniques in use today appear to be those utilizing optical methods, particularly interferometry, for continuously analyzing the changes of concentration with distance and time in a cell. The method which perhaps best combines reasonable experimental simplicity with accuracy is the diaphragm-cell technique. The recent availability of isotopes has aroused interest in self-diffusion measurements, and the peculiar problems of this type of measurement have been best solved by a variety of special techniques.

A number of the earlier experimental methods are described by Williams and Cady (136), and a general review of the experimental aspects of the diffusion field is included in the recent book by Jost (60). The review by Geddes (37) is particularly lucid and includes most of the recent advances in optical techniques. With the availability of the above summaries as well as others, little can be added unless it is in the form of details. For this reason only a brief summary of some major contributions to classical diffusion measurements will be included here, although several methods utilizing radioactive tracers will be discussed in somewhat more detail as they have not generally been reviewed previously.

There have been a number of ways mentioned in the literature for classifying diffusion measurements, but in this discussion experiments will be divided into three broad classes. The first type includes those techniques where diffusion occurs in a quasi-stationary state and it is possible to measure the diffusion rate and concentration gradient. The second type includes all the techniques where a given initial concentration distribution at a starting time is known and the concentration distribution at the end of the experiment can be determined. The third type is similar to the second, except that the concentration distribution is determined continuously or at intervals throughout the experiment. For both of the latter two classifications, the diffusion coefficient can be calculated from solutions of Fick's second law in the form of equation 20 if D can be considered independent of concentration or from the law in the form of equation 31 if D is considered dependent on concentration.

A. QUASI-STATIONARY DIFFUSION MEASUREMENTS

The quasi-stationary method is simpler to calculate and in general requires less equipment. The principles of such a method can be readily illustrated in terms of an experiment utilizing two large vessels connected by a relatively small tube of length l and cross-section A. At the start of an experiment the large vessels are filled with solutions C_0' and C_0'' and after a suitable time there will be a steady concentration gradient through the tube. In early work, after a steady state had been reached with concentrations C' and C'' in the two vessels at a time $t = 0$, diffusion was allowed to proceed until a time t when the concentrations were still substantially unchanged but an amount S of material had diffused. The diffusion flux is then simply $J = S/(\Delta t)(A)$. If D is not dependent on concentration, it can then be immediately calculated from Fick's first law, for $\partial C/\partial x$ is equal to $(C' - C'')/l$.

If D is dependent on concentration, the stationary concentration distribution will not be linear but will be some type of curve. Application of the previous equations will then yield an integral diffusion coefficient which can be converted into a differential coefficient by equation 35. If C can be measured as a function of x, D can easily be determined from the differential concentration differences, because the diffusion flux must be constant at any cross-section for a steady state. Since J is known and $\partial C/\partial x$ can be determined from the slopes of the curve of concentration versus distance, D is immediately calculable.

1. Constant flux methods

Fick (33) formulated his basic diffusion laws on steady-state experiments using a simple apparatus consisting of a vertical tube open at both ends, placed with its upper end in a reservoir of solvent and its bottom end in a reservoir of solution. Clack (18) achieved a high degree of accuracy with the stationary diffusion technique by using a square tube which was set up in such a manner that the refractive index of the system could be measured over the entire length of the tube within which the steady-state gradient was established. With the relation between refractive index and concentration known, $\partial C/\partial x$ could be computed for the entire column and thence the diffusion coefficient at any point. Although the method of Clack is capable of high precision, it has even more serious experimental disadvantages than the relatively complex optical methods and is consequently not used today.

2. Diaphragm cells

Since experimental techniques utilizing solutions of Fick's first law offer an easier approach to measuring diffusion coefficients, considerable work has been done to improve this type of measurement. The most successful has been the diaphragm-cell technique first introduced by Northrop and Anson (89). This is a simple experimental procedure in which diffusion takes place through a porous diaphragm connecting two cells in which the respective liquid concentrations are maintained uniform. Since the diaphragm has a greatly reduced cross-section, the lessened interfacial area between the two liquids eliminates some of the convection errors which often arise during diffusion of liquids in large cells. The diaphragm exhibits an effective cross-section, A, and a path length, l, to the diffusing liquids which must be determined experimentally by studying a system whose diffusion behavior is known. The cell is calibrated and diffusion coefficients are calculated by use of equation 18, which assumes a linear concentration gradient across the diaphragm and an invariant value of D.

Since the above assumptions are not generally true, errors are introduced into the above equation, but these have been analyzed and found to be small in the usual case. Barnes (6) has shown that the influence of the non-linear concentration gradient is ordinarily negligible and in most cases is essentially corrected by the calibration. Gordon (42) in his excellent review of both the experimental and theoretical background of diaphragm-cell measurements has shown how the measured integral coefficient can be converted into a differential coefficient. In particular, if the variation of D may be assumed linear over the concentration range of interest and if equal volumes of solutions are used on both sides of the diaphragm, the measured integral coefficient is equal to the true differential coefficient for the mean concentration.

Although the diaphragm-cell technique has been widely used for diffusion measurements, serious differences exist among data obtained by different investigators using this technique. Recent work on the ethanol–water system by Hammond and Stokes (51) and Smith and Storrow (106) disagree by as much as 100 per cent, yet each pair of investigators considered his results accurate to 1 and 3 per cent, respectively. One source of error no doubt lies in maintaining a constant cross-section for the calibration runs and the actual experimental runs, since entrapment of air or vapor could seriously alter the effective cross-section for diffusion. Another difficulty is the requirement that the logarithm of the ratio of concentration differences be used in equation 18 to calculate D. With small differences in initial concentration, extreme precision is required to reduce the error in D to a tolerable value because of the multiplying effects of the mathematical treatment.

Diaphragm cells have been used for several investigations of self-diffusion, using both non-radioactive and radioactive isotopes. The ability to withdraw samples for isotopic analysis is convenient, as *in situ* measurements of isotopic concentration by radioactivity or other means often pose difficult problems. The diaphragm-cell technique also has promise for work at higher temperatures, where difficulties with optical techniques increase significantly.

B. UNSTEADY-STATE DIFFUSION MEASUREMENTS WITH ANALYSIS AT END OF EXPERIMENT ONLY

The second classification of diffusion measurements comprises those methods in which the initial concentration distribution is known as well as the concentration distribution or an average concentration in parts of the diffusion system at some later time. Although mathematical solutions are theoretically possible for Fick's laws so long as the concentration distribution is a continuous function of distance and time, it was previously observed that for even simple boundary conditions the solutions become complex. For this reason almost all methods of this classification are based on a simple initial concentration distribution, usually that of a uniform C_0' in part of the cell and a uniform C_0'' in the other part. At the end of the experiment either the concentration distribution or the amount of material in various segments of the cell must be measured. Many of these techniques thus allow standard types of analysis to be made of samples removed from the system, but this simplicity is usually achieved at some expense in accuracy.

1. Capillary cells

One of the simplest and oldest methods of this category involves diffusion from a capillary tube into a much larger volume of solvent or solution of different concentration. Capillaries of uniform diameter, sealed at the bottom, are filled with a solution of known concentration. Since the volume in the capillary is so small compared to that in the vessel, the concentration in the latter may safely be assumed to remain constant throughout the experiment. At the end of an experiment the diffusion coefficient can be determined if one can measure either the concentration gradient in the capillary or the total amount of material passing into or out of the capillary. Since the latter is usually easier to determine, it is ordinarily the variable measured. For diffusion times of several days the diffusion coefficient can be simply calculated by using two or three terms of equation 30.

Although this method was used for some of the earliest diffusion measurements (*cf.* 46), the length of the experiments and the analytical difficulties, heightened because of the usual requirement of a rather small difference in initial concentration, caused the method to fall into disfavor. Some recent work by Haycock, Alder, and Hildebrand (53) in measuring the diffusion of iodine into carbon tetrachloride indicated that with modern microanalytical techniques good results can be obtained with this method. For ordinary diffusion measurements, however, it does not appear competitive with either the refined optical techniques or the diaphragm cell.

For self-diffusion measurements, particularly with radioactive materials, the capillary-cell technique has the economic and experimental advantages of requiring only small amounts of diffusing solution. These facts plus the basic simplicity of the method have caused its revival for measurements of self-diffusion of radioactive ions (124, 125, 127, 128) and of compounds tagged with both radioactive and non-radioactive elements (126, 127, 129). With non-radioactive isotopes, exacting density measurements or spectroscopic analyses are necessary, but with radioactive materials the isotopic concentration can be determined by adapting many standard techniques for radiation measurement. For example, in the work of Johnson and Babb (58) and of Wang (127), relatively simple adaptations of Geiger–Mueller tubes were adequate to measure the radioactivity of the small liquid samples.

2. Segmented cells

A method frequently used in earlier studies required that diffusion proceed in a cell of uniform cross-section of such a design that it was possible to determine the amount of material contained in various segments of the cell at the end of an experiment. The calculations for this method are rather laborious, but the tables of Stefan (108) and Kawalki (62), used in conjunction with equation 29, greatly facilitate the work. The general technique of layer analysis was used by the majority of early investigators in the field of liquid diffusion and was perfected by

Cohen and Bruins (19) to yield data with a precision of 1 per cent. The inability to eliminate boundary disturbances with this method, however, has caused it to be generally superseded by techniques of continuous analysis, particularly those based on optical principles.

A modern adaptation of the method of segmented analysis was used by Saxton and Drickamer (102) to measure the self-diffusion of liquid sulfur. They used a cell of fritted glass initially pumped full of liquid sulfur with a known amount of liquid radioactive sulfur-35 in a thin layer on one end of the cell. Diffusion was allowed to proceed, and at the end of an experiment the cell was quenched and the sulfur solidified. Samples of the frit were then sanded off and the radioactivity in each of the various slices was measured. Since this experiment closely approximated diffusion in a cylinder exposed to an instantaneous source of known intensity at one end and diffusion was not allowed to reach the opposite end, the diffusion coefficient could be simply calculated by equation 26.

C. UNSTEADY-STATE DIFFUSION MEASUREMENTS WITH CONTINUOUS OR INTERMITTENT ANALYSIS

In many respects the most desirable method of conducting a diffusion experiment is to use a suitable means of physical analysis to determine the concentration distribution as a function of time at any desired cross-section of a diffusion cell. As previously mentioned, it is desirable from a mathematical point of view to establish a simple initial concentration distribution, usually a uniform C_0' and a C_0'' separated by as sharp an interface as possible. Methods for observing concentration changes as diffusion proceeds are then limited only by the accuracy of the analytical method and the ease and ingenuity with which the analytical equipment can be used in conjunction with the diffusion cell. Although many methods of physical analysis will perform under these conditions, only a few have appeared to be sufficiently accurate for general use. These include measurements of density, of the absorption of light, of the total reflection of light, of radioactivity, and of refractive index. Today refractive index measurements have almost replaced the other types except for radioactivity measurements in self-diffusion studies.

Since all other analytical methods except radioactivity and refractive index are now little used and are reviewed elsewhere, they will be dismissed here with only a reference to a typical investigation using each method. Continuous measurements of density using calibrated floats in the diffusing solutions were performed by Gerlach (38). The absorption of light is discussed by Longsworth (77), and Zuber (138, 139) describes micromethods using both absorption and total reflection of light. A number of special techniques have also been used for diffusion measurements, but these generally appear to offer little utility for wide applications. These methods include measurements of electrical capacitance (120), surface tension (26), and the velocity of sound (61).

1. *Radioactivity measurements*

The availability of radioactive isotopes has made possible an additional technique of analysis for measuring diffusion rates of liquids, particularly for studies of self-diffusion. Using isotopes emitting beta particles, Walker (122) determined the concentration gradient during the diffusion process by measuring the activity through a small slit in a shield surrounding the diffusion cell. This method is subject to the inaccuracy introduced by a finite slit width and is limited to use with pure beta emitters; however, the results of Walker on a phosphoric acid system agreed to within 4 per cent with other published data on this system.

Although the conversion of a conventional diffusion technique for use with radioactive isotopes as shown above is of interest, the ability to measure very small concentrations of radioactive material accurately has allowed the utilization of experimental methods that are not feasible when used with ordinary analytical techniques. In particular, it is possible to both readily establish and determine concentrations of radioactive material in very thin segments of a diffusion cell. One technique based on this fact is the continuous measurement of the amount of material present in a thin layer at the end of a diffusion cell. This is possible if the penetration of the emitted particles is sufficiently small so that only the surface layer contributes to the observed radioactivity. This condition is satisfied by the beta particles emitted from sulfur-35 with an energy of 0.167 m.e.v. and those emitted from carbon-14 with an energy of 0.154 m.e.v. To simplify both experimental procedure and mathematical calculations, the diffusion cell used in this method is ordinarily made of two equal lengths of fritted steel or glass, one of which at the start contains a uniform concentration of radioactive material. The overall chemical concentration is the same in both parts of the cell and is presumed to remain so throughout the experiment. To determine the self-diffusion coefficient it is then necessary only to determine, by any suitable means, the number of particles emitted from the thin surface layer of the solution in the cell.

The method of calculating the diffusion coefficient from such measurements was initially presented by Timmerhaus and Drickamer (118). For a cell with the initial conditions indicated above, the concentration of radioactive material at time t is given by equation 28. With a fritted cell, the length must be determined by diffusion experiments with a system of known diffusion behavior, as the length will in general not be the actual geometric length. With a counting device to measure the rate of particle emission at l, radiation at any point x will be counted with an efficiency relative to the efficiency at l, dependent on the strength of the radiation. If the tracer element gives off only one kind of radiation, the efficiency F may be expressed as:

$$F = \exp -[1 - (x/\lambda)] \tag{36}$$

where λ is the path length of the radiated particle. If λ is very small, the usual case with weak radiation, the intensity of radiation at point l may be expressed as follows:

$$\int_{\infty}^{l} FC\,\mathrm{d}x = \frac{C_0\lambda}{2} + \frac{C_0\lambda}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}[1 - (-1)^n](-1)^{(n-1)/2}\exp\left[(-1)\left(\frac{n\pi^2}{l}\right)Dt\right](-1)^{(n+1)} \tag{37}$$

At equilibrium in the cell when the overall concentration is $C_0/2$, the intensity of counting may be designated as I_f. If observations are restricted to relatively long times after diffusion begins, the following relation holds:

$$I = I_f - (2\pi) \exp [(-1)(n\pi/l)^2 Dt] \tag{38}$$

A plot of $\ln(I_f - I)$ vs. t then gives a line of slope $(\pi^2/l^2)(D)$, from which a value for D is readily obtained. Sometimes it is inconvenient to determine the intensity at equilibrium; if so, it is possible to calculate the diffusion coefficient by a graphical plot of $(\pi^2/l^2)(D)$ versus the quantity $(I_{t_1} - I_{t_2})/(I_{t_3} - I_{t_4})$, with the additional parameter of given values of t_1, t_2, t_3, and t_4. For given values of t and assumed values of D, the required values of the intensity of radiation ratio can be calculated to satisfy equation 38. Once this plot is available, knowledge of the actual radiation intensity ratio for a given set of times equal to those for which the plot was prepared will immediately give the desired diffusion coefficient if l is known from a calibration experiment.

For determinations at atmospheric pressure the counting rate at the end of the cell can be measured by placing the cell adjacent to a thin-walled Geiger–Mueller tube. The most useful application of this technique, however, appears to be for measurements under high pressure where conventional methods for measuring radioactivity are not applicable.

Drickamer and coworkers (21, 68) successfully adapted a scintillation counting technique to such a cell. The cell was placed inside a steel bomb and the cell halves brought together mechanically at the start of an experiment. A crystal of either sodium iodide or anthracene was placed adjacent to the end of the cell. These crystals when exposed to radiation have the property of emitting light, which in the above technique was conducted by means of a lucite or quartz rod to a photomultiplier tube. The energy output from the photomultiplier tube was fed into a counting circuit which essentially registered the number of light pulses emitted from the crystal and hence indicated the number of particles striking the crystal.

2. Refractive index measurements

There is now little doubt that for systems with a suitable difference in refractive index between the two components, measuring the changes in this property as diffusion proceeds in a properly designed cell is currently the most reliable way to determine a liquid-diffusion coefficient. Although the optical techniques are quite important and require considerable experimental equipment and care in both obtaining and analyzing the required refractive index patterns, the material is well treated by Geddes (37) and others, so the comments here will be brief.

With most optical techniques, the experimental diffusion cell is such that a uniform denser solution of concentration C_0' is placed beneath a uniform solution of concentration C_0'' at the start of an experiment with as sharp an interface between the two solutions as possible. Considerable credit for the success of modern methods must go to the improvements in mechanisms for obtaining this sharp boundary, as no method will yield precise results without clearly defined initial conditions. The development of cells is also well summarized by Geddes (37), but mention should be made of the double-slit sharpening technique used by Caldwell and Babb (10). In this work two horizontal slits were built into the cell at the desired interface height from which solution could be withdrawn until the boundary was as sharp as possible. By withdrawing liquid from two slits a sharper interface could usually be attained fairly rapidly.

Although Gouy (45) considered refractive index measurements for diffusion experiments and discussed the expected interference phenomena, Wiener (133) was the first to develop the equation for the curvature of a light beam passing through a diffusing solution and to perform experiments. He developed equation 24 for the case where the refractive index is a linear function of concentration and with suitable optical equipment actually reproduced a photograph on a 45° axis of the refractive index gradient through a diffusing solution. Thovert (116, 117), in the course of his extensive work on diffusion, modified Wiener's technique so that a photograph of the concentration gradient was directly produced in rectangular coordinates. Thovert also used the method whereby the point of maximum curvature of the refractive index gradient was determined from the interference bands. The diffusion coefficient was then calculated from equation 24. Lamm (72) modified this technique in his well-known scale method, in which the displacements of the marks on a uniformly graduated scale are photographed through a diffusing solution. This technique requires very accurate measurements of the scale mark displacements and is extremely laborious to calculate.

It may be mentioned that in most optical techniques, diffusion cells of such a size are used that diffusion does not reach the ends of the cell, so that the simpler mathematical solutions of Fick's laws as given in equations 21 through 24 may be used to calculate the diffusion coefficient.

Although the interference phenomenon was discussed by Gouy (45) in 1880, a quantitative interpretation was not presented until 1947 by Kegeles and Gosting (63) in conjunction with an experimental test of the method by Longsworth (78). Coulson (20) and coworkers have also reported on the same method of observing diffusion. Interferometric methods have since been used by a number of investigators with a precision of 0.1 per cent for non-volatile liquids and better than 1 per cent for volatile liquids.

Several methods of solving for the diffusion coefficient are possible with interferometric methods. The best-known method is to utilize the position of the integral fringes as described by Longsworth (79). Another method, suggested by Svensson (114), has been used successfully by Caldwell and Babb (10, 11); in this method the differential solution of Fick's law as shown in equation 24 is used directly. The required refractive index values are such that they may be expressed in terms of arbitrary fringe numbers directly from the interference photographs.

V. MUTUAL DIFFUSION THEORIES

Many methods for estimating diffusion coefficients for a given system have been proposed since Fick first developed his basic diffusion law. The treatment for diffusion in gases has been adequately developed on theoretical bases (*cf.* 17), and diffusion coefficients in gases have been correlated exceptionally well by an empirical equation proposed by Gilliland (39) and based on the form suggested by several theories of gaseous diffusion. The phenomenon of solid diffusion is also fairly well understood and has been reviewed by several authors (*cf.* Barrer (7) and Jost (60)). In the case of liquids no completely satisfactory method has yet been proposed for estimating diffusion coefficients from either basic molecular data or other physical properties of a system. This is no doubt largely due to the lack of understanding of the liquid state which makes the basic premises of any proposed theory somewhat uncertain.

A. LIQUID-STATE THEORY APPLIED TO DIFFUSION

In recent years a number of authors have presented theories attempting to explain the liquid state, but usually these theories either lack accuracy in their basic assumptions or else are extremely complex. At present, rigorous theories have limited application, unless extensive simplifications and approximations are made. As a result the complex bases of the theories are invalidated. From a practical standpoint, more success often results from a simple "model" structure which is known to be inexact but which can be treated simpler mathematically. Although any detailed discussion of liquid-state theory is beyond the intent of this review, several concepts particularly significant with respect to diffusion will be mentioned briefly. For detailed discussions of liquid-state theory, the reader should refer to one of the many presentations of liquid-state theory, such as those by Born (9), Frenkel (35), Green (48), Jaffe (57), Kirkwood (66, 67), and Yang (137).

Attempts to formulate mathematically the behavior of liquids have usually been based on a model of either a quasi-crystalline state or a condensed gas, but neither approach has yielded entirely satisfactory results. There is some evidence obtained by x-ray investigations that in liquids a tendency toward order exists about any given molecule on a microscopic basis. This order tends to decrease rapidly with distance from the reference molecule and the assumption of an ordered lattice structure in liquids, similar to that in solids, is apparently not justified even on a microscopic basis. Nevertheless, certain phenomena of liquids can be treated rather successfully by assuming an ordered lattice, but the difficulties increase when considering kinetic phenomena because the deviations from an ordered structure are then of the most importance.

In relating liquid structure to an ordered lattice, it is presumed that the holes which exist in the liquid structure introduce apparent disorder as do vacant sites in the analogous case of imperfect crystals. The holes are simply the result of molecules being absent from a given position in the structure, and the number of holes increases with temperature as the liquid becomes less dense. Molecular motion then occurs as molecules move into available holes from a given site in the lattice and create holes in the spaces they vacate.

The treatment of liquids as condensed gases is based on the kinetic theory of fluids originated by Maxwell (84) and Boltzmann (8), highly developed by Chapman (16) and Enskog (28), and summarized in the treatise by Chapman and Cowling (17). The regularity of liquid structure shown by x-rays is explained on a kinetic basis by the existence of a radial distribution function. The mathematical development of such a function is exceedingly complex but has been handled with considerable success by Kirkwood and coworkers (67).

Several assumptions inherent in kinetic theory development make it of questionable value when applied to liquids. The first is that molecules experience only "binary encounters," an assumption which is certainly invalid, since the path followed by a molecule in a liquid is very complex and can only be described in a statistical sense. Another assumption in the theory is that which is required to determine the mean force exerted on a molecule with a definite position and velocity when it collides with other molecules. Boltzmann assumed that the probability was based on the position of the first molecule, but in non-uniform fluids this effect is influenced by local gradients of density, temperature, and macroscopic velocity. It is possible to apply correction terms to include these effects but when clusters of molecules bound by intermolecular forces exist, the mathematical difficulty becomes enormous.

As discussed earlier, diffusion occurs because of the unordered thermal motion of the fluid molecules, causing them to move from point to point in the fluid. Statistically more will move from the region where a given type was originally in a higher concentration to the region where this species was originally in a lesser concentration, resulting in an observable net transport. Since the net diffusion then depends only on the thermal motion of the molecules, it is possible to relate the diffusion coefficient to the velocity distribution functions of the molecular types present in a liquid mixture (*cf.* Green (48)). Although diffusion can be explained solely on the basis of velocity distribution, the molecular structure of the fluid and the intermolecular forces influence this velocity distribution in such a manner that it cannot be evaluated for conditions existing during the diffusion process. The formulation of the distribution function for associated molecules or those with unsymmetrical force fields is particularly difficult. Because of these problems the history of diffusion theory contains many attempts to evaluate diffusivities based on simplified conditions or analogies to other processes.

B. EARLY THEORIES OF DIFFUSION

Historically, attempts to develop suitable expressions for the diffusion coefficient have generally followed either a kinetic, a hydrodynamic, or a thermodynamic approach to the problem. Initial kinetic approaches utilized the fact that in gaseous systems the average kinetic energy of a molecule is a function of the temperature only. Assuming that the rate of diffusion depends only on the translational velocity, the result is Graham's law, which states that the diffusivity varies inversely as the square root of the molecular weight. While valid for gaseous diffusion and reasonably valid for gases diffusing into liquids, it is generally quite inadequate for liquid systems.

The hydrodynamic approach had its start in 1858 when Wiedemann (132) observed that in the dilute solutions then studied D varied inversely as the viscosity of the solvent. Walden (121) combined this observation with Graham's law to establish the relation that $D\eta M^{1/2}$ is a constant for a given solvent, where η is the solvent viscosity and M the molecular weight of the solute.

The classical hydrodynamic development of the diffusion coefficient was made independently by Sutherland (112) and Einstein (27), who showed that:

$$D = RT/6\pi\eta rN \tag{39}$$

where r is the radius of the diffusing molecule. As shown earlier, this relation can be developed by considering the driving force for diffusion to be osmotic pressure and the frictional resistance to be $6\pi\eta r$ as given by Stokes' law.

Equation 39 has been shown to apply accurately for particles of colloidal size by a great number of investigators, but generally its accuracy decreases as the particle size decreases. This is not unexpected, as Stokes' law is based on the premise that the solvent is a continuum, a premise which can no longer be true when the solute particles approach those of the solvent in size. Ordinarily the viscosity considered is that of the solvent alone, and this would further restrict its use to dilute solutions.

C. KINETIC THEORY OF ARNOLD

The first successful approach based on kinetic theory was made by Arnold (4), who applied classical gaseous kinetic theory to diffusion in liquids after making certain corrections for the closer molecular spacing. By making the following assumptions:

1. All collisions are binary,
2. The collision rate is unaffected by the volume occupied by the molecules, and
3. Intermolecular attractions are negligible,

Arnold deduced the following equation:

$$D = \frac{B\sqrt{(1/M_1) + (1/M_2)}}{S^2}\,(V_2) \tag{40}$$

where B is a proportionality constant, M_1 and M_2 are the molecular weights of the solute and solvent, S^2 is the square of the sum of the molecular diameters, and V_2 is the molar volume of the solvent. It is noted that this equation is similar to that developed by Gilliland for gases.

Since the above assumptions are invalid for liquid systems, a correction term F was introduced into the denominator to correct the expression in a semi-empirical manner. The first two assumptions may be handled approximately by the constant B for any given system. The role of the intermolecular forces is complex, and Arnold related the F term to the viscosity of the fluid, which is in turn related to momentum transfer. The following bases were used for evaluating F: (1) in dilute systems F is essentially a function of the solvent properties; (2) F is directly proportional to the square root of the solvent viscosity; (3) when either the solvent or the solute is associated, additional correction factors designated as A_1 and A_2 for the solute and solvent must be introduced. This results in the final equation for D:

$$D = \frac{B\sqrt{(1/M_1) + (1/M_2)}}{A_1 A_2 \eta_2^{1/2} S^2} \tag{41}$$

It is noted that the expression for F includes V_2, so the latter quantity does not appear in equation 41.

Much of the data available at the time his theory was presented was studied by Arnold, and the correlation with the equation was reasonably good. The major difficulty is the fact that many liquids require a correction term for association which must be evaluated experimentally. In general this correction term is approximately a constant for a given substance, although its value differs between the roles of solvent and solute. Arnold pointed out that the method for correcting for association with A factors appeared to yield better results than when a multiplying factor for M and V was used, as required by the usual concept of association for abnormal substances.

On the basis of the limited amount of data then available over a range of temperature, Arnold proposed that the variation of D with temperature was linear. Later work by many authors has shown that in this respect Arnold was in error, as the temperature variation is clearly exponential.

Recently Caldwell and Babb (10) showed that the Arnold equation predicted diffusion coefficients with an average deviation of 10 per cent for dilute concentrations in three ideal systems. Although Arnold apparently did not intend the equation to be used in other than dilute solutions, Trevoy and Drickamer (119) used it to correlate data for some equimolal mixtures with considerable success. While the basic assumptions for Arnold's development are somewhat tenuous, it appears to be one of the best methods yet proposed for estimating diffusion coefficients in dilute solution, providing data are available for the components so that necessary association factors can be assigned.

D. KINETIC THEORY OF EYRING

A recent kinetic approach to the diffusion problem based on reaction-rate theory is due primarily to Eyring. The work was initially presented in a number of papers by Eyring and coworkers (32, 30, 31, 55, 64, 96, 100, 107) and summarized by Glasstone, Laidler, and Eyring (41). The development is based on the hole theory concept of the liquid state, which describes diffusion as a process in which molecules move from a given position into an adjacent hole in the liquid structure. The holes in the liquids are similar to gas molecules in behavior, but the translational motion of the holes in a liquid is not as free as motion in a gas, so the partition function for holes is less than that for gases. If E is the bond strength between liquid molecules, the energy to vaporize a single molecule is $E/2$ if no hole is left in the liquid. This same amount of energy, $E/2$, is required to make a hole in the liquid of a size to accommodate a single molecule.

Eyring and coworkers applied absolute rate theory to diffusion by assuming that the energy of activation for the diffusion process is that energy required to form the extra space in the liquid to allow the molecules to move. In diffusion and also in viscous flow the passing of two molecules requires extra space, which is not necessarily the size of a molecule. The energy of activation for diffusion will then be some fraction of the energy of vaporization, $\Delta E_{\text{diff}} = \Delta E_{\text{vap}}/n$.

The initial development was for the case where the standard free energy is the same in all equilibrium positions occupied by a molecule during the diffusion process, thereby restricting consideration to ideal solutions. Since the Eyring treatment has been widely applied, a brief derivation of the basic equations will be shown in the following paragraphs.

Let λ be the distance between equilibrium positions of a molecule diffusing in the x-direction from an initial concentration of C. The concentration at the next equilibrium stage will be $C + \lambda(\mathrm{d}C/\mathrm{d}x)$. The net flow in this process may be shown to be

$$v = -N\lambda^2\kappa(\mathrm{d}C/\mathrm{d}x) \tag{42}$$

where κ is the specific reaction rate for diffusion and N is Avogadro's number.

Applying the basic form of the expression for rate of reaction, κ may be expressed as:

$$\kappa = \frac{(kTF^{\ddagger})}{(hF)} \exp\,(-\epsilon_0/kT) \tag{43}$$

where ϵ_0 is the activation energy for diffusion per molecule at 0°K. From the basic diffusion law it follows that

$$D = \lambda^2\kappa \tag{44}$$

and this may be combined with equation 43 to give

$$D = \frac{(\lambda^2kTF^{\ddagger})}{(hF)} \exp\,(-\epsilon_0/kT) \tag{45}$$

Assuming that the only degree of freedom is a translational one, the expression for D reduces to:

$$D = \frac{\lambda^2}{V_f^{1/3}}\left(\frac{kT}{2\pi m}\right)^{1/2} \exp\,(-\Delta E_{\text{vap}}/nRT) \tag{46}$$

where the assumption is made that $\Delta E_{\text{diff}} = \Delta E_{\text{vap}}/n$. λ may be approximated by $(V/N)^{1/3}$, where V is the molar volume. The free volume, V_f, may be estimated by one of several methods. Eyring and Hirschfelder (32) showed that it may be approximated by the equation

$$V_f^{1/3} = (cRTV^{1/3})/(N^{1/3}\Delta E_{\text{vap}}) \tag{47}$$

where c is a constant depending on the molecular arrangement, having a value of 2 for a cubical pattern. Kincaid and Eyring (64) also have suggested the relation:

$$V_f = V^{1/3}(U_{\text{gas}}/U_{\text{liq}}) \tag{48}$$

where U is the velocity of sound.

In utilizing the equations developed by Eyring in concentrated solutions, appropriate molar averages must be determined for the various properties.

Although the above method yields results of the proper order of magnitude, a survey of some of the calculated values of diffusion coefficients compared to experimental values reveals its shortcomings. In one of the original papers by Stearn, Irish, and Eyring (107) the observed diffusion rates of approximately twenty substances in dilute aqueous solution were 1.3 to 3.5 times higher than the calculated values, the differences being least for sugars and highest for alcohols. Likewise, data for the diffusion of approximately forty organic substances into benzene and other solvents showed the ratio of observed to calculated diffusion coefficients to be 0.19–0.77. An excellent test of the correlation can be made with self-diffusion data of pure substances, which can be treated as ideal solutions. Data of Graupner and Winter (47), when used to compare calculated with experimental values, showed that for benzene the calculated coefficient was about 30 per cent of the experimental, while for ethanol the calculated coefficient was three times greater and for water, ten times greater. Trevoy and Drickamer (119) calculated the diffusion coefficients for twelve equimolal mixtures of various hydrocarbons and benzene and hydrocarbons with hydrocarbons, most of which formed relatively ideal mixtures, and found the calculated value to be generally three to five times the experimental value. In the recent work of Caldwell and Babb (10) two ideal systems agreed within 10 per cent between the calculated and experimental values; however, when the frequency and exponential factors of the Eyring equation were calculated individually, it was observed that the overall agreement was partly fortuitous. Sufficient data have now been correlated with the Eyring equation to show that at least with present knowledge of molecular parameters the method yields values only of the proper order of magnitude. One factor which may contribute to these shortcomings is that in dilute solutions the solute does not significantly alter the equilibrium length, λ, or the free volume, and yet observation of self-diffusion measurements clearly shows that in dilute solutions the characteristic self-diffusion rate of each component may be greatly different; hence more weight should probably be given to the solute properties. As pointed out by Kincaid, Eyring, and Stearn (65), there may also be changes in the freedom of rotation in the activated state as compared to the normal state; hence the ratio of partition functions based only on translational motion may not be justified.

The Eyring equation does predict an exponential temperature effect on diffusion rates which has been verified by a significant amount of data. The results of Cohen and Bruins (19), Scheffer and Scheffer (103), Graupner and Winter (47), Partington, Hudson, and Bagnall (95), and Caldwell and Babb (10), as well as those of many other investigators, all show that the variation of diffusion with temperature is exponential in form.

Some useful results with the equation for diffusivity are reached by combining it with the equation developed by Eyring (31) for viscosity. The following equation was developed by applying reaction-rate theory to viscosity:

$$\eta = (\lambda_1/\lambda_2\lambda_3)(kT/\lambda^2\kappa_{\text{visc}}) \qquad (49)$$

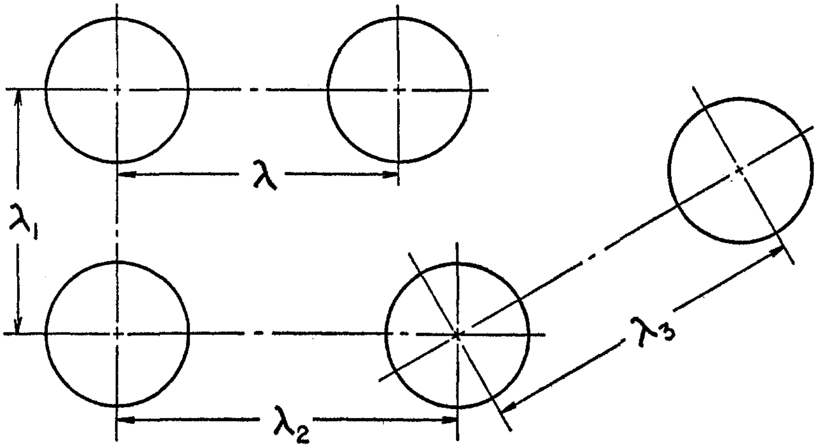

FIG. 1. Intermolecular distances used in the Eyring equation

where λ_1, λ_2, and λ_3 are the three distances between molecules as shown in figure 1. As shown, diffusion is in the dimension of λ_2, and it should be pointed out that λ_2 need not equal λ, the equilibrium distance between molecules moving in that dimension.

By assuming that λ and κ are the same for the processes of diffusion and viscous flow, the following equation can be derived for D:

$$D = \lambda_1 kT/\lambda_2\lambda_3\eta \tag{50}$$

This is a particularly useful relation and has been used by several investigators to develop semiempirical relations for estimating diffusivities. It is observed that the linear relation between D, T, and η is similar in form to that proposed empirically by earlier investigators and even now assigning values for the intermolecular distances for other than a pure liquid requires rather arbitrary assumptions.

By assuming that the liquid structure is made of spherical molecules, with radius r, that are packed to touch, equation 50 may be written as:

$$D = RT/a2r\eta N \tag{51}$$

where a is a factor that is dependent on the size of the solute and solvent molecules. In self-diffusion of simple molecules a should be unity, as the distances λ_1, λ_2, and λ_3 should all be equal. At the other extreme, with the diffusion of large molecules in a solvent of small molecules, it may be assumed that the rate-determining step in the motion of the large molecules is the diffusion of the small molecules around the oncoming large molecules. In this case a in equation 51 becomes 3π and r is the radius of the large molecule, resulting in the familiar Stokes–Einstein equation. For other than self-diffusion of a pure liquid and the diffusion of large molecules, the value for a becomes unpredictable. With molecules of intermediate size it is also difficult to assign an appropriate value for r.

If the assumption of an equal rate constant for viscosity and diffusion is not correct, then equation 51 must be modified to:

$$D = (\lambda_1 kT/\lambda_2\lambda_3\eta)(\kappa_{\text{visc}}/\kappa_{\text{diff}}) \tag{52}$$

where the ratio $(\kappa_{\text{visc}}/\kappa_{\text{diff}})$ must be determined for the system under study. The differences between the phenomena of diffusion and viscous flow have been recently discussed by Li and Chang (76) from the standpoint that Eyring's basic equation for viscosity should include a factor for relative velocity. The previous equations developed by Eyring are restricted to ideal solutions, but by considering the changes in free energy with concentration, the values for the diffusion coefficient were corrected for solution non-ideality. For the case where the diffusion process is considered to be the passing of two molecules the following expression was derived:

$$D_1 = D_i(1 + \partial \ln \gamma_1/N_2\, \partial \ln N_1) \tag{53}$$

where D_i is the ideal coefficient. When the unit process is considered to be the motion of a single molecule, the following equation was derived:

$$D_1 = D_i(1 + \partial \ln \gamma_1/\partial \ln N_1) \tag{54}$$

Rate theory does not indicate which mechanism is preferable, but the development of expressions for diffusivity by thermodynamics indicates that the latter is more probable.

A convenient way of treating this correction is to multiply both sides of equation 54 by the viscosity, η, of the system, thus:

$$D_1\eta = D_i\eta(1 + \partial \ln \gamma_1/\partial \ln N_1) \tag{55}$$

If D_i is replaced by the expression for the ideal diffusivity:

$$D_1\eta = (\lambda_1 kT/\lambda_2\lambda_3)(1 + \partial \ln \gamma_1/\partial \ln N_1) \tag{56}$$

The activity correction may be calculated from partial vapor pressure data, assuming that the behavior of the gas phase is ideal, generally a valid assumption at low pressures.

Powell, Roseveare, and Eyring (96) corrected the observed data of Lemonde (75) for the systems chloroform–acetone, chloroform–ether, and *n*-propyl alcohol–water and found that the $D\eta$ product became more nearly linear after the application of the correction. Unfortunately not all systems are significantly linearized by such a correction. Kincaid, Eyring, and Stern (65) discussed the methanol–water and ethanol–water systems and Caldwell and Babb (11) the methanol–benzene system. No final explanation has been given why there is no significant tendency toward linearity for systems of the above types, but Eyring and coworkers ascribed some of the difference to rotational terms which were neglected in the partition function ratio in the basic development of his theory.

E. RANDOM MOTION DEVELOPMENT OF THE DIFFUSION COEFFICIENT

Although the diffusion coefficient was previously developed from consideration of random molecular motion by an elementary treatment, Ogston (91)

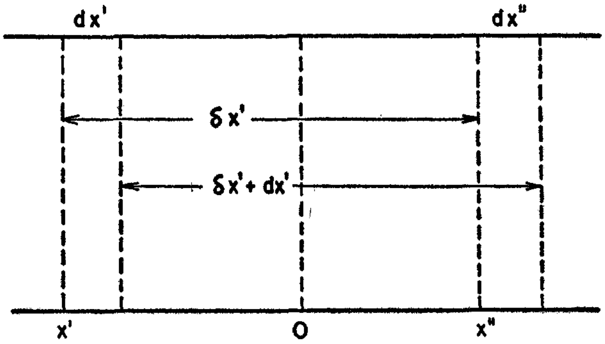

FIG. 2. Molecular displacements in the diffusion process

has recently discussed the problem for non-ideal solutions in the following manner.

With reference to figure 2, consider the displacements taking place between laminae at x' and x'' across a plane within a very short interval of time. All particles moving to the right from between x' and $(x' + \mathrm{d}x')$ will arrive between x'' and $(x'' + \mathrm{d}x'')$ and vice versa. The flux is then:

$$\mathrm{d}J_{x'} = C_{x'}\,\mathrm{d}x'\chi_{x'+} - C_{x''}\,\mathrm{d}x''\chi_{x''-} \tag{57}$$

where $\chi_{x'+}$ and $\chi_{x''-}$ are the frequencies of motion from the positions and directions shown. From the principle of microscopic reversibility, $\chi_{x'+}$ and $\chi_{x''-}$ each contain a factor typical of the point of origin and a factor typical of the transition; hence

$$\chi_{x'+} = \phi(x')\phi''(x', x'') \tag{58}$$

$$\chi_{x''-} = \phi(x'')\phi''(x', x'') \tag{59}$$

The flux may then be expressed as follows:

$$\mathrm{d}J_{x'} = -\phi'(x', x'')\,\frac{\partial}{\partial x}\,(C_x\mathrm{d}x\phi(x))\delta x' \tag{60}$$

It may be shown that:

$$\mathrm{d}x'' - \mathrm{d}x' = \delta'_{x'}(\partial \mathrm{d}x'/\partial x) = \mathrm{d}x'(\partial\delta'_{x'}/\partial x) \tag{61}$$

The flux then becomes:

$$\mathrm{d}J_{x'} = -\phi(x')\phi(x', x'')\delta_{x'}\left[1 + \frac{\partial \ln \delta'}{\partial \ln C} + \frac{\partial \ln \phi(x)}{\partial \ln C}\right]\frac{\partial C}{\partial x}\,(\mathrm{d}x') \tag{62}$$

Integration between the limits of zero and a value of x equal to $(-\delta')$ gives the total flux. The equation is simplified by referring the quantities to the position $x = 0$. The total flux thus obtained is:

$$J = -\phi(0)\phi'(0, 0)\delta_0'^2\left[1 + \frac{\partial \ln \delta'}{\partial \ln C} + \frac{\partial \ln \phi(x)}{\partial \ln C}\right]\frac{\partial C}{\partial x} \tag{63}$$

If the $\phi(0)\phi'(0, 0)$ is represented as $k_0/2$, the total flux becomes:

$$J = \frac{-\delta_0'^2 k_0}{2}\left\{1 + \frac{\partial \ln \delta'}{\partial \ln C} + \frac{\partial \ln \phi(x)}{\partial \ln C}\right\}\frac{\partial C}{\partial x} \tag{64}$$

Since x is a function of C, the above equation may be written as:

$$J = \frac{-\delta_0'^2 k_0}{2}\left[1 + \frac{\partial \ln \delta'}{\partial \ln x} + \frac{\partial \ln \phi(x)}{\partial \ln x}\right]\frac{\partial C}{\partial x} \tag{65}$$

Practically, the term in parentheses can rarely be evaluated, but it serves somewhat the same purpose as the activity correction in other expressions for the diffusion coefficient.

F. HYDRODYNAMIC AND THERMODYNAMIC DEVELOPMENTS OF DIFFUSION COEFFICIENTS

Although the classical efforts to utilize thermodynamics to evaluate diffusion coefficients have usually combined thermodynamic and hydrodynamic principles, efforts have recently been made to develop an expression for the diffusion coefficient by use of the thermodynamics of irreversible processes. This will be discussed after illustrating the usual hydrodynamic approach.

1. *Hydrodynamic development*

The following derivation is adapted from that initially presented by Hartley and Crank (52). Let a concentration C_A of component A in a binary solution be maintained in equilibrium by applying a force F_A per mole of A in the direction of increasing x. This force is purely hypothetical but is useful in applying hydrodynamic principles. In an ideal solution:

$$F_A = RT(\partial \ln C_A/\partial x) \tag{66}$$

If there were no concentration gradient present, F_A would produce a real average velocity v_A of the A molecules in the direction of increasing x where

$$v_A = (F_A/N)(1/\sigma_A\eta) \tag{67}$$

and $\sigma_A\eta$ is a resistance to flow dependent on the composition and viscosity of the solution. The above flow will cause a rate of transfer S_A' moles per second across unit cross-section of area where:

$$S_A' = (F_A/N)(1/\sigma_A\eta)C_A \tag{68}$$

If the concentration gradient assumed above is present but with no corresponding force, the gradient will produce a transfer by diffusion equal in magnitude to that deduced above but opposite in algebraic sign, $S_A = -S_A'$. From the basic diffusion law:

$$S_A = -D_A(\partial C_A/\partial x) \tag{69}$$

and thence:

$$D_A = (RT/N)(1/\sigma_A\eta) \tag{70}$$

In any real solution further complications arise. The force used in the above development must be based on activity; hence,

$$F_A = (RT)(\partial \ln N_A\gamma_A/\partial x) = \text{grad } \mu \tag{71}$$

The velocity of the molecules will affect the randomness of the molecular motion, but this is taken care of empirically by the resistance terms designated σ, which will be a function of the solution composition. The displacement of one molecular species by another must also be considered, as this will introduce mass flow in the general case. When the partial volumes are constant, the following equation results for D_A:

$$D_A = (RT/N\sigma_A\eta)(\partial \ln N_A\gamma_A/\partial \ln C_A) \tag{72}$$

Consideration of some basic relations between volume and concentration allows the above equation to be rewritten as:

$$D_A = (RT/N\sigma_A\eta)(N_A/V_BC_A)(1 + \partial \ln \gamma_A/\partial \ln N_A) \tag{73}$$

An equation similar to that for D_A can be written for D_B:

$$D_B = (RT/N\sigma_B\eta)(N_B/V_AC_B)(1 + \partial \ln \gamma_B/\partial \ln N_B) \tag{74}$$

Hartley and Crank (52) have further shown that under constant volume conditions a mutual diffusion coefficient can be defined by

$$D_{AB} = V_AC_A(D_B - D_A) + D_A \tag{75}$$

where V_A and V_B are assumed to be independent of composition. This relation, when combined with the Gibbs–Duhem equation, yields an expression for the mutual diffusion coefficient for a non-ideal binary solution in the form:

$$D_{AB} = \frac{RT}{N}[1 + \partial \ln \gamma_A/\partial \ln N_A]\left[\frac{N_B}{\sigma_A\eta} + \frac{N_A}{\sigma_B\eta}\right] \tag{76}$$

The resistance factors σ are functions of composition, although in systems where the $D\eta$ product, corrected for solution activity, is a linear function of molar composition, given values for σ_A and σ_B will completely define the behavior of the diffusion coefficient isotherm.

2. Thermodynamics of irreversible processes development

A formalized approach to evaluating diffusion coefficients has been made by use of the thermodynamics of irreversible processes (*cf.* 23 and 24). The general equations for such a process in a mixture of two components are:

$$\vec{J}_1 = L_{11}\vec{X}_1 + L_{12}\vec{X}_2 \tag{77}$$

$$\vec{J}_2 = L_{21}\vec{X}_1 + L_{22}\vec{X}_2 \tag{78}$$

where $\vec{J}_1$ and $\vec{J}_2$ are the mass flow rates of components 1 and 2, L_{11}, L_{22}, L_{12}, and L_{21} are phenomenological coefficients, and $\vec{X}_1$ and $\vec{X}_2$ are the driving forces for the process. Analysis of the problem reveals that for the case of interdiffusion of two components there are no cross-effects, so that the following is true:

$$\vec{J}_1 = -\vec{J}_2 = L_{11}(\vec{X}_1 - \vec{X}_2) = -L_{12}(\vec{X}_1 - \vec{X}_2) \tag{79}$$

For the case with no external forces and no pressure gradient the force difference is as follows:

$$(\vec{X}_1 - \vec{X}_2) = -\partial\left[\frac{\mu_1 - \mu_2}{\partial N_1}\right]_{T,P} \text{grad } N_1 \tag{80}$$

or

$$(\vec{X}_1 - \vec{X}_2) = -\frac{1}{N_2}\left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P} \text{grad } N_1 \tag{81}$$

when the Gibbs–Duhem equation is applied.

Comparing this with the usual diffusion equation:

$$J = -D \text{ grad } N_1 \tag{82}$$

it is observed that the diffusion coefficient D_{12} is defined as:

$$D_{12} = -(L_{12}/N_2)(\partial\mu_1/\partial N_1) \tag{83}$$

Representing the chemical potential in the usual manner in terms of activities results in the following equation:

$$D_{12} = -(L_{12}RT/N_1N_2)(\partial \ln N_1\gamma_1/\partial \ln N_1) \tag{84}$$

Although phenomenological theory gives no indication of the form of L_{12}, consideration of experimental diffusion results shows that it must be a function of concentration. Otherwise, equation 84 would yield results incompatible with experiment or would be indeterminate for the case of dilute solutions.

G. CORRELATION OF DIFFUSION COEFFICIENTS WITH MOLECULAR FREE LENGTHS

A different hydrodynamic approach to estimating diffusion coefficients was proposed by Jacobsen and Laurent (56), who have related various physical properties of liquids to the molecular property of free length or free fluidity length, the latter being defined for use with properties dependent on molecular motion tangential to the molecular surface, such as viscosity and diffusion. The free fluidity length, L_ϕ, the minimum distance between intermolecular surfaces, is defined as:

$$L_\phi = 2(V_T - V_{\phi_0})/Y \tag{85}$$

where V_T is the molar volume at T°K., $Y = (36\pi NVV_{\phi_0}^2)$. V_{ϕ_0} is defined by

$$\phi = (1/\eta) = k_1(V_T^{8/3} - V_{\phi_0}^{8/3})$$

and k_1 is a constant for a given substance. An empirical equation was developed relating fluidity and free length:

$$\phi + c = kL_\phi M^{1/2} \tag{86}$$

where $c = 15.8$ c.g.s. units, $k = 6.85 \times 10^{-11}$ c.g.s. units, and M is the molecular weight. Tests of the above equation on eighty-one non-associated liquids showed it to hold within 5 per cent; for twenty liquid mixtures the fluidity was a linear function of $L_\phi M^{1/2}$ with an average deviation of only 2.4 per cent.

Jacobsen and Laurent indicated that the diffusion coefficient was a linear function of the free fluidity length in different diffusion media. Since it has been demonstrated that the diffusion coefficient is related to the viscosity in dilute solutions, and linearly so for non-associated liquids, such a result is not unexpected. The notion of free fluidity lengths is not likely therefore to add to our present understanding, for, if the viscosity is a linear function of the free fluidity length, the diffusion coefficient also must be for dilute solutions, but undoubtedly no such simple relationship exists for concentrated solutions.

H. ENGINEERING CORRELATIONS OF DIFFUSION COEFFICIENTS

Several authors have suggested engineering correlations to estimate diffusion coefficients in dilute solution. These have been primarily based on the general form of the Eyring equation, but the empirical factors introduced have resulted in several useful and reasonably accurate methods for estimating diffusion coefficients in dilute solution.

1. Wilke correlation

Wilke (134) proposed setting the quantity $(T/D\eta)$ equal to a factor designated as F, a constant for a given solvent–solute system. This follows immediately from equation 50, which can be written as:

$$F = (T/D\eta) = (\lambda_2\lambda_3/\lambda_1 k) \tag{87}$$

The assumption is that the distance parameters do not vary significantly over moderate temperature ranges.

Data (primarily those of Thovert) for approximately 150 solutes in dilute solutions of water, methanol, and benzene were plotted by Wilke in the form of $(T/D\eta)$ versus the molar volume of the solute. For a given solvent the data fall on a smooth curve with an average deviation of 10 per cent but with some deviations up to 20 to 30 per cent. At low molal volumes, values of $(T/D\eta)$ for methanol are 82 per cent of those for water, while for benzene they are 70 per cent of those for water. Both curves merge into that of water at high molal volumes and apparently approach the value predicted by Stokes' law at very high molal volumes. The method can be extended to include curves of other solvent "factors," so the notion can be used for any system in dilute solution. This is a simple and rapid method for obtaining values for diffusion coefficients in dilute solution, and is particularly useful for those solvents where sufficient data are available to evaluate the solvent "factor" accurately.

In a recent paper Wilke and Chang (135) present a general correlation for diffusion in dilute solutions:

$$D = 7.4 \times 10^{-8} \frac{(xM)^{1/2}T}{\eta V^{0.6}} \tag{88}$$

where V is the molal volume, M is the molecular weight, T is the absolute temperature, η is the viscosity, and x is an association parameter to define the effective molecular weight of the solvent with respect to the diffusion process. This correlation was obtained from data for 285 points among 251 solute–solvent systems and is claimed to predict the experimental values with an average deviation of 10 per cent.

2. Othmer correlation

Othmer and Thakar (94) have also developed a correlation based on the general form of Eyring's equation:

$$D = K \exp (E_d/RT) \tag{89}$$

Differentiating the above yields

$$\mathrm{d} \ln D = (E_d/RT^2)\, \mathrm{d}T \tag{90}$$

Recalling that the Clausius–Clapeyron equation is

$$\mathrm{d} \ln P = (L/RT^2)\, \mathrm{d}T \tag{91}$$

where L is the latent heat of vaporization, it follows that

$$(\mathrm{d} \ln D/\mathrm{d} \ln P) = (E_d/L) \tag{92}$$

If E_d/L is assumed to be constant, the following equation is true:

$$\ln D = (E_d/L) \ln P + C \tag{93}$$

Observation of experimental data showed that there was a discontinuity in the plots with water as a solvent at approximately 30°C., so a plot was used with viscosity as a correlating factor:

$$\ln D = -(E_d/E_v) \ln \eta + C \tag{94}$$

For a number of systems logarithmic plots of diffusion coefficient versus viscosity showed straight-line relations with slopes of -1.07 to -1.15. Assuming an average slope the following equation was developed empirically for diffusion into water, where V_m is the molecular volume of the diffusing substance:

$$(D_w \times 10^5) = (14.0/\eta_w^{1.1} V_m^{0.6}) \tag{95}$$

Assuming that diffusion coefficients in other solvents are related to the inverse viscosities of the given solvents, the following empirical equation was developed:

$$D_s \times 10^5 = 14.0/\eta_w^{(1.1L_s/L_w)} V_m^{0.6} \eta_s^{0} \tag{96}$$

The above equation has not been tested extensively, but it appears to be less promising than the previous correlation with molar volume proposed by Wilke.

I. COMPARISON OF VARIOUS THEORIES OF MUTUAL DIFFUSION

In summarizing the work done toward evaluating diffusion coefficients theoretically, it is apparent that the problem is not yet resolved, but it is of interest that considerable similarity in the expressions for the diffusion coefficient are reached by several different approaches, as summarized below:

Eyring theory when combined with expression for viscosity

$$D = \left(\frac{\lambda_1}{\lambda_2\lambda_3}\right)\left(\frac{RT}{N\eta}\right)(1 + \partial \ln \gamma_1/\partial \ln N_1) \tag{97}$$

Thermodynamic

$$D = \left(\frac{N_2}{\sigma_1} + \frac{N_1}{\sigma_2}\right)\left(\frac{RT}{N\eta}\right)(1 + \partial \ln \gamma_1/\partial \ln N_1) \tag{98}$$

Stokes–Einstein

$$D = (1/6\,\pi r)(RT/N\eta) \tag{99}$$

Thermodynamics of irreversible processes

$$D = -(L_{12}/N_1N_2)(RT)(1 + \partial \ln \gamma_1/\partial \ln N_1) \tag{100}$$

The above equations have a number of points in common. The non-ideality of solutions is corrected in all cases by the term $(1 + \partial \ln \gamma_1/\partial \ln N_1)$ except for the Stokes–Einstein equation, which is intended for use in dilute solutions. Eyring (107) has proposed a correction term for this equation involving the above correction factor, but it has been rarely applied. The other common term is the factor RT/N, with most expressions also explicitly including the viscosity. This leaves the other variable or variables such that the effects of molecular size, shape, and intermolecular forces may be included. The net dimension of such a term is one of reciprocal length, although it is not likely that a simple molecular length parameter is sufficient to adequately represent actual conditions.

On the basis of the above equations one might propose the following:

$$D = (\psi)(RT/N\eta)(1 + \partial \ln \gamma_1/\partial \ln N_1) \tag{101}$$

Unfortunately ψ is certainly dependent on molecular size and shape and other variables such that no way is yet known to evaluate such a quantity from basic molecular data.

The relatively simple forms of the above equations do not directly compare with those developed from absolute rate theory and the random-walk treatment. These two equations are repeated below:

Absolute rate theory

$$D = \left(\frac{\delta_0'^2 kT}{h}\right)\exp\left[\frac{-(F_0 - F_0')}{RT}\right]\left(1 + \frac{\partial \ln \gamma_i}{\partial \ln N_i}\right) \tag{102}$$

Random walk

$$D = \left(\frac{\delta_0'^2 k_0}{2}\right)\left(1 + \frac{\partial \ln \delta'}{\partial \ln N_i} + \frac{\partial \ln \phi(N_i)}{\partial \ln N_i}\right) \tag{103}$$

Both of the latter equations require a knowledge of the mean average displacement of a molecule in a given environment, a difficult quantity to evaluate. The terms correcting for the solution non-ideality are also somewhat different from those in the previous equations, and the exact relationship between the variation of activity coefficient and mean displacement length is not well understood.

Although several basic theories lead to similar expressions for the diffusion coefficient, the fact that the end results are not all equal indicates that the exact solution has not yet been attained. It is rather unlikely that a simple equation of the general form of equation 101 will explain diffusion experiments except on a semiempirical basis; however, accurate evaluation of the more involved kinetic treatments does not appear feasible at this time.

VI. SELF-DIFFUSION THEORIES

The self-diffusion coeficient is unlike a mutual diffusion coefficient in that its measurement does not require the existence of an overall chemical concentration gradient. The measurement of self-diffusion rates gives the nearest available approach to the observation of the magnitudes of actual molecular motion in a gross sense. Although it appears that measurement of self-diffusion rates might yield true differential diffusion coefficients, recent experimental evidence indicates that significant differences may exist between mutual and self-diffusion coefficients for the same average solution composition. The following review of recent theoretical contributions pertaining to this problem will also point out why the two types of coefficients should only rarely be equal and why their relationship is in fact probably quite complex.

A. THEORETICAL RELATIONSHIPS BETWEEN MUTUAL DIFFUSION AND SELF-DIFFUSION

The viewpoint that self-diffusion coefficients should have the same value as mutual diffusion coefficients corrected for solution activity has been recently presented by Prager (97). Prager considered that the driving force for diffusion is the gradient of chemical potential but that even in non-ideal solutions this gradient becomes effectively equal to the gradient of isotopic concentration when self-diffusion of one component is occurring. By considering that the difference in the effective gradient would alter the random motion of the molecules, he derived the following equation:

$$(D_{12}/D_{22}) = (D_{12}/D_{11}) = (1 + \partial \ln \gamma_1/\partial \ln N_1) \tag{104}$$

where D_{12} is the differential diffusion coefficient and D_{11} and D_{22} are the self-diffusion coefficients of the respective components.

This same result may be obtained by using a thermodynamic approach. Let a concentration C_A of component A in a binary solution be maintained in equilibrium with a force F_A per mole of A in the direction of increasing x. In general this force may be expressed as

$$F_A = (\partial \mu_A/\partial x) \tag{105}$$

but in an ideal solution it is

$$F_A = RT(\partial \ln C_A/\partial x) \tag{106}$$

and for any solution in terms of activity coefficients:

$$F_A = RT[\partial \ln (\gamma_A C_A)/\partial x] \tag{107}$$

If there were no concentration gradient present, F_A would produce a real average velocity v_A of the A molecules in the direction of increasing x, where

$$v_A = (F_A/N)(1/\sigma) \qquad (108)$$

and σ is a resistance to flow dependent on solution composition. The resulting rate of transfer J'_A moles per second across unit section of area is:

$$J'_A = (F_A/N)(1/\sigma)C_A \qquad (109)$$

If the concentration gradient assumed is present but with no corresponding force, the gradient will produce a transfer by diffusion equal in magnitude to the above but opposite in algebraic sign:

$$J_A = -J'_A \qquad (110)$$

From the basic diffusion law:

$$J_A = -D_A(\partial C_A/\partial x) \qquad (111)$$

In the case of an ideal solution:

$$D_A^* = (RT/N)(1/\sigma) \qquad (112)$$

while for a non-ideal solution:

$$D_A = (RT/N)(1/\sigma)[\partial \ln \gamma_A C_A/\partial C_A](C_A) \qquad (113)$$

When considering the relation between self-diffusion and differential diffusion the resisting force σ from a purely hydrodynamic viewpoint might be considered the same, if the composition of the solution is essentially identical for the two cases. The actual driving force expressed in terms of concentration, however, is different. With tagged molecules in a solution of uniform composition, the solution behaves ideally insofar as diffusion is concerned, but with the presence of a concentration gradient the effect of non-ideality must be considered. Recognizing that C_A may be expressed in terms of N_A and equating the two resisting forces which are presumed equal result in the relation:

$$(D_A/D_A^*) = (1 + \partial \ln \gamma_A/\partial \ln N_A) \qquad (114)$$

This equation is identical with equation 104 developed by Prager.

Lamm (71) developed a relationship between the two types of diffusion coefficients based on the more likely concept that there is a different mechanism acting between the interchange of A molecules compared with the exchange of A and B molecules in a binary solution of A and B. The development has a hydrodynamic basis, with the notion of one force acting between the tagged molecules and the chemically identical non-tagged molecules and another force acting between the tagged molecules and the chemically dissimilar molecules. Using the development shown in an earlier paper by Lamm (70), the mutual diffusion coefficient between molecules 1 and 2 in binary solution may be expressed as:

$$D_{12} = \frac{RT}{\phi_{12}} \frac{n_1 n_2}{n_1 + n_2}\left[1 + \frac{\partial \ln \gamma_1}{\partial \ln N_1}\right] \qquad (115)$$

where n_1 and n_2 are the molar concentrations per cubic centimeter of components 1 and 2 and ϕ_{12} is the frictional resistance per cubic centimeter between components 1 and 2. This is of the same general form as reached by several theories of mutual diffusion mentioned in Section V.

By considering diffusion in a system of three components—1, tagged A; 1′, untagged A; 2, untagged B—an equation was developed by Lamm (71) for the self-diffusion of tagged A (assumed equal to that for untagged A) in the form:

$$D_{11} = \frac{RT}{\phi_{11}'\left[\dfrac{1}{n_1} + \dfrac{1}{n_1'}\right] + \phi_{12}\left[\dfrac{1}{n_1 + n_1'}\right]} \tag{116}$$

where the notation is the same as before except that ϕ_{11}' is the frictional coefficient for the interaction of tagged and untagged molecules of type A.

For this same case the mutual diffusion coefficient is:

$$D_{12} = \frac{RT}{\phi_{12}\left[\dfrac{1}{n_1 + n_1'} + \dfrac{1}{n_2}\right]}\left(1 + \frac{\partial \ln \gamma_2}{\partial \ln N_2}\right) \tag{117}$$

The two coefficients are then related as follows:

$$\frac{D_{12}}{D_{11}} = \frac{\phi_{11}'\left[\dfrac{1}{n_1 + n_1'}\right] + \phi_{12}\left[\dfrac{1}{n_1} + \dfrac{1}{n_1'}\right]}{\phi_{12}\left[\dfrac{1}{n_1 + n_1'} + \dfrac{1}{n_2}\right]}\left(1 + \frac{\partial \ln \gamma_2}{\partial \ln N_2}\right) \tag{118}$$

A comparison of the above equation with equation 104, developed by Prager, shows that they are similar in form except that Lamm has introduced an additional coefficient for the case of self-diffusion. Since it appears that self-diffusion can occur by two types of molecular interchange, the latter equation might be expected to conform more closely to experimental observations.

Several other conclusions can be deduced from the general equations proposed by Lamm. Since the frictional forces are positive quantities, it follows that:

$$\frac{D_{12}}{N_2(1 + \partial \ln \gamma_2/\partial \ln N_2)} > D_{11} \tag{119}$$

for any solution composition. In infinitely dilute solutions, however, the mutual diffusion and self-diffusion coefficients should be equal, since the tagged molecules of a given species would rarely be adjacent to the untagged molecules of the same species and the frictional resistance to motion would be almost entirely determined by the interaction of tagged molecules with chemically dissimilar molecules. This interaction is the same phenomenon occurring in mutual diffusion.

By presuming that the addition of component 2 does not alter the specific frictional properties of component 1, thus allowing the frictional factors to be evaluated on a volume basis, Lamm (71) developed the following equation relating mutual diffusion and self-diffusion:

$$\frac{1}{D_{11}} - \frac{n_1 V_1^0}{D_{11}^0} \cong \frac{N_2}{D_{12}}\left(1 + \frac{\partial \ln \gamma_2}{\partial \ln N_2}\right) \tag{120}$$

where V_1^0 is the molar volume of pure 1 and D_{11}^0 is the self-diffusion coefficient of pure 1. It is emphasized that Lamm indicated that the above should only be approximately true and that the specific frictional properties of a component may be a function of concentration.

It appears that the principal factor to be considered in qualitatively summarizing the relation between mutual and self-diffusion in a binary solution of A and B is that self-diffusion is a measure of both the motion of type A molecules with respect to each other and the interchange of A and B molecules. Unless the rates of molecular motion of A and B are equal or other compensating influences are at work, it is not unexpected that the two measured diffusion rates would be unequal.

B. COMPARISON OF THEORY WITH EXPERIMENT

The earliest clear experimental evidence of differences between self-diffusion and mutual diffusion is probably due to Johnson (59), who studied self-diffusion in a gold–silver alloy of approximately equimolal composition. Johnson found that the mutual diffusion coefficient was significantly larger than that of either self-diffusion coefficient. This behavior was explained by Darken (22) and Seitz (105) on the basis that the behavior of the mixed crystals under study would need to be corrected for their non-ideality. In this case the agreement between the measurements compared on the activity corrected basis was about 15 per cent, a reasonable agreement for measurements of diffusion in a solid. This work led to the development by Prager (97) of the relations between mutual diffusion and self-diffusion coefficients.

In the earlier work on the self-diffusion of electrolytes many of the investigators (*cf.* 1, 3, 131) apparently considered that the observed self-diffusion coefficient was equal in value to the true mutual diffusion coefficient. When significant differences continued to result, particularly in more concentrated solutions, more consideration was given to possible fundamental differences between the two coefficients. For example, Neilson, Adamson, and Cobble (88), in studies of ionic self-diffusion in aqueous sodium chloride and sodium sulfate solutions, ascribed the difference between the two coefficients to a volume effect, as mutual diffusion includes the contribution of the diffusion rate of the solvent as well as the solute. Adamson (2) has recently discussed in more detail some of the general problems of both measuring and relating the various types of diffusion coefficients, particularly for electrolytic solutions.

Experimental data showing relations between mutual diffusion and self-diffusion were presented by Wang (127) in his work with glycine. He observed that with very dilute solutions, his values for self-diffusion agreed closely with the accepted values for mutual diffusion, but that as the concentration increased, his values were consistently higher. He discussed the activity concept briefly and corrected the mutual diffusion coefficients by dividing them by the expression $(1 + \partial \ln \gamma_1/\partial \ln N_1)$. When this was done it was found that the corrected mutual coefficients were always greater than those for self-diffusion. This difference was discussed in terms of the possible interaction of dipolar ions on the equilibrium properties of the solution, but no quantitative calculations were made as a rigorous solution was not thought possible at this time.

Johnson and Babb (58) measured the self-diffusion rates of benzene, methyl alcohol, and ethyl alcohol tagged with carbon-14 in five binary liquid systems at 25°C. by a simple capillary-cell technique. For the relatively ideal systems, benzene–carbon tetrachloride and ethyl alcohol–methyl alcohol, the self-diffusion coefficient varied approximately linearly with molar composition, but the values for mutual diffusion and self-diffusion for the same liquid composition disagreed by as much as 15 per cent. For the non-ideal systems, benzene–methyl alcohol and benzene–ethyl alcohol, the two coefficients disagreed by a factor of 2 or more over much of the composition range. It was observed, however, that when the component being measured was in dilute concentration, the two coefficients in all systems studied agreed within 5–10 per cent and within 2 per cent for the ideal systems. In addition, the relation developed by Prager was found to be without experimental justification, as the mutual diffusion coefficients corrected for solution activity were as much as threefold greater than the corresponding self-diffusion coefficients. The more general relation between mutual diffusion and self-diffusion proposed by Lamm was shown to be approximately true for ideal systems if the forces were assumed to vary linearly with solution composition. The behavior of the non-ideal systems could be rationalized with this theory if the forces were considered to vary with solution composition.

Similar conclusions were reached for the system methyl alcohol–water at 27°C. by Sehmel and Babb (104), who obtained values of the self-diffusion coefficients of methyl alcohol using a capillary-cell technique.

VII. Tabulation of Mutual Diffusion Coefficients for Binary Liquid Systems of Non-Electrolytes

Included in the following tables are experimental mutual diffusion coefficients for binary liquid systems of non-electrolytes. The object was to include all available data for binary systems where both components are non-electrolytes and liquids at the temperature of study. In table 1 are presented diffusion coefficients for some of the more common liquid systems of practical or theoretical interest where data are available over a fairly wide range of compositions. In table 2 systems for which limited experimental data are available have been listed, together with the pertinent literature references.

The criteria for including data for substances that did not conform to being both a non-electrolyte and liquid at the temperature of the study were often based on either reporting all the data obtained in a certain investigation or including results of a study where the data aid in confirming concepts useful to a study of diffusion. While an attempt has been made to include all available data

TABLE 1

Diffusion coefficients of binary liquid non-electrolyte systems

Components		Composition of A†		Type of Coefficient†	Temperature	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
A	B							
					°C.	cm.²/sec.	per cent	
Acetic acid	Benzene	1	WPC	D	15	1.92	5*	47*
		1	N	I	15	1.73	5	30
	Ethyl alcohol	1	N	I	15.3	0.64	5	30
	Methyl alcohol	1	WPC	D	15	1.54	5*	47*
	Water	1	N	I	14	0.90	5	30
		1	WPC	D	15	0.88	5*	47*
Acetone	Chloroform	0.5	VPC	D	15	2.36	2–4	23
		99.5	VPC	D	15	3.92	2–4	23
		2	VPC	D	17	2.42	2–4	23
		20	VPC	D	17	2.87	2–4	23
		40	VPC	D	17	3.20	2–4	23
		60	VPC	D	17	3.51	2–4	23
		80	VPC	D	17	3.71	2–4	23
		98	VPC	D	17	3.91	2–4	23
	Methyl alcohol	20	G/DL	I	18.8	2.57	5	5
	Nitrobenzene	10	G/DL	I	16	0.86	5	5
		10	G/DL	I	17.8	0.91	5	5
	Water	0.5	VPC	D	15	1.22	2–4	23
		0.5	VPC	D	17	1.25	2–4	23
		20	VPC	D	17	1.00	2–4	23
		40	VPC	D	17	0.88	2–4	23
Acetylene tetrabromide	Acetylene tetrachloride	0.068	M/L	I	0.44	0.351	1	3
		0.068	M/L	I	7.70	0.419	1	3
		0.068	M/L	I	15.01	0.497	1	3
		0.068	M/L	I	24.98	0.611	1	3
		0.066	M/L	I	35.61	0.741	1	3
		0.064	M/L	I	51.10	0.954	1	3
Benzene	Carbon tetrachloride (see also paragraphs No. 7, 8, 16, and 30)	2.154	MPC	D	10.00	1.085	1	2
		25.02	MPC	D	10.00	1.093	1	2
		50.51	MPC	D	10.00	1.230	4	2
		74.98	MPC	D	10.00	1.344	1	2
		98.15	MPC	D	10.00	1.466	1	2
		2.154	MPC	D	25.20	1.419	3	2
		25.02	MPC	D	25.26	1.519	1	2
		50.51	MPC	D	25.26	1.651	1	2
		74.98	MPC	D	25.34	1.759	1	2
		98.15	MPC	D	25.26	1.912	1	2
		2.154	MPC	D	40.0	1.775	1	2
		25.02	MPC	D	40.0	1.970	1	2
		50.51	MPC	D	40.0	2.077	1	2
		74.98	MPC	D	40.0	2.284	1	2
		98.15	MPC	D	40.0	2.432	1	2
	Chloroform	0.5	VPC	D	15	2.51	2–4	23
		2	VPC	D	15	2.51	2–4	23
		20	VPC	D	15	2.48	2–4	23
		40	VPC	D	15	2.48	2–4	23
		60	VPC	D	15	2.46	2–4	23
		80	VPC	D	15	2.45	2–4	23
		98	VPC	D	15	2.39	2–4	23

† See Section VII for an explanation of the abbreviations.

‡ The numbers refer to the numbered paragraphs in Section IX.

TABLE 1—*Continued*

Components		Composition of A†	Type of Coefficient†	Temperature	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
A	B						
				°C.	*cm.²/sec.*	*per cent*	
Isobutyl alcohol	Water (see also paragraph No. 6)	0.5 VPC	D	15	0.77	2–4	23
		99.5 VPC	D	15	0.30	2–4	23
		1.0 VPC	D	18	0.85	2–4	23
		8.8 VPC	D	18	0.71	2–4	23
		92.5 VPC	D	18	0.22	2–4	23
		98 VPC	D	18	0.31	2–4	23
n-Butyl alcohol	Water(see also paragraphs No. 6 and 47)	0.5 VPC	D	15	0.77	2–4	23
		0.0501 M/L	D	1	0.4348	1	27
		0.1000 M/L	D	1	0.4243	1	27
		0.2199 M/L	D	1	0.4040	1	27
		0.3000 M/L	D	1	0.3927	1	27
		0.5002 M/L	D	1	0.3657	1	27
		0.7004 M/L	D	1	0.3435	1	27
		0.0502 M/L	D	25	0.9557	1	27
		0.1006 M/L	D	25	0.9390	1	27
		0.1424 M/L	D	25	0.9248	1	27
		0.3006 M/L	D	25	0.8758	1	27
		0.5001 M/L	D	25	0.8147	1	27
		0.7001 M/L	D	25	0.7555	1	27
Chlorobenzene	Bromobenzene	3.32 MPC	D	10.01	1.007	1	2
		26.42 MPC	D	10.01	1.069	1	2
		51.22 MPC	D	10.01	1.146	1	2
		76.17 MPC	D	10.01	1.226	1	2
		96.52 MPC	D	10.01	1.291	3	2
		3.32 MPC	D	26.78	1.342	2	2
		26.42 MPC	D	26.78	1.380	2	2
		51.22 MPC	D	26.78	1.506	1	2
		76.17 MPC	D	26.78	1.596	1	2
		96.52 MPC	D	26.78	1.708	2	2
		3.32 MPC	D	39.97	1.584	1	2
		26.42 MPC	D	39.97	1.691	1	2
		51.22 MPC	D	39.97	1.806	1	2
		76.17 MPC	D	39.97	1.902	1	2
		96.52 MPC	D	39.97	1.996	1	2
Ether	Chloroform	0.5 VPC	D	15	2.07	2–4	23
		17.8 VPC	D	15	2.44	2–4	23
		34 VPC	D	15	3.10	2–4	23
		58 VPC	D	15	4.44	2–4	23
		76 VPC	D	15	4.72	2–4	23
		80.5 VPC	D	15	4.74	2–4	23
		94.5 VPC	D	15	4.59	2–4	23
		99.5 VPC	D	15	4.40	2–4	23
Ethyl alcohol	Benzene	0.5 VPC	D	15	2.25	2–4	23
		1 VPC	D	15	2.13	2–4	23
		2 VPC	D	15	1.67	2–4	23
		2.5 VPC	D	15	1.63	2–4	23
		16 VPC	D	15	0.82	2–4	23
		32 VPC	D	15	0.72	2–4	23
		50 VPC	D	15	0.92	2–4	23
		70 VPC	D	15	1.19	2–4	23
		98 VPC	D	15	1.65	2–4	23
		99.5 VPC	D	15	1.67	2–4	23
		0.916 MPC	D	27	2.910	1	2
		3.270 MPC	D	27	2.080	1	2
		35.370 MPC	D	27	0.920	1	2
		99.522 MPC	D	27	1.994	1	2

TABLE 1—*Continued*

Components		Composition of A†	Type of Coefficient‡	Temperature	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
A	B						
				°C.	*cm.²/sec.*	*per cent*	
Ethyl alcohol—*Continued*	Chloroform	0.5 VPC	D	15	2.20	2–4	23
		2 VPC	D	15	1.96	2–4	23
		20 VPC	D	15	0.98	2–4	23
		40 VPC	D	15	0.98	2–4	23
		60 VPC	D	15	1.29	2–4	23
		80 VPC	D	15	1.62	2–4	23
		98 VPC	D	15	1.63	2–4	23
	Toluene	0.5 VPC	D	15	3.00	2–4	23
		1 VPC	D	15	2.58	2–4	23
		3 VPC	D	15	1.32	2–4	23
		10 VPC	D	15	0.90	2–4	23
		20 VPC	D	15	0.72	2–4	23
		40 VPC	D	15	0.70	2–4	23
		60 VPC	D	15	0.86	2–4	23
		99.5 VPC	D	15	1.60	2–4	23
		80 VPC	D	15	1.27	2–4	23
	Water (see also paragraphs No. 7, 8, and 47)	1 VPC	D	10	0.84	2–4	23
		21 VPC	D	10	0.57	2–4	23
		40 VPC	D	10	0.31	2–4	23
		62.5 VPC	D	10	0.21	2–4	23
		75 VPC	D	10	0.30	2–4	23
		92.5 VPC	D	10	0.66	2–4	23
		99 VPC	D	10	0.85	2–4	23
		0.5 VPC	D	15	1.00	2–4	23
		99.5 VPC	D	15	1.02	2–4	23
		1 VPC	D	18	1.09	2–4	23
		29 VPC	D	18	0.62	2–4	23
		59 VPC	D	18	0.32	2–4	23
		89 VPC	D	18	0.82	2–4	23
		99 VPC	D	18	1.10	2–4	23
		5 MPC	D	25	1.13	3*	42*
		10 MPC	D	25	0.90	3*	42*
		27.5 MPC	D	25	0.41	3*	42*
		50 MPC	D	25	0.90	3*	42*
		70 MPC	D	25	1.40	3*	42*
		90 MPC	D	25	2.0	3*	42*
		95 MPC	D	25	2.20	3*	42*
		0 G/DL	D	25	1.240	1*	14*
		5 G/DL	D	25	1.079	1*	14*
		10 G/DL	D	25	0.935	1*	14*
		15 G/DL	D	25	0.807	1*	14*
		20 G/DL	D	25	0.694	1*	14*
		25 G/DL	D	25	0.595	1*	14*
		30 G/DL	D	25	0.508	1*	14*
		35 G/DL	D	25	0.426	1*	14*
		40 G/DL	D	25	0.377	1*	14*
		45 G/DL	D	25	0.362	1*	14*
		50 G/DL	D	25	0.372	1*	14*
		55 G/DL	D	25	0.407	1*	14*
		60 G/DL	D	25	0.467	1*	14*
		65 G/DL	D	25	0.551	1*	14*
		70 G/DL	D	25	0.760	1*	14*
		75 G/DL	D	25	0.981	1*	14*
		78.51 G/DL	D	25	1.132	1*	14*

TABLE 1—*Continued*

Components		Composition of A†		Type of Coefficient‡	Temperature	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
A	B							
					°C.	cm.²/sec.	per cent	
Hexane	Benzene	2	VPC	D	5	1.78	2–4	23
		18	VPC	D	5	1.78	2-4	23
		34	VPC	D	5	1.90	2–4	23
		50	VPC	D	5	2.20	2–4	23
		66	VPC	D	5	2.54	2–4	23
		98	VPC	D	5	3.20	2-4	23
		2	VPC	D	11	1.89	2–4	23
		50	VPC	D	11	2.36	2–4	23
		0.5	VPC	D	15	2.15	2–4	23
		99.5	VPC	D	15	3.70	2–4	23
Methyl alcohol	Benzene (see also paragraph No. 45)	2	VPC	D	11	1.89	2–4	23
		12.5	VPC	D	11	0.65	2–4	23
		20	VPC	D	11	0.61	2-4	23
		35	VPC	D	11	0.70	2–4	23
		50	VPC	D	11	0.93	2–4	23
		70	VPC	D	11	1.56	2-4	23
		85	VPC	D	11	1.87	2-4	23
		98	VPC	D	11	2.22	2–4	23
		0.5	VPC	D	15	2.50	2-4	23
		99.5	VPC	D	15	2.40	2–4	23
		0.477	MPC	D	11.00	2.875	1	2
		1.572	MPC	D	11.00	2.233	1	2
		0.477	MPC	D	27.06	3.839	1	2
		1.572	MPC	D	27.06	3.345	1	2
		11.432	MPC	D	27.06	1.327	1	2
		25.484	MPC	D	27.06	0.949	1	2
		50.321	MPC	D	27.06	0.901	1	2
		75.167	MPC	D	27.06	1.533	1	2
		99.821	MPC	D	27.06	2.762	1	2
	Water (see also paragraphs No. 7, 8, and 47)	0.5	VPC	D	15	1.26	2–4	23
		0.6	VPC	D	15	1.26	2–4	23
		12	VPC	D	15	1.11	2–4	23
		22	VPC	D	15	0.99	2–4	23
		46	VPC	D	15	0.77	2–4	23
		64	VPC	D	15	0.85	2–4	23
		84	VPC	D	15	1.22	2–4	23
		92.5	VPC	D	15	1.46	2–4	23
		99.5	VPC	D	15	1.75	2–4	23
Isopropyl alcohol	Water	0.5	VPC	D	15	0.87	2–4	23
		99.5	VPC	D	15	0.38	2–4	23
		1	VPC	D	16	0.89	2-4	23
		14.5	VPC	D	16	0.63	2-4	23
		35.5	VPC	D	16	0.280	2-4	23
		53	VPC	D	16	0.155	2–4	23
		64.5	VPC	D	16	0.174	2–4	23
		75	VPC	D	16	0.204	2–4	23
		88	VPC	D	16	0.275	2–4	23
		96	VPC	D	16	0.37	2–4	23

TABLE 1—*Concluded*

Components		Composition of A†	Type of Coefficient‡	Temperature	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
A	B						
				°*C.*	*cm.²/*sec.	*per cent*	
n-Propyl alcohol	Water (see also paragraphs No. 8 and 47)	1.2 VPC	D	11	0.77	2-4	23
		6 VPC	D	11	0.66	2-4	23
		12 VPC	D	11	0.55	2-4	23
		23.5 VPC	D	11	0.33	2-4	23
		45 VPC	D	11	0.11	2-4	23
		59 VPC	D	11	0.08	2-4	23
		79 VPC	D	11	0.15	2-4	23
		89 VPC	D	11	0.28	2-4	23
		98 VPC	D	11	0.47	2-4	23
		0.5 VPC	D	15	0.87	2-4	23
		99.5 VPC	D	15	0.61	2-4	23
Toluene	Chlorobenzene	1.337 MPC	D	10.00	1.346	1	2
		25.01 MPC	D	10.00	1.404	1	2
		49.92 MPC	D	10.00	1.556	1	2
		74.92 MPC	D	10.00	1.652	1	2
		98.62 MPC	D	10.00	1.759	1	2
		1.337 MPC	D	26.96	1.756	1	2
		25.01 MPC	D	26.96	1.852	1	2
		49.92 MPC	D	26.96	1.985	1	2
		74.92 MPC	D	26.96	2.128	1	2
		98.62 MPC	D	26.96	2.264	1	2
		1.337 MPC	D	40.01	2.113	1	2
		25.01 MPC	D	40.01	2.277	1	2
		49.92 MPC	D	40.01	2.435	2	2
		74.92 MPC	D	40.01	2.586	1	2
		98.62 MPC	D	40.01	2.714	1	2
Water	*n*-Butyl alcohol	52.4 MPC	D	30	0.267	U	37
		48.5 MPC	D	30	0.391	U	37
		45.4 MPC	D	30	0.437	U	37
		42.1 MPC	D	30	0.465	U	37
		38.9 MPC	D	30	0.520	U	37
		35.8 MPC	D	30	0.560	U	37
		32.9 MPC	D	30	0.667	U	37
		30.0 MPC	D	30	0.718	U	37
		27.2 MPC	D	30	0.782	U	37
		24.7 MPC	D	30	0.845	U	37
		22.2 MPC	D	30	0.920	U	37
		19.8 MPC	D	30	1.02	U	37
		17.5 MPC	D	30	1.12	U	37
		15.3 MPC	D	30	1.20	U	37
		13.1 MPC	D	30	1.24	U	37

that meet the requirements set forth above, the reader is reminded that for some systems that are electrolytes, or where the solute is a solid, all data are not necessarily included in this tabulation.

The following outline explains in detail the material included in the tables.

Components: The names in the tables are arranged alphabetically in order of the component designated A and thereafter alphabetically for the other component when data exist for more than one system with A. For data on dilute solutions, component A is ordinarily the solute, but where data are available over a wide concentration range this restriction does not apply. It is therefore

TABLE 2

Systems for which limited diffusion data are available

Components		Experimental Method‡	Components		Experimental Method‡
A	B		A	B	
Acetal	Ethyl alcohol	32	Benzaldehyde	Methyl alcohol	47
	Methyl alcohol	47	Benzotrichloride	Benzene	16
Acetamide	Ethyl alcohol (96%)	32		Ethyl acetate	5
	Methyl alcohol	47		Ethyl benzoate	5
	Water	33, 47		Toluene	16
Acetanilide	Methyl alcohol	47	Benzylamine (see Monobenzylamine)		
Acetic acid	Acetonitrile	30			
Acetone	Ethyl benzoate	5	Biphenyl (see also Diphenyl)	Benzene	39
Acetonitrile	Water	47			
	Methyl alcohol	47	Bromal	Methyl alcohol	47
Acetotoluidine	Methyl alcohol	47	Bromoacetic acid	Methyl alcohol	47
Acetyldiphenylamine	Methyl alcohol	47	Bromoaniline	Benzene	47
Acetylphenylhydrazine	Methyl alcohol	47		Methyl alcohol	47
			9-Bromoanthracene	Benzene	16
Aconitine	Ethyl alcohol	32	Bromobenzene	Benzene	16, 47
α-Alanine	Water	26, 25, 13, 24		Cyclohexane	16
				Cyclohexene	16
β-Alanine	Water	24, 25		*p*-Cymene	16
Alloxan	Water	33		Decalin	16
Allyl alcohol	Ethyl alcohol	32		Dioxane	16
	Methyl alcohol	47		Ethylbenzene	16
	Water	47		Ethyl ether	16
Allyl bromide	Methyl alcohol	47	Bromobenzene	Hexane	16
Allyl iodide	Methyl alcohol	47		Mesitylene	16
o-Aminobenzoic acid	Water	26		Methyl alcohol	47
m-Aminobenzoic acid	Water	26		Tetralin	16
p-Aminobenzoic acid	Water	26		Toluene	16
Amyl acetate	Methyl alcohol	47		*m*-Xylene	16
Isoamyl alcohol	Ethyl alcohol	32	Bromocyclohexane	Benzene	16
	Methyl alcohol	47		Cyclohexane	16
	Water	47		Cyclohexene	16
	Benzene	47	*p*-Bromodiphenyl	Benzene	16
Isoamyl bromide	Ethyl ether	16	Bromoethyl ether	Ethyl ether	16
n-Amyl bromide	Benzene	16	Bromoform	Acetone	34
Isoamyl iodide	Methyl alcohol	47		Isoamyl alcohol	34
n-Amyl iodide	Benzene	16		Benzene	34, 47
Aniline	Acetonitrile	30		Ethyl alcohol	34
	Benzene	30		Ethyl ether	34
	Ethyl alcohol	30		Methyl alcohol	34, 47
	Methyl alcohol	47		*n*-Propyl alcohol	34
	Water	47		Chloroform	16
Aniline hydrochloride	Methyl alcohol	47	α-Bromonaphthalene	Benzene	16, 47
	Water	47		Cyclohexane	16
Anisole	Methyl alcohol	47		Decalin	16
Antipyrine	Methyl alcohol	47		Dibenzyl ether	16
	Water	47		Dioxane	16
Azobenzene	Ethyl alcohol (96%)	32		Ethyl alcohol (96%)	32
Benzene	Bromobenzene	16		Hexane	16
	Decane	48		Methyl alcohol	47
	2,4-Dimethylpentane	48		α-Methylnaphthalene	16
	n-Dodecane	48		Tetralin	16
	Octadecane	48		Toluene	16
	Heptane	48	Bromonitrobenzene	Benzene	47
α-Benzene hexachloride	Benzene	16		Methyl alcohol	47
			9-Bromophenanthrene	Benzene	16
Benzoic acid	Methyl alcohol	47			
Benzaldehyde	Benzene	47	Bromophenetole	Phenetole	16

‡ The numbers refer to the numbered paragraphs in Section IX.

TABLE 2—*Continued*

Components		Experimental Method‡
A	B	
Bromophenol	Benzene	47
	Methyl alcohol	47
Bromopropionic acid	Methyl alcohol	47
o-Bromotoluene	Toluene	16
m-Bromotoluene	Toluene	16
p-Bromotoluene	Toluene	16
Brucine	Ethyl alcohol	32
sec-Butyl alcohol	Water	6
tert-Butyl alcohol	Water	6
n-Butyl bromide	Benzene	16
n-Butyl iodide	Benzene	16
Camphor	Ethyl alcohol (96%)	32
Carbon tetrabromide	Benzene	16
	Carbon tetrachloride	16
Carbon tetrachloride	Methyl alcohol	47
	Nitrobenzene	31, 8
Carminic acid	Ethyl alcohol (96%)	32
Cetyl alcohol	Ethyl alcohol (96%)	32
Chloral	Ethyl alcohol (96%)	32
Chloral hydrate	Methyl alcohol	47
	Water	47
Chloroacetal	Methyl alcohol	47
Chloroacetic acid (see Monochloroacetic acid)		
Chloroaniline	Benzene	47
	Methyl alcohol	47
Chlorobenzene	Benzene	47
	Methyl alcohol	47
Chlorobenzoic acid	Methyl alcohol	47
Chlorobromoethylene	Methyl alcohol	47
Chloroform	Benzene	47, 23
	Ethyl alcohol	23, 32
	Methyl alcohol	47, 23
Chlorohydrin (see Monochlorohydrin)		
α-Chloronaphthalene	Benzene	47
	Methyl alcohol	47
Chloronitrobenzene	Benzene	47
	Methyl alcohol	47
Chlorophenol	Benzene	47
	Methyl alcohol	47
Cumaldehyde	Methyl alcohol	47
Dextrose	Water	26
Dibenzylamine	Methyl alcohol	47
p-Dibromobenzene	Benzene	47
	Methyl alcohol	47
Dibromonaphthalene	Benzene	47
	Methyl alcohol	47
Dichloroacetal	Methyl alcohol	47
Dichloroacetic acid	Methyl alcohol	47
Dichlorobenzene	Benzene	47
	Methyl alcohol	47
o-Dichlorobenzene	Benzene	16
m-Dichlorobenzene	Benzene	16
p-Dichlorobenzene	Benzene	16
1,1′-Dichlorohydrin	Methyl alcohol	47
	Water	47
Dichloronaphthalene	Benzene	47
	Methyl alcohol	47
Dicyandiamide	Water	33
Diethyl sulfate	Methyl alcohol	47
2,3-Diiodopentane	Methyl alcohol	47
2,4-Dimethylpentane	Dodecane	48
m-Dinitrobenzene	Methyl alcohol	47
	Benzene	47
Dinitronaphthalene	Methyl alcohol	47
2,4-Dinitrophenol	Methyl alcohol	47
Diphenyl	Methyl alcohol	45
Ether	Benzene	47, 23
	Methyl alcohol	47, 23
	Water	23, 1
Ethyl acetate	Benzotrichloride	5
	Ethyl benzoate	5
	Methyl alcohol	5, 47
	Nitrobenzene	5
Ethylamine sulfate	Methyl alcohol	47
Ethyl benzoate	Acetone	5
	Benzotrichloride	5
	Ethyl acetate	5
	Methyl alcohol	5
	Nitrobenzene	5
Ethyl bromide	Methyl alcohol	47
Ethylbromobenzoic acid	Ethylbenzoic acid	16
Ethyl iodide	Benzene	16
	Methyl alcohol	47
Ethyl nitrate	Methyl alcohol	47
Ethyl trichloroacetate	Methyl alcohol	47
Ethylene bromide	Benzene	47
	Ethylene chloride	16
	Methyl alcohol	47
Ethylene chloride	Benzene	16, 47
	Mesitylene	16
	Methyl alcohol	47
Ethylene iodide	Benzene	47
	Methyl alcohol	47
Formic acid	Benzene	47
	Methyl alcohol	47
	Water	47
Furfuryl alcohol	Methyl alcohol	47
Galactose	Water	24
Glucose	Water	47, 24
Glycerol	Isoamyl alcohol	34
	Ethyl alcohol (96%)	32
	Methyl alcohol	47
	n-Propyl alcohol	32
	Water	47, 33, 21
Glycine	Water	28, 26, 24, 25
Heptane	Dodecane	48
	Hexadecane	48
	Octadecane	48
	Tetradecane	48
n-Heptyl bromide	Heptane	16
Hexachlorobenzene	Benzene	16
	Methyl alcohol	47
n-Hexyl bromide	Hexane	16
Hydrogen peroxide	Acetone	43
	Ethyl alcohol	43

TABLE 2—*Continued*

Components		Experimental Method‡	Components		Experimental Method‡
A	B		A	B	
Hydrogen peroxide—*continued*	Ethyl ether	43	Nitroaniline	Methyl alcohol	47
	Methyl alcohol	43	Nitrobenzene	Acetone	5
	Water	43		Benzene	47
Hydroquinol	Ethyl alcohol (96%)	32		Carbon tetrachloride	8
	Water	33		Ethyl acetate	5
Hydroquinone	Methyl alcohol	47		Ethyl ether	16
	Water	47, 1		Ethyl benzoate	5
o-Hydroxybenzyl alcohol	Ethyl alcohol	32		Methyl alcohol	47, 5, 8, 31
	Water	33	Nitrobenzoic acid	Methyl alcohol	47
Iodine	Acetic acid	29	*m*-Nitrobenzaldehyde	Methyl alcohol	47
	Acetylene tetrabromide	29	α-Nitronaphthalene	Benzene	47
				Methyl alcohol	47
	Isoamyl acetate	29	Nitromethane	Ethyl benzoate	5
	Anisole	29		Methyl alcohol	5
	Benzene	29, 12, 44		Nitrobenzene	5
	Bromobenzene	29	Nitrophenol	Methyl alcohol	47
	Carbon disulfide	29, 12	*n*-Octyl bromide	Benzene	16
	Carbon tetrachloride	29, 44, 15		Octane	16
	Chloroform	12, 29	Oxalic acid	Methyl alcohol	47
	Dioxane	44		Water	47
	Ether	12	Pararosaniline	Methyl alcohol	47
	Ethyl acetate	29	Pentaerythritol	Water	33
	Ethyl alcohol	12	Phenanthrene	Benzene	16
	Ethylene dibromide	29	Phenetole	Methyl alcohol	47
	Heptane	20, 44	Phenol	Benzene	47
	Hexane	44		Carbon disulfide	47
	Mesitylene	44		Chloroform	47
	Methyl alcohol	29		Ethyl alcohol	47
	Phenetole	29		Ethyl ether	47
	Toluene	29, 44		Methyl alcohol	47
	m-Xylene	44, 29		Water	1, 47
Iodobenzene	Benzene	16, 47	Phenolphthalein	Methyl alcohol	47
	Ethyl alcohol	32	Phenyl acetate	Methyl alcohol	47
	Methyl alcohol	47	Phthalic acid	Benzene	47
	Toluene	16		Methyl alcohol	47
Iodoform	Benzene	16, 47	Propionic acid	Methyl alcohol	47
	Methyl alcohol	47	*n*-Propyl alcohol	Benzene	47, 23
Iodopropionic acid	Methyl alcohol	47	*n*-Propyl bromide	Benzene	16
Lactic acid	Methyl alcohol	47	*n*-Propyl iodide	Benzene	16
Lactose	Water	47	Propylene glycol	Methyl alcohol	47
Levulose	Water	24	Pyridine	Ethyl alcohol	32
Mannitol	Water	47, 40, 33		Methyl alcohol	45, 47
Methyl alcohol	Nitrobenzene	8		Water	47
Methyl iodide	Benzene	16	Pyrogallol	Methyl alcohol	47
	Toluene	16		Water	47
Methyl salicylate	Benzene	47	Quinoline	Methyl alcohol	45, 47
	Methyl alcohol	47	Quinone	Benzene	47
Methylene iodide	Methyl alcohol	47		Methyl alcohol	47
	Methylene chloride	47	Raffinose	Water	47, 25
N-Methylglycine	Water	25	Raffinose·$5H_2O$	Water	24
Monoacetin	Ethyl alcohol	32	Resorcinol	Ethyl alcohol (96%)	32
Monobenzylamine	Methyl alcohol	47		Water	47, 33, 32
Monochloroacetic acid	Benzene	47	Salicylaldehyde	Benzene	47
				Methyl alcohol	47
	Methyl alcohol	47	Salicylic acid	Methyl alcohol	47
Monochlorohydrin	Methyl alcohol	47	Salol	Methyl alcohol	47
	Water	47	Stearic acid	Ethyl alcohol	32
Naphthalene	Benzene	16	Sucrose	Water	10
	Methyl alcohol	47	Tartaric acid	Methyl alcohol	47
Naphthol	Methyl alcohol	47		Water	47

TABLE 2—*Concluded*

Components		Experimental Method‡
A	B	
Tetrabromomethane	Toluene	16
1,2,4,5-Tetrachlorobenzene	Benzene	16
Tetraethyllead	Benzene	16
Tetraphenyllead	Benzene	16
Tetrachlorobenzene	Methyl alcohol	47
Tetraphenoltin	Benzene	16
Thymol	Methyl alcohol	47
Thymoquinone	Benzene	47
Toluene	Ethyl alcohol	23
Tribromoacetic acid	Methyl alcohol	47
Tribromobenzene	Methyl alcohol	47
Tribromophenol	Methyl alcohol	47
Trichloroacetic acid	Methyl alcohol	47
1,2,4-Trichlorobenzene	Benzene	16
Trichlorohydrin	Benzene	47
	Methyl alcohol	47
2,4,6-Trichlorophenol	Methyl alcohol	47
2,4,6-Trinitrophenol	Benzene	47
	Methyl alcohol	47
	Water	47
Triphenylmethane	Methyl alcohol	45
Urea	Methyl alcohol	47
	Water	47, 1, 33, 9, 26
Urethan	Methyl alcohol	47
	Water	47
Uric acid	Methyl alcohol	47
Vanillin	Methyl alcohol	47

advisable when searching for data on the system C–D to look for the system under both C and D in the column for component A.

Composition: The composition of the mixture is always given in terms of component A. To avoid discrepancies in converting composition data, these are given in the units used by the original investigators. The abbreviations used are as follows:

G/DL = grams/100 cc. of solution
MPC = mole per cent
M/L = moles/liter
N = normality
VPC = volume per cent
WPC = weight per cent

When the coefficient is designated as differential, the listed composition is that for which the coefficient applies. When the coefficient is listed as integral, the composition is that of the solute (A) at the beginning of the experiment diffusing into pure solvent (B). When no composition is listed, integral diffusion is being measured between the two pure components. The solution composition for which a given integral diffusion coefficient represents a differential coefficient is generally not known, as the value may depend on the type of diffusion equipment, the length of the experiment, and the method of calculation.

Type of coefficient: The type of coefficient is abbreviated as follows: D = differential; I = integral.

Experimental precision: The value given is the average percentage precision listed by the author or else determined from observations of reported duplicate data for given experimental points. Where no data were at hand to estimate the precision, *U* is entered. In many cases where several investigators have worked on the same system, it is apparent that the true value lies outside the range of reported accuracy of some of the investigations. Where this is observed,

TABLE 3

Self-diffusion coefficients of pure liquids

Liquid	Tracer Element	Temperature	Pressure	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
		°C.	atm.	cm.²/sec.		
Benzene	Deuterium	15	1	1.88	5	11
		25	1	2.15	5	11
		35	1	2.40	5	11
		45	1	2.67	5	11
	Carbon-14	25	1	2.18	5	11
n-Butyl alcohol	Deuterium	25	1	0.504	1	36
		35	1	0.649	1	36
		45	1	0.822	1	36
tert-Butyl alcohol	Deuterium	35	1	0.497	1	36
		45	1	0.744	1	36
		55	1	1.070	1	36
Carbon disulfide	Sulfur-35	0	200	2.44	5	19
		0	800	2.18	5	19
		0	1500	2.46	5	19
		0	2000	1.80	5	19
		0	2500	1.70	5	19
		0	3500	1.50	5	19
		0	5000	1.25	5	19
		0	7000	0.75	5	19
		0	10000	0.164	5	19
		20	200	3.29	5	19
		20	800	3.49	5	19
		20	1000	3.49	5	19
		20	1500	3.00	5	19
		20	2000	2.40	5	19
		20	2500	2.78	5	19
		20	3500	2.36	5	19
		20	5000	2.07	5	19
		20	6500	1.57	5	19
		20	7500	1.45	5	19
		20	9100	0.70	5	19
		40	200	4.67	5	19
		40	1000	4.20	5	19
		40	2000	4.05	5	19
		40	2900	3.52	5	19
		40	3500	5.60	5	19
		40	5000	3.58	5	19
		40	7000	2.76	5	19
		40	10000	1.72	5	19
Ethyl alcohol	Deuterium	15	1	0.80	5	11
		25	1	1.05	5	11
		35	1	1.31	5	11
		45	1	1.70	5	11
		15	1	0.768	1	36
		25	1	1.01	1	36
		35	1	1.30	1	36
	Carbon-14	25	1	1.02	5	17
Ethyl bromide	Deuterium	15	1	3.60	20	11
		22.5	1	3.80	20	11
		30	1	3.96	20	11

† The numbers refer to the numbered paragraphs in Section IX.

TABLE 3—*Continued*

Liquid	Tracer Element	Temperature	Pressure	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
		°C.	*atm.*	*cm.²/sec.*		
Methyl alcohol................	Deuterium	15	1	1.93	1	36
		25	1	2.27	1	36
		35	1	2.65	1	36
	Carbon-14	25	1	2.36	5	17
Isopropyl alcohol..............	Deuterium	15	1	0.474	1	36
		25	1	0.649	1	36
		35	1	0.867	1	36
		45	1	1.145	1	36
n-Propyl alcohol..............	Deuterium	15	1	0.504	1	36
		25	1	0.646	1	36
		35	1	0.814	1	36
		45	1	1.017	1	36
Carbon tetrachloride...........	Chlorine-36	25	1	1.41	4	52
		25	200	1.08	4	52
		35	1	1.75	4	52
		37.5	200	1.49	4	52
		45	1	1.99	4	52
		50	200	1.80	4	52
Water..........................	Deuterium	15	1	1.90	1*	36*
		25	1	2.43	1*	36*
		35	1	2.98	1*	36*
		45	1	3.60	1*	36*
		15	1	1.62	5*	11*
		25	1	2.04	5*	11*
		35	1	2.73	5*	11*
		45	1	3.34	5*	11*
		0	1	1.00	2*	49*
		5.2	1	1.23	2*	49*
		16.1	1	1.65	2*	49*
		25	1	2.14	2*	49*
		35	1	2.76	2*	49*
		45	1	3.45	2*	49*
		55	1	4.12	2*	49*
		5.2	1	1.29	2*	49*
		17.5	1	1.77	2*	49*
		25	1	2.12	2*	49*
		35	1	2.76	2*	49*
		45	1	3.52	2*	49*
		55	1	4.39	2*	49*
		0	1	1.1	5*	46*
		28	1	2.5	5*	46*
		17.5	1	1.77	1*	38*
		20	1	2.05	U	22
		1	1	1.128	1*	26*
		25	1	2.261	1*	26*
		0	1	1.46	4*	35*

TABLE 3—*Concluded*

Liquid	Tracer Element	Temperature	Pressure	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
		°C.	*atm.*	*cm.²/sec.*		
Water—*continued*..............	Deuterium	14.2	1	1.94	4*	35*
		25	1	2.64	4*	35*
		35	1	3.88	4*	35*
		45	1	4.75	4*	35*
		10	1	1.57	4*	51*
		18	1	2.06	4*	51*
		25	1	2.34	4*	51*
		45	1	3.87	4*	51*
		55	1	4.95	4*	51*
Water..........................	Tritium	0	136	1.65	5*	4*
		0	252	2.37	5*	4*
		0	600	1.06	5*	4*
		0	900	1.84	5*	4*
		0	1240	1.45	5*	4*
		0	2040	1.08	5*	4*
		0	3500	0.787	5*	4*
		0	5900	0.584	5*	4*
		25	1	2.64	5*	4*
		25	245	2.90	5*	4*
		25	1300	3.24	5*	4*
		25	2050	3.06	5*	4*
		25	2500	3.04	5*	4*
		25	3000	2.62	5*	4*
		25	3000	2.36	5*	4*
		25	3975	1.71	5*	4*
		25	5000	1.15	5*	4*
		25	7000	0.753	5*	4*
		25	7000	0.843	5*	4*
		25	9175	0.515	5*	4*
		50	235	5.15	5*	4*
		50	735	4.17	5*	4*
		50	1300	3.48	5*	4*
		50	2100	2.33	5*	4*
		50	2500	1.88	5*	4*
		50	3500	1.82	5*	4*
		50	4450	2.07	5*	4*
		50	7000	2.25	5*	4*
		50	10050	1.38	5*	4*
		5	1	1.39	4*	51*
		15	1	1.83	4*	51*
		25	1	2.44	4*	51*
		35	1	3.04	4*	51*
		45	1	3.83	4*	51*
Water..........................	Oxygen-18	25	1	2.09	5*	11*
		45	1	3.20	5*	11*
		1.1	1	1.44	6*	51*
		4.9	1	1.55	6*	51*
		10	1	1.90	6*	51*
		25	1	2.66	6*	51*
		35	1	3.49	6*	51*
		45	1	4.38	6*	51*
		55	1	5.45	6*	51*

TABLE 4

Self-diffusion coefficients for components of binary liquid mixtures

Components		Tracer Element	Composition of A†	Temperature	Pressure	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
A	B							
				°C.	atm.	cm.²/sec.		
Benzene	Carbon tetrachloride	Carbon-14	98.6 MPC	25	1	2.20	5	17
			88.6 MPC	25	1	2.03	5	17
			79.9 MPC	25	1	1.99	5	17
			64.4 MPC	25	1	1.87	5	17
			54.2 MPC	25	1	1.75	5	17
			47.9 MPC	25	1	1.73	5	17
			22.0 MPC	25	1	1.58	5	17
			6.7 MPC	25	1	1.47	5	17
	Ethanol	Carbon-14	3.9 MPC	25	1	1.85	5	17
			25.8 MPC	25	1	2.07	5	17
			41.5 MPC	25	1	2.21	5	17
			67.4 MPC	25	1	2.29	5	17
			91.2 MPC	25	1	2.22	5	17
			96.9 MPC	25	1	2.24	5	17
			99.5 MPC	25	1	2.13	5	17
	Methanol	Carbon-14	3.0 MPC	25	1	2.44	5	17
			21.3 MPC	25	1	2.42	5	17
			32.2 MPC	25	1	2.37	5	17
			57.0 MPC	25	1	2.48	5	17
			82.7 MPC	25	1	2.37	5	17
			91.7 MPC	25	1	2.24	5	17
			98.1 MPC	25	1	2.17	5	17
Carbon disulfide (Additional data for higher pressures are available in the reference for each of the systems with carbon disulfide)	Isobutyl alcohol	Sulfur-35	50 MPC	20	200	2.10	5	20
			50 MPC	40	200	2.95	5	20
	1-Butanol	Sulfur-35	50 MPC	20	200	3.06	5	20
			50 MPC	40	210	4.29	5	20
	Chlorobenzene	Sulfur-35	20 MPC	40	200	3.52	5	20
			50 MPC	20	218	2.60	5	20
			50 MPC	40	200	4.63	5	20
	2,4-Dimethylpentane	Sulfur-35	50 MPC	20	200	3.15	5	20
			50 MPC	40	200	4.46	5	20
	Heptane	Sulfur-35	50 MPC	0	100	2.00	5	20
			50 MPC	20	150	2.88	5	20
			50 MPC	40	100	4.36	5	20
	Methylcyclohexane	Sulfur-35	50 MPC	0	50	2.37	5	20
			50 MPC	20	50	2.65	5	20
			50 MPC	40	200	3.00	5	20
	Octane	Sulfur-35	50 MPC	20	200	2.82	5	20
	Toluene	Sulfur-35	50 MPC	20	1	1.93	5	20
			50 MPC	40	200	4.03	5	20
Ethanol	Benzene	Carbon-14	0.7 MPC	25	1	3.07	5	17
			1.9 MPC	25	1	2.91	5	17
			5.4 MPC	25	1	2.47	5	17
			7.7 MPC	25	1	2.25	5	17
			12.7 MPC	25	1	1.91	5	17
			20.8 MPC	25	1	1.72	5	17
			32.0 MPC	25	1	1.67	5	17
			60.5 MPC	25	1	1.40	5	17
			81.4 MPC	25	1	1.21	5	17
	Methanol	Carbon-14	4.6 MPC	25	1	1.91	5	17
			11.0 MPC	25	1	1.87	5	17

† See Section VII for an explanation of the abbreviations.

‡ The numbers refer to the numbered paragraphs in Section IX.

TABLE 4—*Concluded*

Components		Tracer Element	Composition of A†	Temperature	Pressure	Diffusion Coefficient $D \times 10^5$	Experimental Precision	Experimental Method‡
A	B							
				°C.	*atm.*	*cm.²/sec.*		
			22.1 MPC	25	1	1.68	5	17
			46.9 MPC	25	1	1.46	5	17
			72.3 MPC	25	1	1.13	5	17
Glycine	Water	Carbon-14	0.01 M/L	25	1	1.06	2	50
			0.10 M/L	25	1	1.05	2	50
			0.25 M/L	25	1	1.03	2	50
			0.50 M/L	25	1	0.990	2	50
			1.00 M/L	25	1	0.929	2	50
			1.50 M/L	25	1	0.871	2	50
			2.00 M/L	25	1	0.830	2	50
Methanol	Benzene	Carbon-14	0.7 MPC	25	1	4.16	5	17
			3.7 MPC	25	1	3.30	5	17
			8.1 MPC	25	1	2.77	5	17
			22.8 MPC	25	1	2.17	5	17
			41.6 MPC	25	1	2.02	5	17
			68.5 MPC	25	1	2.02	5	17
			86.2 MPC	25	1	2.16	5	17
	Ethanol	Carbon-14	6.2 MPC	25	1	1.16	5	17
			14.3 MPC	25	1	1.30	5	17
			30.5 MPC	25	1	1.42	5	17
			57.1 MPC	25	1	1.75	5	17
			79.6 MPC	25	1	2.04	5	17
	Water	Carbon-14	1.49 MPC	27	1	1.56	5	41
			5.34 MPC	27	1	1.40	5	41
			16.8 MPC	27	1	1.28	5	41
			26.7 MPC	27	1	1.11	5	41
			40.3 MPC	27	1	1.13	5	41
			46.2 MPC	27	1	1.25	5	41
			63.3 MPC	27	1	1.52	5	41
			84.6 MPC	27	1	1.95	5	41
			100.0 MPC	27	1	2.35	5	41

it is pointed out in the discussion of the experimental method. Likewise other considerations may warrant doubting the reported precision of a particular investigation; where this occurs, it is also mentioned in the discussion of the experimental method.

Experimental method: The numbers refer to the paragraph numbers used in listing the experimental methods in Section IX. Where certain of the tabulated data warrant amplification, this is done in the discussion of experimental methods in Section IX and the fact is noted by an asterisk on the paragraph number. To further indicate which specific item is discussed, another asterisk will ordinarily appear in the column of the item of interest. For example, many of the estimated precisions are discussed further, and this is so noted by asterisks on the reported percentage precision figures in the table.

VIII. Tabulation of Self-Diffusion Coefficients for Pure Liquids and Binary Liquid Mixtures

All available experimental self-diffusion coefficients for single liquids and components of binary liquid mixtures of non-electrolytes are included in tables

3 and 4. The items tabulated are similar to those in Section VII, except that the tracer element used in each investigation is indicated in a separate column. In table 4 the compound whose self-diffusion rates were determined is designated as component A.

IX. SUMMARY OF EXPERIMENTAL METHODS

A brief review of the experimental methods used by each investigator whose work is summarized in Sections VII and VIII is given below. Also included are further comments on some investigations where warranted and, in particular, those items marked with an asterisk in Section VII and VIII are discussed in greater detail. The numbers in the columns of tables 1, 2, 3, and 4 which are headed "Experimental method" refer to the following numbered paragraphs.

1. Calvet *et al.* (13, 14, 36) measured the diffusion rates of five substances into water by an interferometric technique. For several of the systems the diffusion rate in dilute solution was shown to be a linear function of $(dc/dx)^2/(d^2c/dx^2)$ and by use of this relation, diffusion coefficients were extrapolated to infinite dilution. No estimate of the precision of the data was given.

2. The differential diffusion coefficients of three ideal organic liquid systems (10) and the systems methanol–benzene (11) and ethanol–benzene (12) were measured by Caldwell and Babb in a single-channel diffusion cell with a Mach–Zehnder interferometer technique. The data are generally consistent to within 1 per cent.

3. The diffusion rates of 0.068 *M* acetylene tetrabromide into acetylene tetrachloride were measured by Cohen and Bruins (19) from 0° to 50°C., using a method suitable for layer analysis. The diffusion cell was made of six glass plates, the middle four having three 2-cm. holes in them so that, when properly aligned, they formed three diffusion cells. The solution was placed in the second plate and the solvent in the next three plates to allow calculations to be made from Kawalki's tables. At the start of an experiment the plates were slid together to form the cells; at the end they were slid apart, and the contents were drained and analyzed with an interferometer. The results were consistent to within 1 per cent.

4. Self-diffusion coefficients of water were measured by Drickamer *et al.* (21) at temperatures of 0° to 50°C. and pressures up to 10,000 atm., using tritium as a tracer element. Measurements were made by allowing diffusion to proceed between two glass frits, one of which at the start contained water with a portion of tritiated water. The frits were brought together mechanically at the start of an experiment and the progress of diffusion was observed by measuring the radioactivity at the end of one of the frits. The effective cell length was determined by calibrating at 25°C. and atmospheric pressure, using the self-diffusion coefficient of water determined by Orr and Butler (93). The cell length was corrected for changes in the density of the water at higher pressures. The average precision of the data was 5 per cent, with a maximum deviation of 10 per cent. It is noted that serious disagreement exists among various investigations of the self-diffusion coefficients of water.

5. Integral diffusion coefficients were determined by Dummer (25) for a number of dilute solutions of binary organic liquid systems by use of a two-layer analysis method in a cell consisting of two glass cylinders each 4 cm. high and 1 cm. in diameter which were filled with the solution and the solvent, respectively. The cylinders were brought together at the start of an experiment and separated mechanically at the completion. The average composition in each of the two halves of the cell after diffusion was determined by refractive index measurements. Temperature control varied, but the average precision of the results appeared to be within 5 per cent. Data on the viscosity of the solvents are included in the paper.

6. Integral diffusion coefficients were measured by Dunning and Washburn (26) at 25°C. for various butyl alcohols in dilute aqueous solution by observing the rate of change of surface tension with time in a manometric capillarimeter 0.025 cm. in diameter with a liquid height of 0.05 cm. The capillarimeter was initially filled with water to a given level and placed in a large reservoir of dilute solution. As diffusion proceeded the changes in pressure needed to keep the liquid level constant allowed the surface tension and hence the concentration to be observed at the meniscus. By assuming a linear concentration gradient the diffusion coefficient was calculated by integration of Fick's second law. Data on the density, surface tension, and viscosity of the solutions are also included. The consistency of the results was not given.

7. Diffusion coefficients were measured by Franke (34) at 20°C. for a number of binary systems of water, aliphatic alcohols, and other organic liquids by the Lamm method in a square glass vessel 1 cm. on a side and 15 cm. high. The diffusion coefficients were calculated by the Boltzmann method assuming that D is a function of concentration. Data for refractive index vs. concentration are given. The precision of the measurements is not given, but plots of data comparing the results with those of Gerlach and Münter show disagreement with the latter investigators by as much as 50 per cent. Likewise, comparison with the measurements of Caldwell and Babb shows that for the benzene–carbon tetrachloride system the data of Franke may be in error by as much as 30 per cent.

8. Diffusion coefficients were measured by Gerlach (38) at 20°C. for a number of binary systems of water, aliphatic alcohols, and other organic liquids in cylinders 70 cm. high and 6 cm. in diameter by observing the density distribution with calibrated floats placed in both layers of liquid at the start of an experiment. Differential diffusion coefficients were calculated by Boltzmann's method, assuming that D is a function of concentration. Density–composition data are given. The precision of the data was not given, but excellent agreement exists where the results overlap those of Münter. The data of Franke, however, disagree by as much as 50 per cent, and the data of Caldwell and Babb on the benzene–carbon tetrachloride system differ by as much as 50 per cent.

9. Differential diffusion coefficients of urea in water were measured by Gosting and Akeley (43) at 25°C. by the Gouy interferometric technique used with a modified Tiselius diffusion cell. Results are consistent to within 0.1 per cent.

10. Differential diffusion coefficients of sucrose in water were measured by Gosting and Morris (44) at 1° and 25°C. by the Gouy interferometric technique used with a modified Tiselius diffusion cell. Results are generally consistent to within 0.1 per cent.

11. Self-diffusion coefficients were measured by Graupner and Winter (47) over a temperature range of 15° to 45°C. for water, benzene, bromoethane, and ethanol by use of deuterium or oxygen-18 as a tracer element. Measurements were made in Northrop–McBain type cells of 4 and 11 cc. capacity calibrated with 0.1 N potassium chloride diffusing into water, using a value for D at 25°C. of 1.838×10^{-5} cm.^{2}/sec. Analyses were made by burning the compounds to water and measuring the densities with a pycnometer. Duplicate measurements agreed within 5 per cent except for variations of up to 20 per cent for bromoethane. It is noted that values for self-diffusion coefficients for water disagree seriously among different investigators.

12. Integral diffusion coefficients of iodine in various organic solvents were measured by Groh and Kelp (49) at 5° to 20°C. by the method of four-layer analysis adapted to calculation from Stefan's tables. Diffusion was conducted in glass cylinders 3 cm. in diameter and 10–12 cm. high. At the conclusion of an experiment the liquid was divided into four layers and the iodine concentration in each determined by titration with sodium thiosulfate. Data for 10°C. obtained by assuming the $D\eta/T$ product constant and that for infinite dilution obtained by graphical extrapolation are also included in the paper, along with some data for diffusion into mixed pairs of solvents. Temperature control at times varied up to 0.4°C., although results appeared consistent to within less than 5 per cent.

13. Differential diffusion coefficients of DL-α-alanine in water at 25°C. were measured by Gutter and Kegeles (50) over a concentration range of 0.25 to 13 weight per cent. Measurements were made with a single-lens convergent-light Gouy interferometric system used with a Tiselius diffusion cell. Values for the diffusion coefficient were consistent to within 0.1 per cent. Some results with D-α-alanine and L-α-alanine indicated no difference in diffusion rate from that of DL-α-alanine.

14. Integral diffusion coefficients were measured by Hammond and Stokes (51) at 25°C. for ethanol–water in stirred Northrop–McBain type diaphragm cells calibrated with 0.1 N or 0.5 N potassium chloride, using values previously given by Stokes. The integral coefficients were converted into differential coefficients by assuming that the differential coefficient was a function of the concentration and that the integral coefficient $\bar{D}$ was related to the differential coefficient D by the following expression:

$$\bar{D} = \frac{1}{W'_m - W''_m} \int_{W''_m}^{W'_m} D \, \mathrm{d}W$$

where W'_m is the mean of the initial and final concentration on one side of the diaphragm and W''_m the mean of the other side. Although the precision of these data was stated to be 0.5 per cent, they disagree with those of Smith and Storrow by up to 100 per cent in the ranges of high alcohol content.

15. Integral diffusion coefficients of a solution of 10 mg./cc. of iodine in carbon tetrachloride diffusing into pure carbon tetrachloride were measured by Haycock, Alder, and Hildebrand (53), using a capillary-cell technique at temperatures from 10° to 50°C. and pressures up to 200 atm. The capillaries used were 6 to 7 cm. long and held approximately 0.25 cc. diffusing into reservoirs of pure carbon tetrachloride of either 430 cc. or 1 liter capacity. Diffusion was allowed to proceed for approximately three days, and the final iodine content in the capillaries was determined by a standard microanalytical technique. The maximum deviation of experimental observations from the reported mean was 5 per cent.

16. Integral diffusion coefficients of many organic liquids in binary solution were measured by Herzog, Ilig, and Kudar (54) at approximately 7°C. by a method suitable for calculation from Stefan's tables. The diffusion was conducted in a cell so constructed that the liquids could be displaced with a column of mercury. At the end of an experiment eight liquid layers of equal height were withdrawn for analysis and the diffusion coefficients calculated from Stefan's tables. From more complete data listed for a few systems the general precision appears to be within 5 per cent. Data for the viscosity of the solvents are given in the paper.

17. Self-diffusion coefficients of benzene, methanol, and ethanol were measured in binary solutions with each other and the benzene as well as in binary solutions with carbon tetrachloride and chloroform by Johnson and Babb (58). A capillary-cell technique was used with capillaries having an internal diameter of 1.5 mm. and a length of 6 cm. The radioactivity of the liquid samples was determined in small counting cells with a thin mica bottom placed adjacent to a thin-window Geiger–Mueller tube. The results were consistent to within 5 per cent.

18. Differential diffusion coefficients of the methanol–water system were measured by Kannuna (61) at 19.3°C. by relating measurements of the speed of sound at various heights along the diffusion cell to changes of concentration with position and time. The speed of sound was determined by passing light through the cell at various heights and measuring its deflection by use of an ultrasonic field. The diffusion coefficient was calculated by the Boltzmann method, assuming D to be a function of concentration. Some individual duplicate experiments disagreed from the average values by as much as 20 per cent.

19. The self-diffusion rates of carbon disulfide were measured by Koeller and Drickamer (68, p. 267) at temperatures of 0° to 40°C. and pressures up to 10,000 atm., using sulfur-35 as a tracer element. The technique and precision were the same as listed previously in paragraph No. 4.

20. Self-diffusion coefficients of carbon disulfide were measured by Koeller and Drickamer (68, p. 575) for mixtures, primarily at 50 mole per cent, of carbon disulfide and various organic liquids at temperatures of 0° to 40°C. and pressures up to 10,000 atm., utilizing carbon disulfide tagged with radioactive sulfur-35 as a tracer element. The technique and precision were the same as described previously in paragraph No. 4.

21. The differential diffusion coefficient of glycerol in water at a concentration of 97.20 weight per cent glycerol was measured at 20°C. by Lamm and

Sjöstedt (74), using the Lamm scale method. The maximum deviation of the average value reported for D was 0.18×10^{-7} cm.^{2}/sec. at long diffusion times.

22. The self-diffusion coefficient of water was measured at 20°C. by Lamm (73), using the Lamm scale method with deuterium as a tracer. The precision of the observations was not given.

23. Differential diffusion coefficients were measured by Lemonde (75) for a number of binary organic liquid systems at temperatures of 5° to 18°C. for both dilute and concentrated solutions. The rate of diffusion was measured by observing the maximum displacement of a light ray passing through the diffusing system. Plots of viscosity, diffusion coefficient, and the diffusion coefficient–viscosity product vs. composition are given. Data are consistent to within 2–4 per cent and agree well with later data for the systems ethanol–benzene and methanol–benzene (11, 12).

24. The differential diffusion coefficients of thirteen amino acids, four peptides, and five sugars were measured in dilute aqueous solution at 1°C. by Longsworth (79), using a Rayleigh interferometric technique in a modified Tiselius diffusion cell. The precision of the results was within 0.1 per cent. Only part of the data is tabulated in Section VII.

25. The differential diffusion coefficients of twenty amino acids, nine peptides, and three sugars were measured in dilute aqueous solution at 25°C. by Longsworth (80), using a Rayleigh interferometric technique in a modified Tiselius diffusion cell. The precision of the results was within 0.1 per cent. Only a portion of the data is included in Section VII.

26. The differential diffusion coefficients of a number of substances were measured in dilute aqueous solution from 1° to 37°C. by Longsworth (81), using an interferometric optical technique in conjunction with a modified Tiselius diffusion cell. The data are consistent to within 1 per cent. Of particular interest was the observation that the diffusion coefficient of deuterium oxide in water was concentration-dependent, the diffusion rate decreasing by approximately 4 per cent as the amount of deuterium oxide was increased from zero to 0.15 mole fraction.

27. Differential diffusion coefficients of n-butyl alcohol in water were measured by Lyons and Sandquist (82) at 1° and 25°C. by the Gouy interferometric technique in a modified Tiselius diffusion cell. The results are consistent to better than 1 per cent. Densities and viscosities are also included in the paper.

28. Differential diffusion coefficients of glycine in water were measured by Lyons and Thomas (83) at 1° and 25°C. by the Gouy interferometric technique in a modified Tiselius diffusion cell. The results are consistent to within 0.1 per cent. Density and viscosity data were also determined at 1°C.

29. The diffusion rates of approximately 0.1 N solutions of iodine in various solvents were measured by Miller (85) at temperatures from 8° to 19°C. by layering a definite volume of solution beneath three times that volume of pure solvent. Four equal layers of solution were removed at the end of an experiment and analyzed by titration with sodium thiosulfate. The diffusion coefficients were calculated by use of Kawalki's tables slightly modified to eliminate some of the convection error. The agreement of the results was generally within 2 per cent.

30. Integral diffusion coefficients of 1.0 N acetic acid and aniline in various organic liquids were measured by Muchin and Faermann (86), using a method suitable to layer analysis. At the end of an experiment the liquid was divided into four layers and the results calculated by use of Kawalki's tables. Analysis of acetic acid was by titration with barium hydroxide and of aniline by refractive index measurements. Temperature control was sometimes only to 0.5°C., but the results appear generally consistent to within 5 per cent.

31. Differential diffusion coefficients were measured by Münter (87) at 20°C. for binary pairs of several common organic liquids by the Lamm scale method in a glass cell 30 cm. long and 1 cm. in diameter. The diffusion coefficients were calculated by the Boltzmann method, assuming D to be a function of concentration. Density–concentration and refractive index–concentration data are given. Results are plotted along with those of Gerlach; where data overlap the agreement is excellent. The data, however, disagree with those of Franke by up to 50 per cent, and with the data of Caldwell and Babb for the benzene–carbon tetrachloride system by as much as 15 per cent.

32. Integral diffusion coefficients of a number of organic substances were measured in ethyl alcohol and 96 per cent ethyl alcohol (aqueous) by Oeholm (90, No. 24) in a cell designed so that the liquid could be separated into equal layers at the end of an experiment. The liquid layers were analyzed by refractive index measurements and the diffusion coefficients were calculated by use of Kawalki's tables. In general the precision of the measurements was within 5 per cent.

33. Integral diffusion coefficients for a number of high-molecular-weight organic compounds were measured in water at 10° and 20°C. by Oeholm (90, No. 23), using a cell suitable for layer analysis and calculation from Kawalki's tables. Not included in Section VII are data for some of the listed compounds at 10°C. and for a number of compounds of very high molecular weight and some colloids at both 10° and 20°C. The precision of results was generally within 5 per cent.

34. Integral diffusion coefficients of glycerol and bromoform were measured in a number of organic liquids by Oeholm (90, No. 26), using a cell suitable for layer analysis and calculation from Kawalki's tables. The data obtained were near 20°C. and were reduced to 20°C. by assuming that the $D\eta/T$ product was a constant. Viscosity data are given in the original paper as well as some additional diffusion data. The precision of the results was generally within 5 per cent.

35. Measurements of the self-diffusion coefficients of water between 0° and 45°C. were made by Orr and Butler (93), using unstirred glass diaphragm cells of the Northrop–McBain type of approximately 24 cc. volume. Cells were calibrated with 0.1 N potassium chloride at 20°C., using a value for D of 1.68 $\times 10^{-5}$ cm.^{2}/sec. Analyses were by measurements of the density by means of a pycnometer. The results were consistent to within 4 per cent, but it is observed that serious diagreement exists among investigators for the self-diffusion coefficients of water.

36. Self-diffusion coefficients for water and a number of aliphatic alcohols were measured by Partington, Hudson, and Bagnall (95) in a magnetically stirred

Northrop–McBain type glass diaphragm cell over a range of 15° to 55°C. The hydrogen atom in the hydroxyl group was replaced with deuterium and analyses were made by combustion to water, followed by density measurements in a micro-float apparatus. The reported overall accuracy of the results was 0.5 per cent, but it is observed that serious diagreement on the self-diffusion coefficients of water exists among various investigators.

37. Differential diffusion coefficients of water in *n*-butyl alcohol at 30°C. were measured by Randall, Longtin, and Weber (98), using a modified Thovert method. Optical measurements of the refractive index gradient were made to determine the concentration gradient in a vertical cell with water in the bottom and the *n*-butyl alcohol on top. The alcohol was added at a uniform rate of 2 cc./min. and sufficient water was added to the bottom to keep the water–alcohol boundary at the same height. When a steady state was reached after approximately one week the diffusion current of water was determined by an interferometric analysis of the alcohol overflow. Knowledge of the diffusion flux, the concentration gradient, and the concentration at any point enabled the diffusion coefficient to be calculated. The precision of the observations was not given.

38. The self-diffusion coefficient of water was measured by Roegener-Leipzig (99) at 17.5°C. by use of deuterium as a tracer element and an interferometric technique to measure changes in refractive index as diffusion proceeded. The average value of D tabulated was within 1 per cent of all experimental data reported, but it is observed that there is considerable disagreement among investigators for the self-diffusion coefficients of water.

39. Differential diffusion coefficients of diphenyl in benzene were measured by Sandquist and Lyons (101) at 25° and 35°C. and at a concentration of 3 N by the Gouy interferometric technique in a modified Tiselius type diffusion cell. The results were consistent to within 1 per cent.

40. Integral diffusion coefficients of mannitol in dilute aqueous solution were measured by Scheffer and Scheffer (103), using a layer analysis technique. Results were consistent to within 2–4 per cent.

41. Self-diffusion coefficients of methanol in methanol–water solutions were measured by Sehmel and Babb (104), using the capillary-cell technique described in paragraph No. 17.

42. Diffusion coefficients of the ethanol–water system were measured by Smith and Storrow (106) over a range of 25° to 72.5°C. in a magnetically stirred glass diaphragm cell of the McBain–Northrop type of approximately 20 cc. capacity. The cells were calibrated by use of various concentrations of potassium chloride at 25°C., using the data of Harned and Nuttall as reference values. The analyses were by specific gravity measurements supplemented by other chemical or physical methods. The diffusion coefficients listed in Section VII were obtained from a published graph of diffusion coefficient vs. concentration and may be slightly in error because of errors in reading the graph. The precision was stated to be within 3 per cent, but disagreement up to 100 per cent exists with data of Stokes and Hammond.

43. Integral diffusion rates of 0.1 N hydrogen peroxide in water and several

organic liquids were measured by Stern (109) from 0° to 30°C. in a simple Anson-type diaphragm cell of 75 cc. capacity calibrated with 0.1 N potassium chloride diffusing into pure water, using a value for D of 1.448 cm.^{2}/day at 20°C. Analyses were by iodometric titration. The hydrogen peroxide used in the tests with water was stabilized with 0.1 per cent acetanilide; additional data for diffusion into water with other stabilizing agents added are given in the paper. More detailed data given for some of the experiments indicated a general precision within 5 per cent.

44. The integral diffusion coefficients for dilute solutions of iodine diffusing into various organic solvents were measured by Stokes, Dunlop, and Hall (111) at 25°C. in stirred Northrop–McBain type diaphragm cells calibrated with potassium chloride solution. Iodine was analyzed by titration with sodium thiosulfate or sodium arsenite. The diffusion coefficients were extrapolated and reported also for infinite dilution. The precision of the results was stated to be within 1 per cent.

45. The integral diffusion coefficients for a number of organic compounds in methyl alcohol were measured by Svedberg and Svedberg (113) at 15°C. by a method in which the solution could be withdrawn in four layers at the end of an experiment. The average concentration in each layer was measured by refractive index determinations and the diffusion coefficient calculated by use of appropriate tables. Where indicated by an asterisk concentrations of solute are given in terms of grams per 100 cc. of solvent in the tabulation of Section VII. Additional data for some of the systems indicated a general precision of approximately 5 per cent.

46. The diffusion rate of heavy water (3 mole per cent) into water was measured by Temkin (115) by allowing diffusion to proceed from a micropycnometer (0.1 mm. inside diameter) into a larger vessel of water and observing the difference in equilibrium hydrostatic pressure for the solution and the heavy water. The changes in pressure were used to calculate the diffusion coefficient after the method was calibrated with potassium chloride. The results were self-consistent within 5 per cent, but it is noted that serious disagreement exists among investigators for the self-diffusion coefficients of water.

47. The diffusion rates of many organic substances were determined in dilute solution (less than 2 weight per cent) of water, methyl alcohol, and benzene by Thovert (116). The changes in concentration with distance and time in a glass diffusion cell were determined by observing the maximum displacement of a beam of light passing through the cell. The data were calculated assuming that D is a constant and generally represent a differential coefficient at a concentration of approximately 0.5 to 1 weight per cent solute. Although obtained at temperatures from 6° to 25°C., the data are usually extrapolated and tabulated at 15°C. by assuming the $D\eta/T$ product constant for each system. Considerable additional data for the diffusion of phenol into various solvents and mixtures of solvents from 10° to 25°C. are given in the paper. The general precision was stated to be within 2 to 3 per cent, but in many cases the error may have been 5 to 10 per cent.

48. Differential diffusion coefficients were measured by Trevoy and Drickamer

(119) at temperatures of 15° to 55°C. for 50 mole per cent mixtures in binary systems of paraffin hydrocarbons, and paraffin hydrocarbons and benzene, in horizontal, unstirred diaphragm cells. The cells had a capacity of approximately 23 cc. and were calibrated by diffusing 0.1 N hydrochloric acid into pure water, using a value of 2.90×10^{-5} as the integral diffusion coefficient at 25°C. Concentrations were determined with a Zeiss water interferometer. Precision was usually within 4 per cent.

49. Self-diffusion measurements were made by Wang (123) on water in the range of 0° to 55°C., using deuterium as a tracer in both capillary and diaphragm cells. The capillaries used were 0.5 mm. in diameter and 4 cm. long. The diaphragm cells were unstirred Northrop–McBain type glass cells holding approximately 50 cc. and were calibrated using a value of 1.77×10^{-5} cm.^{2}/sec. at 17.5°C. as the self-diffusion coefficient of water. Analyses were by density measurements with a gradient tube for the capillary-cell technique and a pycnometer for the diaphragm-cell technique. Reported accuracies were 1 per cent for the capillary-cell technique and 2 per cent for the diaphragm-cell technique, but later data by the same author disagree by as much as 20 per cent.

50. The self-diffusion coefficients of glycine tagged with carbon-14 were measured by Wang (127) in dilute aqueous solution at 25°C. by a capillary-cell technique. Radioactivity measurements were made with a gas-filled Geiger–Mueller tube. The results were generally consistent to within 2 per cent.

51. The self-diffusion of water was measured by Wang, Robinson, and Edelman (129), using a capillary-cell technique in which deuterium, tritium, and oxygen-18 were used as tracers. The capillaries had a cross-section of approximately 0.2 mm.^{2} and were 2 to 5 cm. long. The deuterium samples were analyzed by mass spectrometry and the tritium by measuring the radioactivity of tritiated methane formed with the tritiated water. The oxygen-18 was analyzed by equilibrating the water with carbon dioxide and analyzing the equilibrated gas by mass spectrometry. The data with oxygen-18 were presented in an earlier paper by Wang (126), but an error was present in the calculations which was eliminated in the present paper. The precision was generally 4 per cent with deuterium and tritium and 6 per cent with oxygen-18. It is noted that considerable disagreement exists among values of self-diffusion coefficients of water as reported by various investigators.

52. The self-diffusion rates of carbon tetrachloride tagged with chlorine-36 were measured by Watts, Alder, and Hildebrand (130) from 25° to 50°C. and 1 to 200 atm. pressure with a stated precision of 4 per cent. The technique used with the capillary diffusion cell is described in paragraph No. 15.

The authors wish to express their indebtedness to Dr. J. R. Hall for his helpful comments and assistance with the manuscript.

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