MOLECULAR DIFFUSION IN SOLUTION

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Diffusion is one of the most fundamental properties of substances in solution. If, for example, sugar is placed in a beaker of water and allowed to stand, the sugar will subsequently be found in all parts of the water. The same is true of other soluble substances, and we say that they diffuse throughout the water occupying the volume of the liquid just as any gas occupies the volume in which it is confined. The diffusion of molecules through liquids is a common phenomenon, and it has been extensively studied in a quantitative way. It should be remarked that in many cases the data of these experiments are conflicting and in other ways unsatisfactory, undoubtedly because each figure is usually the result of a prolonged and laborious experiment which is dependent upon the most painstaking precautions and observations.

These data have not always led to conclusions of theoretical importance because the kinetic theory of liquids is extremely difficult compared to that for gases and solids. However, for dilute solutions results of considerable significance can be obtained using the fundamental diffusion laws. In more concentrated solutions the elementary laws do not hold, supposedly because of interactions between dissolved particles and with solvent molecules which lead to association and solvation effects. Thus the situation may be compared to that of solutions of electrolytes, where the ideal limiting laws are known to be obeyed only in extremely dilute solutions and the deviations from them in more concentrated solutions are just beginning to be understood.

But within the limited scope suggested above, the writers feel that the diffusion theory has performed remarkably well in the interpretation of experimental data in a simple and straightforward way. It will be their attempt to treat these achievements in a logical way, discussing the *theory, experiment, interpretation,* and *application* of molecular diffusion in solution. At the same time it is desired to suggest the subject as one worthy and necessary of further investigation and development. It is our regret that in connection with many ideas expressed it will be impossible to give proper reference to excellent articles which, appearing from time to time, have embodied these thoughts.

Diffusion experiments achieved considerable importance in the hands of Graham (27) who used them to differentiate between "crystalloids" and "colloids." Both free diffusion and diffusion through membranes (dialysis) were used for this purpose. At least in the case of the free diffusion this separation depended upon a difference in the diffusion rate, and not on the fact that crystalloids diffuse and colloids do not. As this has become more clearly understood, it has become proper to speak of a "colloidal state of aggregation" rather than to think of "colloidal substances." As a matter of fact, both ordinary solutions and colloidal solutions are now recognized to be dispersed systems that comprise a dispersion medium and a dispersed part to which, among other things, the molecular kinetic theory may be applied. It is meant to imply here that the kinetic energy of suspended particles in a sol should be the same as the kinetic energy of molecules, and the colloidal solutions should give diffusion just as ordinary solutions do. We are thinking therefore in this article of molecular diffusion in its broader sense.

It is also well to mention that, unless noted to the contrary, a free diffusion is being considered. The mathematical theory of obstructed and forced diffusions is quite different from that of free diffusion. This point is emphasized because in several recent investigations the attempt has been made to avoid the experimental inconveniences of free diffusion by studying the rates of diffusion through porous membranes, giving a diffusion constant relative to some arbitrary standard. Diffusion constants obtained in this way hardly can be accepted as final when a demonstration of the sufficiency of the method is not provided.

I. Theory[1]

A. FREE DIFFUSION

In 1855 Fick (18) stated the general law of linear diffusion as follows: The quantity of substance which diffuses through a given area is proportional to the difference between the concentration of two areas infinitely near to each other. Expressed mathematically, if we take two points in a solution at a distance apart dx, with difference in concentration at these two points dc, concentration gradient in the direction x will be dc/dx and

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[1] In the preparation of this section the authors have drawn freely from several sources, among which may be mentioned: Byerly, Fourier Series and Spherical Harmonics, Ginn and Co., New York (1893); Ingersoll and Zobel, Mathematical Theory of Heat Conduction, Ginn and Co., New York (1913); Carslaw, Heat Conduction, The MacMillan Co., New York (1921); Fürth, Diffusion ohne Scheidewände, Handb. d. phys. u. techn. Mech. (Auerbach-Hort), Vol. 7, Barth, Leipzig (1931).

the amount of solute, $\mathrm{d}m$, which diffuses through a cross-section q in time $\mathrm{d}t$ is

$$\mathrm{d}m = -Dq\frac{\mathrm{d}c}{\mathrm{d}x}\,\mathrm{d}t \tag{1}$$

The minus sign means simply that the solute diffuses in the direction of decreasing concentration. This law, sometimes referred to as the first law of Fick, was originally empirical in character, but it has long since been shown to be derivable from osmotic theory. It is a typical "dilute solution" law. The constant D, the so-called diffusion constant or specific diffusion rate, measures the amount of solute which would diffuse across unit area under unit concentration gradient in unit time, provided the rate is constant during that time.

The two independent variables, x and t, and two dependent ones, m and c, make its use somewhat cumbersome. However, it is possible to reduce the number of dependent variables by one, obtaining at the same time the general differential equation of diffusion known as the second law of Fick. If we consider an infinitesimal volume in a space bounded by planes at the distances x and $x + \mathrm{d}x$, the amount of solute which will accumulate in this volume in time $\mathrm{d}t$ will be the difference in the amount which enters across the plane at x and leaves across the plane at $x + \mathrm{d}x$. It will be

$$\mathrm{d}m - \left(\mathrm{d}m + \frac{\partial(\mathrm{d}m)}{\partial x}\,\mathrm{d}x\right) = -\frac{\partial(\mathrm{d}m)}{\partial x}\,\mathrm{d}x$$

Now, since concentration is amount divided by volume, the corresponding concentration increase is

$$\frac{-\dfrac{\partial(\mathrm{d}m)}{\partial x}\,\mathrm{d}x}{q\mathrm{d}x}$$

This concentration increase is also expressed by the quantity $\frac{\partial c}{\partial t}\,\mathrm{d}t$, therefore

$$\frac{\partial c}{\partial t}\,\mathrm{d}t = \frac{1}{q}\,\frac{\partial(\mathrm{d}m)}{\partial x}$$

Combination of this expression with the first law of Fick leads directly to the very important and general result

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2} \tag{2}$$

The diffusion law may also be derived hydrodynamically. If the solution to which it is applied is sufficiently dilute for the use of the ideal gas law to measure its osmotic pressure we have,

$$p = C\frac{RT}{M}$$

where C is the concentration (amount per unit volume) and M is the molecular weight of the solute. Now, if we consider a volume element, $\mathrm{d}V$, the force on the dissolved particles due to differences in p will be

$$F = -\operatorname{grad} p \, \mathrm{d}V$$

But if m is the mass of a single particle, the total number of particles in $\mathrm{d}V$ is $\frac{C}{m}\,\mathrm{d}V$, so that the force on a single particle will be

$$f = -\frac{m}{C}\operatorname{grad} p$$

Now, since $M/m = N$, we can write

$$f = -\frac{RT}{N}\frac{\operatorname{grad} C}{C}$$

For the case of steady motion, that is, where each particle is given a constant velocity v, it is evident that

$$v = Bf$$

where B is the "mobility" of the particle. It depends upon the size and shape of the particle and the viscosity of the medium in which it is suspended. Therefore,

$$v = -\frac{RT}{N}B\frac{\operatorname{grad} C}{C}$$

Expressed in terms of the flow, J, which is by definition the product $C \cdot v$, we have,

$$J = C \cdot v = -\frac{RT}{N}B\operatorname{grad} C = -D\operatorname{grad} C \tag{3}$$

The diffusion equation is sometimes used in this simple and direct form, a good example of its application being found in the recent work of Onsager and Fuoss (66). The identity $D = RT/N \cdot B$ will be established in a later section.

The diffusion law has different solutions according to the conditions imposed by the methods of carrying out the experiment. This may be illustrated best perhaps by working out the most general solution in the infinite first, and then showing how it is applied to specific problems. In another section there are considered the modifications necessary when the diffusion takes place in such a way that the process is limited by the presence of a boundary.

I. Solutions without finite boundary

The conditions which must be met by any physical solution are as follows:

1. $c = c\,(x, t)$.
2. When $t = 0$, $c = f\,(x)$.
3. When $t > 0$, $f\,(x)$ can be differentiated.

The general solution is obtained by assuming

$$C = \Phi(x)\Psi(t) \tag{4}$$

This makes it possible to separate the variables in equation 2, giving two ordinary differential equations whose solutions are

$$\begin{aligned} \Phi(x) &= \beta \cos kx + \gamma \sin kx \\ \Psi(t) &= \alpha \cdot e^{-k^2Dt} \end{aligned} \tag{5}$$

in which α, β, γ, and k are real constants. Since any sum of solutions is also a solution, a new solution results if we add solutions of the form 5 and integrate over all positive values of k. The constants β and γ are taken as functions of k. The result of the operation is

$$C = \int_0^\infty (g(k) \cos kx + h(k) \sin kx)\, e^{-k^2Dt}\, \mathrm{d}k \tag{6}$$

in which $g(k)$ and $h(k)$ are arbitrary functions of k. The problem now is to see whether these functions can be so chosen that the second condition above is fulfilled, that is, we can write

$$f(x) = \int_0^\infty (g(k) \cos kx + h(k) \sin kx)\, \mathrm{d}k \tag{7}$$

Fourier has found this to be the case when the functions $g(k)$ and $h(k)$ are chosen in the following manner:

$$\begin{aligned} g(k) &= \frac{1}{\pi} \int_{-\infty}^{+\infty} f(\alpha) \cos \alpha\, k \mathrm{d}\alpha \\ h(k) &= \frac{1}{\pi} \int_{-\infty}^{+\infty} f(\alpha) \sin \alpha\, k \mathrm{d}\alpha \end{aligned}$$

Substitution of these values in equation 6 leads to the result

$$C = \frac{1}{\pi} \int_0^{\infty} e^{-k^2Dt}\, dk \int_{-\infty}^{+\infty} f(\alpha) \cos k(\alpha - x)\, d\alpha \tag{8}$$

Thus, it can be shown by an integration process that the general solution of Fick's second law for diffusion in the x direction is

$$C = \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{+\infty} f(\alpha)\, e^{-\frac{(\alpha - x)^2}{4Dt}}\, d\alpha \tag{9}$$

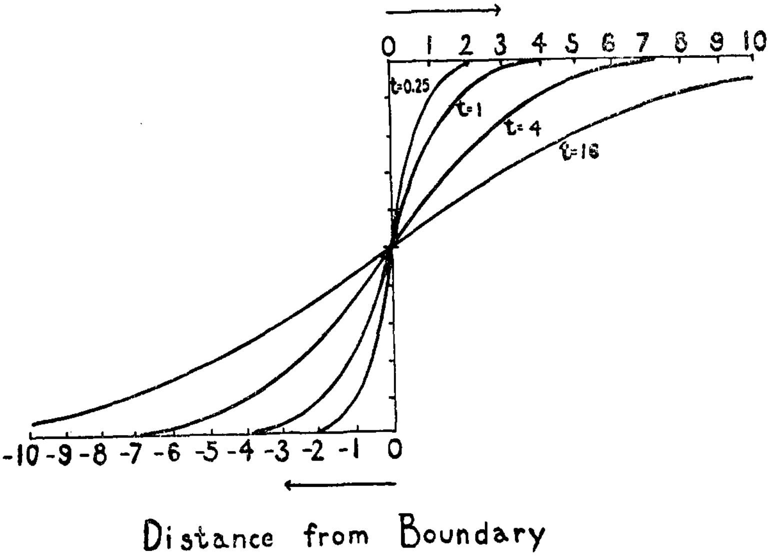

FIG. 1. RELATIVE CONCENTRATION AS A FUNCTION OF DISTANCE FROM BOUNDARY. DIFFUSION FROM SOLUTION ACROSS BOUNDARY INTO SOLVENT

By the introduction of the new variable

$$y = \frac{\alpha - x}{2\sqrt{Dt}}$$

the general solution becomes

$$C = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} f(x + 2y\sqrt{Dt})\, e^{-y^2}\, dy \tag{10}$$

The brief description of two very important special cases of the application of this equation to the diffusion of solutes will illustrate its use. It may be well to recall that in these cases the diffusion is not restricted by the dimensions of the cell in which the process is taking place; in other words, the containing vessels are long enough and the time is short enough so that the concentration changes do not occur at their extreme ends.

Case I. Diffusion from solution into solvent. At time $t = 0$ the concentration of the solute in the positive half of the cell is C_0, but in the negative half it is zero. Thus

$$f(\alpha) = 0, \text{ for } \alpha < 0$$

$$f(\alpha) = C_0, \text{ for } \alpha > 0$$

Under these conditions

$$C = \frac{C_0}{2}\left\{1 - U\left(\frac{x}{2\sqrt{Dt}}\right)\right\} \tag{11}$$

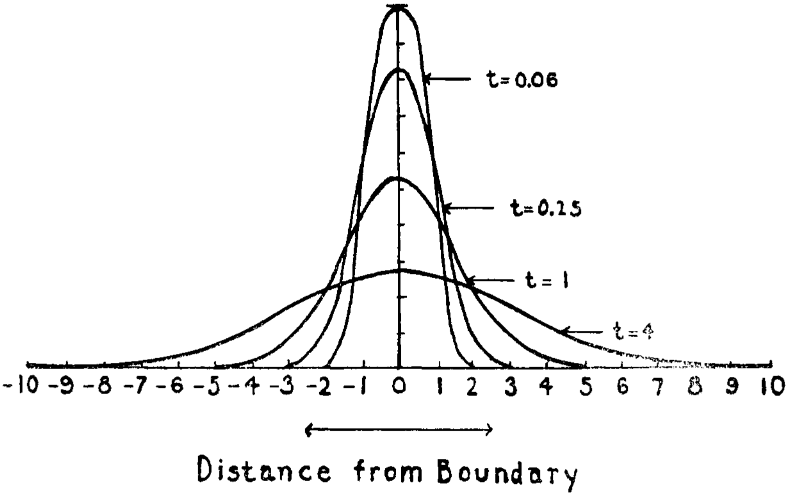

FIG. 2. RELATIVE CONCENTRATION AS A FUNCTION OF DISTANCE FROM BOUNDARY. DIFFUSION FROM THIN LAYER INTO SOLVENT

where

$$U(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2}\, dy$$

The progress of such a diffusion as a function of distance for definite times is shown by the accompanying graph (figure 1) obtained from equation 11.

Case II. Diffusion from thin layer. At time $t = 0$ the concentration of the solute in the cylinder is zero except for an infinitely thin layer of thickness dx between the positive and negative halves of the vessel, in which it becomes infinite as the thickness approaches zero. Thus,

$$f(\alpha) = 0, \text{ for } \alpha \lessgtr 0$$

$$f(\alpha)\, d\alpha = 1, \text{ for } \alpha = 0$$

Under these conditions

$$C = \frac{1}{2\sqrt{\pi Dt}}\, e^{-\frac{x^2}{4Dt}} \tag{12}$$

Figure 2 shows the progress of this type of diffusion. Here $C(x)$ is shown at a number of times t.

II. Solutions with finite boundary

In the general solution of the linear problem it was assumed that the medium in which the diffusion took place extended to infinity in both positive and negative directions. It is not difficult to extend this solution to certain cases where the medium extends to infinity in the one direction but is bounded by a surface on the other side. This surface is conveniently chosen at position $x = 0$. In such an experiment with smooth and impervious boundary at right angles to the direction of the diffusion, $\partial c/\partial x = 0$ for $x = 0$, and the general solution of Fick's law assumes the form

$$C = \frac{1}{2\sqrt{\pi\, Dt}} \int_0^\infty f(\alpha)\, \{e^{-\frac{(\alpha - x)^2}{4Dt}} + e^{-\frac{(\alpha + x)^2}{4Dt}}\}\, d\alpha \tag{13}$$

Corresponding to the second special case considered above, let us assume an experiment in which there is a very thin layer of diffusing solution under a very high column of dispersion medium. As before

$$f(\alpha) = 0, \text{ for } \alpha \lessgtr 0$$

$$f(\alpha)\, d\alpha = 1, \text{ for } \alpha = 0$$

and

$$C = \frac{1}{\sqrt{\pi Dt}}\, e^{-\frac{x^2}{4Dt}} \tag{14}$$

As might have been predicted, the concentration at any distance x in time t is twice that obtained before.

Another important finite boundary problem is the diffusion between parallel boundaries in the YZ planes, $x = 0$ and $x = l$. At time $t = 0$, $c = f(x)$ and $0 \leqq x \leqq l$. It has already been shown that the expression

$$e^{-k^2Dt}\,(A \cos kx + B \sin kx)$$

is a solution of the general diffusion law when A, B, and k are chosen properly. The boundary conditions of the problem demand that $A = 0$ and $kl = n\pi$, where $n = 1, 2, 3, \ldots$ etc. The particular solution then becomes

$$B_n \sin \frac{n\pi}{l} x \cdot e^{-\frac{n^2\pi^2}{l^2} Dt}$$

Any sum of linear solutions is also a solution, therefore

$$C = \sum_{n=1}^{\infty} B_n \sin \frac{n\pi}{l} x \cdot e^{-\frac{n^2\pi^2}{l^2} Dt}$$

Such an infinite sum is a solution provided the series converges. The coefficients B_n may be obtained from conditions at the start of the experiment. It is required that

$$f(x) = \sum_{n=1}^{\infty} B_n \sin \frac{n\pi}{l} \cdot x \text{ in the region } 0 \leqq x \leqq l$$

Fourier has shown that this is fulfilled since $f(x)$ can be represented by a series of sines, cosines or both, and the coefficients are

$$B_n = \frac{2}{l} \int_0^l f(\alpha) \sin \frac{n\pi}{l} \alpha \, d\alpha$$

Thus

$$C = \frac{2}{l} \sum_{n=1}^{\infty} e^{-\left(\frac{n\pi}{l}\right)^2 Dt} \sin \frac{n\pi}{l} x \cdot \int_0^l f(\alpha) \sin \frac{n\pi}{l} \alpha \, d\alpha \qquad (15)$$

This equation is an extremely important one because it is required for the calculation of the diffusion constant in several types of experiment.

An important diffusion experiment makes use of conditions described by Stefan (79), as follows:

At time $t = 0$ the space between planes $x = 0$ and $x = h$ is filled with solution of concentration $C = C_0$ and the corresponding space between $x = h$ and $x = l$ is occupied by solvent, and $c = 0$. In this event,

$$f(x) = C_0, \text{ for } 0 \leqq x < h$$

$$f(x) = 0, \text{ for } h < x \leqq l$$

Transformations not detailed here lead to the final result

$$C = C_0\left(\frac{h}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} e^{-\left(\frac{n\pi}{l}\right)^2 Dt} \cos \frac{n\pi}{l} x \cdot \sin \frac{n\pi}{l} h\right) \qquad (16)$$

The use of this rather complicated formula may be simplified by choosing the experimental conditions in such a way that the ratio h/l is some simple fraction. Its use is also rendered less tedious by the tables of Stefan (79) and Kawalki (40), which are constructed for the case where $h = l/4$. If we know the amount of substance in the several layers into which the diffusing liquid can be divided, the diffusion constant D can be calculated.

In certain experiments it is important to know how much material has diffused from one layer into another in a given time. Thus, for the case in which $h = l/2$, the quantity Q, which has penetrated into the solvent, is

$$Q = -\int_0^t D\left(\frac{\partial c}{\partial x}\right)_{x=\frac{l}{2}} dt$$

$$= \frac{lc_0}{4}\left\{1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} e^{-\left[\frac{(2m+1)\pi}{l}\right]^2 Dt}\right\} \qquad (17)$$

An additional type of experiment in which material is allowed to diffuse into a porous solid or gel from a stirred liquid in contact with it is of considerable chemical interest, but unfortunately the classical methods of Fourier analysis do not always provide adequate solution of the mathematical problem, and other treatments have been necessary. It is largely through the efforts of March and Weaver (49) and of Langer (47) that the coefficients of the several terms can now be determined, with the result that the specific diffusion rate into the porous solid or gel may be calculated from the analysis of the concentration of the stirred liquid above it as a function of the time.

The question may properly be raised at this point whether a free or obstructed diffusion will take place under these conditions. Its answer will depend primarily upon the relative size of the pore and diffusing molecule, because it will determine whether or not the neighborhood of the extensive surfaces within the structure of the solid affects the nature or extent of the diffusion. There may be a suppression of the diffusion through the orientation and immobilization of solvent molecules adjacent to these surfaces; there may be mechanical blocking; there may be orientation effects if the diffusing molecules differ from the spherical shape to any considerable degree—these and other factors would cause an obstructed diffusion where the pore diameters are not very much larger than those of the diffusing molecules. We shall see that experiments which permit the comparison of the obstructed and free diffusion rates may lead to valuable information with regard to the structure of the diaphragm.

In the March and Weaver treatment of the problem there is assumed a mass of a material to be uniformly distributed, at time zero, in such a solid of given depth. The solid is then covered with water to the same depth. The water is kept stirred during the experiment in which the material diffuses into the water. For the mathematical treatment there is obtained a Volterra integral equation of the second kind with discontinuous kernel to express the concentration in the liquid as a function of the time. The solution of this integral equation is obtained in terms of the roots of a transcendental equation and the roots of an infinite system of linear equations. By means of the theory of singular integral equations, it is shown that the differential equation and boundary conditions possess but one solution of the required type. This solution is

$$V = \frac{U + \lambda V_0}{1 + \lambda} - \sum \frac{B_i}{\beta_i} e^{-\beta_i t} \tag{18}$$

where V is the fraction of the material which has diffused from the solid,

λ is the ratio of the height of the solid to the height of the liquid above it, in this case unity,

t is the time,

$U + \lambda V_0 = 1$, and represents the sum of the solute in the solid and water above,

and the quantities B_i and β_i are more complicated functions which depend upon the boundary conditions, the time, and the diffusion constant.

Complete details for the determination of these coefficients are given in the original article. After their evaluation the expression for the concentration in the liquid becomes

$$V = \tfrac{1}{2} - [0.327\, e^{-4.117T} + 0.0766\, e^{-24.14T} + 0.0306\, e^{-63.68T} + 0.0160\, e^{-123T} + \cdots\cdots]$$

where $T = Dt/a^2$, D is the diffusion constant, t is the time, and a is the height of the solid or of the liquid column above it. The diffusion constant is obtained most readily by plotting V as a function of T, according to this equation. The quantity V is the one determined experimentally as the time proceeds. For each value of V there is found on the graph the corresponding value of T, and since both a and t are known, the value of the diffusion constant is thereby fixed.

B. FORCED DIFFUSION

If there acts on a dissolved particle an external force f^*, causing an additional velocity v^*, then the additional flow is $cv^* = cBf^*$ and the diffusion law assumes the form

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v^* \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - Bf^* \frac{\partial c}{\partial x} \tag{19}$$

The statistical equilibrium or the distribution of concentration in the solution which is independent of the time is found by solving the equation

$$D\frac{\partial^2 c}{\partial x^2} - v^* \frac{\partial c}{\partial x} = 0 \tag{19a}$$

In its general form the solution is

$$c = ae^{\frac{v^*}{D}\cdot x} + b \tag{20}$$

in which a and b are arbitrary constants. In many cases the boundary conditions require that $b = 0$. Thus for sedimentation equilibrium the solution takes the form of the well-known hyposometric law:

$$c = c_0 e^{-\frac{N}{RT}f^* x} = c_0 e^{-\frac{Mg}{RT}\cdot x} \tag{20a}$$

In this equation g is the acceleration due to gravity. Particular solutions of the general equation (19) have been obtained for a number of purposes. To mention a single example, they have considerable use in sedimentation studies with colloidal solutions in which the additional forces are either gravitational or centrifugal in character.

Another extremely important case of a diffusion under the influence of an external force is found in the process taking place in a solution containing electrolytes. Onsager and Fuoss (66), in a very complete treatment of the problem, have shown that fundamentally the diffusion and conduction belong together, both being problems involving the general migration of ions. They have concerned themselves with the formulation of the general differential equations directly in terms of the "driving forces" or gradients of thermodynamic potentials, rather than in terms of osmotic pressures which are related to thermodynamic potentials. In the case of an electrolyte containing two kinds of ions where the assumption of complete ionization can be made, Nernst (57) in 1888 derived an expression for the diffusion constant based upon values of the ionic mobilities as determined by conductance and transference number measurements at high dilution. This expression has been generalized by Noyes (30) to give the following result:

$$D = RT\cdot\frac{U_c\cdot U_a}{U_c + U_a}\left(\frac{1}{Z_c} + \frac{1}{Z_a}\right) \tag{21}$$

where U_c and U_a are the mobilities of the cation and anion, and Z_c and Z_a are their valences. This is a typical infinitely dilute solution law. In the region of finite, but very dilute, solutions (Debye-Hückel region), deviations from a random arrangement affect the resistance to the motion of the ions. A dissociation into ions which is practically complete is assumed.

In the conductance problem the mobility directly due to the applied electrical field overcoming the ordinary friction of the solvent is modified, owing to these deviations from a random arrangement by two forces, the electrical force of relaxation and the electrophoretic force. The diffusion of a simple electrolyte will be modified by the second of these forces only, since all the ions now migrate with the same velocity and no asymmetry can be developed in the ion atmospheres about them. The electrophoretic force, on the other hand, is dependent upon a volume force acting in the ionic atmosphere, resulting in an alteration of the forces needed to make both ions move with the same velocity. In a pure diffusion any velocity difference will be eliminated because of space charge effects. Onsager and Fuoss have shown that the electrophoretic effect may be divided into first and second order terms, both due to the deviations of the ions from a random arrangement. The first order effect results because the anions in the neighborhood of a given anion are partially replaced by cations, and vice versa. When one species of ions is more mobile than the other the slower ions will move in a countercurrent and the more mobile ions will be aided by a motion of their environment. This is a typical "square root of the concentration" effect. The second term, which always decreases the resistance to diffusion, depends upon an overall reduction of the mean distances between the ions in the sense that the distances between ions of opposite sign are reduced more than the distances between like ions are increased.

In more concentrated solutions the specific properties of electrolytes make the theoretical study a difficult one. If the amount of solvent is still large in comparison with that of the solute, the resistance offered by the medium will be practically independent of the concentration, but otherwise not. Haskell (30) has treated the situation which exists when both ions and undissociated molecules are present, by assuming that the frictional resistance encountered by an ion is different from that of the undissociated molecules, while the osmotic effects of ions and molecules are determined solely by their number, and has attempted to measure the difference in diffusion rate existing between the dissociated and undissociated portions of the solute. In general, ions are believed to move more rapidly than molecules because the diffusion rate usually increases with dilution. The equation set up is

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2} \tag{22}$$

where the subscripts 1 and 2 refer to neutral molecules and ions, respectively. The equation could be simplified so as to contain only one independent variable c_2, but it had to be used in differential form. Equations containing only D_1 and D_2 were set up by assuming the concentration c_2 to be proportional to the specific conductance and the degree of dissociation to be measured by the classical Arrhenius conductance ratio. The best values of D_1 and D_2 were obtained from these equations using the method of least squares. The values of D_2 obtained agree very well indeed with values calculated using the Nernst equation, and are claimed to confirm the assumptions involved in the calculations, but in the light of more recent theoretical developments it seems well to reserve judgment until further experimental work can be done.

DIFFUSION AND BROWNIAN MOVEMENT

We owe the theory of the Brownian movement from the molecular kinetic point of view to Einstein (17) and to Smoluchowski (76). The displacement of the molecule or particle during a certain interval of time characterizes the movement. Considering linear motion along one direction (x) only, it is evident that positive and negative displacements are equally probable; furthermore the smaller displacements are more probable than the larger ones. The probability of a horizontal displacement having a value between x and $x + dx$ is

$$P = \frac{1}{\sqrt{2\pi\Delta_l^2}} e^{-\frac{x^2}{2\Delta_l^2}} dx \qquad (23)$$

where Δ_l^2 is the mean of the square of the average displacement in a linear direction.

It now turns out that the mean displacement Δ_l is quite simply related to the diffusion constant, a result of tremendous significance. The argument of Einstein is as follows: Suppose the diffusion to take place across a plane in a horizontal tube, with concentrations c_1 and c_2 to the left and right of this plane, respectively. In the time t only those particles closer to the plane than the mean displacement Δ_l can pass through it, and their number will be $1/2\ \Delta_l(c_1 - c_2)$. If Δ_l is small,

$$\frac{c_2 - c_1}{\Delta_l} = \frac{dc}{dx}$$

Therefore the number of molecules passing the plane in unit time is

$$-\frac{1}{2}\frac{\Delta_l^2}{t}\frac{dc}{dx}$$

But, by Fick's first law, the coefficient of diffusion D is the number of molecules passing unit cross-section in unit time when the concentration gradient $-\,\mathrm{d}c/\mathrm{d}x = 1$. Therefore,

$$D = \frac{1}{2}\frac{\Delta_l^2}{t} \tag{24}$$

and

$$P = \frac{1}{2\sqrt{\pi D t}}\, e^{-\frac{x^2}{4Dt}}\,\mathrm{d}x \tag{25}$$

which, as we have seen, is a solution of Fick's second law.

Einstein has also shown the coefficient of diffusion to be related to the size of the molecules and the viscosity of the liquid. If the velocity of a diffusing molecule is v

$$v = Bf$$

where f is the force exerted on the molecule and B is its "mobility" or the reciprocal of the frictional resistance experienced by it. If the concentration of the solution before the plane is c, there will be cN molecules involved, with force F acting upon them, and

$$v = \frac{1}{cN}\,FB$$

In the diffusion the force acting is the osmotic pressure gradient, therefore

$$F = -\frac{\mathrm{d}P}{\mathrm{d}x} = -\,RT\,\frac{\mathrm{d}c}{\mathrm{d}x}$$

and

$$vc = -\,\frac{RT}{N}\,B\,\frac{\mathrm{d}c}{\mathrm{d}x} \tag{26}$$

Again making use of the first law of Fick it is evident that

$$D = \frac{RT}{N}\,B \tag{27}$$

If the molecule can be assumed to be spherical, the frictional resistance may be expressed in terms of its radius, r, and the coefficient of friction of the medium, η, by means of Stokes' law, provided certain other requirements are met, with the final result.

$$D = \frac{RT}{N}\cdot\frac{1}{6\pi\eta r} \tag{28}$$

This equation is known in the literature as the Stokes-Einstein law.

ROTARY DIFFUSION CONSTANT

In addition to the Brownian movement of translation, molecules and particles are undergoing rotational motion, owing to an unequal distribution of molecular impacts upon the faces of the parts of the particle on each side of the axes of rotation, and it follows from kinetic theory that the mean energy of rotation will be equal to the mean energy of translation. It has been shown a number of times that the x of the deduction of the previous section may be replaced by another coördinate a, the angle of rotation, since a itself is not contained in the expression for the kinetic energy, and its derivative with respect to time, da/dt, appears only in terms with constant coefficients. Thus a formula which looks just like equation 24 is obtained, that is,

$$D_r = \frac{1}{2}\frac{\Delta_r^2}{t}$$

where D_r is the rotary diffusion constant, and Δ_r^2 is the mean of the square of the average displacement in a rotary motion.

In the case of the rotational motion, another law of Stokes becomes applicable provided the molecule can be considered to be a sphere. This law says that if a torque of moment I be applied to a sphere of radius r in a medium of viscosity η, the angular velocity acquired by the sphere will be $\frac{I}{8\pi\eta r^3}$. Thus, the mobility of the system, B, referred to the angular motion will be

$$B = \frac{1}{8\pi\eta r^3} \tag{29}$$

and the rotary diffusion constant becomes

$$D_r = \frac{RT}{N}\cdot\frac{1}{8\pi\eta r^3} \tag{30}$$

The experimental determination of D_r is a matter of considerable difficulty. It is true that Perrin (67) was able to make a direct microscopic observation of the mean rotation of particles, using mastic globules having a radius of 6.5×10^{-4} cm. and with small enclosures of impurities on the surface of these globules to enable him to observe the rotary motion, but in general it will not be possible to test the fundamental equations for the motion in this way. Very recently, however, theoretical developments have made available two types of experiment whereby this desired result may be realized, and it seems worth while to outline them. The first development is due to Boeder (6) and depends upon the fact that the optical birefringence induced by flow in solutions arises from the tendency of nonspherical particles to orient, owing to the mechanical stresses within the fluid. This theory should be extended to the double refraction produced by a magnetic field, because it seems possible under these conditions to obtain a higher degree of precision. The second method for the determination of a rotary diffusion constant is based upon the dipole theory of Debye (14). As far as we are aware it has not been specifically mentioned in this connection, although several investigators have proposed to use the dipole theory as a method for the determination of particle size.

The principles upon which the theoretical work of Boeder is based may be given by three statements.

1. The mechanical flow of the solution containing nonspherical molecules or particles causes an orientation of these odd-shaped units.
2. This orientative tendency is opposed by their Brownian movement, the disarraying tendency of which is characterized by the diffusion constant, D_r.
3. If the character of the stresses arising from the viscous flow is known, and if the resulting equilibrium state between the two tendencies can be determined (measurement of double refraction), the diffusion constant can be found.

To these statements a fourth and more obvious one, specifically mentioned by Kuhn (44), may be added:

4. Knowing the diffusion constant, information about the size and also the shape of the molecule or particle should result.

Thus, the problem is one of a rotary diffusion influenced by an external force, in this case produced by the rotation of the inner cylinder of a Stormer type of viscometer. The effect of this rotation upon a particle with direction ϕ is to give it an angular velocity

$$\omega(\phi) = -\beta \sin^2\phi \tag{31}$$

where β is the radial velocity gradient of the fluid motion, and ω is the induced angular velocity of the long axis of the particle.

The directional distribution of the particles is governed by the law of Fick,

$$\frac{\partial \rho}{\partial t} = D_r\left(\frac{\partial^2 \rho}{\partial \phi^2}\right) \tag{32}$$

where ρ is the number of particles whose long axes lie in the interval ϕ and $\phi + d\phi$, or the direction density. The combined effect of these forces is given by the relation

$$\frac{\partial \rho}{\partial t} = D_r\left(\frac{\partial^2 \rho}{\partial \phi^2}\right) - \frac{\partial(\rho\omega)}{\partial \phi} \tag{33}$$

At equilibrium $\partial\rho/\partial t = 0$, therefore

$$D_r\left(\frac{\partial^2\rho}{\partial\phi^2}\right) - \frac{\partial(\rho\omega)}{\partial\phi} = 0 \tag{33a}$$

The solution of this equation, which we will not reproduce, gives the direction density ρ as a function of the direction angle ϕ, the radial velocity gradient of fluid motion β, and the diffusion constant, D_r. The aim to find D_r can be accomplished because means have been provided in the double refraction produced by the molecule or particle orientation to determine the state of equilibrium produced by a given constant rotation of the cylinder.

The second method for the determination of D_r depends upon the frequency dependence of the dielectric constant for a system composed of electrically dissymmetrical molecules suspended in a non-polar solvent medium. In such cases the dipole theory tells us there will be found to be a region in which the dielectric constant decreases as the frequency is increased, because a finite time is required for the orientation of the molecules in the electrical field, owing to the frictional resistance of the medium to the rotation.

The quantitative argument may be suggested by saying that at sufficiently high frequencies the dielectric constant will fall off because the inner friction constant of the medium prevents the orientation of the dipole molecules. The polarization of the system resulting from the suspended molecules consists of two parts, a polarization due to their deformation and a polarization due to their orientation, both of which contribute to the dielectric constant. The transition from the high dielectric constant, ϵ_0, to the low dielectric constant, ϵ_∞, will occur in a frequency region defined approximately by the equation,

$$\nu_c\tau = 1$$

where τ, called the time of relaxation of the molecules, is the time required for $1/e^{\text{th}}$ of the particles to assume a random distribution in the solution after the applied field has been removed, and ν_c is the critical frequency of the alternating field. This means simply that the anomalous dispersion occurs when ν_c and $1/\tau$ are of the same order of magnitude.

Actually the transition between the high and low values of the dielectric constant will take place in the frequency region defined by the expression,

$$0.1 \leqq \chi \leqq 10 \tag{34}$$

In this equation

$$\chi = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2}\,\frac{\pi\zeta\nu}{kT}$$

where ζ is the "inner-frictional" constant, which because of its existence makes necessary the exertion of a torque to rotate the molecules in the solution,
ν is the electrical frequency in cycles per second,
k is the Boltzmann constant, and
T is the absolute temperature.

The theory tells us that the observed dielectric constant will assume a mean value (that is, the dielectric constant–frequency curve will pass through a point of inflection) at the point where $\chi = 1$. Under these conditions,

$$\frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \cdot \frac{\pi \zeta \nu_c}{kT} = 1 \tag{35}$$

with the result that

$$\nu_c \tau = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \cdot \frac{1}{2\pi} \tag{36}$$

In order to obtain this result the quantity ζ has been replaced by its equivalent $\tau \cdot 2kT$. This equality is a consequence of the dipole theory which we cannot discuss here.

We have seen that when a sphere of radius r rotates in a liquid of viscosity η the frictional torque is $8\pi\eta r^3$ times the angular velocity of the sphere. Therefore, for such a sphere,

$$\zeta = 8\pi\eta r^3 \tag{37}$$

This application of the law of Stokes enables us to express the time of relaxation or critical frequency in terms of either the radius of the molecule or the diffusion constant, since

$$\tau = \frac{4\pi\eta r^3}{kT} = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \cdot \frac{1}{2\pi\nu_c} \tag{38}$$

and

$$D_r = \frac{RT}{N} \cdot \frac{1}{8\pi\eta r^3} \tag{30}$$

The determination of the time of relaxation depends upon the experimental observation of ϵ_0, ϵ_∞, and ν_c.

The problem which had to be solved in working out the theory of the anomalous dispersion was how to find the distribution function of the electric moments of molecules affected by a field variable with time. The general mathematical basis for the solution of this problem was found in the theory of the Brownian movement as developed by Einstein (17). The number of molecules whose moments entered in the direction of a given solid angle during an interval of time δt was determined by two causes, one due to the applied alternating field, the other due to the rotary Brownian movement, and the effect of each had to be calculated.

Problems of the type discussed in this article, both as regards linear and rotational displacements, become much more difficult when the shape of the molecule or particle involved deviates from that of a sphere. Some progress has been made in extending the necessary calculations to ellipsoidal and rod-shaped particles, particularly in connection with viscosity problems. Therefore it can be expected that the necessary modifications of the theoretical work described above will be made in the near future, so that the results may be applied to molecules deviating from the spherical or nearly spherical shape. This is particularly necessary in the cases where optical effects produced in solutions are used to study the distribution of the molecules. It is of interest to remark that only very recently the importance of taking the diffusion and Brownian movements into account has been recognized. In a sense these are all problems of a diffusion influenced by an external force, and the effect of the diffusion can be neglected only when it can be shown to be negligible in comparison with the effects produced by the other forces involved.

II. Experiment

A very large number of methods have been worked out for the experimental study of diffusion. Since there is involved the relationship of three variables—concentration, distance, and time—the variations in method are largely reflected in the different ways chosen to measure these variables. The methods also differ in the way in which the boundary conditions postulated in the mathematical formulation are met. It cannot be too strongly emphasized that the mathematical development determines, and hence must precede, the establishment of experimental conditions and the design of the apparatus to be used.

There are several obvious conditions which should be met by any experimental method, as follows:

1. Change in concentration during an experiment should be small.
2. There should be no decomposition, association, or chemical reaction of the components of the system.
3. The diffusion constant must be independent of the concentration of the diffusing material, if Fick's law is to be used.
4. There must be a sharp initial interface.
5. There must be avoided any disturbance or temperature gradient which would cause streaming or mixing.

6. There must be no volume change during the experiment.
7. There must be available methods for accurate concentration determinations.

There exist in the literature several classifications of diffusion experiments. Of these, the methods of Cohen and Bruins (11) and of Fürth (24) have much to recommend them. However, we shall prefer to adopt a double classification, dividing the experiments, first, on the basis of the kind of observation made (measurement of concentration), and second, with respect to the type of diffusion experiment used. The tabulation based upon the kind of observation made to measure the concentration is independent of the way in which the experiment is set up to meet the boundary conditions postulated in the mathematical formulation. Practically all of the methods used to measure the concentration are applicable to either the continuous or interrupted type of experiment.

TABLE 1

Concentration measurement in diffusion experiments

1. Analytical
    a. Gravimetric
    b. Volumetric
    c. Colorimetric
    d. Density
2. Electrical
    a. Potential difference
    b. Resistance
3. Optical
    a. Particle count
    b. Refractive index
    c. Light absorption
    d. Wave length
    e. Optical rotation
    f. Fluorescence

The several kinds of observations made to measure concentration are suggested by table 1. They involve both physical and chemical methods of measurement.

The analytical methods, because of their availability and application to the simpler types of diffusion apparatus, were commonly used by the earlier investigators. The determination of concentration by chemical analysis is usually made at the conclusion of the experiment on samples from different parts of the diffusion system. The course of the diffusion may be followed by chemical analyses only when the removal of the sample will not disturb the diffusion or cause an appreciable change of concentration in the cell. Colorimetric determinations include solutions obtained by the use of indicators and turbid solutions as well as those which follow Beer's law. Both the hydrometer and balance have been used for density determinations.

The electrical methods are restricted to systems whose components carry electrical charges. They are readily adapted to the making of continuous observations, but a small error in the electromotive force measurement represents a significant deviation in the concentration. The potentials are not always readily reproducible at low concentrations; in fact, accurate measurements of density, chemical composition, and potential difference all require rather concentrated solutions.

The optical methods are accurate, may usually be applied without disturbing the diffusing system, and may be used with organic substances. Further, dilute solutions may be used and only small amounts of material are required. The methods depending upon refractive index change are applicable only to those substances which do not absorb light.

Having suggested the means by which concentration may be measured, we are now ready to classify the systems as to type of apparatus used. It is convenient to describe them as:

A. Experiments in which the prevailing average concentration in different finite layers is determined as the process is brought to an end.

B. Experiments in which the diffusion is followed by continuous or intermittent observation, in one or more infinitely thin layers, without disturbing the diffusion process.

TABLE 2

General types of diffusion apparatus

A. Observation of finite layers at the conclusion of the experiment.	B. Continuous or intermittent observation of an infinite number of layers.
1. By separation with a pipet or siphon.	1. By observation along a column.
2. By separation with a mechanical slicer.	2. By observation of the blurring of a boundary.
3. By the use of a porous diaphragm for separation in contact with a quiet liquid.	3. By the use of a porous diaphragm in contact with a stirred liquid.

Table 2 has been prepared to show some of the kinds of diffusion experiments which have been used.

While it will not be possible to include a complete survey of diffusion apparatus and methods, a few representative examples will be given to illustrate the various types of experiment. Because of the variation of diffusion rate with temperature, and the necessity of avoiding a temperature gradient in the solution itself, it is apparent that the temperature must be accurately controlled during any diffusion experiment. Obviously some types of apparatus lend themselves more readily to thermostatic control than do others. While no mention will be made of the various means used to maintain the desired temperature, the importance of its influence must not be overlooked.

Of the first group, the so-called second method of Graham (28) marks the beginning of the quantitative study of diffusion, since the design of the apparatus and the boundary conditions allow a mathematical interpretation of the observations. This experiment, as performed by Graham, consisted of placing 100 cc. of salt solution beneath 700 cc. of water by means of a capillary pipet. A cylindrical glass vessel 152 mm. high and 87 mm. in cross section was used. After a measured time interval, 50 cc. or one-sixteenth of the total solution was removed and the salt content obtained by analysis. Graham recorded the salt concentration found in each of the sixteen layers. Besides salt, Graham used albumin, gum arabic, magnesium sulfate, sugar, and other substances, both in water and in ethyl alcohol.

Later Scheffer (70) modified Graham's apparatus by using a pipet with a stopcock at the top to facilitate introduction and withdrawal of solutions. In addition he used one volume of solution under three volumes of water. This allowed the use of Stefan's tables (79). Concentrations were determined volumetrically.

The apparatus of Scheffer was used by Arrhenius (2), who introduced a mercury layer on the bottom of the flask to assure a flat surface. He added a cork through which he could insert the pipet. This arrangement allowed withdrawal of the solution with less mixing than occurred in former types. Calculations were based on Stefan's tables and concentrations were measured analytically.

The diffusion vessel was further improved by Oeholm (62), who placed a stopcock in the bottom through which mercury could be drawn and liquids emptied, and an air vent in the top. The vessel had a greater length to diameter ratio than the older types. The concentrations were determined volumetrically and Stefan's tables were used in calculating the results. Other experimenters to use this apparatus were Herzog and Polotsky (34), who studied the diffusion of dyes, and Jander and Schulz (38), who determined the molecular weight of potassium tantalate and other amphoteric oxyhydrates.

A slightly different form of Graham's apparatus was used by Svedberg (82). Solutions were admitted and removed through a pipet with side arm. Air pressure was used in the removal of the solutions from the cell. Here again the design was such as to permit the use of Stefan's tables.

An early form of diffusion apparatus was that of Fick (18), who made diffusion measurements by immersing a series of cylindrical tubes to half their length in a saturated salt solution. The upper half was then filled with water. The progress of diffusion was measured by means of an hydrometer. Griffin (29) altered this method slightly by placing several tubes through a partition which divided the upper and lower halves of a box-like container. One medium was placed in one compartment and the other in the second compartment. The partition served to separate solution and solvent except inside the tubes where diffusion took place.

In order to avoid the inevitable mixing which occurred at the beginning of the experiment when the solutions of different concentration were placed in contact with each other, and again at the conclusion of the experiment when the different layers were segregated, various forms of mechanical "slicers" were introduced.

Schuhmeister (72) originated the inverted cylinder method which was later refined by Dummer (16). The diffusion column was built up of two cylinders, one inverted over the other. The diffusing solution was placed in a lower cylinder. The solvent was contained in a similar cylinder which was inverted and placed on a sliding frame. The inverted cylinder was then slid over the first one and the diffusion allowed to start. On completion of the diffusion experiment the frame was slid back again and the contents of the cylinders analyzed.

A distinct type of diffusion cell was devised by von Wogau (97) for use with more viscous solutions. It consisted of eight glass plates with a 2-cm. hole in the center of each. These plates fitted into a frame and, when the holes were lined up, formed a diffusion column the layers of which could be removed at will. It was used to measure the diffusion of zinc, cadmium, lead, tin, and tantalum into mercury. Oeholm (63) adapted this apparatus to the use of the Stefan tables by using four plates. These plates were constructed of brass and carefully ground to insure a perfect fit. Any plate could be removed at will and the solution in it analyzed. This type of apparatus gave more consistent results per layer than the older forms and could be used for viscous liquids and colloidal solutions. Much of Oeholm's diffusion data were obtained with this apparatus.

The diffusion cell described by Cohen and Bruins (12) consisted of six glass plates, the first and sixth acting as bottom and top, respectively. The four middle plates had three 2-cm. holes bored through them. These holes were so spaced that three diffusion columns were formed when the holes were lined up. The diffusing substance was placed in the second plate (from the bottom) and water was placed in the three above it. Additional holes in the plate above allowed the cylinders formed to be filled completely with water or solution. By rotating the plates the water could be slid over the solution. After the diffusion had progressed for the desired length of time, the four layers were separated by merely rotating the plates. Vibration was minimized by the use of a Julius suspension. Concentration was determined by means of an interferometer.

Another type of diffusion system to which mechanical slicing may be applied is that of diffusion into a gel. In this connection the gel will be considered merely as a part of the diffusion apparatus, in so far as its presence offers a solution to several experimental difficulties. With the diffusion taking place in the gel it is possible to get a sharper boundary surface, the danger of mixing is negligible, there is greater freedom from convection currents, and effects due to vibration or other outside disturbances are minimized. The layers may be separated by slicing the gel at the desired points at the conclusion of the experiment. Adsorption of the diffusing molecule by the gel substance and impurities in the gel introduce complications into its use. Further, the assumption that the gel exerts no influence on the rate of diffusion may be open to question.

Graham (28) experimented with gelatin in an apparatus similar to the one that he had used for solutions. One hundred cubic centimeters of 2 per cent gelatin containing 10 per cent sodium chloride was allowed to cool and set in a cylindrical vessel. This was covered with 700 cc. of 2 per cent gelatin and the diffusion allowed to proceed. After several days the gel was removed and cut up into sixteen equal layers for analysis.

Bechhold and Ziegler (4) modified Graham's method by allowing diffusion to take place from the liquid above into the gel. They gauged the concentration by noting the intensity of color of the diffusing substance, by the formation of precipitates in the gel, or by analysis. Stiles and Adair (81) and Stiles (80) used a similar method, allowing the diffusion to proceed from a large quantity of solution upward into narrow glass tubes filled with the gel.

Herzog and Polotsky (34) carried out a large number of experiments on the diffusion of dyes in 5 per cent gelatin where the dye served as its own indicator. Fricke (21) has developed a micro slicing method to study diffusion in agar gels. Ricketts and Culbertson (69) suspended a cylinder of agar gel in a large volume of stirred solution. After diffusion had taken place for a suitable length of time, the gel was removed and sections taken for analysis.

A distinct type of diffusion experiment is that in which the solutions are separated by a porous diaphragm. The diffusion gradient is confined to this porous membrane and the pores may be considered as miniature diffusion columns.

The glass diaphragm method used by Northrup and Anson (60) and later by McBain and Liu (51) has the advantages of speed and simplicity. The apparatus consisted of a sintered glass membrane or alundum disc which separated the two solutions. The more concentrated solution was placed above, thus as diffusion proceeded gravity tended to keep the solutions at a uniform concentration. At the conclusion of the experiment the solution was withdrawn and its concentration determined.

After an adequate mathematical treatment was formulated, it became possible to consider the solution as a series of infinitely close layers. The types of apparatus used in this case are designed primarily to fulfill the boundary conditions and differ according to the method used in determining the concentration over the system.

The electrical methods may be readily adapted to the measurement of concentration along a column in systems containing electrolytes in solution. Weber (91) arranged a cell in such a way that the potential difference between a metal and its ion in the different layers of a diffusing solution could be measured. He also measured the conductivity between two boundary layers as the material diffused. Procopiu (68) extended Weber's method by introducing a third electrode high in the aqueous layer in order to increase the accuracy of the measurement of concentration difference. Haskell (30) measured the conductivity between pairs of electrodes spaced at intervals along his diffusion column.

Clack (9) based his method on the difference in weight between a saturated solution and the same solution after some of the solute had diffused out. A vessel containing salt solution, immersed in a large volume of pure water, was suspended from a balance arm and the loss of weight with time was recorded.

The possibility of a relationship between the refraction of light and the concentration of diffusion layers was early shown by Wollaston (98). Wild and Simmler (95) derived a mathematical relationship between the refractive index and the concentration of the different layers. The first experimental apparatus for measuring diffusion and heat conduction by means of the refraction of light was devised by Wiener (94). He used a solution, covered with water, in a proper optical vessel. Light of definite wave length was passed through a slit and lens system and into the solution. The interference bands were recorded on a photographic plate as the diffusion progressed. The distance that the center of the light band was deflected by the diffusing solution was measured by means of a cathetometer. Wiener derived the relationship between concentration and the displacement of the light band. Thovert (85) improved Wiener's experiment by using a better source of light with collimator, and by changing the angle of the slits. Later Thovert (86) arranged his apparatus in the form of a spectrometer and measured the deviation by means of an ocular with a movable and fixed crosshair. Variations of Wiener's method have been used by Heimbrodt (31), by Clack (10), and by many others.

An apparatus for the microscopic measurement of diffusion was introduced by Westgren (92) for an investigation of gold and selenium sols.

His cell consisted of a microscope slide and cover glass. The sol was thrown to the bottom of the cell by centrifugal force, the apparatus was placed under the ultramicroscope, and the progress of the diffusion was measured by counting the number of particles at different heights over suitable time intervals. Sitte (74) has used a cross-ruled microscope slide for noting the movement of particles of a gold hydrosol.

When two solutions of different concentrations, either molecular or colloidal, are placed in contact without mixing, a sharp boundary is present between them. As diffusion progresses, however, this boundary becomes blurred, and a concentration distribution is obtained which varies with the distance from the boundary.

Svedberg (83, 84) has made very effective use of this boundary blurring as a means of measuring the diffusion coefficients of proteins. In addition to its use in the ordinary type of experiment he has been able to show that the blurring of boundaries in systems subjected to vibrationless centrifugal fields was a result of diffusion, enabling him to evaluate the diffusion coefficient from its quantitative observation as the centrifuging is continued. The registration of the progress of the diffusion was obtained photographically. This is possible because protein materials fluoresce under the influence of ultra-violet light. The relationship between intensity of fluorescence and concentration of the protein must have been obtained previously by independent experiments in order that the variation of concentration with height in the diffusing column may be made available. Lamm (46) has applied the refractive index method to the study of the blurring of the boundary in the ultracentrifuge.

A microscopic arrangement to measure the diffusion of dyes, using the blurring of the boundary method, was designed by Fürth (25). The diffusion apparatus consisted of a divided cell, the diffusion taking place in the left side. A colorimetric standard was located in the right side. As the diffusion proceeded the microscope was successively focused on the layer whose concentration was comparable to that of the standard solution. The rate of diffusion was determined from the observation of the position of this layer as a function of time. A sharp boundary was obtained by means of a metal partition between the two layers which was removed by means of an electromagnet at the start of the diffusion.

The measurement of diffusion between a stirred liquid and a solution contained in a porous solid offers the experimental advantages of being little affected by vibration or convection currents and of giving a sharp boundary between the two solutions.

Friedman and Kraemer (23) have utilized this method in their investigation of gel structure. In a typical experiment a firm gel was formed in the bottom of a 500-cc. bottle and an equal depth of liquid introduced over the gel. Either the liquid or the gel contained the diffusing substance at the start of the experiment. The liquid was kept at a uniform concentration by constant stirring. Its concentration was determined at suitable intervals by means of an immersion refractometer. This method of measuring diffusion is also being used by the authors in the investigation of the capillary dimensions of porous solids. The diffusion cell consists of a water-tight brass cylinder provided with a stirrer. After the pores of the solid have been filled with solvent or solution the solid is fitted into the cell in such a way that only the top surface is exposed. An equal depth of either solution or solvent is placed over the solid and maintained at a uniform concentration by stirring.

III. INTERPRETATION

The ability of a substance to diffuse is frequently mentioned and made use of in connection with other and perhaps better known phenomena. Nevertheless, the diffusion of substances in solution is one of the most fundamental of properties, since it is so closely related to molecular motion. The specific diffusion rate or diffusion constant obtained from its study is a valuable constant, since from it much useful information may be obtained. It has found repeated application in both scientific and technical problems. Among the former may be mentioned the determination of molecular and particle size, the development of electrolytic solution theory, the relation between diffusion rate and the velocity of heterogeneous reactions, and the description of the coagulation of colloidal systems in terms of a time constant whose magnitude depends upon the ability of the particles to diffuse.

Reasons have been suggested why diffusion studies have not been made to an extent which seems to be commensurate with their importance. The experimental difficulties involved and the fact that under different conditions inconsistent values result for the diffusion coefficient are undoubtedly the most important of them. Failure of Fick's law and a variation of the coefficient with concentration are frequently mentioned in connection with the second difficulty, and it is indeed unfortunate that these anomalies persist into such low concentrations that only measurements of highest precision permit the estimation of the proper corrections by extrapolation to zero concentration. But in spite of this situation, means are being found to conduct and interpret the experiments in a manner which leads to a consistent result and the information obtained bids fair to repay the extra effort involved.

A. DIFFUSION AND MOLECULAR RADIUS

As we have seen in an earlier section, kinetic theory leads to the expression

$$D = \frac{RT}{N} B = \frac{RT}{Nf} = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \qquad (27, 28)$$

where f is the reciprocal of the mobility and therefore the frictional coefficient. For a sphere obeying Stokes' law, it is equal to $6\pi\eta r$. Many attempts have been made at a direct experimental confirmation of this law, so that it may be used for the study of the size of molecules. It is a method which should be of considerable value for spherical or nearly spherical molecules, provided the validity of the equation can be established; but unfortunately a rigorous proof of it in such cases does not seem possible. Several methods of test have been recorded in a number of places, and a great deal of experimental work has been done to try to establish it. The more important types of experiment have sought to prove one of the following relationships.

1. In the same solvent and at the same temperature with a number of diffusing substances there should result

$$D \cdot r = \text{const.}$$

2. At constant temperature a given substance diffusing in a variety of solvents should give

$$D \cdot \eta = \text{const.}$$

3. At constant viscosity a substance diffusing at several temperatures should obey the relation

$$\frac{D}{T} = \text{const.}$$

provided the radius of the molecule can be assumed independent of temperature.

Experiments made to test these relationships have usually been as successful as one could reasonably expect. In the very careful experiments of Cohen and Bruins (13) the velocity of diffusion of tetrabromoethane into tetrachloroethane at temperatures ranging from 0°C. to 50°C. was determined, making corrections for the change in the viscosity of the solvent as the temperature was increased. The results of the work are summarized in table 3.

Cohen and Bruins interpret their data to indicate small deviations in the Stokes-Einstein law, but we should prefer to consider these results as a demonstration of the fundamental correctness of the third relationship, considering that the diffusing molecules are not spherical, and that the discontinuities of the medium are not particularly small compared with their size.

To mention a single other example Scheffer and Scheffer (71) studied the temperature dependence of the diffusion constant of mannite in dilute aqueous solutions from 0°C. to 70°C. and found good agreement with the Stokes-Einstein formula. Correcting for the change in viscosity caused by the increase in temperature, the relation D/T = const. is quite exactly obeyed. The radius of the mannite molecule was calculated to be $r = 4 \times 10^{-8}$ cm.

The proof of the relation $D \cdot r$ = const. involves the study of the diffusion of a number of different molecules of known dimension in the same solvent and at the same temperature. Among others, Thovert (85, 86, 87) and Oeholm (62, 64, 65) have made studies of just this kind, the former using water and methyl alcohol, and the latter water and ethyl alcohol, as solvents. The variety of solutes used is suggested by the list of materials which were allowed to diffuse into water by Oeholm, as follows: glycerol, pentaerythritol, mannite, alloxan, resorcinol, hydroquinone, saligenin, inulin, acetamide, carbamide, dicyandiamide, caffeine, ecgonine, salicin, gum arabic, and starch. It is at once apparent that they could not have expected to verify the relationship in question with their experiments because sufficient data concerning the dimensions and shape of these molecules were not available to them. Rather it was their purpose to study the validity of another equation which might appear to have similar significance, namely,

TABLE 3

Diffusion data for tetrabromoethane in tetrachloroethane

	TEMPERATURE					
	273.1°C.	283.1°C.	288.1°C.	298.1°C.	308.1°C.	323.1°C.
η	0.0266	0.0215	0.0195	0.0164	0.0140	0.0113
$r \times 10^8$ cm	2.15	2.15	2.16	2.17	2.19	2.21

$$D\sqrt{M} = \text{const.} \tag{39}$$

where M is the molecular weight of the solute. This relationship may be obeyed by limited numbers of similar molecules, but consideration of the factors involved makes it at once evident that it cannot have general validity. The reason is just the thing we believe but are still attempting to prove, namely, that the diffusion rate of a molecule is determined by its (effective) radius.

It is the opinion of the writers that the numerous attempts to prove the second equation, $D\eta$ = const., have not been as successful as they might have been had the several investigators taken care to choose their systems so that the discontinuities of the medium were small compared with the size of the diffusing solute. The viscosity needed in this equation should be a "microscopic" viscosity and should measure the frictional resistance of the solvent molecules to the linear displacement of the diffusing molecules. Further, there is sometimes considerable doubt as to whether the viscosity as measured in a viscometer and determined by the rate at which the molecules of the medium slip past each other is actually the viscosity that one should use for the required resistance to the displacement of solute molecules. Perhaps the most satisfactory source of information for the present status of the equation involving the coefficient of viscosity is the comparatively recent article of Dummer (16). The results of experiments with acetone, nitromethane, nitrobenzene, ethyl acetate, and ethyl benzoate molecules diffusing into a number of common organic solvents are recorded there.

Remarkable as it may seem, the agreement between theory and fact is often closer and more satisfactory for colloidal systems than it is for ordinary molecular solutions. Measurements on Faraday gold sols having particles of known radius have been carried out by Svedberg (82) in order to test the kinetic formula; he found the particle size calculated by the Stokes-Einstein equation from the diffusion constant to agree within the limit of experimental error with the known radius which had been determined ultramicroscopically, using the Zsigmondy nuclear method. In a representative experiment diffusion gave $r = 1.29 \times 10^{-7}$ cm., and the ultramicroscopic result was $r = 1.33 \times 10^{-7}$ cm. Westgren (93), working in Svedberg's laboratory, carried out a number of similar diffusion measurements with gold and selenium sols, using a method in which a very thin layer of the diffusing solution was placed under a high column of dispersion medium. After a definite period of time the concentrations c_1 and c_2 were determined at the heights X_1 and X_2. It follows from equation 14 that the concentration ratio may be written,

$$\frac{c_2}{c_1} = e^{-\frac{(x_2^2 - x_1^2)}{4\,Dt}} \tag{40}$$

thus the diffusion constant can be determined with comparative ease. The concentrations were determined by counting the number of particles at different heights with the ultramicroscope. The values of the radii calculated with the Stokes-Einstein equation agreed very well with the radii determined by other methods.

The consensus of opinion appears to be that the kinetic theory equation can be applied to the determination of molecular sizes if the limitations imposed upon its use are properly recognized. This is a conclusion of great importance because it makes possible the calculation of the equivalent radii of dissolved particles varying in size from quite small molecules to particles of ultramicroscopic dimension. Such work has been done by Herzog and his collaborators (32, 34), who have studied the diffusion behavior of and calculated the particle size for cellulose esters, rubber, proteins, ferments, and dyes in their proper solvents. More recently Fürth and his associates (25) have developed and used a rapid micro method which permits an estimation of the particle size of dyestuffs in solution.

Svedberg (84) makes very ingenious use of diffusion coefficient determinations in connection with his sedimentation velocity method for the determination of molecular radius and weight. By combining the results of the two studies, made simultaneously in the ultracentrifuge, and by assuming that the frictional resistance exerted by the solvent in diffusion is equal to the frictional resistance, which determines the sedimentation velocity, the equations describing each phenomenon can be combined to eliminate the friction term, giving,

$$M = \frac{RT \ln (x_2/x_1)}{D(1 - V\rho)\,\omega^2 (t_2 - t_1)}, \tag{41}$$

where M is the molecule weight of the solute,

x_1 and x_2 are distances between the axis of revolution and the boundary at times t_1 and t_2,

ω is the angular velocity of the rotor of the centrifuge,

V is the partial specific volume of the particle,

ρ is the density of the solvent, and

D is the diffusion coefficient.

The diffusion constant, which must be determined separately, is obtained from the blurring of the boundary as it recedes. The purpose of this method of procedure is to eliminate the use of Stokes' law to evaluate the frictional resistance to the motion of the particles, involving as it does certain undesirable conditions for validity.

In an extremely interesting table which is here reproduced (table 4), Svedberg (84) has compared values of molecular radii for a number of proteins calculated from sedimentation velocity studies with those determined using diffusion measurements. In certain cases the values of the radius obtained by the two methods are in excellent agreement, indicating a spherical shape for their molecules, but in others there is considerable difference, a result of the failure of the Stokes-Einstein law when it is applied to nonspherical molecules.

In the attempt to accelerate and simplify diffusion methods as applied to biological materials, Northrup and Anson (60) have resorted to the use of a thin porous plate to make the concentration gradient high and at the same time to avoid convection currents. Thus the pores of the diaphragm must be small enough to prevent convection and at the same time large enough to allow free diffusion. The apparatus, after calibration with a hydrochloric acid solution, was used to study the diffusion rate of hemoglobin. Using the Stokes-Einstein law it was found to have a molecular weight of 68,500 ± 1000, which agrees "within the experimental error with that of 67,000 found by Adair by osmotic pressure measurements and of 68,000 found by Svedberg from experiments on the rate of sedimentation." In using the Stokes-Einstein equation, it was assumed that the hemoglobin molecules are spherical and impelled by a force given by an idealized osmotic pressure law against a resistance as given by Stokes' law. But Svedberg has shown in quite convincing manner (table 4) that hemoglobin molecules cannot be spherical. Using Einstein's law, Svedberg calculated the radius of the hemoglobin molecule to be 3.35×10^{-7} cm., while Northrup and Anson gave 2.73×10^{-7} cm. for the same constant. It is true that Svedberg's experiments were made at 20°C., or 15°C. higher than those of Northrup and Anson, but it is difficult to see how this difference in radius could be accounted for on this basis alone.[2] One must therefore feel that results obtained in this way for a diffusion constant or radius can only be accepted as provisional until independent confirmation of the method can be obtained. It is true that McBain and Liu (51) have given a simple and rapid procedure for the use of the Northrup diffusion cell, in which it was shown that the results are independent of the nature and porosity of the diaphragm and equivalent to the best obtained by the more laborious classical methods.

TABLE 4

Molecular radius data for protein molecules

MOLECULE	SPECIFIC SEDIMENTATION VELOCITY AT 20°C.	DIFFUSION CONSTANT AT 20°C.	r (SEDIMENTATION VELOCITY)	r (STOKES-EINSTEIN)
	cm. per second	*cm.² per second*		
Egg albumin	3.32×10^{-13}	9.58×10^{-7}	2.18	2.23
Hemoglobin	4.37×10^{-13}	6.36×10^{-7}	2.44	3.35
Serum albumin	4.21×10^{-13}	6.10×10^{-7}	2.39	3.49
Serum globulin	5.57×10^{-13}	5.40×10^{-7}	2.75	3.96
Phycocyan	5.59×10^{-13}	5.28×10^{-7}	2.76	4.04
Phycoerythrin	11.30×10^{-13}	5.22×10^{-7}	3.93	4.09
Limulus-hemocyanin	35.50×10^{-13}	1.87×10^{-7}	6.96	11.40
Helix-hemocyanin	98.00×10^{-13}	1.78×10^{-7}	12.00	12.20

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[2] Note added in proof: Tiselius and Gross (Kolloid-Z. **66**, 11 (1934)) have shown that the diffusion constant varies with the concentration of solute. Their data make possible an explanation of this difference.

B. DIFFUSION AND ELECTROLYTIC SOLUTION THEORY

It has been seen in an earlier section of this report that an independent diffusion of ions is impossible because of the electrostatic forces between them; thus the problem is more complex than the one involving neutral molecules alone. However, Nernst (57) was able to show that the amount of salt diffusing in a given time could be expressed in terms of the mobilities of the ions, the cross-sectional area of the diffusing medium and the concentration gradient, when 100 per cent dissociation can be assumed. Important experimental studies of the diffusion coefficients of salt solutions have been carried out by Haskell (30), Oeholm (62, 64), Clack (10), McBain (50, 51), Sitte (75), and others. In the verification of the interionic attraction theory of diffusion due to Onsager and Fuoss (66), it is preferable to utilize differential coefficients of diffusion rather than those obtained by allowing a given solution to diffuse into pure solvent, but comparatively few data of this type are available. Those of Clack which meet this particular requirement were made in a concentration region from 0.05 N to saturation, so they hardly permit a test of the theory in the region where the interionic effects predominate. The Onsager theory does account for the general type of the relation between the diffusion constant and concentration, but there are difficulties which must still be overcome. Onsager and Fuoss have discussed this situation in great detail, therefore further reference to it here is unnecessry. We may venture to predict that when precision measurements designed for the express purposes of the theory have been made, the situation will have been considerably improved.

Haskell has studied the interesting and practically important case of a dissociating solute which diffuses in the two parts,—the dissociated and the undissociated. He could show in the first place that the diffusion constant generally becomes larger as the dilution is increased, which is interpreted to mean that the ions move more rapidly than the undissociated portion. The problem Haskell set for himself was to see if during an infinitesimal time these parts could not be considered as moving independently, each having its own diffusibility, so that the total amount of material dm crossing a given area is

$$\mathrm{d}m = \mathrm{d}m_1 + \mathrm{d}m_2$$

where dm_1 represents an amount of unionized salt, and dm_2 represents an amount of ions. The complex differential equation necessary to describe the problem could not be solved directly so that the approximate methods of procedure suggested in Part I were resorted to. Experiments with thallium sulfate and barium nitrate in tenth-normal solution led to the conclusion that the rate of diffusion of the undissociated molecules is of the magnitude one-half that of the ions.

In order to test the Nernst formula, Oeholm investigated the diffusion of a number of strong electrolytes of valence type 1–1 in water solution at concentration 0.01 *N* and found substantial agreement. A portion of the data are collected to form table 5.

The relation between the mobility of the ions under the influence of an electrical field and their ordinary diffusion is therefore justified. The Nernst expression has been generalized by Noyes, who has applied it to the case in which a salt is completely dissociated into any number of ions. This extension is given in detail in the article by Haskell.

TABLE 5

Diffusion of simple electrolytes in dilute aqueous solution at 18°C.

ELECTROLYTE 0.01 *N* IN WATER	*D* (OBSERVED) OEHOLM	*D* (CALCULATED) NERNST
NaCl	1.170	1.173
KCl	1.460	1.460
LiCl	1.000	0.994
KI	1.460	1.467
HCl	2.324	2.431
NaOH	1.432	1.558
KOH	1.903	2.109

C. DIFFUSION AND HETEROGENEOUS REACTION KINETICS

The dissolution of a substance, whether it be a salt dissolving in water, a metal dissolving in an acid, a resin dissolving in acetone, etc., naturally has been the subject of much study. The classical theory for the rate of solution of solids due to Noyes and Whitney (61) and to Nernst (58) has postulated that the rate of this process is very high compared to the rate at which the active component of the solution can reach the solid surface by diffusion, hence the solution rate should be dependent upon that of the diffusion to the surface through the products as they are formed and diffusing away from the surfaces being attacked. However, van Name and Hill (89) and others have recognized that this theory can not be as generally applicable to heterogeneous reactions as had previously been supposed. There are now generally assumed to be three types of heterogeneous reaction, provided that we exclude certain other complicating factors which would certainly interfere, as follows:

1. Those in which the surface reaction is very much faster than the diffusion rate, the observed reaction rate being determined by the latter.
2. Those in which the reaction is very slow compared to the diffusion rate, the latter then being without influence in determining the rate of the process.

3. Those in which the diffusion rate and reaction rate are comparable in magnitude, so that both factors will influence the observed reaction rate.

Interest in this problem has been revived because of the work and discussions of Brönsted and Kane (7), Kilpatrick and Rushton (41), and King and Braverman (42) on the rate of solution of metals in acids. It will be recalled that Nernst (59) had postulated the existence of a "diffusion layer" surrounding the solid, the thickness of which could be calculated from the expression,

$$k = \frac{D}{\delta} \tag{42}$$

where k is the observed solution rate, D is the diffusion coefficient, and δ is the thickness of the layer. Thus, if the thickness of the adhering layer for a given kind and velocity of stirring can once be determined by experiment, the velocity constant of the reaction can be calculated. This constant could be obtained by Brunner (8) from measurements on the rate of solution of magnesia in benzoic acid, after which it was possible to calculate the rate of solution of magnesia in a number of different acids. A further conclusion seems to follow at once: it is not the strength of the acid which regulates the rate of attack, but rather the diffusion coefficient. Further results of experimental work in general agreement with this conclusion have been published by van Name and his associates (88), and by Heymann (36). They all dealt with typical cases in which no other slow processes were involved, so that reasonably good agreement must have been expected.

But while the process of solution of metallic oxides, hydroxides, and carbonates in acids may be so rapid that the observed rate of solution may be controlled by the diffusion process, it could well be that the chemical reaction involved in the dissolution of metals in acids will be slower than the accompanying diffusion. Brönsted and Kilpatrick have therefore begun such experimental studies to determine whether, as heretofore supposed, only the hydrogen ion reacts directly with the metal, or whether other acid ions and molecules enter into such reactions as well. To quote Brönsted and Kane, "There is no reason, however, to assume that the reaction of dissolved molecules with the molecules of a solid substance should be instantaneous or in any way more rapid than the reactions of dissolved molecules between themselves. The diffusion theory is therefore inapplicable for a general explanation of heterogeneous reactions. On the other hand, when the elementary reaction proceeds with sufficient rapidity, there is no doubt that the diffusion of the reacting acid to the interface plays a part more or less important for the dissolving process."

The work of Brönsted and Kilpatrick attempts to deal with the subject from the standpoint of the extended theory of acids and bases, now well known as the result of work by Brönsted and by Lowry. Kilpatrick and

Rushton have observed the rate of dissolution of magnesium in various acids and buffer solutions with results which have to be interpreted to mean that the chemical process is much slower than the diffusion process. In a more complete work Brönsted and Kane have applied this theory to the rate of solution of sodium from sodium amalgam by acids, in which it is concluded that while the diffusion process determines the rate with the stronger acids, the chemical reaction rates are sufficiently lower than the diffusion rates in the case of acids of dissociation constant less than 10^{-7} to be responsible for the observed velocities. King and Braverman, on the other hand, are not convinced of the sufficiency of the arguments which have led to these conclusions. They point out five criteria which are generally accepted for the validity of the "diffusion rate" theory, and insist that neither Kilpatrick and Rushton nor Brönsted and Kane have tested their detailed application. Their own studies on the rate of solution of zinc in acids lead to certain results which are definitely contradictory to the Brönsted-Kilpatrick explanation; at the same time they recognize that the older diffusion rate theory cannot be applied to their data without some modification. Further investigation of these problems will undoubtedly be forthcoming.

The theory of the rate of gaseous reactions at the surface of catalysts has been subjected to similar transitions. A number of individual reactions can not be discussed in the space available to us, but it will be of interest to suggest the changes in viewpoint as to mechanism which one reaction chosen as typical of them has undergone. The reaction chosen is that of the contact sulfuric acid process,

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

In the attempt to explain the observed rates of this reaction under different experimental conditions, Bodenstein and Fink (5) made use of a modification of the Nernst theory of heterogeneous reactions described above. In other words, they assumed that these rates were determined by the rate at which the reacting gases diffused through a film of gas adsorbed on the surface of the catalyst. The mathematical formulation was complicated by the retardation of the reaction by the sulfur trioxide formed in the reaction; nevertheless two expressions could be set up depending upon whether the oxygen or sulfur dioxide was present in excess.

(1) SO_2 *in excess:*

$$\frac{\mathrm{d}[SO_3]}{\mathrm{d}t} = k\frac{[O_2]}{[SO_3]^{\frac{1}{2}}} \tag{43}$$

(2) O_2 *in excess:*

$$\frac{\mathrm{d}[SO_3]}{\mathrm{d}t} = k\frac{[SO_2]}{[SO_3]^{\frac{1}{2}}}$$

Thus, the reaction velocities depend upon the diffusion of oxygen if sulfur dioxide is present in excess and upon the diffusion of sulfur dioxide if oxygen is present in excess, again provided the rate of reaction at the surface is rapid with respect to the diffusion. The term $\frac{1}{[SO_3]^{\frac{1}{2}}}$ is empirical in nature.

There are several serious objections to this explanation. As Langmuir (48) has pointed out, to account for the slowness of this and similar reactions it would be necessary to assume the existence of retarding layers of such thickness that they would be visible. Furthermore, the high temperature coefficient of surface reactions is inconsistent with the much slower variation of a diffusion rate with temperature. Because of these and other difficulties Langmuir was led to seek another explanation, and in a remarkable paper published more than ten years ago he was able to develop an entirely new theory for the kinetics of such reactions, based upon his interpretation of evaporation from and condensation on solid surfaces. According to it the rates of evaporation and condensation are determined by the nature of the forces operative between the solid and gas and the number of active spots available on the surface. The forces involved, which are of chemical nature, are limited in range to distances of the order of molecular thicknesses. The adsorption on the surface is the result of a time lag between condensation and evaporation. Two general cases are considered.

1. Surface of catalyst only slightly covered by monomolecular layer.
2. Surface of catalyst practically completely covered by reacting gases.

The interesting thing for our purpose is that deductions based upon the "monomolecular layer" theory lead to reaction rate equations which are identical in form with those found by Bodenstein and Fink, and for which a diffusion mechanism was postulated. Once more, then, we are faced with the necessity of a differentiation between monomolecular and polymolecular theory. The presumption is decidedly in favor of the monomolecular theory at the present time.

D. DIFFUSION AND KINETICS OF COAGULATION

In the field of homogeneous reaction kinetics the bimolecular reaction has been successfully described by a collision mechanism based upon kinetic theory. The expression for the specific reaction rate of such a reaction is,

$$k = se^{-\frac{E}{RT}} \qquad (44)$$

where s is the number of molecules colliding, and $e^{-\frac{E}{RT}}$ is a numeric representing the fraction of the molecules having energy equal to or greater than the activation energy E. In short, the reaction occurs when activated molecules collide. A similar problem presents itself when we come to study the problem of the coagulation of a colloidal system, which, with respect to the rate of change of the total number of particles, is equivalent to a polymerization reaction of the second order. The solution of this problem was shown by Smoluchowski (77) to be comparatively simple in the case of a rapid coagulation, but it is more complex for slow coagulation.

In considering the coagulation process, two factors must be carefully differentiated. In any colloidal system there is always a definite probability of collision between particles, and there is further a definite probability of adhesion, once collision has taken place. By rapid coagulation is meant that process taking place when the probability of adhesion approaches unity, or when all collisions are effective in reducing the total number of particles. When the probability of adhesion is less than unity, the coagulation is characterized by the word "slow." The quantitative relations for rapid coagulation in a dispersion of spherically shaped particles of uniform size are based upon the assumption that two particles adhere whenever they diffuse to within a certain distance R, which is slightly more than twice the radius of a single particle. These relationships provide an answer to several questions, as follows:

1. The change in the total number of particles,

$$N = \frac{N_0}{1 + \frac{t}{T}} \tag{45}$$

2. The change in the number of single particles,

$$N_1 = \frac{N_0}{\left(1 + \frac{t}{T}\right)^2} \tag{46}$$

3. The change in the number of double particles,

$$N_2 = \frac{N_0\left(\frac{t}{T}\right)}{\left(1 + \frac{t}{T}\right)^3} \tag{47}$$

4. The change in the number of particles of k-order,

$$N_k = \frac{N_0\left(\frac{t}{T}\right)^{k-1}}{\left(1 + \frac{t}{T}\right)^{k+1}} \tag{48}$$

In these equations, N, N_1, N_2, N_k are the numbers of all, single, double, and

k^{th}-order particles, respectively, at time t; k is the number of primary particles in the aggregate; N_0 is the number of particles at the start of the experiment; and T is a constant characterizing the rate of coagulation.

The constant T is of special interest because it is theoretically equal to $\frac{1}{4\pi N_0 DR}$, with D the diffusion coefficient. The constant D is involved because it determines the frequency with which collisions between particles can occur. The probability that one particle considered as stationary in a sol containing N_0 particles per cubic centimeter will be struck by another is

$$P = 4\pi DR$$

Thus, starting with N_0 particles, the number remaining after time t will be

$$N = N_0 e^{-4\pi DRN_0 t} \tag{49}$$

The derivation of the several equations given above follows directly from this statement. The similarity with the expression which describes the bimolecular reaction is now made apparent.

In actual practise the constant T is determined empirically by noting the time at which the total number of particles has fallen to one-half of its original value. In this manner the theory has been confirmed by direct ultramicroscopic count when the coagulation process could be described as a rapid one.

For slow coagulations the application of the theory after its modification to allow for a definite fractional number of effective collisions has not been so successful. In some laboratories this failure of the theory is believed to be due to a sensitivity of slow coagulation to variations in particle size and to deviations from spherical shape. The situation has been considerably improved by the excellent theoretical work of Müller (53), in which these factors are given due consideration. In spite of its shortcomings the coagulation theory is to be considered another triumph of the molecular kinetic point of view as applied to colloidal systems, and improvements in the present situation may be expected.

IV. APPLICATIONS

Diffusion theory has been shown to be of considerable significance for certain fundamental questions of the purely physical sciences. In addition, the application of diffusion measurements to scientific and engineering problems has been attended with success in a number of instances, so much so that it seems worth while to suggest some of them before concluding this report.

An excellent example of an engineering application is found in the wetting and drying of porous solids of all kinds. The wetting of an insulating material by absorption of moisture which exerts a profound effect upon its electrical characteristics, has been described by means of the diffusion law in many instances. Thus, Andrews and Johnston (1) have shown that the process of water absorption when a sheet of rubber is immersed in water follows the diffusion law. As was pointed out by these investigators, it is a further consequence of this law that for a given sample of rubber the time required to reach a specified degree of saturation is proportional to the square of the thickness of the sheet, an important result because it enables the prediction of the behavior of thicker sheets from observations made upon thin sheets which become saturated in comparatively short times.

The inverse problem, that of the drying of a solid, has also been the subject of much discussion. As Sherwood[3] (73) has pointed out in an interesting series of articles dealing with this problem, the water contained in the solid must by some mechanism travel to the surface before it can escape. It has been generally assumed that it travels through the solid by diffusion as a liquid, although the possibility of its diffusing as water vapor has also been considered. In any quantitative consideration of the problem there must be described the mode of transport of the water through the solid, the place and rate of the evaporation, the distribution of moisture in the solid, and the temperature. In the process discussed by Sherwood it is assumed that the temperature, humidity, velocity, and direction of the air are maintained constant, and that the latent heat of vaporization of the water is received by the solid by convection.

The general mechanisms of drying can be classified as follows:

1. Evaporation of the liquid at the surface of the solid, with resistance to internal diffusion of liquid small as compared with resistance to the removal of vapor from the surface.
2. Evaporation at surface, but with resistance to internal liquid diffusion great as compared to the removal of vapor from the surface.
3. Evaporation in the interior of the solid, with resistance to internal diffusion great as compared with resistance to the removal of vapor.

Observations on the rate of drying of a porous slab as a function of the water content led Sherwood to divide the process into a constant rate period and a falling rate period. During the constant rate period the evaporation takes place at the surface of the wet solid much as it does from the surface of a liquid, with the rate of drying being limited by the diffusion rate of water vapor through the surface air film outward. The falling rate period is shown to be further divisible into two zones, a first one in which the rate of drying decreases because of a reduction in the area of

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[3] Many other investigators have considered these and similar problems, and although there has sometimes been uncertainty with regard to detail they are essentially in agreement with the views to be described here.

wetted surface, and a second one in which the drying is controlled by internal liquid diffusion, of which either mechanism or each in turn may prevail. It is also true that the less porous materials show no constant rate period at all, the process being controlled entirely by internal liquid diffusion.

The movement of liquids through solids obeys the same fundamental diffusion laws as hold in the case of molecular diffusion in liquid systems, and equations of the form considered in the theoretical section may be applied to the process. Among other things it can readily be shown that the time required to dry to a given water content is proportional to the square of the block thickness, the diffusion taking place in the direction in which the thickness is measured. A further point of interest has to do with the plane from which the evaporation takes place in the second zone of the falling rate period. This plane of evaporation may move inward from the surface or it may remain effectively at the surface, depending upon whether the solid is porous or fibrous as in the case of paper pulp, or whether it is amorphous as in rubber or clay. In this way diffusion studies can give definite information concerning the structure of solids.

In a somewhat different way this statement also may be illustrated by the work of Friedman and those associated with him (22, 23, 43), who have studied the porosity of dilute gels using diffusion measurements. The problem turns on the very slight hindrance that these gels offer to small molecules diffusing through them. Thus the viscosity theoretically related to the diffusion constant is but slightly greater than that of the liquid itself, and the diffusion must take place in the liquid contained in the pores of the gelatin, agar, and cellulose acetate gels which have been investigated.

The decreased diffusion constant is assumed to have resulted from the operation of three factors:

1. A reduction of diffusion space by the volume of the gel structure.
2. An increased resistance to motion due to the proximity of the cell walls.
3. An increased viscosity of the free liquid due to solution of some of the gel substance.

These factors were taken into account using a relationship of the following form:

$$D_W = D_G\left(1 + 2.4\,\frac{r}{R}\right)(1 + \pi)\,(1 + \alpha) \tag{50}$$

where D_W is the diffusion constant of the solute in pure water,
D_G is that observed in the gel,
r is the radius of the diffusing molecule,

R is the average pore radius in the gel,
π is the correction factor for the mechanical blocking, and
α is the correction factor for the viscosity.

The correction factor α can be calculated from the difference between D_W and the diffusion constant obtained by extrapolation to zero concentration of the data for the dilute gels. The correction for mechanical blocking, which incidentally will depend upon whether a semicrystalline (fibrous) or amorphous structure is involved, was obtained from a formula given by Dumanski (15) some years ago. The third factor is estimated from Ladenburg's correction (45) for the fall of bodies in a capillary tube. The results of the work with gelatin gels are summarized in table 6. The agreement between pore size values obtained with different diffusing molecules will be observed to be satisfactory; furthermore the values themselves are of the expected magnitude.

The authors of this article have been engaged for some time in similar experiments in which lactose and glycerol have been allowed to diffuse both in and out of soaked blocks of wood arranged in the several directions. The samples used up to the present time have been both the sapwood and heartwood of cedar, western hemlock, and white pine. The effective pore size calculations involve several difficult assumptions; nevertheless, preliminary results are in reasonably good agreement with those of Stamm (78), obtained by other and ingenious methods.

TABLE 6

Effective pore size in gelatin gels by diffusion method

DIFFUSING SUBSTANCE	EFFECTIVE PORE DIAMETER		
	5 per cent gelatin	10 per cent gelatin	15 per cent gelatin
	$m\mu$	$m\mu$	$m\mu$
Urea	9.4	3.0	1.6
Glycerol	11.4	3.4	2.0
Sucrose	11.0	2.8	1.0

A problem less closely related to our discussions, but one which is of considerable significance, has to do with the diffusion and electrolytic conduction in crystalline solids, the most recent and satisfactory treatments of which have been given by Hevesy (35) and by Jost (39). If it is assumed with Frenkel (20) that in such systems diffusion and electrolytic conduction are the result of migration of the ions in the interlattice space, and of migration of the vacant places themselves, it is possible to account not only for the temperature dependence, but also for the magnitude of these effects which are known from numerous experiments. In the literature, diffusion and mobility of ions have been represented by a term of the form

$$ae^{-\frac{b}{kT}}$$

in which the constant a depends upon the mobility of a single ion, the ionic concentration, and, in the case of conductivity, the ionic charge, while the constant b determines an energy of liberation required by the ion to leave its normal position.

The applications to physiology and biology are numerous, but necessarily qualitative or semiquantitative in character. Indeed, the complexity of the systems involved is often such that there is difficulty in identifying and segregating the phenomena actually involved. But in spite of this fact much has been accomplished. It was at one time believed that the sorption of materials in biological systems took place as a result of diffusion alone, but the insufficiency of this point of view is recognized, now that negative osmose, selective adsorption, variations in cell structure and composition, and other factors are better understood. Certainly it seems to be true that there is a parallelism between rate of diffusion and the rate of sorption (37, 90). Bechhold (3) and many others (52, 96, 26) discuss diffusion, osmotic pressure, swelling, and shrinking as factors involved in the entry of food into cells and in the circulation of matter. Diffusion is involved in the processes of secretion and excretion, but certainly not in a simple way.

Diffusion studies with enzymes have been made with two objects in view, one in the attempt to obtain a theory for the velocity of enzyme catalysis and the other to separate the enzyme from other crystalloids and colloids. Herzog and Kasarnowski (33) have determined the diffusion coefficients of several enzyme preparations. Fränkel and Hamburg (19) and others have shown that enzyme preparations consist of a diffusible and nondiffusible part; thus enzymatic cleavage may form products which pass into the circulating fluids of an organism by diffusion through membranes. Experiments by Nelson and associates (55, 56), in which the temperature coefficients of enzyme reactions were studied, have led them to conclude that chemical reaction and not diffusion determines the velocity of enzyme catalysis. The study of enzymes from the standpoint of the chemistry of invertase has been reviewed recently in This Journal by Nelson (54).

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