A SURVEY OF DIFFUSION IN FLUID SYSTEM

By

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INTRODUCTION

One of the most important fields in physical chemistry that constitutes a major part in the chemical engineering studies is diffusion. Physics has given much attention and the physical theories entered the different fields of chemistry. Diffusion is one of these fields to which physics has become very important.

With the increasing number and complexity of physical methods for the treatment of diffusion, there has resulted a need for a general survey. It is the object of this paper to provide a description of tested methods, the theoretical background for handling them, and the information necessary for a critical evaluation of the experimental results.

Due to the diversity of the different methods discussed and the relations of few of these to others of different basis, a uniformity of presentation may be noticed in a few cases.

It is hoped that the material will contribute to the understanding and effective application of the respective techniques.

THEORY

Diffusion is a characteristic migratory phenomenon which causes a soluble substance to disperse itself through the entire volume of liquid (or gas) in which it is contained or with which it comes in contact.

The experimental study of diffusion in liquid systems was begun by Graham about 1850. A few years later, Fick[33], from the analogy with Fourier's law of thermal conduction, formed the basic law of diffusion. The formula that was obtained by Fick depends on the assumption that the driving force causing diffusion is proportional to the concentration gradient.

Considering a solution of concentration (C_o) in contact with its solvent, assuming that no external forces other than osmotic pressure, act on the solute molecules and that the solute concentration is in the ideal solution range, the rate of diffusion according to Fick[33] is:

$$\frac{ds}{dt} = -DA\frac{dc}{dx}$$

where A = cross sectional area.

X = distance from the boundary (of first contact).

C = concentration.

D = diffusion coefficient.

$\frac{ds}{dt}$ = quantity of solute diffused in the time (dt).

or $Q = -D\left(\frac{\partial c}{\partial x}\right)$

where Q = the amount of material crossing a plane of unit area per unit time.

When the above equation is combined with the hydrodynamic equation of continuity $\frac{\partial c}{\partial t} = -\frac{\partial Q}{\partial x}$ the general equation which is known as Fick's second law is obtained:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x}\right)$$

When the diffusivity is constant as in the case of very dilute solutions or small concentration ranges, the equation will be

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right)$$

Fick's law was extended to include the effect of the molecular strain by Konobecuskii[103] and the following equation resulted:

$$\frac{\partial c}{\partial t} = D'\left(\frac{\partial^2 c}{\partial x^2}\right) - D''\left(\frac{\partial^2 \epsilon}{\partial x^2}\right)$$

where D' = the classical diffusion coefficient.

D'' = the ascending diffusion coefficient.

ϵ = the strain.

Diffusion may be caused by a gradient of chemical potential (σ) which is a function of concentration, strain and temperature gradient. The general form of the diffusivity equation after including the effect of temperature gradient is:

$$\frac{\partial c}{\partial t} = D'\left(\frac{\partial^2 c}{\partial x^2}\right) - D''\left(\frac{\partial^2 \epsilon}{\partial x^2}\right) + D'''\left(\frac{\partial^2 T}{\partial x^2}\right)$$

where D''' = the thermal diffusion coefficient.

T = the temperature.

Cases of diffusion: To calculate the diffusion coefficient from the experimental data with the use of Fick's law, three cases of diffusion must be considered because the integration of Fick's equation depends on the nature of the diffusion. The following paragraphs discuss briefly the integration forms of the equation for the three general cases of diffusion when diffusion takes place in a vertical column of fluid.

(1) Free Diffusion: Linear diffusion from an initial sharp boundary which separates two solutions of different concentrations with no concentration changes at the column ends. The solution of the equation is:

$$C = C_0'' + \frac{C_0' - C_0''}{2}\left[1 - \frac{2}{\sqrt{\pi}}\int_0^{(x/2)\sqrt{Dt}} e^{-y^2}\,dy\right]$$

where C = concentration at level x.

C_0'', C_0' = the initial concentrations of the upper and lower solutions respectively.

The term in brackets is the probability integral in which (y) is an arbitrary integration variable. If the upper phase is initially pure solvent, the equation is:

$$C_0 = \frac{C_0'}{2}\left[1 - \Psi\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

in which $\Psi\left(\frac{x}{2\sqrt{Dt}}\right)$ represents the probability integral.

Solving this equation for D, the following relation is obtained:

$$D = \frac{x^2}{4t}\left[\frac{1}{\Psi(1 - 2C/C_0')}\right]$$

The same equation applies when the lower phase is maintained at constant concentration.

(2) Restricted Diffusion: Diffusion in the same column mentioned in case of free diffusion with concentration changes occuring at the column ends. Harned et al[48] simplified the equation to the following form:

$$\ln(C' - C'') = -(\pi^2 Dt/L^2) + \text{Constant}$$

where L = length of diffusion column.

$(c' = c'')$ = difference in concentrations between two levels at equal distances from the ends of the diffusion column.

(3) Steady State Diffusion: Diffusion in an open column where the upper end concentration is constant and equal to or greater than zero and the lower end concentration is maintained at a constant value larger than the upper end concentration. In this case, the amount of material crossing a plane of unit area per unit time is constant. If the diffusion coefficient is assumed to be constant, the

concentration gradient will be linear along the column and given by the following equation:

$$c = c' - \frac{x}{L}\left(c' - c'' \right)$$

Since $\partial c/\partial t$ is equal to zero for steady flow, then the Fick's second law is reduced to the first law

$$D = - Q \left(\partial c/\partial x \right)^{-1}$$

Physical Interpretations: The rate of transfer in gases is a combined effect of mass flow because of concentration gradient and pure diffusion. Pure diffusion is defined as that due to the random motion of non-uniformly distributed molecules. In liquids and solids, mass flow is not included in the rate of diffusion relative to surroundings and the diffusivity is calculated in terms of the molecular jump frequencies. A molecular mechanism is suggested for the compensation of mass flow after noticing the distinction between molecular jumps and their oscillations.

The change of energy that the molecules undergo may give an increase in the hydrostatic pressure which is relieved by mass flow.

Yang[157] examined the phenomenon of diffusion in the light of the theory of Brownian motion. Coefficients of self-diffusion, ordinary diffusion, and thermal diffusion were expressed by him in terms of the first and second moment of certain transitional probabilities familiar in Brownian theory.

For self diffusion,

$$D_s = \frac{1}{6}\left(\overline{\Delta x}\right)^2 / \Delta T$$

where ΔT = the mean time of flight.

$\overline{\Delta x}$ = the mean space displacement.

For ordinary diffusion,

$$D_o = \frac{n_1 n_2}{3n}\left\{\left(\frac{\partial}{\partial n_1} - \frac{\partial}{\partial n_2}\right)(\alpha_1 - \alpha_2) + \left(\frac{\alpha_1}{n_1} + \frac{\alpha_2}{n_2}\right)\right\}$$

as explained by Furth[157]. Or

$$D_o = \frac{n_1 n_2}{3n}\left(\frac{\alpha_1}{n_1} + \frac{\alpha_2}{n_2}\right)$$

as explained by Meyer[157].

where α = rate of dispersion and

n = density.

Subscripts 1, 2 refer to the first and the second layer of the fluid.

For Thermal diffusion,

$$D_t = \frac{n_1 n_2}{3 n_2}\left\{1 + n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2} - T \frac{\partial}{\partial T}\right\}(\alpha_1 - \alpha_2)$$

The relation among coefficients of self, ordinary and thermal diffusion was studied for gas mixtures[5], and correlations were obtained.

Arnold has advanced a theoretical equation for estimation of liquid diffusion coefficients based on the application to liquids of a modified kinetic theory for gases. This approach is not entirely satisfactory in view of subsequent work in the liquids theory[6].

Wilke's[154] method for determining liquid diffusion coefficients was based upon relationships suggested by the theory of absolute reaction rates and the Stokes-Einstein equation.

Relations were obtained between diffusion and viscosity by Eyring[31] with the aid of the absolute reaction theory and the concept of hole formation in liquid systems. For self-diffusion, the Eyring relation is:

$$\frac{D\eta}{kT} = \frac{\lambda_1}{\lambda_2 \lambda_3}$$

where λ = distance between molecules on the three axes.

K = Boltzman constant.

η = viscosity of the liquid.

The Stokes-Einstein equation is:

$$\frac{D\eta}{kT} = \frac{1}{6\pi r}$$

r = molecular radius of solute.

Combining these two equations gives the following equation for the diffusion factor (F):

$$F = \frac{T}{D\eta}$$

The proportionality between D & T/η shows that temperature has negligible effect on (F). Thus the equation is limited to application to dilute solutions. Limiting factors on these equations were discussed by Taylor[132].

For the study of concentration effect, ideal and non-ideal solutions were discussed separately by Powell et al[111], and their results are stated in the following equations:

$$\underset{(1)}{\left(\frac{D\eta}{T}\right)_A} = \left[\underset{(2)}{\left(\frac{D\eta}{T}\right)_{B_0}} - \underset{(3)}{\left(\frac{D\eta}{T}\right)_{A_0}} \right] x_A + \left(\frac{D\eta}{T}\right)_{A_0}$$

where (1) = diffusion of A in B at any concentration.

(2) = diffusion of A in dilute solution of A in B.

(3) = diffusion of B in dilute solution of B in A.

For non-ideal solutions, the left side of the equation must be divided by:

$$\frac{d \ln a_A}{d \ln x_A}$$

where a_A = the activity of Component A.

X_A = concentration of A.

A temperature gradient in a solution or in a mixture consisting of a single phase produces a concentration gradient. Diffusion due to such concentration gradient is termed thermal diffusion. If the material is confined between parallel horizontal plates, with the upper plate heated and the lower cooled: the phenomenon is termed the "Soret effect." In the thermogravitational arrangement used by Clausius and Dickel, the material is between hot and cold vertical walls.

Croot[44] developed a theory for the case of dilute solutions based on the "Soret effect" and gives a procedure for deducing the constants of thermal diffusion from statistical measurements.

Thermal diffusion in the critical region[110] was determined using Xenon as a tracer at 4 atm. and 20° above the critical temperature in a modified method which shows the inadequacy of the kinetic theory to explain thermal diffusion.

Most of the above mentioned and other methods were applied to the analysis of binary gas mixtures. Direct or indirect readings were obtained for different systems of binary gases. One of the indirect methods is the one that measures the thermal diffusion ratio by a bending balance.[91]

The theory of thermal diffusion was developed on a kinetic basis and by the method of non-equilibrium thermodynamics using Onsager's[23] relation. It concerns the heat of transport in binary regular solutions.

Whally and Winter[151] extended the elementary theory of thermal diffusion and developed equations for binary mixtures:

$$D_{12} = \left(\frac{KT}{3m_1 m_2}\right)^{1/2} \left(L_1 C_2 m_2^{1/2} + L_2 C_1 m_1^{1/2} \right)$$

where m = molecular mass.

L = free path.

K is derived from $\eta = \frac{0.461}{\pi \sigma^2} \left(\frac{3mKT}{2}\right)^{1/2}$

σ = collision diameter.

η = viscosity.

Eyring and Prager[32] gave equations applying to thermal diffusion in gaseous binary systems when the thermal diffusion occurs in conjunction with mass flow:

$$D(c_1) = -\frac{1}{2}\,\frac{d\lambda}{dc_1}\left[\int_0^{c_1} \lambda\, dc_1 + B c_1 x \int_0^{c_1}\left(\int_0^{c_1} \lambda\, dc_1\right) dc_1\right]$$

where $\lambda = x/t^{1/2}$

$$B = \int_0^{c_1\infty} \lambda \frac{dc_1}{c_1^{\infty}} \int_0^{c_1\infty}\left(\int_0^{c_1} \lambda\, dc_1\right) dc_1$$

For steady state determinations, the approximation is:

$$V = \frac{D_2\,\bar{V}_1\,dc_1}{C_2\,\bar{V}_2\,dx} \quad , \quad P_1 = \frac{D\,dc_i}{c_2\,\bar{V}_2\,dx}$$

$\bar{V}$ = partial molal volume.

To account for mass flow in thermal diffusion:

$$D = D_1 \bar{V}_2 c_2 + D_2 \bar{V}_1 c_1 = \left(D_1^x n_2 + D_2^x n_1\right)\left(\frac{\partial \ln a_1}{\partial \ln n_1}\right)_{P.T.}$$

where a_1 = activity.

n_1 = molal fraction.

D^x = $\lambda^2 \nu_1 (n, T; n, T)$

ν = frequency.

λ = slice thickness (imaginary).

The thermal diffusion factor[45] also can be calculated as a function of pressure and temperature and concentration for binary mixtures of real gases. Among other theories[113,67] and equations[126,26] for thermal diffusion, some depend on the mass[142b] flow and thermal energy[63] (especially for diffusion of direct interchange) but most of them depend on Graham's law of diffusion.[78]

Previous studies for diffusion in gases[58,142a] were extended to give more general mathematical expressions for diffusion in cases involving simultaneous concentration, gravitational and thermal gradient.

A generalization in the diffusion theory involves the following points as discussed by Lamm.[76]

1 - Reference equations of two component systems (general form).

2 - Generalization of Sutherland - Einstein diffusion equation from Wener - Boltzmann diffusion equation,

$$\frac{\partial n_1}{\partial t} = \frac{\partial}{\partial x}\left[D_1 \frac{\partial n_1}{\partial x} \right]$$

where n = Concentration mole/cm^3.

He reaches the conclusion that

$$D_{12} = RTB_{12}\frac{1}{\phi_1 + \phi_2} = RTB_{12}\frac{N_1 N_2}{\rho_{12}\,\bar{V}_{12}}$$

and

$$D_{12} = \frac{n_1 n_2}{\rho_{12}(n_1 + n_2)} = RTB_{12}\frac{N_1}{\phi_2} = RTB_{12}\frac{N_2}{\phi_1}$$

as compared to Sutherland - Einstein equations.

$$\lim_{N_1 \to 1} D_{12} = \frac{RT}{\phi_2}$$

The partial generalization

$$D_2 = \frac{RT}{\phi_2}B_{12}$$

where B_{12} = Thermodynamic factor.

ϕ = frictional coefficient/mole.

ρ = frictional coefficient/amount of substance in 1 cc.

$\overline{V}_{12}$ = mean molar volume of a binary solution.

N = mole fraction.

The diffusion coefficient could be predicted for organic liquids in solution from the $D\eta/T$ plot, the data for which are obtained from the literature and the Langmuir[77] relationship.

The diffusivity for electrolytes may be predicted from Haskell's[56] equation:

$$D = 1.785 \times 10^{-9} \frac{UV}{U+V}\left[\frac{1}{u}+\frac{1}{v}\right] T$$

where U = equivalent ionic conductance of cation at infinite dilution

V = equivalent ionic conductance of anion at infinite dilution.

v = anion valence.

u = cation valence.

T = ° Kelvin temperature.

Haskell's equation does not consider convection, but convection is an important factor. The following equation[138] applies to diffusion in electrolytes when convection is considered:

$$C_{(x,t)} = C_b - \frac{N_d}{\sqrt{\pi D}} \int_0^t \frac{dt}{\sqrt{t}} \; \exp.\left(\frac{-x^2}{4Dt}\right)$$

If $x = o$ at the electrode:

$$C_{(0,t)} = C_b - 1.1285\ N_d \sqrt{t/D}$$

where $C_{(x,t)}$ = concentration at any time.

C_b = original concentration.

N_d = rate of ions removal at the electrode.

X = distance from initial boundary.

For forced convection, other equations had been derived from

$$D = \frac{(n_1 - n_2) D_1 D_2}{n_1 D_1 - n_2 D_2}$$

where N = valence discharge.

D = effective diffusion coefficient.

Diffusion of electrolytes diminishes to a significant extent with increase of concentration. The generalized form of the equation used in the theoretical diffusion of electrolytes was derived from the Nernst-Einstein equations. The Nernst[138] equation for dilute electrolytes,

$$D = \frac{2RT}{1/u + 1/v}$$

where v and u are the ionic mobilities at infinite dilution. The Einstein equation for uncharged spherical particles is:

$$D = \frac{RT}{N_6 \pi \eta r}$$

where r = molecule radius.

η = viscosity.

The generalized equations for diffusion in electrolyte is:

$$D = \frac{iRT}{\text{Sum of Resistances}} = \frac{iRT}{\sum (1/u_m)}$$

The problem of diffusion of electrolytes when the electrolyte contains a radioactive isotope[116] had been discussed with the help of Fick's Law, the Nernst calculation and Debye-Huckel theory to give the following:

$$D = 16.632 \times 10^{10}\, T \left(\frac{\overline{m}}{c}\right)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right)$$

$y_{\pm}$ = mean ionic activity coefficient.

$\frac{\overline{m}}{c}$ = a function of viscosity, concentration and equivalent conductance at infinite dilution.

The equation for self-diffusion of an ion is:

$$D = -n w \frac{\partial \mu}{\partial n}$$

where n = moles/cc.

w = mobility.

μ = chemical ionic potential.

By expressing mobility in terms of equivalent conductance and introducing the activity coefficient, an equation is derived for diffusion of a tracer in any particular case.

EXPERIMENTAL METHODS

Chemical, densimetric, electrical or optical methods of analysis are used to accomplish measurement of concentration or concentration gradient in a system as a function of distance or time. Boundary conditions determine whether the process is free, restricted or steady state diffusion. The following methods are limited to the determination of diffusivity.

Diffusion in Liquids

A - Free Diffusion Cells

(1) Furth cell[22]: For use in microcolorimetric method and is suitable for aqueous systems but not organic liquids. It is made of a glass, metal or plastic spacer cemented between a cover glass and microscope slide. A partition divides the cell into two rectangular chambers. One chamber contains the comparison solution. The other is the diffusion chamber which is divided by a draw slide which is withdrawn by an electromagnet. A layer of grease is necessary in the slot to prevent leakage and reduce friction.

(2) Lamm cell[74]: It is made of a glass, metal or plastic spacer, 1 cm. thick, placed between two circular optical-glass windows that are held tightly by a threaded brass ring and a clamp to form a six cm. high, four mm. wide cell cushioned against the clamp with rubber gaskets.

Vaseline or a suitable cement covers the surfaces where leakage is expected. A small inlet tube reaches above the level of the water and enters the cell through a tight fitting flange. A metal or plastic draw slide fits into a horizontal slot. A recess with heavy oil or mercury filled tube is used to lubricate the slide and prevent leakage. A vaseline filled chamber encloses the metal walls. A reducing gear mechanism accomplishes a slow uniform removal of the slide.

The diffusing solution is introduced to a level above the draw slide, the slide is closed and the other liquid is introduced into the upper compartment. The connecting lines are closed after thermal equilibrium is reached. Leakage is a great problem, especially if refractometric method of analysis is used.

(3) Neurath Cell[100]: A 5 cm. high, 0.5 cm. wide and 1.7 cm. thick cell with two glass plates, one in the front and the other in the back. Two glass, metal or plastic plates hold the cell in place. The upper plate is attached or fixed to a clamp, and the two plates are pressed against the cell by a spring and a screw.

One liquid is introduced to the upper part through one tube and the other liquid to the lower part through another tube. After thermal equilibrium is reached, the two halves of the cell are aligned together. Troubles also arise here from the grease lubricant.

(4) Claesson Cell[18]: is suitable for organic liquids and aqueous solutions because it overcomes grease contamination and leakage. It has two spaces (A, c) each 10 mm. thick held by spring (S). The diffusion chamber is split into two halves (F, G) contained in spaces (A, c) respectively. The upper space (A) can be moved laterally by an eccentric device (B). Liquid is filled through two tubes (D, E) which reach a level (N) near the spring. It is shown in Fugure (1).

(5) Cylindrical Cells: In these cells, leakage is avoided but errors exist in optical method of analysis due to the curved surfaces. The Lamm [75] cylindrical cell has two chambers (A, B). Heavy liquid is applied to (A) and separated from light liquid in (B) by an air lock under the glass dish. After thermal equilibrium is established, stopcock (C) is opened and leveling begins while a slight pressure of air is applied to (A). Disturbances may exist from displacement and leveling of the liquids. It is shown in Figure (2).

Stirred diaphragm cell[127b]: Circulation of the liquid in a diffusion cell may not be adequate since it depends on the density changes due to the diffusion in the cell. To overcome this difficulty a modification was necessary. This resulted in a cell with the denser solution on the lower side and continuous stirring on both sides. The cell has two compartments, each with a glass stirrer. The stirrer in the upper compartment sinks while the one in the lower compartment floats. Each stirrer has sealed in it a piece of iron wire and is rotated by a pulley-driven permanent magnet mounted around the cell. It is shown in Figure (3).

Tiselius Cell[86]: A three-sectioned cell that can be slowly filled with a colloidal suspension by two tubes. First, the lower section is filled with colloid and isolated from the other sections while the middle section is filled with the colloid in one tube and a buffer in the other. The upper section is filled separately with the buffer. After thermal equilibrium is reached, the sections are attached together and the boundaries formed between the liquids. This cell is used for colloids and other dense solutions. This is shown in Figure (4).

Twin diffusion cell[129]: The twin diffusion cell has three side walls (a, b, c). Wall (a) has two horizontal grooves with capillaries (d, e) at the middle and the bottom. Two capillaries go through metal separation wall (k) and connect the two cells together. The capillaries lead to glass containers. Solvent is forced into the cell first. Solution is introduced from the bottom groove. When the boundary is formed and reaches the middle, more solvent is forced in through the upper groove and the intermediate capillary is used for the escape of both solvent and solution until a clear boundary is formed. Figure (5) shows a sketch of this cell. Special selected methods are discussed later in which new or modified cells of this kind are illustrated.

(6) Boundary Sharpening: To improve boundary sharpness, Kahn and Polsun[69] took a two-chambered cell and introduced a fine pipette to the solution chamber in order to draw some solution off and give sharp boundary.

Cox and Ogston[20] took a rectangular cell with two openings to introduce liquids and one opening in between to remove them while another opening was used as an air vent. A sliding plate is used to stop liquid flow simultaneously in all openings. This is shown in Figure (6).

B - Free Diffusion Methods

(1) Method of layer analysis (Bourdillon[9]): This method is used to determine the relation between linearity and concentration at constant temperature. The apparatus is thirteen cm. high. The diffusion tube (B) is three cm. long, one and one-tenth cm. in diameter and five cc. volume, and has a capillary at the upper end one mm. in diameter. Tube (A) and cup (C) are each six cc. capacity, and tube (A) is connected through a rubber tubing to a ten cc. calibrated glass syringe which is operated by a motor connected to a rack and pinion device. Tube (A) is filled with solution and (B) with solvent. Displacement of known amount of solution by the motor brings the boundary to the center of the tube and the stopcock is closed. Analysis is made by samples taken through the capillary by the motor and syringe. From the cell's dimension and ratio of displacement, the samples' distance from initial boundary is calculated. The cell is shown in Figure (7).

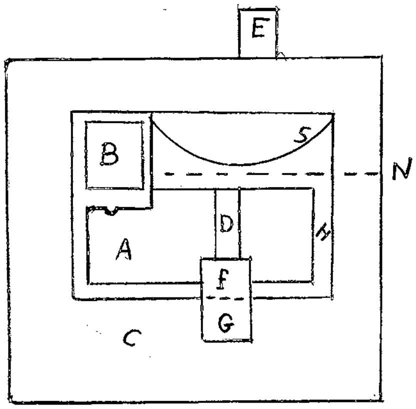


Fig 1

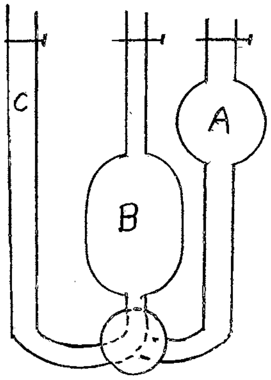


Fig 2

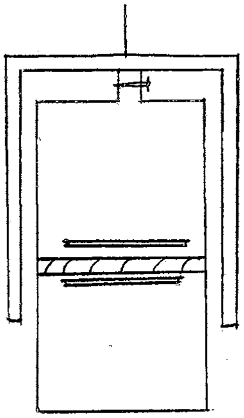


Fig 3

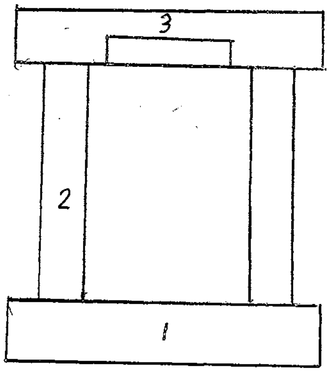


Fig 4

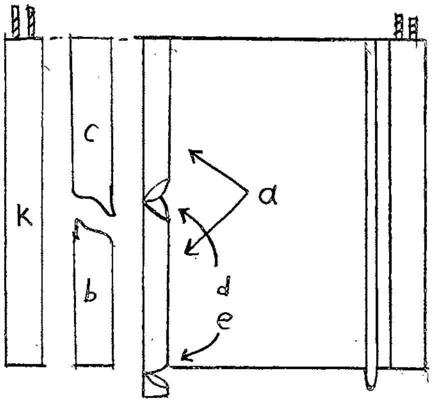


Fig 5

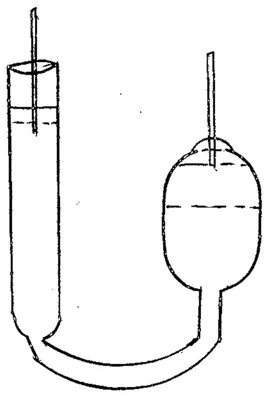


Fig 6

(2) Float Method (Gerlach[36]): This method is to determine the layer distance from the boundary as a function of time at a given concentration which is a good test for the Boltzman relation. The diffusion column is six cm. in diameter, seventy cm. high with a thin sheet of cork placed on the lower liquid surface before the upper liquid is pipetted in. Thirteen floats were made from one mm. capillaries two cm. long with sealed ends. Seven of them ascended the column and six descended during the experiment. The six are introduced before the boundary formation while the seven are introduced after the boundary formation. They are calibrated and their positions determined by a cathetometer or a scale and mirror. A water bath to control the temperature for the fourteen day experiment is needed. The apparatus is not adapted for high precision measurements, but readings can be taken without interrupting the process.

(3) Electrical Conductance Method (Haskell[56]): This is for determination of concentration as a function of time at fixed distances. It is limited to electrolytes. It consists of a one and five-tenths cm. in diameter tube, fifty cm. long through which electrode wires travel. The small tube is surrounded by a five cm. tube (A) for the solution. Electrodes are at distances two, ten, thirteen, sixteen, nineteen, twenty-two, twenty-five, and thirty-two cm. from the bottom of the tube. The eight pairs of electrodes terminate in a mercury cup (M) placed in a commutator (e). A ten cm.

jacket in the bottom contains concentrated salt solution and has four one cm. holes open to tube (A) to allow excess salt solution to diffuse. Salt is placed at the bottom of (A), water introduced at the top slowly, and excess water drained through an outlet in the jacket (D). Conductance measurements at constant temperature are taken as a function of time assuming they correspond to the conductance of a uniform solution of the same concentration as that at the electrode's level.

(4) Light-Absorption Method[79] (Suedberg): Is applicable to materials that exhibit suitable light absorption characteristics and to mixtures of components having characteristic absorption bands at different regions of the spectrum. Measurements do not interrupt the diffusion process. A cell (C) is placed between a camera and light source (S) whose beams are uniformed by two lenses (L_1, L_2) and a diaphragm (D). The camera has a moveable plateholder (P) enabling several exposures to be taken on the same plate. The apparatus is sketched in Figure (9). Flat glass windows enclose the cell in a water bath to permit passage of the light beams without distortion. Monochromatic light is obtained by suitable selection of source and filter. The concentration reference scale is obtained by using a solution of known uniform concentration. Important conditions for the validity of this method are: (1) light intensity must be uniform. (2) pictures must be taken at identical time

intervals. (3) procedure of development and sensitivity of photographic plates must be uniform. (4) development must be made directly after exposure. (5) photometric recording of plate density must be reproducible. This method allows obtaining of concentration distribution along the column at different constant values of time.

(5) Photometric Method (Eversole[29,30]): The cell is formed from two optical glass plates having spaces in three sides and a cover glass for the other side. After introducing the liquid, the cell is inverted and solution begins to pour slowly into the trough. The concentration at the lower end of the cell is kept constant. Vertical movement of the cell is provided by a holder and thumb screw adjustment while reading of the position is accomplished by a cathetometer or scale. A type of photoelectric cell is required which has a characteristic response in the region in which absorption band occurs. A constant-intensity lamp is used to check the photocell. The output of the cell is amplified by an electronic tube direct current amplifier. Calibration is important. Concentration, distance and time can be taken as constant, individually, for readings.

(6) Refractometric Scale Method (Lamm[74]): Suitable for proteins and other micromolecules but not for mixtures. It is an expensive but accurate method. It consists of a uniform light source (M) which emits monochromatic light by means of a filter (G) and a heat absorbing filter (F). A Cell (C) is supported by a vertical sliding device in a

temperature controlled water bath through which the beam of light can pass. The camera (D) is equipped with a slit slide holder (P) allowing 8 or 10 exposures on an optical glass, high speed photographic plate. The cell is filled with liquids, and placed in the bath in such a way that the interface coincides with the system axis. Initial time is recorded at the boundary formation and exposures taken at intervals. When concentration changes occur at the extreme ends, the measurements are discontinued. This is shown in Figure (10).

Calculation of diffusion coefficient (D) is based on Wiener's[153] solution of Fick's Law:

$$\frac{\partial n}{\partial x} = \frac{n_1 - n_0}{2\sqrt{\pi D t}} e^{-x^2/4Dt}$$

where (n_1) and (n_0) are refractive indices of solution and solvent respectively. This equation is adequate when (n) is linear in (C) or they have a known relation. In this case the concentration function can be determined by integration of

$$\int_{x_1}^{x_2} \frac{dc}{dx}$$

Several methods are used to calculate (D) by means of the above equation:

(a) Successive analysis method. $D = \dfrac{x_2^2 - x_1^2}{4t \ln(H_1/H_2)}$

(b) Maximum ordinate method. $D = x^2/2t$

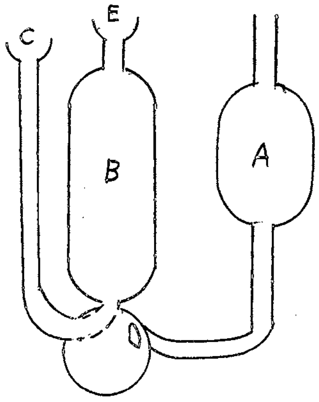


Fig 7

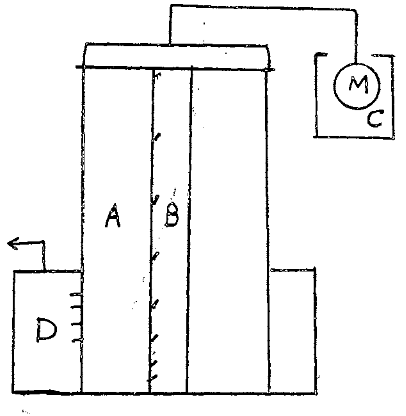


Fig 8

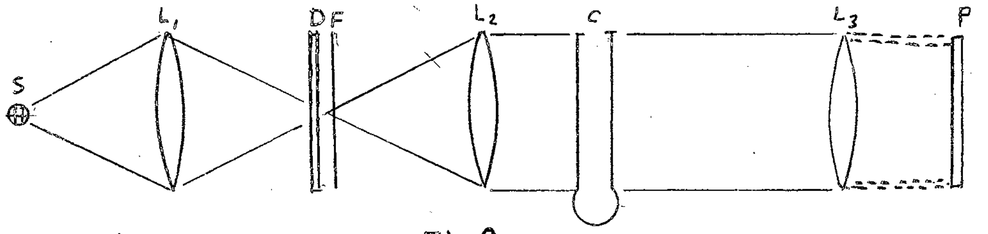


Fig 9

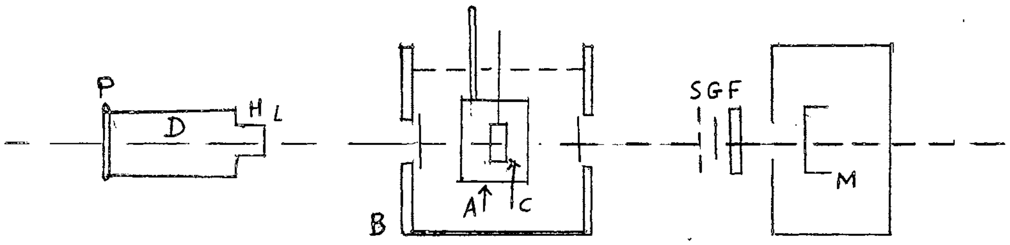


Fig 10

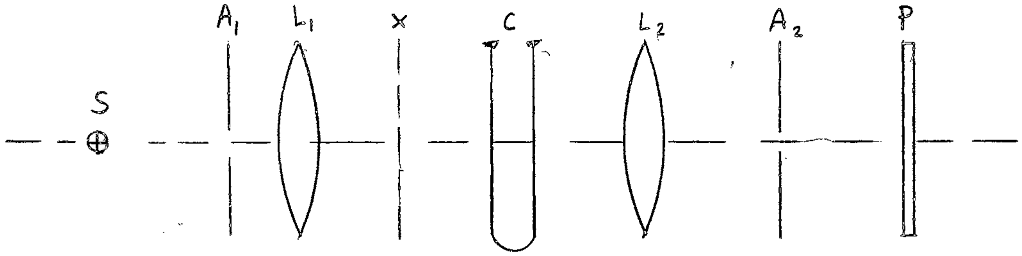


Fig 11

(c) Maximum ordinate area method. $D = (n_1 - n_0)^2/(4\pi t H_m^2)$

(d) Statistical method. $D = \sigma^2/(2t)$

The points of the first three methods are illustrated in the curve (Figure 12); while the statistical method depends on many derivations to obtain (σ) the standard deviation

$$\sigma = \sqrt{\mu_2^{\circ}}$$

where μ_2° = the second moment of curve about arithmatic mean in absolute units. This depends on equation of normal distribution curve of the frequency.

$$S = \frac{N_w}{\sigma\sqrt{2\pi}}(e)^{-(S-\beta)^2\omega^2/2\sigma^2}$$

A modified form of the Lamm method used in a study of aqueous diffusion[37] over temperature range 19 - 25° C. The equation applied gives diffusion coefficient

$$D = \frac{(C_1 - C_0)^2 (dn/dL)^2_{CA}}{4\pi t\ (dn/dx)^2_{max.}}$$

when rearranged gives

$$D = \frac{(C_1 - C_0)^2 G^2 a^2 b^2 (dn/dc)^2_{CA}}{4\pi t Z^2_{max.}}$$

where (Z max.) = maximum scale line displacement produced on photographic plate in (Cm) = Gab (dn/dc) max.

G = optical magnification.

a = thickness of diffusion column in light direction.

b = optical scale distance.

In any experiment, (Z max.) is found by measuring displacement of a few lines on a photographic plate by means of a comparator. Figure (11).

(7) Schlieren - Scanning Method (Longsworth[81,82]): It is based on the phenomena of the curvature of light in a media in which a concentration gradient exists. The system consists of a Schlieren lens (L) located behind the cell (C) through which light passes from a slit (S) to form an image at (Yo) in the plane of the Schlieren diaphragm (D) behind which a camera lens (O) forms an image of the diffusion cell on a photographic plate or ground glass screen (G). A change in concentration will change the refractive index and this will change the position of the image. The diaphragm is moved vertically until all the light is obstructed at the level (Y_o). In the Scanning method, the mechanical movements of the plate and the diaphragm are in a fixed ratio. The formula

$$Y - Y_o = a\,b\left(\frac{dn}{dx}\right)$$

is to relate the index gradient with the diaphragm position, where a = cell thickness.

b = the optical distance from the cell's center to the diaphragm.

A plot of the experimental data gives $({}^{dn}/{}_{dx})$ as a function of (x). Figure (13).

(8) Cylindrical Lens method (Svensson): This method is useful in that the complete refractive-index gradient pattern can be seen at any time during the process. The system consists of an inclined slit (I), located between the camera lens (O) and the cell (C) while a cylindrical lens (R) is located between the camera lens and the plate. This lens displaces the light in the horizontal direction (toward N), the deviation being dependent upon the level through which the light passes slip (I). The light beams from the cell form a curve on the plate and the ordinate scale is related to the refractive index gradient according to:

$$N - N_0 = K\,a\,b\,\frac{dn}{dx}\,\tan\theta$$

where θ = vertical angle of inclination.

K = lateral magnification of the cylindrical lens. Refractive index gradient curve is determined from the experiment. Figure (14).

(9a) Interferometric Method (Gouy): The principles of the system resemble that of Longsworth[83] described previously. It depends on the addition or the cancellation of the light rays from the slit (S). This forms an overall image consisting of an interference pattern of dark and light horizontal lines, each fringe corresponding to a particular conjugate level in the cell. Measurement of the fringe spacings provides a means of determining the diffusion coefficient. The image is projected on the plane of the

Diaphragm. A Schlieren Camera is used to adjust the mask. This helps in making the exposed position twice the thickness of the diffused area which gives uniform exposure on the plate. A filter is used to help in finding the segment of the plate with proper exposure. Monochromatic light is needed as well as a comparator microscope to locate the fringes. The coefficient of diffusion is computed from:

$$D = J_m^2 \lambda^2 b^2 / 4 \pi C_t^3 t$$

where λ = wave length.

C_t = a constant.

J = fringe number.

$J_m = a\ (n_s = n_0)/\lambda$

a, b = cell thickness and optical distance.

(N_s) and (N_0) are refractive indices of boundary solutions. (C_t) is calculated from (J_m) (assumed) till it corresponds at different values of (J).

(9b) Antweiler optical apparatus with Jamin interferometer[118]: In this micrometric method for determining the diffusivity, a white light illumination and a bicameral diffusion cell in which one chamber is for the solvent and the other for the process of diffusion, were used to determine diffusivity of organic solutions at low temperatures. The horizontal interferometric plane was raised and lowered to detect the height of the diffusion layer and to measure the changes in the optical path as a function of height and time. Results are obtained rapidly with small volumes.

(10) Reflectometric Scale Method (Littlewood[80]): A cell (C) is placed in a water container (B) which has a mirror at the bottom that can reflect a light beam, coming from the outside through the cell, back to the objective of the cell. The rotation of the mirror due to the horizontal change of source position is found to be proportional to the refractive indices of the medium at conjugated points of emersion of the light beam. It is found that the angle of emergence and the mirror position are independent of the concentration of the layer between the surface and the point of emergence. Therefore, calibration of the system with a solution of uniform concentration is required. Littlewood[80] used a wire illuminated with sodium and attached close to the telescope objective and rotated the mirror by a mechanical device.

(11) Microcolorimetric Method (Furth[34]): Because of the brief time involved, this method is advantageous in the study of perishable materials. It is based on the proportionality of the time of travel to the square of the distance through which a layer of solution of fixed concentration travels along the diffusion column. The major source of error is the boundary disturbance. It is based on matching of the color of the diffusing solution with the color of a comparison solution of known concentration. It is applicable to dye studies. One or two (as to eliminate the difficulty of using one standard solution at a time)

microscopes are used, with the diffusion cell located in front of one, and the comparison cell in front of the other. Furth's modification is by having eight compartments of the same material and dimensions as the diffusion cell with solutions in them of different known dilutions of the solution under investigation. These are placed in the field of view by one microscope. Readings are taken after the formation of the boundary. A uniform light beam is used with half of a filter and a condenser lens is used to focus the light in the plane of a circular diaphragm placed in front of the collimator that supplies the parallel beam of light. The diaphragm is to control the intensity in the view field. Relations are obtained for distance as a function of time at given concentration.

(12) Microreflectometric Method (Zuber[158]): It consists of a cell mounted on side wall of a prism and having two spacers (D_1, D_2) separated by a slide (S). A beam of light strikes the hypotenuse of the prism and refracts into the liquid. With the use of a solution of uniform concentration and rotation of the prism, a vertical boundary between dark and light areas is obtained across the view field. A relation between the prism position and the concentration is established by calibration. With concentration gradient, a non vertical line is obtained. Many readings of the prism position give relation of concentration to the time at constant values of distance. The system is shown in Figure (15).

C - Restricted Diffusion Methods:

Diffusion coefficient is obtained here by Fick's differential equation and assumed to be constant representing a weight average over the concentration range involved. It could be obtained even at the later stages of the process when the differential of the column and concentrations approach zero. Most methods are of layer analysis type though optical methods are applicable.

(1) Method of Layer Analysis[13] (Cohen and Bruins[19]): The apparatus is formed of a cylindrical cell covered at both ends and divided into four compartments by one cm. thick circular glass plates. The dividing plates have small holes. The solution is placed in the lower chamber and the solvent in the upper three. Samples are to be taken for test during the process after the boundary is formed. Some columns of this type were used with their plates rotating on a common axis.

(2) Electrical Conductance Method (Harned[48]): The cell is made of lucite and in the form of parallelopiped to operate on the shearing principle. The sliding feature is at the bottom and grease contamination is eliminated. The top of the cell and its four sides are screwed and sealed together while brass posts (H) hold the bottom plate (F) against the sliding plate (C) at the cell's bottom. The sliding plate is operated by a brass capstan, wire and pulleys. Platinium electrodes (E) are placed on the sixth

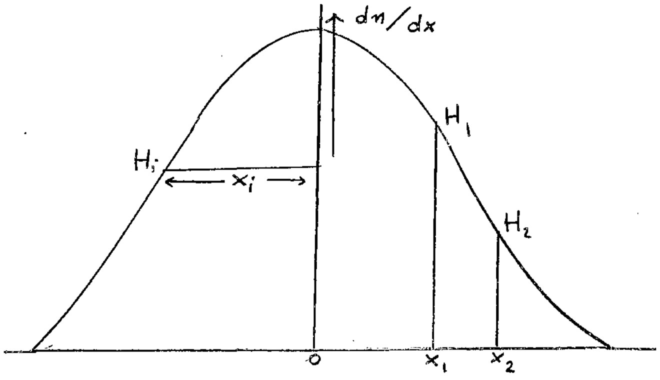


Fig 12

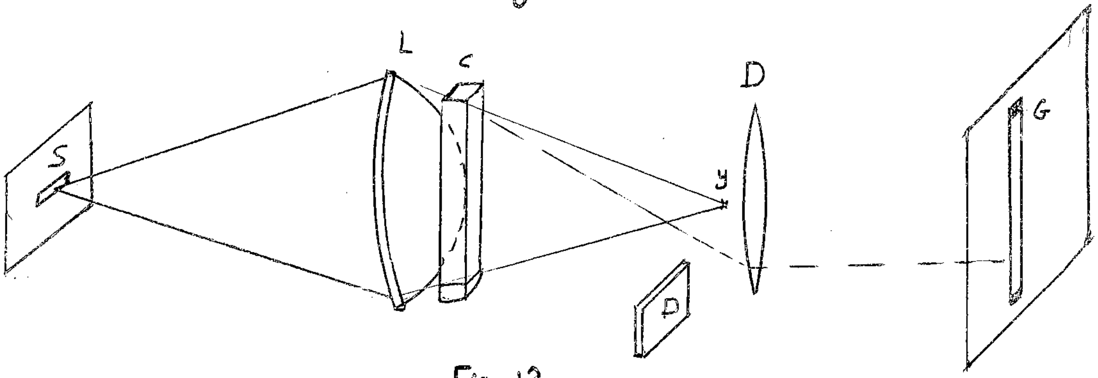


Fig 13

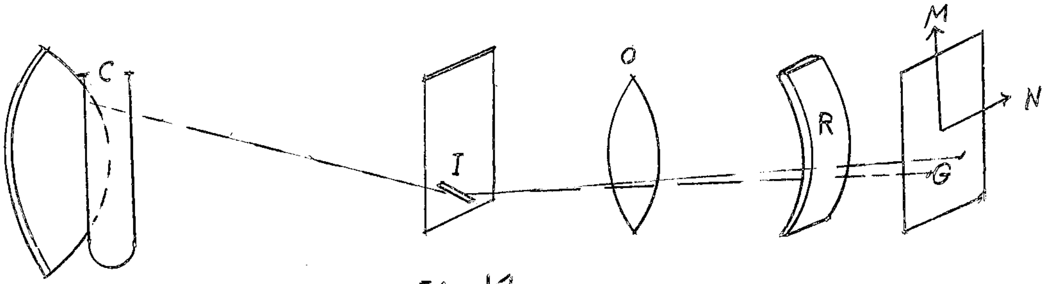


Fig 14

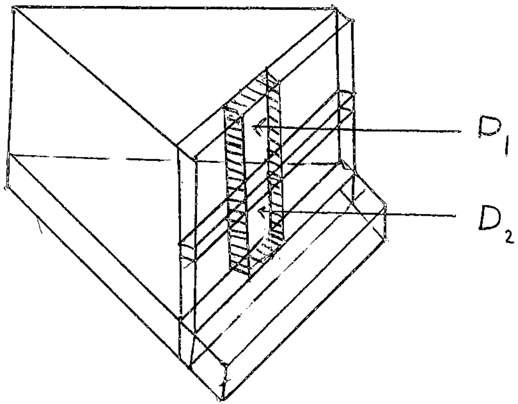


Fig 15

column from each end. The whole system is rested on a block and maintained in a constant temperature bath. The conductance is measured with a calibrated Jones Bridge while the column height is measured with a depth gauge. Conductivity water is introduced to the cell. Excess of water is sheared to a cup (B) while the solution is placed in cup (A) before the sliding of the plate. The system is kept in a constant temperature bath for 24 hours. The slide is removed to let the desired amount of salt diffuse and then the slide goes back to its place. Readings of conductance are taken at desired intervals. Figure (16).

Concentration (determined from its relation with conductance), time and height of the cell determine the diffusion coefficient.

D - Steady-State Diffusion Methods:

The end concentrations of the column are kept constant (with open ends). The flux and concentration gradient are measured experimentally and diffusivity is computed from the equation:

$$D = -Q\left(\partial c/\partial x\right)^{-1}$$

(1) Porous Diaphragm Method (Northrup and Anson[102]): The method is useful for aqueous and non-aqueous solutions but not for dyes or other materials that are absorbed on the membrane surface. There are two types of cells used, single end cell and double end cell[97]. The latter is most used and

modified as described below. The cell is formed of a glass cylinder with a membrane at the middle whose porosity is such that both bulk streaming and semi-permeability are avoided. The tubes for introduction of liquids and the ends of the cylinder are connected by stopcocks. Cell (cylinder) stirring is accomplished by means of two small glass spheres which move through the liquid when the cell is rotated by a belt and pulley mechanism. The time lapse necessary to establish steady state in the diaphragm may be estimated by:

$$t = 1.2\, L^2/D$$

where (L) is the diaphragm thickness. After filling the cells with liquids to the same level in the connecting tube, the system is placed in a constant temperature bath. Time is given for thermal equilibrium and bubble escape, then the stopcocks are closed. Sample analysis may be done after the required period of time has passed or conductometric method may be used for analysis during the process. Figure (17) shows a sketch for the apparatus.

If the diffusivity is constant, two equations apply, one for the short time in which there is a concentration difference across the diaphragm:

$$D = -\frac{q}{Kt}\left(\frac{1}{c' - c''}\right)$$

where q = amount of material passing through the diaphragm.
c', c'' = concentration of upper and lower liquids.

K = is cell constant = A/L.

A = average cross sectional area of the pores.

L = the diaphragm thickness.

For changeable concentration, when the volume of the solution is large:

$$K' D t = \text{Log}\,(C'_0 - C''_0) - \text{Log}\,(C' - C'')$$

(C'_0, C''_0) refer to initial concentrations.

$K' = V' + V''/(2.3\,L\,V'V'')$; ($V'$, V'') are chamber's volumes.

If (D) is not constant and is linear function of the concentration:

Then
$$D' = D_0 - D_0\,\alpha\,\frac{(C' - C'')}{2}$$

where
$$D = D_0\,(1 - \alpha C)$$

(2) Refractometric Method (Clack[17,84]): The cell consists of a (5 x 4 x 1 cm.) column (C) the lower end of which extends into a solution container. Light from slit (S) is collimated by lens (L_1) through the column and focused by lens (L_2) on the ocular plane (E) which has a scale to measure the position of the light band. A sketch of the cell is shown in Figure (18). Twelve days may be required to establish steady state. (Q) is measured for the Fick equation by analysis. The refraction index gradient (dn/dx) is determined from displacement of band position (Z):

$$Z = ab\left(\frac{dn}{dx}\right)$$

where a = cell thickness.

b = focal length of lense (L_2).

(3) Method of Mutual Precipitation of Two Reagents[122]: Two precipitating agents are allowed to diffuse toward each other through a gelatin sheet. A line of precipitate marks the place where the two liquid fronts meet. The equilibrium position of the line depends on the ratio of the diffusivities of the reagents. Three cases result and are discussed.

(1) parallel edges $D_1/D_2 = (c_2/c_1)(d_1/d_2)$

where (d) = distance from solution edge.

(2) Edges at angle $< 90^\circ$ $D_1/D_2 = (c_2/c_1)(\alpha_1/\alpha_2)$

= angle between precipitating lines and edges.

(3) Circular edges $D_1/D_2 = \frac{c_2}{c_1}\left[\frac{(\text{Log } K_1 - \text{Log } K_0)}{(\text{Log } K_2 - \text{Log } K_0)}\right]$

where $K_0 = d_1/d_2$

$K_1 = 1/K_2 = L - \sqrt{(L^2 - r^2)}\,/\,r$

(1) = the distance between centers of the circles and that solution edge.

For the unsteady state other methods must be used. A complete review of the principles and methods for unsteady state diffusion were discussed by Taylor[131].

There are other standard methods[55,68,105,117] for measuring diffusivity in liquids which could be summarized as follows:

(a) Graham second method[55]: The solution of diffusing substance is placed beneath a long water column and different layers are examined at different times.

(b) Over-all absorption by a plane sheet used to determine diffusion rate of direct dyes into cellulose sheet by placing a plane sheet in the solution vapor.

(c) For transfer across a section of fixed composition with respect to one component, then the rate of transfer (S_A) of component (A) through a unit area of the membrane is:

$$S_A = D_A^{\beta} \left(\frac{\partial C_A^{\beta}}{\partial \xi_{\beta}} \right)$$

when (ξ_{β}) is not dependent on (S_A) is steady flow, integration gives:

$$S_A = \frac{1}{a} \int_0^{C_0} D_A^{\beta} \, d C_A^{\beta}$$

where a = unswollen membrane thickness.

(S_A) is determined experimentally for different values of (C_0 , D_A^{β}) obtained from differentiated curve[70] that relates (S_A to C_0).

Radioactive Tracers in Diffusivity Determination Methods

In the last few years, there has been a tendency toward the using of the radioactive tracers for the measurements of concentration through which the diffusivity of a liquid or a gas could be obtained.

(1) Layers Analysis Method (Walker[143]): Since diffusivity depends on concentration as a function of time and distance from the initial boundary between solution and solvent, then concentration determines diffusivity from the following equations:

$$c_x = \frac{c_0}{2}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^y e^{-y^2}\,dy\right)$$

and $$y^2 = \frac{x^2}{4Dt}$$

where Y = parameter related to time.
These equations hold for free diffusion with zero initial concentration.

If the substance whose diffusivity is to be determined is prepared in radioactive form, the counts per minute observed in a thin cross sectional slice in column containing the substance is proportional to the concentration. If activities of many slices are counted, diffusivities can be predicted, even for self diffusion. The apparatus is made of hollow brass tube to shield β-radiation, with a lusteroid tube inside it resting on a vertically adjustable brass disc to adjust the right spot of the tube in front of a slit in the brass wall. Against this slit an end window Geiger tube is placed to measure counts. To form a boundary, the radioactive material is introduced to the bottom with a stainless steel saucer placed carefully on its surface. Then the second layer is added and the free diffusion takes place.

Disadvantages of this method are: slit width is too small to get enough counts; the angle of sight formed through the slit covers a larger volume of liquid than would the slit; beta rays may cloud vision; measurement is limited to beta ray emitters, the resulting curve is not isochronal because of time intervals in any series of counts.

A curve is obtained for distance as a function of concentration from which values are obtained. Figure (19)

(2) Porous Cell Method (Myseles and Slighter[99]): The diffusion cell is formed from two fritted glass cylinders of medium porosity, each covered by lucite plates. Each is filled by gradual displacement, one with tracer solution and the other with solution containing no tracer. The cell is submerged in mercury to prevent evaporation after separation. The amount of tracer in each disc is determined. The diffusion coefficient is computed from the measured transport by comparison with the behavior of a substance of known diffusivity. The calculations are presented by assuming equal ratios (R) of transport across the plane of separation of the discs at time (t_1, t_2) for two substances. Hence,

$$t_1 D_1 = t_2 D_2$$

(t_2, D_1) are known, and (t_1) obtained when the same (R) is obtained in both cases.

(3) Interface Bomb (Tung and Drickman[140]): A bomb of constant dimensions in a constant temperature bath is used.

The bomb has two cavities, one for each component, and an adjustable interface. The diffusion coefficient of a radioactive material must be determined in all layers and across the interface in order to get the interfacial transfer coefficient. A Scintillation counter was used to count the radioactivity from the time the bomb piston was pushed to its diffusion position until the change of counts became negligible.

From the radioactive theory, the following relations are derived to fit the experimental calculations:

$$J = \alpha \left[C\,(o - t) - mc\,(o + t) \right]$$

where J = flux of the diffusing molecule at the interface.

α = transfer coefficient at interface.

m = distribution coefficient of diffusion component between phases at equilibrium.

And:

$$I = I_f - Be^{-D_1 \nu_1^2 t}$$

where I = intensity of radiation

I_f = final radiation's intensity

B = constant

D_1 = diffusion-coefficient in phase 1

$\nu_1 = \pi / 2a$ when (a) = half length of the diffusion cell.

A simpler but similar cell with three compartments was used to determine the diffusion through interfaces in a ternary system. The same theoretical basis was adopted.

(4) Diffusivity measured by radioactive tracers in liquids[35]: The diffusion cell consists of a beaker (B) containing a solution (s). On top of the beaker, the porous plate (P) is bounded by a fiberglass mat or agar gel prepared inside a metal ring (R) on top of which is the Geiger-Muller counter tube (G) to record the process of diffusion within one or two hours through the thin porous plate. The solvent is confined within the porous plate. Figure (20)

To evaluate the rate of increase of counts in term of diffusivity, the following must be considered:
(a) The concentration of solute at each depth from surface and at any time must be evaluated. This depends on conditions of solution below the solvent. If solution is at rest, and has greater depth than that of solvent layer when a fiber glass mat is used.

$$C = 1 - .5\left[\operatorname{erf} \frac{(1 + \frac{x}{L}) / 2(Kt)^{1/2}}{L} + \operatorname{erf} \frac{(1 - \frac{x}{L}) / 2(Kt)^{1/2}}{L} \right]$$

when system is kept at rest.

In case of agar gel and stirring of the solution:

$$C = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \left\{ \left[\frac{(-1)^{n-1}}{(2n-1)} \right] \Big/ (2n-1) \right\} \times$$

$$\left\{ \cos \left[(2n-1)\pi x / 2L \times \exp\left(1 - (2n-1)^2 \pi^2 K t\right) / 4L^2 \right] \right\}$$

The data are plotted as concentration as a function of $^x/_L$ for various values of the parameter $^{kt}/_{L^2}$, when

L = solvent layer depth

k = diffusion constant

(b) Effect of absorption of β-radiation upon activity reaching counter. This must be obtained by calibration. For uranium,

$I = I_o \exp(-6.5\rho x)$.

I_o = initial intensity.

I = intensity after absorption.

ρ = density.

(Approximated for Uranium - UX_2 - while measuring beta-radiation which has a maximum energy of 2.32 Mev. and its maximum range is 1.1 $^g/_{Cm^2}$).

(c) The geometric factor variation with varying depth is also obtained by calibration.

By multiplying the above three mentioned factors, numerical integration over the entire depth gives the relative increase of counts per minute with time. Numerical integration is to proceed to a few times the solvent layer depth because of the limited diffusion layer depth. Further layers contribute a time independent amount to the activity which increases the background counts. Curves are obtained for counts/min. in fractions of the final value as a function of time.

(5) Ionization Currents Method (Amdur et al[3]): Uses the saturation ionization currents as a measure of the extent

of diffusion. The apparatus consists of a diffusion cell mounted horizontally in a thermostat. The cell has a brass tube separated by a slide into two sections, one of which is fixed and the other capable of a limited motion. A shaft is used to rotate the slide and bring a hole of the same diameter as the tube into axial alignment with the sections of the cell. The cell sections contain collecting electrodes insulated from the tube. Radioactive tracers are used because mutual diffusion coefficients can be measured with the tracer concentrations of one of the components of the diffusing mixture. This avoids uncertainties of interpretation which arise from the variation of the mutual diffusion coefficient with composition. After the cell is evacuated, the radioactive mixture is introduced to one section and normal gas into the other (both gases are dried and purified). After equalizing the pressure in both sections, the ionization current is measured in the radioactive section and diffusion allowed to start by opening the separating slide. Decrease in ionization current is measured as a function of time.

Two equations are given to evaluate the data obtained. The easier one to use is:

$$= -S\left(Dt^{x}\right)^{1/2}\Big[1-(1/y)\exp(-y^{2})\int_{0}^{y^{2}}\exp Z^{2}\,dz$$

where s = constant displacement of the time origin.

$t^x = t - .7894\ \tau$

t = original time.

$y = t^x / R_g\ C^{1/2}$

τ = time when slide fully opened.

Rg = effective (d.c) resistance of the ionization chamber.

C = sum of the capacities of the interelated (electrometer) ionization chamber.

Diffusion in Gases

Some of the liquid diffusion methods are applicable to gases. The practical methods that have been used are the sorption-desorption method and the tracer method. Most of the different methods will be discussed separately for each selected system.

(1) Sorption data[106] method: Readings of the weight of vapor absorbed by a film of the material being considered are taken. The film is suspended on a spring at different pressures to calculate diffusivity by:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D_c \quad \frac{\partial c}{\partial x} \right]$$

No analytical solution to this equation exists. Therefore, the following is used:

$$Dr\ (c) = {}^{d}/_{dc}\ (C\ \bar{D}) = \bar{D} + c\,d\bar{D}/_{dc}$$

$\bar{D}$ is $\bar{D}(c)$ average $= \frac{1}{c}\int_0^c D(c)\,dc = \frac{1}{k}\sum_{i=1}^{k} D_i$

(2) Interferometric method: An interferometric method for determining diffusivity in gaseous systems[10] employs a cell comprised of two halves with tubes fitting in the respective sliding plates of each. The bottom half has optical glass windows in the opposite walls of the cell for measuring the refractive index of the filling gas. The cell is mounted on a thermostat and the refractive index is measured by a Machzehnder type optical interferometer. The equation stated to convert the data obtained from the experiment to the data required to obtain diffusivity is:

$$X_1 = \left(\frac{1}{N_1 + N_2}\right)\left\{\left[\frac{2\lambda S}{3L} + \frac{N_1}{\frac{RT}{P} + B}\right]\left[\frac{RT}{P} + B_m\right] - N_2\right\}$$

where N = molar reactivity.

= light wave length.

L = optical path length.

B_m = Virtual coefficient.

S = fringe shifting (number of shifted fringes)

The data obtained from this equation is to be used in a simplified equation of a Fourier series:

$$D = \left(\frac{L^2}{\pi^2 t}\right) \ln\left[\frac{(2/\pi)(\cos \frac{\pi}{c})}{X_1 - \frac{1}{2}}\right]$$

where (X_1) = concentration.

L = cell length.

Monometric Instrument[23]: The cell consists of a chamber containing saturated vapor which is separated by a porous membrane from another chamber in which the vapor pressure (P) is kept very low by cooling. In steady state, the pressure difference between the two chambers at a first approximation is

$$\eta D (P_0 - P) / k P$$

where (k) = the apparatus constant.

η = viscosity.

P = saturated vapor pressure.

Diffusion in Gels

The impedance to diffusion in gels[93] may be due to mechanical blocking, resistance to motion, increase in viscosity of liquid and other variables such as concentration, age, pH, isoelectric point, rate and temperature of gel setting and presence of electrolyte.

(1) Methods of layer analysis[71]: This is based on having the gelatine and the liquid in contact. Analysis of the gelatine is done after diffusion takes place. Plot is made of the fraction of total diffusate across the interface as a function of Dt/L^2

$$V = \frac{1}{2} - \sum \frac{8}{(2n+1)^2 \pi^2} (e)^{-(2n+1)^2 \pi^2 D t / 4 L^2}$$

where V = fraction of total diffusate across the interface.

L = gelatine column height.

(2) Electrical Method: Conductance method similar to Haskell[56] method is employed. Diffusion of colloidal electrolytes was studied.

(3) Optical Method: Only Eversale photometric[29] method used though refractometric and absorption methods are applicable.

(4) Steady State Method (Patrick and Allan[109]): Involves assumption of linear concentration gradient along the column. The apparatus is illustrated in Figure (21). The dilute solution of diffused salt is collected in the over-flow beaker while a slow flow of distilled water flows into the beaker.

(5) Cylindrical Diffusion through a gel[119]: A drop of solution is placed on a thin film of gel which, after diffusion time, is immersed in a solution of a material capable of forming a precipitate with the diffusing salt. The diffusion coefficient is calculated from the resulting spot dimension.

In another method, detection depends on the presence of a precipitating agent in the gel.

Calculations are carried out as follows:

$$C = \sqrt{c_0 / \sqrt{\rho}} \left[1 - \Psi(u) \right]$$

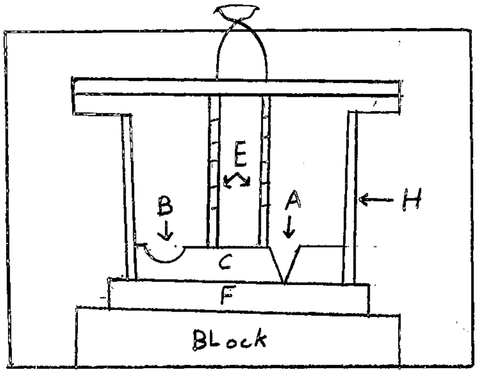


Fig 16

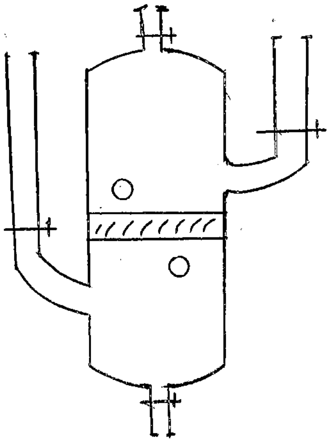


Fig 17

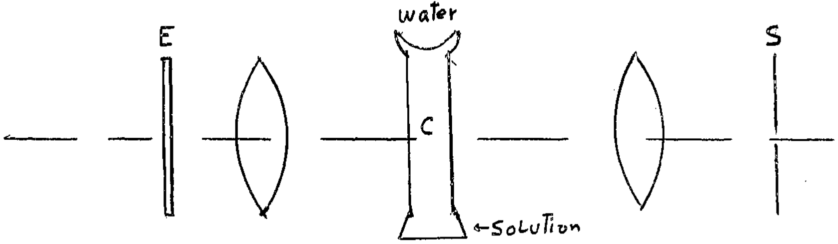


Fig 18

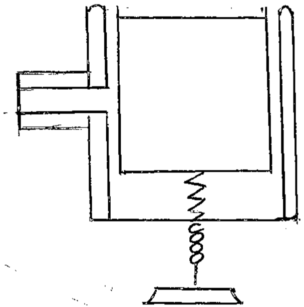
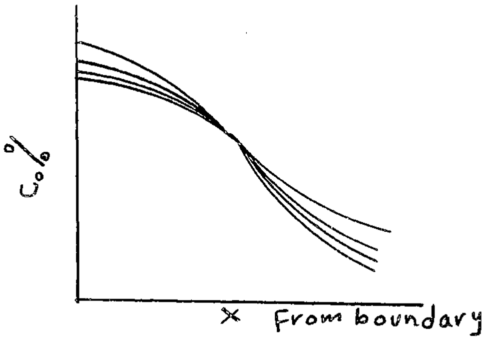


Fig 19



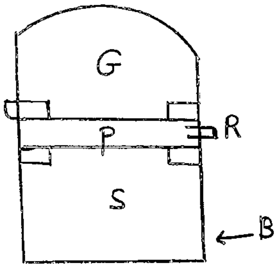


Fig 20

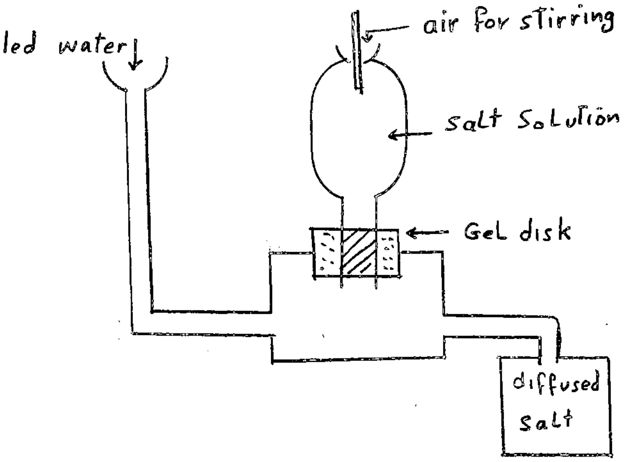


Fig 21

where C_o = original concentration at radius ($^{r}1$).

C = concentration at radius (r) when t = time reached

$$\rho = {}^{r}/_{ro}$$

$$\Psi(u) = \frac{2}{\sqrt{\pi}} \int_0^v e^{-u^2} du$$

$$V = \rho - \frac{1}{2\tau}$$

$$\tau = Kt/r_0^2$$

K is diffusion coefficient

(6) Radioactive indicators have been used to measure diffusivity in gels[120]. This is accomplished by placing an electrolyte of (C_o) concentration in a vertical tube containing a gel layer. At time (t), the concentration of the electrolyte at distance (x) is:

$$C = C_0 \left[1 - \Psi(u) \right]$$

where $\Psi(u)$ is obtained from tables and (c/c_0) ratio is measured by dissolving a slice at distance (x) of the gel in water and taking a radiation count of the resultant solution.

(7) Steady state diffusion in gel caused by mutual precipitation of two reagents, Salvinier[121]. Two reagents were placed on a gel film; precipate was formed between them and ratio of diffusion constant calculated from the concentration and the distance travelled.

Diffusion of Ions

The experimental procedure employed the Northrop's[93b] method to determine the diffusion of electrolytes and colloids[3]. It consists of homogeneous bodies of solution separated by an indifferent membrane with pores of visible or microscopic size, the diffusion gradient being confined within this membrane. Fick's equation was employed for the calculation of diffusion from the experimental data.

Diffusivity calculation from experimental data of concentration, distance and time[14]: True or Boltzman coefficient can be calculated by determining (K) (Fick coefficient) as a function of (C) and making use of relation

$$D = D_o (1 - A_c) \quad \& \quad D_o = K$$

Diffusion of ions in solution was studied with the use of radioactive isotopes[4]. To supress convection currents, narrow capillaries were used as cells for this method. The cells were filled with a solution which has the same properties as the solution in the beaker that contains the cells except for the radioactive isotopes that had been incorporated in the cell. The cell rests on a holder that carries the cell in a position where the top of the cell is just below the beaker's solution level until equilibrium was established. After equilibrium the holder was lowered down to allow diffusion of the two solutions for a period of 3-4 days. At the end of the given period, the cell contents were transferred to a tray to be evaporated leaving the radioactive content for measurements in standard α or β counting equipment. Correction for the decrease in the radioactivity due to the natural decay was considered with the use of a known reference tray subjected to the same process.

Measurements were made with sodium tungstate solutions of different concentration.

SPECIAL METHODS FOR DIFFUSIVITY DETERMINATION OF SELECTED LIQUIDS AND GASES

Among the many different methods that have been used for the determination of diffusion coefficients, certain procedures are selected here with the results.

Some of the important factors that affect the diffusion coefficients are the pressure and temperature. The following few methods deal with the effect of these two factors.

Self diffusion in (CO_2) at moderate pressure[136]: The Lennard-Jones model was employed in evaluating diffusion data for CO_2 - $C^{14}O_2$ system. The low pressure diffusion apparatus consisted of two cells filled with capillary glass rods connected horizontally by a valve. Radioactive gas is introduced to one of the cells, non-radioactive gas to the other cell. One end of the cell containing the non-radioactive gas was fitted with a lucite rod which led to the photomultiplier tube. Considering only beta-radiation (short wave length), the count for a long period of time is:

$$I = I_f - \frac{2}{\pi} \exp - \left(\frac{n\pi}{L}\right) D t$$

where $I_f = C_0/2$ = final number of counts.

A plot of I_f - I as a function of time gives a line of slope $\left(\frac{\pi}{L}\right)^2 D$. The theoretical results on table (1) were calculated from

$$D_{12} = \frac{3(kT)^{1/2}}{16(\pi)^{1/3}(\mu)^{1/2}\, r_0\, n\, W'_{(1)}\, X_{12}}$$

where = reduced mass.

k = Boltzmann's constant.

$W'_{(1)}$ = function of ϵ and T.,

T = absolute temperature.

n = molecules' number/unit volume.

$$X_{12} = 1 + \frac{5}{12}\left(\pi n r_0^2\right).$$

r_0 and ϵ both are evaluated from P. V. T. data.

The experimental and the theoretical results are tabulated in table (1). The agreement of the experimental and theoretical results indicates that even for a nonsymmetrical molecule such as CO_2 the dense gas theory applies at moderate temperature.

Diffusion in system $C^{14}O_2 - CO_2$ [135] under a pressure range 100-1000 atm. and temperature range: The lower range results show little temperature coefficient for diffusion at constant density. At higher densities, temperature coefficients increase rapidly. The Enskog theory is not applicable but the results are correlated in the form:

$$D = D_0 \exp\left[-\frac{E}{RT}\right]$$

when E is activation energy at constant density.

The diffusion cell is a modified form of the one used above[25c]. It consisted of a diffusion bomb with turning mechanism by means of which two cells containing different gases were brought in contact with each other, a scintillation counter which measures the amount of radioactive gas diffused through one of the cells, and equipment for filling and refilling the cells. The results obtained are in table (11).

Diffusion coefficients for $(CO_2 - C^{14}O_2)$[114] under a pressure range (up to 150) with variation in temperature were determined. The theory of Enskog-Chapman (Chapman and Coulins-Mathematical Theory of Non-Uniform Gases) validates the results of this experiment up to a density of 0.067 b/cc. Above this value, the coefficients are higher than those preducted by the theory. The equation employed for self diffusion coefficients is

$$D = \frac{16 (kT)^{1/2}}{3 (2\pi\mu)^{1/2} r_0^2 \, n \, W_{(1)}^{1} \, x}$$

where $x = 1 + \frac{5}{12} \pi n \sigma^3 + 0.1275 (\pi n \delta^3)^2 + \cdots$

D = diffusivity.

k = Boltzmann's constant.

n = molecular number/unit volume.

r_0 = collesion diameter for Lennard Jones model which was employed.

μ = reduced mass.

$W_{(1)}^{1}$ = integral depending on interaction energy and (t) the absolute temperature.

σ = collision diameter for solid elastic spheres.

The apparatus employed consists of a diffusion bomb and a mechanism for bringing two diffusional cells into contact, a scintillation counter to measure radioactive gas diffused into one of the cells and equipment for filling the cells and measuring the pressure. The bomb itself consisted of a steel block with a large hole in the top, a flat metal disk pinned to the bottom above the hole and a rotation cylinder fitted in the hole held by a nut against the insert. The cells were placed in the cylinder and the insert filled with various media whose path length had been measured before. The diffusion for the various media varied with density as the path length did. Radiation was counted continuously and table (9) shows the results.

The same method was employed to determine diffusivities in the CH_4 - TCH_3 system[65] under a pressure up to 300 atm. The equation employed here is a corrected form of the Enskog equation and results are in table (10).

$$D = \frac{3}{16}\left(\frac{kT}{\pi m}\right)\cdot\frac{1}{r_0^2\, W'_{(1)}\, n\, x}$$

The effect of pressure on self diffusion in carbon disulfide[72a, 72b]: A system of (CS_2 - CSS^{35}) was used under pressure (to 10,000 atm.) over known temperatures (0, 20, 40 degrees C.) to measure diffusion coefficients. The apparatus used in this method consists of an intensifier connected to a lower bomb whose bottom has a plug with a synthetic sapphire window. The bomb was located in a temperature bath controlled to ± 0.1° C. The cell is placed on the sapphire window and consists of a lower cylinder whose bottom is occupied by a quartz window, a sleeve sealed with a fritted glass (to be filled with the radioactive liquid) and a piston inserted carefully in the sleeve after it was full. The sleeve was fitted in the cylinder and pressure was applied fifty seconds later. Another fritted glass was used to cover the nonactive liquid before the run started in the cell's cylinder. After the start of the run, molecules diffuse from the upper to the lower fritted glass at a rate indicative of the diffusion coefficient. As the concentration of the radioactive tracer builds up at the surface of the crystal, the frequency of light pulses given off by the crystal increases proportionately. The light pulses pass out of the cell through the quartz window and then through the sapphire window out of the bomb and down the Lucite rod to the photomultiplier tube. Water white petroleum ether was used as a pressure transmitting fluid to allow for the passage of the maximum amount of light between the quartz and sapphire window. The results of the experiment are tabulated in tables (2) and (3). The results of the experiment were not in agreement with answers obtained for the same data by either Stokes-Einstein or Arnold's equations.

Other systems used the above method for determination of pressure effect on diffusivities.

(a) Self diffusion in water and sulfate solution[21a], table (4).

(b) Diffusion in aqueous and alcoholic and salt solutions using (Hg^{203}, Ca^{45} - Tl^{203}) as tracers to determine the diffusivities of HNO_3, $CaCL_2$, Ca $(NO_3)_2$ and $TINO_3$ at different temperatures and pressures[21b], table (5).

Diffusion of Iodine in Carbon Tetrachloride under Pressure[57]: Two methods were used to study the iodine diffusion in carbon tetrachloride over a temperature range of 10-55° C. and pressure range 1-200 atm. In the first method, the capillary cell technique was employed, using the capillary cells containing the diffusate and submerged in a large volume of the diffusent. Measurement of total diffusate transferred in a given time were accomplished by chemical microanalysis methods. The accurately calibrated cells ranged in length from 6-7 cm. Each had a capacity of approximately (0.25) cc. and were supported in a liter reservoir of CP carbon tetrachloride which was thermostated to ± 0.02° C. Temperature equilibrium was reached while the capillary ends were still above the liquid surface. The cells were next filled with 10 mg/cc iodine solution in carbon tetrachloride which was at the same temperature as the reservoir and carefully lowered beneath the surface of the carbon tetrachloride. Diffusion proceeded for three days, then iodine concentration was determined on the removal of the cells.

The integral diffusion coefficients were calculated using the relationship:

$$\frac{C_{av.}}{C_o} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left[\frac{1}{(2n+1)^2} \exp\left\{ \frac{-(2n+1)^2 \pi^2 D T}{4L^2} \right\} \right]$$

where Cav. = average concentration of iodine in capillary after time (t).

Co = initial concentration of iodine in the capillary after zero time.

L = cell's length.

D = integral diffusion coefficient.

The values of (D) expressed in cm^2/day are tabulated in table (6).

The second method is a direct optical comparison method. Two capillary tubes (approximately 40 cm. in length and of equal internal diameter 0.2 cm. were used at one end and supported side by side in a water bath thermostated to 0.01° C. One tube was left open to the atmosphere and the other was connected, by a means of a metal to glass pressure seal, to a pressurizing device. An interface was set up simultaneously in both tubes between an iodine solution at the bottom of the tubes and pure carbon tetrachloride at the top. A sharp interface was achieved by lowering a glass hair capillary until its end was below the diffuse interface initially formed, and slowly withdrawing liquid. Diffusion proceeded for 7-10 days, then a series of photographs were taken, and the density gradients obtained on the photographic negatives were analyzed. Equal densities on the negatives correspond to equal concentrations in the capillary tubes. The depression of the diffusivity is calculated by the following expression:

$$D_1/D_2 = (h_1/h_2)^2$$

where h_1 and h_2 are distances from original interface at which equal densities are measured. The results of the experiment at a temperature of 29.3° C. are tabulated in table (7).

Variation of $D\eta/T$ (cm². poises/abs.) with variation of pressure and temperature is given in table (8).

Glycin Diffusion in HCl and H_2O was studied[64c]. Using Northrup and Anson[102] technique, the results were obtained and are tabulated in table (12).

The differential diffusion coefficients of HCl[64] and H_2SO_4[62] were studied. Using Northrop-McBain type cell[149] the values were obtained with the use of the equation:

$$D = D_0 \left(1 + c\frac{\partial \ln f}{\partial c}\right)\left(\frac{\eta_0}{\eta}\right)$$

where $(1 + c\,\partial \ln f/\partial c)$ is obtained from Ehler's[54b] data and from the international critical tables, D_0 (at infinite dilution) = (Nernst value). Experimental values are in table (13).

Some measurement of self-diffusion coefficients of liquids[155,108]: Two Northrop-McBain cells[94] were used for 18 hour runs for each compound at each temperature. Deuterium was used as a tracer in all cases. The concentration was chosen so that the maximum deuterium content encountered was less than 1 atom %. Density measurements were furnished by combustion of the samples obtaining combustion water to be analyzed after purification. Results are in tables (14) and (15).

Diffusion of Hydrocarbons in Polyisobutylene[108b]. Diffusion coefficients are calculated from sorption and desorption data with a film of polyisobutylene suspended from a sensitive spring in an evacuated weighing chamber. At certain pressure, vapor of the considered hydrocarbon was introduced and the increasing weight of the spring is measured as a function of time. The experiment depends on Eyrings theory[38] which explains diffusion as taking place by a molecule leaving its current position and jumping into one of the holes that are in the liquid body. The data is on table (16).

With the same procedure the diffusion of acetone into polyvinyl acetate[73] above and below second order transition was studied. The results were calculated using a reduced form of Crank and co-worker's empirical equation

$$D' = \frac{\pi}{32}\left[K_s^2\,(0,c) + K_d^2\,(c,0) \right]$$

where K is described as $(\Delta Q t / \Delta Q_\infty) = K_{(c_i, c_f)}\, t^{1/2}/L$ L = film thickness, $K_{(c_i, c_f)}$ represents an effective diffusion coefficient for constant initial and final equilibrium concentrations; with ΔQ_t= weight of vapor sorbed (or desorbed) at time (t). The integral form of the above equation:

$$D' \equiv \frac{1}{c}\int_0^{c_0} D\, dc$$

The results are in table (17).

Diffusion studies on dilute aqueous sucrose solutions at 1° C. and 25° C. with Gouy interference method were carried out. Sucrose solution diffusivities were measured as a function of concentration. In this method, the cell (with initial sharp boundary between solvent and solute) was placed in the path of light from a lens that was illuminated with monochromatic light from a horizontal slit, and the interference fringes formed in the focal plane of the lens were photographed at intervals. In evaluating (D), the image formed when a homogeneous solution filled the cell and the total number of fringes were considered before the spacing of fringes for (D) calculations were taken. Other data required for obtaining (D) by this method were given, and the results are tabulated (table 21) with the theoretical results that were obtained by Gordon[39b, 64b]:

where D is limiting values as concentration approaches zero.

η/η_0 is the relative viscosity of the solution.

f = activity coefficient.

With Gouy interference method[41], the following diffusivitus were calculated:

(a) Urea in water[43b] - Table (20)

(b) Dilute aqueous glycine solution[89] at 1° and 25° - Table (19)

(c) KCl in water at 25° C. using Tiselius cell[42] - Table (30)

The diffusion coefficient of potassium chloride in dilute aqueous solution[48,49b]: Using the conductance method, the diffusivity of this electrolyte was determined for restricted diffusion. The apparatus has been explained previously. The diffusion coefficients were computed by the following equation:

$$D = \frac{a^2}{\pi^2} \cdot \frac{1}{\tau}$$

where $\frac{1}{\tau}$ is the slope of the line of $\ln(K_B - K_A)$ as a function of t or

$$\frac{1}{\tau} = \Delta\left[\ln(K_B - K_A)\right] / \Delta T$$

considering K_B & K_A the conductances at the bottom and the top of the cell (corrected for the cell constant ratios) and (a) the distance from the boundary.

The conditions of the apparatus furnish boundary conditions in a way to make possible integration of the differential equation of diffusion. The theoretical values were computed by Onsager and Guoss[104] equation.

$$D = 16.6288 \times 10^{10}\, T \left(\frac{\bar{M}}{c}\right)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right)$$

where

$$\frac{\bar{M}}{c} \times 10^{20} = 1.0748\, \frac{(\Lambda_{+}^{\circ})(\Lambda_{-}^{\circ})}{(\Lambda_{+}^{\circ} + \Lambda_{-}^{\circ})} - \frac{32.148}{\eta_0 (DT)^{1/2}}$$

$$\left(\frac{\Lambda_{+}^{\circ} - \Lambda_{-}^{\circ}}{\Lambda_{+}^{\circ} + \Lambda_{-}^{\circ}}\right)\frac{\sqrt{c}}{1 + A'\sqrt{c}} + \frac{2.304 \times 10^{7}}{\eta_0 (DT)^{2}}\, c_{\phi}\left(A'\sqrt{c}\right)$$

where Λ = equivalent conductance at infinite dilution.

D = dielectric constnat.

η_0 = viscosity.

$\bar{A}\sqrt{c} = K_a$

a = distance.

K = Debye Heuckel reciprocal distance.

The theoretical and experimental values of diffusivities of KCl at different concentrations are tabulated in Table (22).

Using the conductance method, the following systems were studied:

(a) calcium chloride[49] - Results do not agree with theoretical predictions. - Table (23).

(b) LiCl, NaCL [51] in dilute aqueous solutions at 25° C. - Table (25).

(c) KNO_3 in water[52] at 25° C. - Table (25).

(d) Silver nitrate in various dilute solutions[54] - Table (26).

(e) Zinc sulphate (as a 2-2 valence type electrolyte[53]) in which the conductance indicates considerable ion-pair formation which effects the identity of the theoretical (Onsager-Fuoss equation). Table (27).

(f) KCl in water[46] at 4° C. - Table (28).

Self diffusion of water (deuterium as a tracer[144]): Apparatus: Fine flat bottom scaled capillaries with their upper ends open, to be filled with deuterium oxide (as tracer) and held vertically in constant temperature bath. The solution (of original known concentration) is to be taken out to determine the deuterium concentration (by gradient tube method). This gives a determination of the density from a standard curve of the density as a function of the height of equal position in gradient tube-curve.

Results are in Table (24). Following the same procedure, the following systems have been studied:

(a) Potassium chloride (aqueous solution[146]) - Table (31).

(b) (Cl) ion in aqueous sodium chloride at 25° C.[147] - Table (33).

(c) Ca^+ and Cl^- in aqueous calcium chloride at 25° C.[145] – Table (37).

(d) Na^+ in aqueous NaCl[148], using a diffusion tube modification[66] of the diaphragm cell to avoid the difficulties encountered such as cell constant changes due to density gradient if no stirring is applied and the convection error. Results obtained at 25° C. are in Table (34).

Self diffusion equation for sodium Na^+ (by means of radio-sodium[1]) is

$$D = n w \frac{\partial \mu}{\partial n}$$

where W = molality potential of the ion.

n = moles/cc.

Introducing activity coefficient: $D = 8.97 \times 10^{-10} \lambda_+ T(1+c)\frac{\partial \ln y}{\partial c}$ using the limiting law expression

$$\operatorname{Log} y_+ = 0.508\, c^{1/2}$$

Then $$D = 0.0231 \lambda_+ \left[1 - 0.583 (C)^{1/2}\right]$$

This method does not relate the net movement of tracer ion to that of charged ion by the requirement of electroneutrality necessary when bulk concentration gradient exists. It is the differential diffusivity of the ion rather than the mean diffusivity of salt obtained and for smaller concentrations. McBain-Northrop[149] sintered glass diaplragm cell is calibrated with HCl diffusing in H_2O. (Na^{22}) was used as tracer in the upper compartment and (NaI) solution in both compartments. Tracer measurements were taken in the lower part to calculate diffusivity. A curve of diffusivity as a function of the square root of the concentration is obtained. For a concentration of tracer at a given time is represented by:

$$D = D_0 \left(1 - 1.4\, c^{1/2}\right)$$

where $D_0 = 1.24\ \mathrm{Cm}^2/\mathrm{day}$.

Radio chemical analyses were made by evaporation of aliquots on watch glass and counting by means of mica window tube and scaling circuit. (Y) was evaluated for the above equation.

The limiting law equation for self-diffusion of $(Na^+)^1$ used here is

$$D = 7.75 \times 10^{-5} \lambda_{+} T \left(1 + c\left[\frac{\partial \ln n}{\partial c}\right]\right)$$

(Na^+) diffusion in NaCl was obtained[2] as follows:

At 25° C. $D = 1.15\ (1 - 1.41\ c^{1/2})$
35° C. $D = 1.47\ (1 - 1.43\ c^{1/2})$

The diffusion coefficients of highly concentrated sucrose[28] in supersaturated solutions has been measured at 25° C. and 35° C. by two optical methods. Schlieren method[81] of observing refraction index and hence concentration gradient was applied to diffusion measurements in dilute solutions and Gouy[83] interference fringe method. The latter gave more accurate values from the standpoint of internal consistency. The values of the first method are plotted on Figure (22) while the values of the second method are tabulated in Table (18). Two figures (23) were furnished, one of which shows comparison of the results with the calculated results from Gordon's equation

$$D = D \left[1 + \frac{d \ln f}{d \ln C} \right] \frac{\eta_0}{\eta}$$

A new cell was developed for this study. It is a modified Neurath type. Its optically flat glass windows were rigidly attached to the cell and sealed with a rubber gasket to prevent water leakage. A sliding partition between upper and lower liquids was used instead of the entire lower block sliding to remove the boundary. The interference fringe method modification consists of varying the exposure of the photographic plate by moving an opaque shield over the light source at a speed controlled by an electric motor (instead of the step filter in front of the camera plate) to obtain a gradual change in the blackening of the photographic plate.

Diffusion in liquid Sulfur[25]. The diffusion of (S^{35}) into two varieties of ordinary sulfur was studied and the diffusion coefficients obtained in the following manner:

Cylinders of coarse fritted glass were pumped full of sulfur and placed in a close fitting stainless steel cell, and the edges were filled with sulfur. The cell was inserted into a furnace and heated with a small amount of (S^{35}) injected on the surface. Chromel-alumel thermocouples were used for temperature measurements. Samples of the frit were sanded off after a 20-90 minute period and placed on an emery cloth to count the slices under a Geiger counter. The frit was measured before and after each sample was removed to give the slice thickness and the sample position on the frit. The equation for diffusion from an instantaneous source is

$$C = \frac{Q}{\pi (Dt)^{1/2}} \exp\left(- Dt/4x^2\right)$$

where Q = intensity of source.

X = the distance.

t = time.

c = concentration.

The results are in Table (36).

Measurement of the diffusion coefficient of hydrogen peroxide vapor in to air[95] and the diffusion in a water-hydrogen system at different temperatures: The diffusion takes place through a stagnant gas in a glass tube with liquid at the bottom to provide vapor of know concentration while the top of the tube is fixed at zero concentration affected by conducting a stream of the second gas across the end of the tube. The rate of diffusion is determined from the rate of liquid loss with time. This is a case of steady unidirectional diffusion of one gas through a second stagnant gas under a fixed concentration gradient. The results are in Table (35).

Diffusion of common electrolytes in aqueous solutions:

(a) The diaphragm method has been used in many cases and special modifications were introduced in the specific methods. The following are selected systems.

1. Ca Cl_2[115], at 25° with the porous diaphragm cell. Table (32).
2. NaCl and Na_2 SO_4[101], at 25° C. Using isotopic labelling of the Anion, (Na^{24}, Na^{24} - as tracers). Counts were measured by means of a glass jacketed Geiger counter connected to a standard high voltage supply, amplifier and scaling circuit. Results are in Table (38).
3. Univalent electrolytes at 25°[127]: Determination of concentrations in the upper and lower parts of the modified diaphragm cell by potentiometric titration of weighed samples against silver nitrate using capillary reference electrode with valve voltmeter as null indicator. Table (39).

(b) McBain procedure has been employed for:

1. K Cl[94]: A simple cell was employed with a sintered glass membrane placed in a beaker of the solution and analysis was accomplished by gravimetric method when crystals of KCl were weighed after the evaporation of the solvent. Table (40) gives the results.

2. Ag NO_3 and Ag^+ ion[152]

(Ag^+) ion diffusion between Ag NO_3 solutions of identical concentrations (self-diffusion) was followed with a radioactive isotope (Ag^{110}; half life 225 days) and all counting was done on aliquots with an end window Geiger-Muller tube. Required stirred was furnished by density differences. Results plotted in Figure (24).

3. Ca Cl_2 [61], Table (41).

(c) Longsworth method[83] (which has been described before). Diffusion coefficient of (0.6) N into (6.4) N KCl at .5° C. was obtained = 9.287 $Cm^2/_{sec.}$ with average deviation = 0.15%. Table (42) gives results for different concentrations of the system.

NaCl diffusion coefficient was obtained for different temperatures and concentrations by Burrage[13] method (described before). Table (43) shows the results. With the same method, the diffusivities of (Cu SO_4)[30] were obtained for different concentrations at 25°. The results are shown in Table (44).

Diffusion in some common systems: Table (29) gives results obtained for hydrogen, nitrogen-organic compound systems obtained by Boyd[10] et al.

Diffusivity of butyl alcohol in aqueous solutions[27]: Using a monometric cappillarimeter, the solute particles were diffused through a column of liquid contained in the calibrated capillary. An approximate equation is:

$$D = \left(m^2 \times \frac{dc}{dt} \right) \Big/ 2 \left(C_o - C_h \right)$$

(C_o and C_h) are concentrations at the end of the capillary and the hypothetical plane, (m) is the distance of the hypothetical plane from the end of the capillary in direction of diffusion (cm). At average of 0.0082 g/cm³ concentration, the butyl alcohol values are tabulated against other values obtained theoretically by the Stokes-Einstein equation with viscosity = 1.482 weight % and the given radii. Results are in Table (45).

Using Gouy interference method[40], diffusivities of butyl alcohol were obtained for different concentrations. Tisellius cell was employed. Table (46) shows the results.

Diffusion in $CO_2 - CO_2$, $CO_2 - N_2O$[3] systems:

Using saturation ionization currents as a measure of diffusion, the results are in Table (48).

Diffusion of 2-naphthol in H_2O[98]. A double end diaphragm diffusion cell was used and was capable of rotation in a constant temperature bath. Two glass spheres were introduced in each chamber of the cell. After calibration (KCl in upper chamber and H_2O in the lower), 2-naphthol solution was introduced in the upper chamber of diffusivity measurement and water in the lower. After period of time, analysis (by titration) was made of the liquid in each chamber. Many readings for different temperatures were obtained and the following equation employed:

$$KDt = \operatorname{Log} \frac{C_0' - C_0''}{C' - C''}$$

where K = cell constant.

Co = initial concentrations.

(C) = final concentration.

Results are in Table (47).

Diffusion of sucrose in air-saturated water[40]: With a single lens convergent light apparatus, diffusion in liquids (sucrose) was studied using a Tiselius cell[137,86] with a mask to prevent superposition of successive fringe system photographs. Polson[69] technique was employed for sharpening the boundary. The results, obtained for sucrose in air-saturated water at an average concentration of 2.252 g./100 ml of solution and temperature of 1° C. (when J_m value = 33.41), are tabulated giving a mean result of 2.33 x 15^{6} cm^2/sec.

CONCLUSIONS

All the problems of diffusion depend on the diffusivity of the material being considered. Graham's law was the earliest definition for diffusion which enables the later workers to form their theories. All the derivations and equations that were applied in determining diffusivity were based on Fick's laws.

Among the different procedures that have been discussed, there are very few of them which agree with the theoretical results very closely. Most of them depend on the study of concentration of the system. For that reason, the basic difference among these methods is the method of determining the concentration of the solution under study at a particular region. Using most of the factors that are related to concentration like surface tension, refractive index, vapor pressure equivalent conductance, etc., the workers obtained methods for computing the concentration from the data of the employed factor.

One of the most important methods that has been developed in the recent years is the one that employs radioactive tracers to determine the concentration. This method gave accurate results with reasonable deviation from the theoretical estimations. The radioactive tracers were used in gases, liquids and solids. The errors that were encountered in the other methods due to the environmental effect on a system were eliminated since the measuring devices employed are attached closely to the systems. Organic and inorganic systems were discussed and studied by using the tracers while changable conditions as temperature and pressure applied. Other methods may fail to apply in such conditions.

For gases, the sorption-desorption method is used very widely and considered to be very important for its simplicity and also for the accurate data obtained.

The most important optical method is the interferometric method which has been modified to the study of different liquids. This method is like the other optical methods in depending on the refractive index of the liquid being considered.

The conductance methods are specified to the study of electrolytes. Special conductance methods were modified to be applied to the study of diffusion of particular ions.

Among the different cells that have been used in determination of diffusivity, some of them are of particular importance. Few important factors have to be determined before selecting the cell. The system under study is the major factor. Some cells are provided with different devices to prevent leakage or disturbance of the fluid's boundary.

The study of diffusion of fluids is very wide. For the different methods, the related subjects have to be considered with the theory behind that particular method.

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APPENDIX

TABLE 1

SELF DIFFUSION OF CARBON DIOXIDE AT MODERATE PRESSURE

Cell Length	P atm	T °K	Obs. D cm^2/sec	Calc. D cm^2/sec
33.75 cm	1.243	296.2	.0847	.847
	2.49	296.9	.0424	.0422
	2.77	296.1	.032	.038
	6.38	296.6	.015	.0164
	9.33	296.4	.0104	.0111
	18.49	296.5	.0071	.0055
21.35 cm	6.34	295.7	.0163	.0165
	9.24	296.2	.0101	.0112
	18.59	296.5	.00494	.00546
	21.4	296	.00476	.0046
	28.1	296	.00384	.00328
60.05 cm	.506	297.1	.206	.212
	.98	296	.103	.109
	1.18	295.7	.091	.091
	2.18	295.9	.05	.049
	2.46	295.6	.0437	.0435

TABLE 2

SELF DIFFUSION OF CARBON DISULFIDE

T °K	P atm	Effective Cell Length cm	Obs. D cm^2/sec x 10^5	Density g/cc
293	3500	.557	2.36	1.483
293	6500	.661	1.57	1.58
293	1500	.504	3.00	1.389
293	5000	.611	2.07	1.537
293	9100	.665	.70	1.646
293	7500	.665	1.45	1.606
293	800	.504	3.49	1.340
293	200	.504	3.29	1.284
273	7000	.611	.75	1.618
273	5000	.611	1.25	1.562
273	3500	.557	1.5	1.51
293	2000	.504	2.4	1.417
273	2500	.557	1.7	1.467
273	1500	.504	2.46	1.414
273	800	.504	2.18	1.366
273	200	.504	2.44	1.312
273	2000	.504	1.8	1.442
273	10000	.665	.164	1.691
313	7000	.611	2.76	1.569
313	3500	.557	5.6	1.461
313	5000	.611	3.58	1.513
313	1000	.504	4.2	1.323
313	2000	.557	4.05	1.389
313	200	.504	4.67	1.250
313	10000	.665	1.72	1.642
313	2900	.557	3.52	1.435
293	2500	.557	2.78	1.44
293	1000	.504	3.49	1.356

TABLE 3

DIFFUSIVITY OF CS_2 IN SEVERAL HYDROCARBONS

Organic Mixture	T °K	P atm	D x 10^5 cm^2/sec
50% CS_2 in $n\text{-}C_7H_{16}$	293	150	2.88
	293	5000	.515
	293	7000	.375
	293	600	2.75
	293	1200	2.53
	293	2800	1.18
	273	100	2.
	273	1200	1.46
	273	3050	.455
	313	100	4.36
	313	1200	4.17
	313	3500	1.92
	313	5200	1.01
	313	7000	.526
	313	10000	.43
50% CS_2 in $n\text{-}C_8H_{18}$	293	200	2.82
	293	600	2.59
	293	1200	2.62
	293	2000	1.45
	293	4000	.628
	293	6100	.282
50% CS_2 in 2,4 dimethylpentane	293	200	3.15
	293	1200	1.78
	293	3500	1.22
	293	6700	.479
	313	200	4.46
	313	900	3.52
	313	2000	2.37
	313	3500	1.8
	313	4900	1.26
	313	7000	.842
	313	7000	.763
	313	10200	.657
50% CS_2 in Toluene	293	1	1.93
	293	50	1.93
	293	300	1.49
	293	900	.742
	293	3300	.575
	293	7150	.53

TABLE 3 (continued)

Organic Mixture	T °K	P atm	D x 10^5 cm^2/sec	
	313	200	4.03	
	313	900	1.97	
	313	1500	1.49	
	313	3500	.85	
	313	5750	.71	
	313	9100	.669	
50% CS_2 in methylcyclohexane	273	50	2.37	
	273	1200	.621	
	273	3000	.236	
	293	50	2.65	
	293	900	1.83	
	293	3000	.585	
	293	7000	.192	
	313	200	3.0	
	313	900	1.97	
	313	2000	1.34	
	313	4000	.965	
	313	5000	.69	
	313	6300	.54	
	313	7750	.485	
	313	10000	.351	
50% CS_2 in chlorobenzene	293	218	2.6	
	293	1530	.943	
	293	3500	.87	
	293	7000	.33	
	313	200	4.63	
	313	900	2.59	
	313	2000	1.84	(2.02)
	313	3000	2.18	
	313	3500	1.66	
	313	4850	1.05	
	313	8200	.422	
	313	10000	.254	
20% CS_2 in chlorobenzene	313	200	3.52	
	313	900	2.42	(1.78)
	313	2000	1.29	
	313	2800	1.3	
	313	4400	.912	
	313	7000	.565	
50% CS_2 in n-butanol	293	200	3.06	
	293	1500	1.21	
	293	3500	.714	

TABLE 3 (continued)

Organic Mixture	T °K	P atm	D x 10^5 cm^2/sec	
	293	7000	.192	
	313	210	4.29	
	313	950	2.1	
	313	2000	1.42	
	313	3500	1.21	
	313	5450	.963	
	313	7000	.534	
	313	9000	.315	
50% CS_2 in iso-butanol	293	200	2.1	
	293	2000	1.03	
	293	3500	.876	
	293	5000	.454	
	293	5650	.235	
	313	200	2.95	
	313	1500	2.34	
	313	2500	1.84	
	313	3500	.494	(.565)
	313	5000	.368	
	313	5700	.333	
	313	8000	.232	

TABLE 4

SELF DIFFUSION OF WATER AND SULFATE SOLUTIONS

Compound	T °K	P atm	$D \times 10^5$ cm^2/sec	
H_2O	273	136	1.65	
	273	252	2.37	
	273	600	1.05	
	273	900	1.84	
	273	1240	1.45	
	273	2040	1.08	
	273	3500	.787	
	273	3900	.584	
	298	1	2.64	
	298	245	2.9	
	298	1300	3.24	
	298	2050	3.06	
	298	2500	3.04	
	298	3000	2.62	(2.36)
	298	3975	1.71	
	298	5000	1.15	
	298	7000	.753	(.843)
	298	9175	.515	
	323	235	5.15	
	323	735	4.17	
	323	1300	3.48	
	323	2100	2.33	
	323	2500	1.86	(1.89)
	323	3500	1.82	
	323	4450	2.07	
	323	7000	2.25	
	323	10050	1.38	
0.1N H_2SO_4	273	238	.678	
	273	338	.265	
	273	500	.506	
	273	666	.836	
	273	800	.956	
	273	1340	.764	
	273	1850	.786	
	273	2500	.656	
	273	4050	.65	
	273	5500	.415	
	278	100	1.05	
	278	250	.94	
	278	303	.741	
	278	355	.956	
	278	515	1.38	
	278	1000	.982	

TABLE 4 (continued)

Compound	T °K	P atm	D x 10^5 cm^2/sec
	298	238	2.22
	298	370	2.36
	298	803	2.62
	298	1000	2.47
	298	3000	1.76
	298	5000	1.13
	298	6850	.721
	298	8500	.502
	323	524	3.2
	323	1500	3.11
	323	2050	2.67
	323	3400	2.47
	323	5100	1.66
	323	6900	1.13
	323	8900	.806
	323	10150	.631
0.1N Na_2SO_4	273	100	.99
	273	238	.91
	273	377	.59
	273	510	1.08
	273	652	.84
	273	803	.69
	273	1304	.72
	273	1650	.65
	273	2050	.54
	273	4000	.49
	273	6000	.47
	298	1	1.41
	298	252	1.58
	298	640	1.92
	298	1200	2.18
	298	1900	2.89
	298	2500	1.92
	298	4550	1.16
	298	6525	1.27
	298	9000	.96
	323	120	4.32
	323	510	2.90
	323	1005	2.25
	323	1950	1.44
	323	2500	1.43
	323	3500	2.93
	323	4500	1.75
	323	7000	1.57
	323	10500	1.3

TABLE 4 (continued)

Compound	T °K	P atm	D x 10^5 cm^2/sec	
1 N Na_2SO_4	273	20	.28	
	273	210	.33	
	273	400	.29	
	273	600	.39	
	273	1000	.56	
	273	1800	.91	
	273	3050	.55	
	298	34	.9	
	298	238	1.01	(.86)
	298	605	.76	
	298	1000	1.07	
	298	2000	1.6	
	298	3225	.78	
	298	4500	1.03	
	298	6050	.8	
	323	20	4.86	
	323	265	1.24	
	323	640	1.14	
	323	1000	1.34	
	323	2200	1.88	
	323	3000	2.24	(2.27)
	323	4050	1.46	
	323	5100	1.26	
	323	6550	1.81	
	323	6950	1.54	
	323	10000	1.25	
0.1 N K_2SO_4	273	10	.33	
	273	100	.67	
	273	265	.71	
	273	390	.5	
	273	415	.4	
	273	600	.9	
	273	775	.86	
	273	1060	.83	
	273	1800	.82	
	273	3075	.66	
	298	100	1.4	
	298	252	.98	
	298	258	1.04	
	298	610	1.3	(1.44)
	298	1000	.9	
	298	1210	.84	
	298	1900	1.17	
	298	2850	1.59	
	298	3800	.82	
	298	4650	.87	

TABLE 4 (continued)

Compound	T °K	P atm	$D \times 10^5$ cm^2/sec
	323	100	3.92
	323	230	2.48
	323	1000	.87
	323	1500	.75
	323	1970	1.46
	323	3000	2.06
	323	4050	2.37
	323	4950	1.44
	323	6550	1.04
	323	10250	.58

TABLE 5

SELF DIFFUSION OF SOME ELECTROLYTES

Compound	T °K	P atm	D x 10^5 cm^2/sec
0.1 N $H_g(NO_3)_2$	273	20	.54
	273	250	.33
	273	600	.41
	273	1200	.48
	273	2000	.6
	273	3000	.75
	273	4250	.4
	273	5000	.57
	298	20	.86
	298	50	1.24
	298	250	2.05
	298	600	1.26
	298	1000	.92
	298	2000	1.02
	298	3000	1.17
	298	4000	.7
	298	5000	1.16
	298	7000	1.45
	298	9000	.79
	323	20	1.17
	323	250	2.13
	323	600	1.32
	323	1200	1.17
	323	2000	1.54
	323	3000	1.87
	323	4000	.9
	323	5500	1.85
	323	7000	1.95
	323	8500	1.29
	348	20	2.56
	348	250	3.28
	348	600	5.17
	348	1000	3.56
	348	2000	3.87
	348	3000	1.81
	348	4000	2.34
	348	5500	2.98
	348	7000	2.54
0.1 N $CaCl_2$	298	100	1.08
	298	250	.83
	298	600	.82
	298	1000	.94
	298	2000	.84

TABLE 5 (continued)

Compound	T °K	P atm	D x 10^5 cm^2/sec
	298	3000	1.16
	298	4250	.49
	298	5500	.44
	298	7000	.33
	298	9000	.49
	323	100	1.25
	323	250	1.37
	323	600	1.14
	323	1000	1.22
	323	2000	1.5
	323	3000	1.41
	323	4250	1.82
	323	5500	1.48
	323	7700	.83
0.1 N $Ca(NO_3)_2$	298	100	.72
	298	250	1.49 (1.6)
	298	600	1.32 (1.5)
	298	1000	1.43
	298	2000	1.13
	298	3000	1.17
	298	4000	1.47
	298	5000	.75
	298	7100	1.04
	298	9000	1.24
0.1 N $TlNO_3$	298	20	2.07
	298	250	1.35
	298	600	1.8 (1.69)
	298	1000	.95
	298	2000	2.00
	298	3000	1.67
	298	4000	1.03
	298	5700	.88
	298	7000	1.48
	298	9000	1.73
0.1 N H_gCl_2 in C_4H_9OH	298	200	1.61
	298	1000	.68
	298	2000	.4
	298	3500	.18
	298	5000	.084
	298	7000	.041
	323	200	3.75
	323	1000	2.29

TABLE 5 (continued)

Compound	T °K	P atm	$D \times 10^5$ cm^2/sec
	323	2000	1.26
	323	3500	.7
	323	5000	.35
	323	8500	.088

TABLE 6

DIFFUSION OF IODINE IN CARBON TETRACHLORIDE

P = 1 atm		P = 65 atm		P = 200 atm	
T °C	D cm²/day	T °C	D cm²/day	T °C	D cm²/day
10.2	.95	14	.91	18.6	.88
17.0	1.12	22	1.09	31.5	1.19
25.1	1.25	27	1.19	50.7	1.65
31.0	1.45	35.2	1.44		
37.8	1.59	42.6	1.64		
43.3	1.79	50.1	1.84		

TABLE 7

DIFFUSION OF I_2 IN C Cl_4 AT 29.3° C.

Density (arbitrary units)	h_1 (cm)	h_{65} (cm)	D_{65}/D
3	6.78	6.36	.88
7	5.28	4.98	.89
10	3.78	3.59	.9
14	2.59	2.51	.94
		Average	.9

TABLE 8

VARIATIONS OF $D\eta/T$ WITH VARIATION OF PRESSURE AND TEMPERATURE FOR THE DIFFUSION OF I_2 IN C Cl_4

Molar Volume in cc	P = 1 atm		P = 65 atm		P = 200 atm	
	T °C	$10^5(D\eta/T)$	T °C	$10^5 \times D\eta/T$	T °C	$10^5 \times D\eta/T$
95.3	10	3.82	16.5	3.79	25.3	3.69
96.5	20	3.86	26.7	3.82	36.2	3.78
97.7	30	3.89	36.4	3.89	47.1	3.87
98.9	40	3.96	46.0	3.94	58.1	3.92

TABLE 9

SELF DIFFUSION OF CARBON DIOXIDE

T °C	P atm	Density g/cc	D cm^2/sec
23	16.05	.0313	.0065
44.7	9.7	.016	.0111
24.9	9.5	.0174	.011
44.6	9.2	.0157	.0131
24.9	16.7	.0346	.00577
44.8	16.3	.0295	.00529
45.2	16.3	.0291	.00519
44.8	27.2	.0522	.00415
25.3	34.2	.0756	.00325
45.3	34.3	.068	.0034
25.2	34.3	.0757	.00271
25.1	47.6	.1235	.00179
.3	34.3	.0956	.00131
.4	34.3	.0955	.00183
13.6	47.8	.147	.00119
21	36.4	.088	.0026
22	38.4	.092	.00197
30.2	47.2	.1155	.00166
44.7	47.7	.1045	.00197
30.2	47.7	.118	.00158
23.8	16.7	.0328	.0041
.75	34.3	.095	.0013
13.4	47.5	.145	.00114
43.8	61.2	.152	.00148
44.6	68.1	.18	.00105
44.5	68.1	.18	.00130
25	61.2	.21	.00106
22.8	36.4	.0855	.00228
22.5	36.4	.0855	.00250
22.4	30.6	.0675	.00306
23.3	47.7	.128	.0015
30.2	59.5	.173	.00126
30.3	61.2	.1835	.00105
30.3	65.5	.217	.000822
40.4	80.8	.297	.000638
23.8	70.6	.058	.00269
30.8	45.6	.1093	.00192
40.6	57.6	.1415	.00154
40.6	68.00	.189	.00113
41.5	75	.23	.000924
40.5	79.5	.275	.000804
40.4	85.6	.3602	.00053
32.06	74.3	.3898	.000563

TABLE 9 (continued)

T °C	P atm	Density g/cc	D cm^2/sec
32.06	74.65	.4535	.000538
40.25	86.05	.4	.000507
40.08	96.3	.608	.000293
25.3	124.9	.852	.000105
32.06	73.6	.3335	.000345
40.26	86.05	.4	.0003
40.26	108.5	.68	.000182
40.26	129.9	.745	.000149
25.1	65.1	.722	.000216
25.1	90.2	.802	.000104
25.1	90.2	.802	.0000822
.2	71.07	.96	.0000456
.3	38.4	.922	.0000599
.2	137.9	.998	.0000404
40.21	144.9	.774	.000104
25.1	89.05	.8	.000103
25.2	149.9	.878	.0000702
25.2	65.1	.72	.000133
40.1	107.9	.68	.000166
40.2	119.8	.72	.000130
25.4	65.1	.716	.000111

TABLE 10

SELF DIFFUSION OF CARBON TETRACHLORIDE

P atm.	T °C	Density g/cc	Obs. D cm^2/sec x 10^3	Calc. D cm^2/sec x 10^3
40	50	.026	3.65	3.5
60	50	.0392	2.46	2.36
80.3	50	.0532	1.6	1.64
100	50	.0686	1.13	1.22
124.8	50	.085	.94	.93
150	50	.103	.664	.715
46.5	25	.03	2.9	2.91
60	25	.044	1.98	1.9
80	25	.0596	1.38	1.36
100	25	.0828	.98 (.87)	.91
125	25	.099	.69 (.71)	.715
150	25	.1192	.57	.56
200	25	.1585	.368	.374
300	25	.214	.21	.231
20	0	.0156	5.3	5.5
40.2	0	.0322	2.48	2.55
60	0	.051	1.51	1.52
81	0	.0716	1.09	1.02
100	0	.0916	.75	.734
125	0	.1184	.575	.535
150	0	.1445	.4	.413
200	0	.188	.248	.27
300	0	.242	.15	.177

TABLE 11

SELF DIFFUSION OF CARBON DIOXIDE

T °K	P atm	Density g/cc	D cm^2/sec x 10^5
298	113.2	.862	9.05
302.1	103.1	.782	13.7
300.6	178.9	.883	7.02
298.1	103.1	.822	9.34
297.9	130.3	.858	7.64
298.1	562	1.054	5.12
323.2	232.3	.824	9.16
323.2	250	.840	8.84
323.1	270.5	1.025	7.04
298.0	402.5	1.003	4.09
298.2	402.5	1.003	4.34
298	562	1.054	3.54
298.2	752	1.106	3.18
298.2	1023	1.159	2.53
272.9	137.1	.999	4.04
273.2	307.1	1.06	3.2
273.2	512	1.103	2.46
273.1	802	1.157	1.98
323	470.5	.955	4.98
322.9	596.5	.993	4.53
322.9	837	1.056	3.92
322.9	1029	1.102	3.48
298.2	561	1.057	3.51
298.1	1030.5	1.16	2.45

TABLE 12

DIFFUSION OF 0.1 GLYCINE INTO HCl AND HCl INTO GLYCINE

C	H^+ in G	Diffusivity cm^2/day	
HCl	after Diffusion	G	Cl
.0014	.000005	1.04	7.3
.006	.00009	1.02	6.9
.012	.00009	1.06	6.5
.024	.0002	1.17	5.7
.026	.0002	1.23	5.75
.0526	.0005	1.18	4.08
.1	.008	1.18	3.59
.252	.002	1.61	3.45
.52	.01	1.82	3.19
1.03	.04	2.24	3.14
2.06	.24	1.92	2.82

TABLE 13

SELF DIFFUSION OF HCl AND H_2SO_4

		Temperature			
Acid	Concentration	10° C.	15° C.	25° C.	35° C.
HCl	0	2.16	2.48	3.14	3.87
	.02	2.05	2.35	2.97	3.66
	.05	2.02	2.33	2.93	3.61
	.1	2.03	2.33	2.92	3.6
	.2	2.05	2.35	2.98	3.65
	.35	2.11	2.4	3.06	3.77
	.5		2.45	3.18	
	.75		2.56	3.37	
	1.0		2.68	3.58	
H_2SO_4	.15	1.28	1.49	1.94	2.35
	.2	1.25	1.45	1.88	2.31
	.3	1.21	1.4	1.83	2.26
	.4	1.19	1.38	1.81	2.25
	.6	1.21	1.41	1.86	2.29
	.8	1.27	1.47	1.94	2.39
	1	1.36	1.57	2.05	

TABLE 14

DIFFUSION OF SOME ORGANIC LIQUIDS

System	T °C	Diffusivity (cm^2/sec) x 10^5
D_2O-H_2O	15	1.62
	25	2.04
	35	2.73
	45	3.34
$H^{18}{}_2O-H_2O$	25	2.09
	45	3.2
$C_6H_5\ D-C_6H_6$	15	1.88
	25	2.15
	35	2.4
	45	2.67
$C_2H_4\ D\ Br-C_2H_5Br$	15	3.6
	22.5	3.8
	30	3.96
$C_2H_5\ OD-C_2H_5OH$	15	.8
	25	1.05
	35	1.31
	45	1.7
$C\ Cl_4-C_6H_6$	20	1.77
	20	1.74

TABLE 15

SELF DIFFUSION OF SOME HYDROCARBONS

Hydrocarbon	T °C	Diffusivity (cm^2/sec) x 10^9
n-Butane	25	1.17
	35	3.29
	46.5	7.54
isobutane	25	.53
	35	1.46
	46.5	3.75
n-Pentane	25	1.08
	35	2.59
	46.5	6.55
isopentane	25	.47
	35	1.34
	46.5	3.6
Neopentane	25	.2
	35	.6
	46.5	1.2

TABLE 16

DIFFUSION OF SOME HYDROCARBONS IN POLYISOBUTYLENE

Hydrocarbon	P (mm)	Film Thickness (cm)	Equilibrium Concentration of Vapor	Diffusivity $(cm^2/sec)\ 10^9$
Propane	496	.0234	.0061	5.6
	941	.0234	.0116	6.4
	1446	.0272	.0185	8.0
	1452	.0234	.0183	7.4
n-Butane	242	.0309	.0126	4.5
	503	.0309	.0288	6.8
	662	.0355	.0392	9.1
	763	.0309	.0466	10.9
	994	.0309	.0653	18.6
	1243	.0309	.0905	33.0
	1448	.0309	.1162	56.8
isobutane	210	.0218	.0069	1.7
	488	.0218	.0171	2.2
	712	.0218	.0260	2.5
	767	.0254	.0281	2.8
	980	.0218	.0373	3.6
	1246	.0218	.0509	4.7
	1460	.0218	.0622	6.4
n-pentane	32	.0269	.0061	3.1
	104	.0269	.0213	4.4
	207	.0269	.0474	8.2
	212	.0244	.0478	7.3
	306	.0269	.0787	18.1
	388	.0269	.1132	33.7
isopentane	106	.0244	.0156	1.9
	222	.0244	.0353	2.9
	324	.0269	.057	3.9
	333	.0244	.0587	4.7
	333	.0271	.0596	5.1
	422	.0244	.0808	7.3
	666	.0244	.1795	39
neopentane	489	.0082	.0373	1.1
	703	.0309	.0595	1.4
	1052	.0082	.1104	3
	1240	.0082	.1515	5.4

TABLE 17

DIFFUSION OF ACETONE INTO POLYVINYL ACETATE AT 20° C.

Concentration g.solvent/g.polymer	Log $\bar{D}$ + 12
.113	3.76
.095	3.2
.073	2.4
.055	1.6

TABLE 18

SUCROSE DIFFUSIVITIES IN SUPER SATURATED LIQUIDS

T °C	t sec	Concentration Weight % (av.)	Moles H_2O/mole sucrose	Diffusivity (cm^2/sec) 10^7
25	231	.729	2587	51.74
	251	61.05	12.1	10.71
	0	66.22	9.69	7.8
	90	70.44	7.97	5.42
	68	72.21	7.31	4.51
	398	74.5	6.5	3.14
35	144	61.05	12.1	15.88
	12	65.95	9.81	12
	213	70.4	7.99	8.61
	39	72.2	7.32	7.33
	114	72.77	7.11	6.7

TABLE 19

DIFFUSION OF DILUTE AQUEOUS GLYCINE SOLUTION AT 1° C. AND 25° C.

Temp.	Concentration g/100 ml.	Diffusivity (cm^2/sec) x 10^6
1° C.	.2501	5.169
	.6001	5.107
	.6002	5.097
	1.8008	4.941
	1.8012	4.942
	3.0015	4.793
	4.2003	4.665
25° C.	.2503	10.575
	.7203	10.443
	1.99	10.327
	1.7997	10.175
	2.9999	9.885
	4.2017	9.547

TABLE 20

DIFFUSION OF UREA IN H_2O

Concentration moles/liter	Diffusivity cm^2/sec x 10^5
.12501	1.3725
.2475	1.3628
.5	1.3433
.75001	1.3264
.9782	1.3086
1.00003	1.3074
1.50009	1.274
2.00005	1.2448
3.00016	1.189
3.99994	1.1425

TABLE 21

DIFFUSION OF DILUTE SUCROSE SOLUTION

T °C	ΔC	$\bar{C}$	$\left[\frac{\Delta n}{\Delta C}\right] \times 10^6$	Obs. D $cm^2/sec \times 10^6$	Calc. D $cm^2/sec \times 10^6$
24.95	1.5019	.7507	1430.7	5.170	5.227
	1.5016	1.0011	1430.8	5.148	5.224
	1.5016	2.2521	1429.8	5.049	5.221
	1.5018	3.7537	1429.4	4.934	5.222
	1.5025	5.2546	1429.3	4.821	5.224
1	.50042	.2502	1468.9	2.918	2.428
	.50096	1.2513	1468.8	2.378	2.429
	.5008	2.2512	1466.5	2.303	2.422
	.5012	3.2539	1467.5	2.292	2.432
	.5011	4.2551	1465.1	2.251	2.428
	1.4017	.7009	1468.5	2.3920	2.420
	1.5009	.7505	1468.4	2.3928	2.4232
	1.502	.7510	1468.4	2.3937	2.4241
	1.5018	1.5018	1466.8	2.362	2.4231
	3.0037	3.7593	1466.3	2.3704	2.4262

$$\Delta C = C_s - C_o$$

$$\bar{C} = \frac{C_o + C_s}{2}$$

C_o = Concentration of above initial boundary.

C_s = Concentration of below initial boundary.

TABLE 22

DIFFUSION OF KCl IN DILUTE AQUEOUS SOLUTION

T	C	Calc. D $cm^2/sec \times 10^5$	Obs. D $cm^2/sec \times 10^5$
25° C.	0	1.9958	
	.00125	1.9605	1.612
	.00194	1.9531	1.9545
	.00325	1.9430	1.9433
	.00585	1.9293	1.9308
	.00704	1.9246	1.9241
	.00980	1.9155	1.9180
	.01261	1.907	1.908
	.02654	1.883	1.879
	.03992	1.870	1.877
	.04620	1.866	1.872
	.0545	1.861	1.860
	.06074	1.858	1.856
	.1298	1.840	1.838
	.3323	1.839	1.842
	.5276	1.853	1.852
20° C.	0	1.7652	
	.00125	1.734	1.736
	.00248	1.7235	1.7245
	.00367	1.716	1.719
	.00451	1.712	1.709
	.01121	1.69	1.6885
30° C.	0	2.2334	
	.00326	2.173	2.172
	.0065	2.155	2.154
	.00896	2.145	2.146
	.01236	2.133	2.139

TABLE 25

DIFFUSION OF SOME ELECTROLYTES IN AQUEOUS SOLUTIONS AT 25° C.

Electrolyte	C	Obs. D cm^2/sec x 10^5	Calc. D cm^2/sec x 10^5
LiCl	0		1.368
	.000634	1.348	1.349
	.00179	1.331	1.339
	.00229	1.335	1.335
	.00235	1.335	1.335
	.00263	1.334	1.334
	.00302	1.331	1.331
	.00339	1.327	1.329
	.00496	1.326	1.323
	.00568	1.319	1.321
	.00732	1.320	1.317
	.00792	1.315	1.316
	.00834	1.313	1.315
	.00935	1.312	1.313
	.11	1.313	1.31
NaCl	0		1.612
	.000746	1.586	1.589
	.00161	1.576	1.58
	.0033	1.576	1.568
	.0045	1.562	1.563
	.0052	1.559	1.56
	.0065	1.557	1.556
	.0077	1.555	1.552
	.009	1.544	1.549
	.0093	1.544	1.548
	.01	1.547	1.546
	.01473	1.542	1.537
KNO_3 in water	0		1.9308
	.000904	1.9	1.933
	.00121	1.895	1.928
	.00163	1.891	1.927
	.00221	1.885	1.937
	.00259	1.882	1.921
	.00268	1.882	1.927
	.00403	1.872	1.929
	.00452	1.869	1.93
	.00503	1.866	1.942
	.00515	1.865	1.923
	.00538	1.864	1.939
	.006	1.861	1.938
	.00728	1.855	1.932
	.00868	1.849	1.929

TABLE 26

DIFFUSION OF SILVER NITRATE

Concentration	Obs. D cm^2/sec x 10^5	Calc. D cm^2/sec x 10^5
0		1.7675
.00285	1.718	1.721
.00322	1.719	1.718
.00427	1.711	1.712
.00496	1.708	1.708
.00628	1.701	1.702

TABLE 27

DIFFUSION OF ZINC SULFATE AT 25° C.

Concentration	Obs. D cm^2/sec x 10^5	Calc. D cm^2/sec x 10^5
0		.8486
.00108	.747	.721
.00139	.739	.708
.00192	.733	.69
.00256	.728	.673
.0026	.731	.672
.00263	.732	.671
.00308	.721	.664
.00439	.714	.647
.00471	.707	.644

TABLE 28

DIFFUSION OF KCl AT 4° C.

Concentration (mole)	Obs. D $cm^2/sec \times 10^5$	Calc. D $cm^2/sec \times 10^5$
.0166	1.08	1.082
.168	1.038	1.039
.307	1.036	1.036
.379	1.037	1.036
.558	1.042	1.04

TABLE 29

DIFFUSION OF H_2 AND N_2 IN DIFFERENT SOLUTIONS

System	T °C	Obs. D $cm^2/sec \times 10^5$	Calc. D $cm^2/sec \times 10^5$
H_2-CO_2	20	.629	
N_2-CO_2	20	.16	
H_2-CH_4	25	.726	
H_2-C_2H_6	25	.537	
H_2-CO_2	25	.696	.631
N_2-CO_2	25	.165	.152
H_2-SF_6	25	.418	.464
N_2-C_2H_6	25	.148	.139
N_2-C_2H_4	25	.163	.156
N_2-C_4H_{10}	25	.096	.0986
N_2-isoC_4H_{10}	25	.0908	.0961

TABLE 30

DIFFUSION OF KCl IN WATER AT 25° C.

Concentration	ΔC	Obs. D cm^2/sec x 10^5	Calc. D cm^2/sec x 10^5
.1	.2	1.8512	1.8469
.225	.2	1.8382	1.8396
.33196	.19965	1.84	1.8443
.50001	.2	1.8497	1.8588
1.00005	.2	1.8923	1.9206
1.50021	.20014	1.9427	2.0024
2.00034	.20017	1.9994	2.104
2.50043	.70008	2.0569	2.2271
3.0008	.20014	2.112	2.3727
3.50087	.20022	2.1603	2.5416
3.9008	.1996	2.1956	2.6941

TABLE 31

SELF DIFFUSION OF KCl

Concentration g/liter	Diffusivity cm^2/sec x 10^5
.00494	1.313
.0125	1.32
.0375	1.3
.055	1.29
.09375	1.28
.1035	1.3
.15	1.32
.25	1.31
.375	1.33
.564	1.36
.8	1.4
1	1.42
1.5	1.43
2	1.4
3	1.34
4.14	1.26

TABLE 32

DIFFUSION OF $CaCl_2$ IN AQUEOUS SOLUTION AT 25°C.

Concentration	Obs. D cm^2/sec x 10^5	Calc. D cm^2/sec x 10^5
.05	1.129	1.172
.1	1.120	1.189
.2	1.117	1.247
.3	1.119	1.316
.4	1.124	1.382
.5	1.132	1.458
.6	1.148	1.532
.7	1.167	1.621
.8	1.189	1.706
.9	1.215	1.78
1.0	1.243	1.89

TABLE 33

Cl^- DIFFUSION IN AQUEOUS NaCl

Normality of NaCl	Cl^- diffusivity cm^2/sec x 10^5
.03	1.975
.05	1.96
.1	1.94
.25	1.91
.5	1.85
1	1.77
2	1.61
3	1.44
4	1.24
5	1.06

TABLE 34

SELF DIFFUSION OF Na^+ IN AQUEOUS NaCl

Normality of NaCl	Diffusivity of Na^+ $cm^2/sec \times 10^5$
.005	1.32
.01	1.31
.05	1.3
.1	1.31
.175	1.313
.2	1.32
.3	1.35
.35	1.34
.35	1.32
.625	1.31
1	1.25
2	1.13
3	1.02
4	.904
5	.796

TABLE 35(a)

DIFFUSION OF HYDROGEN PEROXIDE VAPOR INTO AIR

Air Flow Rate (cc/min)	Weight of Peroxide (% in liquid)	D cm^2/sec at 60° C.
1200	99 - 98.4%	.191
1000	99.4 - 98.6%	.189
1050	99 - 96.8%	.183

TABLE 35(b)

WATER-HYDROGEN DIFFUSION

T °C	Hydrogen Rate cc/min	Diff. Rate g/cm^2 sec x 10^6	D cm^2/sec
30	2200	1.55	.882
	2150	1.53	.87
	2050	1.57	.897
55	2100	6.45	.996
	3300	6.34	.979
60	3000	8.75	1.059
	2050	8.8	1.067

TABLE 36

DIFFUSION OF LIQUID SULFUR

Temperature °C	Diffusivity cm^2/sec x 10^6
122.5	1.05
125	1.95
139	2.52 (2.47)
148	3.85
153	2.45
154.5	2.9
158.5	1.45
163	1.31
167.5	1.17
170	1.53
180	1.03
183	.9
185	.863
192	.714
199	.710
206	.871
215	.946
231	.804
236	.826
273	1.52
316	2.26

TABLE 37

SELF DIFFUSION OF Ca^{++} AND Cl^- IN AQUEOUS $CaCl_2$

Normality $CaCl_2$	Diffusivity ($cm^2/sec \times 10^5$) Ca^{++}	 Cl^-
.01	.778	
.0705	.782	1.89
.282	.767	1.72
.803	.646	1.6
1.41	.56	1.42
2.68	.405	.907
4.02	.225	.447
5.36	.1	.159

TABLE 38

SELF DIFFUSION OF Na^+ AND Cl^- IN AQUEOUS NaCl AND SELF DIFFUSION OF Na^+ AND SO_4^{--} IN AQUEOUS Na_2SO_4

Normality	D $(Na)^+$ cm^2/day	D (Cl^-) cm^2/day	D $(Na)^+$ cm^2/day	D (SO_4) cm^2/day
.005	1.135	1.705		
.01			1.125	.83
.02	1.13	1.66	1.12	
.03				.75
.04	1.12			
.05			1.095	.72
.1		1.63		.65
.16	1.09			
.2		1.62	1.05	.61
.3	1.087			
.4			1.00	.57
.5		1.58		
.55				.57
.6	1.05			
.7		1.5	.935	.555
.8	1.05			
1	1.04	1.46		
1.2			.845	.53
1.4	1.035	1.43		
1.5	1.03		.8	.5
2.0	1.015	1.41	.77	.525
3.0			.73	.59
3.5	1	1.41		

TABLE 39

SELF DIFFUSION OF SOME UNIVALENT ELECTROLYTES

Mole liter	KBr	HCl	HBr	LiCl	LiBr	NaCl	NaBr	KCl
.00								
.05	1.892	3.073	3.156	1.28	1.300	1.506	1.533	1.863
.1	1.874	3.050	3.146	1.269	1.279	1.484	1.517	1.848
.2	1.87	3.064	3.190	1.267	1.285	1.478	1.507	1.835
.3	1.872	3.093	3.249	1.269	1.296	1.477	1.515	1.826
.5	1.885	3.184	3.388	1.278	1.328	1.474	1.542	1.835
.7	1.917	3.286	3.552	1.288	1.360	1.475	1.569	1.846
1.0	1.975	3.436	3.869	1.302	1.404	1.483	1.596	1.876
1.5	2.062	3.743		1.331	1.473	1.495	1.629	1.951
2.0	2.132	4.046		1.363	1.542	1.514	1.668	2.011
2.5	2.199	4.337		1.397	1.597	1.529	1.707	2.064
3.0	2.28	4.658		1.430	1.65	1.544		2.110
3.5	2.354	4.92		1.464	1.693	1.559		2.152
4.0	2.434	5.17				1.587		

TABLE 40

DIFFUSION OF KCl IN AQUEOUS SOLUTION

Normality	Diffusivity cm^2/day
.01	1.714
.02	1.687
.1	1.631
.2	1.62
.5	1.585
1.0	1.653
1.5	
2	1.698

TABLE 41

DIFFUSION OF $CaCl_2$ IN AQUEOUS SOLUTION

T °C	Inner Molality	Outer Molality	Diffusivity cm^2/sec x 10^5
15	.00565	0	.904
15	.01025	0	.905
15	.05	0	.885
15	.1522	.0515	.87
15	.3001	.2023	.874
15	.05023	.401	.901
25	.00513	0	1.201
25	.01024	0	1.174
25	.0206	0	1.161
25	.0483	0	1.154
25	.1517	.051	1.129
25	.302	.1982	1.138
25	.5043	.4034	1.156
35	.00559	0	1.538
35	.01045	0	1.488
35	.0488	0	1.449
35	.1491	.0368	1.423
35	.2999	.2002	1.431
35	.4962	.4	1.456

TABLE 42

SELF DIFFUSION OF KCl AT 5° C.

Normality of KCl	Solvent Normality	Diffusivity cm^2/sec x 10^6
.2	Water	9.016
.4	.2	9.056
.6	.4	9.111
.8	.6	9.259
1	.8	9.41

TABLE 43

SELF DIFFUSION OF NaCl

Molality NaCl	Temperature °C	Diffusivity $cm^2/sec \times 10^5$
.1012	14.7	.986
.198	13.6,14.4	.944,.968
.498	13.6	.936
1.005	13.6,13.0	.927,.912
1.501	13.7	.93
2.072	15,12.8	.973,.905
2.936	13.5,13.8	.918,.95
4.259	13.3	.93
5.503	16,17,13.3	1.026,1.075,.94
5.81	13.5	.952
.1004	16.2,16.6	2.153,2.166

TABLE 44

SELF DIFFUSION OF C_2SO_4 AT 25° C.

Molarity	Diffusivity cm^2/sec x 10^6
.0028	7.474
.0042	7.314
.0056	7.159
.007	7.049
.0084	6.922
.0098	6.805
.0112	6.726
.0126	6.646
.014	6.579
.0154	6.497
.0196	6.375
.0258	6.27
.028	6.208
.0308	6.159
.0336	6.113
.0364	6.079
.042	6.012
.07	5.786
.098	5.644
.14	5.493
.168	5.418
.21	5.349
.252	5.312
.28	5.238
.35	5.231

TABLE 45

SELF DIFFUSION OF BUTYL ALCOHOL

Alcohol	Obs. D cm^2/sec x 10^5	Calc. D cm^2/sec x 10^5
n-butyl	.81	.81
isobutyl	.8	.8
s.butyl	.76	.8
t.butyl	.73	.78

TABLE 46(a)

DIFFUSION OF n-C_4H_9OH IN H_2O

Temperature	Molarity	Diffusivity $cm^2/sec \times 10^6$
1° C.	.0501	4.348
	.1	4.243
	.2199	4.04
	.3001	3.941
	.3	3.927
	.5002	3.657
	.7004	3.435
25° C.	.0502	9.557
	.1006	9.3
	.1424	9.248
	.3006	8.758
	.5001	8.147
	.7001	7.555

TABLE 46(b)

DIFFUSIVITY MEASUREMENT OF BUTYL ALCOHOL BY SURFACE TENSION METHOD AT 25° C. AND 8.2 g/l. CONCENTRATION

Alcohol	Diffusivity $cm^2/sec \times 10^6$
n-butyl	8.1
isobutyl	8.0
s.butyl	7.6
t.butyl	7.3

TABLE 47

DIFFUSION OF 2-NAPHTHOL IN H_2O

Temperature °C	Diffusivity cm^2/day
7	.679
14.6	.774
31.6	1.12
39.75	1.37
40.05	1.39
60.02	2.03
71.6	2.58

TABLE 48

DIFFUSION OF CO_2 IN CO_2 AND N_2O

System	T °K	P mm.	D cm^2/sec
CO_2-CO_2	194.8	157	.0516
	273.2	307.2	.097
	312.8	490.4	.1248
	362.6	468.4	.1644
CO_2-N_2O	194.8	203.7	.0531
	273.2	319.7	.0996
	312.8	510	.128
	312.8	323.3	.128
	362.6	507.4	.1683

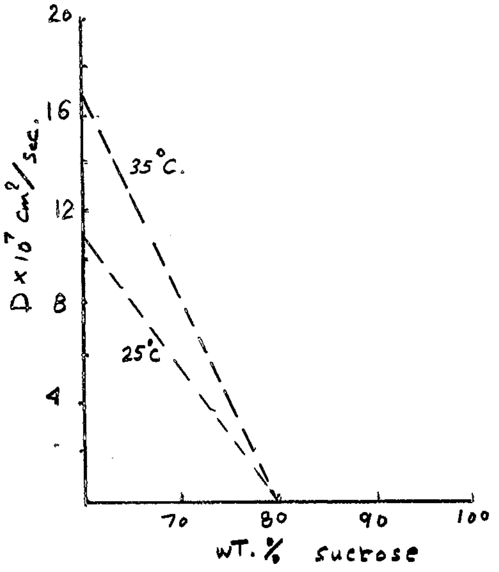

Fig 22

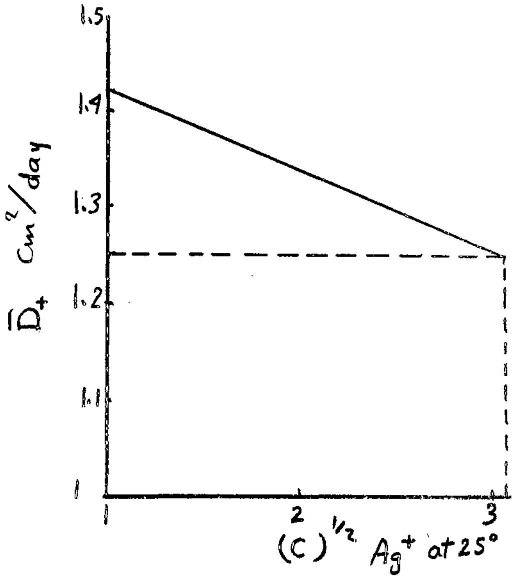

Fig 24

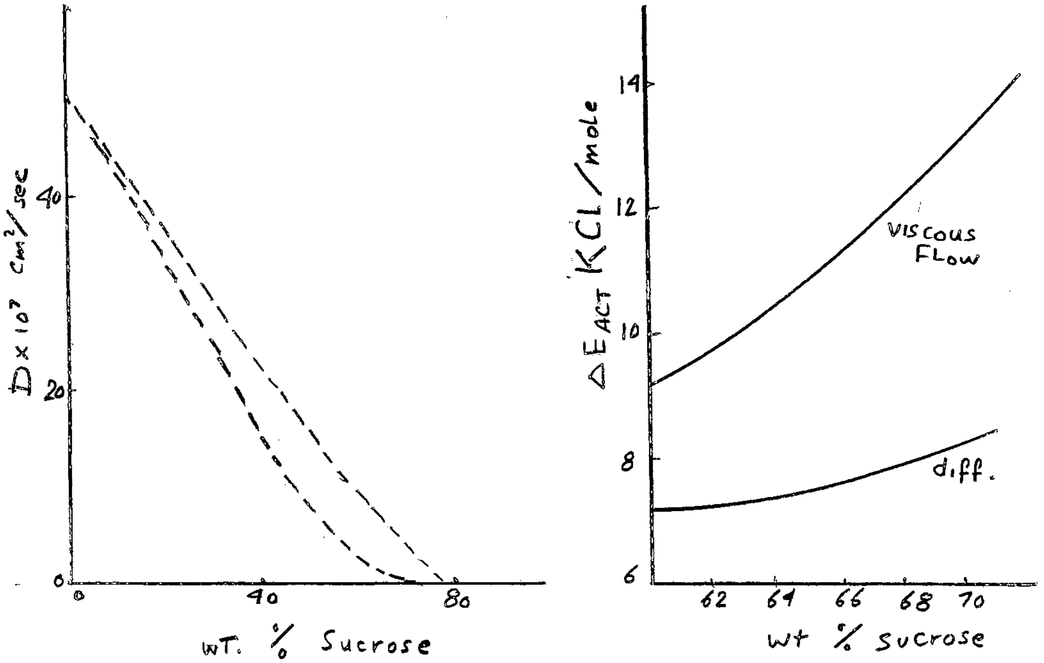

Fig 23

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