Liquid Diffusion of Nonelectrolytes:

Part I

This review covers the field of liquid diffusion from the time of the publication of the review article by Johnson and Babb in 1957. In Part I a concise introduction is given to the phenomenological description of the diffusion process, followed by a review of the various theories of and model approaches to diffusion in binary mixtures. These are treated in the following categories: hydrodynamic theories, Eyring's theory and the friction coefficient theories. The predictions are compared with the experimental results throughout the review. Part I will be followed by Part II in November reviewing self-diffusion, empirical predictive equations, and experimental techniques. A supplement of critical tabulations of all experimental diffusion data since 1956 has been prepared.

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SCOPE

Diffusion plays an important role in chemical engineering as well as in many other disciplines. Knowledge of diffusion coefficients and also the mechanism of diffusion is of great and general practical significance. Liquid diffusion is more difficult to handle than diffusion in solids and gases mainly because of the closeness of mobile molecules in the liquid. The differences in the rate of diffusion between the various states of matter are also significant. Typical diffusivity values are $10^{-14}m^2/s$ for solids, 10^{-9} m^2/s for liquids, and $10^{-4}m^2/s$ for gases. The intermolecular forces, and the shape and size of the molecules are all important factors which are very difficult to account for quantitatively as the literature survey has also indicated. For mutual diffusion, most of the efforts have been concentrated on the study of concentration dependence and less on temperature dependence. Studies of the effect of pressure on mutual diffusivity has received the least attention. A generally applicable predictive equation for mutual diffusion has not yet evolved.

CONCLUSIONS AND SIGNIFICANCE

The various theoretical approaches to diffusion in liquid mixtures have helped to provide increasing insight into the diffusion process. Disregarding certain relatively minor differences there are basically four different approaches in use at the present time: The Stokes-Einstein relation, the Darken and Hartley-Crank approaches, Eyring's approach, and the various friction coefficient approaches. In the last category there are the hydrodynamic-thermodynamic theory of Lamm, the statistical mechanical theory of Bearman and Kirkwood, and the developments based on irreversible thermodynamics. All of these result in essentially identical relations between the three friction coefficients and the three diffusion coefficients in binary solutions. The mutual diffusion coefficient, which is by far the most important from the applications point of view, is related only to the friction coefficient between molecules of the two dissimilar components. There is no general method to calculate this friction coefficient from the other two giving the friction between like molecules. The viscosity of a binary solution is related to all three friction coefficients, and therefore there is no general method to calculate the mutual diffusion coefficient from viscosities. Calculation of the friction coefficients from molecular theory faces similar difficulties as the calculation of equilibrium properties. Possibly a better understanding of the relationships between molecular interactions and thermodynamic properties, on the one hand, and molecular interactions and friction coefficients, on the other, might eventually result in thermodynamic correlations for the friction coefficients, using activity coefficients.

It appears that the rest of the approaches to liquid diffusion represent special cases of the more general, friction coefficient approach. These permit certain correlations of the mutual diffusion coefficient which, however, rapidly loose their validity for solutions of increasing nonideality.

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1. INTRODUCTION

The study of liquid diffusion is of great interest to engineers and scientists alike. Diffusion plays a large role in many chemical processes involving mass transfer. For instance, distillation, mixing, extraction, condensation, chemical reactions, etc. are influenced to various degrees by diffusion. Diffusion is also important in many other fields, for example, in biological systems, in pollution control, and in the separation of isotopes.

The necessity of predicting liquid diffusivities, therefore, often arises. Theoretical approaches have not yet been successful in accurately predicting liquid diffusivities. For dilute gases and for solids, diffusion is more amenable to mathematical treatment, but rigorous treatment has met with great difficulties in the case of liquids because in liquids the molecules are both closely spaced and in chaotic motion. The effects of intermolecular forces cannot be taken into account accurately as yet. However, theoretical approaches have served as starting points for some of the empirical and semi-empirical formulations.

Since the last extensive review of this subject by Johnson and Babb (1956), concerted efforts—theoretical as well as experimental—have been made. For a long time these two aspects have not been put together in one place except for some very simple liquids of monatomic molecules (Ar, for example) diatomic molecules (O_2, for example) and a few polyatomic molecules which were reviewed by Rice, Boon, and Davis (1968). The systems covered in their article have not been included here.

In this review we have confined ourselves to one- and two-component systems of nonelectrolytes, water being an exception.

Several theoretical approaches which have been reduced for numerical prediction of diffusion data are presented and discussed, along with some more-or-less empirical correlations, in the light of agreement between predicted and experimental data. The basic assumptions and the final formulae are stated in every case. For further details the reader is referred to the original papers. All available experimental data have been collected and compiled in tabular form.*

New developments in the experimental techniques for measuring diffusion coefficients are also described in Part II (to appear in the November *AIChE Journal*).

There has been some ambiguity in the literature in the use of some terms pertaining to diffusion. In this paper, the terminology used by Albright and Mills (1965) is followed: The term *intradiffusion coefficient* is used for a system in which the diffusion of a labeled component is followed in a chemically homogeneous mixture. The term *tracer diffusion coefficient* is also used frequently for this case in the literature. *Self diffusion* is the special case of intradiffusion where the system consists of only one chemical component. *Interdiffusion coefficient* is sometimes used when following the diffusive mixing of two different chemicals. The term *mutual diffusion coefficient* is used more often in the literature for this case.

2. PHENOMENOLOGICAL DESCRIPTION OF DIFFUSION PROCESSES

Diffusion measurements in liquid systems have been usually described by Fick's law. According to this law the flux of a component *A*, or the rate of passage of the component, with respect to the cell, along a given axis per unit cross-sectional area, under isothermal conditions, is given by

$$J_A^c = -D_F \nabla C_A \tag{2.1}$$

where ∇C_A is the concentration gradient of component *A* along the given axis, and D_F is known as the Fickian diffusivity. Although this phenomenological law has been found satisfactory for certain experimental conditions, it does not always describe diffusion in an adequate manner (Tyrrell, 1970).

It is more consistent to define a diffusion coefficient D_{AB} for a binary mixture of components *A* and *B* as (for example, Robinson, 1964)

$$J_A^v = -D_{AB} \nabla C_A \tag{2.2}$$

where the superscript v refers to the volume fixed frame of reference. The analogous expression for component *B* is

$$J_B^v = -D_{BA} \nabla C_B \tag{2.3}$$

It may be shown (Tyrrell, 1961, Ch. 3) that $D_{AB} \equiv D_{BA}$, which means that in a volume fixed frame of reference the diffusion coefficient D_{AB}, usually known as mutual or interdiffusion coefficient, is one and the same value regardless of which of the two components is followed. The equivalence of D_{AB} and D_{BA} can also be shown to be true for the mass fixed or barycentric and the mole or number fixed frames of reference (Tyrrell, 1961, Ch. 3). This equivalence is not true for the Fickian diffusion coefficient except for systems of composition independent partial molar volumes (Tyrrell, 1961, Ch. 3).

A relation for D_{AB} in terms of a flux J_A^c with respect to a coordinate fixed frame of reference can be obtained from Equation (2.2) (Robinson, 1964)

$$J_A^c = -D_{AB} \nabla C_A + C_A (J_A^c \overline{V}_A + J_B^c \overline{V}_B) \tag{2.4}$$

The terms in parentheses on the right-hand side of Equation (2.4) represent the net bulk flow v_v past a stationary plane. In the event that pure diffusion takes place in a constant partial volume system, such volume flow is absent and Equation (2.4) reduces to Equation (2.1) so that

$$D_{AB} = D_F \tag{2.5}$$

In case of self- or intra-diffusion studies where there is no difference in the chemically identifiable components Equation (2.1) is always correct because, the overall composition of the solution staying constant, there cannot be a volume change.

Equation (2.1) is not valid for describing diffusion in multicomponent systems (Dunlop and Gosting, 1955, 1959). Cross diffusion-coefficient terms may become very significant. Adequate description of diffusion in these systems has been made by the use of irreversible thermodynamics.

Another frame of reference, introduced by Darken (1948), Hartley and Crank (1949), and subsequently used by several investigators, (for example, Adamson, 1958; Bennett, 1958; Carman, 1967; Baranowski and Curowski, 1968; Kett and Anderson, 1969) is generally known as the convection fixed frame of reference. There is no diffusion-generated bulk flow across this frame of reference. The existence of such a bulk flow (the so-called "Kirkendall effect") has been experimentally established in gases (Irani and Adamson, 1958) and in solids (Darken, 1948). There has not been so far any clear demonstration for the existence of such bulk flow in liquid systems.

With respect to this frame of reference, flux J_i^m is given by

$$J_i^m = -D_i \nabla C_i \quad (i = A, B) \tag{2.6}$$

where D_i is known as the intrinsic diffusion coefficient for component *i* in the mixture.

The diffusion generated bulk volume flow v_m of the medium w.r.t. the stationary coordinate system is given by

$$J_i^m = J_i^c - v_m C_i \quad (i = A, B) \tag{2.7}$$

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* The Supplement has been deposited as Document No. 02172 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., N.Y., N.Y. 10017 and may be obtained for $1.50 for microfiche or $2.00 for photocopies.

Usually the flows are described with respect to a volume fixed frame of reference. If $\mathbf{v}_v$ is the bulk volume flow w.r.t. stationary coordinates, then, according to Equation (2.4)

$$\mathbf{J}_i^v = \mathbf{J}_i^c - C_i\,\mathbf{v}_v \tag{2.8}$$

where

$$\mathbf{v}_v = \Sigma\,\mathbf{J}_i^c\,\overline{V}_i \tag{2.9}$$

Equations (2.7) and (2.8) may now be combined to give (Kett and Anderson, 1969)

$$\mathbf{J}_i^m = \mathbf{J}_i^v - (\mathbf{v}_m - \mathbf{v}_v)C_i \quad (i = A, B) \tag{2.10}$$

The only kind of diffusion induced bulk volume flow indicated by diffusion experiments in liquids is due to volume change on mixing. Hence, in a usual diffusion experiment $\mathbf{v}_m = \mathbf{v}_v$, and $\mathbf{J}_i^m = \mathbf{J}_i^v$.

As far as purely phenomenological relations are concerned, Fick's law and its generalized forms are adequate, but when attempts are made to relate the diffusion coefficients to other observable properties it becomes necessary to investigate the nature of the driving force of diffusion more thoroughly. It is now well established from irreversible thermodynamics (Denbigh, 1971) that the driving force of diffusion is the gradient of chemical potential, instead of the concentration gradient. As a consequence, D_{AB} as defined by Equation (2.2) must be corrected. The corrected diffusivity D_{AB}^{id} was shown (for example, Dullien, 1960, p. 72) to be

$$D_{AB}^{id} = D_{AB}/\beta \tag{2.11}$$

where

$$\beta = \frac{d\,\ln a_i}{d\,\ln x_i} \quad (i = A, B) \tag{2.12}$$

a_i in this equation is activity on the mole fraction scale and x_i is the mole fraction. β is generally called the thermodynamic factor.

There are, however, some authors (for example, Danckwerts, 1971) who question how the gradient of chemical potential can exert a force on a molecule, arguing that diffusion is a randomizing process and not a flow of matter subject to a driving force. It is an incontrovertible fact, however, that a randomizing tendency may result in a real and sometimes very powerful force. For example, randomizing tendency is responsible for the elasticity of elastomers, such as rubber.

3. LIQUID STATE THEORIES AND DIFFUSION

The complications in the structure of liquids are partly due to the dense packing of the molecules. Unlike in gases the time-average distance between molecules in liquids is very small, and the molecules are always in the range of intermolecular forces. However, the effect of these intermolecular forces in liquids cannot be easily taken into account mathematically because the molecules are not confined to fixed lattice sites as they are in solids.

The case of dilute gases in which the assumption of binary collisions is valid has been treated by Chapman and Enskog (Chapman and Cowling, 1970). For fluids of liquid densities interactions between more than two molecules have to be considered for an exact description of the transport properties. These problems and the recent approaches have been discussed by Mazo (1967) and others (for example, Rehman, 1964; Bruin, 1969; Raveche and Mayer, 1970). Kirkwood (1946) obtained a mathematically tractable solution by time-smoothing procedure. Although theories such as Green's (1952) which make an attempt to solve N-body nonequilibrium problems in a rigorous manner appear to be of enormous consequences, they have not yet reached a stage where they can be applied for direct comparison with the experiment. These kinds of theories, therefore, will be omitted from our discussions.

In view of the difficulties in the theories mentioned above, model approaches such as the cell model, free volume model, small-step diffusion model, and the rate process theory have been resorted to. Model approaches discussed in Part II may help to visualize diffusion processes and the structure of liquid.

4. MUTUAL AND INTRADIFFUSION THEORIES AND THEIR COMPARISON WITH EXPERIMENTAL DATA

Most theories of diffusion proposed so far have had either hydrodynamic, kinetic, statistical-mechanical, or thermodynamic foundations, or combinations of these. Although the various theories originated from entirely different concepts, it has been possible (Bearman, 1961; McLaughlin, 1969) to show striking similarities between them under certain restricted conditions. These theories have also been discussed in the light of the experimental data.

Hydrodynamic Theories

The Stokes-Einstein Equation. The basic Stokes-Einstein equation was developed by Einstein (1905) using random-walk motion as a model. According to this motion, the diffusion coefficient is given by

$$D_{AB} = kTq = kT\,\frac{v}{F} \tag{4.1}$$

where q is the mobility or average velocity v of the diffusing particle per unit frictional force F acting on the particle. q can also be recognized as the reciprocal of certain friction coefficients appearing in other theories (Lamm, 1952; Bearman, 1961; Laity, 1959). In spite of the fact that concerted efforts have been made to relate mobility or friction coefficients to molecular properties, little success has been achieved so far. Calculating mobilities form Stokes' equation (Lamb, 1945) for the two limiting cases of the coefficient of sliding friction β_f and substituting them in Equation (4.1), the following equations are obtained:

$$D_{AB} = \frac{kT}{6\pi r_A \eta_B} \quad \text{when} \quad \beta_f = \infty \tag{4.2}$$

and

$$D_{AB} = \frac{kT}{4\pi r_A \eta_B} \quad \text{when} \quad \beta_f = 0 \tag{4.3}$$

Equation (4.2), generally known as the Stokes-Einstein equation, and Equation (4.3) have been applied to describe both self-, intra, and mutual diffusion data with varying degrees of success. The validity of these equations will now be discussed in the light of the mutual and intradiffusion data. The validity of these equations with regard to the self-diffusion data is discussed in Part II.

The Stokes-Einstein equation should be applicable to describe diffusion strictly for spherical or nearly spherical molecules in solvents of considerably smaller molecules. The diffusivities of colloid particles in a variety of solvents compare favorably with this equation. It has thus become general practice to calculate the size of the diffusing particles using the Stokes-Einstein equation. In a

TABLE 1. STOKES' LAW RADII FOR SOLUTES IN DILUTE AQUEOUS SOLUTIONS FROM MEASUREMENTS OF MUTUAL DIFFUSION COEFFICIENTS AT DIFFERENT TEMPERATURES (FROM LONGSWORTH) (TYRRELL, 1961, P. 173)

	Stokes' law radius A				$r \times 10^{10}$
Substance	T, 1°C	T, 13°C	T, 25°C	T, 37°C	m
HDO	1.021	—	1.072	—	1.93
Urea	1.672	1.718	1.758	1.802	2.59
Glycine	2.235	2.269	2.296	2.332	2.58
Alanine	2.667	2.661	2.664	2.676	2.88
Dextrose	3.670	3.643	3.601	3.584	3.53
Cyclo-hepta-amylose	7.716	7.588	7.516	7.467	6.56
Bovine plasma albumin	37.55	37.30	36.84	—	27.0

TABLE 2. EXPERIMENTAL INTRA-DIFFUSION COEFFICIENT-TO-STOKES-EINSTEIN RATIOS IN CCl_4 SOLUTIONS (AGISHEV AND EMEL'YANOV, 1964)

	Concentration (mole fraction)					
Substance	1	0,8	0,6	0,4	0,2	0
C_6H_{14}	1,73	1,86	1,95	2,00	2,36	2,90
C_8H_{18}	1,95	1,83	1,86	2,02	2,28	2,60
$C_{10}H_{22}$	2,18	2,05	2,00	2,02	2,16	2,30
$C_{12}H_{26}$	2,49	2,26	2,18	2,11	2,10	2,20
$C_{14}H_{30}$	2,85	2,61	2,41	2,20	2,10	2,02

study made by Longsworth (1954) on diffusion in aqueous solution, (see Table 1), it was shown that for large molecules the radii calculated from the Stokes-Einstein equation are a little larger than those available from the independent estimates. The difference is attributed to the hydration of the solute molecules and to the departure of these molecules from spherical shapes. The radii calculated from Equation (4.2) were found to decrease with increase in temperature, as expected, since the hydration number is likely to decrease as temperature increases (Tyrrell, 1961, p. 173).

It is now clear from the studies of several investigators (for example, see Table 2) that the Stokes-Einstein equation fails to describe intradiffusion of solutes of molecular dimensions. The range of validity of this equation for mutual diffusion has been discussed in considerable detail by Longsworth (1955). See Section 5, Part II for the failure of this equation in the case of self-diffusion.

Stokes' equation calculates the frictional force acting on a large, nonattractive spherical particle when it moves in a continuum, but the frictional forces acting on a particle of molecular dimensions cannot be expected to obtain accurately from this expression. Generally, the predicted values of diffusivities from Equation (4.2) are lower than the actual values. Equation (4.3) predicts a little larger values which are closer to the actual ones. However, some large deviations from this equation have also been noted (Tyrrell, 1961, p. 159). It is therefore believed that, in general, Equations (4.2) and (4.3) both fail to properly account for the frictional forces acting on solutes of molecular dimensions.

Several investigators have attempted to modify the Stokes-Einstein equation for shapes other than spherical. The reader is referred to Tyrrell's book on diffusion (1961, Ch. 6) for detailed discussion of this subject.

Other theoretical approaches, discussed later, such as those due to Hartley and Crank (1949), Eyring and coworkers (Glasstone et al., 1941), Dullien (1963), among others, yield expressions similar to the Stokes-Einstein equation under certain conditions (see Section 5.6, Part II).

Darken's Equation. Employing the concept that the diffusion of each component in a binary mixture is related to its mobility, Darken (1948) derived for solid metallic solutions a relation between mutual and intra-diffusion coefficients. This relation has also been widely used for liquid systems. According to Darken's theory, transport of each component across a fixed plane is different depending on the mobility of the species, resulting in bulk volume flow of the medium. In order to separate the diffusional flux from the bulk flow, Darken derived an expression for the velocity v_m of the medium with the assumption of constant C

$$v_m = \frac{1}{C} (D_A \nabla C_A + D_B \nabla C_B) \qquad (4.4)$$

where D_A and D_B are the so-called "intrinsic" diffusion coefficients for component A and B, respectively, and C is the total concentration $C = C_A + C_B$ (moles/unit volume). Darken obtained the following relationship between mutual and intrinsic diffusion coefficients

$$D_{AB} = x_B D_A + x_A D_B \qquad (4.5)$$

According to Darken the intrinsic diffusion coefficients can be equated to the intra-diffusion coefficient D_{i*} multiplied by the thermodynamic factor $\beta = d\ln a_i / d\ln x_i$, giving

$$D_{AB} = (x_B D_{A*} + x_A D_{B*})\beta \qquad (4.6)$$

Even though there are some legitimate questions regarding the applicability of the Darken approach in the case of liquids, Equation (4.6) has often been used.

Since precise values of intra-diffusion coefficients have been obtained experimentally, several investigators have tested the adequacy of the Darken equation. The ideal or nearly ideal systems on which the Darken equation has been tested are, for example, benzene + bromobenzene (Miller and Carman, 1959), n-hexane + n-dodecane

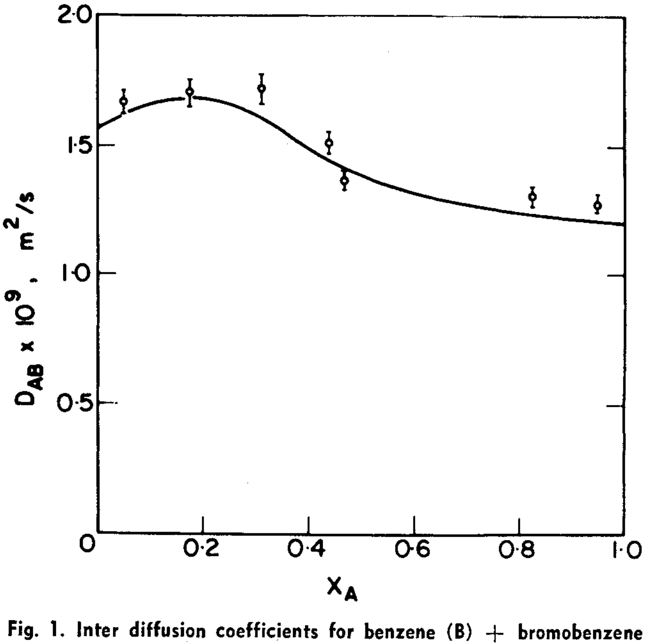

Fig. 1. Inter diffusion coefficients for benzene (B) + bromobenzene (A) system. Curve calculated from Darken's equation; O expt. values (Miller and Carman, 1959).

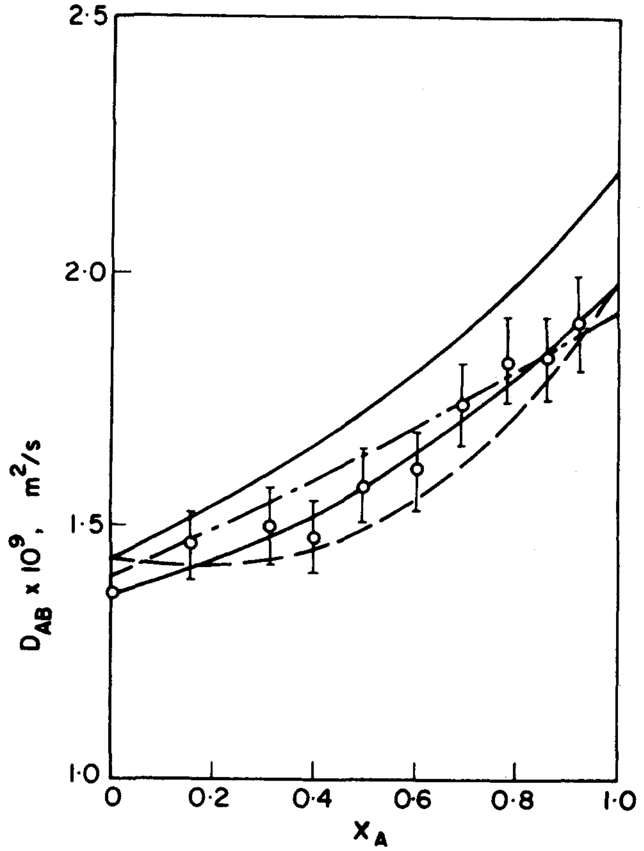

Fig. 2. Diffusion in the benzene (A) -carbon tetrachloride (B) system at 25°: — · —, mutual diffusion (Anderson et al., 1958); — —, Darken's equation; ——; inter diffusion of benzene (Johnson and Babb, 1956); O, intradiffusion of carbon tetrachloride (Hardt, et al., 1959).

Table 3. Comparison of Experimental D_{AB} Values With Predictions of the Darken Equation (4.6) and Equation (4.8) for the System Benzene-Diphenyl at 25°C (Mills, 1963)

$C_A \times 10^{-3}$ mol m^{-3}	$D_{AB} \times 10^9$ (m^2 s^{-1}) Expt.	Equation (4.6)	Equation (4.8)	D_B^*/D_A^*
0.5	1.450	1.421	1.439	1.45
1.0	1.342	1.301	1.331	1.45
1.5	1.242	1.200	1.241	1.45
2.0	1.147	1.103	1.148	1.46
2.5	1.062	1.021	1.066	1.46
3.0	0.977	0.940	0.984	1.46

(Shieh and Lyons, 1969), benzene + CCl$_4$ (Hardt et al., 1959), octane + decane (Van Geet and Adamson, 1964), heptane + cetane (Miller and Carman, 1962) and benzene + diphenyl (Mills, 1963). The experimental data for the system benzene + bromobenzene (see Figure 1) is approximately in accord with Darken's equation. For some other nearly ideal systems such as *n*-hexane + *n*-dodecane, octane + decane the maximum deviation was found to be, respectively, 2.3% at 25° (and 11.7% at 35°) and 0.63% at 25° (and 0.72% at 60°). For the system heptane + cetane the intradiffusion values corresponding only to equimolar composition were measured by Miller and Carman (1962). The D_{AB} value of 0.90 ± 0.08 × 10^{-5} cm^2/sec calculated from the Darken equation was in accord with the experimental value of 0.90 ± 0.03 × 10^{-5} obtained by Trevoy and Drickamer (1949) but differed from their own value of 0.98 ± 0.03 × 10^{-5}. Miller and Carman attributed this difference to experimental error. The mutual diffusion data for the system benzene + diphenyl, as shown in Table 3, is also in reasonable agreement with the Darken equation (average error 3.2%), but the agreement is poorer (average error 6%) for the

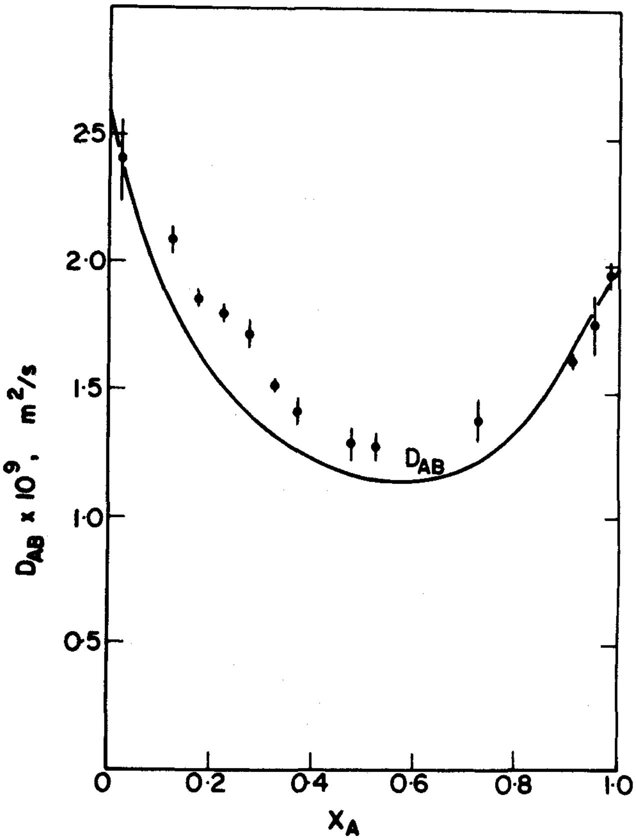

Fig. 3. Inter diffusion coefficients for benzene (B) + nitromethane (A) system. Curve calculated from Darken's equation; ● expt. values (Miller and Carman, 1959).

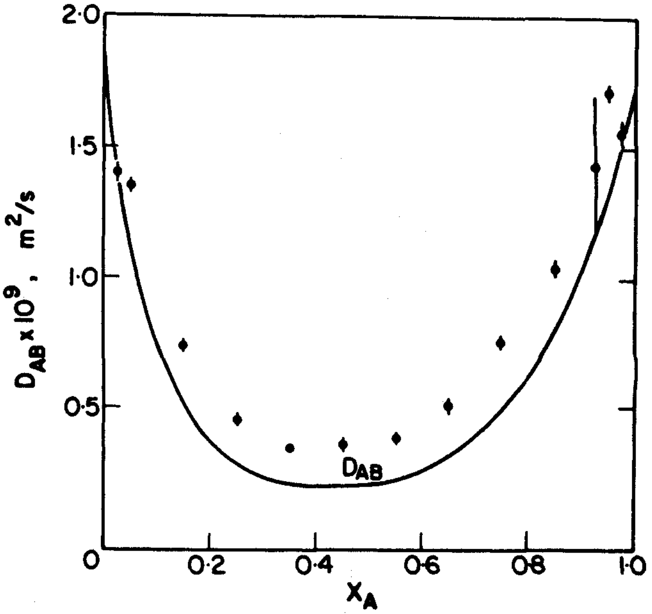

Fig. 4. Inter diffusion coefficients for CCl$_4$ (B) + nitromethane (A) system. Curve calculated from Darken's equation; ● expt. values (Carman and Miller, 1959).

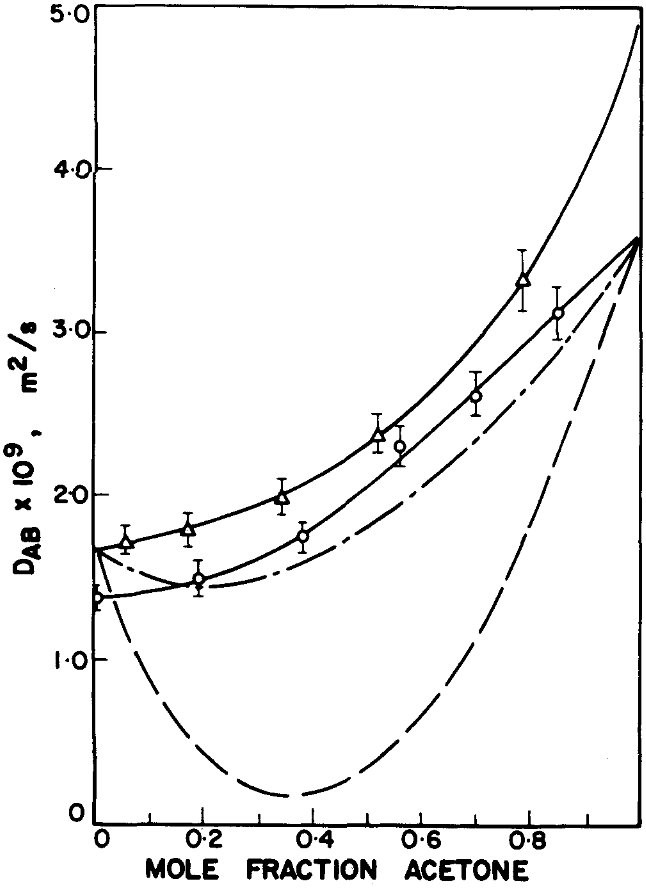

Fig. 5. Diffusion in the acetone-carbon tetrachloride system at 25°: — · —, mutual diffusion (Anderson et al., 1958); ——, Darken's equation; △, intradiffusion of acetone; O, self-diffusion of carbon tetrachloride (Hardt et al., 1959).

system benzene + CCl_4 (see Figure 2).

For the systems which depart widely from thermodynamic ideality the Darken equation breaks down, sometimes by a factor of eight. Comparisons of the Darken equation with experimental values are shown in Figures 3 to 7 for the systems nitromethane + benzene (Miller and Carman, 1959), nitromethane + CCl_4 (Carman and Miller, 1959), acetone + CCl_4, acetone + $CHCl_3$, and ethanol + CCl_4 (Hardt et al., 1959), and in Table 4 for the system benzene + cyclohexane (Kamal and McLaughlin, 1966).

For nonideal systems in which association or complex formation is known to occur, the Darken equation has been modified (Carman, 1967). The modified form of this equation, however, does not apply to other nonideal systems in which such effects are absent.

Hartley and Crank's Equation. The Hartley-Crank (1949) treatment of liquid diffusion is similar to Darken's treatment except that the former postulated that the velocity of the medium in a constant volume system, w.r.t. fixed coordinates is

$$v_m = D_A \overline{V}_A \nabla C_A + D_B \overline{V}_B \nabla C_B \qquad (4.7)$$

Evidently, Equation (4.7) simplifies to Equation (4.4) if $\overline{V}_A = \overline{V}_B = V$. The existence of v_m has not so far been demonstrated in liquids although some attempts have been made to that effect (Irani and Adamson, 1958; Freise, 1958). It is therefore best regarded as a fictitious quantity.

Applying similar arguments, as was done in Darken's treatment, the following relation has been obtained in place of Equation (4.6):

$$D_{AB} = (\phi_B D_{A*} + \phi_A D_{B*})\beta \qquad (4.8)$$

where ϕ is volume fraction. In the development of Equation (4.8), an assumption of constant partial molal volumes was made. This equation, however, can be developed also without making such an assumption (Ghai, 1973). As shown in Table 3, Equation (4.8) was found to be superior to the Darken equation and remarkably accurate by present day standards (averge error 0.5%) for the system benzene + diphenyl (Mills, 1963). The same

TABLE 4. COMPARISON OF CALCULATED AND EXPERIMENTAL MUTUAL DIFFUSION COEFFICIENTS FOR THE SYSTEM BENZENE (A) + CYCLOHEXANE (B) AT 25°C (KAMAL AND MCLAUGHLIN, 1966)

x_A	$D_{AB} \times 10^9$ ($m^2 s^{-1}$) Expt.	$D_{AB} \times 10^9$ ($m^2 s^{-1}$) Darken's Equation 4.6
0	1.880	1.88
0.1	1.859	1.75
0.2	1.833	1.66
0.3	1.809	1.60
0.4	1.796	1.58
0.5	1.797	1.60
0.6	1.815	1.63
0.7	1.847	1.68
0.8	1.903	1.75
0.9	1.991	1.87
1.0	2.101	2.07

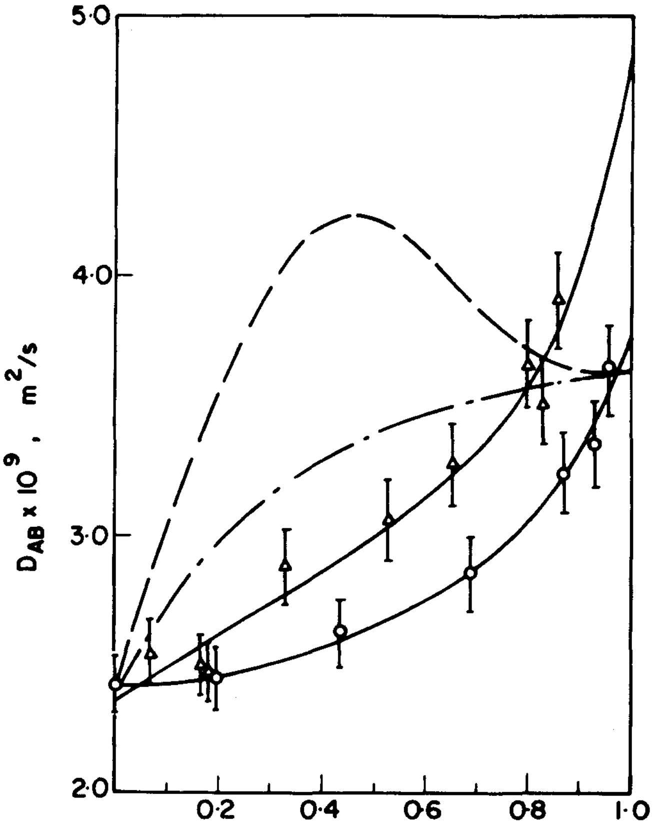

Fig. 6. Diffusion in the acetone-chloroform system at 25°: — · — mutual diffusion (Anderson et al., 1958); ——, Darken's equation; △, intradiffusion of acetone; O, intradiffusion of chloroform (Hardt et al., 1959).

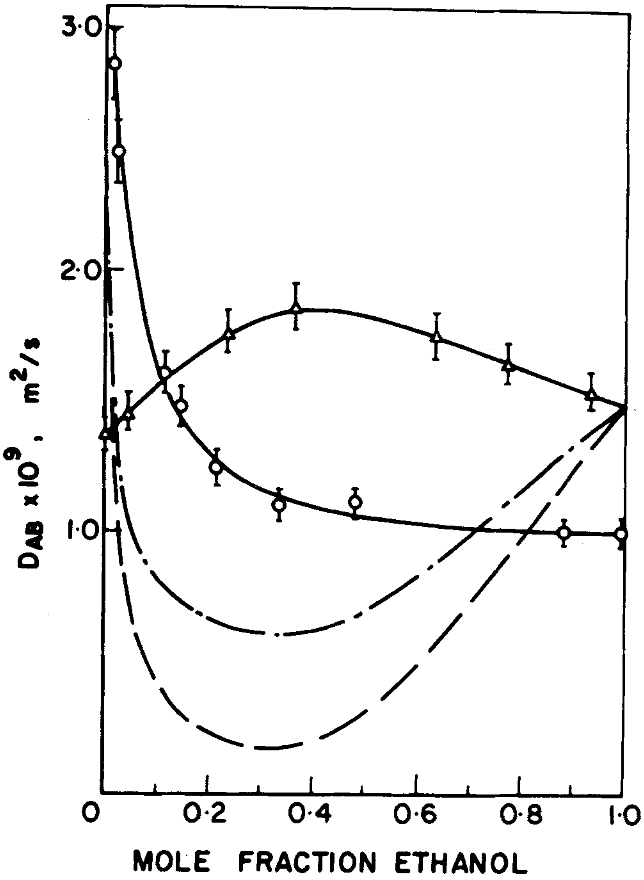

Fig. 7. Diffusion in the ethanol-carbon tetrachloride system at 25°: — · —, mutual diffusion; — — —, Darken's equation; △, intradiffusion of carbon tetrachloride; O, intradiffusion of ethanol (Hardt et al., 1959).

was found to be true for the system n-octane + n-dodecane (Van Geet and Adamson, 1964).

Another form of the Hartley-Crank equation is obtained (Carman and Stein, 1956) if the following assumption is made:

$$D_i = \frac{kT}{\sigma_i \eta} \frac{d\ln a_i}{d\ln C_i} \quad i = A, B \tag{4.9}$$

where σ_i is usually called *friction factor.* Noting that

$$\frac{d\ln a_A}{d\ln C_A} = \frac{V}{\bar{V}_B} \frac{d\ln a_A}{d\ln x_A} = \frac{V}{\bar{V}_B}\beta \tag{4.10}$$

the result is

$$D_{AB} = \frac{kT}{\eta}\left\{\frac{x_A}{\sigma_B} + \frac{x_B}{\sigma_A}\right\}\beta \tag{4.11}$$

Assuming that

$$D_{i*} = \frac{kT}{\sigma_i \eta} \tag{4.12}$$

where σ_i is composition-independent, Carman and Stein (1956) showed that Equation (4.11) leads to the Darken equation (4.6).

If $D_{AB}{}^0$ and $D_{AB}{}^\infty$ are the limiting mutual diffusion coefficients for $x_A \rightarrow 0$ and $x_A \rightarrow 1$, respectively, then according to all known theories of diffusion (with the assumption that the effect of mass difference due to labeling is negligible)

$$D_{AB}{}^0 = D_{A*}{}^0 \tag{4.13}$$

and

$$D_{AB}{}^\infty = D_{B*}{}^0 \tag{4.14}$$

where $D_{A*}{}^0$ and $D_{B*}{}^0$ are the limiting tracer diffusion coefficients for $x_A \rightarrow 0$ and $x_A \rightarrow 1$, respectively. The equality of the limiting values has been tested also experimentally with the help of accurate diffusion data (for example, Harris et al., 1970; Aoyagi and Albright, 1972).

It follows from Equation (4.12) (Carman and Stein, 1956).

$$D_{A*}\eta = D_{AB}{}^0 \eta_B = D_A{}^0 \eta_A \tag{4.15}$$

and

$$D_{B*}\eta = D_{AB}{}^\infty \eta_A = D_B{}^0 \eta_B \tag{4.16}$$

where $D_A{}^0$ and $D_B{}^0$ are self-diffusion coefficients of pure A and pure B, respectively.

With the help of Darken's equation (4.6) and Equations (4.15) and (4.16), a relationship for D_{AB} in terms of limiting values was obtained by Carman and Stein

$$D_{AB} = \frac{1}{\eta}(x_B \eta_B D_{AB}{}^0 + x_A \eta_A D_{AB}{}^\infty)\beta \tag{4.17}$$

One should bear in mind that in addition to the assumption of constant σ_i values, all those restrictions which apply to Darken's equations also apply to Equation (4.17).

Several investigators have tested their experimental data with the Hartley-Crank equation (4.11). The values of the friction factors σ_A and σ_B appearing in this equation were almost always calculated from the infinitely dilute component data, and the assumption was made that the influence of concentration on these factors was not significant. The mutual diffusivities were calculated using this equation for nonideal systems such as methyl-ethyl-ketone + carbon tetrachloride (Anderson and Babb, 1962) and diethyl ether + chloroform (Anderson and Babb, 1961), (see Figures 8 and 9). The calculated and the experimental values differ significantly. Since in this type of systems one of the components is known to be of associating or complex-forming type, it was assumed that the kinetic unit for diffusion is not a monomer. Anderson and Babb (1961, 1962), therefore, modified the Hartley-Crank equa-

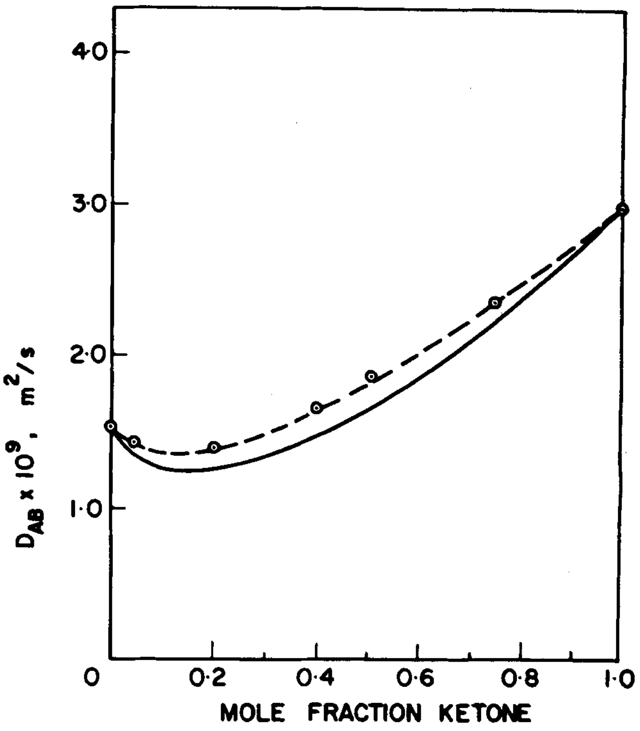

Fig. 8. Diffusion coefficients for the system methyl ethyl ketone-carbon tetrachloride: O, experimental; ——, calculated from Equation (4.11) (Anderson and Babb, 1962).

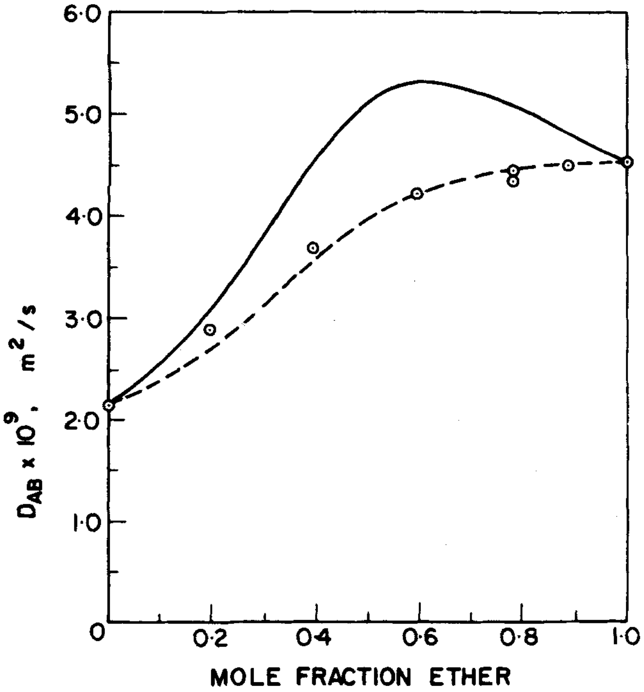

Fig. 9. Mutual diffusion data for the diethyl ether-chloroform system: O, experimental, 25°; ——, calculated from Equation (4.11) (Anderson and Babb, 1961).

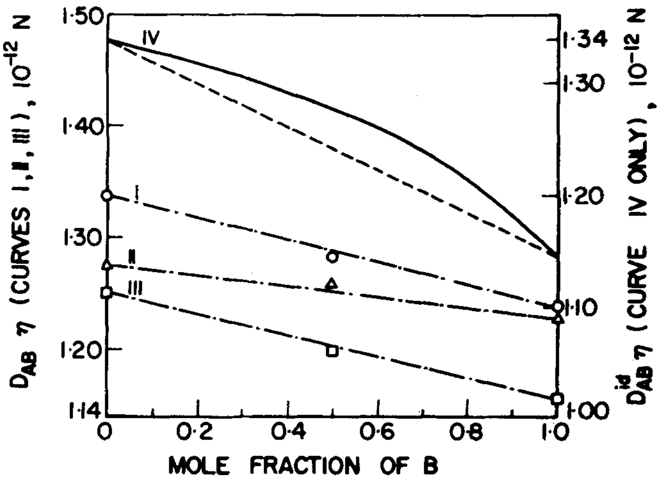

Fig. 10. Variation of $D_{AB}\eta$(or $D_{AB}^{id}\eta$) with composition for nearly ideal binary mixtures (Tyrrell, 1961). Curve I: C_6H_5Cl (A) + C_6H_5Br (B); Curve II: $C_6H_5CH_3$ (A) + C_6H_5Cl (B); Curve III: C_6H_6 (A) + CCl_4 (B); Curve IV: CCl_4 (A) + Cyclohexane (B).

tion and were successful in rationalizing the deviation from the experimental diffusion values for some systems (see the dotted lines in Figures 8 and 9). For the system sucrose-water (Carman, 1967) a series of complexes of AB_n type (where n can vary from 1 to 6) had to be assumed.

The Hartley-Crank equation has also been tested by plotting the group $D_{AB}\eta/\beta$ against molar composition. If σ_A and σ_B remain constant with composition, then according to Equation (4.11) the group $D_{AB}\eta/\beta$ should be a linear function of the mole fraction for isothermal diffusion. Bearman (1961) showed that the Bearman-Kirkwood theory and Eyrings' theory also lead to the same linear function for regular solutions. Since the thermodynamic factor β is unity for ideal solutions, the product $D_{AB}\eta$ has been plotted against molar composition for several ideal or nearly ideal systems such as chlorobenzene + bromobenzene, toluene + chlorobenzene, benzene-carbon tetrachloride (Caldwell and Babb, 1956), and carbon tetrachloride + cyclohexane (Hammond and Stokes, 1956). Except for the last system the product varies linearly with the mole fraction, Figure 10. For the other nearly ideal systems hex-

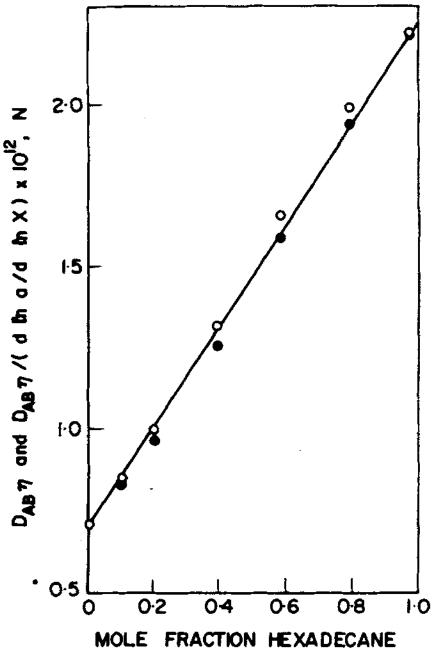

Fig. 11. $D_{AB}\eta$ and $D_{BA}\eta/\beta$ as a function of mole fraction for the system heptane-hexadecane: ——, linear or ideal behavior; O, $D_{AB}\eta$; ●, $D_{AB}\eta/\beta$ (Bidlack and Anderson, 1964a).

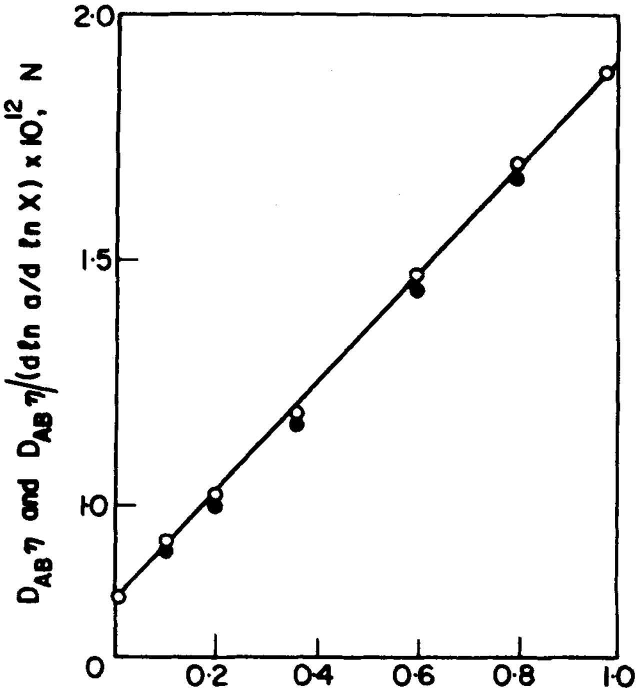

Fig. 12. $D_{AB}\eta$ and $D_{AB}\eta/\beta$ as a function of mole fraction for the system hexane-dodecane: ——, linear or ideal behavior; O, $D_{AB}\eta$; ●, $D_{AB}\eta/\beta$ (Bidlack and Anderson, 1964a).

ane + dodecane, heptane + hexadecane, and hexane + hexadecane, linear or nearly linear plots were obtained (Figures 11 to 13). The deviation from the straight line is, however, pronounced for increasingly nonideal systems. The plots of $D_{AB}\eta/\beta$ for the nonideal systems acetone + water, acetone + CCl_4, acetone + benzene, and acetone + chloroform (Anderson et al., 1958) are displayed in Figures 14 to 17.

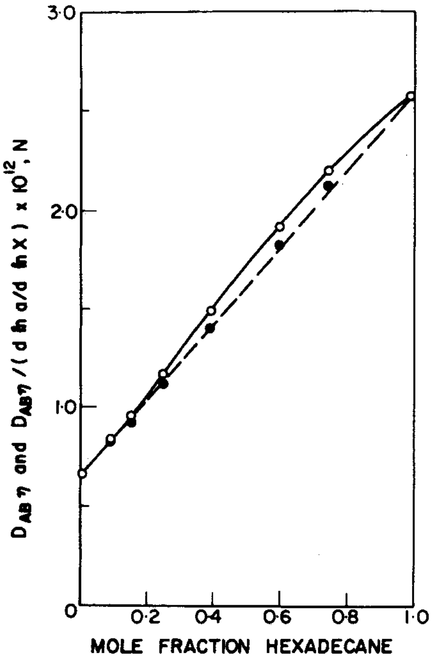

Fig. 13. $D_{AB}\eta$ and $D_{AB}\eta/\beta$ as a function of mole fraction for the system hexane-hexadecane; ———, ideal or linear behavior; O, $D_{BA}\eta$; ●, $D_{AB}\eta/\beta$ (Bidlack and Anderson, 1964a).

The introduction of the thermodynamic factor generally overcorrects the diffusion data regardless of the nature of the system. The departure from linearity was attributed to the formation of the molecular aggregates which are customarily believed to be the kinetic units. While the existence of such aggegates in some solutions has been firmly established from the study of a variety of equilibrium properties, there is very little known about the kinetic properties of the complexes.

Critical experimental study of the diffusion of acetic acid and its homomorphs in dilute CCl_4 solutions (Dullien and Shroff, 1972) has indicated, however, that the kinetic units of diffusion are not likely to be the acetic acid dimers. These findings cast some doubts on the general validity of assuming molecular aggregates as kinetic units of diffusion in associating solutions. It is more likely that the monomers forming a complex are kinetically independent neighbors in most cases (Dullien, 1963).

In some binary nonideal systems there exists no evidence that molecular aggregates are formed. Nonideality in these systems is caused by differences in shape and size of the molecules. It is of interest to see whether for such binary systems the Hartley-Crank equation is obeyed. A few such systems, for example, hexane + CCl_4 (Bidlack and Anderson, 1964a, 1964b), and benzene + OMCTS and CCl_4 + OMCTS (Marsh, 1968) were used to test the Hartley-Crank equation with negative results. See Fig-

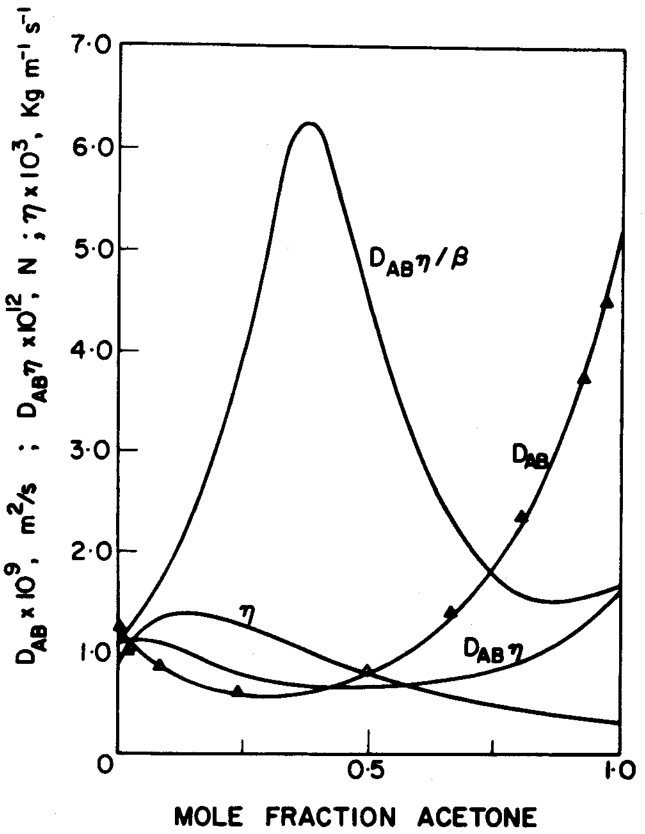

Fig. 14. Mutual diffusion, viscosity, and uncorrected and activity corrected $D_{AB}\eta$ products for acetone-water system at 25.15° (Anderson et al., 1958).

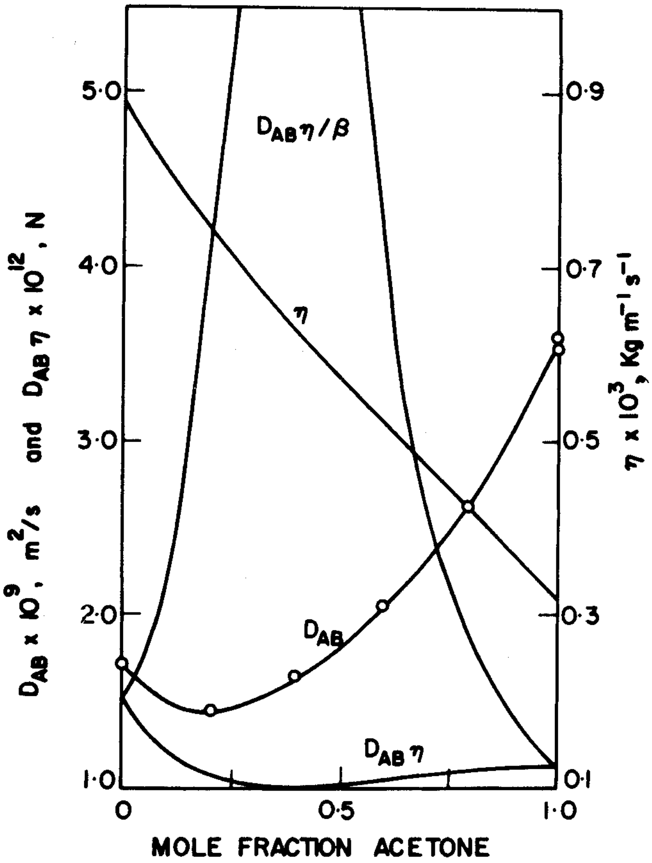

Fig. 15. Mutual diffusion data for acetone-carbon tetrachloride system at 25.15°; uncorrected and activity corrected $D_{AB}\eta$ products, left hand scale; viscosity on right hand scale (Anderson et al., 1958).

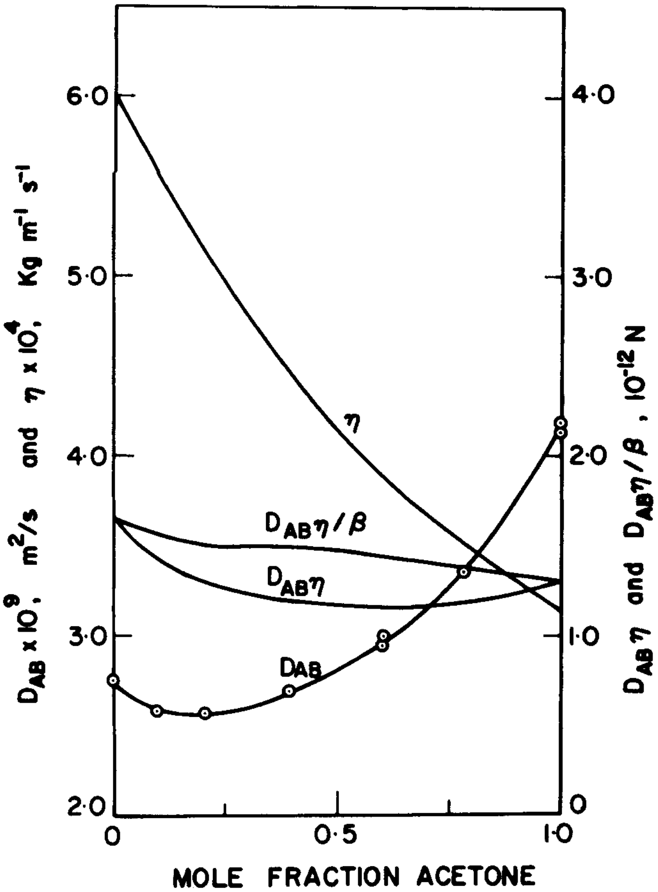

Fig. 16. Diffusion and viscosity data for the acetone-benzene system at 25.15°; D_{AB} and η, left-hand scale; $D_{AB}\eta$ and $D_{AB}\eta/\beta$, right-hand scale (Anderson, et al., 1958).

ures 18, 19, and 20. The failure of the Hartley-Crank equation might be due to composition dependence of the friction factors. Rodwin, Horpst, and Lyons (1965) and Kulkarni, Allen, and Lyons (1965) assumed a linear dependence of the friction factors and applied the Hartley-Crank equation for the systems benzene + cyclohexane and CCl_4 + cyclohexane, respectively. They found that the calculated values agreed fairly well with their experimentally measured values, primarily because of the four adjustable parameters used.

Now we shall examine the validity of Equations (4.12),

Table 5. Values of $D_{A^*}\eta$, $D_{B^*}\eta$ and D_{A^*}/D_{B^*} at 25°C (Kamal and McLaughlin, 1968)

Benzene (A) + Toluene (B)				Cyclohexane (A) + Toluene (B)			
x_A	$D_A^*\eta$ $10^{-12}N$	$D_B^*\eta$ $10^{-12}N$	D_A^*/D_B^*	x_B	$D_B^*\eta$ $10^{-12}N$	$D_A^*\eta$ $10^{-12}N$	D_B^*/D_A^*
0	1.33	1.27	1.05	0	1.56	1.31	1.19
0.1	1.35	1.29	1.05	0.1	1.50	1.31	1.15
0.2	1.35	1.29	1.05	0.2	1.46	1.30	1.12
0.3	1.36	1.31	1.04	0.3	1.44	1.31	1.10
0.4	1.37	1.31	1.05	0.4	1.41	1.30	1.09
0.5	1.37	1.31	1.05	0.5	1.38	1.28	1.08
0.6	1.37	1.31	1.05	0.6	1.36	1.28	1.06
0.7	1.37	1.31	1.05	0.7	1.35	1.28	1.06
0.8	1.36	1.31	1.04	0.8	1.33	1.26	1.06
0.9	1.36	1.31	1.04	0.9	1.32	1.24	1.07
1.0	1.35	1.30	1.04	1.0	1.30	1.21	1.07

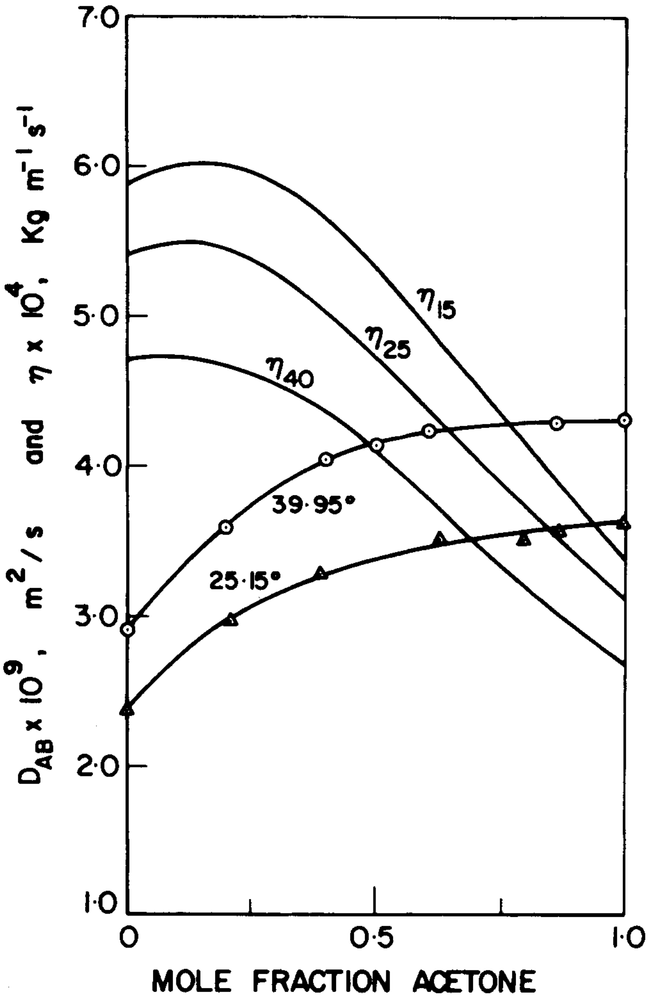

Fig. 17. Mutual diffusion and viscosity data for the acetone-chloroform system: O, expt. values at 39.95°; △ expt. values at 25.15° (Anderson et al. 1958).

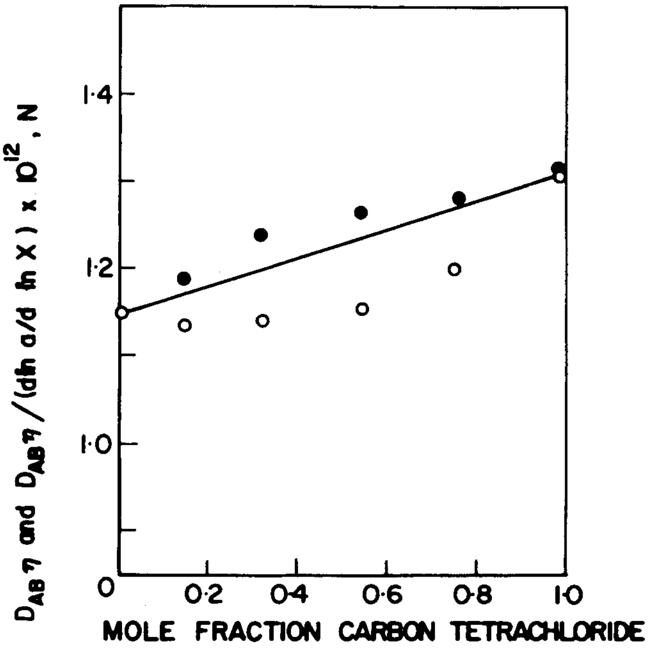

Fig. 18. $D_{AB}\eta$ and $D_{AB}\eta/\beta$ as function of mole fraction for the system hexane-carbon tetrachloride; ——, Hartley-Crank equation; O, $D_{AB}\eta$ expt.; ●, $D_{AB}\eta/\beta$ expt. (Bidlack and Anderson, 1964b).

(4.15), and (4.16). Equations (4.15) and (4.16) can also be obtained from Equation (4.1) if the friction coefficient (reciprocal of mobility) appearing in the latter equation is assumed to be linearly related to the viscosity of the solution. The same result has been obtained from the Bearman-Kirkwood theory (Bearman, 1960) for regular solutions. By virtue of Equation (4.15), Equation (4.12) may also be written as

$$\frac{D_{AB}{}^0\,\eta_B}{kT} = \frac{1}{\sigma_i} \tag{4.18}$$

According to this, the group $D_{AB}{}^0\,\eta_B/T$ should be independent of T for a given system if the friction factor σ_i remains unaltered. There is no apparent reason for this to be a constant, and the scarcity of accurate mutual diffusion data over an extended temperature range has so far prevented a thorough investigation of this equation.

Some attempts have been made to correlate the group $D_{AB}{}^0\,\eta_B/T$ with the properties of the solutes in the same solvent (Wilke and Chang, 1955; Hayduk and Cheng, 1971; Innes and Albright, 1957). Wilke and Chang (1955) correlated this group with the molal volume of the solute. The recent empirical study of Hayduk and Cheng (1971) has found that the group $D_{AB}{}^0\,\eta_B{}^A$ under isothermal conditions is fairly constant for a mixture of normal components (that is, components in which no molecular aggregation occurs). The relationship they found is of the form

$$D_{AB}{}^0\,\eta_B{}^A = B \tag{4.19}$$

where the values of parameters A and B depend solely on the properties of the solute.

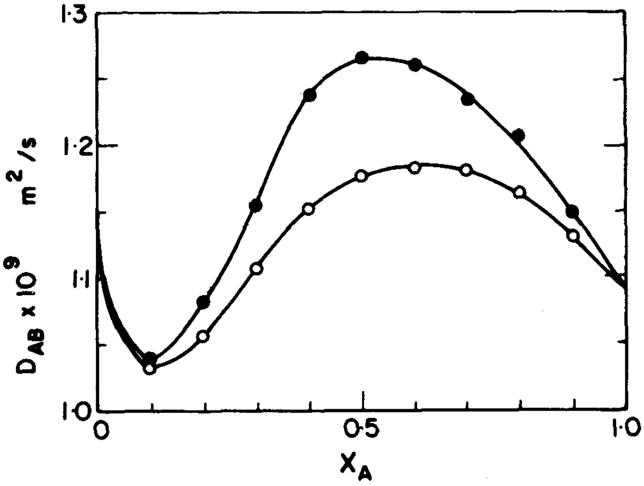

Fig. 19. Mutual diffusion coefficients for the system OMCTS (A) + benzene (B) at 25°C: ○, D_{AB} expt.; ●, D_{AB} calc. from Hartley-Crank equation (Marsh, 1968).

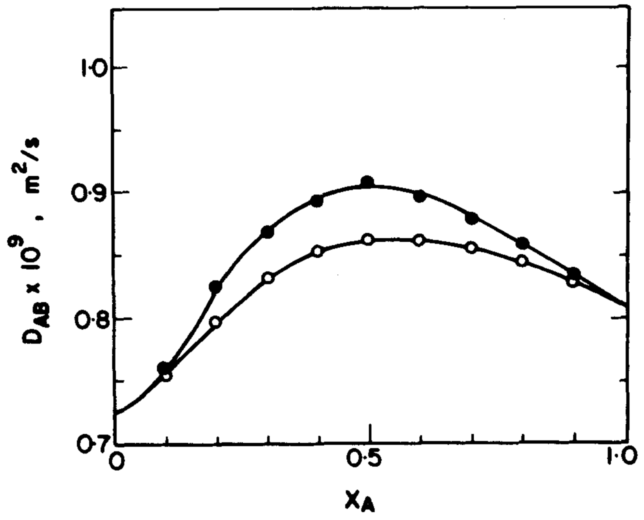

Fig. 20. Mutual diffusion coefficients for the system OMCTS (A) + carbon tetrachloride (B) at 25°C: ○, D_{AB} expt.; ●, D_{AB} calculated from Hartley-Crank equation (Marsh, 1968).

TABLE 6. PRODUCTS $D^*\eta$ AT 19.35°C, USING VALUES OF D^* FROM SMOOTHED CURVES (CARMAN AND STEIN, 1956)

x_A	$D_{EtI}{}^*\eta \times 10^{12}$ N	$D_{BuI}{}^*\eta \times 10^{12}$ N
1.0	1.31	1.23
0.8	1.32	1.21
0.6	1.33	1.18
0.4	1.31	1.18
0.2	1.31	1.19
0	1.30	1.18

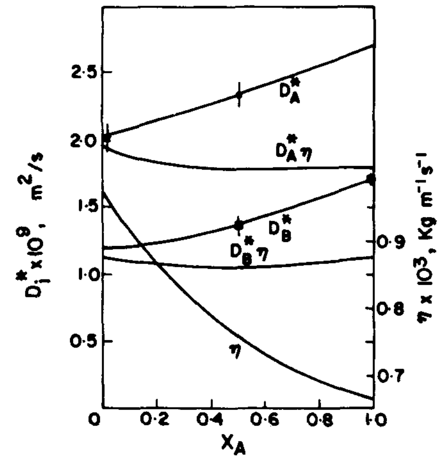

Fig. 21. Intra-diffusion coefficients for CCl_4(B) + nitromethane (A) system; ●, nitromethane; ■, CCl_4. Also curve for viscosity η of the mixture and curves for $D_{A*}\eta$ and $D_{B*}\eta$ (Carman and Miller, 1959).

Some attempts to relate the group $D_{AB}{}^0\,\eta_B$ either to the properties of the solvent (Hammond and Stokes, 1955; Stokes et al., 1953) or both to the properties of solute and solvent (Lusis and Ratcliff, 1968) have been made. They all fail for the associating and complex forming type of solutions.

The product $D_{i*}\eta$ has also been frequently plotted against composition at a constant temperature for a variety of mixtures, categorized as (1) ideal systems, (2) nonideal systems, and (3) associating and complex-forming systems. This product, according to Equation (4.12), should be composition independent only if σ_i is insensitive to composition changes. The assumption that σ_i is composition independent is likely to be valid only for a highly restricted class of solutions in which the radial distribution functions do not change with the composition. For this type of systems, this product, as shown in Table 5 for the system benzene + toluene (Kamal and McLaughlin, 1968) and in Table 6 for the system ethyl iodide + butyl iodide (Carman and Stein, 1956), does not vary with composition. For n-octane + n-dodecane (Van Geet and Adamson, 1964), the products $D_i\eta$ vary about 30%

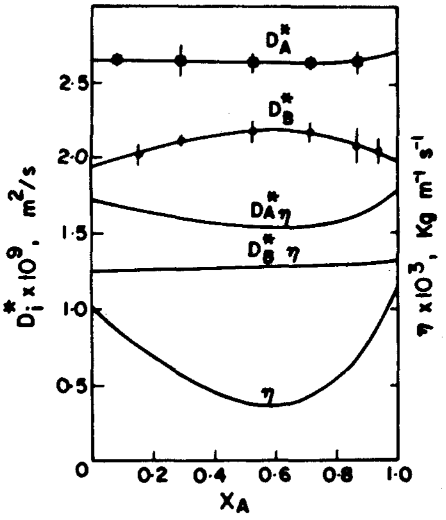

Fig. 22. Intra-diffusion coefficients for benzene (B) + nitromethane (A) system. ■, nitromethane; ●, benzene. Also curve for viscosity η and curves for $D_A*\eta$ and $D_B*\eta$ (Miller and Carman, 1959).

TABLE 7. INTRADIFFUSION AND RELATED DATA FOR BENZENE AT 25°C (MILLS, 1971)

mol % OMCTS	$D^* \times 10^9$ $m^2\,s^{-1}$	$\eta \times 10^3$ $kg\,m^{-1}\,s^{-1}$	$D^*\eta \times 10^{12}$ N
0.0	2.207	0.602	1.33
10.16_3	2.107	0.672	1.42
19.18_5	1.992	0.762	1.52
40.41	1.713	1.024	1.75
60.77	1.464	1.336	1.96
80.50	1.268	1.724	2.19
97.98	1.110	2.140	2.38
100 (extrap)	1.095	2.190	2.40

over the entire composition range for both the components, although this may be regarded as an almost ideal mixture. Similar deviations have been observed for other nearly ideal systems such as benzene + bromobenzene (Miller and Carman, 1959), benzene + carbon tetrachloride (Horrocks and McLaughlin, 1962), and carbon tetrachloride + cyclohexane (Horrocks and McLaughlin, 1962; Nishi et al., 1971).

Although near constancy of the products $D_{i*}\eta$ have been observed for the nonideal systems nitromethane + carbon tetrachloride (Carman and Miller, 1959) and nitromethane + benzene (Miller and Carman, 1959), see Figures 21 and 22, it should be noted that the data for the above systems are associated with large errors. Indeed it is very important that the data for both the intradiffusion and the viscosity coefficients should be highly accurate for these calculations.

In the nonideal systems toluene + cyclohexane and benzene + OMCTS, as shown in Tables 5 and 7, and in some others (Agishev and Emel'yanov, 1969) the product $D_{i*}\eta$ has been found to vary with composition. The reason for this behavior may be attributed to the invalidity of the assumption of the constancy of the friction factor σ_i.

Eyring's Theory

Eyring et al. applied the absolute reaction rate theory to the problem of describing diffusion and viscosity in liquids (Glasstone et al., 1941; Kincaid et al., 1941). This work has been reviewed extensively (Johnson and Babb, 1956a; Tyrrell, 1961; McLaughlin, 1960). During the past few years some modifications and some corrections to this theory have been proposed.

According to the absolute reaction rate theory, diffusion is considered as an activated rate process, taking place by jumping of a molecule from one position to another. This theory assumes that both diffusion and flow ordinarily involve only one molecule at a time. Although this may be true for solids, there are reasons to believe that a large number of molecules cooperate in diffusion and flow in liquids (Tyrrell, 1970; Fehder et al., 1971).

As suggested originally by Eyring et al., their equations should hold in dilute or ideal solutions. It has been pointed out, however, that they should rather apply to solutions in which there is a uniform concentration (Ree et al., 1958; Bearman, 1961; Hirschfelder et al., 1964), for only in this case is a diffusing molecule in a uniform environment and can it move across a given plane in either direction with equal likelihood.

In Eyring's original theory of viscosity, the effect of velocity of the neighboring molecules in the same layer was neglected. This was pointed out by Li and Chang (1955) who obtained the following equation:

$$D_{AB}{}^{id} = \frac{a-b}{2a}\,\frac{kT}{\eta}\left\{\frac{N}{V}\right\}^{1/3} \tag{4.20}$$

where a is the number of nearest neighbors in all the directions and b is the number of nearest neighbors in one layer. For simple cubic packing ($a = 6$, $b = 4$), Equation (4.20) reduces to

$$D_{AB}{}^{id} = \frac{kT}{6\eta}\left\{\frac{N}{V}\right\}^{1/3} \tag{4.21}$$

This equation has the same form and the same numerical factor as the Stokes-Einstein equation.

For a nonideal solution, Eyring et al. postulated

$$D_{AB} = D_{AB}{}^{id}\,\frac{\partial \ln a_A}{\partial \ln x_A} \tag{4.22}$$

If the activation energy is related to vaporization energy $\Delta U_{\rm vap}$, Eyring's equation for diffusion becomes (Kincaid et al., 1941).

$$D_{AB} = \left\{\frac{V}{N}\right\}^{2/3}\frac{1}{V_f{}^{1/3}}\left\{\frac{RT}{2\pi m}\right\}^{1/2}\exp\left\{-\frac{\Delta U_{\rm vap}}{nRT}\right\} \tag{4.23}$$

where V_f is the free volume, m is the mass of a molecule, and n is an adjustable parameter.

Another form of Equation (4.23) which has been used for self-diffusion is

$$D = \frac{\lambda^2}{V_f{}^{1/3}}\left\{\frac{kT}{2\pi m}\right\}^{1/2}\exp(-e/kT) \tag{4.24}$$

where e is the activation energy for the diffusion process (McLaughlin, 1959). The activation energy was calculated from the Devonshire theory of liquids (Lennard-Jones and Devonshire, 1937). The activation energy was believed to arise from two contributions. The first contribution is a function of the number density of unoccupied lattice sites, and the second contribution represents the potential barrier for diffusion and is expressed as some fraction w of the lattice energy. If ϵ is the depth of L-J potential-well, the following equation has been obtained by McLaughlin (1959). See also Collings and Mills (1970):

$$\frac{e}{kT} = \frac{\epsilon}{kT}(N\lambda^3/V)^4 + \frac{w\epsilon}{kT}\{14.454(N\lambda^3/V)^2 - 6.066\,(N\lambda^3/V)^4\} \quad (4.25)$$

There were two approximations made in determining w. As a first approximation w was empirically chosen to be 1/3, and as a second approximation w was expressed as a function of the reduced temperature,

$$w = 0.28\ T/T_c + 0.169 \quad (4.26)$$

where T_c is the critical temperature.

McLaughlin showed that Equation (4.24) predicts self-diffusion data of benzene, carbon tetrachloride, and argon within about 10% in the first approximation, and within 8% in the second approximation. Eyring's equation (4.23) predicts the values with about twice the error for the same systems. Table 8 shows the recent and most accurate values of the self-diffusion of benzene and carbon tetrachloride at several temperatures measured by Collings and Mills (1970) together with the diffusion values calculated from Equation (4.24) in the first and second approximations.

An important assumption in Eyring's theory is that the free energies of activation for diffusion and viscous flow ($\Delta G_D\#$ and $\Delta G_v\#$, respectively) are equal. Olander (1963a) and Gainer and Metzner (1965) have suggested approximate methods to calculate the difference between $\Delta G_D\#$ and $\Delta G_v\#$ which are discussed briefly in Part II.

Even for ideal or nearly ideal systems the assumption of equal free energies of activation was found to be invalid (Van Geet and Adamson, 1964; Shieh and Lyons, 1969). In mixtures of n-alkanes $\Delta G_D\#$ for intradiffusion was found to be the same for each component at a given concentration and the ratio $\Delta G_D\#/\Delta G_v\#$ fairly constant over the entire composition range. Both $\Delta G_v\#$ and $\Delta G_D\#$ were found to be linearly related to the mole fraction.

Lamm-Dullien Approach

A completely different approach than those employed by Hartley and Crank and Darken, involving no assumption of independent intrinsic mobilities, was put forward by Lamm (1943a, 1943b, 1952, 1954). According to his approach, diffusion is governed by mutual friction between the components. The gradient of the chemical potential was set proportional to the relative velocity of the diffusing species, the proportionality coefficient being the friction coefficient. To describe mutual and intradiffusion in binary mixtures, Lamm considered a three-component system consisting of A, B, and either tagged A, or tagged B. He obtained the following three equations:

$$\frac{D_{AB}}{\beta} = \frac{RT}{\phi_{AB}} = \frac{RT\,x_A}{\phi_{B(A)}} = \frac{RT\,x_B}{\phi_{A(B)}} \quad (4.27)$$

$$D_{A*} = \frac{RT}{\phi_{A^0A*} + \phi_{A(B)}} \quad (4.28)$$

and

$$D_{B*} = \frac{RT}{\phi_{B^0B*} + \phi_{B(A)}} \quad (4.29)$$

where A^0 and B^0 represent untagged A and B molecules, and A^* and B^* represent tagged A and B molecules, respectively; $\phi_{i(j)}$ and $\phi_{j(i)}$ are, respectively, the molar friction coefficients between components i and j per mole of i and per mole of j; ϕ_{ij} is given by

$$\phi_{ij} = \phi_{i(j)} + \phi_{j(i)} \quad (4.30)$$

i and j can be any one of A^0, B^0, A^*, B^*, $A = A^0 + A^*$, or $B = B^0 + B^*$.

Table 8. Comparison of Experimental Diffusion Coefficients With Those Calculated from Equation (4.25) Using First and Second Approximations Mentioned in this Paper (Collings and Mills, 1970)

		$D \times 10^9$ (m² s⁻¹)			
Liquid	T (°C)	Expt.	First App.	Second App.	Equation (4.24)
Benzene	15	1.86	1.40	1.61	3.10
	25	2.21	1.80	1.95	3.80
	35	2.61	2.28	2.33	4.54
	45	3.01	2.86	2.76	5.24
Carbon tetrachloride	15	1.09	1.06	1.16	2.60
	25	1.30	1.42	1.49	2.97
	30	1.42	1.61	1.65	3.21
	40	1.68	2.01	1.98	3.77
	50	1.93	2.50	2.31	4.51

With the assumption that the friction between the molecular species of the same component is not affected by the amount of the other component present in the mixture, Lamm (1954) obtained the following equation:

$$\frac{1}{D_{A*}} \simeq \frac{1}{V}\left\{\frac{x_A V_A{}^0}{D_A{}^0} + \frac{x_B V}{D_{AB}}\right\}\beta \quad (4.31)$$

where $D_A{}^0$ and $V_A{}^0$ are, respectively, self-diffusion coefficient and molal volume for pure component A.

It will be seen later that with a similar assumption the Bearman-Kirkwood theory also simplifies to the above equation. Because of the assumption used, the above equation is not expected to conform closely to the experimental data. The observed and calculated intradiffusion coefficients for the system benzene + carbon tetrachloride were found to agree within 10% (Johnson and Babb, 1956b). Miller and Carman's measured intradiffusion values of 0.54×10^{-5} cm²/sec for cetane and 1.18×10^{-5}, for heptane, in an equimolar cetane-heptane mixture, do not compare favorably with the calculated values of 0.38×10^{-5} and 1.43×10^{-5} cm²/sec.

As can be seen from Lamm's equations (4.27) to (4.29), while in tracer diffusion friction between both the like and the unlike molecules is involved, in mutual diffusion only friction between unlike molecules is of importance. The same holds true for the statistical-mechanical theory and the diffusion theory based on irreversible thermodynamics. In viscous flow, on the other hand, all three friction coefficients may be expected to play a role.

Assuming that the friction coefficients in diffusive and viscous flow are the same, Dullien (1963) proposed a simple relation between viscosity and diffusion coefficients. He first evaluated the molar average friction coefficient η^* in terms of the molar frictions appearing in Lamm's equations (4.27) to (4.29)

$$\eta^* = x_A\left(\phi_{A(B)} + \frac{1}{2}\phi_{A^0A*}\right) + \frac{1}{2}x_B\,\phi_{B^0B*} \quad (4.32)$$

Noting that η^* and η are, in fact, two ways of averaging the same friction coefficients, he arrived at the following relationship

$$\eta^* = \eta\frac{V}{\delta^2} \quad (4.33)$$

where δ is the mean distance of momentum transfer between the colliding molecules, measured in the direction normal to the transport plane.

On combining Equations (4.28), (4.29), (4.32), and (4.33) the following equation was obtained:

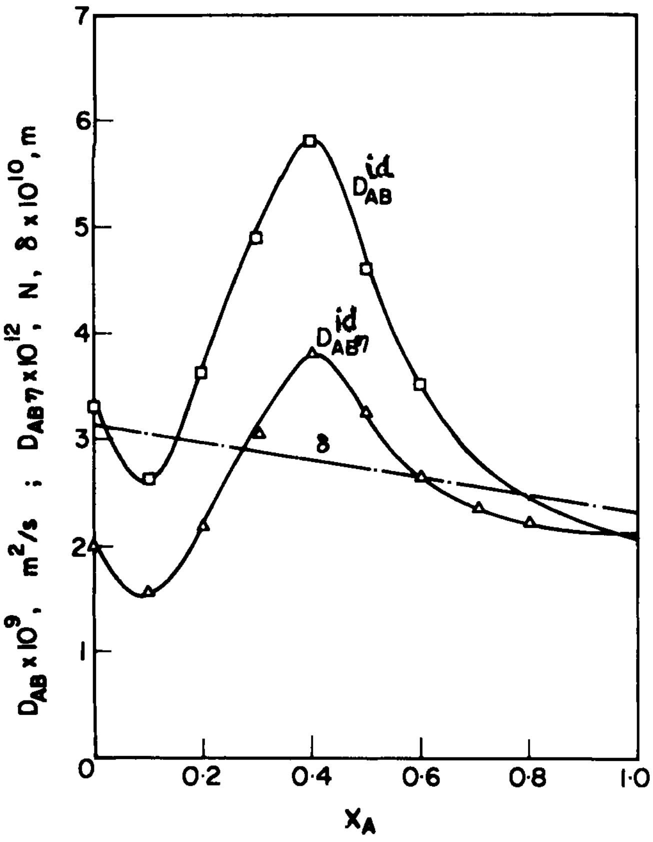

Fig. 23. Curves for D_{AB}, $D_{AB}\eta$, and δ as functions of composition for the system ethanol (A) + benzene (B), 25°.

$$\frac{2\,V\eta}{RT\left\{\dfrac{x_A}{D_{A*}}+\dfrac{x_B}{D_{B*}}\right\}} = \delta^2 \qquad (4.34)$$

Since no molecular model was assumed in the development of Equation (4.34), it is therefore applicable to both gases and liquids (Dullien, 1963, 1972; Ertl and Dullien, 1973).

It is quite interesting that, as shown in Figures 23 and 24, δ has been found to be a linear function of mole fraction even for such highly nonideal systems as ethanol + benzene and methanol + benzene.

Snell and Spangler (1967) have also found that, of necessity, new molecular parameters, such as δ in Dullien's equation, appear in the formulation expressing explicit connection between intradiffusion and viscosity coefficients.

Recently, Albright (1969) extended Dullien's treatment to multicomponent systems.

Statistical-Mechanical Theory

Statistical-mechanical theories which envisage diffusion taking place in small steps in a random walk fashion, have been successfully applied for the gaseous state by Chapman and Cowling (1970) and have been discussed by Hirschfelder et al. (1964). Kirkwood (1946) formulated a theory for dense media which was further developed by Irving and Kirkwood (1950), Bearman and Kirkwood (1958), and Rice and Kirkwood (1959).

Bearman (1960) later obtained equations in a form that could be compared with numerical data. A brief review of Bearman's theory—perhaps it is more accurate to call it Bearman-Kirkwood theory—is given below.

Based on statistical-mechanical arguments, it was shown (Bearman, 1960, 1961) that the frictional force $\mathbf{F}_i$ acting on a species i, in a mixture of n components is given by

$$\mathbf{F}_i = -\sum_{j=1}^{n} C_j\,\xi_{ij}\,(\mathbf{v}_i - \mathbf{v}_j) \qquad (4.35)$$

where ξ_{ij} is the coefficient of friction between component i and j. Evaluation of these friction coefficients has not been possible from the Bearman-Kirkwood theory. The friction coefficients are related to the deviation of the pair correlation function from its equilibrium value. The only difference between Equation (4.35) and the starting point for Lamm's derivations is that Lamm treated the product $C_j\,\xi_{ij}$ as the friction coefficient. As it will be discussed later, $C_j\,\xi_{ij}$ has a more direct physical meaning than ξ_{ij}.

Bearman obtained the following expressions for the mutual diffusivity:

$$D_{AB} = \frac{\overline{V}_B\,kT}{\xi_{AB}}\,\frac{d\ln a_A}{d\ln C_A} = \frac{\overline{V}_A\,kT}{\xi_{AB}}\,\frac{d\ln a_B}{d\ln C_B}$$

$$= \frac{kT}{\xi_{AB}}\,V\beta \qquad (4.36)$$

These are equivalent to Equation (4.27). Note that $\phi_{A(B)} = NC_B\,\xi_{AB}$, where N is Avogadro's number.

The corresponding expressions for the intra-diffusion coefficients are

$$D_{A*} = \frac{kT}{C_A\,\xi_{A^0A*} + C_B\,\xi_{AB}} \qquad (4.37)$$

and

$$D_{B*} = \frac{kT}{C_B\,\xi_{B^0B*} + C_A\,\xi_{AB}} \qquad (4.38)$$

where A^0 and A^* represent untagged and tagged A mole-

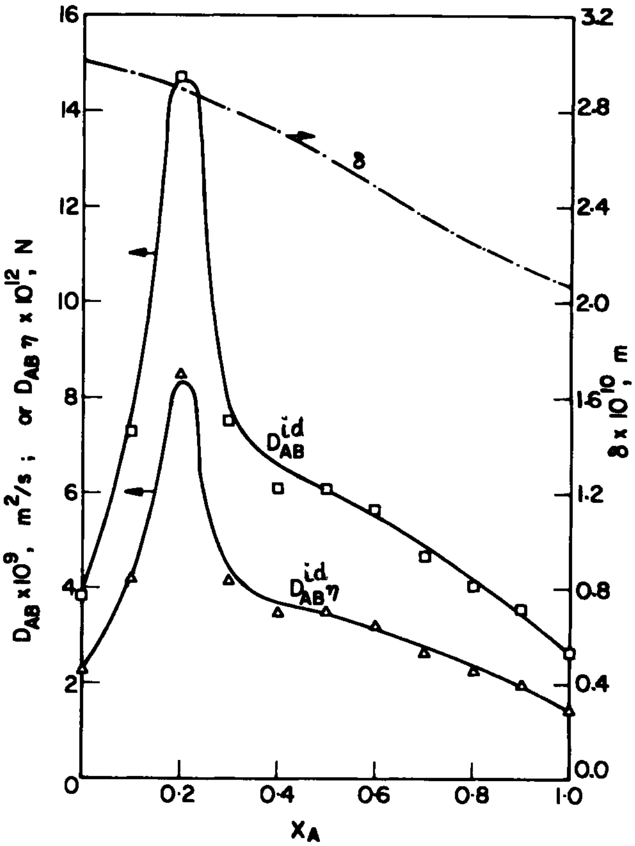

Fig. 24. Curves for D_{AB}, $D_{AB}\eta$, and δ as functions of composition for the system methanol (A) + benzene (B), 25°.

cules, respectively. These equations are equivalent to Equations (4.28) and (4.29). Note that $\phi_{i^0 i^*} \approx \phi_{i^*(i^0)} = NC_i\, \xi_{i^0 i^*}$. (See Discussion of the Various Friction Coefficients.)

For a highly special class of solutions in which (1) there is no volume change on mixing and (2) radial distribution functions are independent of mole fraction, Bearman (1960) showed that

$$\frac{D_{A^*}}{D_{B^*}} = \frac{V_B{}^0}{V_A{}^0} \tag{4.39}$$

The constancy of this ratio implies a geometric mean relationship between the friction coefficients, that is,

$$\xi_{AB} = \sqrt{\xi_{A^0A^*}\, \xi_{B^0B^*}} \tag{4.40}$$

and

$$\left.\begin{aligned} D_{AB} &= D_{i^*} \frac{d\ln a_i}{d\ln C_i}, \quad \text{and} & (4.41)\\ D_{AB} &= D_{i^*} \frac{V}{\overline{V}_i}\, \beta & (4.42) \end{aligned}\right\} \quad i = A, B$$

Bearman termed this type of solutions regular, which is a different definition from the one originally introduced by Hildebrand et al. (1970).

The radial distribution functions will be rigorously composition independent only if the two species are identical; if, however, the molecules are similar in size, shape and intermolecular potential, Bearman's assumption may still be approximately valid. In a recent paper Bearman and Bearman (1970) tested the above equations over a wide range of densities. By testing their theory with Ar-Kr mixture they found that only in a narrow region of densities does the theory turn out to be approximately valid.

Generally, Equation (4.39) has not been found to conform to the experimental data (for example Van Geet and Adamson, 1964; McCall and Douglass, 1967); however, the ratio D_{A^*}/D_{B^*} has been found to be constant for a few systems such as ethyl iodide + butyl iodide and benzene + diphenyl. Even for these systems, however, the value of this ratio was not identical to $V_B{}^0/V_A{}^0$, see Table 9.

Bearman (1961) showed that Equations (4.39) and (4.42) may be combined to result in Darken's equation. For a few nonideal systems, McCall and Douglass (1967) calculated the thermodynamic factor β both from the activity coefficients and from the Darken equation. Their results plotted in Figure 25 show large disagreement between the two values, the disagreement being relatively less for the system benzene + cyclohexane.

The Bearman-Kirkwood theory also provides an expression for viscosity (Bearman and Jones, 1960). It was shown that the product $D_{i^*}\eta$ for regular solutions should be independent of composition. This is consistent with Equation (4.12) which was used by Carman and Stein (1956).

Equations (4.36) to (4.38) may also be combined to give the following expression (Loflin and McLaughlin, 1969):

$$D_{AB} = (x_A\, D_{B^*} + x_B\, D_{A^*})\beta$$
$$\left[\frac{x_A\, \xi_{AB}}{x_A\, \xi_{AB} + x_B\, \xi_{B^0B^*}} + \frac{x_B\, \xi_{AB}}{x_B\, \xi_{AB} + x_A\, \xi_{A^0A^*}}\right]^{-1} \tag{4.43}$$

Equation (4.43) simplifies to Darken's equation if the geometric mean relation between the friction coefficient, Equation (4.40), holds (Loflin and McLaughlin, 1969).

TABLE 9. RATIOS OF $V_A{}^0/V_B{}^0$ AND D_{B^*}/D_{A^*} (MILLS, 1963)

Component	$V \times 10^6$ m^3 mol^{-1}	$V_A{}^0/V_B{}^0$	$D_B{}^*/D_A{}^*$	$\dfrac{V_B\, D_A{}^*}{V_A\, D_B{}^*}$
Benzene (B)	89.44	1.67	1.45	1.15
Diphenyl (A)	149.00			
Ethyl iodide (B)	80.51	1.41	1.14	1.24
n-Butyl iodide (A)	113.87			

Bearman (1961) showed that Eyring's equation (4.22) is essentially equivalent to his Equations (4.41) and (4.42). If it is conjectured as was done by Mills (1963) and Bearman (1961) that the intrinsic diffusion coefficients D_A and D_B are identical with the mutual diffusion coefficient, the Hartley-Crank equation (4.9) and Bearman's equation (4.41) become identical. Assuming that the absence of experimentally demonstrable volume bulk flow, other than that due to volume change on mixing, may be construed as evidence that there does not exist any other kind of volume bulk flow under the conditions used in the usual diffusion measurements, there follows immediately from the comment after Equation (2.10) that $D_{AB} = D_A = D_B$.

Another attempt to calculate theoretically the ratio of the friction coefficients was made by Loflin and McLaughlin (1969). They employed the Rice and Alnatt (1961) extension of the Rice and Kirkwood theory (1959). The resulting expression was obtained in terms of the Lennard-Jones parameters ϵ and σ, and intra-diffusion coefficients. Assuming the usual combining rules for the Lennard-Jones parameters for a binary mixture, the following expression was obtained:

$$\xi_{A^0A^*}\, \xi_{B^0B^*}$$
$$= 4\, \xi_{AB}{}^2 \frac{\sigma_{A^0A^*}\ \sigma_{B^*B^0}}{(\sigma_{A^0A^*} + \sigma_{B^*B^0})^2} \quad \frac{m_A + m_B}{m_A\, m_B} \quad \frac{D_{A^*}\, D_{B^*}}{(D_{A^*} + D_{B^*})^2} \tag{4.44}$$

Systems consisting of species of the same diameter and the same mass have been assumed to have equal values of D_{A^*} and D_{B^*}. For such systems, the geometric mean relation between the friction coefficients again follows from Equation (4.44). Any further quantitative extension of the usefulness of Equation (4.44) is possible only if the friction coefficients can be predicted theoretically or by independent measurements.

If it is assumed that the friction coefficients are independent of composition, one can obtain from Equation (4.37) the following expression for the self-diffusion coefficient of component A

$$D_A{}^0 = \frac{V_A{}^0\, kT}{\xi_{A^*A^0}} \tag{4.45}$$

This equation may be combined with Equations (4.37) and (4.36) to give the approximate form of Lamm's equation, Equation (4.31) (Loflin and McLaughlin, 1969).

Use of Irreversible Thermodynamics

The science of irreversible thermodynamics has aided in the study of the coupling phenomena, such as thermal diffusion, which is beyond the scope of this article. Fick's law, as mentioned earlier, is inadequate to deal with multicomponent diffusion. A set of generalized flow equations has been suggested for the description of this process (Onsager, 1945; Baldwin et al., 1955; Lamm, 1957). Only the equations for ternary diffusion will be given here. All of these equations may also be used for binary mixtures by assuming two of the components chemically identical. One of the main preoccupations in the study of ternary isothermal diffusion has been to test the Onsager reciprocal *relations* (Dunlop and Gosting, 1955; Dunlop, 1964; Cussler and Dunlop, 1966; Mills and Ellerton, 1966). The other main aim of such a study has been to formulate flow equations in terms of friction coefficients in binary mixtures.

Applications of Ternary Diffusion Equations to Binary Systems. For a ternary system there are two independent flow equations

$$J_1 = - D_{11}\, \nabla C_1 - D_{12}\, \nabla C_2 \qquad (4.46)$$

$$J_2 = - D_{21}\, \nabla C_1 - D_{22}\, \nabla C_2 \qquad (4.47)$$

where J_i and D_{ij} represent the flows and diffusion coefficients with respect to a volume-fixed frame of reference such that

$$\sum_{i=0}^{2} J_i \overline{V}_i = 0 \qquad (4.48)$$

In general, $D_{ij} \neq D_{ji}$. However, there exists a relationship between the coefficients because of the principle of microscopic reversibility (Dunlop and Gosting, 1955).

For intradiffusion of component 1 in a three-component system where components 1 and 2 are chemically identical and the sum of the concentrations of 1 and 2 is constant (Albright and Mills, 1965)

$$\nabla C_1 = - \nabla C_2 \qquad (4.49)$$

and Equation (4.46) reduces to

$$J_1 = - (D_{11} - D_{12})\, \nabla C_1 \qquad (4.50)$$

$$= - D_{1*}\, \nabla C_1 \qquad (4.51)$$

where D_{1*} is the intra diffusion coefficient of component 1.

$$\therefore\ D_{1*} = D_{11} - D_{12} = D_{22} - D_{21} \qquad (4.52)$$

In a ternary system where chemically identical components 1 and 2 interdiffuse with component 0 under conditions such that

$$\frac{C_i}{C_s} = \text{constant} \quad (i = 1, 2) \qquad (4.53)$$

where $C_s = C_1 + C_2$, it has been shown by the above authors that

$$D_{21} = \frac{C_2}{C_s}\,(D_{01} - D_{1*}) \qquad (4.54)$$

$$D_{22} = \frac{C_2}{C_s}\,(D_{01} - D_{1*}) + D_{2*} \qquad (4.55)$$

The analogous equations for D_{12} and D_{11} can also be obtained in a similar manner.

When the concentration of component 2 becomes infinitely dilute it can be shown from the above that

(i) $D_{21} \rightarrow 0$
(ii) D_{22} becomes equal to intradiffusion coefficient of component 2
(iii) D_{11} becomes equal to mutual diffusion coefficient.

These limiting cases have been tested experimentally (Dunlop, 1957; O'Donnell and Gosting, 1959; Woolf et al., 1962). Since for a binary mixture, according to our previous notation, components 1 and 2 are equivalent to A^* and A^0, the preceding conclusions for $C_{A^*}/C_s \rightarrow 1$, lead (Harris et al., 1970) to the equations

$$D_{AB} = D_{A*} + D_{A*A} \qquad (4.56)$$

and

$$D_{AB} = D_{B*} + D_{B*B}, \qquad (4.57)$$

where D_{A*A} and D_{B*B} are cross-diffusion coefficients.

On multiplying Equation (4.56) with x_B and Equation (4.57) with x_A, (Harris et al., 1970) showed that

$$D_{AB} = x_A\, D_{B*} + x_B\, D_{A*} + x_A\, D_{B*B} + x_B\, D_{A*A} \qquad (4.58)$$

which is similar to Darken's equations except that it contains cross diffusion coefficients.

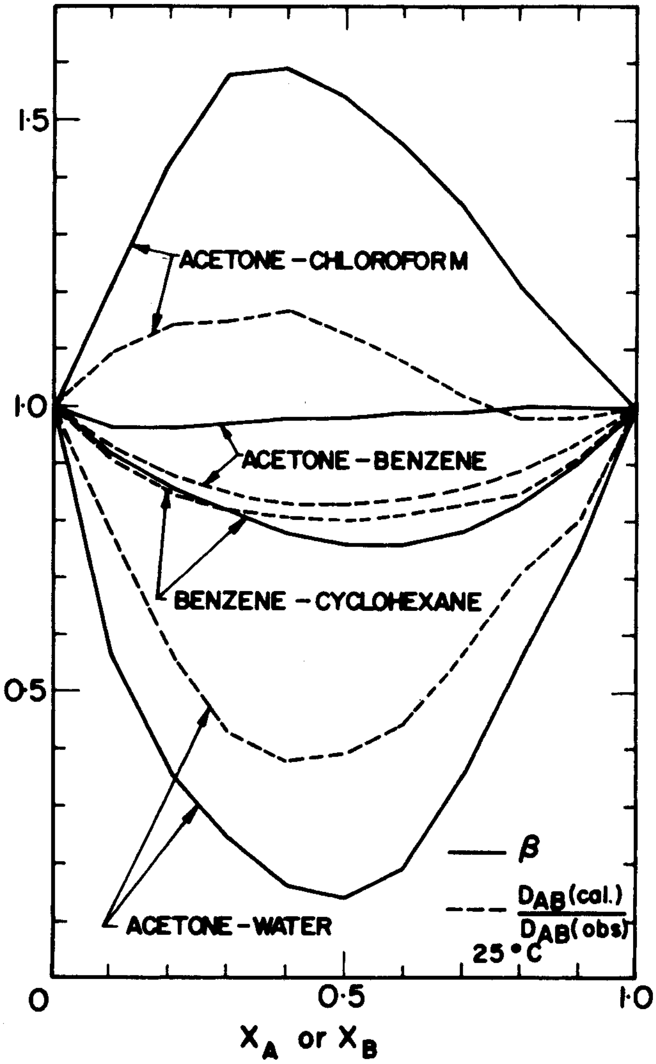

Fig. 25. Comparison of the thermodynamic factor β with the diffusion ratio $D_{AB}/(x_A D_{B*} + x_B D_{A*})$ at 25° (McCall and Douglass, 1967).

Friction Coefficients. According to Onsager (1945) the friction coefficients R_{ij} are related to the dissipation function (that is, half the rate at which the energy is dissipated) S as

$$S = \tfrac{1}{2} \sum_{i,j}^{n} R_{ij}\,(J_i \cdot J_j) \qquad (4.59)$$

where J_i and J_j are local fluxes and the summation is taken over all the possible combinations. According to Onsager (1945), $R_{ij} = R_{ji}$ and

$$\sum_{j=1}^{n} R_{ij}\, C_j = 0 \tag{4.60}$$

This restriction represents the condition of no dissipation when all the velocities are equal. Laity (1959) combined Equations (4.59) and (4.60) to obtain

$$\nabla \mu_i = \sum_{j=1}^{n} R_{ij}\, C_j\, (\mathrm{v}_j - \mathrm{v}_i) \tag{4.61}$$

Equation (4.61) is equivalent to Equation (4.35).

A similar equation was obtained also by Klemm (1953). The following equations have been obtained (Laity, 1959) to calculate the three friction coefficients from the experimental mutual and intra-diffusion coefficients:

$$R_{AB} = -\, RT \frac{V}{D_{AB}} \beta \tag{4.62}$$

$$R_{A^*A^0} = RT \left\{ \frac{V x_B}{D_{AB} x_A} \beta - \frac{V}{D_{A^*} x_A} \right\} \tag{4.63}$$

and

$$R_{B^*B^0} = RT \left\{ \frac{V x_A}{D_{AB} x_B} \beta - \frac{V}{D_{B^*} x_B} \right\} \tag{4.64}$$

Evidently, $R_{ij} = N\, \xi_{ij}$, and Equations (4.62) to (4.64) may be derived also from Equations (4.36) to (4.38).

Discussion of the Various Friction Coefficients

In recent years stress has been laid on the study of friction coefficients in addition to that of diffusion coefficients. As pointed out in the literature (Laity, 1959; Mills, 1965 and 1971a), there are several advantages in this type of study. The friction coefficients in this formalism are independent of frame of reference, and each of them represents a specific interaction between molecules of the species. Furthermore, these are the coefficients which appear in the microscopic theory of liquids.

It is helpful to have some degree of feel for the physical meaning of friction coefficients. Without attempting to go into any detailed quantitative analysis it seems nevertheless plausible to assume that the value of a friction coefficient between the species i and j should generally increase with the average amount of interaction between these species in the solution. Therefore, it is convenient to express the friction coefficients in a form that reflects this anticipated dependence. This objective has been met by Lamm's formulation of the friction coefficients $\phi_{i(j)}$ and $\phi_{j(i)}$ which are based on one mole of i and j, respectively. [See Equations (4.27) to (4.30).] Thus, the value of $\phi_{i(j)}$ reflects the average amount of interaction between i and j molecules per mole of i molecules. Evidently, for $x_i = 1$ one expects $\phi_{i(j)} = 0$, and the normal behavior of $\phi_{i(j)}$ is to decrease with increasing x_i. The converse may be said about $\phi_{j(i)}$.

The friction coefficients $R_{ij} = N\, \xi_{ij}$ do not appear to have such intuitively appealing properties. [See Equations (4.35) to (4.38), and Equations (4.61) to (4.64).]

The relationships between the various friction coefficients can be easily shown through the use of the friction coefficient ϕ_{ij}^{v}, representing the friction between molecules of species i and j per unit volume of the solution, which was also introduced by Lamm. Evidently

$$\phi_{ij}^{v} = \phi_{i(j)}\, C_i = \phi_{j(i)}\, C_j \tag{4.65}$$

and

$$\phi_{i(j)}/\phi_{j(i)} = C_j/C_i = x_j/x_i \tag{4.66}$$

Hence, from Equation (4.30)

$$\phi_{ij} \equiv \phi_{i(j)} + \phi_{j(i)}$$

there follows

$$\phi_{ij} = \phi_{i(j)}/x_j = \phi_{j(i)}/x_i = R_{ij}\, V = N\, \xi_{ij}\, V \tag{4.67}$$

where the identities

$$R_{ij} = \phi_{i(j)}/C_j = \phi_{j(i)}/C_i \tag{4.68}$$

have been used. For the special case of tracer diffusion

$$\phi_{i^0 i^*} = \phi_{i^0(i^*)} + \phi_{i^*(i^0)} = \frac{x_i}{x_{i^0}}\, \phi_{i^*(i^0)} \cong \phi_{i^*(i^0)} \tag{4.69}$$

as $x_i = x_{i^0} + x_{i^*} \cong x_{i^0}$.

Hence

$$\phi_{i^0 i^*}/C_i = R_{i^0 i^*} = N\, \xi_{i^0 i^*} \tag{4.70}$$

Equations (4.67) to (4.70) establish the equivalence of Equations (4.27) to (4.29) with Equations (4.36) to (4.38), and Equations (4.62) to (4.64).

In order that the friction coefficients be meaningful, it is essential that the diffusivity measurements be accurate to a few tenths of 1% (Tyrrell, 1963). Since this magnitude of accuracy is now accessible, friction coefficients have been calculated for a few binary systems at several concentrations.

A relatively early attempt to calculate and utilize friction coefficients is due to Dullien (1963) who calculated the friction coefficients $\phi_{i(j)}$ and ϕ_{ij}, using the experimental diffusion data for two highly nonideal solutions, ethanol + benzene and methanol + benzene. By comparing these friction coefficients with those corresponding to an hypothetical equivalent random solution, Dullien discussed qualitatively the spatial distributions of *A*-*A*, *A*-*B*, and *B*-*B* molecular pairs. The conclusions thus reached were in accord with independent thermodynamic data (Tyrrell, 1970).

The friction coefficients $R_{A^0A^*}$ and R_{AB} for the system urea (*A*) water (*B*) were calculated by Albright and Mills (1965) using their own measured intra-diffusion values and the mutual diffusivity data reported by Gosting and Akeley (1952). Both $R_{A^0A^*}$ and R_{AB} were found to vary linearly with molar concentration of the component *A*. The friction coefficients were also calculated for the binary systems α-alanine and β-alanine and mannitol and thiourea (Tilley and Mills, 1967). In these systems the

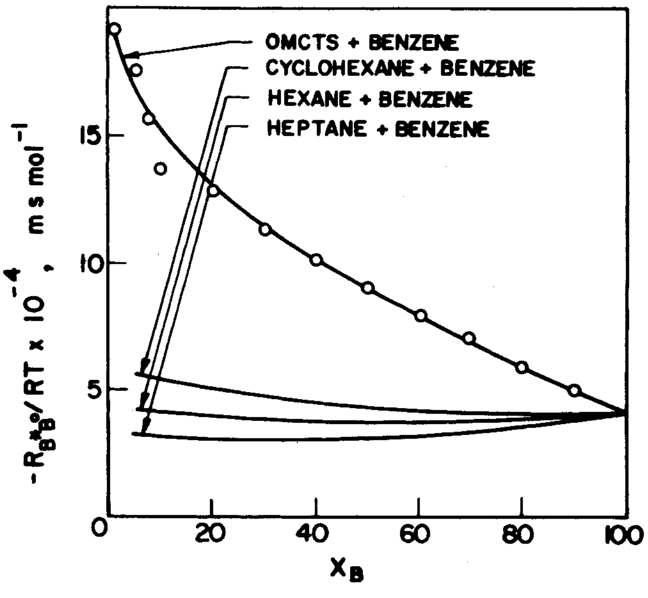

Fig. 26. $R_{B^*B^0}/RT$ values for benzene in various organic liquids as a function of mole fraction (x_B) of benzene. O, OMCTS (Mills, 1971).

friction coefficients R_{A*A0} and R_{AB} were found to have non-linear dependence on molar concentration. The R_{A*A0} values were found to be much larger than the R_{AB} values in the above systems and also in the system diphenyl-water (Mills, 1965). This may be because of the smaller size of the solvent molecules.

Very recently Mills (1971a) and Harris et al. (1970) extended such measurements to binary systems in which both of the components were organic. Harris et al. calculated the friction coefficients for the binary systems of benzene in chlorobenzene, *n*-hexane, and *n*-heptane. Mills calculated the same for the systems benzene + OMCTS and benzene + cyclohexane. Figure 26 shows the composition dependence of the friction coefficients R_{i*i0} of benzene in mixtures with a number of solvents. These R_{i0i*}'s values change very sharply with the composition in the case of the system benzene + OMCTS. In other systems, however, the R_{i0i*} values vary only gradually. This is not surprising because the OMCTS molal volume is much larger than the volumes of the other components.

Another interesting correlation was obtained when the limiting friction coefficients were plotted against the solute molar volume (Tilley and Mills, 1967) with water as the solvent. Excepting R_{i0i*} for β-alanine, all the other three R_{i0i*} values for mannitol, α-alanine and urea fell on the straight line. The exception of β-alanine may be ascribed to its large dipole moment.

ACKNOWLEDGMENTS

Grants in aid by the National Research Council of Canada are gratefully acknowledged by the authors.

NOTATION

A = adjustable parameter, Equation (4.19)
a = number of nearest neighbors in all directions
a_i = activity of component i
B = adjustable parameter, Equation (4.19)
b = number of nearest neighbors in one layer
C_i = molal concentration of component i
D, D_{i0} = self-diffusion coefficient of pure component i
D_i = intrinsic diffusion coefficient of component i
D_{i*} = intradiffusion coefficient of component i
D_{AB} = mutual- or interdiffusion coefficient
D_F = Fick diffusion coefficient
e = activation energy, Equation (4.25)
F = friction force
$\Delta G_D^{\#}$ = energy of activation for diffusion
$\Delta G_v^{\#}$ = energy of activation for viscous flow
J_i = molal flux vector of component i
k = Boltzmann's constant
M = molecular weight
m_i = molecular mass of component i
N = Avogadro's number
n = adjustable parameter, Equation (4.23)
q = mobility
R = universal gas constant
R_{ij} = friction coefficient, Equation (4.59)
r = molecular radius
S = dissipation function
T = absolute temperature
T_c = critical temperature
ΔU_{vap} = molal energy of vaporization
V = molal volume of solution
V_f = free volume
V_i^0 = molal volume of pure component i
$\overline{V}_i$ = partial molal volume of component i
v = velocity vector
w = fraction of lattice energy, Equations (4.25) and (4.26)
x_i = mole fraction of component i

Greek Letters

β = thermodynamic factor, Equation (2.12)
β_f = coefficient of sliding friction
δ = mean distance of momentum transport
ϵ = Lennard-Jones potential parameter
η = viscosity
η^* = molar average friction coefficient
λ = intermolecular distance
μ = chemical potential
ξ_{ij} = friction coefficient, Equation (4.35)
σ = Lennard-Jones distance parameter
σ_i = friction factor of component i
ϕ_{ij} = molal friction coefficient, Equation (4.30)
ϕ_{ij}^v = friction coefficient per unit volume of solution

Superscripts

c = coordinate-fixed frame of reference
id = ideal
m = convection-fixed frame of reference
v = volume fixed frame of reference
0 = untagged component; infinitely dilute solution w.r.t. component A
∞ = infinitely dilute solution w.r.t. component B
$*$ = tagged component

Subscripts

$A, B, 1, 2, i, 0$ = refer to various components in a mixture

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THE AUTHORS

The occasion that made this review possible was provided by the fortunate coincidence of having two Ph.D. students present at the same time, both working in the field of diffusion. As it happened, H. Ertl did his thesis by using the nuclear magnetic resonance technique for measuring self-diffusion whereas R. K. Ghai used the radiotracer method to measure diffusion in mixtures. Since these two dedicated researchers had to cover for their theses, between the two of them, almost the entire literature of liquid diffusion it was natural to use the material gathered by them to write this review paper. Both of them came from overseas for this occasion, Ertl from Germany and Ghai from India. As far as F. A. L. Dullien is concerned, he was very lucky to be able to host two such excellent co-workers and provide them with the opportunity to do this job. He also came from overseas, though somewhat earlier from Hungary, possibly to be ready for the arrival of his two co-authors of this paper.