Liquid Diffusion of Nonelectrolytes:

Part II

Part II of the review paper covers the self-diffusion theories and their comparison with experimental results. This is followed by a review of empirical and semi-empirical predictive equations of mutual and self-diffusion coefficients. Recent developments in experimental techniques for measuring liquid diffusivities are discussed in the last section. A supplement of experimental diffusion data since 1956 is available.

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SCOPE

For an overall description of the intent and objectives of this Review, refer to the Scope for Part I (*AIChE Journal*, September, 1973, page 881).

CONCLUSIONS AND SIGNIFICANCE

There exist various model approaches to self-diffusion in liquids. With the exception of a few, these approaches treat liquids either as a dense gas or a disordered solid. More rigorous approaches to liquid diffusion have yet failed to yield workable equations. Most of the approaches can be classified as hard sphere models (Louguet-Higgins and Pople; Ascarelli and Paskin), free volume models (Cohen and Turnbull), and cell models (Houghton). Other approaches arise from combinations of these, while some others have a different basis, for example, Significant Structure Theory of Eyring and co-workers. In the majority, the resulting equations contain adjustable parameters. The values of the parameters cannot be predicted a priori. Most of the approaches result in equations similar to the Stokes-Einstein relation.

A number of empirical and semi-empirical equations have been proposed. Leffler and Cullinan's equation is probably the best on the average, for the estimation of mutual diffusion coefficients of most systems except for the systems containing *n*-alkanes where Vignes' correlation is more satisfactory. Both Vignes' and Leffler and Cullinan's equations require values of limiting mutual diffusion coefficients. Hayduk and Cheng's correlation is useful to predict diffusivities of a solute in dilute solutions in various solvents if the diffusivities in at least two solvents of known viscosities are known. Van Geet and Adamson's equation predicts self-diffusion coefficients of *n*-alkanes satisfactorily. Dullien's correlation is applicable to a wider variety of liquids.

Since 1956, *significant developments in the* experimental techniques for measuring diffusion coefficients have occurred. With these developments it is now possible to obtain an increased accuracy in the diffusivity values of organic systems. The introduction of the nuclear magnetic resonance method (nmr) has facilitated to a large extent the study of temperature and pressure dependence of self-diffusion (and also intradiffusion) coefficients.

5. SELF-DIFFUSION THEORIES AND THEIR COMPARISON WITH EXPERIMENTS

Self-diffusion is the term used to describe the motion of molecules in an environment which consists of one chemical species only.

As discussed in Section 3 (Part I) rigorous theoretical treatment of transport properties of liquids represents, at the moment, mathematically insurmountable difficulties in most of the cases.

In the various model approaches to self-diffusion the liquid is, with a few exceptions, either considered as a dense gas or a disordered solid.

Among the exceptions are the random packing models by Bernal (1959), and others (for example, Scott, 1964), which, however, have not yet been used for quantitative work. The 'molecular dynamics' method (Alder and Wainright 1959, 1967) also falls in this category. With the aid of digital computers, this method is used to calculate the trajectories of a limited number of molecules after each collision. This approach, as well as the Monte Carlo method (Wood and Parker, 1957) and particularly the approach by Born and Green (1946, 1949) appear to be the most rigorous ways to describe the liquid state at the present time. However, the practical applications of these approaches require assumptions to be made which often do not appear to leave much of the rigor of the original treatment.

Neither the dense gas nor the quasi-crystalline models

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can be expected to represent the liquid state satisfactorily. In a real liquid many body collisions occur, yet the basic assumption for dense gas models are binary collisions. As found from the radial distribution functions obtained by diffraction experiments, liquids exhibit a so-called "short-range" order, which, contrary to the case of solids, is rapidly lost with distance. The much greater mobility of molecules in the liquid state as compared to the molecules in the solid state is also a distinct difference between the two phases.

The only way to determine the usefulness of the equations obtained from different models is to compare their predictions with experimental values. This test has become possible with the availability of new experimental techniques utilizing either radioisotopes or nuclear magnetic resonance. Both techniques have contributed a great deal to the interpretation of the liquid state in general.

Hard Sphere Models

Longuet-Higgins and Pople (1956) have developed a model for transport processes in dense fluids. In addition to the self-diffusion coefficient D, they were able to derive expressions for the viscosity η and thermal conductivity λ.

The development is based on the assumption of molecules consisting of nonattractive hard spheres undergoing random walk motion. Furthermore, in the case of self-diffusion it is assumed that the velocity correlation function decays exponentially via binary collisions. The final result for the self-diffusion coefficient is

$$D = \frac{r}{2}\,\frac{\pi RT}{M}\left(\frac{PV}{RT} - 1\right)^{-1} \tag{5.1}$$

where r is the radius of the sphere. McLaughlin (1969) has shown that Equation (5.1) is also obtained in the limiting case of identical molecular masses of the species from the expression for the mutual diffusion coefficient. Combination of the equations for the self-diffusion coefficient and the viscosity yields a formula akin to the Stokes-Einstein relation.

Equation (5.1) gives results which are too large probably due to the neglect of attractive forces, the contribution of which is already important at moderate densities (Davies and Rice, 1961). Equation (5.1) predicts a temperature dependence of the diffusion coefficient which has been found to be too small (McCall et al., 1959; Douglass et al., 1961; Kessler et al. 1967). This is clearly illustrated in Figure 1 for the tetramethyl-(group IV) liquids.

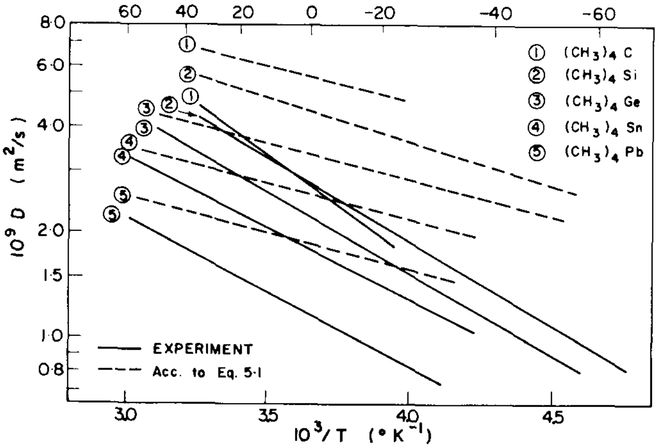


Fig. 1. Self-diffusion coefficient D as a function of temperature (Kessler et al., 1967).

TABLE 1. COMPARISON BETWEEN CALCULATED [EQUATION (5.7)] (γ/η) VALUES AND EXPERIMENTAL VALUES (LONGUET-HIGGINS AND VALLEAU, 1958)

Liquid	Temp., °K	10^{-6} (γ/η) exptl., erg g^{-1} deg^{-1}	10^{-6} (γ/η) theor., erg g^{-1} deg^{-1}
Argon	84.2	4.5	5.2
	87.3	4.8	5.2
Helium I	2.5	51.0	52.0
	4.0	94.0	52.0
Nitrogen	69.2	6.6	7.4
	77.3	8.8	7.4
Oxygen	74.0	5.5	6.5
	83.6	7.0	6.5
	90.2	8.0	6.5
Hydrogen	16.7	61.0	103.0
	20.4	95.0	103.0
Deuterium	20.2	31.0	51.6
	23.2	43.2	51.6

Several modifications have been proposed to improve this shortcoming. The inclusion of the intermolecular attractive forces through a square-well potential function has been performed by Longuet-Higgins and Valleau (1958), resulting in

$$D = \frac{3n}{32}\sqrt{\frac{RT}{\pi M}}\,\{\gamma_1 a_1^2 + \gamma_2 a_2^2 \Xi\}^{-1} \tag{5.2}$$

where γ_1 and γ_2 are the values of the pair correlation function at the two discontinuities. Ξ is a function depending on the reciprocal reduced temperature ϵ/kT. It can be seen from Table 1 that when the counterparts of Equation (5.2) for shear viscosity η and thermal conductivity λ are applied to some simple liquids the right order of magnitude for λ/η is obtained, but they fall short of predicting temperature dependence.

Naghizadeh and Rice (1962) have also tested Equation (5.2) for simple liquids. In contrast to Table 1 they have found that Equation (5.2) predicted the experimental temperature dependence for argon along the saturated liquid line (Figure 2); however, the predicted D did not agree with the experimental values.

The pressure P in Equation (5.1) has been replaced by the so-called "thermal" or "kinetic" pressure $P_t = T(\partial P/\partial T)_V = P + (\partial U/\partial V)_T$ (McCall et al., 1959; Kessler et al., 1967) yielding a marked improvement with regard to the magnitude of predicted values of D, Table 2. However, it has been found unsatisfactory when applied to polar liquids (McCall et al., 1959).

For the case of van der Waals liquids, Kessler et al. (1957) introduced another approach by replacing P_t with the cohesive energy density $\Delta H_v/V$. ΔH_v is the enthalpy of vaporization.

Douglass et al. (1961) have suggested the superposition of an oscillating function on the exponentially decaying velocity correlation function used in the derivation of Equation (5.1). In a different article, Douglass (1961) has obtained approximate expressions for the self-diffusion coefficient by using this proposed modification. The calculation for neopentane revealed a marked improvement of the temperature dependence, but the diffusion coefficients were still predicted only to the right order of magnitude (Figure 3).

The original model of Longuet-Higgins, along with its modifications, assumes molecules of spherical shape and smooth surface, and hence, does not allow transfer of rotational energy. Valleau (1958) and Brown and Davies (1971) extended Longuet-Higgins and Pople's model to perfectly rough spherical molecules. Transfer of rotational energy may also be simulated by adding a load to the sphere (Brown and Davies, 1971), in which case the center of mass does not coincide with the geometric center. Brown and Davies found that loading a sphere increases the self-diffusion coefficient compared to the hard sphere model, while the rough sphere model decreases the self-diffusion coefficient. The authors have pointed out, however, that due to the small effect of rotational energy on the magnitude of D its inclusion does not seem worthwhile unless diffusion coefficients can be calculated to better than 10% accuracy.

TABLE 2. COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED VALUES USING EQUATION (5.4) AND THE KINETIC PRESSURE APPROXIMATION (FROM MCCALL ET AL., 1959)

Liquid	$10^5 D$ (cm²/sec) Theory	$10^5 D$ (cm²/sec) Exptl.
n-Pentane	6.3	5.5
n-Hexane	3.8	4.2
n-Heptane	3.2	3.1
n-Octane	2.8	2.0
n-Nonane	2.2	1.7
n-Decane	2.0	1.3
2-Methyl pentane	5.0	4.0
3-Methyl pentane	5.0	3.6
2,2-Dimethyl butane	5.0	3.4
2,3-Dimethyl butane	5.0	3.5
Benzene	3.8	2.2
Carbon disulfide	5.2	4.1
Carbon tetrachloride	2.8	1.4

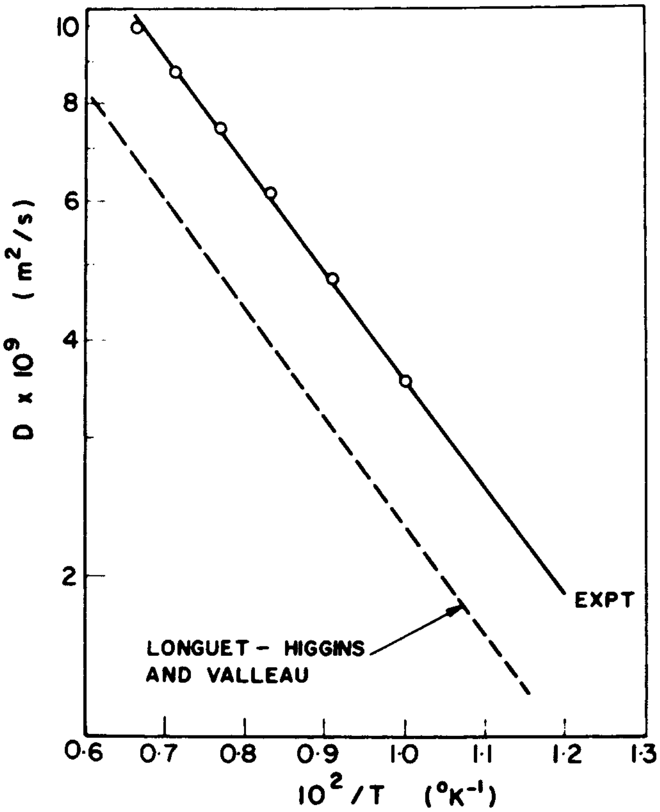


Fig. 2. Diffusion coefficient of liquid argon (Naghizadeh and Rice, 1962). The theoretical (dashed) line is according to Equation (5.7).

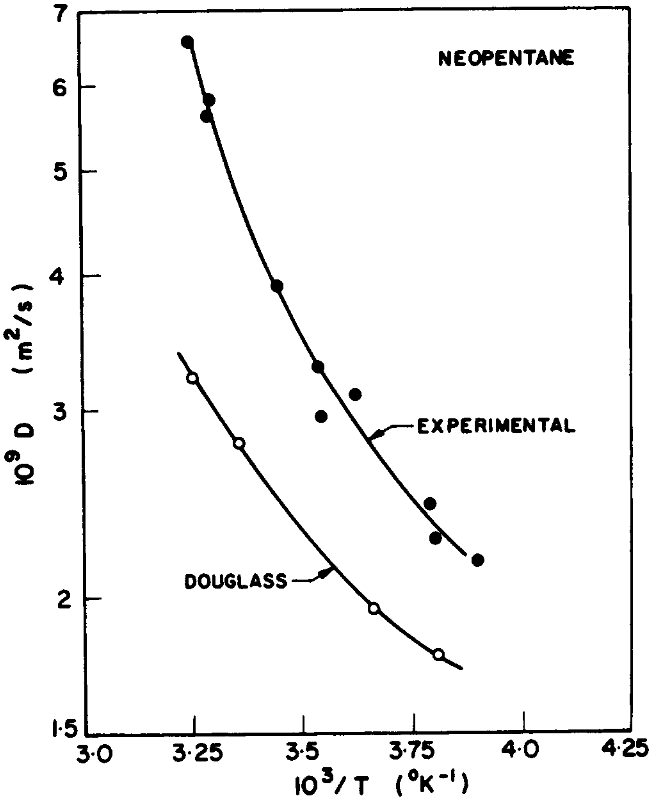


Fig. 3. The logarithm of the self-diffusion coefficient (m_1^2/s) of neopentane vs. reciprocal temperature (K). Dots indicate experimental data, circles indicate coefficients calculated using the modified velocity correlation function (see text) (Douglass, 1961).

The approach due to Ascarelli and Paskin (1968) is just the reverse of that of Longuet-Higgins and Pople (1956). They start with the diffusion coefficient of an ideal gas D_g and take into account real fluid properties through the Enskog high-density correction. They obtained the following expression for the self-diffusion coefficient

$$D = 0.28\, b_m \sqrt{\pi RT/M}\, (\xi_m/\xi) \left(\frac{10 T_m n}{T n_m} - 1 \right)^{-1} \qquad (5.3)$$

where $b = (3/4\pi) V^{1/3}$ and V is atomic volume.

Equation (5.3) has not been applied to organic liquids. When applied to liquid metals, Figure 4, Equation (5.3) yielded good results both in magnitude and temperature dependence.

Free Volume Model

Pressure dependence studies of the viscosity have revealed that this property is strongly governed by the free volume of the liquid (Doolittle, 1951) and Williams et al. (1955).

Cohen and Turnbull (1959) assigned the dominant role to the free volume also in the diffusion process. They envisage the diffusion process taking place in the following way: Adjacent to each molecule there is thought to be a free volume of variable size. The continuous motion of the molecules gives rise to density fluctuations on a molecular scale, that is, a redistribution of the free volume occurs. It is assumed that the redistribution energy is zero. A molecule undergoes a diffusive displacement at the instant when a void of at least critical size V^* (assumed to be equal to the volume of a molecule) is formed adjacent to it.

The redistribution of the free volume is equivalent to

TABLE 3. VALUES DETERMINED FROM EQUATION (5.14); FROM KESSLER ET AL. (1967)

Substance	Temp. range studied, °K	$D_1$¹) cm² sec⁻¹	E_a¹) kcal/mol	T_0 °K	$\frac{\gamma V^*}{V/N}$
$(CH_3)_4Pb$	250-325	$4.27 \cdot 10^{-4}$	1.96	35.80	0.583
$(CH_3)_4Sn$	240-330	$5.87 \cdot 10^{-4}$	1.90	58.04	0.544
$(CH_3)_4Ge$	220-310	$9.31 \cdot 10^{-4}$	2.02	77.66	0.472
$(CH_3)_4Si$	210-300	$1.58 \cdot 10^{-3}$	2.19	84.55	0.701
$(CH_3)_4C$	260-305	$3.85 \cdot 10^{-3}$	2.69	133.12	0.524
$(CH_3)_3Cl$	240-345	$2.03 \cdot 10^{-3}$	3.13	107.00	0.673
$(CH_3)_3CBr$	260-330	$1.82 \cdot 10^{-3}$	2.87	100.68	0.711
$(CH_3)_3CCl$	250-315	$1.45 \cdot 10^{-3}$	2.49	80.11	0.823
$(CH_3)_3COH$	295-355	$9.71 \cdot 10^{-1}$	7.51	212.0	0.582
$(CH_3)_3CNO_2$	215-330	$1.97 \cdot 10^{-3}$	2.58	79.38	0.763
$(CH_3)_3SiBr$	230-330	$9.79 \cdot 10^{-3}$	2.40	72.25	1.649
$(CH_3)_3SiCl$	220-315	$1.47 \cdot 10^{-3}$	2.39	85.80	1.415
$(CH_3)_3SiF$	200-295	$1.35 \cdot 10^{-3}$	2.05	80.34	1.268
$(CH_3O)_4Si$	275-370	$1.16 \cdot 10^{-3}$	2.62	76.75	1.068
$(CH_3O)_4Ge$	290-380	$6.96 \cdot 10^{-4}$	2.47	58.43	0.806

¹) $D = D_1 \exp(-E_a/RT)$

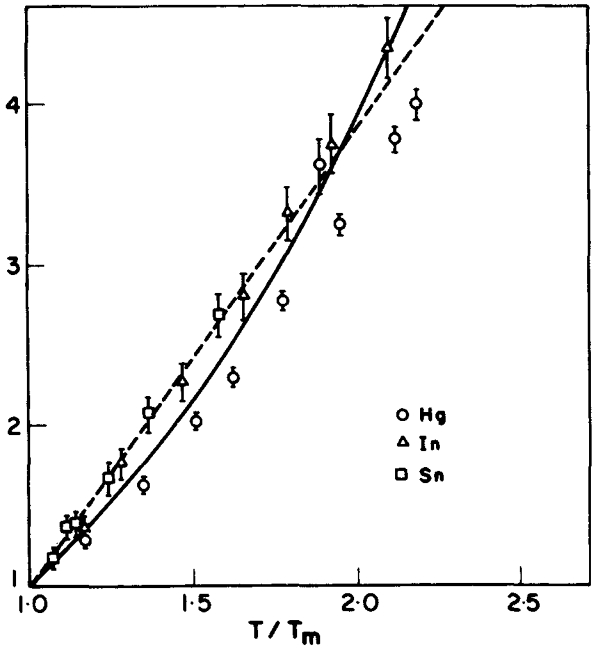


Fig. 4. Comparison of the temperature dependence of D for In, Sn and Hg with theory. The full curve is the hard-sphere calculation and the dashed curve is the phenomenological activated form $D \propto (T/T_m)^{1/2} e^{-2T_m/T}$. It may be noticed that this last form is also approximated by a linear temperature dependence (Ascarelli and Paskin, 1968).

a redistribution of the molecules. The diffusion contribution arising from this has not been considered in this model. Their final expression for the self-diffusion coefficient has the form

$$D = g\,\sigma\sqrt{3kT/m}\exp(-\gamma V^*/V_f) \qquad (5.4)$$

where γ is a numerical factor to correct for overlap of free volume V_f. Equation (5.4) has been applied to liquid metals (Cohen and Turnbull, 1959) and to nonelectrolytes (Naghizadeh and Rice, 1962; Robinson and Stewart, 1968; Kessler et al., 1967; Collings and Mills, 1970).

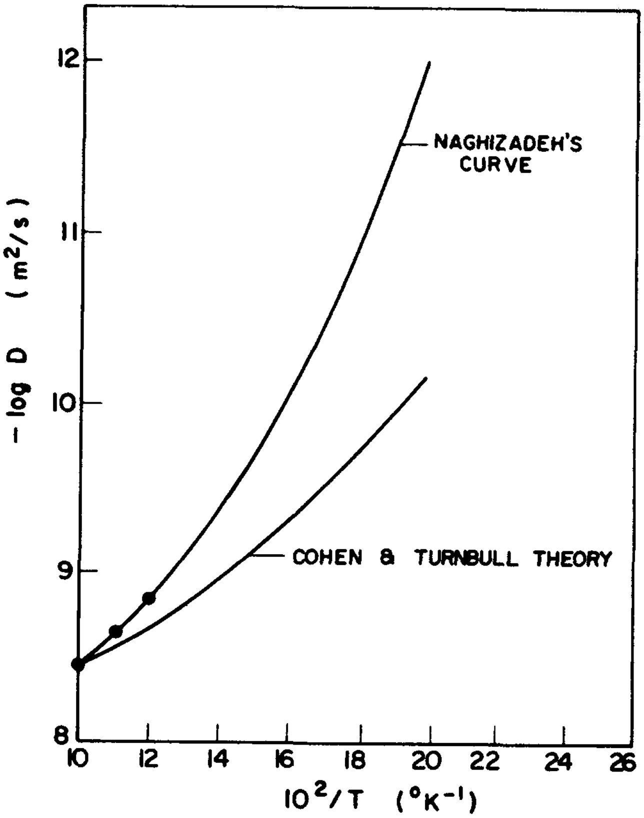


Fig. 5. Fit of Cohen and Turnbull's theory and Naghizadeh's modification to argon. Dots are experimental data. From Naghizadeh (1964).

Since Equation (5.4) contains two disposable parameters γV^* and T_0, the good agreement usually found between experimental data and the predicted values is not surprising. To be in accord with the model, γV^* of Equation (5.4) must be close to the molecular volume. This was borne out by a number of experiments (Cohen and Turnbull, 1959; Kessler et al., 1967; Robinson and Stewart, 1968). Table 3 illustrates the results for molecules of almost spherical shape (Kessler et al., 1967).

The trimethyl silicone halide group of this table has values for γV^* which are too large. As a possible explanation for this, it has been suggested (Kessler et al., 1967) that the kinetic unit in the diffusion process contains, on the average, more than one molecule. The trimethyl carbon halides, of identical structure, have values which agree far better with theory. On the other hand, for methane $\gamma V^*/(V/N)$ has also been found to be considerably larger than unity (Naghizadeh and Rice, 1962).

In a later paper, Cohen and Turnbull (1961) have attempted to analyze their theory in terms of the Lennard-Jones potential. The region near the inflection point of the potential curve has been approximated by a straight line. Thus, no energy is required for the redistribution of the free volume in this region. The linear region increases with the steepness of the repulsion branch of the potential function. Hence, Cohen and Turnbull's model, in which the redistribution energy is zero, can be expected to fit data best for molecules whose repulsion forces resemble those of hard spheres. As expected, the theory was found rather inaccurate when applied to softer molecules (Ar, Kr, Xe) (Naghizadeh and Rice, 1962). This shortcoming is demonstrated in Figure 5 for the case of argon. On the other hand, the good agreement often found for polyatomic molecules (Cohen and Turnbull, 1959; Kessler et al., 1967) may be interpreted to imply that for this type of molecules the intermolecular potential varies more rapidly than a (6-12) potential.

Naghizadeh (1964) has modified Cohen and Turnbull's theory in order to take into account the shape of the potential function as found for monatomic liquids. The derivation is similar to that of Cohen and Turnbull, but it includes the energy of redistribution of free volume, which arises from the curvature of the potential function. The result of the modification along with the original model is seen in Figure 5 for argon. The modified equation contains now three adjustable parameters.

By a different approach, Adam and Gibbs (1965) have obtained an expression for the self-diffusion coefficient which is similar to Equation (5.4). Their derivation assumes that the system consists of independent and equivalent subsystems. In their model the motion of a molecule occurs by the rearrangement of a group of molecules. These authors have shown that the size of such a cooperative region can be given in terms of the configurational entropy of the liquid. Their approach led to

$$D = D_0 \exp\left(-A/(T - T_0)\right) \qquad (5.5)$$

where D_0, T_0, and A are constants. T_0, here, is defined as temperature at which the configurational entropy vanishes.

Equations (5.4) and (5.5) differ by the term $T^{1/2}$ in the pre-exponential factor. Since this temperature dependence is weak, particularly at higher temperatures, both equations are compatible. The insignificance of the temperature dependence of the pre-exponential factor D_0 has been demonstrated by Gaven et al. (1962) for ethane (Figure 6). V_0 of 35.4 cm^3/mole has been found from diffusivity data, and 40.2 cm^3/mole from viscosity data, which is inconsistent with the assumption made in deriving Equation (5.4) that diffusion and viscous flow have the same mechanism.

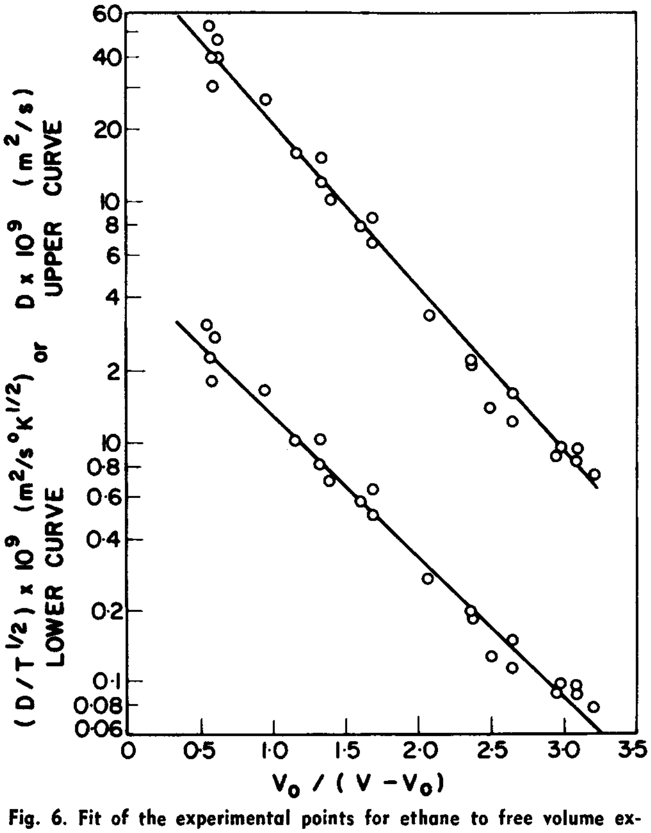


Fig. 6. Fit of the experimental points for ethane to free volume expressions with (lower curve) and without (upper curve) explicit theoretical temperature dependence. Here V_0 = 35.4 cm^3/mole. From Gaven et al. (1962).

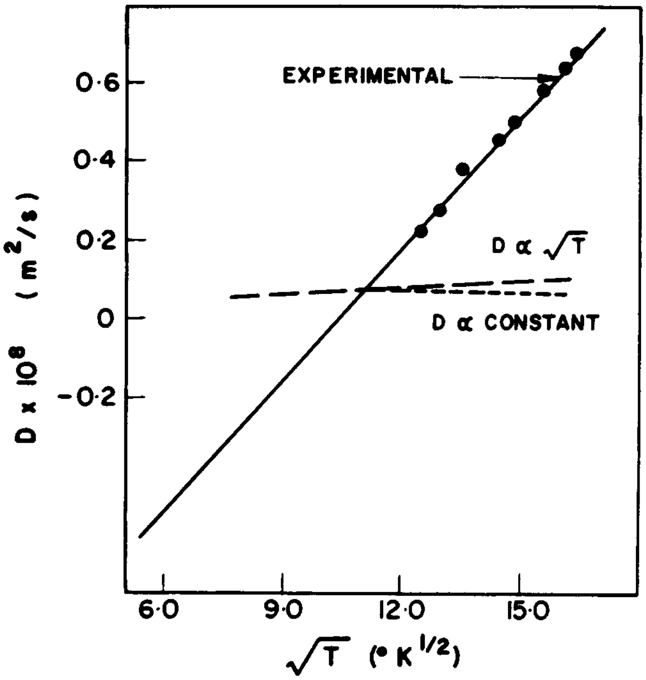


Fig. 7. Plot of D vs. $-_3T^{1/2}$ for ethane at a constant density of 0.65 g cm^{-3}. The dotted line is predicted from the simple free volume theory, using the parameters which fit the temperature dependence of D for ethane under its own vapor pressure. The dashed curve is similar except that the modified free volume theory was used (from Wade and Waugh, 1965).

According to Equation (5.4) the diffusion coefficient should be constant or vary only as $T^{1/2}$ at constant volume. Experimental work on ethane (Wade and Waugh, 1965), with density kept constant, has shown that the free volume theory in the form of Equation (5.4) is unsatisfactory in describing diffusion, Figure 7.

Macedo-Litovitz Approach

Macedo and Litovitz (1965) have combined aspects of both Eyring's reaction rate theory approach (Glasstone et al., 1941) and Cohen and Turnbull's (1959) free volume theory. According to their model, diffusion is presumed to occur only if two conditions are met simultaneously: (1) a molecule must acquire an energy greater than some critical value, and (2) a free volume V_f greater than a critical value V^* must be formed adjacent to it.

By assuming independence of the two events and using the probability of occurrence of condition 1 (Weymann, 1962) and Cohen and Turnbull's (1959) probability for condition 2, the following equation for the self-diffusion was obtained:

$$D = A \exp\left(-\frac{E}{RT} - \frac{\gamma V^*}{V_f}\right) \qquad (5.6)$$

where E is the activation energy at constant volume and V^* should be close to the van der Waals volume of the molecule V_0. The temperature dependence of the pre-exponential factor A is a matter of dispute. However, it is generally much weaker than the exponential term. Most workers agree to $A \propto T^{1/2}$. $V_f = V/N - V_0$ is the free volume per molecule. By assuming that the increase in free volume is due to thermal expansion and if V_0 is considered to be temperature independent, the free volume is given by $V_f = \alpha\,(T - T_0)\,V/N$.

In deriving Equation (5.6) it was further assumed that the Einstein relation holds, that is, $D \propto 1/\eta$. Equation

(5.6) has been also derived by using statistical mechanical arguments (Chung, 1966).

Macedo and Litovitz reason that the dependence of D on both E and V_0/V_f should account for the non-Arrhenius behavior of certain liquids and also for the weakness of the free volume theory in describing the temperature dependence at constant volume. Part of the success of the hybrid equation [Equation (5.16)] is of course due to the increased number of adjustable parameters.

A modification of Equation (5.6) has been presented by Gubbins and Tham (1969). In contrast to the conclusions reached by Matheson (1966), V_0 here has been shown to decrease with increasing temperature. It was found (Gubbins and Tham, 1969) using the viscosity data of argon and nitrogen that their modification represented an improvement for densities greater than approximately twice the critical value. No attempt has yet been made to apply a similar modification to liquids consisting of polyatomic molecules.

Significant Structure Theory

The newer liquid-state theory by Eyring, the Significant Structure Theory (Eyring and March, 1963; Eyring and John, 1969; John and Eyring, 1971; Faerber et al., 1972) also represents a model approach. The volume expansion, excess volume, upon melting and increasing temperature is accounted for by assuming vacancies in the liquid. These vacancies are, however, of quite a different nature than those in solids; they are continually changing their positions and sizes. The liquid is envisaged to be composed of solid-like molecules possessing vibrational degrees of freedom and gas-like molecules with translational degrees of freedom.

The theory postulates that any property X of a liquid can be calculated by

$$X = X_s V_s / V + X_g (V - V_s) / V \tag{5.7}$$

where X_s and X_g are the values of the property in the solid and gas state, respectively, and V_s is the solid volume. This equation has been successfully applied to thermodynamic (equilibrium) properties as well as some transport properties, such as viscosity and thermal conductivity. However, the equation for the self-diffusion coefficient

$$D = \frac{kT}{\xi \dfrac{\lambda_2 \lambda_3}{\lambda_1} \eta} \tag{5.8}$$

which is customarily quoted (Eyring and March, 1963; Eyring and John, 1969) as belonging to the significant structure theory was not derived from Equation (5.7) but rather by use of the defining equations for viscosity ($\eta = f/(dv/dX)$, f being the shear stress, and diffusion ($D = J/(\partial C/\partial X)$). Besides the usual symbols in Equation (5.8), ξ is the number of nearest neighbors in the plane of shear.

A significant structure approach to diffusion would have to start from

$$D = D_s V_s / V + D_g (V - V_s) / V \tag{5.9}$$

Since diffusion theories for the solid and gaseous state are well established, application of Equation (5.8) should be possible.

Equation (5.8) is of similar form as that derived from reaction rate theory, the only difference being ξ. Practical application of Equation (5.8) is curtailed by the fact that a packing structure has to be assumed in order to be able to express the λ's in terms of the volume. Furthermore, a variation of ξ with temperature has not been considered in the theory.

Other Model Approaches

Swalin's Model. The model of Swalin (1959) is similar to that of Cohen and Turnbull (1959), and it yields the expression

$$D = CT^2/\Delta H_v \alpha^2 \approx C'T^2 \tag{5.10}$$

where ΔH_v is the enthalpy of vaporization and α is related to the curvature of the intermolecular potential. C is a constant containing the coordination number. Reynik (1966) has pointed out an alleged oversight in the derivation of Equation (5.10). According to him the correct form of the equation should be

$$D = C'T \tag{5.11}$$

A polemic of the small fluctuation model of Swalin and Reynik has been given recently (Solar and Guthrie, 1972). There it has been demonstrated that the diffusion coefficients of dissolved hydrogen, oxygen, and carbon in pure molten iron as predicted by these models are grossly in error, particularly for hydrogen. For this case, Reynik's model even predicts a negative value for D.

Houghton's Model. Houghton (1964) has developed a cell model which treats diffusion and viscous flow as continuous stochastic processes. The model assumes a cubic cell of volume λ^3 and restricts considerations to the interactions of the nearest neighbors of the central molecule. Based on x-ray measurements of atomic distributions, Houghton considers $\lambda = 2(V/N)^{1/3}$ a reasonable approximation for the cell size and obtains

$$D = \frac{RT\rho}{6\eta M} \left(\frac{V}{N}\right)^{2/3} \tag{5.12}$$

Equation (5.12) is similar to the Stokes-Einstein equation, and it contains no adjustable parameter.

Houghton's equation has been tested by him for 25 liquids (including hydrogen-bonded liquids and liquid metals) at 25°C (most of them). It predicts the self-diffusion coefficients from viscosity and density data with an average deviation of 9%. It has been tested over a large temperature interval for HCl only (Krynicki and Powles, 1972); the agreement was less satisfactory than at constant temperature, as it is illustrated in Figure 8.

Model by Walls and Upthegrove (1964). In the model of Walls and Upthegrove, the mobility of an atom or

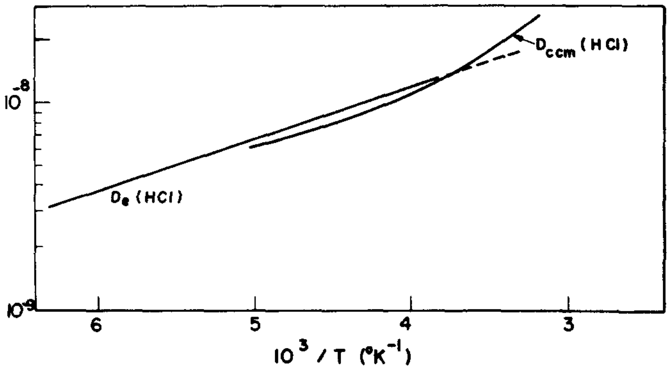


Fig. 8. Self-diffusion coefficient for liquid HCl, plotted on a log scale against $10^3/T$ where T is the absolute temperature. D_e are experimental results for HCl by O'Reilly (1968). D_{ccm} are calculated results from the cubic cell model. From Kryniki and Powles (1972).

TABLE 4. COMPARISON BETWEEN EQUATIONS

	Equation No.	$\frac{kT}{D\eta} =$	Assumptions	Explanation
Stokes-Einstein (Lamb, 1945)	4.2	$6\pi r$		
Sutherland (Lamb, 1945)	4.3	$4\pi r$		
Gierer & Wirtz (1953)		$6\pi r f_t$		$f_t = 0.16 + 0.4\, r/r_s$ r rad. of diff. part.
		$3.36\pi r$	$r/r_s = 1$	r_s rad. of solvent part.
Li & Chang (1955)	4.20	$\frac{2a}{a-b}\left(\frac{V}{N}\right)^{1/3}$		a number of all closest neighbors b number of closest neighbors in one layer
Eyring et al. (1960) Reaction rate theory		$\frac{\lambda_b\lambda_c}{\lambda_a}$	$\lambda_a = \lambda_b = \lambda_c = (V/N)^{1/3}$	
Significant Structure Theory (Eyring and John, 1969)	5.8	$\xi\frac{\lambda_2\lambda_3}{\lambda_1}$		
Dullien (1963)	4.34	$= 16r\left(\frac{r}{\delta}\right)^2$	$r = 0.5(V/N)^{1/3}$	
		$= 3.54\pi r$	$\delta/r = 1.2$	
Longuet-Higgins-Pople (1956)	5.1	$= \frac{5}{2}\frac{(V/N)}{r^2}$		
		$= \frac{10}{3}\frac{\pi r}{c}$	$c\left(\frac{V}{N}\right) = \frac{4\pi}{3}r^3$	c fraction of volume occupied by molecules
Houghton (1964)	5.12	$= \frac{24(V/N)}{\lambda^2}$		
		$= 6(V/N)^{1/3}$	$\lambda = 2(V/N)^{1/3}$	
Walls and Upthegrove (1964)	5.13	$= 2\pi r(2b + 1)$		

molecule is expressed in terms of the viscosity and geometry. By use of the Einstein relation, the following equation results

$$D = \frac{kT}{2\pi r(2b + 1)\eta} \tag{5.13}$$

where r is the atomic radius and b is a geometrical factor, namely, the ratio of the atomic radius to the intermolecular distance. Factor b is postulated to be the same for one given class of liquids. Equation (5.13) has been modified further by introducing an expression for η as had been found by the absolute reaction rate theory.

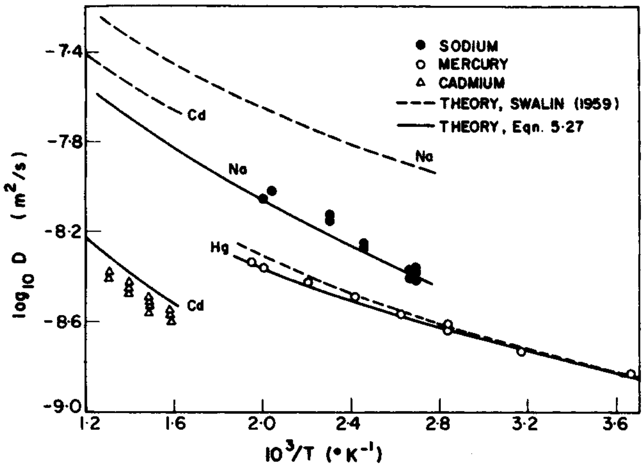


Fig. 9. Comparison of theory with liquid metals self-diffusion data (Walls and Upthegrove, 1964).

Equation (5.13) has been derived on the basis of a liquid metal model. For the case of atoms b is clearly defined, but it is very doubtful if b offers an adequate description for liquids consisting of polyatomic (rigid or nonrigid) molecules. As can be seen in Figures (5.9), it predicts diffusion data for liquid metals (Walls and Upthegrove, 1964) better than Swalin's (1959) fluctuation model.

Discussion of Various Self-Diffusion Equations

A great number of diffusion coefficient equations contain the viscosity as independent variable. Most of them, when suitably rearranged, lead to expressions which are similar or almost identical to the Stokes-Einstein relation, as shown in Table 4.

The Stokes-Einstein equation [Equation (4.2)], although based on the assumption of a spherical particle diffusing in a solvent consisting of a continuum, has often been used to test self-diffusion data pertaining to the diffusion of molecules of equal size. It has also been applied to the self-diffusion of extremely nonspherical molecules.

There is a large body of evidence now to show that the Stokes-Einstein equation yields too small values for the molecular radius. Similarly, no satisfactory agreement has been reached if the radius is taken proportional to the cube root of the molal volume. This has been observed for ethane (Gaven et al., 1962), carbon tetrachloride, methanol, ethanol, benzene (Rathbun and Babb, 1961). Figure 10 shows a plot for ethane (Gaven et al., 1962) in the form of the Stokes-Einstein relation. The failure of this relation is clearly seen by the curvature. The radius is often taken as proportional to the cube root of the spe-

Table 5. Values for $D\eta$ and $D\eta/T$ as Calculated from Experimental Data for $(CH_3)_4Sn$ (= 1) and $(CH_3)_4Pb$ (= 2) (from Bambynek, 1960)

T	$D_1\eta_1 \times 10^8$	$D_2\eta_2 \times 10^8$	$\frac{D_1\eta_1}{T} \times 10^{10}$	$\frac{D_2\eta_2}{T} \times 10^{10}$
°K	dynes	dynes	dynes/grad	dynes/grad
288	9,8 ± 0,3	10,4 ± 0,3	3,39 ± 0,10	3,61 ± 0,10
293	9,8 ± 0,2	10,3 ± 0,3	3,36 ± 0,07	3,50 ± 0,10
298	9,8 ± 0,2	10,2 ± 0,3	3,30 ± 0,07	3,43 ± 0,09
303	9,9 ± 0,2	10,1 ± 0,3	3,26 ± 0,04	3,34 ± 0,07

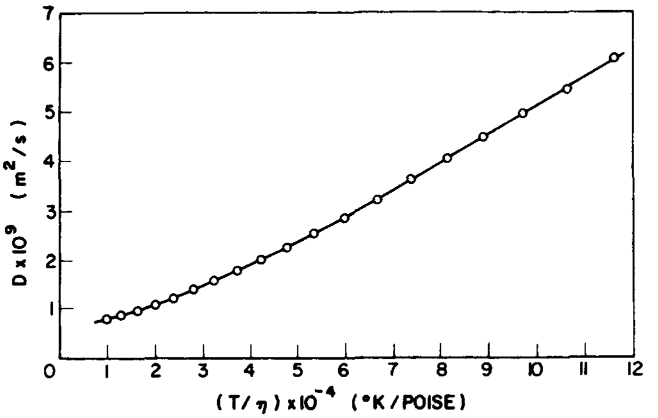


Fig. 10. Failure of the Stokes-Einstein relation to describe diffusion in ethane. The points are taken from smoothed diffusion data (from Gaven et al., 1962).

cific volume. If such a dependence were included in the plot of Figure 10 the curvature would become even more pronounced.

The agreement becomes much better with respect to the magnitude of D when using the Sutherland equation [Equation (4.3)]. However, this equation does not change the temperature dependence. The product $D\eta/T$ as well as $D\eta\ V^{1/3}/T$ usually found to increase with temperature, but exceptions have been noticed for tetramethyl tin and tetramethyl lead (Bambynek, 1960). Table 5 shows $D\eta$ and $D\eta/T$ for these two compounds as a function of temperature.

The Stokes-Einstein relation when tested for water up to 10^4 atm, at constant temperature, has been found to hold approximately (Benedek and Purcell, 1954), Figure 11. The conclusion regarding the closeness of viscous flow and diffusion for water is confirmed by independent information (Dass and Varshneya, 1969) since the same value for the temperature T_0 (see free volume theory) was found from the viscosity and from the diffusion data.

From experimental data Dullien (1963) found δ/r = 1.2 (see Section 4.3 in Part I). By substituting this value into his general formula, a numerical factor approximately equal to that in the Sutherland relation and Gierer and Wirtz's equation (for $r/r_s = 1$) was obtained. In a later article by Dullien (1972) a relation between δ and the molecular diameter has been presented. This relation is discussed in the section on Estimation of Self-Diffusion Coefficients. In contrast to the other equations, Dullien's equation does not imply a constant numerical factor because, as pointed out by him, δ/r is dependent upon temperature and pressure. With the increased amount of experimental data available, recent work (Ertl, 1973) on the temperature dependence of δ/r for a variety of different liquids over their normal liquid range has revealed that a constant value for $\eta D/kT$ obtained for pure liquids is fortuitous. This is due to the coincidence that δ [see Equation 6.17)] exhibits a very flat minimum between $0.45 \leq T_r \leq 0.50$, where $T_r = T/T_c$, and rises slowly for higher temperature. For $T_r < 0.45$ δ increases sharply. The minimum region corresponds approximately to temperatures where most of the earlier measurements were taken and the Stokes-Einstein relation was tested. All of the Stokes-Einstein type equations which assume a constant factor can be expected to apply only for a limited range of temperature.

For an homologous series of liquids, the temperature dependence of the diffusion coefficient normally increases with molecular weight (Douglass and McCall, 1958; McCall et al., 1961; Kessler et al., 1967; Ertl, 1973). An exception to this has also been noted for $(CH_3)_4X$ (X = Group IV elements) (Kessler et al., 1967). These trends are clearly evident in Figures 12 and 13 in which D is plotted versus $1/T$.

For the vast majority of the liquids investigated, the temperature dependence of the diffusion coefficient can be represented in the form of an Arrhenius equation within experimental error. There are enough reasons to believe (Hildebrand and Scott, 1962) that no physical significance should be attached to the form of this equation and its implication of an activation energy. This is supported, for example, by data (Watts et al., 1955) which gave jump lengths considerably smaller than one

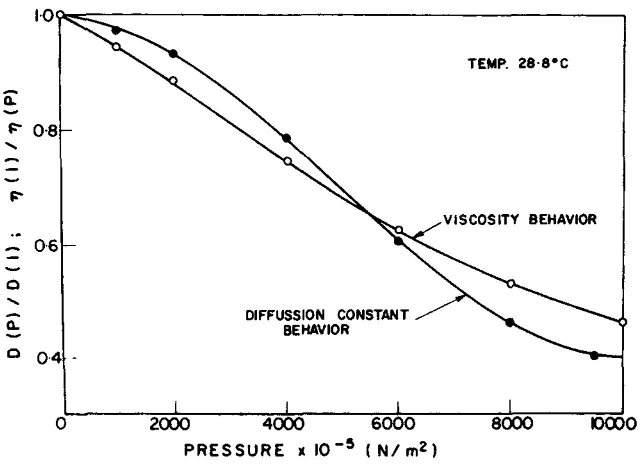
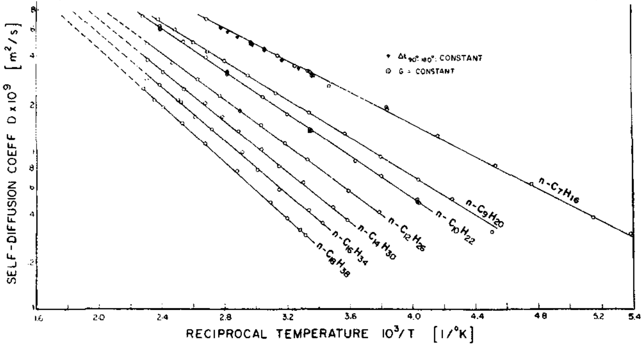


Fig. 11. Reciprocal of normalized viscosity and normalized diffusion constant vs. pressure for water. $D(1)$ and $\eta(1)$ are the diffusion coefficient and viscosity at 1 atm (from Benedek and Purcell, 1954).



EXPERIMENTAL DIFFUSIVITIES OF N-PARAFFINS

Fig. 12. Self-diffusion coefficients for n-paraffins vs. reciprocal temperature (Ertl, 1973).

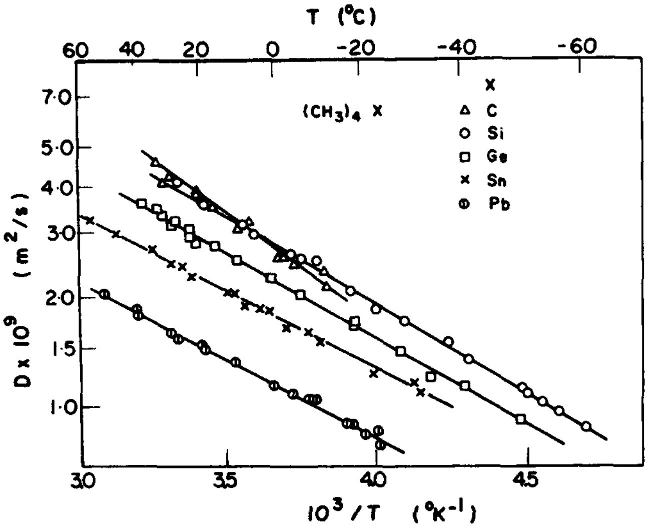


Fig. 13. Self-diffusion coefficients for $(CH_3)_4X$ vs. $10^3/T$. (X-c, Si, Ge, Sn, Pb). From Kessler et al. (1967).

molecular diameter as expected from models based on the concept of activation energy. The Arrhenius equation has been used in the tabulation section (see Supplement) as a mere convenience because most investigators have reported their results in this form. As is well known, other forms of equations are—in general—also suitable, for example, the free volume equation.

Some liquids exhibit a marked deviation from the constant activation energy. Both increases and decreases with temperature have been observed. Examples for the first case are, for example, water (Simpson and Carr, 1958), toluene, Figure 14, and diglycoldimethyl ether (Krüger and Weiss, 1970); and for the latter, ethane (Gaven et al., 1962), neopentane (Douglass et al., 1961), Figure 3, and sulphurhexafluoride (Hackleman and Hubbard, 1963). Normal paraffins also show a departure (latter case) close to the critical temperature (Panchenkov et al., 1969).

Measurements of the volume of activation of the *n*-paraffins (Fishman, 1955; Douglass and McCall, 1958) and linear dimethylsiloxanes (McCall et al., 1961) suggest a diffusion process by which the diffusing unit is not the entire molecule, but rather single methyl groups. Segmental motion is thus largely responsible for diffusion of this class of flexible molecules. Such a result is not unexpected because, as the length of a molecule increases, the orientations and movements of the ends become increasingly independent.

Several investigators (Gaven et al., 1963; Rugheimer and Hubbard, 1963; Robinson and Stewart, 1968) have attempted to correlate diffusion coefficients on the basis of the corresponding state principle. The work is partly encouraging but still inconclusive due to the lack of experimental data over wide ranges of density. Some agreement has been noted for the liquified noble gases and simple spherical ployatomic molecules. The extension of the corresponding state principle to liquids with nonspherical molecules is likely to require additional quantities to characterize the geometrical structure. This is supported by recent work (Doan and Brunet, 1972) on *n*-alkanes.

Self-diffusion at or near the critical point has been recently reviewed (Hamann et al., 1972). Thus, we restrict ourselves to only a few remarks. Measurements of the diffusion coefficient in the region of the critical point are still scarce. In the majority of cases (Hamann et al., 1966; Trappeniers and Oosting, 1966; Hausser et al., 1966; Tison and Hunt, 1971), no anomaly has been observed. However, Noble and Bloom (1965) reported a marked decrease of D close to T_c for ethane. The experimental data for methane are contradictory; normal behavior (Trappeniers and Oosting, 1966 as well as an anomaly (Cini Castagnoli et al., 1970)—similar to ethane—have been observed.

6. EMPIRICAL AND SEMI-EMPIRICAL EQUATIONS

Mutual Diffusion Coefficients at Infinite Dilution

The rigorous theoretical approach has not provided as yet practical predictive equations. However, some of the theories have served as starting points for developing semi-empirical or empirical equations. Most of the empirical correlations are limited to the estimation of mutual diffusion coefficients at infinite dilution. Several of them which are useful in the predictive sense have been discussed in Reid and Sherwood's book (1966, Ch. 11) including the Wilke-Chang equation, the Scheibel equation, and others.

Wilke-Chang's equation was found to fail for highly viscous solvents. The approach used by Olander (1963) and Gainer and Metzner (1965) is more successful for such systems.

Equations of Lusis and Ratcliff. Recently, Lusis and Ratcliff (1968) suggested an equation which expresses the group $D_{AB}{}^0\eta_B/T$ as a function of the ratio of molal volumes of the solute and the solvent

$$D_{AB}{}^0\eta_B/T = 8.52 \times 10^{-10}\,(V_B)^{-1/3}\left[1.40\left(\frac{V_B}{V_A}\right)^{1/3} + \frac{V_B}{V_A}\right] \tag{6.1}$$

where V_A and V_B are LeBas molal volumes (Reid and Sherwood, 1966, p. 86) in cm³/gm-mole. This equation was shown (Lusis and Ratcliff, 1968) to give better results than the previous correlations for some systems.

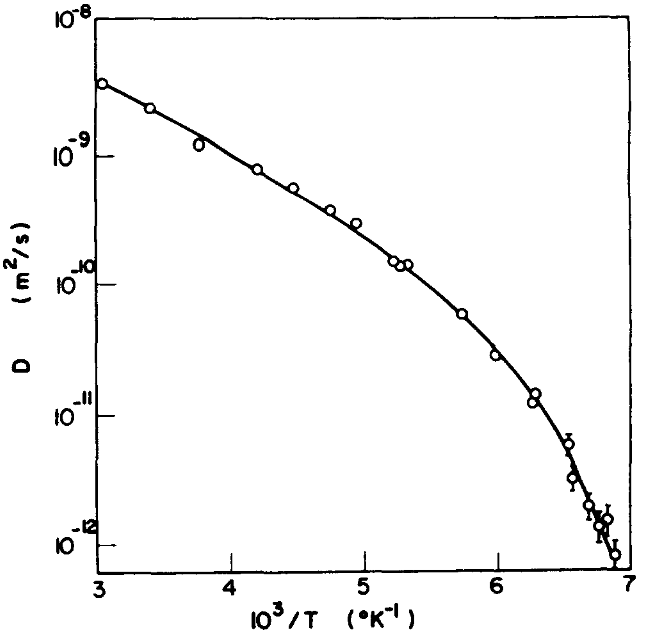


Fig. 14. Self-diffusion coefficient of toluene as a function of reciprocal temperature (Kruger and Weiss, 1970).

Large errors were obtained in the estimation of D_{AB}^0 of short straight-chain molecules in long chain solvents (~39% for the diffusivity of hexane in hexadecane). Like other correlations, this equation also fails with associating systems. It was shown (Hayduk and Cheng, 1971) that Equation (6.1) resulted in larger errors than the Wilke-Chang equation for the diffusion of ethane in hexane, heptane, octane, dodecane, and hexadecane. Both equations deviated increasingly from the experimental results as the viscosity of the solvent increased.

More recently, Ratcliff and Lusis (1971) developed an equation for systems in which 1:1 complex is formed. Such a complex may be formed in systems in which one of the components contains an active hydrogen atom but no donor atoms (for example, $CHCl_3$), and the other component contains donor atoms but no active hydrogen atom (for example, ethers, ketones, esters, and aldehydes). Their equation is

$$D_{AB}^0 = \frac{1}{1+K} D_{A_1} + K\, D_{A_1B_1} \qquad (6.2)$$

where K is an association constant which may be determined from vapor-liquid equilibrium data, as

$$K = \frac{1-\gamma_A^0}{\gamma_A^0} \qquad (6.3)$$

where γ_A^0 is activity coefficient at infinite dilution. D_{A_1} and $D_{A_1B_1}$ may be found from the following empirical equation which is of similar form as Equation (6.1)

$$\frac{D_i\, \eta_B}{T} = 8.52 \times 10^{-10}(V_B)^{-1/3}\, 1.40\, R_i^{1/3} + R_i \qquad (6.4)$$

where

$$R_i = \frac{V_B}{V_A} \quad \text{if} \quad i = A_1$$

and

$$R_i = \frac{V_B}{V_A + V_B} \quad \text{if} \quad i = A_1B_1$$

Equation (6.2) has been tested for a few systems. An average error of about 6% was reported. The average error of the Wilke-Chang equation with the same systems was shown to about 27% (Ratcliff and Lusis, 1971). Equation (6.2) needs modifying for systems in which complexes of different sizes are formed.

Correlation of Hayduk and Cheng. In an interesting empirical study by Hayduk and Cheng (1971), a hypothesis that the solute diffusivity in dilute solutions depends only on the solvent viscosity was tested. Study was made by plotting the logarithm of D_{AB}^0 against the logarithm of solvent viscosity. A variety of solutes such as organic acids and alcohols, among others, and a number of solvents were tested. A relation of the following form was generally found to apply to systems in which there is no association or complexing

$$D_{AB}^0\, \eta_B^A = B \qquad (6.5)$$

Here, A and B are constants which depend only on the solute properties. There are, however, some systems for which Equation (6.5) gives rather large errors: for example, CCl_4 in ethanol and dioxane (~18%); benzene in CCl_4, chlorobenzene, and bromobenzene (>20%); toluene in CCl_4, chlorobenzene, and bromobenzene (~20%). While organic acids are known to associate, their diffusivities in different solvents were also found to follow Equation (6.5).

Equation (6.5) is useful to predict diffusivities of a solute in various solvents if D_{AB}^0 values in at least two solvents of known viscosities are known.

Hammond and Stokes (1965) observed that the product $D_{AB}^0\, \eta_B$ is a linear function of the molal volume of the solute for CCl_4 in a variety of solvents consisting of (1) spherical molecules, (2) elongated molecules, and (3) alcohols. This relation was also found to apply to benzene in *n*-hexane, *n*-heptane, and *n*-octane (Harris et al., 1970).

Mutual Diffusion Coefficients as Functions of Composition

Estimation of mutual diffusion coefficients at concentrations other than infinitely dilute solutions is also very important. Often mutual diffusivity D_{AB} has been correlated with the two limiting values D_{AB}^0 and D_{AB}^∞. The limiting values can either be obtained experimentally or estimated from the empirical or semiempirical equations discussed above. For thermodynamically ideal or nearly ideal systems D_{AB} is found to be a nearly linear function of composition (Caldwell and Babb, 1956; Burchard and Toor, 1962; Shuck and Toor, 1963; Van Geet and Adamson, 1964). Mostly mole fractions have been used; however, for some systems weight fraction was found to give a little better linearity (for example, Van Geet and Adamson, 1964). Based on this empirical fact, the following relation has been suggested for ideal or nearly ideal systems

$$D_{AB} = x_B\, D_{AB}^0 + x_A\, D_{AB}^\infty \qquad (6.6)$$

Vignes Correlation. Equation (6.6) does not fit experimental diffusion data adequately for nonideal systems. Vignes (1966) found, for a variety of binary systems, that the activity-corrected diffusion coefficients are exponential functions of mole fractions. He proposed

$$\frac{D_{AB}}{\beta} = (D_{AB}^0)^{x_B}\, (D_{AB}^\infty)^{x_A} \qquad (6.7)$$

Dullien (1971) performed a thorough statistical analysis of the predictions by Equation (6.7). A simpler comparison with experimental data has been given by Leffler and Cullinan (1970). These are shown in the first column of Table 6. Equation (6.7) generally predicts lower values than the actual ones.

Leffler and Cullinan's Equation. Cullinan (1966) showed that the Vignes correlation may be rationalized on the basis of Eyring's theory if the free energy of activation $\Delta G_D^{\neq}$ is assumed to be a linear function of the mole fraction and if λ is assumed to be invariant with composition.

Instead of assuming λ to be constant, Leffler and Cullinan (1970) proposed

$$\lambda = \lambda_A^{x_A}\, \lambda_B^{x_B} \qquad (6.8)$$

where λ_A and λ_B correspond to pure components. On combining Eyring's equation,

$$\frac{D_{AB}\eta}{\beta} = \frac{kT}{\lambda} \exp\,(\Delta G_V^{\neq} - \Delta G_D^{\neq})/RT \qquad (6.9)$$

with (6.8) Leffler and Cullinan obtained

$$\frac{D_{AB}}{\beta} = (D_{AB}^\infty \eta_A)^{x_A}\, (D_{AB}^0 \eta_B)^{x_B} \qquad (6.10)$$

In another paper, Cullinan (1971) showed that additional restrictions on the use of Equation (6.10) are

TABLE 6. COMPARISONS OF EQUATIONS (6.7), (6.10), AND (6.11) WITH EXPERIMENTAL DATA

System	(Predicted—Experimental) Max. % deviation Equation (6.7)	Equation (6.10)	Equation (6.11)
Cyclohexane + carbon tetrachloride	−4.1	1.5	—
Hexane + carbon tetrachloride	−12.7	−1.9	—
Acetone + benzene	−6.0	−1.5	—
Cyclohexane + benzene	−12.0	4.0	—
Benzene + carbon tetrachloride	−7.0	−7.5	—
Toluene + chlorobenzene	−3.0	−4.0	—
Chlorobenzene + bromobenzene	−4.1	−4.1	—
Methanol + propanol	−5.0	−6.5	—
Butanol + propanol	1.5	2.0	—
Methyl ethyl ketone + carbon tetrachloride	1.5	−1.0	−9.01*
Acetone + carbon tetrachloride	−18.5	−19.6	6.20*
Hexane + hexadecane	9.0	−18.0	—
Methanol + carbon tetrachloride	—	—	12.5*
Methanol + benzene	—	—	10.0*
Ethanol + benzene	—	—	15.4*

* The values with the superscript "*" were taken from Ref. (Rathbun and Babb, 1966), and the other values were taken from Ref. (Leffler and Cullinan, 1970).

that the partial molar volumes and the coefficient of thermal expansion of the system be composition independent. Equation (6.10) predicts better than Equation (6.7) for some systems (see Table 6) for example, *n*-hexane + carbon tetrachloride (errors 1.9% and 12.7%, respectively), and benzene-cyclohexane (errors 4.0% and 12%, respectively). On the other hand, Equation (6.10) predicted diffusion values with rather large errors for *n*-alkane systems. For example, for *n*-hexane + *n*-hexadecane the error with this equation is 18%, while it is only 9% with Vigne's correlation.

Rathbun and Babb's Equation. Rathbun and Babb (1966) suggested the equation

$$D_{AB} = (D_{AB}^0 x_B + D_{AB}^{\infty} x_A)\left(\frac{d \ln a}{d \ln x}\right)^s \qquad (6.11)$$

where s is an adjustable parameter. This equation can be used with the recommended value of $s = 0.6$ for binary systems containing an associated and a nonpolar component. With this value Equation (6.11) has reproduced the diffusion data for methanol, ethanol, and acetone in mixtures with carbon tetrachloride and benzene at temperatures between 10° and 55°C (see Table 6). The difference between the predicted and actual values was usually within ± 12.5% except for ethanol + carbon tetrachloride at 10°C (23.6%) and methanol + benzene (23.6%). For acetone + carbon tetrachloride, for which both Equations (6.10) and (6.7) failed to estimate satisfactorily, Equation (6.11) predicted better (error 6.2% at 25°C).

Rathbun and Babb (1966) suggested the value $s = 0.3$ for systems exhibiting negative deviations from Raoult's law. The calculated diffusion values for diethyl ether + chloroform were reasonably close to the experimental values (within 2 to 5%).

Haluska and Colver's Equation. Haluska and Colver (1971) proposed that the friction factor ξ_{AB} appearing in Equation (4.36) be estimated in the following manner

$$\xi_{AB} = \eta \frac{x_A}{\eta_A} \xi_{AB}^{\infty} + \frac{x_B}{\eta_B} \xi_{AB}^0 \qquad (6.12)$$

where

$$\xi_{AB}^{\infty} = \frac{RTV_A^0}{D_{AB}^{\infty}}, \qquad (6.13)$$

and

$$\xi_{AB}^0 = \frac{RTV_B^0}{D_{AB}^0}$$

Using essentially Hartley-Crank's equation, they obtained the following expression:

$$D_{AB} = \frac{\eta_A \eta_B RT(V_A^0 x_A + V_B^0 x_B)}{\eta(x_A \eta_B \xi_{AB}^{\infty} + x_B \eta_A \xi_{AB}^0)} \qquad (6.14)$$

Equation (6.14) has been tested only with a few systems such as toluene + methylcyclohexane, toluene + aniline, methylcyclohexane + aniline, and chloroform + carbon tetrachloride. Generally the error was of the same magnitude as that obtained by the Vignes correlation.

Estimation of Self-Diffusion Coefficients

Presently no empirical or semi-empirical equation exists which could reliably predict self-diffusion coefficients as a function of temperature and pressure. Several attempts have been made but the equations proposed are applicable only to limited classes of liquids and/or over limited temperature ranges. An equation containing the pressure explicitly is not found in the literature.

From the engineering point of view, equations relating the self-diffusion coefficient to the mutual diffusion coefficient are most desirable. Only in few instances have such equations been proposed (Lamm, 1954; Van Geet and Adamson, 1965).

Dullien's Equation. The starting point in deriving the predictive equation is Equation (4.34). For the case of a one component system this equation simplifies to

$$\delta = \sqrt{2\eta VD/RT} \qquad (6.15)$$

where D is now the self-diffusion coefficient and the other symbols have the usual meaning.

The derivation of Equation (6.15) did not require the assumption of a liquid model. It has been shown (Dullien, 1963) that for the gaseous state Equation (6.15) yields an expression in agreement with the kinetic gas theory. A liquid model has been assumed (Dullien, 1972) to find a relation between δ [Equation (6.15)] and more directly measurable parameters. In this model the molecules are assumed to be rigid and the molecular diameter is considered to be temperature independent.

For molecules of any arbitrary shape

$$\delta = 0.63d \qquad (6.16)$$

where

$$d = \int l(\mathbf{\Omega})p(\mathbf{\Omega})d(\mathbf{\Omega}) \qquad (6.16a)$$

is a momentum-transfer-average molecular diameter. $l(\mathbf{\Omega})$ is the center-to-center distance of two touching molecules for a particular mutual orientation defined by the vector $\mathbf{\Omega}$, and $p(\mathbf{\Omega})$ is the probability of occurrence for this orientation.

Combination of Equations (6.16) and (6.15) has resulted in the following relationship (Dullien, 1972)

$$d = 2.24\sqrt{\eta VD/RT} \qquad (6.17)$$

The values for the effective molecular diameter d calculated from this equation were found (Dullien, 1972) to be in close agreement with values obtained by some other methods.

Empiricism has been introduced when the expression for δ as obtained from the kinetic gas theory and that for the liquid ($\delta = 0.63d$) have been combined at the critical temperature. As a result, d has been obtained in terms of the critical volume V_c. Combination with Equation (6.17) has resulted in the following simple relation:

$$\eta VD/RT = C \times V_c^{2/3} \qquad (6.18)$$

where C is a constant. A value of 0.124×10^{-16} for C was obtained from the best fit to the data of a large number of liquids where the necessary properties were available. The correlation is shown in Figure 15. The scatter is remarkably small considering the large variety of the liquids. Equation (6.18) fits the experimental data of 32 liquids with a mean deviation of 4%. This is a distinct improvement considering the wide variety of liquids studied.

As it has already been mentioned in Section 5, the quantity $\eta VD/RT$ is—contrary to the assumption made in deriving Equation (6.18)—dependent on temperature. The temperature dependence becomes increasingly pronounced for reduced temperatures $T_r = T/T_c < 0.45$ (Ertl, 1973) and also in the proximity of the critical temperature T_c.

Van Geet and Adamson's Equation. Van Geet and Adamson's (1965) equation is limited to normal paraffins. Their approach is based on the regularities which are found for this class of liquids. Adamson (1960) noticed earlier a linear relation between log D_0 and the activation energy E, namely,

$$\log D_0 = -3.28 + 0.82 \times 10^{-3}\, E/2.3R \qquad (6.19)$$

where D_0 is the preexponential factor of the Arrhenius type equation

$$D = D_0 \exp(-E/RT) \qquad (6.20)$$

R = 1.9872 kcal/mole is the gas constant. Equation (6.20) has been found to hold for n-paraffins.

Combining the Equations (6.19) and (6.20) gives the empirical equation proposed by Van Geet and Adamson (1965)

$$\log D = -3.28 - \frac{10^{-3}E}{2.3R}\left(\frac{10^3}{T} - 0.82\right) \qquad (6.21)$$

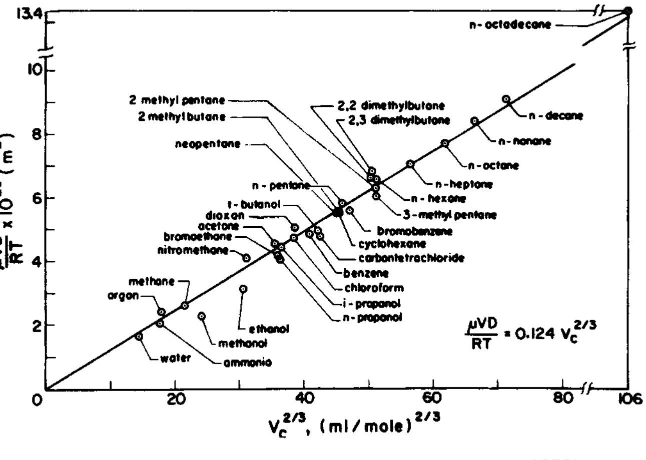


Fig. 15. Self-diffusivity correlation for liquids (Dullien, 1972).

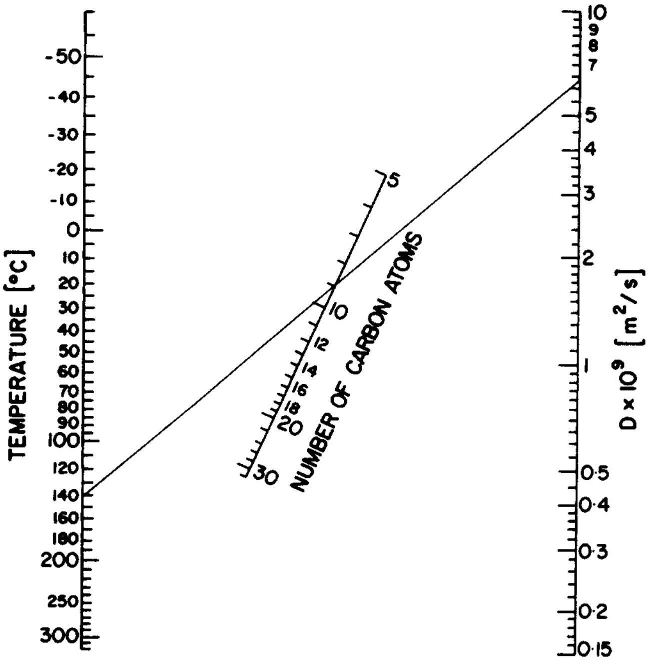


Fig. 16. Nomograph for the prediction of self-diffusivities for n-parffins (from van Geet and Adamson, 1965).

The authors stated that this equation provides self-diffusion coefficients with an accuracy of about 5% for n-paraffins (n-C_nH_{2n+2}) from n = 5 to 32 and for temperatures between −50°C and 300°C. The simple form of Equation (6.21) facilitated the construction of a nomograph (Figure 16). It has been suggested (Van Geet and Adamson, 1965) to extend this approach to other homologous series.

Values from the nomograph have been compared with experimental values recently determined (Ertl, 1973). Agreement is good at low temperatures but the values disagree at high temperatures by more than the stated error.

Although applicable over a wide temperature range the monograph does not cover the whole liquid range.

7. DEVELOPMENTS IN EXPERIMENTAL TECHNIQUES FOR MEASURING LIQUID DIFFUSION COEFFICIENTS

Almost all the methods employ Fick's first and/or second law for determining diffusion coefficients. The difference between the methods lies mainly in the boundary conditions and in the analytical procedures used. Depending on the boundary conditions, diffusion can be classified as free diffusion, restricted diffusion, or steady state diffusion. The differential equations describing the diffusion process have been solved analytically for various boundary conditions (Crank, 1956; Geddes and Pontius, 1959; Jost, 1960; Tyrrell, 1961). In order to obtain the solutions, the diffusion coefficient has been mostly assumed to be independent of composition. This assumption is justifiable in cases involving very dilute solutions or small concentration ranges. Highly accurate diffusion measurements were not obtained until a short time ago. Difficulties used to arise because of convection currents or bulk movement of the medium due to vibration, temperature fluctuations, or interfacial boundary formations.

Diaphragm Cell Technique

First developed by Northrop and Anson (1929), later improved by McBain (1931 and 1935), Gordon (1937), Hartley and Runnicles (1938), and others and brought by Stokes (1950) to a stage where it is now recognized as an exact method for the measurement of diffusion coefficients. Gordon (1945) wrote a comprehensive article on this technique. Recent developments have been reviewed by Mills and Woolf (1968).

Correct stirring is very important for this method. For viscous solutions, Henrion (1954) used an extra stirrer which floated in the bulk of the solution in the lower compartment. Holmes et al. (1963) and Mills and Boland (1968) also used new methods of stirring. The cell used by Holmes et al. contains a vertical diaphragm instead of a horizontal one. This cell was found to be successful for most systems; however, it may not be equally successful for solutions of high viscosity and low diffusivity. The method of external stirring by means of a pump as used by Mills and Boland may be helpful in the study of diffusion in viscous solutions. Pumping, however, is a difficult technique requiring great care and much testing to avoid pumping liquid through the diaphragm.

Recently Sanni and Hutchison (1968) described a modified diaphragm-cell in which the composition in the top compartment is determined continuously by measuring changes in the conductivity or capacitance of the solution. Another rapid method for measuring liquid diffusivity was described by Hollander and Barker (1963). In this method the concentrations are monitored outside the diaphragm cell. The contents of the diaphragm cell are circulated periodically through a scintillation counting chamber and the concentration differences are measured.

A technique reported by Rao and Bennett (1971) also employs a sintered glass diaphragm. Steady state concentrations in the two compartments are achieved by a continuous supply of solution to one compartment and making the other compartment an infinite sink. The design of this cell also permits diffusion measurements under a pressure gradient. An apparatus utilizing a filter paper diaphragm has been described in the literature (Kreevoy and Wewerka, 1967). This type of cell needed only an hour or so for a diffusion measurement, and diffusion coefficients reproducible to ± 2% have been obtained.

Surface effects in the diaphragm have been investigated by Stokes (1950a). It appears that the phenomenon may be limited to charged species at low concentrations, although there is some evidence that dipolar molecules may also cause surface effects (Mills and Woolf, 1968, p. 36). The reasons for surface effects may be attributed to the inhomogeneities and defects in the surface rather than to the material of the diaphragm.

Through error-analysis, Stokes (1950b) and Robinson, et al. (1965) showed that initial large concentration differences reduce the relative error in the diffusivity measurements. The condition for this relative error to be a minimum is a diffusion time

$$t_{\text{opt}} = \frac{1.1}{\beta_c \overline{D}_{AB}} \tag{7.1}$$

This relationship and other considerations require that for precise results the product $\overline{D}_{AB}t$ for calibration runs be the same as for the actual runs. (D_{AB} is a time-and-concentration-average diffusion coefficient.)

For the systems in which the partial molal volumes are composition dependent, an account has to be made for the bulk flow in order to calculate D_{AB} values from $\overline{D}_{AB}$ values. Equation (2.4) instead of Equation (2.1) was, therefore, used in a Gordon type analysis. With the general, rigorous equations developed by Robinson et al. (1965) it is now possible, although laborious, to calculate differential coefficients for highly nonideal systems from diaphragm cell measurements performed with large concentration differences. The only assumption in their equation is the existence of steady state conditions during the diffusion experiment.

Isotope Effects

Strictly speaking, self- or intra-diffusion coefficients can not be measured by the radioactive isotope methods because the radioactive and stable isotopes of different masses have somewhat different diffusion rates. If large amounts of radioactive isotopes are present, especially in an isotopic mixture of lighter elements (such as normal water and deuterium oxide), the diffusivity of radioactive isotopes is measurably different from that of the unsubstituted compounds (Tyrrell, 1961, p. 152). Variation of deuterium oxide concentration in mixtures with normal water has a significant effect on its intra-diffusion coefficient (Adamson and Irani, 1957; Douglass and McCall, 1959). Other physical properties, particularly viscosity (Tyrrell, 1961), also change significantly with the concentration of deuterium oxide.

McLaughlin (1960) suggested the equation

$$\frac{D_c^*}{D_0^*} = \left(\frac{M_0}{M_i}\right)^{1/2} \tag{7.2}$$

to obtain a corrected value of self- or intra-diffusion coefficient D_c^* from an observed value D_0^*. M_0 and M_i in Equation (7.2) are molecular weights of the labeled and unlabeled molecules, respectively. The difference in the limiting mutual and tracer diffusion values observed by Mills (1963) and Aoyagi and Albright (1972) was attributed to the isotope effect and to the assumed systematic error introduced by calibration with aqueous potassium chloride solution (Eppstein, 1969). Eppstein thus rationalized Mills' data with the following equation

$$\frac{D_c^*}{D_0^*} = \frac{1}{1.020}\left(\frac{M_0}{M_i}\right)^{1/2} \tag{7.3}$$

where the factor 1.020 corrects for the assumed systematic error in the calibration. Harris, Pua, and Dunlop (1970) demonstrated the absence of any such error in calibration. They used both KCl and urea for calibration and obtained almost identical results. They measured self-diffusion coefficients of benzene with labeled samples of different average molecular weights, namely, 81, 84, and 88 and obtained all values within the range of 2.203 to 2.218 (10^{-5} cm^2/s). The approximately 4% deviation expected from Equation (7.3) is much too large compared to the observed range.

When very small amounts of radioactive isotopes are used to measure self- or intra-diffusion coefficients, as is usually done, the isotope effects can be assumed to be negligible. The diffusion coefficients obtained in this manner should indeed be very close to the true values. The great virtue of the radiotracers is that they can be assayed accurately even when they are present in very small concentrations.

Assay of Radioactivity

Measurements of coefficients can be carried out by following the diffusion of radiotracers in the diaphragm cell or in the capillaries. Very precise determination of the radiotracer concentrations has not been possible until the development of liquid scintillation counter.

The principle virtues of the liquid scintillation counters are their high efficiency and excellent sensitivity. The efficiency is high because the sample and the scintillation phosphors are dissolved in the same solution resulting in a 4π geometry. The success and popularity of this method has been largely due to recent improvements in the photomultiplier tubes and to the discovery of efficient phosphors in liquid form. The desirable characteristics of the photomultiplier tubes are low dark current and high signal-to noise ratio. High efficiency of the phosphors is necessary, particularly if the solution is of quenching type. Mills (1963) and others (Harris et al., 1970; Aoyagi and Albright, 1972) were able to measure radiotracer concentrations with an accuracy of a few tenths of 1%. The details of Mills' apparatus and his techniques have been outlined by Mills and Woolf (1968, p. 74-81) and have been discussed in detail by Ghai (1973).

Nuclear Magnetic Resonance (nMR) Method

Soon after the discovery of the nmr phenomenon (Bloch, 1946; Blombergen et al., 1948) Hahn (1950) demonstrated successfully its applicability towards diffusion measurements. In contrast to the existing nmr experiments Hahn's experiment consisted of multiple 90° pulses. The ensuing theoretical analysis of the experiment led to a powerful technique for measuring diffusion coefficients.

The observation of the nmr phenomenon is possible in systems that contain atomic nuclei with both magnetic moment and angular momentum. This condition is not fulfilled for nuclei with an even mass and an even number of protons. The inherent advantages of the nmr method are: (1) no disturbing effects due to labeling since this is achieved by the direction of the magnetic moments of some of the atoms of the molecule; (2) the diffusion times are extremely short and are in the range of milliseconds; (3) no macroscopic change occurs during the measurements; (4) only a small quantity of the substance is required (<1 cm^3); and (5) great potential for temperature and pressure studies.

The disadvantages are that: (1) only certain nuclei are suitable; but, fortunately hydrogen is one of the most suitable nuclei; (2) the labeled nuclei have to be in a chemically equivalent environment (Hahn and Maxwell, 1952); (3) a minimum number of labeled nuclei are required for detection; (4) when measuring intradiffusion coefficients the two compounds must, in general, possess distinct nuclei for labeling. A lucid description of the principles of the pulsed nmr or spin echo experiment has been given by Hahn (1953).

The effect of diffusion is taken into account by including the diffusion terms into the equations of motion of the macroscopic magnetization. The equations have been solved for different pulse sequences by using different mathematical treatments (Hahn, 1950; Das and Saha, 1954; Carr and Purcell, 1954; Torrey, 1956; Douglass and McCall, 1958; Muller and Bloom, 1960; Woessner, 1961; Stejskal and Tanner, 1965; Tanner, 1970). Solutions, however, are only known for the case where the inhomogeneity is represented by a linear field gradient G. The solution for the 90° − 180° pulse sequence is

$$A(t, G) = A_0 \exp\left(-t/T_2 - \gamma^2 G^2 D t^3/12\right) \quad (7.4)$$

where A is the amplitude of the signal (voltage) and D is the diffusion coefficient.

By knowledge of T_2 Equation (7.4) is immediately suitable for the evaluation of the diffusion coefficient. The usual procedure, however, is to calculate the ratio of the echo amplitudes as they have been determined for two different, known field gradients. One of the field gradients is approximately zero when using a very homogeneous magnet, and the other one is much larger. The following expression, in which relaxation effects cancel out, is obtained:

$$A_0/A = A(G = 0, t)/A(G, t) = \exp\left(\gamma^2 G^2 D t^3/12\right) \quad (7.5)$$

To obtain an appreciable decay of the spin echo the inequality $D\gamma^2 G^2 t^3/12 > t/T_2$ should be satisfied.

D can be calculated from the slope of ln (A_0/A) versus t^3 and by knowledge of γ and G. The alternate procedure (Woessner, 1960) uses the slope of ln (A_0/A) versus G^2. A limitation may arise for this method due to the condition that H_1 has to be larger by several times than total field variation across the sample $2aG$ (a is radius of sample). Highly viscous substances (short T_2's) or substances with small diffusion coefficients require a large field gradient in order to fulfil the inequality mentioned. The above condition applies then to either method and normally restricts the steady field gradient method to liquids with $D > 10^{-7}$ cm^2/s.

McCall et al (1963) suggested a time dependent field gradient to circumvent this restriction. Stejskal and Tanner (1965) presented the mathematical formulation and the experimental technique for the case of two rectangular gradient pulses.

Diffusion coefficients, which were beyond the capacity of the steady gradient method, have been measured down to the magnitude of 10^{-10} cm^2/s (Stejskel and Tanner, 1965; Boss et al., 1967; Kruger and Weiss, 1970; Tanner, 1972) with the pulsed field gradient technique. Other time dependences for the field gradient (than rectangular pulses) have been suggested (Stejskal and Tanner, 1965; Gross and Kosfeld, 1969) and applied (Anderson and Gerritz, 1970). In a very recent paper, Burnett and Harmon (1970) have demonstrated successfully a different technique which is applicable to systems having even smaller diffusion coefficients.

Equation (7.4) has been derived on the assumption that the diffusing molecules move in an infinite sample, that is, that the size of the sample container is much larger than the average displacement a molecule undergoes during the time interval t. Normally, this condition is well satisfied, but there exist experimental conditions where it might not be fulfilled. Examples in which the diffusion coefficient is affected due to the presence of barriers are the diffusion in adsorbed liquids, of a solvent in a polymer, in porous materials, in a thin layer etc. Experimental work (Woessner, 1963; Boss and Stejskal, 1965; Stejskal, 1965a; Boss et al., 1967; Freude, 1968; Murdy and Cotts, 1968; Tanner and Stejskal, 1968; Karger, 1969) in this category is mainly carried out by use of the time-dependent field gradient technique. Packer et al. (1970) have recently suggested a modification of the two gradient pulse sequence of Stejskal and Tanner (1965). They adopted the Carr-Purcell/Meiboom-Gill (1958) pulse sequence and employ the gradient pulses at appropriate times. For extremely small diffusion times, Gross and Kosfeld (1969) have pointed out that the use of alternating gradient pulses becomes advantageous. The mathematical description of the spin echo for the case of restricted diffusion in a pulsed magnetic field gradient has been described by Stejskal (1965a). Solutions for different boundary conditions have also been reported for the steady field gradient (Wayne and Cotts, 1966; Robertson, 1966) and for the pulsed field gradient (Murdy and Cotts, 1968).

Tanner (1970) has treated the decay of the spin echo due to a three 90° pulse sequence in a time dependent field gradient. The echo, occurring an interval after the third rf-pulse equal to that between the first two pulses, is called stimulated echo (Hahn, 1950). This pulse sequence can prove advantageous (Tanner, 1972) if for the diffusing substance the spin lattice relaxation time $T_1 > T_2$. For example, this condition may apply in surface diffusion, diffusion in viscous liquids and in plastic crystals. The nmr method is also suitable for relative density measurements (Luszczynski et al., 1962; Ruggheimer and Hubbard, 1963; Wade and Waugh, 1965; Hamann et al., 1966). For a sample of fixed volume within the rf-coil, the amplitude of the free induction decay following a 90° pulse is proportional to the number of spins in the volume (number density) and inversely proportional to the absolute temperature.

The intra-diffusion coefficient is also accessible to measurement by the spin echo technique. For systems consisting of components with different resonating nuclei the diffusion of the components can be studied separately. The procedure is the same as for self-diffusion measurements. If, however, the resonance condition applies to nuclei contained in both components the spin echo is made up of contributions of both. Measurements of this type have been reported (McCall et al., 1963a; Valiev et al., 1964; Valiev and Emelyanov, 1964; Boss et al., 1967). The separation of the contributions becomes less accurate for similar values of the diffusion coefficients and it is impossible when they are equal. The signal to noise ratio limits the accuracy in dilute systems.

The design of sample holders, some (Benedek and Purcell, 1954; McCall et al., 1959) capable of very high pressures (up to 10000 atm) have been described (Luszczynski et al., 1962; Odle and Flynn, 1964; Hausser and Noak, 1965; Panchenkov et al., 1968; Woessner et al., 1969; Dietriech and Kosfeld, 1969; Gerritsma and Trappeniers, 1971). The construction material of the sample holder should be non-magnetic in order to avoid distortion of the rf-field; a Be-Cu alloy has proved satisfactory for high pressure work (Benedek and Purcell, 1954; McCall et al., 1959). Detailed description of the nmr apparatus and the circuitry required has appeared in the literature (Schwartz, 1957; Buchta et al., 1958; Garwin and Reich, 1959; Pfeiffer and Weiss, 1961; Lowe and Howard, 1962; Gerritsma and Trappeniers, 1971).

Interferometric Methods and Other Techniques

Interferometric and other optical methods, reviewed extensively by Tyrrell (Tyrrell, 1961, Ch. 5), Geddes and Pontius (1959), and Longworth (1968), employ free diffusion boundary conditions. The interferometric methods are absolute in the sense that they require no calibration. They have grown in popularity because of their high accuracy. The Gouy diffusiometry is particularly suited for the study of ternary systems (Longworth, 1968, p. 99). The Gouy diffusiometer and the method of calculating diffusion coefficients from it have been discussed lately by Woolf et al. (1962) and Ellerton et al. (1964). A modification of the Tiselius cell used with the Gouy diffusiometer has been described by Harris et al. (1970). Thomas and Furzer (1962) have used the more refined treatment of Gosting and Morris (1949) in the Gouy method.

Rayleigh, Jamin, and Mack-Zehnder interferometers are similar to each other in that they all use two cells and give the refractive index profiles. The Jamin (Garner and Marchant, 1961) and Mach-Zehnder (Caldwell and Babb, 1956) instruments utilize half-silvered mirrors to split the light for the two cells and are described as amplitude splitting interferometers, whereas in the Rayleigh interferometer two vertical slots in the cell mask do this job. The optically more complex wave-front shearing interferometer developed by Bryngdahl and co-workers (1957, 1958, 1960, 1962) uses only one diffusion cell and gives the finite difference gradient as a function of the distance from the interface. This method was later discussed by Gustafsson et al. (1965) and Thomas and Nicholl (1965, 1967). In order to initiate the experiment a method called bottom layer diffusion has been employed (Gustaffson et al., 1968; Arvidsson et al., 1970).

Very recently a method has been put forward by which the sensitivity of Savart plate interferometers can be increased by a factor to two (Wallin and Wallin, 1970). In another method use of the Fabry-Perot interferometer was reported. In the Fabry-Perot interferometer (Born and Wolf, 1965) multiple beam interference fringes are obtained.

In order to establish a sharp, flat initial boundary between two fluids, many different types of cells have been designed and used (Bryngdahl, 1958; Geddes and Pontius, 1959). Among these are the draw slide cell, the sliding solvent cell, the capillary withdrawal cell, and the flowing junction cell. Analytical as well as graphical methods have been used for the necessary zero time correction (Geddes and Pontius, 1959; Haluska and Colver, 1970). With some diffusion experiments (Mullin and Nienow, 1964; Secor, 1965), it is preferable to use the concentration distribution data to determine the position of initial contact. This procedure has been applicable only to systems with no volume change on mixing, although recently equations have been presented to take into account the effect of volume change on mixing (Duda and Vrentas, 1966).

The mathematical analysis of the photographs used to deduce diffusion coefficients has been extensively reviewed by several workers (Geddes and Pontius, 1959; Mullin and Nienow, 1964; Longworth, 1968).

A new type of interferometric technique based on the formation of interference pattern by a thin wedge has appeared in the literature (Duda et al., 1969; Travnicek and Fan, 1969; O'Brien et al., 1970). Duda et al. (1969) give a list of references and discuss critically the accuracy, limitations, and other problems associated with this technique. This method seems also to be effective for polymer solutions. However, it is difficult to get as accurate data as by the other methods discussed above because of initial mixing effects caused by boundary disturbances (Duda et al., 1969). In the method used by O'Brien et al. (1970) the wedge is used as an electrochemical cell where the two plates of the wedge serve as electrodes.

The hologram interferometry (Heflinger et al., 1966) has been applied to diffusion measurements very recently (Maddux and Becsey, 1970; Becsey et al., 1971). The diffusion coefficients measured by this technique for some electrolytes in aqueous solutions are in very close agreement with the values obtained by other accurate techniques.

The development of the laser technique has made it possible to measure diffusion coefficients from the spectral broadening of the line after light scattering by the solution. This method has been applied to solutions consisting of macromolecules (Dubin et al., 1967; Herbert et al., 1968). From the analysis of the broadened lines of distinctly different frequencies the diffusion coefficient is deduced (Chu and Schoene, 1968; Hyde, 1971).

Dreyer et al. (1968, 1968a) have recently reported a new experimental technique. This technique is based on the fact that in the presence of a pulsating liquid flow in a porous or capillary cell very stable liquid layers are formed along the walls.

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NOTATION

A = constant
A = amplitude
a = activity
a_1, a_2 = repulsive, attractive radii, Equation (5.2)
B = constant
b = geometric factor, Equation (5.13)
C = constant
C = concentration
D = self-diffusion coefficient
D_{AB} = mutual diffusion coefficient
$\overline{D}_{AB}$ = integral diffusion coefficient
D_{AB}^0 = limiting mutual diffusion coefficient when $x_A \rightarrow 0$
D_{AB}^∞ = limiting mutual diffusion coefficient when $x_B \rightarrow 1$
D_0 = constant
d = effective molecular diameter
E = activation energy
F = shear stress
G = magnetic field gradient
$\Delta G_D^{\ddagger}$ = activation energy for diffusive flow
$\Delta G_v^{\ddagger}$ = activation energy for viscous flow
g = geometric factor, Equation (5.4)
H_v = enthalpy of vaporization
J = flux
K = constant
k = Boltzmann's constant
M = molecular weight
m = molecular mass
N = Avogadro's number
n = number density
P = pressure
P_t = thermal pressure
R = gas constant
r = radius of molecule
T = absolute temperature
T_0 = constant
T_2 = spin-spin relaxation time
t = time
$t/2$ = pulse separation time
U = internal energy
V = molal volume
V_f = free volume
v = velocity
X = physical property
X = coordinate
x = mole fraction

Greek Letters

α = thermal expansion coefficient
β = thermodynamic factor
β_c = call constant of the diaphragm cell
γ = activity coefficient
γ_1, γ_2 = particular values, Equation (5.2)
γ = gyromagnetic ratio
γ = numerical factor, Equation (5.4)
δ = momentum transfer distance
ϵ = depth of attractive potential
η = viscosity
λ = thermal conductivity
λ_i = intermolecular distance
λ = cell dimension, Equation (5.12)
ξ_{AB} = friction coefficient between A and B molecules
ξ = nearest neighbor number, Equation (5.8)
ξ = packing fraction
ρ = density
σ = molecular diameter, Equation (5.4)

Superscripts

0 = pure component

Subscripts

A = component A
B = component B
C = critical
g = gas
m = melting
r = reduced
s = solid

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JOURNAL REVIEW

Molecular Thermodynamics for Chemical Reaction Design

Various techniques of molecular thermodynamics and solution theory have been applied, through the transition state theory, to problems in chemical kinetics. These include experimental techniques for ascertaining the structure and properties of the transition states for various classes of reactions, plus analytical methods for using this information to predict the effect of solvents or reactant structure on chemical reaction rates. Such methods provide the chemical engineer with an additional parameter to use in the optimal design of reaction systems—that is, the chemistry of the reaction itself.

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One of the foremost aspects of chemical engineering practice is the design of processes involving chemical reaction steps. The reaction design engineer is well accustomed to considering the important mathematical and physical parameters in such a process, but the purpose of this review is to stress that the chemical parameters—although frequently neglected—may often be at least as important. A number of examples are now available where a knowledge of the molecular chemistry of the reaction has been applied to a rational design of the reaction system.

Such process improvements and optimization have most often been implemented by using transition state theory to reduce the rate problem to an equilibrium problem, tractable by the many approaches of thermodynamics. Often this involves the use of a thermodynamic method to characterize the mechanism of the reaction or the properties of the transition state, as from a determination of the activation parameters. An outstanding example of the application of such information is in the area of solvent selection and design. Commonly, solvent effects on chemical reactions are a factor of several orders of magnitude in the rate, and cases have been reported with factors as high as 10^9 (Brown and Okamoto, 1958; Cram et al., 1961). Thus a proper choice of a reaction solvent can have a very large effect on reaction rates, and molecular solution theories have been shown to be useful in designing solvents or solvent mixtures to optimize yields or selectivities of reactions or sets of reactions (Eckert, 1967; Wong and Eckert, 1969). For instance, often a solvent mixture is better than either pure component for separation processes (Grieger and Eckert, 1967), and correspondingly, examples exist where solvent mixtures markedly accelerate reaction rates (see Figure 1). Yet another extremely useful application of a thermodynamic approach

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