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STUDIES IN DIFFUSION. II. A KINETIC THEORY OF DIFFUSION IN LIQUID SYSTEMS

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The experimental study of diffusion in liquid systems was begun by Graham about 1850. A few years later Fick,[1] from analogy with Fourier's law of thermal conduction, enunciated the basic law of diffusion. In 1879 Stefan[2] showed that the data of Graham harmonized with Fick's Law, and developed the theory of liquid diffusion further along the same lines as his theory of diffusion in gaseous systems.[3] The equation given

$$dN/d\Theta = DA\,dc/dx$$

by Fick rests upon the assumption that the driving force causing diffusion is proportional to the concentration gradient. The use of the equation requires the evaluation, by measurement or estimation, of the proportionality constant D, usually termed the diffusion coefficient or diffusivity.

TABLE OF NOMENCLATURE

(1) — Subscript referring to diffusing substance (solute)
(2) — Subscript referring to solvent medium
A — Area of contact; abnormality factor for compounds containing active oxygen or nitrogen
a, A', B' — Proportionality constants
B — Universal constant in the equation for D
b — Temperature coefficient
c — Concentration, in moles per cubic centimeter
D — Diffusion coefficient (diffusivity), cm.^{2}/sec. or cm.^{2}/day
d — Differential operator
F — Factor used to allow for resistance due to intermolecular forces
M — Molecular weight
m — Weight of a single molecule
N — Number of moles of substance transferred
R — Gas constant, in $pV = RT$
r — Radius of diffusing particle
S — $V_1^{1/3} + V_2^{1/3}$; represents the sum of the molecular diameters
T — Absolute temperature, degrees Kelvin
t — Temperature, degrees centigrade
u — Net forward velocity of diffusion
V — Volume of one mole of liquid: refers to b. p. for the calculation of S
v — Specific volume
w — Molecular velocity of thermal agitation
x — Distance, measured in the direction of diffusive flow
Z — Solvent viscosity, in centipoises
Θ — Time, in seconds or days

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[1] Fick, *Ann. Phys.*, **94**, 59 (1855).

[2] Stefan, *Wien. Ber.*, **79**, 161 (1879).

[3] Lewis and Chang, *Am. Inst. Chem. Eng.*, **21**, 135 (1928).

Numerous attempts to correlate the values of D obtained experimentally and the properties of the substances involved have been made during the past fifty years; none has been a pronounced success, and all have lacked generality. The principal difficulty in the way of the development of a rational theory of diffusion in liquid systems has been the absence of a kinetic theory of liquids corresponding to that of gases. Attempts at correlation have proceeded along two diametrically opposite lines, the kinetic and the hydrodynamic, as represented by the Exner Rule and the Stokes–Einstein Equation.

From kinetic theory it is known that in any gaseous system the average kinetic energy of a molecule is a function of temperature only

$$mw^2 = \text{constant}$$

It is seen from this that the translational velocity of the molecule is inversely proportional to the square root of the molecular weight; if we make the simple assumption that the rate of diffusion varies directly as the translational velocity, the diffusivity varies inversely as the square root of the molecular weight (Graham's Law). In 1875 Exner[4] applied this rule to the diffusion of gases through liquids, and showed that it is in agreement, approximately, with the experimental data. This work was continued by Hüfner,[5] who later extended it to substances other than dissolved gases, as did Euler[6] and Pickering.[7] The rule has been exploited by a number of other investigators, among them Thovert,[8] Öholm,[9] and Carlson.[10] More recently, Smith,[11] using Öholm's data, defined D/M as the "ideal diffusion coefficient," which was then shown proportional inversely to the 3/2 power of M.

In 1858, Wiedemann[12] found that D varied inversely as the solvent viscosity, thereby laying the foundation for numerous attempts at correlation along hydrodynamical lines. This fact was combined by Walden[13] with the Exner Rule, giving the relation

$$DZM^{1/2} = \text{constant}$$

The equations of Wiedemann and Walden were tested for a large number of systems by Thovert,[14] and found to conform approximately to the observed facts.

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[4] Exner, *Ann. Phys.*, **155**, 443 (1875).

[5] Hüfner, *ibid.*, **16**, 253 (1882); **60**, 134 (1897); *Z. physik. Chem.*, **27**, 227 (1898).

[6] Euler. *Ann. Phys.*, **63**, 273 (1897).

[7] Pickering, *Phil. Mag.*, **35**, 127 (1893).

[8] Thovert, *Compt. rend.*, **135**. 579 (1902).

[9] Öholm, *Z. physik. Chem.*, **70**, 378 (1910).

[10] Carlson, THIS JOURNAL, **33**, 1027 (1911).

[11] Smith, *ibid.*, **36**, 847 (1914): **37**, 722 (1915)

[12] Wiedemann, *Ann. Phys.*, **104**, 170 (1858).

[13] Walden, *Z. Elektrochem.*, **12**, 77 (1906).

[14] Thovert, *Compt. rend.*, **138**, 481 (1904); *Ann. de Phys.*, **2**, 369 (1914)

In 1905 Sutherland[15] and Einstein[16] independently derived what is now known as the Stokes–Einstein equation. Sutherland applied the relation

$$D = \frac{RT}{6\pi NZr}$$

(N here is Avogadro's number) to the existing data, but finding the agreement poor, discarded it in favor of the empirical equation

$$D = A'/V + B'/V^{1/3}$$

Einstein, who derived the relation in the course of his investigation of the Brownian movement of colloidal particles, indicated its possible usefulness in molecular diffusion, but did not apply it to the existing data; this has been done by von Wogau,[17] Groh and Kelp, Svedberg [18] and Miller, resulting in the conclusion that the equation is only approximately true for the diffusion of molecules, though accurate for colloidal particles. Its breakdown is due to the inapplicability of Stokes' law, which assumes the solvent to be a continuum, a postulate no longer satisfied when the diffusing particle approaches the solvent molecules in size. It also possesses the obvious fault of including only the viscosity of the solvent and the radius of the diffusing particle, which are certainly insufficient to specify the behavior of the system; similar objections apply to the Exner Rule. It may be noted that Gapon and Muchin[19] have derived an equation similar to the Stokes–Einstein, but including other variables than r and z.

Riecke[20] found a relation between the diffusivity and the mean free path of the diffusing molecule, but as he did not evaluate the free path length, the theory is incomplete. His theory is essentially the same as the usual kinetic theory of diffusion in gases. Enskog[21] has also made a preliminary attempt to apply gas theory to liquid diffusion.

In the absence of a classical kinetic theory of liquids, there has arisen in recent years a tendency to apply the kinetic theory of gases directly to liquid systems, usually with the introduction of a free space factor to take account of the fact that the close packing of the molecules must necessarily interfere with their freedom of motion. In this manner Christiansen,[22] Norrish and Smith[23] and Jowett[24] have made use of the gas theory expression for collision rate in their studies of reaction velocity

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[15] Sutherland, *Phil. Mag.*, **9**, 781 (1905).

[16] Einstein, *Ann. Phys.*, **17**, 549 (1905).

[17] Von Wogau, *Ber. physik. Ges.*, **6**, 542 (1908).

[18] Svedberg, "Existenz der Moleküle," p. 60.

[19] Gapon and Muchin, *Ukrainskii Khem. Zhur.*, **2**, 459 (1926).

[20] Riecke, *Z. physik. Chem.*, **5**, 564 (1890).

[21] Enskog, *Svenska Vet. Ak.*, **63**, 4 (1922).

[22] Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

[23] Norrish and Smith, *J. Chem. Soc.*, 129 (1928).

[24] Jowett, *Phil. Mag.*, **8**, 1059 (1929).

in liquid systems. Lenard[25] follows a similar course in his consideration of ionic mobility.

It is the purpose of this paper to demonstrate that the classical kinetic theory expression for gaseous diffusivity may be applied to liquid systems, provided that due regard be taken of the complications introduced by the close packing of the molecules. We shall first apply gas theory directly to liquid diffusion, later modifying the equation so obtained to allow for the failure of several assumptions made for gases. The derivation which follows closely parallels that of Stefan[26] for gaseous diffusion.

Fick's law states that the diffusion rate is proportional to the concentration gradient

$$\mathrm{d}N_1/A\mathrm{d}\Theta = D\mathrm{d}c_1/\mathrm{d}x$$

If we represent by u_1 the net forward velocity of a molecule in the diffusion stream

$$\mathrm{d}N_1/A\mathrm{d}\Theta = c_1 u_1$$

It may easily be shown by calculation that the acceleration of the diffusing molecules is negligibly small; in the absence of external forces, the driving force $\mathrm{d}c/\mathrm{d}x$ is used solely to overcome the resistance to diffusion, measured in terms of the momentum transferred from the diffusing solute to the solvent. This momentum transfer is equal to the product of the total number of collisions of unlike molecules by the momentum loss per collision. From gas theory the number of collisions per second is proportional to the concentration of each type of molecule, to an "average" molecular cross-sectional area, and to the root mean square molecular velocity; that is, to

$$c_1 c_2 S^2 \sqrt{w_1^2 + w_2^2} \tag{3}$$

where S^2 represents the square of the sum of the molecular diameters. At constant temperature, all the molecules in the system have, on the average, the same kinetic energy; w^2 therefore varies inversely as the molecular weight, since Mw^2 is constant, and Expression 3 becomes

$$c_1 c_2 S^2 \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \tag{4}$$

For forceless spheres, the momentum loss per collision is

$$2/3\, \frac{m_1 m_2}{m_1 + m_2} (u_1 + u_2) \tag{5}$$

Since the mass of a single molecule, m, is proportional to the molecular weight, M, Expression 5 may be written

$$\frac{(u_1 + u_2)}{\dfrac{1}{M_1} + \dfrac{1}{M_2}} \tag{6}$$

$u_1 + u_2$ being the relative velocity of unlike molecules.

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[25] Lenard, *Ann. Physik*, **61**, 665 (1920).

[26] Stefan, *Wien. Ber.*, **65**, 323 (1872); cf. Sutherland, *Phil. Mag.*, **38**, 1 (1894).

Assuming no volume change on mixing, we may write the equation of continuity to express the constancy of volume

$$c_1V_1u_1 - c_2V_2u_2 = 0 \tag{7}$$

since the sum of the partial volumes equals the total volume

$$c_1V_1 + c_2V_2 = 1 \tag{8}$$

Combining Equations 7 and 8

$$(u_1 + u_2) = u_1\left(1 + \frac{c_1V_1}{c_2V_2}\right) \tag{9}$$

From 4, 6 and 9 the resistance to diffusion is found to be proportional to

$$\frac{c_1c_2\, S^2\, u_1}{c_2V_2\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}} \tag{10}$$

From Equations 1 and 2

$$\mathrm{d}c_1/\mathrm{d}x = c_1u_1/D \tag{11}$$

On setting the driving force $\mathrm{d}c_1/\mathrm{d}x$ equal to the resistance and solving for D we have

$$D = \frac{B\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{S^2}\,(V_2) \tag{12}$$

where B is a proportionality constant. Except for the V_2, this is identical with the expression derived by Stefan for gaseous diffusion.

In the derivation of Equation 12 three assumptions relative to the collision rate have been made, *viz.*, (1) that all collisions are binary, involving two molecules only; (2) that the collision rate is unaffected by the volume occupied by the molecules, which in a gas is negligibly small compared to the total volume; and (3) that the intermolecular attractions do not come into play. While in the kinetic theory of gases these assumptions may be allowable, in the treatment of liquid diffusion none of them can be considered valid because of the greater molecular density in the liquid state. As far as the writer is aware, no molecular analysis of the problem of collision rate in liquid systems has been made; in this paper we shall take account of the failure of the three assumptions mentioned in a semi-empirical way, by means of a factor F to be inserted in the denominator of Equation 12, this factor being evaluated by a study of the available data on liquid diffusion.

Since roughly one-third of the volume of a liquid is occupied by the molecules themselves, it is apparent that a fairly large fraction of the collisions will be of an order higher than the second, on account of the very close packing. It has been shown by Syrkin[27] that the expression for the rate of higher order collisions is of a form similar to Equation 4; as will be seen later, we may assume to a sufficient approximation that the simpler expression (4) is applicable.

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[27] Syrkin, *Physik. Z.*, **24**, 236 (1923).

The effect on collision rate of the volume occupied by the molecules was first evaluated for gases by van der Waals[28] in developing his equation of state. For gases, the correction factor obtained is always a function of the ratio b/V, where b is proportional to the actual volume of the molecules and V is the apparent volume. In the gaseous state, b/V is very small, while for a liquid it is roughly unity; however, in a liquid, V is no longer constant as required by Avogadro's law, but varies from liquid to liquid over a wide range. At the boiling points, or other corresponding temperatures, the actual volume of the molecules is the same fraction of V for all liquids, hence b/V becomes the same for all liquids. The correction factor therefore varies from liquid to liquid only in so far as V at the given temperature differs from V at the boiling point; because of the low coefficients of expansion of liquids, this variation will not be large. Moreover, the correction factor is probably quite insensitive to moderate variations in b/V, and, since most liquids are not far removed from their boiling points at ordinary temperatures, we may safely suppose that this factor is constant for all systems, as a working approximation; exceptions will be met with in the case of high-boiling solvents.

The third assumption, that intermolecular forces may be neglected, is not tenable even in the theory of gaseous diffusion, and much less so in the case of liquids. Presumably because of induced curvature in the molecular paths, such forces cause a very considerable increase in the collision rate; the effect is a specific one, depending on the nature of the molecules composing the system, and varying over an extremely wide range. The effect of molecular forces on gaseous viscosity and diffusion was considered by Sutherland,[29] who arrived at a dynamical solution of the problem; the application of Sutherland's equations to gaseous diffusion is treated in the first paper of this series.[30] In the present state of liquid kinetic theory, a dynamical analysis of the problem is impossible; we shall therefore evaluate the factor F in terms of other properties of the system as parameters, thereby avoiding the necessity for such an analysis. Since F is intimately connected with the total transfer of momentum within the fluid, it is logical to relate it to the viscosity of the medium, which is a measure of such transfer.

By the empirical examination of the existing data on the diffusion of non-electrolytes, several rules for the variation of F with the nature of the system have been determined. In this paper we shall be concerned only with the data for low concentrations of diffusing substance, *i. e.*, for dilute systems, a condition satisfied by practically all the existing data.

[28] Jeans, "Dynamical Theory of Gases," pp. 125 *ff.;* Loeb, "Kinetic Theory of Gases," pp. 130 *ff.*

[29] Sutherland, *Phil. Mag.*, **36**, 507 (1893); **38**, 1 (1894).

[30] Arnold, *Ind. Eng. Chem.*, **22**, 1091 (1930).

1. For dilute systems, F is *essentially* a function of the solvent properties only, being nearly independent of the nature of the diffusing substance; thus the diffusion data for a number of solutes in any given solvent obey the same law found for gaseous diffusion, except for the proportionality constant. This rule is not strictly true, some dependence of F on solute properties being noted, but the meagerness of the available accurate data prevents the more accurate determination of the nature of this dependence.
2. F is directly proportional to the square root of the solvent viscosity. For high-boiling solvents indications are that some modification of this rule is necessary; this also is hampered by scarcity of data.
3. When either solvent or solute, or both, belongs to the class of substances commonly regarded as "associated," factors A_1 and A_2 (for solute and solvent, respectively) must be inserted in the expression for F. Such substances are those containing an unsaturated oxygen or nitrogen atom, *e. g.*, water, alcohols, acids, amines, etc., whose molecules as a result of this unsaturation possess unduly large attractive forces, and consequently show anomalies in many physical properties. With such substances the resistance to diffusion is found to be higher than can be accounted for by the first two rules, necessitating the use of the "abnormality factor," A.

The complete expression for F is therefore

$$F = A_1A_2V_2Z_2^{1/2} \tag{13}$$

the V_2 in this expression canceling that in Equation 12, as is found necessary for proper correlation. The final equation for D to be tested is then

$$D = \frac{B\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{A_1A_2Z_2^{1/2}S^2} \tag{14}$$

As a standard temperature of comparison, we shall use 20°, conversions to this temperature being made with the aid of the coefficients discussed later. Z_2 is expressed in centipoises at 20°; S is the sum of the cube roots of the molecular volumes of solute and solvent, found with the aid of the Kopp–Le Bas system of calculation as described in the previous paper.

To test the first rule governing F, we require data on the diffusion of normal substances in a single solvent; these are supplied by the experiments of Thovert,[31] using benzene as the solvent. Table I contains values observed at 15°, in cm.^{2}/sec., $\times 10^{-5}$ together with $D_{\text{calcd.}}$ found with the aid of a graphically determined value of B of 0.00918 at 15°, or 0.0100 at 20°. The agreement is not exact, the ratio of calculated to observed D tending to rise with increasing molecular weight; the median deviation is 8%, which is not to be considered serious inasmuch as the probable

[31] Thovert, *Ann. phys.*, [9] **2**, 415 (1914).

experimental error is about 5% or even more. We shall therefore assume that F is approximately independent of solute nature, for normal solutes.

TABLE I

DIFFUSION IN BENZENE (THOVERT)

Diffusing solute	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$
Chloroform	92.3	83.4	0.1456	2.00	2.11
Bromoform	99.5	85.0	.1295	1.74	1.62
Iodoform	129.5	92.9	.1238	1.53	1.38
Ethylene dichloride	93.6	83.2	.1514	2.08	2.45
Ethylene dibromide	98.4	84.5	.1347	1.83	1.97
Ethylene di-iodide	118.4	90.1	.1280	1.63	1.40
Trichloropropane	136.7	94.9	.1400	1.69	1.72
Ethyl ether	107.2	87.2	.1623	2.10	2.21
Methyl salicylate	161.5	100.6	.1392	1.59	1.56
Chlorobenzene	116.9	89.9	.1474	1.87	2.15
Dichlorobenzene	137.8	95.3	.1400	1.68	1.90
Bromobenzene	119.3	90.4	.1384	1.75	1.86
Dibromobenzene	142.6	96.4	.1307	1.56	1.37
Iodobenzene	129.3	92.9	.1330	1.64	1.50
Chloronaphthalene	170.1	102.6	.1383	1.54	1.20
Dichloronaphthalene	191.0	107.0	.1338	1.43	1.40
Bromonaphthalene	172.5	103.2	.1330	1.47	1.30
Dibromonaphthalene	195.8	108.0	.1277	1.35	1.25
Nitrobenzene	122.7	91.4	.1447	1.81	1.84
Dinitrobenzene	149.4	97.8	.1370	1.60	1.54
Trinitrobenzene	176.1	103.8	.1310	1.44	1.39
Chloronitrobenzene	143.6	96.6	.1430	1.70	1.70
Bromonitrobenzene	146.0	97.2	.1332	1.57	1.33
Nitronaphthalene	175.9	103.8	.1363	1.50	1.39
Dinitronaphthalene	202.6	109.4	.1320	1.38	1.23

The relation of F to solvent viscosity is well shown by the data of Miller[32] on the diffusion of iodine (Table II). The values for diffusion in ether and ethyl alcohol are due to Groh and Kelp,[33] whose values for benzene, carbon disulfide, and chloroform agree closely with those of Miller. The units of D are cm.^{2}/day, at 20°; converted to these units, the B found from Thovert's data is (0.01) (86400) or 864, which is found to be satisfactory for the correlation of Miller's data as well. The last column of Table II contains the ratio of calculated to observed D, assuming A_1 and A_2 of Equation 14 to be unity; for most of the solvents the ratio is seen to be nearly unity, indicating the correctness of our theory. Heptane is anomalous, for no apparent reason, while the high-boiling solvents anisole, phenetole, ethylene dibromide and acetylene tetrabromide show rather large deviations which will be mentioned further below. For

[32] Miller, *Proc. Roy. Soc.* (London), **106**, 724 (1924).

[33] Groh and Kelp, *Z. anorg. Chem.*, **147**, 321 (1925).

acetic acid, methanol, ethyl alcohol and water, the ratio is much larger, since these substances are abnormal and A_2 is greater than unity. As will be shown below, A_2 is a constant characteristic of the solvent, paralleling in magnitude the familiar "association factor" found from surface tension or similar anomalous properties of abnormal liquids.

TABLE II

DIFFUSION OF IODINE (MILLER)

Solvent	V	$Z^{1/2}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	Calcd./Obs.
Benzene	96.0	0.801	1.81	1.670	1.08
Toluene	118.2	.763	1.67	1.686	0.99
m-Xylene	140.4	.802	1.41	1.454	.97
Bromobenzene	119.3	1.065	1.01	1.038	.97
Chloroform	92.3	0.761	1.83	1.831	1.00
Carbon tetrachloride	113.2	.976	1.11	1.177	0.94
Carbon disulfide	66.0	.613	2.70	2.697	1.00
Heptane	162.8	.693	1.58	2.386	0.66
Ethyl acetate	108.2	.675	1.96	1.859	1.06
Amyl acetate	174.8	.934	1.04	1.071	0.97
Ether	107.2	.493	2.88	2.90	.99
Anisole	129.2	1.040	1.11	0.977	1.14
Phenetole	151.4	1.147	0.91	.843	1.08
Ethylene dibromide	98.4	1.310	.81	.719	1.13
Acetylene tetrabromide	145.0	3.127	.255	.1576	1.62
Acetic acid	63.8	1.120	1.65	.887	1.86
Ethyl alcohol	59.2	1.100	1.91	1.02	1.88
Methanol	37.0	0.781	3.64	1.572	2.325
Water	18.4	1.005	4.48	0.832	5.38

Table III contains the data of Öholm[34] for the diffusion of bromoform through various solvents, with the calculated values of A_2 shown in the last column. Table IV gives the data of Dummer,[35] whose work is of especial interest because of his use of several substances both as solvent and as solute. Although he used 10 and 20% solutions, the effect of

TABLE III

DIFFUSION OF BROMOFORM (ÖHOLM)

Solvent	V	S^2	$Z^{1/2}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	A_2
Ethyl ether	107.2	88.0	0.493	2.64	2.98	(0.89)
Benzene	96.0	85.0	.801	1.65	1.53	(1.08)
Acetone	74.0	78.2	.570	2.83	2.37	1.19
Water	18.4	53.0	1.005	3.98	0.85	4.70
Methanol	37.0	63.6	0.781	3.27	1.71	1.91
Ethyl alcohol	59.2	73.0	1.100	1.74	0.85	2.04
Propyl alcohol	81.4	80.7	1.492	1.03	.76	1.36
Amyl alcohol	103.6	87.2	2.00	0.62	.54	1.14
(Bromoform)	99.5	..	..	..	..	..

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[34] Öholm, *Medd. Nobelinst.*, **2**, 23 (1913).

[35] Dummer, *Z. anorg. Chem.*, **109**, 49 (1919).

concentration on D is not great, and the agreement throughout is satisfactory. For methanol, nitrobenzene and acetone, values of A_2 of 2.0, 1.35 and 1.15 are required for good correlation. All values in Tables III and IV are in cm.²/day at 20°.

TABLE IV

DIFFUSION OF ORGANIC SUBSTANCES (DUMMER)

System	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$
In ethyl acetate: (1) (0.675) $= AZ^{1/2}$					
Nitrobenzene	117.6	93.8	0.1395	1.91	1.94
Benzo-trichloride	180.9	108.6	.1282	1.52	1.69
Ethyl benzoate	174.6	107.0	.1340	1.61	1.60
In ethyl benzoate: (1) (1.48)					
Nitrobenzene	117.6	110.0	0.1217	0.65	0.63
Nitromethane	51.2	86.7	.1517	1.02	.91
Benzo-trichloride	180.9	126.0	.1085	.51	.41
Ethyl acetate	108.2	107.0	.1340	.74	.77
Acetone	74.0	96.0	.1544	.95	.91
In benzo-trichloride: (1) (1.53)					
Ethyl acetate	108.2	108.6	0.1282	0.67	0.66
Ethyl benzoate	174.6	126.0	.1085	.49	.45
In methanol: (2.0) (0.781)					
Nitromethane	51.2	49.8	0.194	2.16	2.39
Nitrobenzene	117.6	68.0	.197	1.61	1.56
Ethyl acetate	108.2	65.5	.206	1.74	1.79
Ethyl benzoate	174.6	79.7	.195	1.36	1.37
Acetone	74.0	56.9	.220	2.14	2.31
In nitrobenzene: (1.35) (1.41)					
Nitromethane	51.2	74.5	0.1562	0.95	0.83
Ethyl acetate	108.2	93.8	.1395	.68	.68
Ethyl benzoate	174.6	110.0	.1217	.50	.50
Acetone	74.0	83.0	.1590	.87	.80
In acetone: (1.15) (0.570)					
Nitrobenzene	117.6	83.0	0.1590	2.54	2.54
Ethyl benzoate	174.6	96.0	.1544	2.13	2.13

Table V contains data from Thovert[31] for the diffusion of normal solutes in methanol, in cm.²/sec. × 10^{-5} at 15°. Using the abnormality factor 2.0 found from Dummer's data for methanol, satisfactory correlation is obtained, the deviations being of the same nature and magnitude as in Table I. It may be noted here that Thovert's results are somewhat erratic, with considerable errors in some instances; the general accuracy of his work is quite uncertain.

TABLE V

DIFFUSION OF NORMAL SOLUTES IN METHANOL (THOVERT)

Substance	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$
Carbon tetrachloride	113.2	67.0	0.1940	1.70	1.69
Chloroform	92.3	62.0	.1993	1.90	2.07
Ethylene di-iodide	118.4	68.0	.1865	1.62	1.56
Trichloropropane	136.7	72.2	.1954	1.59	1.76
Allyl bromide	89.9	61.1	.1990	1.92	2.22
Allyl iodide	99.0	63.9	.1930	1.78	1.78
Acetonitrile	56.3	51.5	.2360	2.70	2.64
Ethyl ether	107.2	65.4	.2120	1.92	2.00
Ethyl nitrate	85.9	60.0	.2060	2.02	2.18
Quinone	108.4	66.0	.2015	1.80	1.84
Methyl salicylate	161.5	77.1	.1972	1.51	1.56
Nitrobenzene	122.7	69.2	.1985	1.69	1.81
Dinitrobenzene	149.4	74.8	.1930	1.52	1.56
Nitronaphthalene	175.9	80.0	.1925	1.42	1.50
Dinitronaphthalene	202.6	85.0	.1892	1.32	1.32
Chloronaphthalene	170.1	79.0	.1940	1.45	1.38
Dichloronaphthalene	191.0	83.0	.1905	1.35	1.52
Chlorobenzene	116.9	66.1	.2005	1.79	2.07
Bromobenzene	119.3	68.4	.1940	1.67	1.79
Iodobenzene	129.3	70.5	.1903	1.59	1.65

As noted above, when the *solvent* is abnormal, the calculated D must be brought into agreement with the observed D by the use of the abnormality factor A_2; it is also found that abnormal *diffusing substances* require the introduction of a factor A_1, quite independently of the abnormal or normal nature of the solvent. This is clearly shown by Table VI, the values of D calculated on the assumption of an A_1 of unity being uniformly too high; the ratio $D_{\text{calcd.}}/D_{\text{obs.}}$ is then equal to the factor A_1. The last column contains values of A_1 found similarly from Thovert's data on diffusion in methanol; in most cases these agree closely with the values for benzene solution, indicating that the abnormal diffusional behavior of the solute is not greatly influenced by the nature of the solvent (see, however, the discussion of Table X).

Table VII contains data by Öholm[34] for the diffusion of both normal and abnormal solutes in ethyl alcohol; values of D are given in cm.^{2}/day, at 20°, extrapolated to zero concentration. To a close approximation, the A_2 for ethyl alcohol may be taken as 2.0, as for methanol. The last column gives, for the abnormal solutes, the values of A_1 calculated from Thovert's data on diffusion in methanol, as in Table VI.

We have next to consider the data for diffusion in aqueous solution. In order to arrive at an abnormality factor A_2 for water, we are limited to the consideration of normal solutes only; unfortunately, nearly all substances which are water-soluble are also abnormal. In Table III

TABLE VI

DIFFUSION OF ABNORMAL SOLUTES IN BENZENE (THOVERT)

Substance	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	A_1	A_{MeOH}
Formic acid	41.3	64.6	0.1567	2.78	2.16	1.29	1.53
Acetic acid	63.7	73.6	.1716	2.66	1.92	1.38	1.53
Chloro-acetic acid	94.6	83.4	.1530	2.10	1.48	1.42	1.28
Benzoic acid	130.2	92.9	.1450	1.79	1.36	1.32	1.26
Phthalic acid	164.4	101.2	.1372	1.55	1.37	1.13	1.12
Benzaldehyde	122.8	91.6	.1490	1.86	1.73	1.07	1.03
Salicylaldehyde	130.2	93.3	.1450	1.78	1.78	1.00	0.94
Quinone	108.4	87.6	.1485	1.94	1.68	1.15	.98
Propyl alcohol	103.6	86.3	.1720	2.28	1.60	1.42	..
Amyl alcohol	125.8	92.0	.1522	1.91	1.48	1.29	1.29
Phenol	103.4	86.1	.1530	2.04	1.54	1.32	1.35
Chlorophenol	124.3	91.8	.1437	1.79	1.42	1.26	1.26
Bromophenol	126.7	92.3	.1363	1.69	1.34	1.26	1.21
Chloro-aniline	131.1	93.5	.1440	1.76	1.56	1.13	1.18
Bromoaniline	133.5	93.9	.1363	1.66	1.41	1.18	1.15

TABLE VII

DIFFUSION IN ETHYL ALCOHOL (ÖHOLM)

Substance	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	A	A_{MeOH}
Iodobenzene	129.3	80.6	0.163	0.79	0.85	(0.93)	..
Bromonaphthalene	172.5	90.0	.163	.71	.68	(1.04)	..
Chloroform	92.3	71.2	1.73	.95	1.07	(0.89)	..
Bromoform	99.5	73.0	.160	.86	0.85	(1.01)	..
Azobenzene	205.6	96.2	.165	.67	.65	(1.03)	..
Stearic acid	419	129.3	.159	.48	.50	(0.96)	..
Acetal	162.6	88.0	.174	.78	.98	(.80)	..
Camphor	214.5	97.6	.168	.67	.62	1.08	..
Pyridine	93.1	71.2	.185	1.02	.95	1.07	1.26
Allyl alcohol	74.0	65.7	.197	1.18	.83	1.42	1.27
Amyl alcohol	125.8	79.0	1.79	0.89	.68	1.31	1.29
Chloral	114.5	76.8	.169	.86	.56	1.53	1.40
Saligenin	133.0	81.0	.172	.83	.53	1.57	..
Acetamide	71.1	65.0	.197	1.19	.57	2.08	1.54
Acetin	144	83.7	.171	0.80	.48	1.67	..
Glycerin	99.5	73.0	.181	.97	.45	2.15	1.65
Hydroquinone	110.8	76.0	.175	.90	.42	2.14	1.43
Resorcinol	110.8	76.0	.175	.90	.38	2.36	..
Cetyl alcohol	370	122.5	.160	.51	.30	1.70	..
Ethyl alcohol	59.2	..	..	..	..	2.00	..

an A_2 of 4.70 was found, which on further trial proves to be correct, giving excellent agreement with the experimental results for the diffusion of the fixed gases (Table VIII). The molecular volumes used in this table have been taken from the previous paper on gaseous diffusion, and were calculated from gaseous viscosity data; Kopp's law is rather difficultly applicable to substances of low molecular complexity. The values of $D_{\text{obs.}}$ are taken as the most reliable of those cited in Table VIII-A, which was compiled from data given by Tammann[36] in his recent review of the subject, together with values for oxygen and carbon dioxide given by

TABLE VIII

DIFFUSION OF GASES IN WATER

Gas	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$
Hydrogen	14.3	25.7	0.745	5.34	5.13 (av.)
Oxygen	25.6	31.2	.294	1.73	1.80
Nitrogen	31.2	33.5	.302	1.66	1.64
Carbon dioxide	34.0	34.5	.280	1.50	1.50
Nitrous oxide	36.4	35.5	.280	1.45	1.51
Acetylene	(37.0)	35.8	.307	1.58	1.56
Ammonia	25.8	31.4	.338	1.98	1.76
Hydrogen sulfide	(33.0)	34.2	.291	1.57	1.41
Chlorine	(49.2)	39.6	.264	1.23	1.22
Water	18.4	..	...	..	..

TABLE VIIIA

DIFFUSION OF GASES IN WATER (AFTER TAMMANN)

	D_t	t	D_{20}
Hydrogen			
Hagenbach	2.95	14	3.48
Exner	5.81	13	7.04
Tammann	2.95	17.5	3.17
Hüfner	4.09	16	4.58
Hüfner	4.45	21	4.32
Hüfner	7.53	16	8.44
Ammonia			
Scheffer	1.06	4.5	1.55
Arrhenius	1.42	12	1.76
Hüfner	1.106	15	1.27
Abegg	1.575	16	1.76
Hagenbach	1.594	17	1.74
Exner	1.93	17	2.10
Voigtländer	1.26	20	1.26
Hydrogen sulfide			
Hüfner	1.24	15.5	1.41
Hagenbach	1.53	16	1.71
Chlorine			
Hüfner	1.10	16.3	1.22
Euler	1.22	12	1.51
Acetylene			
Tammann	1.45	17.5	1.56
Carbon Dioxide			
Hagenbach	0.770	0	1.23
Hagenbach	.843	15	0.97
Stefan	1.38	17	1.50
Tammann	1.25	17.5	1.34
Hüfner	1.383	15.2	1.60
Hüfner	1.264	10.3	1.63
Hüfner	1.542	20.4	1.52
Carlson	1.378	16	1.50
Oxygen			
Hüfner	1.62	21.7	1.54
Tammann	2.05	17.5	2.20
Exner	1.91	15	2.20
Carlson	1.607	16	1.80
Nitrogen			
Hüfner	1.73	21.7	1.64
Exner	1.68	15	1.93
Tammann	1.56	25	1.36
Nitrous oxide			
Hüfner	1.35	16.2	1.51
Hagenbach	0.634	14	0.748

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[36] Tammann, *Z. anorg. Chem.*, 179, 125 (1929).

Carlson,[37] all data being reduced to 20° with the aid of a temperature coefficient of 0.030, and expressed in cm.^{2}/day. Especially in the case of hydrogen, disagreements among the various experimenters are apparent, and are traceable to the difficult technique involved and the low solubility of most of the gases.

Representative of the diffusion of abnormal solutes in aqueous solution, Table IX contains the data of Thovert. The dependence of A on the functional groups in the molecule is clearly shown; the aliphatic alcohols show nearly the same value of A throughout, as do formic and acetic acids. In the multiple-functioned compounds such as tartaric acid, glycerin and the sugars, internal neutralization of the abnormal forces operates to give a lower A than would be expected. When such neutralization becomes complete, an A of unity is to be expected; this is the case for

TABLE IX

DIFFUSION OF ABNORMAL SOLUTES IN WATER (THOVERT)

Substance	V	S^2	$\sqrt{\frac{1}{M_1}+\frac{1}{M_2}}$	$D_{\text{calcd.}}$	$D_{\text{obs.}}$	A_2
Formic acid	41.3	37.2	0.278	1.37	1.04	1.32
Acetic acid	63.7	44.0	.269	1.12	0.88	1.27
Tartaric acid	135	60.3	.249	0.76	0.61	1.24
Methyl alcohol	37.0	35.6	.295	1.52	1.28	1.19
Ethyl alcohol	59.2	42.6	.278	1.24	1.00	1.24
Propyl alcohol	81.4	48.7	.269	1.01	0.87	1.16
Butyl alcohol	103.6	53.8	.263	0.90	.77	1.16
Amyl alcohol	125.8	58.5	.259	.81	.69	1.16
Allyl alcohol	74.0	46.7	.270	1.06	.90	1.17
Glycerin	96.2	52.2	.258	0.91	.72	1.25
Chlorohydrin	109.7	55.2	.254	.84	.76	1.11
Dichlorohydrin	123.2	58.0	.252	.80	.75	1.06
Chloral hydrate	129.3	59.0	.248	.77	.58	1.33
Phenol	103.4	53.8	.257	.88	.72	1.21
Hydroquinone	110.8	55.3	.254	.84	.66	1.27
Pyrogallol	118.2	57.0	.252	.81	.56	1.45
Glucose	178	68.3	.247	.66	.52	1.27
Mannite	185	69.4	.247	.65	.50	1.30
Lactose	340	92.7	.246	.49	.38	1.28
Raffinose	503	112	.240	.39	.33	1.19
Aniline	110.2	55.2	.257	.85	.69	1.23
Aniline hydrochloride	138.5	61.0	.252	.76	.79	0.96
Urethan	103.8	53.8	.258	.88	.80	1.10
Urea	58.0	42.5	.269	1.16	.94	1.23
Acetamide	66.0	44.6	.269	1.10	.96	1.15
Acetonitrile	56.3	42.0	.283	1.23	1.26	0.98
Pyridine	93.1	51.5	.261	0.93	0.58	1.60
Antipyrine	230.8	77.0	.247	.59	.54	1.09
Trinitrobenzene	176.1	68.0	.245	.66	.69	0.96

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[37] Carlson, *Medd. Nobelinst.*, **2**, 2 (1913).

aniline hydrochloride, trinitrobenzene and acetonitrile. A similar effect is noted with phthalic acid and salicylic aldehyde (Table VI).

Because of the cumulative errors in experiment and theory, accurate generalizations concerning the abnormality factor A are difficult to formulate. For a given substance, A_2 is greater than A_1; that is, the abnormality is more pronounced when the substance is the solvent than when it is the solute. Thus, methyl and ethyl alcohols have an A_2 of 2.0, and an A_1 in aqueous solution of only 1.2; acetone and nitrobenzene show an A_2 of 1.15 and 1.35, respectively, but as diffusing substances are apparently nearly normal. The magnitude of A_1 is dependent to some extent on the solvent, as shown in Table X; it is seen that the tendency is for A_1 to increase as the A_2 for the solvent decreases, A_1 being generally smallest in aqueous solution. Pyridine, however, shows the opposite tendency. The usual behavior is in accord with the Nernst–Thomson rule,[38] which is based on the diminution of molecular forces when the molecule is surrounded by a medium of high dielectric constant; as commonly expressed, good ionizing media, such as water, have high dielectric constants, while solvents with low constants favor association. Thus, intermolecular attractions will be weak, and A_1 consequently low, when the solvent dielectric constant is high.

TABLE X

SOLUTE ABNORMALITY FACTORS (A_1)

Solute	Water	Methanol	Ethyl alcohol	Benzene
Phenol	1.21	1.35	..	1.32
Amyl alcohol	1.16	1.29	1.31	1.29
Hydroquinone	1.27	1.43	2.14	..
Chloral	1.33	1.40	1.53	..
Glycerin	1.25	1.65	2.15	..
Formic acid	1.32	1.53	..	1.29
Acetic acid	1.27	1.53	..	1.38
Acetamide	1.15	1.54	2.08	..
Pyridine	1.60	1.26	1.07	..

It is to be emphasized that much better correlation is obtainable by the use of the factors A_1 and A_2 than by the use of an "association factor" as a multiplier for M and V in Equation 12, as would be required by the usual concept of the association of abnormal substances. For example, to fit the value of 1.22 for Cl_2 in Table VIII, an association factor for water of 12.6 would be required—far higher than any such factor found heretofore by other methods; using this factor for bromoform (Table III) gives a $D_{\text{calcd.}}$ of 0.68, with 0.85 observed, while for H_2 (Table VIII) the calculated value is 8.33, the observed average 5.13, and the value using our A factor, 5.34. Thus, granting the fundamental soundness of the present method of correlation, it appears that the hypothesis of molecular asso-

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[38] Turner, "Molecular Association," Longmans, Green and Co., 1915, p. 42.

ciation is insufficient to explain the data. In this connection, it is noteworthy that Longinescu[39] has apparently abandoned the concept of an actual physical combination of molecules, replacing it by the idea of an abnormally high "molecular concentration" in abnormal liquids. In the opinion of the present writer, all the anomalous properties of abnormal substances are fully as readily explainable by the concept of an abnormally strong force field around the molecule as by the assumption of association.

It is noteworthy that evidence of such association is usually very indirect, and that the several available methods for the quantitative estimation of degree of association give widely differing values of this quantity. It is hardly to be expected that such relationships as, for instance, the familiar Eötvös–Ramsay–Shields equation, will give a true value of molecular weight when the surface tension and critical temperature used in the equation are themselves abnormally high because of excessive intermolecular attraction; attempts to balance the equation by assuming an abnormal molecular weight can be productive of nothing more than empirical correlations, since a new, non-existent abnormality is assumed to compensate for the two existing ones. Similar criticisms may be applied to the related hypothesis of solvation. Inspection of Table II shows the absence of complications due to solvation, which is often assumed to be the cause of the diverse colors of iodine solutions. For instance, Hildebrand[40] has even determined equilibrium constants of solvation reactions from colorimetric data. It is evident that any actual attachment of solvent molecules to the diffusing iodine molecules would be shown by the failure of the diffusion equation to apply when the normal molecular weights and volumes are used.

The variation of diffusivity with temperature has never received a thorough investigation over a wide range. It is usual to assume D a linear function of t, according to the Nernst equation

$$D = D_0(1 + bt) \tag{15}$$

where b is the usual temperature coefficient. This relation is sufficiently accurate over short ranges, but for wide variation in temperature D is not linear in t. The Stokes–Einstein equation provides the relation

$$D \propto T/Z \tag{16}$$

Cohen and Bruins,[41] investigating the diffusion of acetylene tetrabromide in acetylene tetrachloride, found the relation to be true over the range 0–50°; Scheffer,[42] for mannitol diffusing in water, verified it from 0 to 70°.

Taking the logarithm of both sides of the last equation and differentiating gives

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[39] Longinescu, *Chem. Reviews*, **6**, 381 (1929).

[40] Hildebrand, THIS JOURNAL, **42**, 2180 (1920).

[41] Cohen and Bruins, *Z. physik. Chem.*, **103**, 404 (1923).

[42] Scheffer, *V. Kon. Ak. Wet. Amst.*, **19**, 148 (1916).

$$\frac{1}{D}\frac{dD}{dT} = \frac{1}{T} - \frac{1}{Z}\frac{dZ}{dT} \tag{17}$$

whence, by definition

$$b = 1/T - b_z \tag{18}$$

where b_z is the corresponding temperature coefficient of viscosity. Also if instead of using the Stokes–Einstein equation, we choose to express the variation of D solely in terms of the change in Z, let

$$D = a\bar{Z}^n \tag{19}$$

from which

$$b = -nb_z \tag{20}$$

To test these relations, we may use the data of Miller, over the range 10–20°. In Table XI the first column shows values of b_z calculated from the solvent viscosities. The second column gives values of b found from the Stokes–Einstein, relation, Equation 18, taking T to correspond to 15°, while the third column gives values of b from Equation 20, taking n as 3/2. The fourth column contains values of b given by the empirical equation

$$b = 0.020(Zv^{2/3})^{1/2} \tag{21}$$

Z and v both being at 20°. A study of this table indicates that the relation last given is the most satisfactory, and the Stokes–Einstein the least, though all agree fairly well with the observed values.

TABLE XI

TEMPERATURE COEFFICIENTS (MILLER)

Solvent	$-b_z$	Eq. 18	Eq. 20	Eq. 21	$b_{\text{obs.}}$
Benzene	0.0139	0.018	0.021	0.017	0.018
Toluene	.0113	.015	.017	.016	.016
Xylene	.0113	.015	.017	.017	.017
Anisole	.0147	.018	.022	.021	.024
Phenetole	.0154	.019	.023	.023	.023
Bromobenzene	.0119	.016	.018	.019	.017
Ethylene dibromide	.0144	.018	.022	.020	.020
Acetylene tetrabromide	.0333	.037	.050	.043	.041
Chloroform	.0084	.012	.013	.013	.013
Carbon tetrachloride	.0138	.018	.021	.017	.019
Carbon disulfide	.0071	.011	.011	.011	.012
Heptane	.0108	.015	.016	.016	.016
Ethyl acetate	.0104	.014	.016	.014	.014
Amyl acetate	.0140	.018	.021	.020	.021
Methanol	.0128	.017	.019	.017	.018

A study of the temperature coefficients found by Öholm[43] for diffusion in aqueous solution indicates that, like the factor F, b is (for dilute solutions) a function of the solvent properties only, converging to a value of 0.030 as solute concentration approaches zero. For concentrated solutions, b becomes greater or less than 0.030, depending on the nature of the

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[43] Öholm, *Z. physik. Chem.*, **70**, 378 (1910); *Medd. Nobelinst.*, **2**, 23, 24 (1913).

Z–c curve. For dilute solutions, since b is independent of solute nature, the relations deduced from Miller's data may be used for any diffusing substance.

It is apparent from an inspection of the tables given that the theory here presented is still incomplete, and can make no claim to mathematical exactness; nevertheless, the agreement with experiment is considerably better than any hitherto attained, and indicates that the method of approach is fundamentally sound and practicable. We have now to consider the several causes to which the deviations noted may be attributed.

Experimental errors in diffusion measurements are considerable, of the order of 5% for ordinary work, and undoubtedly are responsible for much of the disagreement. The use of a Kopp law V as representing the cube of the molecular diameter is open to some criticism; it has, however, been shown in the previous paper of this series that this volume corresponds closely with that calculated from gas viscosity, and is therefore probably satisfactory for diffusion calculations. The importance of errors in V is lessened by the fact that it appears in the equation for D as a cube root. The selection of 20° as a standard reference temperature is quite arbitrary, but in the absence of a more definite knowledge of the variation of D with T, it seems advisable to choose a constant temperature near that used experimentally. The further development of the present theory will undoubtedly require the expression of F as a function of T; it is to be noted that Equation 14 is correct only at 20°, and does not completely express the variation of D with T. The factor F is analogous to the $(1 + C/T)$ of the Sutherland theory of gaseous diffusion, both representing the effect of intermolecular forces on diffusional resistance.

The greater part of the observed discrepancy is probably traceable to three causes: (1) the assumption of binary, elastic collisions in a liquid system is inexact; (2) the van der Waals correction factor is not, as assumed, constant for all systems; (3) the functional relation between F and Z is not accurately given over a wide range by Equation 13. Of these, (1) and (2) are not remediable except by further analysis of the problem, while (3) awaits further data on diffusion in viscous, high-boiling solvents. Further, neglect of the dependence of F on the solute nature introduces some error, comparable in magnitude with the experimental errors and hence not yet subject to exact evaluation. It is also to be mentioned that F may be a function of molecular volume as well as molecular force, allowing for the mean free path shortening due to the space occupied by the molecules as well as that due to intermolecular attractions. Macleod[44] has shown that liquid viscosity is very simply related to the free space within the liquid, while Equation 13 is seen to contain the solvent molecular volume as a variable affecting F. The more exact

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[44] Macleod, *Trans. Faraday Soc.*, 19, 6 (1923); 21, 151 (1925).

evaluation of this factor, together with the applications of the principles above discussed, to the closely related problems of diffusion in mixed solvents, ionic mobility and the diffusion of electrolytes, will be considered in a later paper.

The writer is indebted to Mr. James J. Hogan for his careful reading of the manuscript and his many helpful suggestions; to Professor Warren K. Lewis for his continued interest in the work; and to the host of experimental investigators in this field during the past eighty years, whose contributions of painstaking and accurate work have made possible the present correlation.

Summary

The classical kinetic theory of gases has been applied to diffusion in liquid systems, assuming that the resistance to diffusion is due wholly to binary collisions, and that the mean free path shortening due to the volume occupied by the molecules is the same for all systems. Allowance is made for the retarding effect of intermolecular forces by introducing a factor F, which has been found empirically to be essentially independent of the nature of the diffusing substance and directly proportional to the square root of the solvent viscosity. "Associated" substances are found to require the use of abnormality factors in the expression for F; it is found that the usual hypothesis of molecular association is incapable of explaining the diffusional behavior of these substances, and that the related hypothesis of solvation of certain substances is unnecessary for good agreement with theory. The variation of diffusivity with temperature is discussed, and several rules are given for the prediction of temperature coefficients. Comparison of the observed diffusion coefficients with those calculated from the theory shows good agreement over a wide range of molecular weights and viscosities; the sources of the deviations observed are discussed.

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