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HUGH S. TAYLOR

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

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The Eyring concept of holes in liquids and his theory of absolute reaction rates indicate that diffusion coefficients should vary exponentially with temperature. Data in the literature indicate that this is true. It is shown that empirical observations concerning the relation between diffusion velocity and its temperature coefficient, hitherto generally assumed to be linear, are readily explained upon the basis of holes in liquids as a controlling factor. As with viscosity, in liquids containing hydrogen bonds relatively high activation energies of diffusion are found. Data for small diffusing molecules should not show a constant diffusion-viscosity product as required by the Stokes-Einstein relation at constant temperature, but a product varying within restricted ranges with the dimensions of the solvent molecules. Data already available tend to confirm this conclusion.

THE concept of holes in liquid systems has been shown by Eyring[1] to lead straightforwardly to a theory of viscosity, plasticity and diffusion in condensed systems with the aid of the Eyring theory of absolute reaction rates.[2] The application of this theory of viscosity to a number of experimental data over a range of temperature and pressure has been examined by Ewell and Eyring[3] and the activation energy of the viscosity process related to the energy of vaporization of the liquid, by employing the relation, developed by Eyring and Hirschfelder,[4] between free volume and energy of vaporization.

In his original communication,[1] dealing with diffusion, Eyring pointed out that the diffusion coefficient D is

$$D = \lambda^2 k_1, \tag{1}$$

where λ is the average difference between two successive minima in the potential energy curve representing the flow of a diffusing molecule past a molecule of the medium, when both types of molecule are approximately the same size. The constant k_1 is the absolute rate of reaction for the transition. For ordinary viscous flow, it was shown that, to a sufficient approximation, the viscosity η could be represented by the equation

$$\eta = \lambda_1 kT(\lambda^2\lambda_2\lambda_3 k_1)^{-1}, \tag{2}$$

where λ_1 is the perpendicular distance between two neighboring layers of molecules sliding past each other, λ_2 the distance between neighboring molecules in the direction of flow and λ_3 the intermolecular distance in the plane normal to the direction of motion. In this way the relation between diffusion and viscosity, from Eqs. (1) and (2) becomes

$$D = \lambda_1 kT / \lambda_2\lambda_3\eta \tag{3}$$

for molecules of similar sizes. This is to be compared with the well-known relationship for the diffusion of very large molecules in a medium of smaller molecules,

$$D = kT / 6\pi r\eta. \tag{4}$$

In the light of Eq. (3) Eyring examined the data of Orr and Butler for the diffusion of heavy into light water[5] at 0 and 45° and found that the results indicated that, in viscous flow, the plane of the water molecule tended to coincide with the plane of flow and that λ_1 the perpendicular dimension was the small one, equal to 1.44×10^{-8} cm whereas $(\lambda_2\lambda_3)^{\frac{1}{2}}$ had the value 4.54×10^{-8} cm. Eq. (4) leads to unreasonably small values of r. Eyring also emphasized that, for the diffusion of ions in solutions of electrolytes, Eq. (3) should normally be employed.

The variation of viscosity with temperature was tested by Ewell and Eyring by means of the approximate formula

$$\eta = 1.090 \cdot 10^{-3} \frac{M^{\frac{1}{2}}T^{\frac{1}{2}}}{V^{\frac{2}{3}}\Delta E_{vap}} \exp\frac{\Delta E_{vap}}{nRT}, \tag{5}$$

where ΔE_{vap} is the heat of vaporization in calories per mole and n is a constant for a given substance

[1] H. Eyring, J. Chem. Phys. **4**, 281 (1936).
[2] H. Eyring, J. Chem. Phys. **3**, 107 (1935).
[3] R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).
[4] H. Eyring and J. Hirschfelder, J. Phys. Chem. **41**, 249 (1937).
[5] Orr and J. E. V. Butler, J. Chem. Soc. 1273 (1935).

(3–4) which can be interpreted as expressing the fraction $(1/n)$ of the heat of vaporization necessary for the production of a hole of suitable size for the flow process to occur. Diffusion therefore should show a similar exponential variation with temperature since it is related to viscosity by either Eqs. (3) or (4).

In the older treatments of diffusion in liquid systems[6] the data on the effect of temperature have normally been represented as a linear function of temperature and not as an exponential function even though, in contrast to viscosity, the subject of diffusion has generally been treated in sections dealing with reaction velocity in heterogeneous systems. This doubtless arises from the restricted material on temperature variation, measurements of the diffusion coefficient being often only available at two temperatures, the data being represented by an equation of the form

$$D_2/D_1 = 1 + \alpha(T_2 - T_1). \qquad (6)$$

In the precision measurements of Cohen and Bruins[7] on the diffusion of tetrabromethane in tetrachlorethane solutions, extended over the range 0–55°C it was found that the series of six measurements could not be represented by a linear interpolation formula and an equation in t and t^2 was derived by the method of least squares. These data of Cohen and Bruins form the best material with which to test the variability of diffusion with temperature. By plotting the logarithm of the mean diffusion constants against the reciprocal of the absolute temperature in the range above indicated, an excellent linear plot is obtained from which an activation energy of diffusion = 3490 calories can be derived.

Cohen and Bruins simultaneously determined with great precision the viscosity of the tetrachlorethane employed as medium, also representing their data over the same range of temperature by means of an equation with powers of t and t^2. Plotting the logarithm of the viscosity against the reciprocal of the temperature again yields an excellent straight line, whose slope, however, leads to a somewhat lower value for the activation energy of the viscosity process,

2995 calories. The molecular heat of vaporization of this compound has been determined from vapor pressure measurements of Herz and Rathmann[8] who found 9134 calories, giving a Trouton constant of 21.8 indicating a normal liquid. The relation between the activation energy of the flow process and the heat of vaporization leads to a value of $n = 3.0$ in Eq. (5) in agreement with the viscosity results for $C_2H_4Cl_2$ and $C_2H_4Br_2$ examined by Eyring and Ewell. The same Trouton constant for tetrabromethane gives for the heat of vaporization at the boiling point $(T \sim 515°K)$ the value 11230 calories. Using the above value of $n = 3$, the activation energy of the flow process in tetrabromethane would then be 3745 calories. It is significant that the activation energy of diffusion is fairly close to the mean of these two activation energies of viscous flow $(E_D = 3490; \frac{1}{2}E_{vis}(-Cl_4 + -Br_4) = 3370)$ suggesting that, in the diffusion process, the motion of the diffusing molecule past the medium molecule demands a free volume approximately the mean of that required by the two molecules in their separate viscous flows.

Other data expressing diffusion coefficients over a range of several temperatures are very meager. From the *International Critical Tables*[6] we select data on the diffusion of mannitol in aqueous solutions containing 0.3 gram moles per liter. These data[9] are the most extensive as to temperature range (0–70°) of those recorded. Plotting log D against $1/T$ over this range we obtain, not a straight line, but one slightly curved toward the $1/T$ axis. Calculation of activation energies from point to point over the temperature range shows a value for the activation energy decreasing steadily toward a constant value somewhat greater than 3000 calories.

$T =$	273	283	293	303	313	323	333	343
$E_D =$	6590	5530	4460	4230	4035	3900	3774.	

These values show the same trend noted by Ewell and Eyring[3] for the activation energy of viscous flow of water and accounted for, by them, on the basis of the hydrogen bond structure of the liquid. The actual values for the activation energy of diffusion are upwards of 1 kcal. larger than the activation energies of viscous flow at the same temperature which is readily under-

[6] See, for example, Taylor, *Treatise of Physical Chemistry*, second edition (1931), pp. 1022–1028. Also, *International Critical Tables*, Vol. 5, (McGraw-Hill and Co., New York, 1929), p. 63.

[7] E. Cohen and H. R. Bruins, Zeits. f. physik. Chemie **103**, 404 (1923).

[8] Herz and Rathmann, Chem. Zeits. **36**, 1417 (1912).

[9] Scheffer and Scheffer, Proc. Acad. Sci. Amsterdam, **19**, 148 (1916).

TABLE I. *Temperature coefficients and activation energies of diffusion.*

$D(\text{cm}^2/\text{day})$	2.4	1.2–1.1	0.2–0.1
α	0.018	0.025	0.040
D_{t+10}/D_t	1.20	1.28	1.48
E_D	2875	4070	6470

standable when the size of the diffusing mannitol molecule and its hydrogen bond forming capacity are borne in mind.

Recently some data have been obtained using the technique developed by Northrop and Anson,[10] using a porous glass disk to separate the two solutions. Cole and Gordon[11] employed this technique to measure the diffusion of copper sulphate in dilute solution into sulphuric acid solutions containing 0.1 gram equivalents of acid per liter. Measurements made at 283, 291 and 298°K give a fair linear plot, $\log D$ vs. $1/T$, from the slope of which an activation energy of 5140 cal. is derived. This value is to be compared with an activation energy of viscous flow of water in the same temperature range somewhat less than 5000 cal. The abnormally high values of these activation energies, approximately one-half of the heat of vaporization ($\sim$10 kcal.) is again to be accounted for by the hydrogen bond structure of the liquid. Similar data recently given by Anson and Northrop[12] at several temperatures in the range 278–295°K for the diffusion coefficients of $2n$ NaCl, $1n$ and $0.1n$ HCl into water also give, approximately, a linear relationship, $\log D$ vs. $1/T$, with slopes corresponding to activation energies of 5450, 4850 and 4760 cal., respectively.

Although the data for the temperature variation of diffusion coefficients are scanty, there are nevertheless in the generalizations from the data obtained at only two temperatures results which are at once comprehensible from the standpoint of diffusion as a velocity process depending upon hole formation in the liquid medium. Thus, Öholm[6] on the basis of data at two temperatures with a wide variety of media, pointed out that substances showing a high value for the diffusion coefficient always showed a small temperature coefficient (α in Eq. (6)) and *vice versa*. Öholm's generalization is exemplified in Table I.

This is exactly what is to be anticipated on the basis of Eyring's theory. The more slowly diffusing materials require larger holes than the fast-diffusing species and the activation energy to produce these holes is correspondingly greater. The generalization of Öholm for the diffusion process is identical with the observation of Kohlrausch on ionic mobility. The greater is the ionic mobility the less the temperature coefficient. Herein lies also the reason for the observation that, with increased temperature, the transport numbers of the ions all approach 0.5; for, the ions with values less than 0.5 at a given temperature will have a larger temperature coefficient of mobility than those greater than 0.5.

Riecke[13] in 1890 attempted to formulate a kinetic theory of diffusion in dilute solutions and obtained an expression for the diffusion coefficient,

$$D = \text{const.} \ (1/M)^{\frac{1}{3}}l,$$

where M is the molecular weight and l the mean free path. Values for l of the order of 0.1A were obtained with this equation. That it cannot have real validity is evident from a selection of data compiled by Öholm in which diffusion coefficients for molecules with molecular weights between 50 and 300 showed entirely random variations on the molecular weight basis. Certain of these data are shown in Table II for $1.0N$ solutions in ethyl alcohol.

Qualitatively all these data are in agreement with anticipations based upon the concept of holes. It is the shape and volume of the diffusing molecule rather than its mass which determines the diffusion velocity in a given medium. Comparison of bromoform and stearic acid illustrates this. Comparison of chloroform with glycerine shows how greatly this latter is retarded by reason of its hydrogen bond forming capacity.

The influence of the medium on the rate of

TABLE II. *Diffusion coefficients and molecular weights.*

SUBSTANCE	MOLECULAR WEIGHT	$D_{20°}(\text{CM}^2/\text{DAY})$
Pyridine	79	0.89
Glycerine	92	0.35
Chloroform	119	1.08
Chloral	147	0.53
Camphor	152	0.58
Iodobenzene	204	0.81
Brom-naphthalene	207	0.60
Bromoform	252	0.83
Stearic acid	284	0.34

[10] Northrop and Anson, J. Gen. Physiol. 12, 543 (1928).
[11] Cole and Gordon, J. Phys. Chem. 40, 733 (1936).
[12] Anson and Northrop, J. Gen. Physiol. 20, 575 (1937).
[13] E. Riecke, Zeits. f. physik. Chemie 6, 564 (1890).

TABLE III. *Diffusion coefficients of bromoform in various media.*

SOLVENT	NORMALITY	α	$D_{20°}$	ΔE_{vap}
Ether	0.5	0.017	2.93	6.26
Acetone	0.5	0.018	2.32	7.27
Methyl alcohol	0.5	0.022	1.67	8.44
Benzol	1.0	0.024	1.46	7.45
Ethyl alcohol	1.0	0.028	0.835	9.97
Propyl alcohol	1.0	0.030	0.665	9.99
Amyl alcohol	1.0	0.034	0.446	10.6
50% EtOH : 50% H_2O	0.25	0.038	0.267	~10.0

TABLE IV. *Diffusion-viscosity data for 0.1N solutions of iodine in various solvents.*

SOLVENT	$D_{(19.9°)}$	α	$D\eta_{(19.9°)}$	MOLE VOL.	ΔE_{vap} KCAL./MOL.
Tetrabromethane	0.1576	0.041	1544	117	11.2
Dibromethane	0.719	0.020	1232	87	8.25
Phenetole	0.843	0.023	1111	126	—
Anisole	0.977	0.024	1056	109	8.8
Iso-amyl acetate	1.071	0.021	933	149	9.0
Brombenzene	1.038	0.017	1176	105	8.8
Carbon tetrachloride	1.177	0.019	1128	97	8.0
m-Xylene	1.454	0.017	935	123	8.8
Methyl alcohol	1.572	0.018	960	40	8.44
Benzene	1.670	0.018	1072	89	7.45
Toluene	1.686	0.016	981	106	7.99
Chloroform	1.831	0.013	1062	81	7.08
Ethyl acetate	1.859	0.014	850	98	7.78
Heptane	2.386	0.016	1148	140	7.59
Carbon disulphide	2.697	0.012	1014	60	6.6

diffusion of a given substance can be illustrated by Öholm's[14] data for the diffusion of bromoform in various media at 20°C.

Table III again illustrates the inverse trend of α with D and indicates the decreasing value of the diffusion coefficient with increasing energy of vaporization of the medium and increasing association of the liquid.

The data of Miller[15] on the diffusion of 0.1N iodine solutions in various organic solvents illustrate the same inverse variation of α with D as shown in Table IV. Measurements of the viscosity of the solvent were simultaneously obtained in order to test the validity of the Stokes-Einstein Eq. (4) according to which the product $D\eta$ should be constant at constant temperature. The fourth column in Table IV shows that this is only approximately true, the value $D\eta$ varying between 850 and 1544. While this variation is small compared to the variation in D(0.1576 to 2.697), it is nevertheless indicative that the Stokes-Einstein relationship is not applicable. A twofold variation in r, the radius of the diffusing molecule, would be deduced from the data. The Eyring expression (3)

$$D\eta = kT\lambda_1/\lambda_2\lambda_3$$

is, in reality, only applicable to the case of self-diffusion and viscous flow. In this equation the term λ^2, in the expression for each, cancels in the product, λ being the distance between successive potential energy minima in the particular type of motion involved. In the case of diffusion of a solute through a solvent it is not necessarily true that the λ for the solute molecule in a solution is the same as the λ for the process of viscous flow. This would be true if λ was the distance between single molecules in the liquid. For a given solute in various solvents, it is

[14] Öholm, Medd. Vet. Akad. Nobel Inst. **2**, 16 (1912).
[15] C. C. Miller, Proc. Roy. Soc. **A106**, 724 (1924).

evident, however, that, even granting the invariance of λ, the presence of λ_1, λ_2 and λ_3, the dimensions characteristic of the solvent, in the equation, means that the diffusion-viscosity product shall not necessarily be constant but vary from solvent to solvent within a certain restricted range. Miller has already pointed out that, when the data for solvents of similar chemical nature are compared, the product $D\eta$ increases as the molecular volume increases. Dibromethane and tetrabromethane, chloroform and carbon tetrachloride, ethyl acetate and iso-amyl acetate of the preceding Table IV may thus be compared. Anomalous in this respect are the data for benzene, toluene and *m*-xylene which do not show the progressive variation with volume or with heat of vaporization that might be expected. The experimental data in such a series should be restudied using the more recent techniques. Similar studies with suitably chosen solvents would serve more precisely to define the influence of the λ factors on the viscosity-diffusion product. From such data, over a range of temperatures, we can expect a material increase in our knowledge of the structural characteristics of liquids.

The data on the activation energy of viscous flow in tetrachlorethane and on the activation energy of diffusion of tetrabromethane in tetrachlorethane, already discussed, indicate that the differences in activation there found will also enter into the magnitude of the diffusion-viscosity product. Since this factor enters as an exponential, $e^{-\Delta E/RT}$, it may be of controlling importance in determining the magnitude of the variations in the value of the product for various solutions of a given solute, and, specifically, in the data for iodine just presented.