13. Ebach, E. A., and R. R. White, *Chem. Eng. Progr.*, 4, 161 (1958).
14. Glaser, M. B., and I. Lichtenstein, *A.I.Ch.E. J.*, **9**, 30 (1963).
15. Glaser, M. B., and Mitchell Litt, *ibid.*, 103.
16. Gottschlich, C. H., *ibid.*, 88.
17. Green, D. W., R. H. Perry, and R. E. Babcock, *ibid.*, **10**, 645 (1964).
18. Hoffman, H., *Chem. Eng. Sci.*, **14**, 193 (1961).
19. Hoftyzer, P. J., "Joint Symposium on Scaling-up," p. S73, Inst. Chem. Engrs., London (1957).
20. Hoogendoorn, C. J., and J. Lips, *Can. J. Chem. Eng.*, **43**, 125 (1965).
21. King, R. P., M.Sc. thesis, Univ. Witwatersrand, Johannesburg, South Africa (1962).
22. Kramers, H. and G. Alberda, *Chem. Eng. Sci.*, **2**, 173 (1953).
23. Levenspiel, O., and K. B. Bischoff, "Advances in Chemical Engineering," Vol. 4, p. 95, Academic Press, New York (1963).
24. Loomis, A. L., "International Critical Tables," Vol. 3, p. 260, McGraw-Hill, New York (1928).
25. McHenry, K. W., and R. H. Wilhelm, *A.I.Ch.E. J.*, **3**, 83 (1957).
26. Miyauchi, Terukatsu, and Theodore Vermeulen, *Ind. Eng. Chem. Fundamentals*, **2**, 113 (1963).
27. Morris, G. A., and J. Jackson, "Absorption Towers," p. 143, Butterworths, London (1953).
28. Norman, W. S., "Absorption, Distillation and Cooling Towers," pp. 192, 193, Longmans, London (1961).
29. Rixon, F. F., *Trans. Inst. Chem. Engrs.* (*London*), **26**, 119 (1948).
30. Schwartz, C. E., and J. M. Smith, *Ind. Eng. Chem.*, **45**, 1209 (1953).
31. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2 ed., p. 291, McGraw-Hill, New York (1952).
32. Shulman, H. L., C. F. Ullrich, A. Z. Proulx, and J. O. Zimmerman, *A.I.Ch.E. J.*, **1**, 253 (1955).
33. Sinclair, R. J., and O. E. Potter, *Trans. Inst. Chem. Engrs.* (*London*), **43**, T3 (1965).
34. Uchida, S., and S. Fujita, *J. Soc. Chem. Ind.* (*Japan*), Suppl., **37**, 274 (1934); **39**, 432 (1936); **41**, 275 (1938).

Manuscript received June 8, 1965; revision received January 5, 1966; paper accepted January 12, 1966. Paper presented at A.I.Ch.E. Philadelphia meeting.

Diffusion of Gases in Electrolytic Solutions

KEITH E. GUBBINS, KAMLESH K. BHATIA, and ROBERT D. WALKER, JR.

University of Florida, Gainesville, Florida

Measurements of the diffusion coefficients of hydrogen and methane in strong aqueous electrolytes have been made with the use of the diaphragm cell method. The variation of the diffusion coefficients with electrolyte concentration, type of ion, and temperature has been studied over the electrolyte concentration range zero to saturated, and for temperatures in the range 25° to 65°C.

The results have been interpreted with the Eyring rate theory. The presence of ions in water increases the activation energy for diffusion which results in a decrease in the diffusion coefficient. The increase in activation energy is represented by terms that are additive for the ions involved. The influence of ions on the diffusion coefficient increases rapidly with ionic charge, but seems to be little affected by temperature or solute for the systems studied.

The prediction of the rate of diffusion of nonelectrolytes through aqueous electrolytes is of interest in a number of practical problems, for example, the study of mass transfer limitations at electrodes. Although the Wilke-Chang equation (*1, 2*) provides a means of estimating binary diffusion coefficients in liquids, it is not immediately applicable to electrolytes, since it involves the solvent molecular weight and an association parameter. The Eyring theory (*3, 4*) of reaction rates provides a starting point for the development of correlations for diffusion in electrolytes, and has been used by Podolsky (*5*) and Ratcliff (*6*) in developing relationships for the fluidity of electrolytes and also for the diffusion of nonelectrolytes. Very few experimental studies of diffusion of dissolved gases in electrolyte solutions are available, and the measurements reported have been made at a single temperature (*6, 7*). The object of the present work is to examine the variation of gaseous diffusion coefficients with solute gas, electrolyte, concentration, and temperature.

THEORY

According to the Eyring reaction rate theory, the fluidity of a liquid ϕ and the binary diffusion coefficient in dilute solution D are given by

$$\phi = \frac{1}{\eta} = k_\phi \lambda^2 e^{-\Delta G_\phi{}^*/RT} = k_\phi \lambda^2 \frac{h}{(2\pi mkT)^{1/2} v_f{}^{1/3}} e^{-\epsilon_\phi/kT} \tag{1}$$

$$D = k_d \lambda^2 e^{-\Delta G_d{}^*/RT} = k_d \lambda^2 \frac{h}{(2\pi mkT)^{1/2} v_f{}^{1/3}} e^{-\epsilon_d/kT} \tag{2}$$

Weyman (*8*) recently has derived equations similar to (1) and (2) by more rigorous statistical mechanical methods. The diffusion coefficient (or fluidity) is determined primarily by the activation energy for the process and the temperature.

Podolsky (*5*) has derived an expression for the fluidity of an electrolyte solution using Equation (1), and Ratcliff (*6*) has proposed a corresponding equation for the diffusion coefficients of gases in electrolytes. Their derivation is outlined below.

K. K. Bhatia is with Procter and Gamble Company, Cincinnati, Ohio.

The presence of ions in the solution is assumed to cause changes in the free energy of activation for the process; changes in the lattice spacing λ due to the presence of ions are assumed to have a negligible effect on the transport coefficient as compared to the effect of changes in free energy of activation. The free energy of activation in Equations (1) and (2) is replaced by a free energy of activation which is averaged over all possible configurations of the molecule undergoing diffusion or viscous flow.

$$<\Delta G^*> = \sum_i p_i \Delta G_i^* \tag{3}$$

In considering the case of diffusion, a solute gas molecule is assumed to interact with n surrounding solvent molecules; on replacing one of the surrounding water molecules by an ion of type i, the free energy of activation is supposed to be perturbed by an amount δ_i, so that the free energy of activation for diffusion becomes $(\Delta G_o^* + \delta_i)$. If it is assumed that the distribution of ions in the neighborhood of the solute molecule is the same as that in the bulk solution, the average free energy of activation for the diffusion of sparingly soluble gases is obtained from Equation (3) as

$$<\Delta G_d^*> = \Delta G_o^* + \frac{nx(\nu_1\delta_1 + \nu_2\delta_2)}{(1-x) + (\nu_1 + \nu_2)x} \tag{4}$$

The second term in Equation (4) represents the change in the free energy of activation for the solute molecule in water due to the electrolyte. By combining Equations (2) and (4) and by assuming the second term in Equation (4) is small and that λ is not affected appreciably by the presence of electrolyte, we obtain

$$\frac{D}{D_o} = \exp\left[1 - \frac{nx(\nu_1\delta_1 + \nu_2\delta_2)}{RT[(1-x) + (\nu_1 + \nu_2)x]}\right] \simeq 1 - \frac{Ax}{(1-x) + (\nu_1 + \nu_2)x} \tag{5}$$

The plot of D vs. $x/[(1-x) + (\nu_1 + \nu_2)x]$ at a given temperature should therefore be approximately linear at electrolyte concentrations that are not too high. The corresponding equation for fluidity has been obtained by Podolsky (*5*) as

$$\frac{\phi}{\phi_o} = 1 - \frac{x(1 + r')(\nu_1 n_1 \delta_1' + \nu_2 n_2 \delta_2')}{RT[(1-x) + (\nu_1 + \nu_2)x]} \tag{6}$$

The perturbation terms δ_i and δ_i' are generally different since they represent ion-solute and ion-water interactions, respectively. Equation (6) is formally similar to equations proposed by Jones and Dole (*9*) and Bingham (*10*). The latter has tabulated the contributions (corresponding to $n_1\delta_1'$ and $n_2\delta_2'$) of the separate ions to the fluidity.

Recently McCall and Douglass (*11*) measured the self-diffusion coefficient of water as a function of concentration for several electrolytes at 23°C. With the use of Podolsky's approach (*5*), the effect of electrolyte on the self-diffusivity of water D_w is given by

$$\frac{D_w}{D_{wo}} = 1 - \frac{x(\nu_1 n_1 \delta_1' + \nu_2 n_2 \delta_2')}{RT(1-x)} \tag{7}$$

The perturbation terms δ_i' will be the same as in the case of fluidity. McCall and Douglass tabulated the contributions of the separate ions for self-diffusion of water.

EXPERIMENTAL

Measurements of the diffusion coefficients were made by the diaphragm cell method (*12* to *14*). The cells were filled under vacuum with gas-free electrolyte solution, and the liquid on one side of the cell was saturated with the gas under study. Diffusion was then allowed to take place for 24 to 48 hr. Afterward the concentration of gas in each compartment was determined by gas chromatography; the analysis method used has been described elsewhere (*15*). Experiments were carried out in water baths controlled to ± 0.05°C. and the solution on each side of the diaphragm was stirred by means of magnetic stirrers at a rate of 100 rev./min. (*16*). The cells were calibrated with potassium chloride solution at 25°C.

To check the possibility of gas adsorption on the frit, the concentration of dissolved gas in both compartments was measured both before and after a diffusion experiment. A mass balance indicated no measurable loss of gas. The cell calibration of each of the cells used was checked periodically (about once for each ten diffusion measurements). During the course of the experiments reported here, the calibration constants of each of the cells used changed by less than 1%.

The usual practice in measuring diffusion coefficients by the diaphragm cell method is to allow diffusion to occur until a linear concentration gradient has been established across the diaphragm. The solution in the compartment of lower concentration is then replaced by fresh solvent, and the time of diffusion under quasistationary conditions is measured from the time of replacement. This procedure is unsatisfactory when studying the diffusion of gases in liquids because of the difficulty of replacing the solution on one side of the diaphragm with gas-free solvent. In addition it is difficult to avoid creating temperature fluctuations in the cell when replacing solutions; this effect is particularly prone to lead to difficulties when measurements are made at temperatures appreciably different from ambient.

To overcome this difficulty the time of diffusion was measured from the time at which the cell was filled with the gas-saturated solution. At the end of the experiment a correction was applied for the initial period of unsteady state operation. The required correction may be estimated with sufficient accuracy by solving the diffusion equation with the following initial and boundary conditions:

$$\begin{array}{lll} c' = 0 & t \leq 0 & 0 \leq x \leq L \\ c' = c_o & t > 0 & x \leq 0 \\ c' = 0 & t > 0 & x \geq L \end{array}$$

The solution of the diffusion equation is (*17*):

$$c' = c_o - \frac{c_o x}{L} - \frac{2}{\pi} \sum_{j=1}^{\infty} \frac{c_o}{j} \sin \frac{j\pi x}{L} e^{-j^2 D\pi^2 t/L^2} \tag{8}$$

From a knowledge of the cell constant the necessary correction to be applied for the unsteady state period was obtained from Equation (*8*). In most cases this correction represented about 1% of the total time of diffusion (*14*), so that the use of the above boundary conditions should not cause appreciable error.

RESULTS

The diffusion coefficients of hydrogen and methane in aqueous solutions of potassium chloride, magnesium chlo-

TABLE 1. DIFFUSION COEFFICIENTS OF HYDROGEN IN AQUEOUS ELECTROLYTES AT 1 ATM.

Values reported are $D \times 10^5$, sq. cm./sec.

Electrolyte	c	x	$\frac{x}{1-x+(\nu_1+\nu_2)x}$	D_{25}	D_{45}	D_{65}
Pure water	0	0	0	4.10	6.30	9.44
Potassium chloride	1.0	0.01821	0.0178	3.79	5.97	
	2.0	0.03693	0.0356	3.60	5.73	8.90
	3.0	0.05623	0.0532	3.34	5.27	8.30
Magnesium chloride	0.75	0.01355	0.01319	3.36		7.39
	1.5	0.02724	0.02583	3.09	4.13	6.04
	2.25	0.0412	0.03806	2.18	3.38	4.95
	3.0	0.0565	0.05788	1.45	2.71	3.47
Magnesium sulfate	0.5	0.00894	0.00878	3.90	5.29	7.18
	1.0	0.01783	0.01721	2.86	4.41	6.34
	2.0	0.03556	0.0332	1.57	2.90	4.27

ride, and magnesium sulfate have been determined at temperatures of 25°, 45°, and 65°C. Each electrolyte has been studied at a number of concentrations in the range zero to near saturation. The results are given in Tables 1 and 2, together with the diffusion coefficients of the gases in water at these temperatures. Concentrations of electrolyte *c* are values determined at 20°C. Since the concentration of both hydrogen and methane in these solutions was of the order 10^{-3} molar or less, the diffusion coefficients obtained from the diaphragm cell method may be regarded as the differential diffusion coefficients at infinite dilution.

The experimentally determined diffusion coefficients for hydrogen in water appear to be in agreement with data reported by other workers, although there is some scatter in the published data. Thus for hydrogen in water at 25°C. Vivian and King *(18)* report 4.8×10^{-5}, Baird and Davidson *(19)* give 4.27 and 5.52×10^{-5}, and Ipatev *(20)* gives 3.43×10^{-5} sq.cm./sec. Ipatev also reports a value of 5.7×10^{-5} sq.cm./sec. for hydrogen in water at 45°C. The measured diffusion coefficient for methane in water at 25°C. agrees well with the value of 1.88×10^{-5} sq.cm./sec. recently obtained by Witherspoon and Saraf *(21)*, who used the capillary cell technique.

The values reported for the diffusion coefficient of hydrogen in water represent the mean value derived from three separate experiments. The values of *D* for methane in water at 25° and 45°C. are mean values for two determinations. The standard deviation of the measured values of *D* for each of the gases in water was approximately 3% of the arithmetic mean. It is estimated that the absolute values given in Tables 1 and 2 are probably accurate to within ± 10%. Since the effect of electrolyte concentration on the diffusion coefficient is small in the case of potassium chloride solutions, no measurements were made at low potassium chloride concentrations for the diffusion of methane.

DISCUSSION

According to Equation (5) the plot of D/D_o vs. $x/[1 - x + (\nu_1 + \nu_2)x]$ should be linear if the concentration is not large; the slope will be $n(\nu_1\delta_1 + \nu_2\delta_2)/RT$. Figures 1 and 2 show D/D_o as a function of $x/[1 - x + (\nu_1 + \nu_2)x]$; the latter function is approximately proportional to concentration for concentrations that are not too high. In most cases the data seem to fall on straight lines within experimental error; in some cases the data are fitted somewhat better by curves. In general the data showed slightly better linearity when plotted as D/D_o vs. $x/[1 - x + (\nu_1 + \nu_2)x]$ than when plotted as $\ln D/D_o$.

TABLE 2. DIFFUSION COEFFICIENTS OF METHANE IN AQUEOUS ELECTROLYTES AT 1 ATM.

Values reported are $D \times 10^5$, sq. cm./sec.

Electrolyte	c	x	$\dfrac{x}{(1-x)+(\nu_1+\nu_2)x}$	D_{25}	D_{45}	D_{65}
Pure water	0	0	0	1.81	2.78	3.84
Potassium chloride	2.40	0.04454	0.04264			3.86
	3.55	0.06703	0.0628	1.65		
	3.65	0.06904	0.06458		2.52	3.29
Magnesium chloride	1.025	0.01852	0.01786	1.60	2.44	3.36
	2.02	0.03690	0.03436	1.41	1.68	2.34
	2.95	0.05545	0.04990	0.79	1.42	1.70
Magnesium sulfate	0.5	0.00894	0.00878	1.88	2.58	3.56
	1.0	0.01783	0.01721	1.42	1.73	2.86
	2.0	0.03556	0.0332	0.73	1.27	1.97

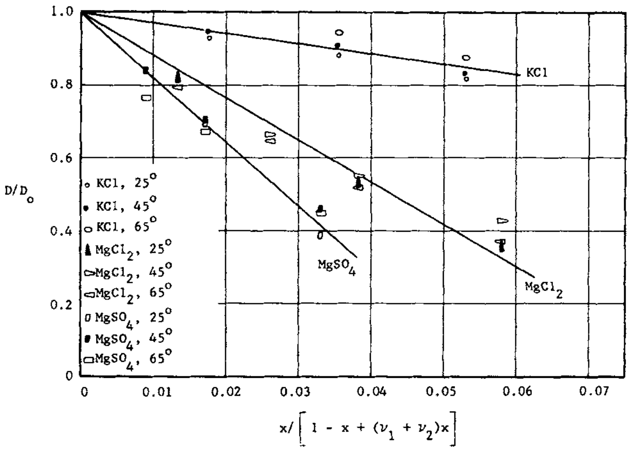

Fig. 1. Diffusion coefficients of hydrogen.

A plot of $\ln D$ vs. $1/T$ gave good straight lines for the data in Tables 1 and 2. In principle the measured slopes of these lines should enable the perturbation of activation energy due to the electrolyte to be determined. Since the change in slope with electrolyte concentration is small, however, the perturbations are more accurately determined by plotting *D* as in Figures 1 and 2. Plotting the data for diffusion of hydrogen and methane as $\ln D$ vs. $1/T$ yielded measured activation energies of 4.22 and 4.01 kcal./g.-mole for hydrogen and methane, respectively.

Table 3 shows the slopes *A* of the lines obtained on plotting the data of Tables 1 and 2. The values of *A* show only small changes with temperature for a particular electrolyte, and some of these changes may arise from experimental errors which become magnified in measuring the slope. The values of *A* for carbon dioxide at 25°C. included in Table 3 are those given by Ratcliff and Holdcroft *(6)*. Also included in Table 3 are the standard deviations of the estimate of *D* obtained from the straightline plots. The results indicate that the effect of the electrolyte on *D* is greatest for magnesium sulfate, somewhat less for magnesium chloride, and considerably less for potassium chloride. This suggests that the perturbation terms are strongly affected by the charge of the ions involved, and to a lesser extent by the ionic radius.

These results may be interpreted in a qualitative manner as follows. The term δ_i represents the change in the free energy of activation for a solute molecule when one of the water molecules surrounding the solute is replaced by an ion type *i*. δ_i should therefore be related to the difference between the ion-solute and water-solute interac-

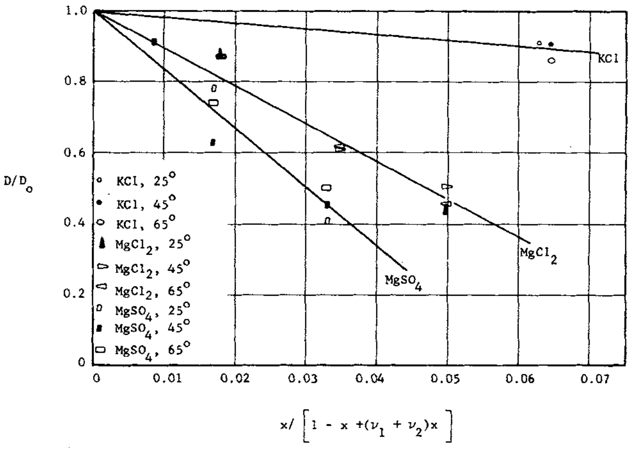

Fig. 2. Diffusion coefficients of methane.

TABLE 3. VALUES OF SLOPE A

$$A = \frac{n(\nu_1\delta_1 + \nu_2\delta_2)}{RT}$$

Gas	Electrolyte	25°C. A	25°C. $\sigma_e(D)$†	45°C. A	45°C. $\sigma_e(D)$	65°C. A	65°C. $\sigma_e(D)$
Hydrogen	Potassium chloride	3.4 ± 0.2‡	0.03×10^{-5}	3.0 ± 0.3	0.07×10^{-5}	2.2 ± 0.5	0.18×10^{-5}
	Magnesium chloride	11.3 ± 0.9	0.16×10^{-5}	10.4 ± 1.5	0.39×10^{-5}	11.2 ± 1.0	0.42×10^{-5}
	Magnesium sulfate	18.7 ± 2.4	0.26×10^{-5}	16.4 ± 0.5	0.08×10^{-5}	16.5 ± 2.3	0.51×10^{-5}
Methane	Potassium chloride	1.4		1.4		1.9 ± 1.4	0.26×10^{-5}
	Magnesium chloride	10.2 ± 2.4	0.17×10^{-5}	10.3 ± 1.4	0.14×10^{-5}	11.3 ± 1.2	0.17×10^{-5}
	Magnesium sulfate	17.4 ± 3.1	0.14×10^{-5}	17.3 ± 3.3	0.23×10^{-5}	15.0 ± 1.3	0.13×10^{-5}
Carbon dioxide*	Magnesium chloride	11.1					
	Magnesium sulfate	17.8					

* Data reported by Ratcliff and Holdcroft (*6*).
† $\sigma_e(D)$ is the standard deviation of the estimate of D obtained from the straight line plot of D vs. $x/[1 - x + (\nu_1 + \nu_2)x]$.
‡ The precision shown is the standard deviation of estimate.

tion potentials. For a nonpolar solute molecule, the ion-solute electrostatic interaction is given by an equation of the form (*22*)

$$u_{is} = -\frac{\alpha(z_i e)^2}{2r^4} \tag{9}$$

and the water-solute interaction is given by

$$u_{ws} = -\frac{\alpha \mu_w^2}{r^6} \tag{10}$$

Equation (9) suggests that δ_i should increase rapidly with z_i, and this appears to explain the much greater effect on D of magnesium sulfate over potassium chloride. In addition, an increase in the temperature of the solution will cause a small increase in the average distance r, separating the solute molecule from the ion or water molecule with which it interacts. Since r appears to the fourth and sixth powers in Equations (9) and (10), respectively, a temperature rise may cause an increase in $(u_{is} - u_{ws})$ and therefore in δ_i. The results in Table 3 show no clear trend with change in temperature, so this effect appears to be small.

Since the values of A in Table 3 show only small temperature variations, it should be possible to use an average value for the temperature range 25° to 65° with little error. Table 4 shows average values of A for hydrogen and methane for each electrolyte, together with the data of Ratcliff and Holdcroft for carbon dioxide in magnesium chloride and magnesium sulfate solutions. The effect of each electrolyte on the diffusion coefficient appears to be litle influenced by the solute gas for the gases studied, and further work with other solutes is needed to clearly determine the effect of solute. The results shown in Table 4 should therefore enable a fairly good estimate to be made of the diffusion coefficients of other gases in these electrolytes, provided that the diffusion coefficient in water D_o is known; in cases where no experimental measurements have been made, D_o may be estimated from the Wilke-Chang equation.

TABLE 4. AVERAGE VALUES OF A

	Hydrogen	Methane	Carbon dioxide*
Potassium chloride	2.9 ± 0.5†	1.6 ± 0.2	
Magnesium chloride	11.0 ± 0.4	10.6 ± 0.5	11.1
Magnesium sulfate	17.2 ± 1.1	16.6 ± 1.1	17.8

* Data of Ratcliff and Holdcroft (*6*).
† The precision shown is the standard deviation of the arithmetic mean of A values given in Table 3.

The form of Equation (5) suggests that the effect of the electrolyte on the diffusion coefficient may be separated into perturbations characteristic of the individual ions, which may be expressed as $n\delta_i$. Both the conductivity and fluidity of electrolyte solutions at moderate concentrations have been found to be made up of approximately additive contributions from water molecules and the separate ions (*10*). From mutual diffusion studies involving a relatively small number of electrolytes it should be possible to construct a table of ionic contributions, from which the diffusion coefficients in other electrolytes could be predicted.

Unfortunately it is not possible to obtain the values of $n\delta_i$ directly from the values given in Table 3, since we have in general only $(y - 1)$ independent linear equations involving $n(\nu_1\delta_1 + \nu_2\delta_2)$ for y unknowns. It is therefore necessary to know the value of $n\delta_i$ for one ion before values for the others may be evaluated. Since the limiting conductivities of potassium and chloride ions are almost equal, these two ions would be expected to have an almost equal effect on the mutual diffusion coefficient of a solute molecule.

By assuming potassium and chloride ions to have equal values of $n\delta_i$, the values shown in Table 5 have been calculated. The values of $n\delta_i$ for carbon dioxide presented in Table 5 were calculated from the data of Ratcliff and Holdcroft by assuming values of $n\delta_i$ for potassium and chloride ions that are the mean of those for hydrogen and

TABLE 5. VALUES OF $n\delta_i$ IN KCAL./G.-ION

Gas	Temperature, °C.	K^+	Cl^-	Mg^{++}	SO_4^{--}
Hydrogen	25	1.0	1.0	4.6	6.4
	45	0.9	0.9	4.7	5.7
	65	0.7	0.7	6.1	5.0
Methane	25	0.4	0.4	5.2	5.1
	45	0.4	0.4	5.6	5.3
	65	0.6	0.6	6.3	3.8
Carbon dioxide*	25	0.7	0.7	5.1	5.4
Water† (self-diffusion)	23	0.3	0.3	7.7	6.1

* Data of Ratcliff and Holdcroft (*6*). The values of K^+ and Cl^- were taken as being the average of the values for hydrogen and methane.
† Calculated from data of McCall and Douglass (*11*) for self-diffusion of water.

methane; this appears to be justified, since the values of A in Table 4 for carbon dioxide, methane, and hydrogen are very similar. The values of $n\delta_i'$ for the self-diffusion of water obtained from the data of McCall and Douglass are also included in Table 5.

The values of $n\delta_i$ indicate a marked increase with ionic charge, as expected from Equation (9), but seem to be little affected by solute or temperature. If the number of molecules with which a solute molecule interacts is taken as 10, the values of δ_i are in the range 40 to 600 cal./mole; this represents a change of approximately 1 to 15% from the activation energy of diffusion for pure water.

CONCLUSIONS

For the electrolytes and solutes studied the diffusion coefficient varies approximately linearly with electrolyte concentration. The influence of the electrolyte on the diffusion coefficient seems to be an additive effect for the ions involved, and increases rapidly with ionic charge. The change in D/D_o produced by a given electrolyte is little affected by temperature or solute for the solutes studied. By tabulating values of $n\delta_i$ for individual ions it should be possible to estimate diffusion coefficients for solute-electrolyte systems that have not been studied experimentally. Further measurements are needed to obtain values of $n\delta_i$ for other ions and to determine clearly the effect of solute.

ACKNOWLEDGMENT

Financial support of part of this work by Harry Diamond Laboratories is gratefully acknowledged.

NOTATION

A = slope of plot of D/D_o vs. $x/[1 - x + (\nu_1 + \nu_2)x] = n(\nu_1\delta_1 + \nu_2\delta_2)/RT$
c = concentration of electrolyte at 20°C., g.-mole/liter
c' = concentration of solute gas at position x
c_o = initial concentration of solute gas in high concentration side of diaphragm cell
D = diffusion coefficient of solute in electrolyte at temperature T
D_o = diffusion coefficient of solute in water at temperature T
D_w = self-diffusion coefficient of water in electrolyte solution
D_{wo} = self-diffusion coefficient of pure water
e = electronic charge
ΔG_ϕ^* = free energy of activation for viscous flow/mole
ΔG_d^* = free energy of activation for diffusion/mole
ΔG_o^* = free energy of activation for diffusion in pure water
h = Planck's constant
i = possible configurations of the molecule transported
k = Boltzmann's constant
k_ϕ = constant in Eyring equation for fluidity
k_d = constant in Eyring equation for diffusion
L = length of a cylinder of stagnant liquid having a resistance to diffusion equal to that of the diaphragm
m = molecular mass
n = number of molecules or ions with which a single solute molecule interacts
n_i = number of water molecules with which an ion of type i interacts
p_i = probability of configuration i in which activation free energy is ΔG_i^*
R = gas constant
r = distance between two molecules (or molecule and ion)
r' = constant = 0.055
T = temperature
t = time
u_{is} = intermolecular potential between ion of type i and solute molecule
u_{ws} = intermolecular potential between a water molecule and a solute molecule
v_f = free volume
x = mole fraction of electrolyte
z_i = valency of ion i

Greek Letters

α = polarisability of solute molecule
δ_i = perturbation of diffusional activation energy/mole, due to single ion of type i interacting with solute molecule
δ_i' = perturbation of activation free energy for viscous flow/mole, due to single ion of type i interacting with water molecule
ϵ_ϕ = activation energy for viscous flow/molecule
ϵ_d = activation energy for diffusion/molecule
η = viscosity
λ = average jump distance of molecule in flow
μ_w = dipole moment of water molecule
ν_i = number of g.-ions of ion of type i/g.-mole of electrolyte
$\sigma_e(D)$ = standard deviation of estimate of D obtained from the straightline plot of D vs. $x/[1 - x + (\nu_1 + \nu_2)x]$
ϕ = fluidity
ϕ_o = fluidity of water

LITERATURE CITED

1. Wilke, C. R., *Chem Eng. Progr.*, **45**, 218 (1949).
2. ———, and P. Chang, *A.I.Ch.E. J.*, **1**, 264 (1955).
3. Glasstone, S., K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York (1941).
4. Ree, H. R., R. Taikyue, and H. Eyring, *Ind. Eng. Chem.*, **50**, 1036 (1958).
5. Podolsky, R. J., *J. Am. Chem. Soc.*, **80**, 4442 (1958).
6. Ratcliff, G. A., and J. G. Holdcroft, *Trans. Inst. Chem. Engr. (London)*, **41**, 315 (1963).
7. Gubbins, K. E., and R. D. Walker, Jr., *J. Electrochem. Soc.*, **112**, 469 (1965).
8. Weyman, H. D., *Kolloid Z*, **181**, 131 (1962).
9. Jones, G., and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).
10. Bingham, E. C., *J. Phys. Chem.*, **45**, 885 (1941).
11. McCall, D. W., and D. C. Douglass, *J. Phys. Chem.*, **69**, (6), 2001 (1965).
12. McBain, J. W., and T. H. Liu, *J. Am. Chem. Soc.*, **53**, 59 (1931).
13. Gordon, A. R., *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).
14. Bhatia, K. K., M.S. thesis, Univ. Florida, Gainesville (1965).
15. Gubbins, K. E., S. N. Carden, and R. D. Walker, Jr., *J. Gas Chromatog.*, **3**, 98 (1965).
16. Stokes, R. H., *J. Am. Chem. Soc.*, **72**, 763 (1950).
17. Carslaw, H. S., and J. C. Jaeger, "Conduction of Heat in Solids," p. 99, Oxford Univ. Press, England (1959).
18. Vivian, J. E., and C. J. King, *A.I.Ch.E. J.*, **10**, 220 (1964).
19. Baird, M. H. I., and J. F. Davidson, *Chem. Eng. Sci.*, **17**, 476 (1962).
20. Ipatev, V. V., and S. I. Drushina-Artemovich, *Z. Anorg. Allgem. Chem.*, **216**, 66 (1933).
21. Witherspoon, P. A., and D. N. Saraf, *J. Phys. Chem.*, **69**(11), 3752 (1965).
22. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).

Manuscript received July 23, 1965; revision received January 7, 1966; paper accepted January 10, 1966.