[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Interdiffusion of Acid and Base in Aqueous Solution

BY CECIL V. KING AND WILLIAM H. CATHCART

The interdiffusion of hydrochloric acid and glycine has been studied in some detail by McBain and Dawson.[1] An interesting feature of this double diffusion is the greatly increased rate of passage of material (notably the chloride ion) through the porous partition of the diffusion cell due to the chemical reaction. McBain and Dawson have interpreted the increased diffusion rates in terms of increased over-all diffusion coefficients. In view of the fact that the hydrogen-ion concentration falls to a low value at the point within the porous disk where it meets the glycine, the increased diffusion rates should be interpreted in terms of sharpened concentration gradients rather than enhanced diffusion coefficients. Analysis of the data from this viewpoint is impossible since sufficient details are not given by the authors. The presence of the glycinium ion is a complicating factor and also, as shown below, the experimental method used was probably inadequate for obtaining correct diffusion rates in this type of system.

The present paper reports measurements of the interdiffusion rates of hydrochloric acid and sodium hydroxide in the porous disk cell.[1] It is assumed that the diffusion coefficients are unaffected by the neutralization (the heat of reaction is unimportant with the dilute solutions used), and this assumption is confirmed by the results. The diffusion coefficients are affected, however, by the sodium and chloride ions accumulating in the disk, and this factor must be taken into account.

The interdiffusion of hydrochloric acid and sodium hydroxide has been studied previously by Barry and Smith,[2] by a method of superposing one solution upon the other and following the movement of the boundary and the heat evolved by the neutralization. For our purpose experiments in the porous disk cell are much easier to interpret since under suitable conditions the diffusion gradients are confined to the porous partition.

If A and δ are the effective (not the measured) area and thickness, respectively, of the porous disk, we may assume that the neutralization of acid and base occurs in a plane at a distance y from the surface in contact with base, $\delta - y$ from the surface in contact with acid. The rates are then given, assuming Fick's law to be valid for the experimental arrangement, by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{AD_{\mathrm{A}}}{\delta - y}\,\frac{a - x}{V_{\mathrm{A}}} = \frac{AD_{\mathrm{B}}}{y}\,\frac{b - x}{V_{\mathrm{B}}} \qquad \text{(1a)}$$

where a, b = initial moles acid and base in cell compartments of volumes V_{A}, V_{B}; x = moles neutralized at time t; D_{A}, D_{B} = diffusion coefficients of the acid and base.

Solving for y and substituting,

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{A}{\delta}\left[\frac{V_{\mathrm{B}}D_{\mathrm{A}}(a - x) + V_{\mathrm{A}}D_{\mathrm{B}}(b - x)}{V_{\mathrm{A}}V_{\mathrm{B}}}\right]$$

If D_{A} and D_{B} are constants under the conditions of the experiment, this expression can be integrated as follows

$$kt = \frac{V_{\mathrm{A}}V_{\mathrm{B}}}{V_{\mathrm{B}}D_{\mathrm{A}} + V_{\mathrm{A}}D_{\mathrm{B}}}\ln\frac{V_{\mathrm{B}}D_{\mathrm{A}}a + V_{\mathrm{A}}D_{\mathrm{B}}b}{V_{\mathrm{B}}D_{\mathrm{A}}(a - x) + V_{\mathrm{A}}D_{\mathrm{B}}(b - x)}$$

where $k = A/\delta$, a "cell constant" dependent on the characteristics of the porous disk only and not on the volumes of the cell compartments. This equation may be rewritten

$$kt = \frac{V_{\mathrm{A}}V_{\mathrm{B}}}{V_{\mathrm{B}}D_{\mathrm{A}} + V_{\mathrm{A}}D_{\mathrm{B}}}\ln\frac{D_{\mathrm{A}}C_{\mathrm{A}} + D_{\mathrm{B}}C_{\mathrm{B}}}{D_{\mathrm{A}}C'_{\mathrm{A}} + D_{\mathrm{B}}C'_{\mathrm{B}}} \qquad (1)$$

where C_{A}, C_{B} are initial concentrations of acid and base, C'_{A}, C'_{B} are concentrations at the time t.

The corresponding equation for a single diffusion is, in a form convenient for use

$$kt = \frac{V_{\mathrm{A}}V_{\mathrm{B}}}{(V_{\mathrm{A}} + V_{\mathrm{B}})D}\ln\frac{C_{\mathrm{A}}}{C_{\mathrm{A}} - (1 + V_{\mathrm{B}}/V_{\mathrm{A}})C''_{\mathrm{A}}}$$

where C''_{A} is the concentration of diffusing solute in the cell compartment which initially contained pure solvent. This equation was used in establishing cell constants and for the other single diffusions reported.

Experimental

Several cells were used in the course of this work, but all the final experiments were run in one rotating cell of the type described by Mouquin and Cathcart.[3] McBain and Dawson have given 2.71 sq. cm./day as the diffusion coefficient of 0.1 molar hydrochloric acid into pure water at 25°,

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[1] McBain and Dawson, THIS JOURNAL, **56**, 52 (1934).

[2] Barry and Smith, *ibid.*, **55**, 2215 (1933).

[3] Mouquin and Cathcart, *ibid.*, **57**, 1791 (1935).

and this value was used in determining all cell constants.

Rotating Cell Constant.—The volumes of the cell compartments were V_A = 69.6 cc., V_B = 71.2 cc. The cell was rotated approximately forty times per hour, both in determining the cell constant and in the double diffusion experiments. Data are given in Table I.

TABLE I

ROTATING CELL CONSTANT DETERMINATION (25 ± 0.02°)

C_{HCl}, *M*	Time, hours	C'_{HCl}, *M*	*k*
0.1002	17.75	0.00962	3.78
.0995	18.25	.00996	3.85
.0983	26.67	.01377	3.87
.0982	26.83	.01380	3.88

Salt Effect on the Diffusion Coefficients.—The diffusion coefficient of an electrolyte varies somewhat with its own concentration, but, in general, this variation amounts to only a few per cent. up to 0.1 *N* solution. The variation has been explained quantitatively for very dilute solutions in terms of the interionic attraction theory. The effect of salts on the diffusion coefficients of dilute acids and bases is much greater and has not yet been accounted for quantitatively. Since in the interdiffusion experiments acid and base diffuse into the disk, sodium and chloride ions outward in both directions, the diffusion coefficients will vary continuously with the concentration gradients unless the experiments are carried out in such a medium that the salt formed will not have this effect.

For this reason, the diffusion coefficients of acid and base were determined in solutions containing added sodium chloride. This was first done in stationary cells but, as shown below, it was found necessary to establish the curves with the rotating cell also. The coefficients of both acid and base reach maxima between 0.2 and 0.4 molar salt and apparently decrease again at higher concentrations. Measurements in the rotating and stationary cells check well with sodium hydroxide, but this is not true with hydrochloric acid. Presumably the coefficients of both should continue to rise with increasing salt concentration, the hydrogen ion reaching a value near 8 sq. cm./day when freed of all retarding effects of the negative ion.[1] This value assumes, however, no effect due to the increased viscosity of the concentrated salt solution, and ionic mobilities of the same value as at infinite dilution. In practice, 6 sq. cm./day is about the highest value reached in sodium chloride (Table II); the decrease at higher salt concentration may be real or may be due to inadequacy of the experimental method. Since the rotating cell gives higher values than the stationary cell and results below show that these higher values are substantially correct, it is possible that inadequate stirring in the cell compartments of even the rotating cell is responsible for the decreasing values obtained at high salt concentrations.

TABLE II

THE DIFFUSION COEFFICIENTS OF HYDROCHLORIC ACID (0.0492 *M*) AND SODIUM HYDROXIDE (0.0530 *M*) IN SODIUM CHLORIDE SOLUTIONS (BOTH SIDES OF CELL) AT 25°

HCl			NaOH		
C_{NaCl}, *M*	Cell	*D* (sq. cm./day)	C_{NaCl}, *M*	Cell	*D* (sq. cm./day)
0	..	(2.71)[a]	0	S	1.73 1.735
0.01	S	3.34	0.04	S	2.41
.02	S	3.26	.08	S	3.18
.04	S	3.85 4.17	.12	S	3.34
.06	S	3.98	.16	S	3.39
.10	S	4.65	.20	S	3.50
.20	S	5.36	.40	S	3.54
.30	S	5.60	.72	S	3.43
.40	S	5.46	.30	R	3.55
.50	S	5.69	.40	R	3.58
1.0	S	5.53	.50	R	3.56
1.5	S	5.08			
2.0	S	4.65 4.68			
3.0	S	3.65 3.50			
0.24	R	5.82			
.40	R	5.90 6.10			
.56	R	6.09			
1.0	R	5.94 6.09			
2.0	R	5.18			
3.0	R	4.34 4.32			

[a] Approximately the same as 0.1 *M* HCl. S = stationary, R = rotating cell.

Interdiffusion Experiments.—All these experiments were run with 0.4 molar sodium chloride in both compartments of the rotating cell, since the diffusion coefficients have their maximum value at this concentration and the higher concentration accumulating within the disk cannot affect the coefficients much. Three experiments were run, in duplicate, with acid and base concentrations between 0.04 and 0.06 molar, since the single diffusions were run at approximately 0.05 molar. The values do not change much with acid or base concentration, however, and one pair of experiments was run with 0.1 molar acid, 0.05 molar base. The values D_A = 6.05, D_B = 3.55 were selected as the approximate maxima from Table II and Fig. 1 and used in equation (1) in calculating the cell constant *k* as shown in Table III.

TABLE III

CELL CONSTANTS FROM INTERDIFFUSION EXPERIMENTS IN ROTATING CELL (25°). 0.4 *M* NaCl IN BOTH CELL COMPARTMENTS

Expt.	C_A	C_B	Time, hours	C'_A	C'_B	k
6	0.0498	0.0497	22.33	0.0301	0.0304	3.915
7	.0498	.0497	41.5	.01915	.0200	3.955
8	.0598	.0397	18.5	.04225	.0220	3.89
9	.0598	.0397	25.0	.0378	.0172	3.86
10	.04025	.0595	25.17	.0195	.0383	4.06
11	.04025	.0595	24.6	.0199	.0388	4.03
4	.0997	.0537	23.0	.0679	.02185	3.685
5	.0997	.0537	26.75	.0641	.0183	3.67

Samples of both acid and base were titrated before and after the diffusion, and a comparison of the values in Table III shows that the method is not very precise unless more precautions are taken than were thought necessary for the present purpose. The greatest discrepancy in moles of acid and base disappearing is 4.4% in experiment 9. The error in k caused by an error of 1% in any one term of equation 1 (*i. e.*, in D, V, C, C', etc.) is approximately 1%.

In Table IV are given the results of two interdiffusion experiments carried out in the same cell without rotating, the first with the acid in compartment A above, the second with base in compartment B above. The density of the sodium hydroxide solution was found by measurement to be greater than that of the acid. More moles are neutralized in less time with the base above the acid; in neither case does the diffusion proceed with the theoretical speed as shown by the very low values of k. The constant of this cell was not determined (with 0.1 molar hydrochloric acid diffusing into water) with the cell stationary, but it should be approximately 3.65.[3]

TABLE IV

INTERDIFFUSION WITH CELL STATIONARY, 25°C., 0.4 *M* NaCl

Expt.	C_A	C_B	Time, hours	C'_A	C'_B	k
20[a]	0.04925	0.0484	27.33	0.0367	0.0360	1.89
21[b]	.04925	.0484	24.17	.0348	.03405	2.53

[a] HCl above. [b] NaOH above.

Discussion.—While the greatest variation of k in Table III is 5.6% from the mean value of Table I, the average of all results is only 1.0% different. The variations are evidently due largely to the difficulty of choosing correct values of D_A, D_B and the change of the latter with acid and base concentration. The picture of the interdiffusion represented by equation (1) is fully substantiated.

The fact that the maximum coefficient for hydrochloric acid obtained with the rotating cell must be used to obtain the agreement of cell constants, as well as the fact that interdiffusion experiments in the stationary cell give abnormal results, indicates that the rotating cell has a wider range of applicability. The latter experiments especially indicate that the diffusion gradients are not confined to the porous disk unless the density relations allow adequate stirring to be maintained by convection currents, or mechanical stirring is introduced.

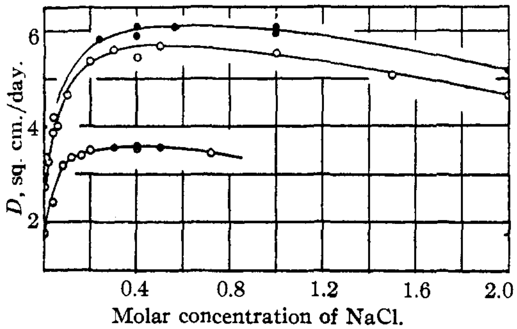

Fig. 1.—Diffusion coefficients in sodium chloride solutions: lower curve, NaOH; upper curves, HCl; ○, stationary cell; ●, rotating cell.

The point within the disk at which the neutralization occurs varies with the diffusion coefficients and concentrations of the reagents, and can be calculated from equation (1a). In the present case with equal acid and base concentrations in the presence of 0.4 molar sodium chloride, it occurs at a distance 0.37 δ from the surface in contact with the base.

Since this paper was written, an interesting and useful "multimembrane" method of studying diffusion processes has been published by Teorell.[4] In one interdiffusion experiment, the "diffusion layer" between equimolar hydrochloric acid and sodium hydroxide solutions was separated into seven portions by cellophane membranes; samples from the several compartments were analyzed after twenty-four hours, and the concentration gradients of the various ions thus recorded. The solutions contained no added salt; the neutralization occurred 0.375 of the total distance from the base compartment.

Summary

The diffusion coefficients of hydrochloric acid and sodium hydroxide have been measured in the presence of added sodium chloride over a wide concentration range.

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(4) Teorell, *J. Biol. Chem.*, **113**, 735 (1936).

The rate of interdiffusion of the same acid and base in sodium chloride solution has been studied. It is shown that the diffusion coefficients are unchanged if sufficient sodium chloride is present initially; in the porous disk cell, the diffusion *rates* are, however, greatly increased since the concentration gradients become much sharper because of the neutralization within the disk.

Some limitations of the porous disk diffusion cell are demonstrated. Adequate mixing must be maintained in the cell solutions either by natural convection or by auxiliary stirring.

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The Conductance of Salts (Potassium Acetate) and the Dissociation Constant of Acetic Acid in Deuterium Oxide

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The accurate calculation of the dissociation constant of a weak acid, like acetic acid, in deuterium oxide requires values of comparable accuracy of the limiting conductances Λ_0, of deuterochloric acid, potassium chloride and potassium acetate. In ordinary water the problem is solved by measuring a series of conductance values at increasing dilutions and controlling the extrapolation to infinite dilution by the Onsager[1] equation.

The limited quantities of heavy water available do not permit execution of this tedious and experimentally difficult problem at this time. We are accordingly interested in establishing the validity of two approximate rules, which will permit the calculation of Λ_0 for the deuteronium ion and for the anion of the weak acid with sufficient precision for present purposes from a single measurement at an experimentally convenient concentration ($C = 0.01$) in heavy water which is not necessarily 100% D_2O.

These rules are

$$[\Lambda_c/\Lambda_0]_{H_2O} = [\Lambda_c/\Lambda_0]_{D_2O} \qquad (1)$$

valid for acids and salts in pure D_2O, but presumably accurate only for salts in intermediate mixtures of D_2O–H_2O, owing to the complication of the exchange reactions which acids suffer in the mixed waters.[2]

$$\Lambda\eta = \text{Constant};\ \eta = \text{Viscosity}. \qquad (2)$$

valid for interpolation and for extrapolation to pure D_2O of the data obtained for the salts in H_2O–D_2O mixtures.

The justification of (1) follows from the Onsager equation[3]

$$\Lambda_c = \Lambda_0 - [\alpha\Lambda_0 + 2\beta]\sqrt{C} \qquad (3)$$

where

$$\alpha = \frac{8.173 \times 10^5}{(DT)^{3/2}} \text{ and } \beta = \frac{41.7}{(DT)^{1/2}} \times \frac{1}{\eta} \qquad (4)$$

Let $\beta' = 2\beta\eta$, then α and β' differ in H_2O and D_2O only by the ratio of the dielectric constants of H_2O and D_2O which ratio appears to be almost unity.[4,5]

$$\Lambda_c/\Lambda_0 = 1 - [\alpha + \beta'/\Lambda_0\eta]\sqrt{C} \qquad (5)$$

and

$$\frac{[\Lambda_c/\Lambda_0]_{H_2O}}{[\Lambda_c/\Lambda_0]_{D_2O}} = 1 + \frac{\beta'\sqrt{C}\,[1/(\Lambda_0\eta)_{H_2O} - 1/(\Lambda_0\eta)_{D_2O}]}{1 - [\alpha + \beta'/(\Lambda_0\eta)_{D_2O}]} \qquad (6)$$

The experimental data on potassium chloride and on potassium acetate presented below show that $(\Lambda_0\eta)_{H_2O}$ differs from $(\Lambda_0\eta)_{D_2O}$ by only 1.93%. Hence equation (6) reduces without appreciable error to equation (1).[6]

The error in $\Lambda_0(D_2O)$ calculated through equations (1) and (6) is thus less than 0.1% and less than our present experimental errors. The Λ_c *vs.* $\sqrt{C}$ curves in D_2O are, therefore, sensibly parallel to those in H_2O, and the D_2O curve can be constructed from a measurement of Λ at a single low concentration.

Since the only difference in the limiting conductance of non-acid ions in D_2O and in H_2O appears to be resident in the change in β, the electrophoretic part of the Onsager equation, we expect

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[1] Onsager, *Physik. Z.*, **27**, 288–292 (1926); **28**, 277–298 (1927).

[2] Baker and La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

[3] MacInnes, Shedlovsky and Longsworth, *Chem. Rev.*, **13**, 29 (1933), eq. (7).

[4] Horst Müller, *Physik. Z.*, **36**, 1009–1011 (1935).

[5] P. Abadie and G. Champetier, *Compt. rend.*, **200**, 1387 (1935).

[6] η does not change significantly on passing from $C = 0.01$ to $C = 0$.