Ion Diffusion in Mass Transfer Between Phases

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Mass transfer between phases has become a subject of broad technical importance, particularly in industrial operations involving gas absorption, extraction, ion exchange, and other separation processes. Many such operations involve simultaneous mass transfer and chemical reaction, as in the absorption of carbon dioxide by an alkaline solution, the absorption of hydrogen sulfide by amine solutions, or the absorption of NH_3 by sulfuric acid. The theory of such cases has been discussed in recent years by many writers, notably by Danckwerts(*2*) and by Pigford(*6*), and a considerable amount of experimental data has been collected, especially by Van Krevelen(*8*) and by Pozin(*7*).

The general mechanism of simultaneous mass transfer and chemical reaction was outlined by Hatta (*4*) in 1928. Hatta pictured the solute A entering a phase with a concentration p at the phase boundary and reacting with a second solute B present in concentration q in the bulk of the fluid. In the special case of a rapid irreversible reaction between A and B, the reaction is presumed to occur at a plane near the interface where the concentrations of both A and B are zero: A diffuses to this zone as a result of the concentration potential (p-0) and B as the result of the concentration difference (q-0). This relatively simple picture leads to the rate equation

$$N_A = \frac{D_A p + D_B q}{x_L} = k^\circ{}_{LA}\left(p + \frac{D_B}{D_A} q\right) \qquad (1)$$

where N_A represents the flux as gram moles/(day) (square centimeter), D_A and D_B are the effective diffusion coefficients of A and B, square centimeter/day, and x_L is the "effective thickness" of the "stagnant film," which corresponds to the diffusional resistance. $k^\circ{}_{LA}$ is the coefficient of mass transfer of A into the phase when B is not present and no reaction occurs.

This picture has been described many times, usually in terms of the oversimplified stagnant-film model. The basic concept, however, permits allowance for combined molecular and eddy diffusion provided D_A, D_B, and x_L are properly defined, without reference to the molecular-diffusion – stagnant-film model. Danckwerts's surface-renewal theory(*2*), for example, leads to a more complex relation but gives approximately the same quantitative relationship between N_A and $(D_A p + D_B q)$.

DIFFUSION IN MIXED ELECTROLYTES

In cases of neutralization involving ionic reactions, as, for example, the absorption of hydrochloric acid gas by an aqueous solution of sodium hydroxide, it is diffusion of ions that is important, and allowance must be made for the fact that individual ions in the presence of other ions may diffuse at rates which are quite different from those of their original "partners." Allowance for this effect is the subject of the present paper. The subject will be developed within the framework of the classical stagnant-film picture presented by Hatta, with later comments on the errors in this approach.

Diffusion in mixed electrolytes has been discussed by several authors(*3, 5*); the treatment of Vinograd and McBain(*9*) will be used here. Following the Nernst theory, these authors write diffusion equations for each ion, the diffusion potential for each involving both the concentration gradient of the particular ion and the gradient of the electrical potential in the solution. Imposing the condition of electrical neutrality for the ion mixture, they obtain the following equation for diffusion of cations:

$$n_+N_+ = -\frac{RT}{F}\frac{u_+}{n_+}\left(G_+ - n_+C_+ \frac{\Sigma u_+G_+/n_+ - \Sigma u_-G_-/n_-}{\Sigma u_+C_+ + \Sigma u_-C_-}\right) \qquad (2)$$

A similar relation is given for anions, the minus becoming a plus within the parenthesis. Here N_+ is the ion flux of a particular cation of valence n_+, concentration C_+, and mobility u_+; G_+ is the concentration gradient dC_+/dx of this cation in the direction of diffusion; and the minus signs as subscripts refer to anions. The derivation is subject to the limitation that activity coefficients and collision effects are ignored, as are the effects of ion pairs or ionic complexes. Such approximations are well within the precision of an approach to mass transfer problems by use of the stagnant-film model.

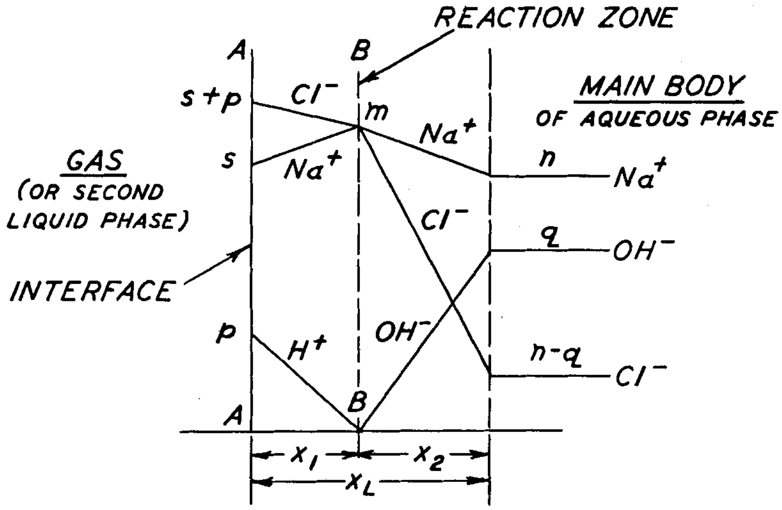

Fig. 1. Concentrations in double film during absorption of hydrochloric acid by aqueous sodium hydroxide.

Vinograd and McBain demonstrate the use of these equations in the analysis of data on simultaneous diffusion of barium chloride and hydrogen chloride and of potassium chloride and hydrogen chloride in the same direction through the fritted-glass disk of a diffusion cell. Since the concentration gradient G varies with distance x through the disk, the calculation is simplified if G is assumed to be represented by $\Delta C/\Delta x$; furthermore, C is taken as the arithmetic mean of the concentrations of the ion in the bulk fluid on the two sides of the cell, and ionization is assumed to be complete. In spite of these several simplifying assumptions, the data and theory are found to check within a few per cent.

In the barium chloride–hydrogen chloride system, D for the H^+ ion decreased from 10.6 to 4.2 sq.cm./day as the ratio of H^+ to Ba^{++} was increased from 0 to 1.3; these values may be compared with the value for free H^+ ion, which is 8.05 sq.cm./day, and the value 2.87 sq.cm./day for hydrogen chloride at the same temperature (25°C.). The presence of the slow-moving Ba^{++} ion accelerates the H^+ ion; hydrogen chloride retards the Ba^{++} ion. D for Cl^- increases with increase in the ratio H^+/Ba^{++}, and D for Ba^{++} decreases and even becomes negative. Similar data are quoted for the system hydrogen chloride–potassium chloride.

Ions of a single ionized solute, such as hydrogen chloride, must diffuse at the same rate to maintain electrical neutrality at any plane in the solution. Under such circumstances it is allowable to define a molecular diffusivity of the compound hydrogen chloride, even though ions rather than molecules are diffusing. In a system of mixed ions, as in the simultaneous diffusion of hydrogen chloride and sodium chloride, the faster moving H^+ may move ahead of its Cl^- partner, essential electrical neutrality being maintained by the presence of the slower moving Na^+ ions, which now lag behind their own Cl^- partners. At very low H^+ concentration in a solution of sodium chloride the electrical potential in the direction of diffusion may cause the effective diffusivity of H^+ to be even greater than that of a free hydrogen ion.

STEADY STATE DIFFUSION OF HYDROGEN CHLORIDE INTO SODIUM HYDROXIDE

An example of a possible approach to the problem of absorption with chemical reaction is the case of steady state absorption of hydrogen chloride gas from air by an aqueous solution of sodium hydroxide. The modified Hatta picture is illustrated by Figure 1, where A-A is the gas-liquid interface and B-B the zone in the liquid where H^+ and OH^- ions meet. Concentrations of the several ions at different planes are represented by the symbols shown on the figure. The symbol p, for example, represents the H^+ ion concentration at the liquid surface, and q is the OH^- ion concentration in the main bulk of the alkaline solution. Na^+ and Cl^+ concentrations must be equal at the reaction zone in order to maintain electrical neutrality.

In order to make the analysis more understandable, specific values of the several variables will be assumed and the results compared quantitatively with the simple Hatta theory. Thus for the system hydrogen chloride–sodium hydroxide at 25°C. the mobilities are $u_+(H^+) = 350/F$, $u'_+(Na^+) = 50/F$, $u_-(Cl^-) = 76/F$, and $u'_-(OH^-) = 198/F$ sq.cm./(sec.) (volt), where F is the Faraday. The assumptions employed by Vinograd and McBain regarding linear concentration gradients and arithmetic mean concentrations will be adopted. First is considered the region near the interface in film of thickness x_1:

$$G_+ = -\frac{p}{x_1}; G'_+ = \frac{m-s}{x_1};$$

$$G_- = \frac{m-s-p}{x_1}$$

$$C_+ = p/2; C'_+ = \frac{m+s}{2};$$

$$C_- = \frac{m+s+p}{2}; C'_- = 0$$

Substituting in Equation (2) and simplifying give

$$N_+ = 8.05\frac{p}{x_1}\left[\frac{100m+152s+152p}{426p+126m+126s}\right] \qquad (3)$$

Here the number 8.05 is the diffusion coefficient for free H^+ ion (RTu_+/Fn_+) and has the units sq.cm./day; N_+ is expressed as g. equivalents/(day) (sq.cm.)

Similar equations are obtained for Na^+ and Cl^- diffusion. Since

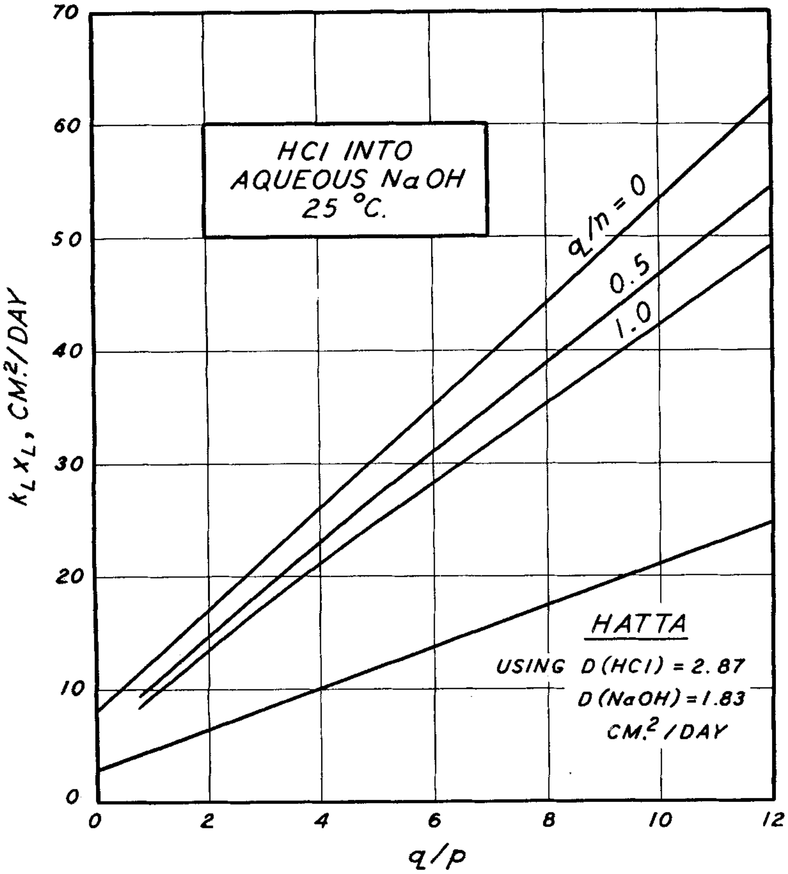

Fig. 2. Comparison of ion-diffusion theory with original version of Hatta theory; effect of sodium hydroxide concentration on rate of hydrochloride absorption.

there is no net diffusion of Na⁺ in this region, N'_+ may be set equal to zero; whence

$$s = -\frac{p}{2} + \sqrt{\frac{p^2}{4} + m^2 + 4.61\,pm} \tag{4}$$

This same relation is obtained by equating N_+ and N_- (H⁺ and Cl⁻).

Following this procedure, diffusion equations are written for the x_2 region, for OH⁻, Na⁺, and Cl⁻. Since Na⁺ is not diffusing, N'_+ is again set equal to zero; whence

$$m = n\sqrt{1.605\frac{q}{n} + 1} \tag{5}$$

which is also obtained by equating N'_- and $-N_-$.

If N is the rate of absorption of hydrogen chloride and k_L the mass transfer coefficient for hydrogen chloride crossing the liquid layer x_L then

$$k_L x_L = \frac{N x_L}{p} = \frac{N_+ x_1 = N'_- x_2}{p} \tag{6}$$

It follows from Equation (5) that m/n is a function of q/n, and from Equation (4) that s/m is a function of the product $p/q \cdot q/n \cdot n/m$. The fraction in square brackets in Equation (3) can, therefore, be expressed in terms of q/p and q/n. The corresponding term in the equation for N'_- is a function of q/n only but is multiplied by q instead of p. From Equation (6) then

$$k_L x_L = 4.54\frac{q}{p}f_1\left(\frac{q}{n}\right) + 8.05 f_2\left(\frac{q}{n}, \frac{p}{q}\right) \tag{7}$$

where the number 4.54 is the diffusion coefficient RTu'_-/Fn'_- for OH⁻ ion, corresponding to the 8.05 for H⁺ ion.

Figure 2 shows values calculated from this relation for the diffusion of hydrogen chloride into aqueous sodium hydroxide at 25°c., by use of the values of ion mobilities quoted earlier. For comparison with the simple form of the Hatta theory, values of $k_L x_L$ are also shown as the lowest line on the graph. These are calculated from Equation (1) in the form

$$k_L x_L = \frac{N_A x_L}{p} = D_A\left(1 + \frac{D_B}{D_A}\frac{q}{p}\right) \tag{8}$$

D_A for molecular hydrogen chloride and D_B for sodium hydroxide are calculated from the Nernst equation to be 2.87 and 1.83 sq. cm./day, respectively.

Figure 2 indicates that the rapid diffusion of H⁺ and OH⁻ ions in the presence of Na⁺ and Cl⁻ ions may lead to an absorption rate more than twice that predicted by the use of molecular diffusion concepts and the Hatta theory. The limiting value of $p = 0$, at which the gas-side resistance controls, is

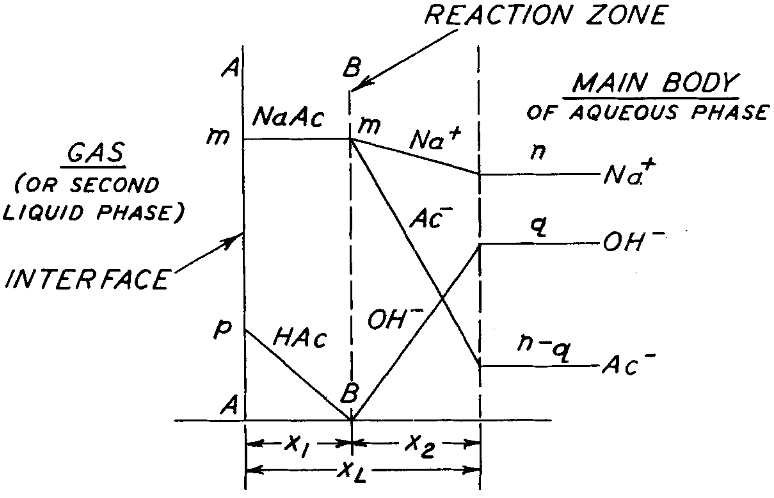

Fig. 3. Concentrations in double film during absorption of nonionizing acetic acid by aqueous sodium hydroxide.

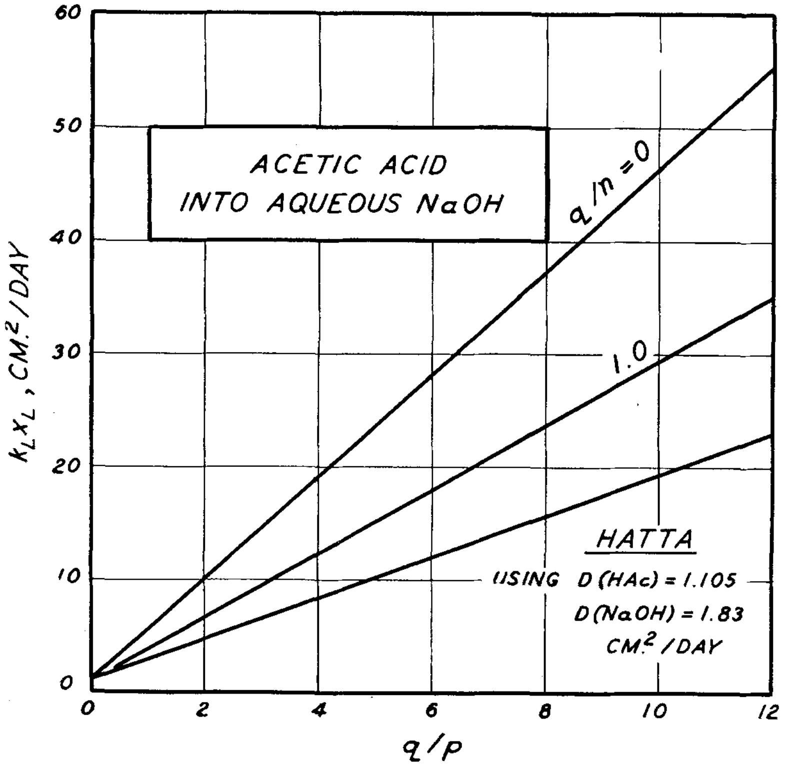

Fig. 4. Effect of sodium hydroxide concentration on rate of absorption of acetic acid.

reached at a lower value of q (or C_B) than predicted by the Hatta theory by use of diffusion coefficients for pure compounds.

In the calculation of the values plotted in Figure 2 it is noted that m, the sodium normality at the reaction zone, varies from n at $q = 0$ to about $1.6n$ at $q = n$. Because chloride ion diffuses more slowly than the H⁺ ion, sodium ion tends to accumulate near the interface in concentrations greater than in the bulk liquid. The concentration s at the liquid surface may be more than twice that in the bulk liquid.

STEADY STATE DIFFUSION OF ACETIC ACID INTO SODIUM HYDROXIDE

There are several possible variations of the hydrogen chloride–sodium hydroxide case, as, for example, to allow for different valences. Allowance for the variation of ionization with concentration might be made, although this would be difficult. One of the reacting solutes may not dissociate, whereupon the ion diffusion equations apply only to part of the film. As an example of this last possibility, one may consider the diffusion of acetic acid into aqueous caustic, neglecting the ionization of acetic acid in layer x_1. The picture of the double diffusion layer is given in Figure 3.

As in the previous illustration, steady state will be assumed, with p, the surface concentration of acetic acide, held constant. Then in region x_1

$$N_A = \frac{D_A}{x_1} p \qquad (9)$$

where the subscript A now refers to acetic acid. In the region x_2

$$\text{for Na}^+;\ u'_+ = \frac{50}{F};\ G'_+ = \frac{n-m}{x_2};$$
$$C'_+ = \frac{n+m}{2}$$

$$\text{for OH}^-;\ u'_- = \frac{198}{F};\ G'_- = \frac{q}{x_2};$$
$$C'_- = \frac{q}{2}$$

$$\text{for Ac}^-;\ u_- = \frac{41}{F};\ G_- = \frac{n-q-m}{x_2};$$
$$C_- = \frac{m+n-q}{2}.$$

Substituting these values into Equation (2) (and the corresponding equation for anions) yields for the OH⁻ ion:

$$N'_- = -\frac{4.54}{x_2}\left[\frac{50nq+41mq}{45.5m+45.5n+78.5q}\right] \qquad (10)$$

with similar equations for Na⁺ and Ac⁻. Since Na⁺ does not diffuse, N'_+ may be set equal to zero (or N'_- put equal to $-N_-$), whence

$$m = n\sqrt{3.82\frac{q}{n}+1} \qquad (11)$$

For the entire layer x_L

$$N_{\text{HAc}}\, x_L = N_{\text{HAc}}\, x_1 = N_{\text{OH}^-}\, x_2 \qquad (12)$$

and

$$k_L x_L = \frac{N_{\text{HAc}}\, x_L}{p} = D_{\text{HAc}} + \frac{4.54q}{p}\left[\frac{50n+41m}{45.5n+45.5m+78.5q}\right] \qquad (13)$$

As in the case of hydrogen chloride–sodium hydroxide, $k_L x_L$ is seen from Equations (10) and (12) to be a function of q/p and q/n, but the relation is not only simpler, but, as shown by Figure 4, the rate is somewhat nearer that predicted by the simple Hatta theory for molecular diffusion.

OVER-ALL COEFFICIENTS

The effect of ion diffusion has been illustrated by considering its effect on the aqueous-side mass transfer coefficient k_L. Over-all mass transfer coefficients may be defined for cases where the transfer is to or from a second gas or liquid phase, and these are easily related to the individual coefficients k_L and k_G if Henry's law applies.

Let the gas solubility at the interface be represented by $P_i = Hp$, and let C^* be the aqueous concentration corresponding to the main gas composition P_G. For the hydrogen chloride–sodium hydroxide illustration, K_L is defined as $N/C^* - 0$). Then if the gas-side transfer coefficient is k_G, it follows that

$$\frac{1}{K_L} = \frac{C^*}{N} = \frac{1}{Hk_G} + \frac{D_A}{k^\circ_L\,(k_L\,x_L)} \qquad (14)$$

and

$$\frac{K_L}{K^\circ_L} = \frac{Hk_G + k^\circ_L}{k^\circ_L + \frac{Hk_G\,D_A}{(k_L\,x_L)}} \qquad (15)$$

Here k°_L is the aqueous-side transfer coefficient D_A/x_L for *molecular* diffusion of solute A and K°_L is the corresponding over-all coefficient.

Figure 2 illustrates the dependence of $k_L x_L$ on p, q, and n; p may be eliminated by combining this with Equation (14) and the division of C^* into parts proportional to resistances:

$$p = \frac{C^* D_A K_L}{k^\circ{}_L\,(k_L x_L)} \qquad (16)$$

The expression for the over-all coefficient in the acetic acid–sodium hydroxide case is simpler. $k_L x_L$ is represented by

$$k_L x_L = D_A + \frac{q}{p} Q \qquad (17)$$

where Q is defined by comparison with Equation (13). Then from Equation (14)

$$\mathrm{K}_L = \frac{\left(1 + \dfrac{qQ}{C^* D_A}\right)}{\dfrac{1}{Hk_G} + \dfrac{1}{k_L{}^\circ}} = K^\circ{}_L \left(1 + \frac{qQ}{C^* D_A}\right) \qquad (18)$$

In this case Q does not depend on p, and so no trial-and-error method is required. In both examples, however, the Henry-law constant H is properly defined as the solubility of the diffusing substance in the aqueous solution at the interface. This may in some instances be a rather strong electrolyte, containing more sodium, for example, than the main bulk of the solution.

The discussion has emphasized that allowance for ion diffusion may increase the rate of transfer above values predicted from the Hatta theory or other analyses based on molecular diffusion. It should be pointed out that the reverse can also happen, as in cases involving chemical reaction of a metal ion which, in the presence of other ions, has an effective diffusivity less than that for the unionized molecule.

IONIC REACTIONS IN DIFFUSION CELLS

The Hatta model can evidently be represented experimentally by the operation of a diffusion cell in which two reacting solutions are used. Preliminary studies of this kind have been made by means of the standard type of porous-glass disk apparatus commonly employed in measurements of diffusion coefficients in liquids. Several tests were made in which sodium hydroxide was neutralized by acetic and by hydrochloric acids.

The apparatus consisted of a vertical glass cylindrical vessel divided into two halves by a porous glass disk approximately 2 mm. thick. The solutions were placed in the two compartments, and the whole was placed in a bath at 25 ± 0.02°C. for 14 to 24 hr., when the solutions in both compartments were withdrawn and analyzed. Cell constants were obtained by preliminary tests using 0.1N potassium chloride and water, by reference to the established values of the integral diffusion coefficient for potassium chloride. The two liquids were not stirred, but natural convection was assisted by placing the heavier sodium hydroxide solution in the upper compartment and the lighter acid in the lower compartment. The lower compartment was first filled with the acid solution to the top of the porous disk. The upper compartment was rinsed and then filled with the alkaline solution, the volumes of both solutions being 68.0 ml. Inclusion of air bubbles was carefully avoided. At the end of the test the solutions were titrated with standard sodium hydroxide, hydrogen chloride, and silver nitrate to determine OH^-, H^+, and Cl^-. Bulk flow between the two compartments, resulting from volume changes of the solutions, was estimated and found to be negligible. Results are shown in Table 1, which gives the arithmetic average rate of neutralization for the period of the test.

Application of the ion diffusion theory is complicated by the fact that a steady state does not prevail. Figures 1 and 3 illustrate the conditions in the porous disk at any instant, but the concentrations change continuously with time. For the sodium hydroxide – hydrogen chloride case Equation (2) may be employed for both H^+ and Na^+ in region x_1 but the corresponding equation for Cl^- is not independent. In region x_2 independent rate equations may be written for Na^+ and OH^-. In addition to these four rate equations, the following apply:

$$N_{Na^+} \text{ through } x_1 = N_{Na^+} \text{ through } x_2 \qquad (19)$$

$$N_{H^+} = -N_{OH^-} \qquad (20)$$

$$x_1 + x_2 = x_L \qquad (21)$$

$$(p_O - p)\,V_L = \int_0^\theta N_+\,d\theta \qquad (22)$$

Table 1.—Results of Neutralization Tests in Diffusion Cells

	Measured concentrations, normality					Average neutralization rate, m. e. / (liter) (day)	
	Initial		Final				
Run	Upper	Lower	Upper	Lower	Time, hr.	Obs.	Calc.
1	0.0971 NaOH	0.1046 HCl	0.0768 OH^- 0.0123 Cl^-	0.0844 H^+ 0.0925 Cl^-	23.7	0.0204	0.0225
2	0.0486 NaOH	0.1046 HCl	0.0339 OH^- 0.0101 Cl^-	0.0900 H^+ 0.0954 Cl^-	23.2	0.0151	0.0174
3	0.0971 NaOH	0.1082 HAc	0.0837 OH^-	0.0959 HAc	23.87	0.0124	0.0128
4	0.0971 NaOH	0.0523 HCl	0.0822 OH^- 0.0078 Cl^-	0.0377 H^+ 0.0452 Cl^-	22.35	0.0157	0.0158
5	0.0486 NaOH	0.1082 HAc	0.0392 OH^-	0.0991 HAc	23.72	0.00922	0.00891
6	0.4898 NaOH	0.4935 HCl	0.431 OH^-	0.437 H^+	13.85	0.102	0.113
7	0.0924 NaOH	0.0936 HCl	0.0701 OH^-	0.0730 H^+	21.5	0.023	0.0222

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*Test 7 was carried out by Thibaut Brian (*1*) with magnetic stirring of both compartments and $V_L = 75$ ml. Calibration tests with potassium chloride to obtain the cell constant with and without stirring checked within 1%. However, the material balance in this test is off by 8%, as was true of run 3; the other balances checked within 4% for the acetic acid tests and within 2% when HCl was used.

$$sV_L = -\int_0^\theta N'_+ \, d\theta \qquad (23)$$

Equation (19) neglects holdup in the porous disk. Equation (21) relates x_1 and x_2 to x_L, obtainable from the cell constant (in terms of the unknown cross section of the diffusion path). Equation (22) assumes the bulk concentration of H^+ ion in the lower compartment to be the same as the surface concentration p of Figure 1. This compartment has an initial H^+ concentration p_0 and a volume V_L ml.

With the variable p retained, these nine equations may be solved simultaneously to obtain the neutralization rate $dp/d\theta$ for any specific values of p, s, q, and n. New concentrations can be calculated after a short time increment, and numerical stepwise integration employed to relate all concentrations to time.

In comparison of the theory with the test results, the foregoing procedure was followed to calculate the neutralization rate at the beginning and end of each test, and the average of these two calculated rates is shown in Table 1. As in the earlier discussion, linear concentration gradients and average concentrations were assumed in applying the ion-diffusion-rate equations.

The deviation of the calculated from the observed average rates averages 7.7%, which is believed to be excellent in view of the several approximations made to simplify the application of the Vinograd-McBain equations. By contrast, the neutralization rates predicted by the Hatta theory, by use of molecular diffusivities, show an average deviation of 18% from the experimental values. In the light of these results it must be concluded that allowance for the effects of multiple-ion diffusion requires a substantial modification of the Hatta picture of mass transfer with chemical reaction in electrolytes, as in the neutralization of an acid by a base. As suggested by Figure 3, the deviation from the Hatta theory under some circumstances may be much greater than in the diffusion-cell tests here reported.

APPLICATION TO MASS TRANSFER WITH TURBULENCE

As applied to mass transfer into a stirred or moving fluid, the Hatta model is, of course, an incorrect idealized picture of the actual situation. Transfer is accomplished in large part by mixing or eddy diffusion, though final contact of reacting molecules or ions must be accomplished by molecular or ion diffusion. Eddies are damped out by the presence of the surface, and so equations for molecular or ion diffusion apply only in the limit as the distance from the surface approaches zero.

One can only speculate as to the effect of mixed ion diffusion in the case of mass transfer with chemical reaction in a moving liquid. It is not obvious, for example, that the stipulation of electric neutrality would be valid for macroscopic eddies. A rough approximation might be made by dividing the phase-boundary resistance arbitrarily into two parts (*10*), one involving D to the first power and one not involving D, and then applying the corrections indicated by Figures 2 and 4 to the first of these. In such cases as that illustrated by Figure 3, however, the effect of ion diffusion might be expected to be minor because ionization is small in the region near the interface, where D is important.

Attempts have been made in this laboratory to study the applicability of the ion-diffusion theory to the case of mass transfer between two stirred immiscible liquids with acid-base neutralization of diffusing solids. These have failed because in such cases the interface is violently agitated by the tendency of the phases to emulsify spontaneously and it would appear that no diffusion equations apply. The results, which throw considerable light on phenomena of solvent extraction with simultaneous chemical reaction, will be reported at another time.

ACKNOWLEDGMENT

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NOTATION

C = concentration, g. equiv./cu.cm.
C^* = liquid concentration in equilibrium with other phase, g. moles/cu.cm.
D = diffusivity, sq.cm./sec., or sq. cm./day, diffusion rate per unit area per unit of concentration gradient, where the concentration employed is that of the species (ion or molecule) diffusing
F = Faraday = 96,500 coulombs/g. equiv.
G = concentration gradient, g. equiv./cm.^{4}
H = Henry's law constant, g.moles/(cu.cm.) (atm.)
k_L = mass transfer coefficient, cm./day
$k°_L$ = mass transfer coefficient in absence of chemical reaction, cm./sec. or cm./day
K_L = over-all coefficient in absence of chemical reaction, cm./sec. or cm./day
m = sodium ion concentration, g. equiv./cu.cm.
n = valence
N = mass transfer rate, g.moles/(sec.) (sq.cm.) or g.moles/(day) (sq.cm.)
p = concentration of reactant A at boundary, g.moles/cu.cm.
q = concentration of reactant B at boundary, g.moles/cu.cm.
Q = quantity in square brackets in Equation (13)
R = gas constant, joules/(°K.) (g. mole)
T = temperature, °K.
u = ion mobility, sq.cm./(sec.) (volt)
V_L = diffusion cell volume, cu.cm.
x = distance normal to diffusion flux, cm.
x_L = effective film thickness, cm.
θ = time, sec. or days

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