# Mass Transfer Between Two Liquids with Chemical Reaction

**RICHARD SEARLE and KENNETH F. GORDON,** University of California, Berkeley, California

The subject of mass transfer between two phases with chemical reaction is only partially developed, as shown by the fact that absorption and extraction processes with chemical reaction are apparently designed on the basis of laboratory and pilot plant runs rather than on more basic premises. Examples of the processes would be found in the Solvay process, the manufacture of dry ice, and the production of nitric acid.

Whitman and several coauthors (*18, 19, 20*) set forth the fundamentals of mass transfer between two phases on the basis of the two-film theory, in which the resistance of each phase was represented by an equivalent film. More recently several authors (*5, 10*) have shown evidence for the existence of an appreciable interfacial resistance at high rates of transfer. Several years ago Danckwerts (*4*) suggested another model for the process of interphase mass transfer. Instead of an equivalent two-film picture he postulated an unsteady state situation with eddies of one fluid momentarily resting at the interface until displaced by other eddies coming from the bulk of the same fluid phase. During the period when the eddy rests at the interface unsteady state mass transfer takes place. This viewpoint, known as the penetration theory, results in equations of the same general form as those of the film theory. The available evidence does not indicate which picture is closer to the truth. Probably both views have partial validity, and a more accurate picture may well be a compromise between the two.

Hatta (*8*) pioneered with the application of the two-film concept to the case of absorption of carbon dioxide in potassium hydroxide and showed how the concept could qualitatively explain the experimental results. In their fairly recent text Sherwood and Pigford (*15*) devote a chapter to the subject of mass transfer with chemical reaction, giving an excellent summary of the mathematical and experimental developments in the field. Recently several studies on gas absorption with chemical reaction (*1, 14, 16*) have been published. There seems to be much less experimentation in liquid-liquid extraction with chemical reaction.

The steady state picture of two solutes $A$ and $B$ diffusing through stagnant films close to the interface between phases $W$ and $I$, where $W$ contains $B$ and $I$ has $A$, and undergoing instantaneous reaction in one of the films results in the following equations:

for reaction in phase $W$

$$\frac{k_{AW}}{k_{AW}'} - 1 = \frac{D_{BW}C_{BW}}{D_{AW}C_{AW_i}} \qquad (1)$$

and for reaction in phase $I$

$$\frac{k_{BI}}{k_{BI}'} - 1 = \frac{D_{AI}C_{AI}}{D_{BI}C_{BI_i}} \qquad (2)$$

Naturally, for the case of reaction in phase $W$ the transfer coefficient $k_{AI}$ equals $k_{AI}'$. The other coefficient in $W$, namely $k_{BW}$, which is greater than $k_{BW}'$, follows from $k_{AW}$, $k_{BW}'$, and the film concept. The parallel derivation holds for reaction in phase $I$.

The other picture, that of unsteady diffusion into an eddy which is momentarily resting at the interface, gives the same numerical result if the molecular diffusivities of each solute are equal.

The main difference between the two pictures of the transfer process without chemical reaction is that the strict film theory indicates that the individual transfer coefficient should be proportional to the first power of the molecular diffusivity while the penetration or transient state theory yields the result that the individual-phase mass transfer coefficient should vary as the square root of the molecular diffusivity.

An exact solution is available for the equations which result when the case of second-order infinitely rapid irreversible reaction is considered by the penetration theory (*2, 3, 4*). The solution is complicated and so makes an approximation convenient to use. Peaceman (*13*) and Sherwood and Pigford (*15*) have found that a close approximation is given if the square root of the molecular diffusivities is substituted for the first power in Equations (1) and (2). Thus for reaction in phase $W$ a good approximation is

$$\frac{k_{AW}}{k_{AW}'} - 1 = \sqrt{\frac{D_{BW}}{D_{AW}}}\,\frac{C_{BW}}{C_{AW_i}} \qquad (1a)$$

and for reaction in phase $I$

$$\frac{k_{BI}}{k_{BI}'} - 1 = \sqrt{\frac{D_{AI}}{D_{BI}}}\,\frac{C_{AI}}{C_{BI_i}} \qquad (2a)$$

In the present sodium hydroxide-acetic acid system where $D_{BW}/D_{AW} = 1.6$, when $D_{BW}\ C_{BW}/D_{AW}\ C_{AW_i}$ or $D_{AI}\ C_{AI}/D_{BI}\ C_{BI_i}$ is unity, Peaceman has found that these approximations are good to within 10% and to within 5% when the ratios are greater than ten. They continue to become even better as the ratios increase.

The purpose of this study is not to choose one model as being preferable but to determine the value of the equations in predicting and correlating data for extraction with chemical reaction. A rapid irreversible reaction is the neutralization reaction between sodium hydroxide and acetic acid. In a study of this system with an apparatus very similar to that used in the present investigation, Osborne (*12*) working with T. K. Sherwood and K. F. Gordon has found mass transfer rates higher than would be predicted by theory. When the concentration of each component was about $0.45N$, transfer rates were found to be more than twice as great as those which would be predicted by the two-film theory. His data were all for a concentration of about $0.45N$ acetic acid, so only a partial picture of the behavior of this system was obtained.

The reaction was studied in a system consisting of a layer of alcohol-saturated water containing sodium hydroxide beneath a layer of water-saturated 2-methyl-1-propanol (isobutanol) containing acetic acid. The distribution coefficients $m = C_I/C_W$ were 0.0051 for the sodium hydroxide and 1.18 (*6*) for the acetic acid. As shown in Figure 1, the solvents were in a cylinder having a stirrer with a single arm in each phase rotating at such a speed that the interface was smooth and of known constant area. Values for the individual transfer coefficients $k_W'$ and $k_I'$ were obtained by a previously described technique (*7*). To obtain the individual transfer coefficients, thirteen runs without chemical reaction were made with five solutes.

## APPARATUS

The apparatus, similar to one previously described (*7*), consisted of a glass cylinder, 6.09 in. I.D. suspended in a constant-temperature bath at 25°C. The stirring arms, of 3/16 in. stainless steel rod, were mounted at right angles in a 5/16-in.-diam. circular stainless steel shaft. The upper arm was 4 in. long, mounted with its center line 2¾ in. above the lower end of the rod while the lower stirrer, 2⅞ in. long, with its center line ½ in. above the end of the rod, was placed at a right angle to the upper stirrer. The shaft ended ½ in. from the center of the floor of the glass cylinder which was slightly curved, being ¼ in. higher at the center than at the edge. The end of the rod and the stirrer arms were slightly beveled. The

---

Richard Searle is at present with Rocketdyne Division of North American Aviation, Inc., Canoga Park, California, and Kenneth F. Gordon with the University of Michigan, Ann Arbor, Michigan.

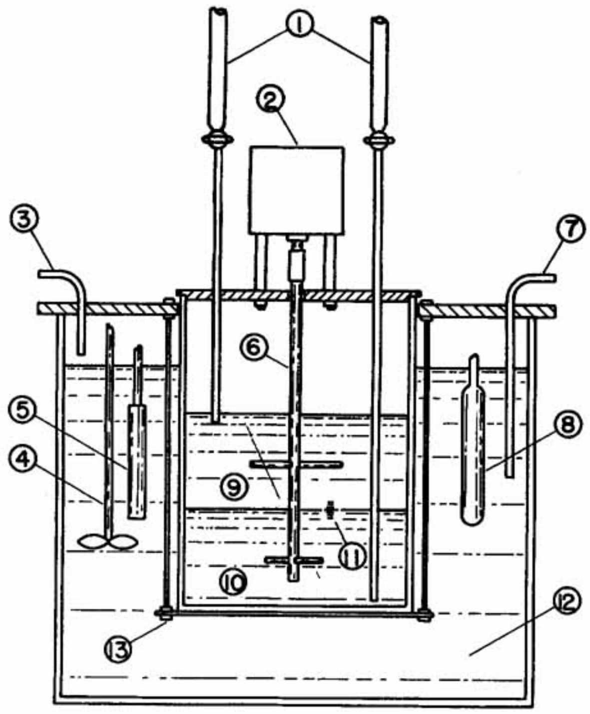

Fig. 1. Schematic diagram of apparatus. (1) burets; (2) stirrer motor; (3) water inlet to bath; (4) bath stirrer; (5) immersion heater; (6) reaction vessel stirrer; (7) constant head siphon; (8) mercury thermostat; (9) isobutanol phase; (10) water phase; (11) etched scale on reaction vessel; (12) thermostat bath; (13) reaction vessel supports.

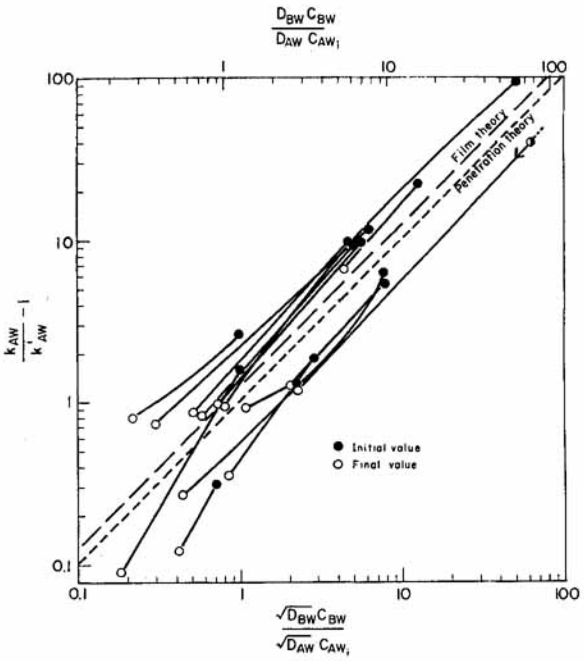

Fig. 2. Experimental increase of aqueous-phase mass transfer coefficient vs. theoretical increase.

stirrer was driven at 75 rev./min. by a constant-speed motor.

Extended tips from burettes containing solvent ran into each phase.

## PROCEDURE

One liter of the alcohol phase, containing the acetic acid, was added to the cylinder, and the water containing the sodium hydroxide was placed slowly beneath the alcohol through a bent glass tube from a separatory funnel so that there was a minimum of initial mass transfer between the two phases. The stirrer was started, and periodically 10-ml. samples of each phase were taken and solvent was added to the phase in order to keep the total phase volume constant. Usually samples were taken every 10 min., but when the transfer rate was high the interval would be 5 min. or even as low as 2 min.

In order to reduce the possible interference of solvent transfer on the transfer process being studied the solvents were 90 vol. % saturated with the second solvent when the initial solutions were being prepared; likewise the replacement solvents were also 90% saturated.

All samples were diluted with neutralized 50 vol. % ethanol in water and titrated with sodium hydroxide or hydrochloric acid in 50 vol. % ethanol. This avoided titrations involving two phases.

## RESULTS

The values for the over-all transfer resistance of various solutes were plotted against the distribution coefficient. The solutes were acetic acid, valeric acid, tetraethanol ammonium hydroxide, tetramethylammonium hydroxide, and sodium hydroxide. A straight line of intercept equal to the resistance of one phase and of slope equal to the resistance of the other phase resulted. This is to be expected from the equations for the additivity of resistances. As the solutes had various diffusivities the result would be more accurate if a correction for differences in diffusivity were made. This is done by converting each resistance to that for a solute with a molecular diffusivity of $3.6 \times 10^{-2}$ sq. cm./hr. This value, while arbitrary, is an intermediate value of those solutes used. The factor used to make this correction is the ratio of the square root of the diffusivities. Thus $1/K_{corrected}$ is equal to $(1/K)(D/3.6 \times 10^{-2})^{1/2}$.

The experimental values for the individual transfer coefficients were 9.5 cm./hr. for $k'_I$ and 10.0 cm./hr. for $k'_W$ for a substance having a diffusivity of $3.6 \times 10^{-2}$ sq. cm./hr. These values may be compared with the values of 9.0 and 10.4 cm./hr. (7) for the respective values in a similar, but not quite identical, apparatus after a minor correction for the difference in stirrer speeds.

For the runs with chemical reaction, as broad a range as possible was taken for concentrations and concentration ratios. Analytical techniques limited the lower concentration, and the effect of solute concentration on properties such as viscosity and density, which would in turn affect the hydrodynamics, limited the upper concentration, which was arbitrarily set as $1.4N$, for all but one run.

A total of twenty-four reaction runs was made. In fourteen the initial acetic acid concentration was greater than that of the sodium hydroxide. In one of these runs the reaction zone, which was initially in the isobutanol phase because of the high diffusivity of sodium hydroxide, moved into the water phase as the ratio of the acetic acid concentration to that of the sodium hydroxide increased. In the other thirteen runs of this set the reaction zone remained in the aqueous phase. Nine runs were made where the sodium hydroxide concentration was larger than that of the acetic acid, and one was made where it was equal, and so reaction took place entirely in the alcohol phase for these runs.*

On a hydrodynamical basis there is no clear choice between the film and penetration theories. However, the evidence from transfer without chemical reaction indicates that the transfer coefficient is more nearly proportional to the square root of the molecular diffusivity as required by the penetration theory, rather than to the first power (7). In the present systems the conditions postulated by either theory could exist. Therefore, the results will be considered in the light of both views.

The results in Figure 2 are plotted as suggested by the penetration theory [Equations (1*a*) and (2*a*)]. This plot shows all the runs which, according to theory, occurred in the aqueous phase, the solid circles representing values at the beginning of a run and the open

---

*Supplementary data may be obtained as document 4834 from the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

circles conditions later in the run. This figure contains the complete data for thirteen runs and part of the data for the single run where the reaction zone, which was originally in the isobutanol phase, crossed the interface to the water phase. It is the latter portion which is shown here. The dotted line represents that predicted by the penetration theory. It will be noticed that many of the lines are straight and nearly parallel to the theoretical line.

The runs where the reaction took place in the isobutanol phase are shown in Figure 3. The vertical line at $\sqrt{D_{AW}}\, C_{AI}/\sqrt{D_{BW}}\, C_{BI_i} = 642$ shows where the bulk concentrations of each phase are equal. Runs where the reaction zone moves toward the water phase and eventually enters it would lie to the right of this. The line for the run where the bulk concentration of each phase is equal plots as a vertical line. The curve for that run connects the two points shown on the plot, but, instead of being a vertical line, it lies to the right of the vertical except at the terminal points, because the bulk concentrations did not remain precisely equal except fortuitously at both terminal points. It is noticeable that the slopes of the connecting lines between initial and subsequent values tend toward the vertical as the dotted line is approached. For the case of almost equal bulk concentration of each reactant where

$$\sqrt{D_{AW}}C_{AI}/\sqrt{D_{BW}}C_{BI_i} = 642$$

the deviation between theory and experiment decreases as the reactants are consumed. Here the reaction is in the alcohol phase and the reaction product, sodium acetate which has a distribution coefficient $m < 0.1$ in favor of the water phase, is transferred to the aqueous phase as the reaction proceeds, and total solute concentration in the alcohol phase decreases as does the deviation.

Except for data close to the dividing-line region, the discrepancy between the calculated and experimental values seems to be independent of the value of $D_{BW}C_{BW}/D_{AW}C_{AW_i}$ or $D_{AI}C_{AI}/D_{BI}C_{BI_i}$.

The theoretical equations for mass transfer with chemical reaction, Equations (1*a*) and (2*a*), suggest that

$$\left(\frac{k_{AW}}{k_{AW}'} - 1\right) \Big/ \sqrt{\frac{D_{BW}}{D_{AW}}\frac{C_{BW}}{C_{AW_i}}}$$

and

$$\left(\frac{k_{BI}}{k_{BI}'} - 1\right) \Big/ \sqrt{\frac{D_{AI}}{D_{BI}}\frac{C_{AI}}{C_{BI_i}}}$$

should equal unity. In Figures 4 and 5 the value of the appropriate function at the beginning is plotted against the bulk concentration in the phase where the reaction takes place. For most runs subsequent values during a run would fall on about the same point as the initial value or a little lower.

Figures 6 and 7 show the effect of bulk concentration on the fractional increase in mass transfer coefficient at constant interfacial concentration. Figures 8 and 9 show the effect of interfacial concentration on the fractional increase in mass transfer coefficient at constant bulk concentration. The constant concentrations were chosen to give the maximum number of data points.

The deviation of the experimental fractional increase from the simple theoretical is seen to be a strong function of the bulk concentration in the phase in which reaction is taking place, as shown by the results in Figures 4 and 5 and by the slopes appreciably different from unity in Figures 6 and 7, but to have much less correlation with the interfacial concentration, as shown by the slopes close to $-1$ in Figures 8 and 9.

These results may be compared with those of Stephens and Morris (*16*), who found that for the absorption of chlorine in aqueous ferrous chloride the fractional increase in transfer coefficient was proportional to $(C_{BW}/C_{AW_i})^{0.83}$, and with those of Roper (*14*), who for the absorption of chlorine by carbon tetrachloride solutions of 2-ethylhexene-1 or oleic acid found the fractional increase to be proportional to $(k_c C_B/C_{A_i})^{0.5}$. The reaction rate constant $k_c$ is fairly high, 152 to 3,200 liters/(g. mole)(sec.), but Roper suggests that the exponent might approach unity for a very rapid reaction.

Before these correlations are considered further, it would be well to examine the basic equations used to obtain the data which are plotted in Figures 2 and 3. At higher values of $(k_{AW}/k_{AW}') - 1$

$$\left(\frac{k_{AW}}{k_{AW}'} - 1\right) \rightarrow \frac{k_{AW}}{k_{AW}'}$$

$$= \frac{N_A}{AC_{AW_i}k_{AW}'} = \frac{N_A}{AC_{AW_i}} \text{ (constant)} \tag{3}$$

and

$$\frac{D_{BW}C_{BW}}{D_{AW}C_{AW_i}} = \frac{C_{BW}}{C_{AW_i}} \text{ (constant)} \tag{4}$$

Thus, if data are correlated by the methods used here, by Stephens and Morris, and by Roper, essentially $N_A/AC_{AW_i}$ is plotted as a function of $C_{BW}/C_{AW_i}$.

For reactions occurring near the interface large fluctuations in $C_{AW_i}$, with relatively smaller changes in $N_A$ and $C_{BW}$, produce large parallel shifts of data points in a single run with a 45-deg. slope on a log-log plot. This effect is seen clearly in Figures 2 and 3. The most interesting characteristic of the present data is the deviation from the theoretical line. As mentioned above in the discussion of Figures 4 to 9, the bulk concentration seems to be the significant factor in the deviation rather than the interfacial concentration.

From Figures 2 through 5 it is seen that, for this particular system, the penetration or transient-state theory predicts values for $(k/k') - 1$ which are about 100% high at 0.005 *N* bulk concentration, correct at about 0.1*N*, and about 60% low at 1*N*.

## DISCUSSION

It is seen that theory has good qualitative agreement with the present experimental results; however, at very low concentrations it gives predictions which are too high, and at the higher concentrations the theoretical results are too low. At the higher concentrations the viscosity would be greatest and the molecular diffusivity would be smallest. Both of these effects would be expected to reduce the experimentally observed fractional increase below the theoretically calculated value rather than to increase it. The more obvious explanations for possible discrepancies between theoretical and calculated transfer coefficients lead to the expectation of theoretical coefficients higher than experimental, but the reverse is true at concentrations above about 0.1*N*.

It would be wise to consider the possible errors that might arise from the use of an incorrect diffusivity. The values used for the diffusivities $D_{AW}$ and $D_{BW}$ were taken from the International Critical Tables after employing the Stokes-Einstein equation for a temperature correction. Allowances were made for the variation of diffusivity with concentration. The square root of the diffusivity was always within 3% of the mean value.

The diffusivities enter into the calculation of the interfacial concentration by means of an equation of the form

$$C_{BI_i} = \frac{k_{BW}'C_{BW} - k_{AI}'C_{AI}}{k_{BI}' + \dfrac{k_{BW}'}{m_B}} \tag{5}$$

A diffusivity correction to $k_W$ and $k_I$ must be made to obtain values for $k_{AW}'$, $k_{BW}'$, $k_{AI}'$, and $k_{BI}'$. This may be derived from the two-film theory as shown in the Appendix. As mentioned earlier the interfacial concentration appears in both ordinates and abscissas in Figures 2 and 3. The effect of using different values for the diffusivity would be to shift the data points along a 45-deg. line. For the few points where $k/k'$ is appreciably different from $(k/k') - 1$ the angle would be somewhat different from 45-deg. Errors in diffusivity would also alter the scale of the abscissas in those figures. As the most significant point about the data is not the absolute values of the data but rather the deviation from the theoretical line, moderate errors in diffusivity will not be important.

In the calculation of the individual transfer coefficients a correction for the diffusivity differences is made for both the water- and isobutanol-phase coefficients. In making the correction for the isobutanol-phase transfer coefficient it is necessary to know the ratio of the appropriate diffusivities in both water and isobutanol. The ratios are assumed to be the same in both phases, an assumption that is probably valid for members of a homologous series, where the association effects might be expected to be similar. This assumption is used for the ratio of the diffusivities for sodium hydroxide or acetic acid to those of the various carboxylic acids used to make the runs for mass transfer without chemical reaction which gave values for the individual phase transfer coefficients. The assumption is probably fairly good for acetic acid, for sodium hydroxide with its dissociation and possible variable solvation the accuracy is not known.

For reaction in the water phase, the diffusion coefficient for acetic acid through isobutanol is required to obtain the interfacial concentration using the counterpart of Equation (5). The small diffusivity correction for acetic acid is believed accurate. All the other diffusivities required are those in the water phase, which are also believed to be known accurately enough for the present calculation. Thus for reaction in the water phase it seems impossible to explain the discrepancy between theory and experiment on the basis of diffusivity if constant hydrodynamics are assumed. It is most likely that the similar deviation which results when reaction takes place in the isobutanol phase is due to the same cause rather than to erroneous diffusivities of the pure components in the pure solvents.

The calculations for this study have been made by use of the diffusivities of the pure components. This method cannot be precisely correct, for as soon as reaction starts there will be reaction product, sodium acetate in this case. It is known that the diffusivity of sodium hydroxide, an ionic material, should be affected by the presence of sodium acetate, another ionic material. Here the hydroxide and acetate ions may be diffusing while the sodium ions may not be diffusing. Thus the ionic diffusivities become important.

A paper by Sherwood and Wei (*15a*) provides a helpful insight to the problem. They show calculations based on the theory of diffusion in mixed electrolytes including some for the aqueous-phase reaction between sodium hydroxide in water and acetic acid being absorbed or extracted from another phase. They calculate that for the case when the ratio of sodium hydroxide to sodium acetate bulk concentration is low the rate of mass transfer will be about 2.4 times

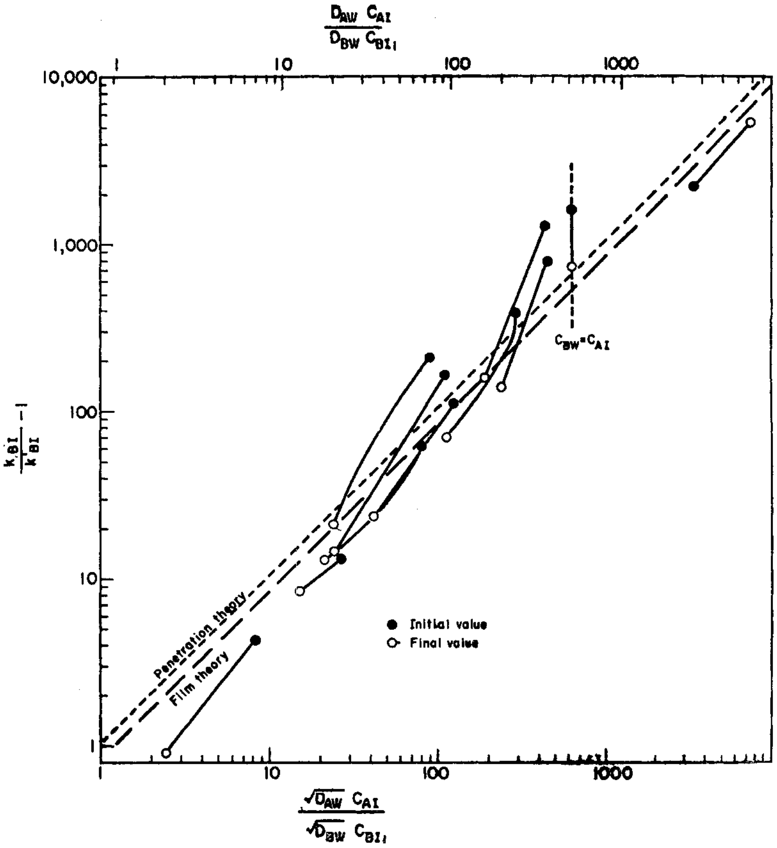

Fig. 3. Experimental increase of alcoholic-phase mass transfer coefficient vs. theoretical increase.

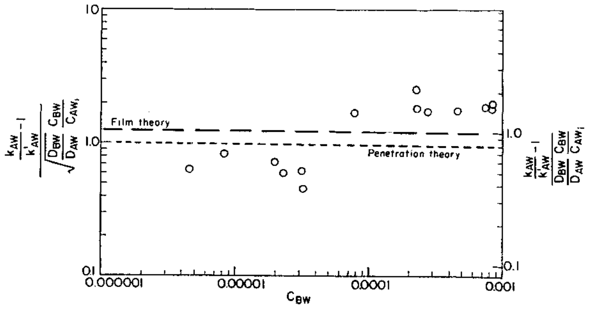

Fig. 4. Effect of bulk aqueous-phase concentration on the ratio of experimental to theoretical increase of aqueous-phase mass transfer coefficient.

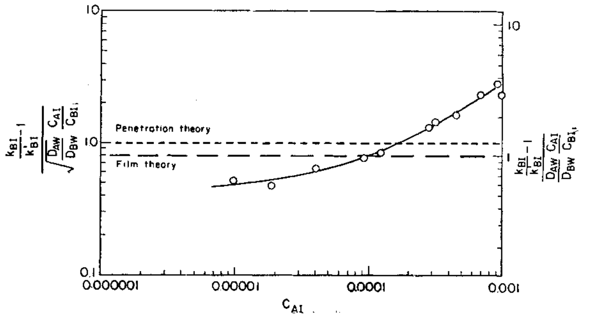

Fig. 5. Effect of bulk alcoholic-phase concentration on the ratio of experimental to theoretical increase of alcoholic-phase mass transfer coefficient.

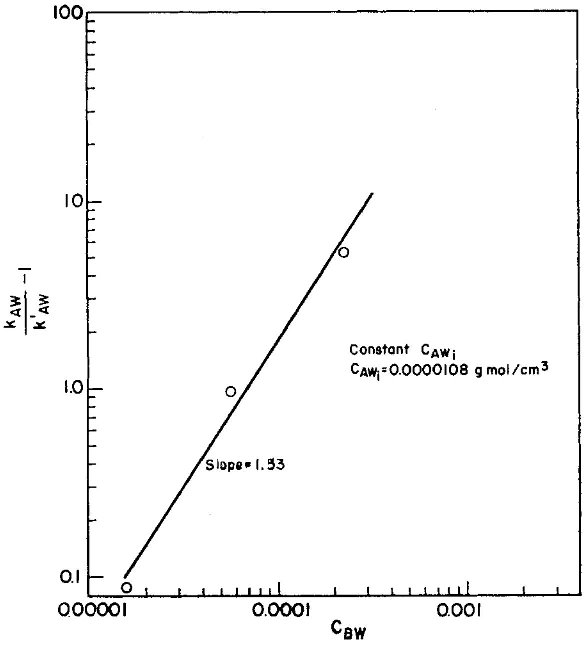

Fig. 6. Effect of bulk aqueous-phase concentration on increase of aqueous-phase mass transfer coefficient.

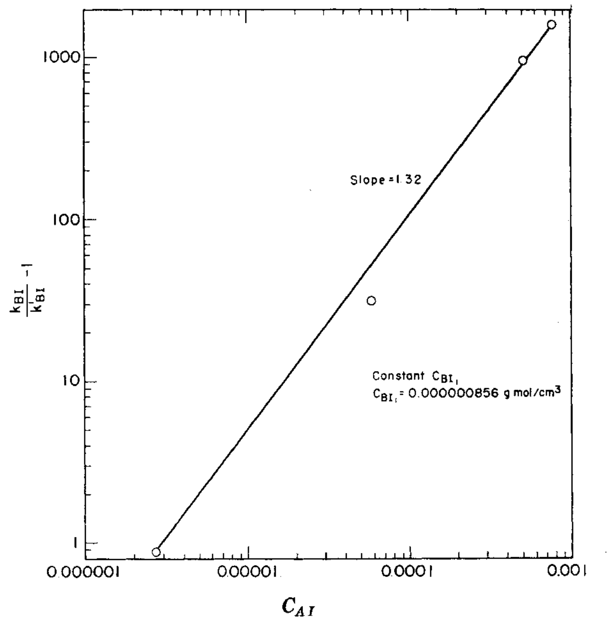

Fig. 7. Effect of bulk alcoholic-phase concentration on increase of alcoholic-phase mass transfer coefficient.

that predicted from the film theory. As the ratio of sodium hydroxide to sodium acetate becomes very large this ratio becomes about 1.5. The increase in transfer rate is due to an increase in the effective diffusivity.

They point out the difficulty in applying these results for a film to a moving or agitated liquid and conclude that for the sodium hydroxide–acetic system "the effect of ion diffusion might be expected to be minor because ionization is small in the region near the interface, where the diffusivity is important."

Thus far the experimental results have been compared with the predictions of the penetration theory. As pointed out earlier, instead of exact solutions of the penetration theory, approximations are used which are good to within 10% for all the data and within 5% for most of it. For comparison of the results with the two-film theory, by use of half-power diffusivity corrections for the individual film coefficients, $(k_{AW}/k_{AW}') - 1$ could be plotted against $D_{BW}C_{BW}/D_{AW}C_{AW_i}$ as indicated by Equation (1). This could be demonstrated in Figure 2 by shifting the abscissa of each data point to a value identical to that derived by multiplying by $(D_{AW}/D_{BW})^{1/2}$, and keeping the same line for the theoretical line of both theories. It is convenient to show the equivalent operation by multiplying the scale of the abscissa by the factor $D_{BW}/D_{AW})^{1/2}$. As the factor varies over the limited range 0.785 to 0.814, it will be taken as 0.80. This is shown on the upper scale. The theoretical line predicted by the penetration theory is given by the dotted line. The data may be compared with either theory on the same plot. Figure 3 is treated in a parallel manner. Similar reasoning, with adjustments to the ordinates rather than the abscissas, yields the theoretical lines of the penetration theory in Figures 4 and 5.

It is seen that the discrepancy between theory and experiment remains for both theoretical views.

A calculation using the enthalpy of reaction, the rate of reaction, and the analogy between heat and mass transfer with two-thirds exponents on the Schmidt and Prandtl numbers will show that a temperature difference of up to about 1.4°C. would be sufficient to transfer all the heat evolved across the equeous resistance. This is for the case where the concentrations and rates of transfer are highest. Presumably this represents a maximum temperature rise in the water phase because it would be expected that the heat of reaction would be dissipated in two directions. The maximum so calculated for the isobutanol phase is 3.6°C. What effect this temperature rise should have on the fluid dynamics and the mass transfer coefficient is not yet known. It may be noted that the higher the concentration of reactants the higher will be the temperature rise and, as the experimental results show, the greater the increase in transfer rate over that predicted by theory, which assumes constant fluid dynamics without added thermal convection.

There is no evidence to support the two-thirds exponent on the Schmidt and Prandtl groups for a liquid-liquid system. If half-power exponents are used, then the temperature rise would be about 2.4 times larger. If the half power is used on the Schmidt group and two thirds on the Prandtl group, a temperature difference three times larger would result. Thus a temperature difference of up to 11°C. might be calculated as the rise due to chemical reaction. These values are given solely to show an order of magnitude and are not meant to imply any reliability.

It is of interest to note that another case has been reported where mass transfer with chemical reaction gives coefficients higher than would be expected. Peaceman (*13*) studied the desorption of chlorine from water where the chlorine is in the form of chlorine, hydrochloric acid, and hypochlorous acid. Basing his liquid film coefficients on the total chlorine present, that is as chlorine, hydrochloric acid, and hypochlorous acid, he obtained liquid-phase mass transfer coefficients higher than those obtained without chemical reaction. The coefficients without chemical reaction were obtained from the desorption of carbon dioxide from water and the desorption of chlorine from hydrochloric acid, which represses the reaction to form hydrochloric acid and hypochlorous acid. After a diffusivity correction the carbon dioxide data were in excellent agreement with the chlorine data.

Peaceman's data for the desorption of chlorine from water showed that the liquid-film mass transfer coefficient, based on the total chlorine present, approaches zero as the concentration of chlorine approaches zero, equals the maximum expected value at about a total chlorine concentration of 0.06 g. mole/liter, and continues to increase with increasing concentration. This behavior is very surprising, for the reaction between hydrochloric acid and hypochlorous acid to form chlorine would be expected to constitute a chemical resistance which would reduce the liquid-phase coefficient if it had any effect. The diffusivity used by Peaceman for hydrochloric acid is about twice that for chlorine or hypochlorous acid. This prevents an elucidation based on differences of diffusivities. He could offer no explanation for the anomalous behavior of this system.

## CONCLUSIONS

For the case of extraction with rapid second-order chemical reaction between sodium hydroxide and acetic acid, the two-film theory and the transient-state theory give a good qualitative picture of the experimental results. However, theory predicts values for $(k/k') - 1$ which are about 100% high at 0.005*N*, correct at 0.1*N*, and about 60% low at 1*N*. The magnitude of the discrepancy appears to be a function of the bulk concentration of the phase in which the reaction is occurring rather than the interfacial concentration.

## NOTATION

$A$ = area for mass transfer, sq. cm.
$C$ = concentration, g. moles/cu. cm.
$D$ = diffusivity, sq. cm./hr.
$k'$ = individual mass transfer coefficient without chemical reaction, cm./hr.
$k$ = individual mass transfer coefficient with chemical reaction, cm./hr.
$m$ = distribution coefficient, $C_{SI}/C_{SW}$ at equilibrium
$N$ = mass transfer rate across interface, g. moles/hr.

### Subscripts

$A$ = of component $A$ or acetic acid
$B$ = of component $B$ or sodium hydroxide
$I$ = of or in component $I$ or isobutanol
$i$ = at the interface
$S$ = of solute $S$
$W$ = of or in component $W$ or water

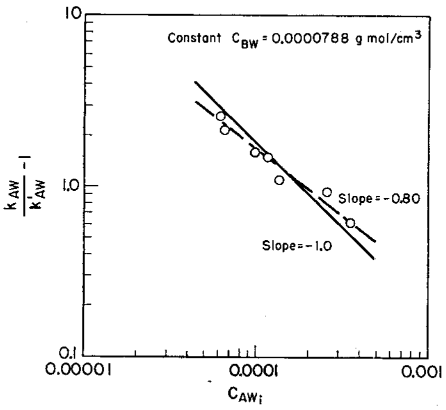

Fig. 8. Effect of aqueous-phase interfacial concentration on aqueous-phase mass transfer coefficient.

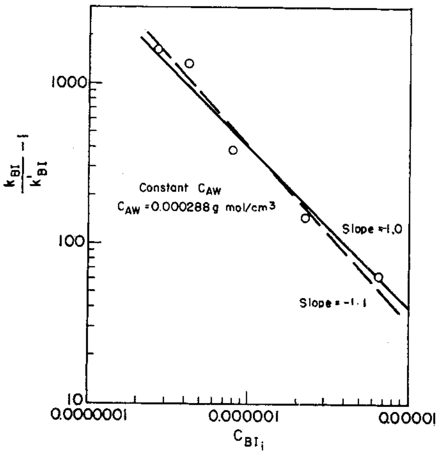

Fig. 9. Effect of alcoholic-phase interfacial concentration on alcoholic-phase mass transfer coefficient.

## LITERATURE CITED

1. Caudle, P. G., and K. G. Denbigh, *Trans. Faraday Soc.*, **49**, 39 (1953).
2. Danckwerts, P. V., *loc. cit.*, **46**, 300 (1950).
3. *Ibid.*, 701.
4. ———, *Ind. Eng. Chem.*, **43**, 1460 (1951).
5. Emmert, R. E., and R. L. Pigford, *Chem. Engr. Progr.*, **50**, 87 (1954).
6. Gordon, K. F., *Ind. Eng. Chem.*, **45**, 1813 (1953).
7. ———, and T. K. Sherwood, *Chem. Eng. Progr. Symposium Series*, No. 10, **50**, 15 (1954).
8. Hatta, S., *Tech. Repts., Tohoku Imp. Univ.*, **8**, 1 (1928–29).
9. Heertjes, P. M., W. A. Holve, and H. Talsma, *Chem. Eng. Sci.*, **3**, 122 (1954).
10. Higbie, R., *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
11. Lewis, J. B., A.E.R.E. C.E./R. 1120. Atomic Energy Establishment, Harwell, England (1954), quoted by T. K. Sherwood and K. F. Gordon, *A.I.Ch.E. Journal*, **1**, 129 (1955).
12. Osborne, R., M.S. thesis, Mass. Inst. Technol., Cambridge, Mass. (1951).
13. Peaceman, D., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Mass. (1951).
14. Roper, G. H., *Chem. Eng. Sci.*, **2**, 18, 247 (1953).
15. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2 ed., McGraw-Hill Book Company, Inc., New York (1952), and correction sheet.
15a. Sherwood, T. K., and J. C. Wei, *A.I.Ch.E. Journal*, **1**, 522 (1955).
16. Stephens, E. J., and G. A. Morris, *Chem. Eng. Progr.*, **47**, 232 (1951).
17. Wang, J. H., C. V. Robinson, and I. S. Edelman, *J. Am. Chem. Soc.*, **75**, 466 (1952).
18. Whitman, W. G., *Chem. Met. Eng.*, **29**, No. 4, p. 146 (July 23, 1923).
19. ———, and D. S. Davis, *Ind. Eng. Chem.*, **16**, 1233 (1924).
20. ———, and W. K. Lewis, *loc. cit.*, 1215.

*Presented at A.I.Ch.E. New York Meeting.*

## APPENDIX

### Calculation of Transfer Coefficients Without Chemical Reaction

*Calculation of the Over-all Transfer Coefficient for a Run.* The calculation of $K$ for a run is elementary when a continuous analysis of each phase is available without sample removal. If, as is often the case, the analyses are taken by removing a sample of each phase and replacing it with pure solvent, a correction must be made for the solute removed from the phase in sampling.

Let

$C^*$ = concentration of one phase that would be in equilibrium with the other, g. moles/cc.
$p$ = number of intervals
$v$ = volume of sample removed from the phase, cc.
$\Theta$ = volume of a phase, cc.
$V$ = time, hr.

$K_W$ for Transfer from Water to Isobutanol:

$$N = K_W A(C_W - C_W^*) \qquad \text{(A-1)}$$

Remembering $m = C_I/C_W^*$ and $V_I = V_W$ = constant and letting the zero subscript refer to the beginning of the interval being considered, one obtains from a substitution of $C_I/m$ for $C_W^*$ followed by a substitution of $C_{I_0} + C_{W_0} - C_W$ for $C_I$, based on a total material balance,

$$N = K_W A\left[\frac{1+m}{m}C_W - \frac{1}{m}(C_{W_0} + C_{I_0})\right] \qquad \text{(A-2)}$$

Considering the interval from $n$ to $n+1$, at $n+1$

$$N = K_W A\left[\frac{1+m}{m}C_{W_{n+1}}' - \frac{1}{m}(C_{W_n}' + C_{I_n}')\right] \qquad \text{(A-3)}$$

where the primes on the concentrations refer to the actual concentrations of the phases at the beginning and end of the interval.

The rate of transfer from the water phase

$$N = -V_W \frac{dC_W}{d\Theta} \qquad \text{(A-4)}$$

Substituting this in Equation (A-3), collecting concentration terms, and integrating over the interval $n$ to $n + 1$ gives

$$\ln \frac{\left(1 + \frac{1}{m}\right)C_{W_n}' - \frac{1}{m}(C_{I_n}' + C_{W_n}')}{\left(1 + \frac{1}{m}\right)C_{W_{n+1}}' - \frac{1}{m}(C_{I_n}' + C_{W_n}')}$$

$$= \left(1 + \frac{1}{m}\right)K_W\frac{A}{V}(\Theta_{n+1} - \Theta_n) \qquad \text{(A-5)}$$

Let the unprimed concentrations refer to those given by the actual analysis of samples taken at the beginning and end of each interval. In the interval $n$ to $n + 1$ the concentrations at the beginning will be $(V - v)/V$ times the concentration just given by analysis because the fraction $v/V$ of the volume of each phase is removed in sampling and is immediately replaced by pure solvent. Therefore

$$C_{W_n}' = \frac{V - v}{V} C_{W_n}$$

and

$$C_{I_n}' = \frac{V - v}{V} C_{I_n}$$

At the end of the interval the actual concentration is that given by the analsyis making

$$C_{W_{n+1}}' = C_{W_{n+1}} \quad \text{and} \quad C_{I_{n+1}}' = C_{I_{n+1}}$$

Substituting the foregoing results in Equation (A-5) gives

$$\ln \frac{\left(\frac{V - v}{V}\right)\left[\left(1 + \frac{1}{m}\right)C_{W_n} - \frac{1}{m}(C_{I_n} + C_{W_n})\right]}{\left(1 + \frac{1}{m}\right)C_{W_{n+1}} - \frac{1}{m}(C_{I_n} + C_{W_n})\left(\frac{V - v}{V}\right)}$$

$$= \left(1 + \frac{1}{m}\right)K_W \frac{A}{V}(\Theta_{n+1} - \Theta_n) \qquad \text{(A-6)}$$

Owing to solute removal during sampling

$$\left(\frac{V - v}{V}\right)(C_{I_n} + C_{W_n})$$

$$= C_{I_{n+1}} + C_{W_{n+1}} \qquad \text{(A-7)}$$

Substituting Equation (A-7) in the denominator of Equation (A-6) and writing similar equations for each of $p$ periods or intervals and adding gives

$$\ln \left(\frac{V - v}{V}\right)^p \frac{\left(1 + \frac{1}{m}\right)C_{W_n} - \frac{1}{m}(C_{I_n} + C_{W_n})}{\left(1 + \frac{1}{m}\right)C_{W_{n+p}} - \frac{1}{m}(C_{I_{n+p}} + C_{W_{n+p}})}$$

$$= \left(1 + \frac{1}{m}\right)K_W \frac{A}{V}(\Theta_{n+p} - \Theta_n) \qquad \text{(A-8)}$$

If the time intervals are of equal length

$$\Theta_{n+p} - \Theta_n = p(\Theta_{n+1} - \Theta_n)$$

and Equation (A-8) can be written

$$K_W = \frac{V}{\left(1 + \frac{1}{m}\right)A}\left\{\frac{\ln \frac{V - v}{V}}{\Theta_{n+1} - \Theta_n} - \frac{\Delta\left\{\ln\left[\left(1 + \frac{1}{m}\right)C_W - \frac{1}{m}(C_I + C_W)\right]\right\}}{\Delta\Theta}\right\} \qquad \text{(A-9)}$$

The second term in the braces is the slope of a plot of ln $(C_W - C_W^*)$ vs. $\Theta$ and the first term is a correction to allow for solute being removed from both phases, which decreases the driving force without any interphase transfer. Equation (A-9) is written so that it is dependent on $C_W$, for $(C_I + C_W)$ changes slowly. A similar equation could be written dependent on $C_I$. It could be used when the percentage of $C_I$ changes more rapidly than that of $C_W$. This would give greater accuracy than Equation (A-9). There the numerator of the second term in the braces would be

$$\Delta\left\{\ln\left[(C_{I_n} + C_{W_n}) - \left(1 + \frac{1}{m}\right)C_{I_n}\right]\right\}$$

$K_W$ for Transfer from Isobutanol to Water:
A similar derivation yields

$$K_W = \frac{V}{\left(1 + \frac{1}{m}\right)A}\left\{\frac{\ln \frac{V - v}{V}}{\Theta_{n+1} - \Theta_n} - \frac{\Delta\left\{\ln\left[\left(1 + \frac{1}{m}\right)C_{I_n} - (C_{W_n} + C_{I_n})\right]\right\}}{\Delta\Theta}\right\} \qquad \text{(A-10)}$$

$K_I$:

$K_I$ is obtained from $mK_I = K_W$ (A-11)

*Calculation of Individual Transfer Coefficients.* From the equations for the additivity of individual phase resistances

$$\frac{1}{K_W} = \frac{1}{k_W'} + \frac{1}{mk_I'} \qquad \text{(A-12)}$$

$$\frac{1}{K_I} = \frac{1}{k_I'} + \frac{m}{k_W'} \qquad \text{(A-13)}$$

it is seen that for a series of solutes a plot of the over-all resistance against the distribution coefficient $1/K_W$ vs. $1/m$ and $1/K_I$ vs. $m$ should yield straight lines, the slope of which equals the resistance of one phase and the intercept that of the other. Also the slope of one plot should equal the intercept of the other.

For greater accuracy a correction is made for the variation in $K$ due to diffusivity by taking $K$ as being proportional to the square root of the molecular diffusivity and putting all resistances on the basis of the same diffusivity.

## Calculation of Mass Transfer Coefficient with Chemical Reaction

First the rate is calculated. The logarithm of the concentration of each phase is plotted against time in order to allow interpolation and to check for consistency.

The rate at

$$\Theta = \frac{\Theta_{n+1} + \Theta_n}{2}$$

is taken as

$$N = \left[\frac{\frac{V - v}{V} C_n - C_{n+1}}{\Theta_{n+1} - \Theta_n}\right] V \qquad \text{(B-1)}$$

where $(V - v)/V$ allows for the dilution on sampling.

Two sets of values for $N$ may be obtained, one from each phase. Both are plotted as log $N$ vs. $\Theta$. The data are usually in good agreement, yielding a straight line allowing $N$ to be read with adequate precision.

For instantaneous reaction in the $W$ phase where one molecule of $A$ reacts with one of $B$

$$k_{AI}'A(C_{AI} - C_{AI_i}) = N_A = N_B$$

$$= k_{AW}'A\left[C_{AW_i} + \left(\frac{D_{BW}}{D_{AW}}\right)^{1/2} C_{BW}\right] \qquad \text{(B-2)}$$

As $C_{AI_i} = m_A C_{AW_i}$, this yields

$$C_{AW_i} = \frac{k_{AI}'C_{AI} - k_{BW}'C_{BW}}{k_{AW}' + k_{AI}'m_A} \qquad \text{(B-3)}$$

Then the value for $k_{AW}$ is obtained from

$$N_A = k_{AW}A(C_{AW_i} - O) \qquad \text{(B-4)}$$

In a similar way values for $k_{BI}$ for reaction in the $I$ phase may be obtained after calculating $C_{BI_i}$ from

$$C_{BI_i} = \frac{k_{BW}'C_{BW} - k_{AI}'C_{AI}}{k_{BI}' + \frac{k_{BW}'}{m_B}} \qquad \text{(B-5)}$$

In all cases $k'$ is obtained from the runs to determine the individual transfer coefficients with the assumption that $k'$ is proportional to the square root of the molecular diffusivity.