Gas Absorption Accompanied by a Liquid-phase Chemical Reaction

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The rate of absorption of chlorine from chlorine-nitrogen mixtures into solutions of ferrous chloride in 0.203 N aqueous hydrochloric acid was studied in a short wetted-wall column. Dimensional analysis and the film and penetration theories were used to infer, from the absorption rate data, that the chemical reaction between chlorine and the ferrous ion is second order. The absorption-rate results for experiments with a dilute gas phase agreed with theoretical predictions for absorption accompanied by a second order reaction with a reaction rate constant of 188 liters/(g. mole)(sec.). The results for experiments with pure chlorine gas deviated from the rest of the results, and they did not agree with the theoretical equations. It was shown that the assumption of a three-step mechanism for the chemical reaction, including the formation of a complex ion and the decomposition of this complex ion, explains, at least qualitatively, the deviations observed for the pure chlorine gas runs.

In recent years, an increased emphasis has been placed on solving the problem of predicting the effect of a simultaneous chemical reaction on the rate of gas absorption. This is due, in part, to the increasing number of industrial applications in which a gas absorption rate is appreciably affected by a simultaneous chemical reaction; it is also due to the feeling that studying the effect of a chemical reaction offers a means of learning more about the mechanism of the absorption process.

The general problem of simultaneous gas absorption and chemical reaction has been studied by a number of investigators over the last thirty-five years, and many of the investigations are reviewed by Sherwood and Pigford (*8*). In general, the method of analysis used was to compare experimental data with the predictions of the film theory and, in more recent years, the penetration theory. For general discussions of the film theory and its application to the prediction of the effect of a chemical reaction, reference may be made to Sherwood and Pigford (*9*) and to Van Krevelen and Hoftijzer (*13*); for the penetration theory, reference may be made to Sherwood and Pigford (*10*) and to Perry and Pigford (*7*). While the two theories often proved to be useful in qualitatively interpreting the absorption rate data, quantitative agreement between theoretical equations and experimental data has been rare indeed, and, in one investigation (*6*), the absorption coefficient was observed to increase with increasing concentration when the film-theory equations predicted that the coefficient should decrease. The reasons for disagreement between theory and experiment were often obscured by uncertainties about many of the important system parameters, such as the kinetics and equilibrium of the chemical reaction, the interfacial area for mass transfer, and the liquid density, viscosity, and diffusivity which changed as the chemical reaction proceeded. There was also considerable uncertainty about the ability of the simplified theories to describe the complex liquid- and gas-flow patterns in the experimental systems.

In order to eliminate some of these uncertainties about the system parameters, several recent investigations have been conducted using a short wetted-wall column as the absorption apparatus (*6, 4*). The liquid-flow pattern in such a column would be expected to be somewhat similar to that described by the penetration theory, and it has been shown that physical-absorption results in such a column can be predicted within 10 to 30% by the penetration theory and streamline-flow mathematical equations (*14*). Even with the short wetted-wall column, however, quantitative agreement between experimental results and theoretical equations for absorption accompanied by a chemical reaction has eluded investigators.

This investigation was undertaken in order to gain a clearer insight into the manner in which a chemical reaction affects the rate of gas absorption. In order to accomplish this, it was necessary to eliminate as many as possible of the uncertainties about the experimental system. Thus, it was decided to consider only the liquid-phase resistance to absorption and the effect of a liquid-phase chemical reaction on this resistance. The short wetted-wall column was chosen as the absorption apparatus because the interfacial area can be evaluated, the absorption coefficient in such a column is of the same order of magnitude as the absorption coefficients encountered in industrial absorbers, and physical-absorption results in the column had been shown to be in fair agreement with penetration theory and streamline-flow equations. The chemical system chosen was chlorine-ferrous chloride. In this system, chlorine gas is absorbed into an aqueous solution of ferrous chloride, and the absorption rate is affected by the oxidation reaction

$$Cl_2 + 2Fe^{++} = 2Cl^- + 2Fe^{+++} \quad (1)$$

This system had been studied by Stephens and Morris (*12*), who used a disk column absorber. All the data reported by Stephens and Morris were for experiments in which the sum of the ferric and ferrous ion concentrations was equal to 2.84 g. ions/liter; thus, the liquid viscosity was quite high. Under these conditions, Stephens and Morris found that the chemical reaction rate was essentially "infinite"; however, their results did not agree quantitatively with either the film theory or the penetration theory. While they did not report the results, Stephens and Morris mentioned that some data had been taken in which the sum of the ferrous and ferric ion concentrations was much lower than 2.84 g. ions/liter; in these experiments, the liquid viscosity was considerably lower than in the previous experiments, and the results of these experiments indicated that the reaction rate was not infinite. It appeared, therefore, that the chlorine-ferrous chloride system offered the possibility of taking data in the region where the chemical reaction rate is essentially infinite and also in the region where the reaction rate is not infinite. Other advantages of the system include the fact that the gas-phase resistance to absorption is a small fraction of the total resistance and the fact that the chemical reaction is essentially irreversible. The irreversible reaction is advantageous not only because the need for precise evaluation of the equilibrium constant is eliminated but also because the film and penetration theory differential equations have been solved for more cases for absorption accompanied by an irreversible reaction than for absorption accompanied by a reversible reaction.

EXPERIMENTAL

The experimental program was a study of the rate of absorption of chlorine gas from chlorine-nitrogen mixtures into aqueous solutions of ferrous chloride in 0.203 *N* hydrochloric acid. The chemical reaction affecting the absorption rate was the oxidation of the ferrous ion by chlorine [see Equation (1)]; the hydrochloric acid was added to the liquid phase to suppress the chlorine hydrolysis reaction so that it would not affect the absorption rate. The absorption apparatus was a short wetted-wall column.

The wetted-wall section of the short wetted-wall column was a glass cylinder of 3.02 cm. diam. Liquid flowed onto the wall through an upper slot, which was kept full of liquid, and liquid flowed from the wall through a lower slot, which was also kept full of liquid. In this manner, gas-liquid contact occurred only on the wetted wall. The height of the wetted wall, which was taken as the distance from the top of the upper slot to the bottom of the lower slot, was equal to 4.61 cm. plus the upper slot width, which varied from approximately 0.01 to 0.13 cm. The column design was the same as that described by Vivian and Peaceman (*14*), and it will not be described in this paper. In the terminology of Vivian and Peaceman, the liquid inlet slot was of the "downflow" type.

In operation, the column was supplied with liquid and gas streams at 25°C. The liquid stream was 0.203 *N* aqueous hydrochloric acid containing varying concentrations of ferrous chloride. Liquid feed was prepared in 50-liter batches in a carboy and brought to the proper temperature. It was pumped to a constant-head tank, from which it flowed through a capillary flowmeter and into the short wetted-wall column. From the column the liquid passed to a collecting tank. Thermometers were installed in the inlet and exit lines to measure the liquid temperature before and after the column, and samples of the inlet and exit liquid streams were collected and analyzed. The liquid flow rate, which was measured by means of the capillary flowmeter, was varied over a fifteen-fold range.

The gas stream was a mixture of chlorine and nitrogen, with the chlorine gas-phase mole fraction varying from 0.06 to 1.0. The pure gases were withdrawn from cylinders at constant rates, metered through capillary flowmeters and mixed in a mixing "tee." The mixture was then passed through several dilute hydrochloric acid bubblers to saturate the gas stream with water. From the bubblers, the gas flowed through a 28-in. calming section and into the short wetted-wall column. From the column, the gas was exhausted to the atmosphere through two packed water scrubbers. The gas calming section was jacketed with water at 25°C. to insure that the gas entered the short wetted-wall column very near that temperature. The mass flow rate of gas was maintained at approximately 2 lb./hr. at all chlorine mole fractions; thus, the gas stream Reynolds number was of the order of 650. Under this condition, the liquid-phase mass transfer coefficient should be insensitive to gas flow rate (*14*). This gas flow rate was sufficiently high, however, to insure that the change in chlorine gas-phase mole fraction was negligible as the gas stream passed through the column. Also, the gas-phase resistance to mass transfer was quite small. The gas-phase composition was calculated from the metered flow rates of chlorine and nitrogen. The column pressure was approximately atmospheric.

In most of the runs the liquid stream samples were analyzed for ferrous and ferric ion concentrations. Ferrous ion was determined by titrating the sample with potassium dichromate by the use of barium diphenylamine sulfonate as an indicator. The titration was performed in the presence of phosphoric acid. Ferric ion was determined by adding potassium iodide to the sample and titrating the liberated iodine with sodium thiosulfate. The oxidation of the iodide ion by the ferric ion was catalyzed by cuprous iodide, which was added to the sample. In the chemical absorption experiments, the absorption rate was determined from the liquid flow rate and the difference between the ferric ion concentrations in the outlet and inlet liquid streams.

In the physical absorption experiments, in which the liquid phase contained no ferrous chloride, the exit liquid contained free chlorine. In these cases, the exit liquid sample was collected beneath the surface of an aqueous solution of potassium iodide and sodium hydroxide. The sample was then acidified, and the liberated iodine was titrated with sodium thiosulfate.

In addition to the absorption rate experiments, experiments were also performed to determine the effect of ferric chloride concentration on the solubility of chlorine in dilute hydrochloric acid solutions and to determine the effect of ferrous chloride concentration on the viscosity of hydrochloric acid solutions.

A summary of the original data and calculated results of this investigation is tabulated in reference (*3*), a thesis available at the M. I. T. Library.

RESULTS AND DISCUSSION

Figure 1 shows a plot of the physical absorption results; in these experiments, no ferrous chloride was added to the liquid phase. The variables are plotted as

$$k_L^* \sqrt{h/D_A} \text{ vs. } \Gamma/\sqrt{\xi}$$

in order to correct for minor variations in the column height, the chlorine liquid-phase diffusivity, and the liquid density and viscosity. It should be emphasized, however, that variations in these quantities were slight; the true variables are liquid flow rate and liquid-phase absorption coefficient. The liquid-phase absorption coefficient, k_L^*, is defined as the chlorine absorption rate in moles per unit time divided by the entire interfacial area in the column and by the liquid phase driving force at the top of the column. Since the entering liquid was always free of chlorine, the driving force was simply the interfacial concentration of chlorine in the liquid phase, calculated from the gas-phase partial pressure and the chlorine-solubility relationship, a small correction being applied for gas-phase resistance. In order to make the gas-phase-resistance correction, the gas-phase coefficient was calculated from the theoretical results of Boelter (*2*), but it should be noted that the correction never exceeded 6.4% in any of the runs, including runs with and without the chemical reaction accompanying the absorption process. The diffusivity of chlorine in water at 25°C. was taken as 1.48×10^{-5} sq. cm./sec., as reported by Vivian and Peaceman (*14*). This value was corrected for temperature variations and also for variations in liquid viscosity due to the presence of hydrochloric acid, ferrous chloride, and ferric chloride by the Stokes-Einstein equation:

$$D \propto T/\mu$$

In one series of runs, 0.22 moles/liter of ferric chloride were added to the liquid phase in order to test, somewhat, the corrections applied for variations in diffusivity, viscosity, density, and chlorine solubility.

The experimental results of Vivian and Peaceman (*14*) and the theoretical equation

$$k_L^* \sqrt{h/D_A} = (2/\sqrt{\pi})(9g/8\mu_w\rho_w)^{1/6}(\Gamma/\sqrt{\xi})^{1/3} \qquad (2)$$

are plotted in Figure 1 for comparison with the experimental results of this study. Equation (2) is derived from the penetration theory and from streamline-flow theory (*14*). It can be seen from Figure 1 that the results of this study substantiate the conclusion of Vivian and Peaceman that the agreement between Equation (2) and experimental physical absorption coefficients in the short wetted-wall column is encouraging. These authors attributed the deviation observed to the probable deviation of the true liquid exposure time on the column wall from the exposure time predicted by the theoretical equation for well-

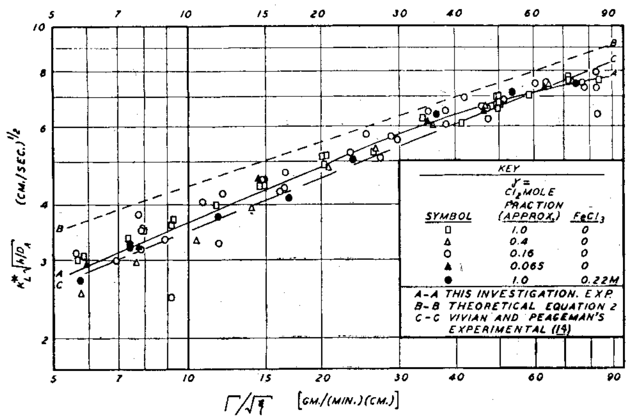

Fig. 1. Physical absorption results. Absorption of chlorine into dilute hydrochloric acid.

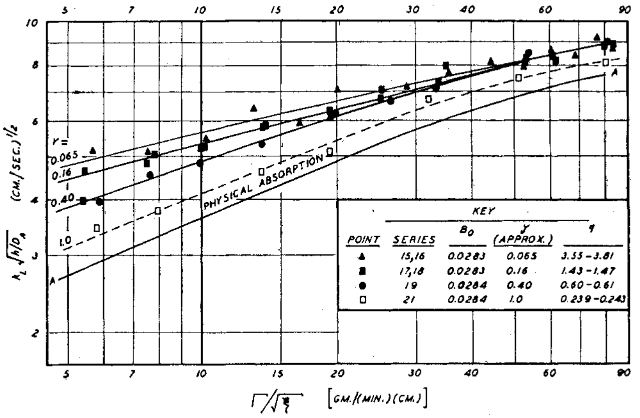

Fig. 2. Absorption of chlorine into 0.028 *M* ferrous chloride.

developed streamline flow, which was used in deriving Equation (2). Such an explanation seems quite reasonable, especially considering the fact that it is the surface layer velocity which is of prime importance. Right at the end of the liquid inlet slot, the liquid surface velocity would be expected to be zero, due to the drag of the slot wall. The surface layer should accelerate, perhaps reaching the theoretical velocity for well-developed flow further down the wall, but the effect of the entrance slot should cause the surface-layer exposure time to be greater than that used in deriving Equation (2); thus, the absorption coefficient should be lower. Another departure of the actual liquid flow pattern from the idealized one used in deriving Equation (2) is the presence of a standing wave which was observed to form on the column wall near the bottom of the column. While the presence of a standing wave was not reported by Vivian and Peaceman, it has been reported by subsequent investigators (*4*, *1*). The standing wave can be eliminated under certain conditions, but it is felt that it does have an effect on the rate of gas absorption in a short wetted-wall column (*3*).

Figures 2, 3, 4, and 5 show the chemical absorption results; ferrous chloride was present in the liquid phase during these experiments. The variables plotted are the same as the variables in Figure 1, except that the liquid-phase absorption coefficient in the presence of a chemical reaction, k_L, has replaced the physical absorption coefficient, k_L^*. The variables are grouped as $k_L\sqrt{h/D_A}$ vs. $\Gamma/\sqrt{\xi}$ in order to facilitate comparison with the physical absorption results; it should not be inferred that such a grouping corrects for variations in column height, viscosity, density, and diffusivity for absorption in the presence of a chemical reaction. In the calculation of k_L, the chlorine solubility relationship was corrected for the presence of ferric chloride in the liquid phase. It was assumed, for this correction, that the ferric chloride concentration at the gas-liquid interface was equal to the inlet concentration of ferrous chloride. This assumption, based on the film theory model for an infinitely rapid reaction and for equal diffusivities for the ferrous and ferric ions, was probably adequate for making this small correction which never exceeded 9%.

The experimental curve for physical absorption, Curve *A*-*A* from Figure 1, is shown in Figures 2 through 5 for comparison with the chemical absorption results. It can be seen from these graphs that the presence of ferrous chloride in the liquid phase causes the absorption coefficient to be greater than that which would be expected if no chemical reaction took place. It can be seen also that the absorption coefficient in the presence of the chemical reaction is, in general, less sensitive to variations in the liquid flow rate than is the physical absorption coefficient. Finally, it should be noted that the chemical absorption coefficient is not insensitive to variations in the chlorine gas phase mole fraction, y, as is the physical absorption coefficient.

THEORETICAL CONSIDERATIONS

It is constructive to consider the dimensionless groups involved in the problem of gas absorption accompanied by an irreversible chemical reaction. For the case in which the absorbing species, A, dissolves into the liquid phase and then reacts irreversibly with the nonvolatile solute, B, consuming ν molecules of B for each molecule of A, according to the kinetic equation

$$-dA/dt = k_1 A^n B^m \qquad (3)$$

the penetration theory predicts (*3*) that, for fixed values of n and m

$$\phi \equiv k_L/k_L^*$$

is a unique function of the following variables:

$$\sqrt{M} \equiv \sqrt{k_1 D_A B_0^m A_i^{n-1}}/k_L^*$$

$$q \equiv B_0/\nu A_i$$

$$r \equiv D_B/D_A$$

The variable ϕ is the ratio of the absorption coefficient in the presence of a chemical reaction to that which would be expected if the reaction did not take place; thus, it is an index of the effect of the reaction on the absorption rate. That ϕ is a unique function of $\sqrt{M}$, r, and q could be derived by dimensional analysis if it were assumed that the liquid flow pattern could be characterized by a single parameter, k_L^*. The film theory predicts (*3*) that r and q enter only as their product, ϕ being a unique function of $\sqrt{M}$ and rq.

For the particular case of a second-order reaction in which n and m are both equal to unity, the film-theory solution can be closely approximated by the equation:

$$\phi = \frac{\sqrt{M}\sqrt{1 - (\phi - 1)/rq}}{\tanh[\sqrt{M}\sqrt{1 - (\phi - 1)/rq}]} \qquad (4)$$

Equation (4) was first presented by Van Krevelen and Hoftijzer (*13*), and its accuracy was shown by Peaceman (*6*). For the particular case in which r is equal to unity, Equation (4) is also a good approximation to the penetration-theory solution (*3*).

Figure 6 shows a graph of Equation (4). The graph shows that ϕ approaches unity at low values of $\sqrt{M}$; this indicates that a slow reaction has no effect on the absorption coefficient. At large values of $\sqrt{M}$, it can be seen that ϕ approaches an asymptote for each value of rq. This asymptotic region corresponds to the condition of an "infinitely rapid" reaction, a further increase in the value of k_1 having no effect on the absorption rate. In the infinitely rapid reaction region, ϕ is given by the equation

$$\phi_a = 1 + rq \qquad (5)$$

For any fixed value of $\sqrt{M}$, ϕ approaches an asymptote at large values of the parameter rq. The curve for rq equal to infinity shows the locus of these asymptotic values. As this asymptote is approached, the concentration of species B becomes essentially constant throughout the liquid phase at a value of B_0; thus, species A reacts pseudo first order. For values of ϕ greater than 2, the pseudo first-order reaction curve is seen to be closely approximated by the equation

$$\phi = \sqrt{M} \qquad (6)$$

or

$$k_L/k_L^* = \sqrt{k_1 D_A B_0}/k_L^* \qquad (6a)$$

or

$$k_L = \sqrt{k_1 D_A B_0} \qquad (6b)$$

Therefore, in the pseudo first-order region, k_L becomes independent of k_L^* and thus independent of liquid flow rate.

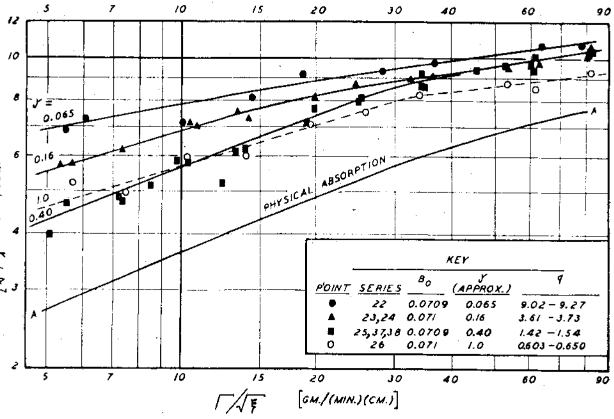

Fig. 3. Absorption of chlorine into 0.07 M ferrous chloride.

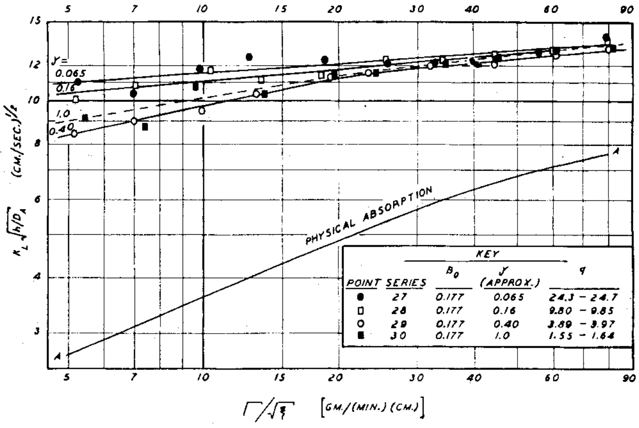

Fig. 4. Absorption of chlorine into 0.177 M ferrous chloride.

COMPARISON OF THEORY AND EXPERIMENT

In a comparison of the experimental results in Figures 2 through 5 with these theoretical predictions, several observations can be made. First, while the physical absorption coefficient varies with approximately the 0.4 power of the liquid flow rate, the chemical absorption coefficient is seen to be relatively insensitive to liquid flow rate in some of the runs. For Series 27 in Figure 4 and Series 31 in Figure 5, it can be seen that the absorption coefficient is almost independent of the liquid flow rate, Γ. The value of q for each of these series is approximately 25, the highest value studied. It would appear, then, that the pseudo first-order region was closely approached. Since the inlet ferrous chloride concentration, B_0, was 0.177 M in Series 27 and 0.442 M in Series 31, Equation (6*b*) would predict that the ratio of the values of $k_L\sqrt{h/D_A}$ for Series 31 and Series 27 should be the square root of the ratio 0.442/0.177, or 1.58. This is very nearly the case, the mean value of $k_L\sqrt{h/D_A}$ being approximately 19 for Series 31 and approximately 12 for Series 27. It should be emphasized that, for the case of the more general kinetic equation, in which n and m are not necessarily equal to unity [Equation (3)], the equation corresponding to Equation (6*b*) takes the form (*3*)

$$k_L = \sqrt{2/(n+1)}\sqrt{k_1 D_A B_0{}^m A_i{}^{n-1}} \qquad (7)$$

Thus, the fact that the ratio of the values of $k_L\sqrt{h/D_A}$ for Series 31 and 27 is approximately 1.58 supports the idea that the value of m is near unity. Inspection of Figures 4 and 5 shows that the absorption coefficient is a weak function of the chlorine gas-phase mole fraction, y, and thus the value of A_i, in the region near Series 27 and Series 31. This suggests, according to Equation (7), that the value of n is near unity. Substitution of a value of $k_L\sqrt{h/D_A}$ equal to 19 (cm./sec.)$^{1/2}$, B_0 equal to 0.442 M, and h equal to 4.64 cm. into Equation (6*b*) yields a value of 176 liters/(g. mole)(sec.) for the reaction rate constant, k_1.

The preceding analysis indicates that the results of Series 27 and 31 suggest that the chemical reaction is second order, both n and m being unity, with a rate constant of 176 liters/(g. mole)(sec.). The analysis was approximate because Equations (6*b*) and (7) apply only to the asymptotic region at large values of rq, and this region was only approached in the experimental system. The following analysis, which is not limited to large values of rq, will test these conclusions further. It was pointed out earlier that, for the case in which the chemical kinetics are described by Equation (3), ϕ should be a unique function of $\sqrt{M}$, r, and q. It follows, then, that if experiments be conducted in which B_0 and A_i are both varied but the ratio B_0/A_i is maintained constant, ϕ should be a unique function of the variable

$$\sqrt{D_A B_0{}^{m+n-1}}/k_L^*$$

if the diffusivity ratio, r, and the reaction rate constant, k_1, remain constant. In this study, B_0 was varied by adding ferrous chloride to the liquid phase, and A_i was varied by diluting the gas phase with nitrogen, but a number of series was made with the same ratio B_0/A_i. For all such series made at the same value of q, the separate effects of liquid flow rate and concentration level should be correlated by plotting ϕ vs. $\sqrt{D_A B_0^{m+n-1}}/k_L^*$. Figure 7 shows a plot of ϕ vs. $13.7\sqrt{D_A B_0}/k_L^*$ for Series 27 and 31. The points for the two series can be seen to agree quite well with a single curve, supporting the choice of unity for the exponent of B_0 under the square root sign and indicating that the sum of n and m is 2. The factor 13.7 in the abscissa for the experimental points was chosen so that the points would agree with the solid curve shown, which represents Equation (4) for a value of rq equal to 25. In a comparison of the abscissas plotted for the theoretical curve and the experimental points, the factor 13.7 indicates that the reaction rate constant, k_1, is equal to

$$k_1 = (13.7)^2 = 188 \text{ liters/(g. mole)(sec.)}$$

Figures 8 through 11 show the rest of the chemical absorption results plotted as ϕ vs. $13.7\sqrt{D_A B_0}/k_L^*$. Each figure is for a different value of q, and the solid curve in each figure represents Equation (4) for the value of q in question and for a value of r equal to unity. It can be seen from Figures 7 through 11 that the results correlate well in this manner and that they agree with the film theory equation for a second-order reaction with a rate constant of 188 liters/(g. mole)(sec.), except for the marked deviations shown by the series made with pure chlorine gas.

The runs made with pure chlorine gas are seen to deviate quite seriously from the correlation of Figures 7 through 11 and from the theoretical curves; in these graphs, all of the pure chlorine-gas results appear to be too high. Also, the results of the pure chlorine-gas runs appear to be too high in Figures 2 through 5, and the series that they are compared with in Figures 2 through 5 are different from the series that they are compared with in Figures 7 through 11. Thus, the pure chlorine-gas runs show positive deviations from the general pattern of the other results. Some of the runs with 40% chlorine gas show a similar deviation, but to a much less extent.

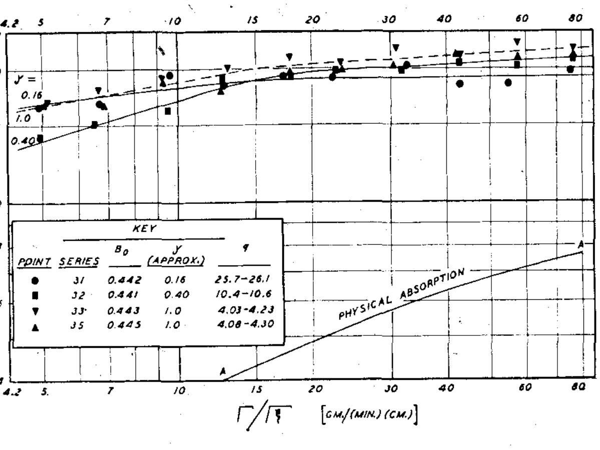

Fig. 5. Absorption of chlorine into 0.44 M ferrous chloride.

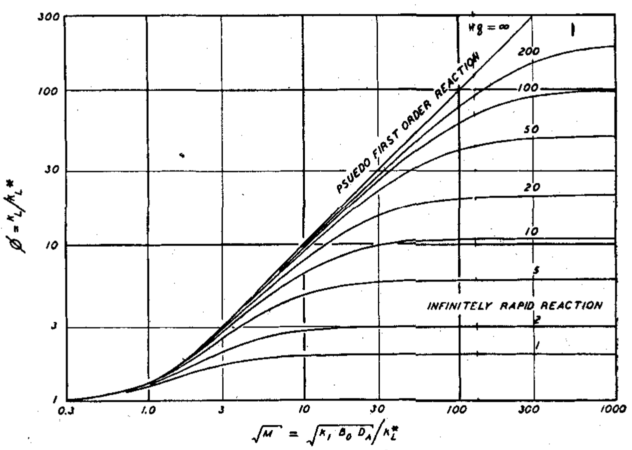

Fig. 6. Film-theory solution for a second-order irreversible reaction (*13*) [Equation (4)].

At first it was suspected that the reason for the high results of the pure chlorine-gas runs might be changes in the reaction rate constant due to temperature rise caused by the heat of reaction. The heat of the chemical reaction caused the mixed mean temperature of the liquid to rise as it passed through the short wetted-wall column. This temperature rise was much greater in the pure chlorine-gas runs than it was in any of the other runs; the maximum mixed mean temperature rise encountered was approximately 3.5°C. However, experimental measurements of the effect of temperature on the absorption rate and a theoretical analysis of temperature gradients within the liquid layer on the column wall indicate clearly that temperature rise could not have caused deviations as large as those of Series 33 and 35 in Figure 9. For example, Figure 12 shows the results of Series 33 and 35 compared with the results of two other series which were made under the same conditions as Series 33 and 35 except that the inlet liquid and gas temperatures were different from 25°C. From Figure 12 it can be seen that $k_L\sqrt{h/D_A}$ increases approximately 2.2% for each degree Centigrade rise in temperature. A theoretical analysis indicates (*3*) that, for the lowest liquid flow rate of Series 33 and 35, in which the mixed mean liquid temperature rose from 25 to 28.5°C., the hottest point within the liquid layer on the column wall was cooler than 28.7°C. Thus, temperature rise could have increased the coefficients determined in Series 33 and 35 by only 8%. The use of an average temperature in evaluating the chlorine solubility, the chlorine diffusivity, and the liquid viscosity and density might have introduced an error as great as 7% into the calculations, but temperature rise can account for no more than a 15% deviation in the results of Series 33 and 35; it cannot account for a deviation as great as that observed in Figure 9. A theoretical analysis (*3*) also indicated that natural convection, caused by the temperature and concentration gradients in the liquid layer, had a negligible effect on the absorption coefficient.

If the diffusivity ratio, r, is less than unity, both the film and the penetration theories predict that ϕ_a, the asymptotic value of ϕ at large values of $\sqrt{M}$, must be less that the quantity $(1 + q)$:

$$\phi_a < 1 + q \quad (\text{for } r < 1)$$

It can be seen in Figures 9, 10, and 11 that the experimental results obtained in the pure chlorine-gas runs exceeded the limitation of the above inequality, even though the value of r is thought to be less than unity. It should be emphasized that such a deviation from the theories cannot be explained in terms of a varying reaction rate constant or in terms of uncertainties about the reaction rate equation. The deviation could be explained if r were really considerably greater than unity, but this is very unlikely in this system.

If r is taken as the ratio of the salt diffusivity of ferrous chloride to the diffusivity of chlorine, a value of 0.65 results. The effective diffusivity of the *ferrous ion in the* experimental system would be expected to be different from the salt diffusivity of ferrous chloride, however, because the experimental system involved "counter-ion" diffusion. With the techniques employed by other investigators (*11*, *5*) and the adoption of the film-theory model for an infinitely rapid reaction, counter-ion diffusion considerations lead (*3*) to the conclusion that the effective diffusivity of the ferrous ion in the experimental system is only 59% as great as the salt diffusivity of ferrous chloride, thus indicating that the value of r is only 0.38.

The penetration-theory solution for absorption accompanied by a second-order reaction is not available for the case in which r is different from unity and the reaction rate is not infinite, but an approximation to the solution can be obtained by using Equation (4) with rq replaced by $(\phi_a - 1)$, where ϕ_a is obtained from the penetration-theory solution for an infinitely rapid reaction. Thus, the solution becomes

$$\phi = \frac{\sqrt{M}\sqrt{1-(\phi-1)/(\phi_a-1)}}{\tanh[\sqrt{M}\sqrt{1-(\phi-1)/(\phi_a-1)}]} \tag{8}$$

where ϕ_a is obtained from the parametric equations

$$\phi_a = 1/\text{erf}\,(\sigma)$$

$$q\sqrt{r} = \frac{1 - \text{erf}\,(\sigma/\sqrt{r})}{\text{erf}\,(\sigma)e^{\sigma^2(1-1/r)}}$$

The dotted curves and the dashed curves in Figures 7 through 11 were obtained from these equations for values of r equal to 0.65 and 0.38, respectively, with the use of the values of q shown under the titles of the graphs. It can be seen that the theoretical curves are not very sensitive to the value of r in the range of variables covered, and the true value of r in the experimental system cannot be readily deduced by comparing these curves with the experimental results.

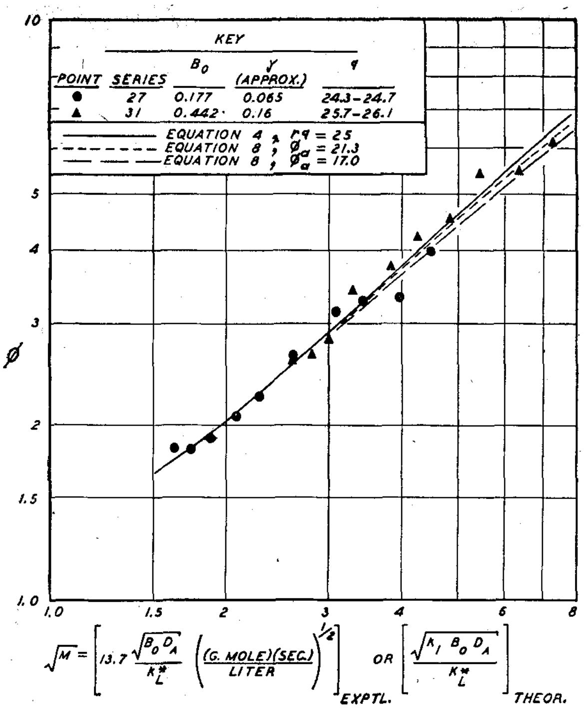

Fig. 7. Correlation of results, $q = 25$.

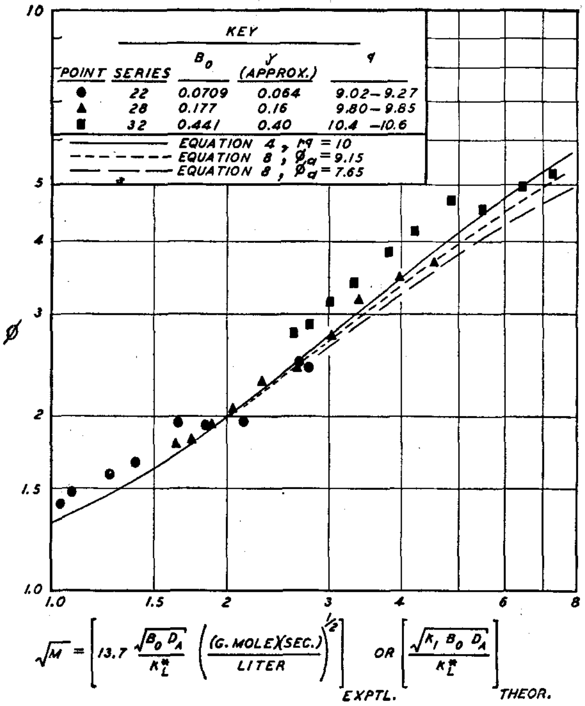

Fig. 8. Correlation of results, $q = 10$.

REACTION MECHANISM

One possible reason for the fact that the experimental values of ϕ exceeded the values of $(1 + q)$ is that the q values were really greater than those calculated. The values of q were calculated as

$$q = B_0/2A_i$$

a value of 2 being used for the stoichiometric factor, ν, as indicated by the over-all reaction expressed in Equation (1). It is possible, however, that the effective value of the stoichiometric factor may have been less than 2. If the over-all reaction expressed by Equation (1) proceeded according to the two-step mechanism

$$\text{Cl}_2 + \text{Fe}^{++} = \text{Intermediate} \tag{9}$$

$$\text{Intermediate} + \text{Fe}^{++} = 2\,\text{Cl}^- + 2\,\text{Fe}^{+++} \tag{10}$$

and if the first step were irreversible and the second step were very slow, then the first step would be the only reaction affecting the rate of chlorine absorption. The effect on the absorption rate would be that of an irreversible reaction with a stoichiometric factor of unity. Of course, eventually two ferrous ions would be consumed for each chlorine molecule reacted, but if the second step were very

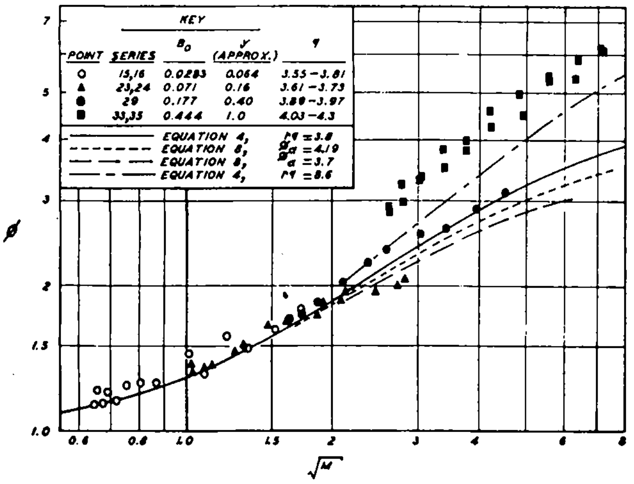

Fig. 9. Correlation of results, $q = 3.8$.

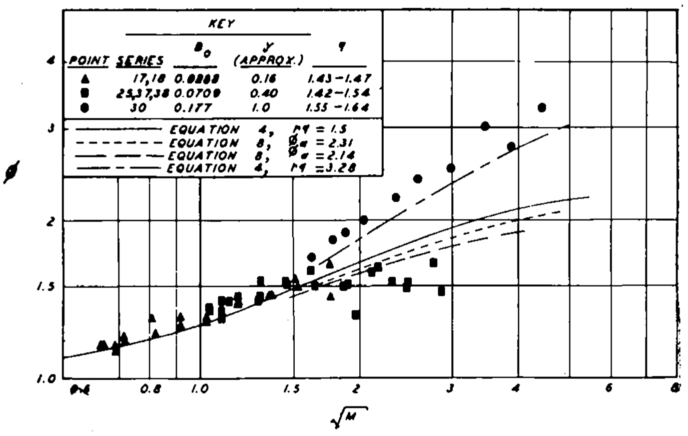

Fig. 10. Correlation of results, $q = 1.5$.

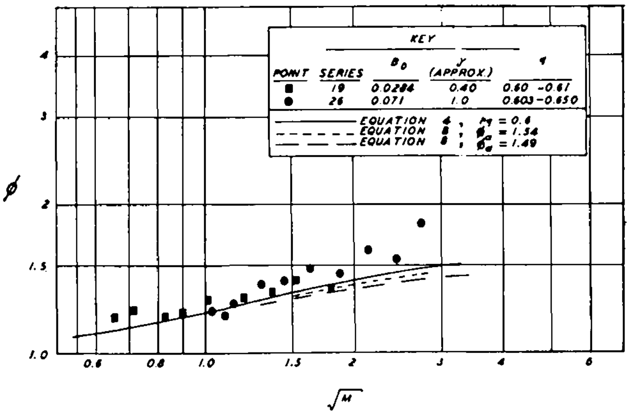

Fig. 11. Correlation of results, $q = 0.6$.

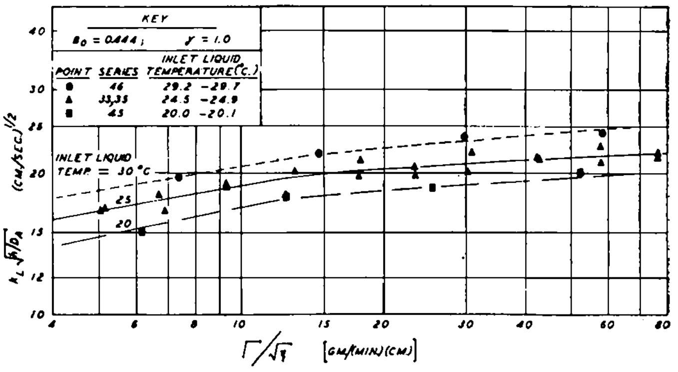

Fig. 12. Effect of temperature.

slow it would not affect the concentration profile of the ferrous ions, and the effective stoichiometric factor would be unity. If, on the other hand, the second reaction step were very fast compared to the first step, two ferrous ions would be consumed instantaneously as each chlorine molecule reacted, and the effective stoichiometric factor would be 2. It is clear that the effective value of the stoichiometric factor could take on any value from 1 to 2 as the rate of the second reaction step varied from very slow to very fast, relative to the rate of the first reaction step. It is possible that, with an intermediate reaction rate for the second step, the effective value of ν might vary with concentration level, thus destroying the correlation of Figures 7 through 11. This would occur only if the kinetic equations for the two reaction steps were of different order. For example, if the first reaction step were second order and the second reaction step were first order, the dimensionless parameter which would depict the relative rates of the two reaction steps would be

$$k_2/B_0k_1$$

Thus, a decrease in the concentration level would have the same effect as an increase in the ratio k_2/k_1, namely to increase the rate of the second reaction step, relative to that of the first; thus a higher value of ν and a lower value of ϕ would result. For such a system, the correlation of Figures 7 through 11 would not hold because ϕ would not be a unique function of B_0/A_i, r, and $\sqrt{M}$; the group k_2/B_0k_1 would also be a variable, and it would vary even if k_2/k_1 were constant. Thus, in the correlation of Figures 7 through 11, the series made at high concentration levels would have higher values of ϕ than the series with lower concentration levels, even at the same values of B_0/A_i and $\sqrt{M}$. This is the kind of deviation exhibited by the pure chlorine-gas series in Figures 9 through 11. The correlation would not be destroyed in the vicinity of the pseudo first-order reaction region, however, because the value of ν is unimportant in that region.

Thus, it is seen that the reaction mechanism of Equations 9 and 10, with the first step being second order and the second step being first order, would explain, at least qualitatively, the deviations observed in the experimental results. The first reaction step, Equation (9), would be expected to be first order in ferrous ion concentration and first order in chlorine concentration; this is in agreement with what was inferred earlier from the experimental results. The second step would be expected to be second order it it proceeded according to Equation (10), and so it would probably involve several steps if it were first order.

The most likely form of the "Intermediate" in Equation (9) is a complex ion. Since both iron and chlorine have strong tendencies toward complex ion formation, it does not seem unreasonable that the complex ion, $Cl_2 \cdot Fe^{++}$, would form:

$$Cl_2 + Fe^{++} = Cl_2 \cdot Fe^{++} \qquad (9a)$$

This complex ion could then oxidize another ferrous ion:

$$Cl_2 \cdot Fe^{++} + Fe^{++} = 2Cl^- + 2Fe^{+++} \qquad (10a)$$

Since the indication is that the second step would have a kinetic equation of order less than two, this step might proceed according to two steps, the first of which is the first-order decomposition of the complex ion:

$$Cl_2 \cdot Fe^{++} = Cl^- + Cl \cdot Fe^{+++} \qquad (11)$$

$$Cl \cdot Fe^{+++} + Fe^{++} = Cl^- + 2Fe^{+++} \qquad (12)$$

Thus, a likely form of the reaction mechanism is

$$Cl_2 + Fe^{++} = Cl_2 \cdot Fe^{++} \qquad (9a)$$

$$Cl_2 \cdot Fe^{++} = Cl^- + Cl \cdot Fe^{+++} \qquad (11)$$

$$Cl \cdot Fe^{+++} + Fe^{++} = Cl^- + 2Fe^{+++} \qquad (12)$$

in which the first step is essentially irreversible, the second step is slow, relative to the first step, and the third step is fast, relative to the second step. Such a mechanism seems reasonable; it would explain the second-order kinetic equation found for a trimolecular over-all reaction; and it would allow the effective stoichiometric factor to decrease with increasing concentration, perhaps becoming as low as unity.

If the effective value of ν is taken as unity, all of the q values become twice the values presented, and none of the experimental values of ϕ surpass the expected values of ϕ_a. The "dashed-dotted" curves in Figures 9 and 10 are plots of Equation (4) in which r was taken as unity and q was taken as twice the value reported for the pure chlorine-gas series on the graph, thus corresponding to a value of ν equal to unity. While the experimental results for the pure chlorine-gas series are still 12 to 15% higher than these dashed-dotted curves, this smaller discrepancy could have been caused by temperature rise. It is quite possible, then, that a reaction mechanism such as the one expressed by Equations (9*a*), (11), and (12) could be responsible for the deviations of the results of the pure chlorine-gas series and for these results exceeding the expected asymptotic values.

It should be emphasized that the complex ions shown in Equations (9*a*), (11), and (12) have neither been isolated nor shown to exist, and the reaction mechanism has not been proven to be in accordance with these equations. The proposed mechanism is presented as a plausible one which is in agreement with the curious behavior of the absorption rate data, but other mechanisms could presumably meet this requirement also.

CONCLUSION

From the results of this study, it is concluded that the film and penetration theories and dimensional analysis can be used to infer the order of a chemical reaction and the reaction rate constant from data on the rate of gas absorption accompanied by the chemical reaction. It is also concluded that the absorption rate data for the chlorine-ferrous chlorine system are in good agreement with theoretical predictions for absorption accompanied by a second-order reaction with a rate constant of 188 liters/(g. mole)(sec.), except for the data taken with pure chlorine gas. The assumption of a three-step reaction mechanism, involving the formation of a complex ion and the decomposition of the complex ion, explains, at least qualitatively, the apparent deviations of the pure chlorine gas runs.

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NOTATION

A = concentration of species A, the gas being absorbed in general and chlorine in the experimental system, g. moles/liter.
B = concentration of species B, the nonvolatile solute in general and ferrous chloride in the experimental system, g. moles/liter.
D = liquid-phase diffusivity, sq. cm./sec.
e = 2.71828 . . .
erf (σ) = $(2/\sqrt{\pi}) \int_0^\sigma e^{-x^2}\,dx$
g = acceleration due to gravity, (cm.)/(sec.)^2
h = height of the short wetted-wall column, cm.
k_1 = reaction rate constant, in general and also for the first reaction step, liters/(g. mole)(sec.) for a second-order reaction.
k_2 = reaction rate constant for the second reaction step.
k_L = liquid-phase absorption coefficient, cm./sec.
M = $k_1 \; D_A B_0{}^m A_i{}^{n-1}/(k_L{}^*)^2$, theoretically.
= $(13.7)^2 \; D_A B_0/(k_L{}^*)^2$, for experimental values, (g. mole)(sec.)/(liter).
m = exponent of B in the reaction rate equation.
n = exponent of A in the reaction rate equation.
q = $B_0/\nu A_i$ in general and $B_0/2A_i$ for experimental values.
r = D_B/D_A
T = absolute temperature, °K. or °R.
t = time, sec.
tanh (x) = $(e^x - e^{-x})/(e^x + e^{-x})$
y = gas phase mole fraction of chlorine, dry basis.

Greek Letters

Γ = liquid flow rate per unit perimeter of the column, g./(min.)(cm.).
μ = liquid viscosity, g./(cm.)(sec.).
ν = moles of species B consumed per mole of species A reacted.
ξ = $(\mu/\mu_w)(\rho/\rho_w)$
π = 3.14159 . . .
ρ = liquid density, g./cc.
σ = parameter in parametric equations.
ϕ = $k_L/k_L{}^*$

Subscripts

A = species A, the gas being absorbed in general and chlorine in the experimental system.
a = asymptotic value at large values of $\sqrt{M}$.
B = species B, the non-volatile solute in general and ferrous chloride in the experimental system.
i = the gas-liquid interface.
0 = film theory, the bulk liquid. penetration theory, the liquid at the start of a time of exposure. experimental, the liquid entering the short wetted-wall column.
w = the properties of water at 25°C.

Superscripts

* = physical absorption.

LITERATURE CITED

1. Beecher, Norman, Sc.D. thesis, Mass. Inst. Technol., Cambridge (1957).
2. Boelter, L. M. K., *Trans. Am. Inst. Chem. Engrs.*, **39**, 557 (1943).
3. Brian, P. L. T., Sc.D. thesis, Mass. Inst. Technol., Cambridge (1956).
4. Emmert, R. E., Ph.D. thesis, Univ. Del., Newark (1954).
5. Goldstein, D. J., Sc.D. thesis, Mass. Inst. Technol., Cambridge (1956).
6. Peaceman, D. W., Sc.D. thesis, Mass. Inst. Technol., Cambridge (1950).
7. Perry, R. H., and R. L. Pigford, *Ind. Eng. Chem.*, **45**, 1247 (1953).
8. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2nd ed., 339, McGraw-Hill Book Co., Inc., New York (1952).
9. *Ibid.*, p. 321.
10. *Ibid.*, p. 328.
11. Sherwood, T. K., and J. C. Wei, *A.I.Ch.E. Journal*, **1**, 522 (1955).
12. Stephens, E. J., and G. A. Morris, *Chem. Eng. Progr.*, **47**, 232 (1951).
13. Van Krevelen, D. W., and P. J. Hoftijzer, *Rec. trav. chim.*, **67**, 563 (1948).
14. Vivian, J. E., and D. W. Peaceman, *A.I.Ch.E. Journal*, **2**, 437 (1956).

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