Interfacial Resistance in Gas Absorption

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A laminar jet method for contracting a liquid with a gas for contact times down to 1 msec. has been developed. A jet is formed with a very thin square-edged orifice to minimize boundary-layer effects, and the rate of absorption of carbon dioxide into water is found to depend only upon contact time, an indication that the method is self-consistent.

The rate of absorption of carbon dioxide into pure water is 1 to 4% lower than the theoretical rate for absorption into a jet in rodlike flow the surface of which is instantaneously saturated. This indicates that, at most, interfacial resistance in this system is small and justifies the common assumption of interfacial equilibrium.

Jets with thick boundary layers were formed with other types of orifices, and the absorption rates into these jets were lower than the theoretical value because of the decreased surface velocity. This effect can be easily mistaken for an interfacial resistance.

The presence of a commercial surface-active agent causes an apparent interfacial resistance which is due at least partly to a hydrodynamic effect.

INTERFACIAL RESISTANCE IN GAS ABSORPTION

When two molecular systems which are not in equilibrium with one another are brought into contact, equilibrium between the material on either side of the interface can be attained only when the entire system comes to equilibrium. More specifically, if a gas is contacted with a liquid which is unsaturated with respect to the gas, then, even if there were no transfer of the molecules from the liquid surface to the bulk of the liquid, a finite time would be necessary to saturate the liquid interface because of the finite rate at which the gas molecules strike the interface. In reality gas molecules are continuously transferred from the interface to the bulk liquid until equilibrium is attained, and during this entire time the interface must be unsaturated in order for transfer to take place.

This nonequilibrium at the interface appears as an extra resistance to mass transfer and under certain conditions acts like the usual individual mass transfer coefficient. Because of the lack of knowledge of interfacial phenomena it has been commonly assumed that the interface is always saturated, that is, in gas absorption the gas side of the interface is in equilibrium with the gas molecules dissolved in the liquid surface. This procedure essentially combines any surface resistance with either the liquid or gas side resistance. One reason for separating the surface resistance from the other resistances is that it would be expected to vary in a manner quite different from the other resistances.

The *simplest* mechanism that will describe the transfer across the interface is a first-order process described by

$$N_A = k_s'(C_i^* - C_i) \qquad (1)$$

Physical significance can be given to k_s by using the kinetic theory of gases to compute the rate at which soluble molecules strike and leave the interface. The net rate is the difference between these rates, and it is found that

$$k_s' = \frac{\alpha H}{\sqrt{2\pi RTM}} \qquad (2)$$

where α, the condensation coefficient, is the fraction of the molecules striking the surface which actually condense. Henry's Law has been assumed.

Another interpretation is that there is a very narrow region in the liquid adjacent to the interface where the diffusivity is very low and Fick's Law holds; so

$$N_A = \frac{D_i}{y_0}(C_i - C_{y0}) = k''(C_i - C_{y0}) \qquad (3)$$

and from Equations (1) and (3)

$$N_A = k_s(C_i^* - C_{y0}) \qquad (4)$$

where

$$\frac{1}{k_s} = \frac{1}{k_s'} + \frac{1}{k_s''} \qquad (5)$$

and y_0 is the thickness of the region of resistance.

Thus interfacial resistance may be described by either or both of two first-order processes: one is due to nonequilibrium at the interface, which leads to an apparent resistance at $y = 0$; and the other is due to an extra diffusional type of resistance which leads to nonequilibrium between the interface and y_0, over and above the usual small nonequilibrium which would exist between those two points.

If the over-all process is at a steady state, the rate of transfer from the gas to the interface must be equal to the rate across the interface and in turn to the rate from the interface to the liquid. For the over-all process then,

$$N_A = K_L(C^* - C_L) \qquad (6)$$

$$\frac{1}{K_L} = \frac{1}{Hk_g} + \frac{1}{k_s} + \frac{1}{k_L} \qquad (7)$$

Since k_s can never be infinite, C_i^* and C_i can never be equal when transfer is taking place, and K_L is always less than the value corresponding to zero surface resistance ($k_s = \infty$). However if k_s is much greater than Hk_g or k_L, its effect on K_L is negligible, and, since the transfer rate is then controlled by the other resistance in the system, C_i approaches C_i^* and interfacial equilibrium is essentially attained. For example, if there is no diffusional resistance at the interface, the lack of equilibrium is due only to the finite rate at which gas molecules strike the interface, and if α is one, k_s is enormous and can be completely neglected.

To measure k_s the other resistances in the system must be made as small as possible and should be known. The gas-side resistance can be eliminated by using a pure gas, but owing to the low diffusivities of gases in liquids the liquid side is more difficult to handle. The best method appears to be to use a liquid in laminar flow so that the transfer with and without surface resistance may be directly calculated from diffusion theory and to make the liquid-side resistance as small as possible by reducing the gas-liquid contact time to a minimum.

A number of workers have attempted to measure k_s in gas absorption, and Higbie (*9*), Emmert and Pigford (*6*), and Danckwerts and Kennedy (*5*) have all reported appreciable interfacial resistances in the carbon dioxide–water system; Emmert and Pigford have also reported a large resistance in the O_2–water system. Matsuyama's data, on the contrary, indicated negligible resistance in the carbon dioxide–water system (*12*).

This work was carried out with unsteady state methods in short and long wetted-wall columns, rotating drums, laminar jets, and gas bubbles moving in tubes. Although the results of the vari-

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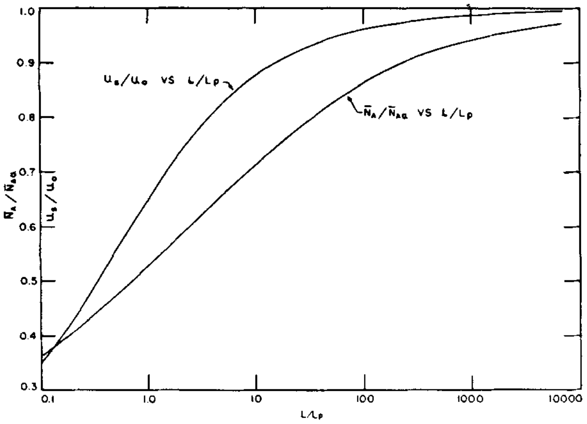

Fig. 1 Effect of boundary layer on the surface velocity and on the average rate of absorption.

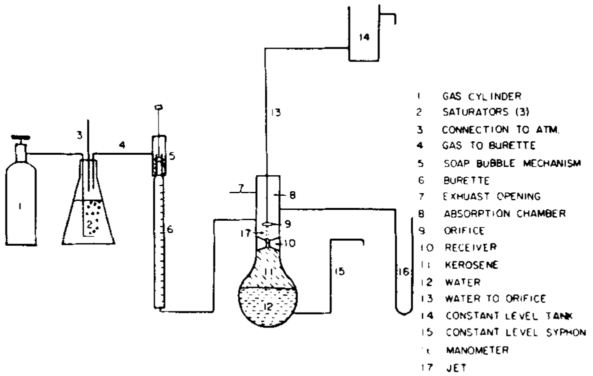

Fig. 2 Flow diagram of the apparatus.

ous methods, except for Matsuyama's, are in rough agreement for carbon dioxide–water, the sensitivity of the conclusions to experimental error makes them inconclusive. More particularly it will be shown that boundary-layer effects, which make the true gas-liquid contact time greater than the apparent contact time, may cause a reduction in the absorption rate which may easily be interpreted as an interfacial resistance. Thus the initial objects of this work were to develop a self-consistent method for measuring gas absorption at short contact times and to determine whether or not the apparent resistances which have been observed for carbon dioxide–water are real.

Since the completion of this work a number of related studies have become available. Cullen and Davidson (*3*), Nijsing (*13*), and Scriven (*17*) have used laminar-jet techniques and concluded that interfacial resistance in the carbon dioxide–water system is negligible. The various techniques differ among themselves and from the work reported here mainly in the method of forming the jet and in treating the effect of the boundary layer.

THEORY

In this work a laminar jet is passed through a pure gas for a short distance and is removed by being directed into a small receiver. The jet method used by Matsuyama was not self-consistent, but it was believed that minimizing end effects would increase the reliability.

To determine the rate of absorption by the jet as a function of k_s the following assumptions are made:

1. Fick's Law for unsteady state diffusion holds.
2. The initial liquid concentration is uniform or zero. There is no gas side resistance.
3. During the exposure period the maximum depth of the liquid at which any appreciable concentration changes have occured is small compared with the diameter of the jet.
4. There is no chemical reaction in the liquid.
5. The rate of transfer across the interface is assumed to be given by Equation (4), and if there is a finite region of interfacial resistance it is thin enough so that the accumulation in the region occurs very rapidly and may be neglected.
6. There is no relative motion within the fluid; that is the jet moves as a rod.
7. Henry's Law holds.

The solution to Fick's Law for these conditions gives the instantaneous rate of absorption, which may be integrated to give the average rate over the jet. When the interfacial resistance is zero, the point rate is given by the well-known equation (*9*)

$$N_A = (C^* - C_0)\sqrt{\frac{D_L}{\pi\theta}} \qquad (8)$$

and the mean rate is

$$\bar{N}_A = 2(C^* - C_0)\sqrt{\frac{D_L}{\pi\theta'}} \qquad (9)$$

When there is an interfacial resistance described by Equation (4), the point and mean rates are lower than the values of Equations (8) and (9) (*5*). The theoretical rates for various values of k_s are shown in Figures 6 and 8. The amount of gas absorbed per unit area of jet surface when there is no interfacial resistance is, from Equation (*9*),

$$Q = 2(C^* - C_0)\sqrt{\frac{D_L\theta'}{\pi}} \qquad (10)$$

The first assumption is satisfied by use of carbon dioxide–free water and absorbing pure carbon dioxide saturated with water. The water vapor would not be expected to cause a gas-phase resistance, since it is at its saturation point, but this assumption will be checked experimentally. The third assumption may be justified by solving the diffusion equations in cylindrical coordinates; it is found thereby that for the short contact times used in this work the penetration distance is so small that the curvature of the jet has negligible effect (*16*). The fourth assumption follows from the small amount of dissociation and reaction of carbon dioxide in water, even at equilibrium. The fifth assumption is a working hypothesis, and more complicated surface mechanisms may be dicated by experimental results.

When a liquid leaves an orifice, the surface of the liquid must leave at a velocity approaching zero, since it was in contact with a fixed wall, and a finite distance will be necessary before the surface can be accelerated to its final velocity by the bulk of the jet. Since the sixth assumption assumes instantaneous acceleration, an estimate of the error introduced is necessary. The formation of a boundary layer in a square-edged orifice and its dissipation in the jet are closely related to the boundary layer on a flat plate and the wake behind the plate. The symmetry line in the wake is analogous to the surface of the jet, since the shear stress at the jet surface is negligible. Although the two cases are not identical, the solution for the midpoint of a wake should give an approximate description of the surface velocity of a jet. The surface velocity determined from Goldstein's solution (*7, 8*) for a wake is shown in Figure 1 as a function of distance along the jet.

If the surface velocity is varying, the the mean absorption rate (*18*) is

$$\bar{N}_A = \frac{1}{A'}\int_0^{\theta'} 2\pi r u_s N_A \, d\theta = \frac{2\pi r}{A'}\int_0^{L} N_A \, dx \tag{11}$$

where θ' is the true contact time of any surface element and the jet radius r is taken outside the integral, since it is found to be constant.

If u_s increases from zero to its final value, $\bar{N}_A$ has a lesser value than it would have if the velocity instantaneously attained its final value. However when a boundary layer is present, N_A is not given by the solution to Fick's Law, since the axial velocity varies with axial and radial position, and, in addition, by continuity there must be radial velocity components. These effects tend to increase the point transfer rates so that there are two opposing effects on the mean rate. (The results below indicate that the decrease due to a lowered surface velocity predominates.)

Thus if Equation (8) is used in Equation (11), the result should show the maximum boundary-layer effect. When Equation (11) is integrated by means of the point rate for no interfacial resistance and the surface velocity from Figure 1, the resulting equation is (*16*)

$$\bar{N}_A = 2(C^* - C_0)\sqrt{\frac{D_L u_0}{\pi L}}\, f\!\left(\frac{L}{L_p}\right) \tag{12}$$

Since L/u_0 is the apparent contact time, the ratio of the mean rate with a boundary layer to the rate, if the velocity were constant at u_0, is $f(L/L_p)$, and this result is shown in Figure 1. For a plate thickness of about 0.01 cm., as used in this work, the surface velocity reaches 95% of its final value in a distance less than 1 cm., but a jet over 10 cm. long is theoretically needed to bring the mean absorption rate up to the 95% point. These figures cannot be taken too literally, but the general characteristics of the curves would be expected to be correct.

When L/L_p is large, it can be seen that the mean absorption rate depends only upon L/u_0, which is θ' in this limit, and the rate at equal values of L/u_0 should be independent of L and the jet diameter. This result is independent of the transfer mechanism at the surface and gives a general criterion for self-consistency. In the region where the mean absorption rate is greater than about 95% of the constant surface-velocity rate, this technique will not be precise, since Figure 1 shows that the length effect will be small; below the 95% point a significant length effect should appear.

APPARATUS AND EXPERIMENTAL TECHNIQUE

In essence the equipment is designed to contact a laminar jet with a gas for a short period of time under conditions in which the jet area, contact time, and absorption rate can be determined. The length, diameter, and velocity of the jet can all be varied. A flow diagram of the apparatus is shown in Figure 2, with further details in Figure 3.

The gas is taken from a standard cylinder (1), through a pressure regulator, and passed through water saturators. The saturated gas is then led to the soap-bubble mechanism (5), through the measuring burette (6), and to the absorption chamber. An excess of gas is always passed through the saturators. Before a run was made, the connection to the atmosphere was closed off, and all the gas was forced to the absorption chamber and out through the exhaust opening (7). During a run opening (7) was closed, and excess gas was passed to the atmosphere at (3) so that all the gas absorbed by the jet flowed through the connecting tube (4). The pressure in the absorber, therefore, was atmospheric less the small pressure drop across the lines and soap bubble. The gas-flow rate was measured directly by timing the motion of the soap bubble which could be placed on the top of the burette by a wire ring.

Originally the rate of absorption was obtained by measuring the pressure drop across a precision-bore capillary tube insterted in the gas line to the absorption chamber. A two-fluid U-tube manometer which could read a pressure drop of 0.0005 cm. of water was used. This device was calibrated by a liquid-displacement method, and the calibration checked Poiseuille's Law to within 1%. However it was later found that in use the manometer gave readings between 5 and 8% low owing to the time lag in reaching equilibrium. The equilibrium readings on the manometer checked the soap-bubble readings within 1%.

Four types of orifices were used. Orifice 1, which produced approximate rodlike flow, was a square-edged orifice 0.01 cm. thick. Orifice diameters of 0.0851 and 0.0571 cm. were used and there were no visible surface curves on the jets. Orifice 2, which produced surface waves, was a slightly elliptical orifice of average diameter 0.0851 cm., and these jets had visible standing waves. The orifice plates were mounted on the end of a 1-cm.-I.D., 60-cm.-long glass tube (Figure 3*a*) in which the flow was always laminar and the length Reynolds numbers in the orifices were always far below the critical value for turbulence. Orifice 3, producing a thick boundary layer, was a bell-mouthed orifice as shown in Figure 3*c*, and orifice 4, producing an initial parabolic velocity profile, was a precision-bore capillary tube long enough to give a fully developed parabolic velocity profile (Figure 3*b*). All the jets could be raised and lowered by a screw mechanism.

The absorption chamber is the male part of a ground-glass joint, with the lower part fitted with a Lucite core having a center hole to receive the jet (Figure 3*a*). Hole

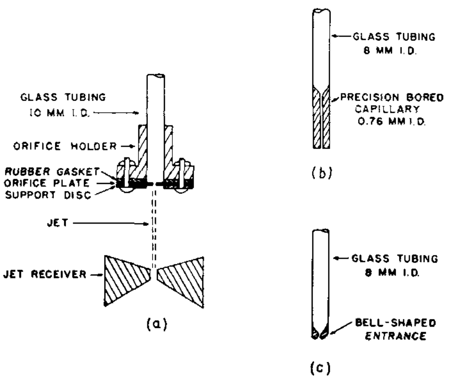

Fig. 3

(*a*) **Sections 7, 8, 9, and 10 of Figure 2 in detail.**
(*b*) **Capillary tube entrance.**
(*c*) **Tube with bell-shaped entrance.**

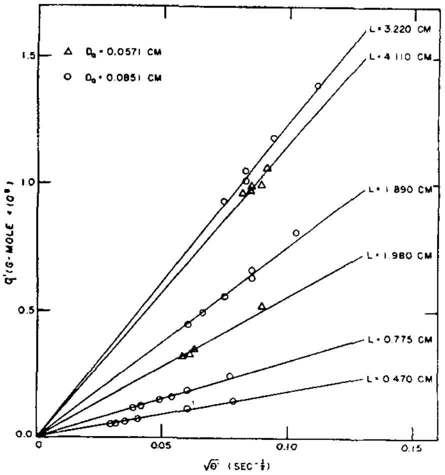

Fig. 4 Amount of carbon dioxide absorbed for typical jet lengths and diameters vs. square root of contact time.

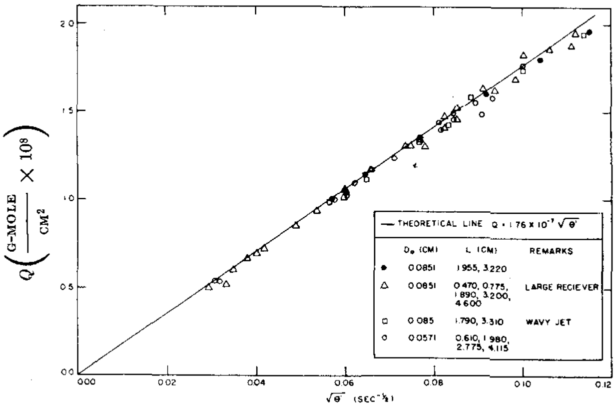

Fig. 5 Absorption of carbon dioxide in water plotted against the square root of the contact time.

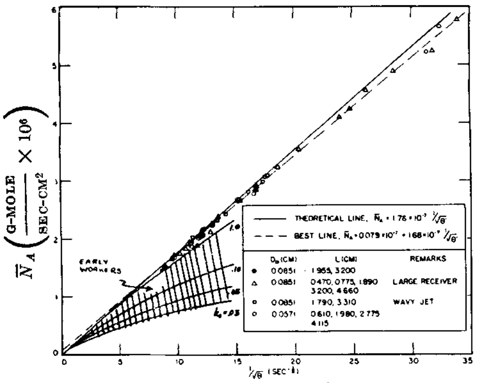

Fig. 6 Rate of carbon dioxide absorption in water, plotted against the inverse of the square root of the contact time.

diameters of 0.30 and 0.10 cm. were used, and the surface of a layer of kerosene was held at the top of the receiving hole by a constant-level siphon (Figure 1). The system was built in a constant-temperature room held at 22.2°C. ± 0.25°C., ordinary distilled water was used, and the carbon dioxide had a purity of 99.8%.

The diffusivity of carbon dioxide in water at 22.2°C. was taken as 1.84×10^{-5} sq. cm./sec. and the solubility as 3.65×10^{-5} g.-mole/cc. (*14*).

The jet length was measured from the top of the kerosene level to the orifice with a cathetometer which could be read to 0.005 cm. The water flow rate was measured by noting the time to fill a 1,000-ml. flask. The jet diameter was obtained by using a previously prepared calibration chart determined with a microscope.

The jet area and apparent contact time were calculated directly from the measurements of jet length, diameter, and water flow rate. The absorption rate was calculated by subtracting the water vapor from the measured gas flow rate, and it was then corrected to a carbon dioxide partial pressure of 1 atm. as indicated by Equation (9). (Carbon dioxide was always zero.) It was assumed in this calculation that the entering water vapor condensed in the absorber as the carbon dioxide was absorbed.

RESULTS

Contact times from 1 to 20 msec. were obtained by varying the jet length over a tenfold range and the jet velocities over a sevenfold range. Some typical results with a square-edged orifice are shown in Figure 4, where the amount of gas absorbed ($q' = A'Q$) is plotted against $(\theta')^{1/2}$. The data for the various jet lengths and diameters are combined in Figure 5 by plotting the amount of gas absorbed per unit area of jet and are compared to the theoretical line for no interfacial resistance and rodlike flow [Equation (10)]. On this figure are shown the data obtained with the square-edged orifice and the eliptical orifice. Part of the data were obtained with the 0.3-cm.–diameter receiver and part with the 0.1-cm.–diameter receiver.

With the large receiver there was an effect of a jet length on the absorption rate which indicated that measurable transfer was taking place at the gas-kerosene interface. This extra absorption was made negligible by decreasing the receiver diameter until no length effect could be observed. Replacing the kerosene in the small receiver by water had no effect on the results. The data with the large receiver were corrected for the absorption into the receiver (*16*).

The data of Figure 5 are also shown in Figure 6, where N_A is plotted against $1/(\theta')^{1/2}$ to spread out the data in the important region of short contact times. The theoretical line for no interfacial resistance and rodlike flow is again shown [Equation (9)]. The standing waves which occur with the elliptical orifice have little effect on the absorption. The range of data of some workers (*5, 9*) who reported a possible interfacial resistance is also shown here as well as the theoretical lines for various values of $k_s{}^5$. The results with the small receiver and the square-edged orifice, which needed no correction for absorption into the kerosene, are shown separately in Figure 7.

The absorption rates with the capillary orifice are shown in Figure 8, and those with a bell-mouthed orifice are given in Figure 9. Absorption rates in three solutions of Petrowet, a commercial surface-active agent, were obtained and are shown in Figures 10 and 11.

All the original data are given by Raimondi (*16*).

The following additional results were obtained: (1) using dry instead of saturated gas had no measurable effect on the absorption; (2) the effect of inerts accumulating in the absorber during a run was negligible; (3) dye studies on a large-scale model of the square-edged orifice indicated steady, rectilinear flow in the jet; (4) the jet diameter at a constant flow rate contracted in the first 0.05 cm. or less and then remained constant with length. The diameter decreased slowly as the flow rate was increased and was not changed by the addition of the surface-active agent.

DISCUSSION

The results obtained by using a thin orifice plate follow very closely the theoretical line of no interfacial resistance as shown in Figures 5 to 7. Since the effect of interfacial resistance should increase as the contact time decreases, the fact that the data follow the theoretical line so closely down to a contact time of less than a millisecond indicates a very small interfacial resistance and perhaps none at all for practical purposes. This agrees with the conclusions of other recent workers (*3, 17, 13*).

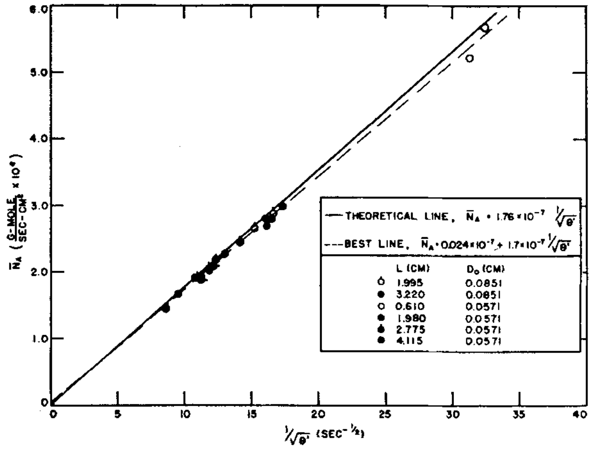

Fig. 7 Rate of absorption of carbon dioxide in water. Wave-free jet and small receiver.

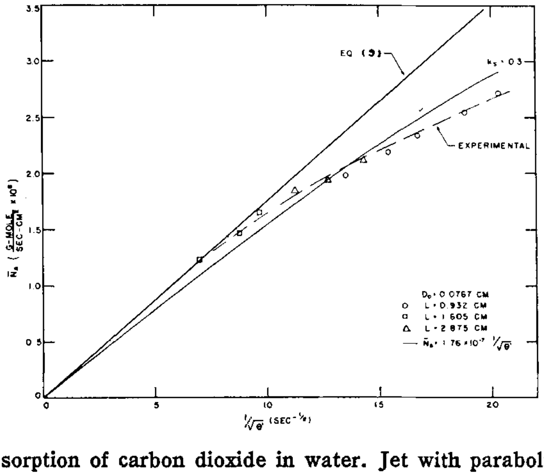

Fig. 8 Rate of absorption of carbon dioxide in water. Jet with parabolic velocity profile.

In an attempt to establish whether or not the results indicate the presence of a small interfacial resistance, a statistical treatment of the data was carried out. The best line obtained by the least-squares method for all the runs with a thin orifice plate is $\bar{N}_A = 0.079 \times 10^{-7} + 1.68 \times 10^{-7}\, 1/(\theta')^{1/2}$, where the standard deviations of the intercept and of the slope are 0.0434×10^{-7} and 0.0263×10^{-7}, respectively. Equation (9) requires that if there is no interfacial resistance, in a plot of $\bar{N}_A$ vs $1/\theta'^{1/2}$ the intercept of the straight line through the data should be zero. In this case the intercept is 0.079×10^{-7}, but a *t* test shows that at the 95% confidence level there is insufficient evidence that the intercept differs from zero by more than can be accounted for by the experimental error. There is stronger support that the data actually give a zero intercept if one considers only those data taken with a waveless jet by use of a small receiver. In this case the equation of the best straight line (Figure 7) is $\bar{N}_A = 0.024 \times 10^{-7} + 1.71 \times 10^{-7}\, 1/\theta'^{1/2}$, the standard deviation of the intercept and of the slope being 0.0233×10^{-7} and 0.0175×10^{-7}, respectively. This intercept is negligibly different from zero, but the range of slope owing to experimental error is not sufficient to include the theoretical slope of 1.76×10^{-7}. However this is not a conclusive proof that there is, in this range, a small interfacial resistance, since the physical constants D_L and C^* used in the theoretical equation might be in error by a few per cent, and the surface velocity must be somewhat less than the bulk velocity.

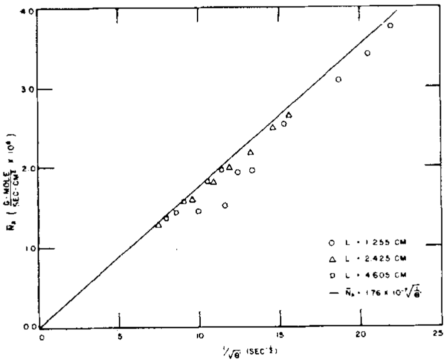

Fig. 9 Rate of absorption of carbon dioxide in water. Jet formed with bell-shaped entrance.

If the lower absorption rate is an indication of a true interfacial resistance, then k_s is in the range of 2.6 to 11.8 cm./sec., with corresponding α's of 0.35×10^{-3} to 1.6×10^{-3}. These values are two to three orders of magnitude larger than those reported in early studies (*5, 6, 9*), and for many purposes this small surface resistance can be neglected in the range of practical contact times, since most liquid or gas side resistances would be appreciably greater.

Since the absorption rate should be entirely dependent on the contact time, a critical factor in this type of investigation is the velocity at the surface of the jet. The very short orifice used should develop a thin boundary layer which should rapidly accelerate to the bulk jet velocity. With an orifice plate thickness L_p of 0.01 cm., Figure 1 shows that the surface velocity of the jet should be, for example, 95% of the jet bulk velocity at a jet length of 0.5 cm. However the process of averaging rates of absorption over all the elements of different age shows that the average rate at a jet length of 0.5 cm. is only 82% of the theoretical, that is, of the rate that would be obtained if the surface velocity of the jet had reached the bulk jet velocity instantaneously. If these calculations were correct, then in the range of jet length used here the absorption rate should have varied from 82 to 92% of the theoretical, and a significant length effect should have been detected.

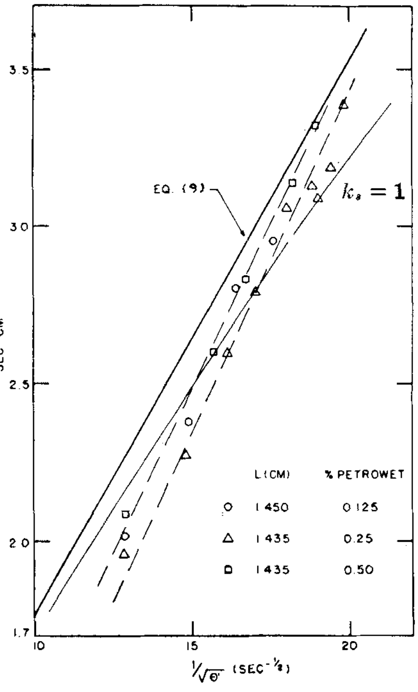

Fig. 10 Effect of Petrowet concentration on the absorption rate at constant jet length.

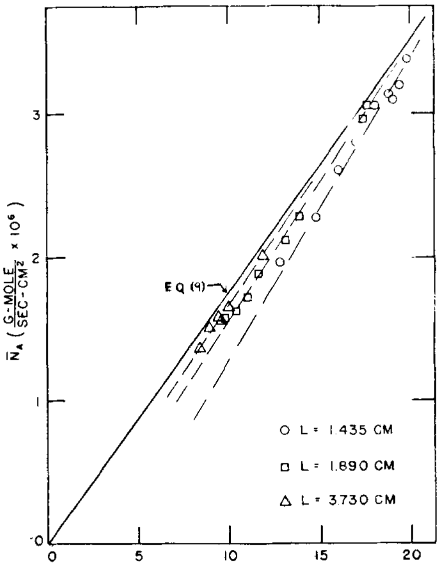

Fig. 11 Rate of carbon dioxide absorption in water containing 0.25% Petrowet.

A cross plot of Figure 4 at a constant contact time gives Figure 12, where the amount of carbon dioxide absorbed per unit area is plotted against the jet length at a constant contact time. The horizontal line indicates no effect of jet length over the range studied. The cross plot was made for a contact time in which the various jet lengths overlap, but, since the data in Figure 4 yield straight lines going through the origin, the results should be true over a wide range of contact times. This absence of a length effect indicates that the boundary layer accelerated faster than calculated or that the *y* components of velocity caused the absorption rate to be higher than calculated. Figure 1 shows that after 96% of the theoretical absorption rate is reached, the rate remains practically constant over a large variation of jet length. Therefore if the boundary layer did accelerate faster than was calculated, and the region of 96 to 99% of the theoretical was reached with a relatively short jet length, then the rate would continue to remain almost constant but about 1 to 4% lower than the theoretical. Thus it is quite possible that the slightly lower than theoretical rates were caused by the boundary layer.

In an attempt to find any errors which would cause the absorption rate to be higher in this work than in others, the possibility that there was some turbulence was considered. That this is not due to unobserved surface waves is shown by the fact that the results obtained with a wavy jet are the same as those obtained on a wave-free jet. The Reynolds number in the tube was always well below the critical, and the Reynolds number based on the length of the orifice was also far below the critical value for a flat plate, and so no turbulence should occur. It would be expected that if a low level of turbulence does exist, it would increase with jet velocity. The data in Figure 12, for example, show no such effect over a variation of velocity of 700%.

It is unlikely that the radial-velocity components which exist when the jet surface is accelerating cause an increase in absorption rate large enough to overcome the decrease in rate brought about by the lowered surface velocity. If this were the case, the rate when a boundary layer is present should be greater than the theoretical value, but work with jets with thick boundary layers always gave a rate below the theoretical, an indication that the increased surface age caused by a lowered velocity is the predominant factor. Thus boundary-layer effects, when they exist, give an apparent resistance and cannot be used to explain why negligible resistance was found.

Other possible effects which could increase the absorption rate were shown earlier to be negligible.

BOUNDARY-LAYER EFFECTS

Work on jets formed with a capillary tube and with a bell-mouthed orifice was undertaken in an attempt to determine the effect of hydrodynamic conditions on the rate of absorption.

The jet formed with a long capillary tube will leave the tube with a parabolic velocity profile. The velocity of the surface of the jet will start out at zero, but in this case the boundary layer is the radius of the jet, and the distance to accelerate the surface to the bulk velocity will be much greater than in the case of a jet formed with a short orifice.

Figure 8 shows the results obtained on this type of jet. Here the measured rate is plotted against an apparent contact time which was calculated from the jet bulk velocity. The actual contact time was longer, since the surface velocity was lower than that of the bulk of the jet. In this type of plot there is an apparent interfacial resistance because of the lower surface velocity. At the shorter contact times (higher velocity or shorter jet length) the apparent resistance is very high, but at the longer contact times (lower velocity or longer jet length) the rate approaches the theoretical. In the same figure the theoretical line for an interfacial resistance is shown for k_s = 0.3 cm./sec. It can be seen that this line and the line through the data are close to each other and have the same characteristic curvature. Thus it appears that the type of surface resistance described by early investigators could very well have been the result of unknown hydrodynamic conditions rather than the result of the physico-chemical behavior at the interface.

Actually these data on a jet with initial parabolic velocity profile do not follow exactly any constant resistance line, since the constant resistance line for a k_s of 0.3 intersects the line through the data. Moreover a close look at the points in Figure 8 shows a discontinuity from one jet length to the other, as would be expected. Unfortunately there is no solution to the equation for the velocity distribution in a free liquid jet with an initial parabolic velocity profile, and so it is not possible to interpret these results quantitatively. However it is clear that the low rate is not due to any constant surface resistance and that the increase in rate due to radial-velocity components is less than the decrease caused by a lowered surface velocity.

The results obtained with the bell-shaped orifice are shown in Figure 9. This orifice is expected to give a boundary layer of thickness intermediate between the orifice plate and the capillary. With the longer jet the rate is as close to the theoretical line as the rate with the short orifice. At the intermediate jet length the effect of the boundary layer begins to appear, as indicated by a slightly lower rate than with the longer jet. With the shortest jet length the rate falls still lower. Thus the rates with the bell-shaped orifice fall between the rates with the short orifice and the capillary, as was expected from boundary-layer considerations. It should be noted that with a carefully designed nozzle Cullen and Davidson were able to go down to lengths of 1.6 in. without detecting any boundary-layer effect (*3*).

SURFACE-ACTIVE AGENTS

Emmert and Pigford (*6*), using a long wetted-wall column to measure interfacial resistance, added Petrowet to the water to reduce the ripples on the surface, since the ripples caused the absorption rate to exceed the theoretical; their absorption rates were then found to be well below the theoretical. To determine whether or not the surface-active agent actually hindered the transfer across the interface, they compared rate data in a short wetted-wall column with the surface-active agent present to data obtained without the surface agent. Since there were no ripples present in either case, they found only an 11% decrease owing to the surface active agent and concluded that the lower than theoretical values in the long column were not due to the hindering effect of the surface active agent but indicated a true interfacial resistance for pure water with an α of 1.9×10^{-6} for carbon dioxide. This was close to the value obtained on the short column without surface-active agent, and although it can be argued that the resistance reported in the short column was due to boundary-layer effects, the long-column results cannot be explained in this fashion.

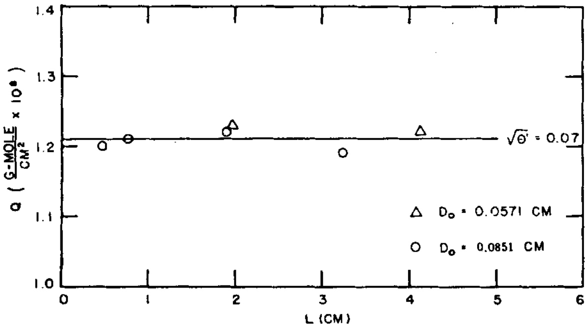

Fig. 12 Comparison of carbon dioxide absorbed per unit area at different jet lengths for the same contact time.

Cullen and Davidson, using a wetted sphere, have recently concluded that Petrowet does cause an interfacial resistance in the carbon dioxide–water system (*2*). The results with three concentrations of Petrowet are shown in Figure 10 for a fixed jet length. The absorption rate diverges increasingly from the theoretical as the contact time increases, just the reverse of what would be expected if there were a constant interfacial resistance, and the lowest rate occurs at the intermediate concentration. Furthermore there is a marked length effect which is shown in Figure 11 for the 0.25% Petrowet solution. At a constant contact time the rate decreases as the jet length decreases.

The length effect must be at least partly hydrodynamic in nature, since any diffusional or surface-resistance mechanism should depend only upon contact time. Lynn et al. (*11*) and Cullen and Davidson (*3*) have observed that in the presence of surface-active agents a stagnant film forms on the surface of a moving liquid when it enters a stagnant liquid. If the absorption rate into this film is relatively small, the effective jet length in this work would be less than the actual value, as found in wetted-wall columns (*11*), and the absorption rate would vary with jet length and diverge from the theoretical in the observed manner.

By assuming that the lowered rate at the shortest jet length for each Petrowet concentration is due entirely to the stagnant film at the receiver, one might calculate the apparent stagnant film height and use it to correct the results for the longer jets. This correction brings all the jet lengths and Petrowet concentrations into rough agreement with the theoretical line, an indication that the lowered absorption rate might be explained entirely as a receiver effect.

Actually there is stronger evidence that part of the lowered rate may be due to an interfacial resistance, for if only half the apparent stagnant-film height is used to correct the jet lengths, the correlation is greatly improved and the length effect is eliminated with the rate data still below the theoretical.

When a fresh surface is formed from

a solution containing a surface active agent, the initial surface concentration is the bulk concentration, and as the surface ages, the interfacial concentration of surface-active agent increases until the surface attains its final large excess of surface-active agent (*15*). Thus if there is a resistance due to the hindering effect of the surface-active agent, it should increase from a very small value at the orifice to its final value when the interface is saturated.

The surface ages in this work are much less than those studied by Emmert and Pigford (*6*) or by Cullen and Davidson (*2*), and so even if negligible resistance were found here, this would not imply that none would exist in a relatively old surface. Thus these results, although inconclusive, are not inconsistent with the conclusions of Cullen and Davidson (*2*) that the addition of Petrowet causes a true interfacial resistance in the carbon dioxide–water system and that the interfacial resistance reported by Emmert and Pigford is due to the hindering effect of the surface-active agent.

It is interesting to note that at a fixed contact time and jet length (Figure 10) the rate of absorption goes through a minimum as the concentration of surface-active agent increases. This is very similar to the results of Cullen and Davidson (*2*) and Emmert and Pigford. Since in this work there is a definite hydrodynamic effect present, the question arises as to whether this minimum may not be due at least partly to a hydrodynamic effect rather than entirely to a hindering effect as concluded by Cullen and Davidson (*2*). Unfortunately, as Emmert and Pigford and Cullen and Davidson (*2*) worked with a constant length of flow, their data cannot be checked for a length effect.

It does not seem very likely that the minimum is due to a change in the surface waves, since it was shown earlier that even large waves in the jet have little effect on the absorption, and the stagnant film at the receiver is hardly likely to be significant in the long column used by Emmert and Pigford. Since a hydrodynamic effect that could be significant in all the widely different types of apparatus used is not readily apparent (the surface viscosity of water has been reported to be unaffected by Petrowet (*2*)), the possibility that the minimum in the present work is due entirely to a hindering effect cannot be rejected.

CONCLUSIONS

1. An accurate, self-consistent method of obtaining gas-liquid contact times down to 1 msec., under known hydrodynamic conditions, has been developed.
2. There is at most a very small interfacial resistance at a clean carbon dioxide–water interface. For practical purposes interfacial equilibrium is immediately attained when the gas and liquid are brought into contact.
3. Boundary-layer effects can be easily mistaken for an interfacial resistance, but the two phenomena can be distinguished from each other by varying the jet length and velocity.
4. The presence of a surface-active agent lowers the absorption rate. This is due at least partly to a change of the flow pattern.

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NOTATION

A = gas-liquid contact area, sq. cm.
A' = total gas-liquid contact area, sq. cm.
C = solute gas concentration, g.-mole/cc.
C_0 = initial concentration of solute gas, g.-mole/cc.
C_i = concentration of solute gas in liquid at interface, g.-mole/cc.
C_L = concentration of solute gas in bulk of liquid, g.-mole/cc.
C_{y0} = concentration of solute gas at $y = y_0$, g-mole/cc.
C^* = concentration of solute gas in liquid which would be in equilibrium with gas, g.-mole/cc.
C_i^* = concentration of solute gas in liquid at the interface in equilibrium with gas adjacent to interface, g.-mole/cc.
D_0 = orifice diameter, cm.
D_i = diffusivity of dissolved gas in the hypothetical film of thickness y_0, sq. cm./sec.
D_L = diffusivity of solute gas in liquid, sq. cm./sec.
f = functional symbol
H = Henry's Law constant, atm. cc./g.-mole, or erg./g.-mole in Equation (2)
k_g = gas-side mass transfer coefficient, g.-mole/sec.-sq. cm.-atm.
k_L = liquid-side mass transfer coefficient, cm./sec.
k_s = Interfacial mass transfer coefficient, cm./sec.
k_S' = restricted interfacial mass transfer coefficient, cm./sec.
k_S'' = D_i/y_0, cm./sec.
K_L = over-all mass transfer coefficient, cm./sec.
L = jet length, cm.
L_p = thickness of orifice plate, cm.
M = molecular weight
N_A = local mass transfer rate per unit area, g.-mole/sec.-sq. cm.
$\bar{N}_A$ = average mass transfer rate per unit area, g.-mole/sec.-sq. cm.
$\bar{N}_{Aa}$ = average mass transfer rate per unit area based on a constant jet surface velocity, in Figure 1, g.-mole/sec.-sq. cm.
q' = total amount of carbon dioxide absorbed by jet. g.-mole
Q = amount of carbon dioxide absorbed per unit area, g.-mole/sq. cm.
r = jet radius, cm.
R = gas constant, erg./(g.-mole)(°K.)
T = temperature, °K.
u_0 = mean jet velocity, cm.
u_s = jet surface velocity, cm./sec.
x = distance along the axis of the jet
y = distance measured from surface of liquid, cm.
y_0 = thickness of hypothetical film at liquid surface, cm.

Greek Letters

α = condensation coefficient
θ = gas-liquid contact time, sec.
θ' = total gas-liquid contact time, sec.

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