Transient Absorption at Small Contact Times: Moving-Band Absorber

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In the last ten years several ingenious techniques have been reported for measuring transient absorption rates (*3*). The primary purpose of these studies has been to test the assumption of chemical equilibrium at a freshly formed interface through which there is a net transfer of mass. As noted by several authors (*9*) a net transfer through the interface implies a nonequilibrium state, and the question of importance is therefore how rapidly is a state indiscernible from equilibrium established at the interface.

Dynamic experiments have been carried out with short, wetted-wall columns (*4*), flow over a wetted sphere (*2*), laminar liquid jets (*6, 7*), and a rotating drum (*1*). Of these techniques it would appear that the laminar liquid jet is best suited for short liquid-gas contact times, and that the smallest contact time attainable is of the order of a millisecond. In all of these experiments there is relative motion between the gas and the liquid, and therefore an interpretation of the mass transfer results calls for a detailed knowledge of the flow field in the vicinity of the interface. Two other difficulties encountered in dynamic experiments are end effects and, where the rate of absorption is measured by analyzing the liquid effluent for dissolved gas, the analysis of the extremely small concentrations of absorbed gas.

The purpose of this investigation was to develop an apparatus for measuring transient absorption rates over a wide range of contact times extending to times less than a millisecond. The improvements over existing techniques which the apparatus was to feature were a high ratio of surface area to volume for the liquid phase and minimal end effects.

The technique, described below, used in the absorption experiments consisted of contacting a soluble gas with a thin liquid film carried on a metal ribbon, rotating as an endless belt. The film was exposed to the gas, scraped from the belt and analyzed for dissolved gas.

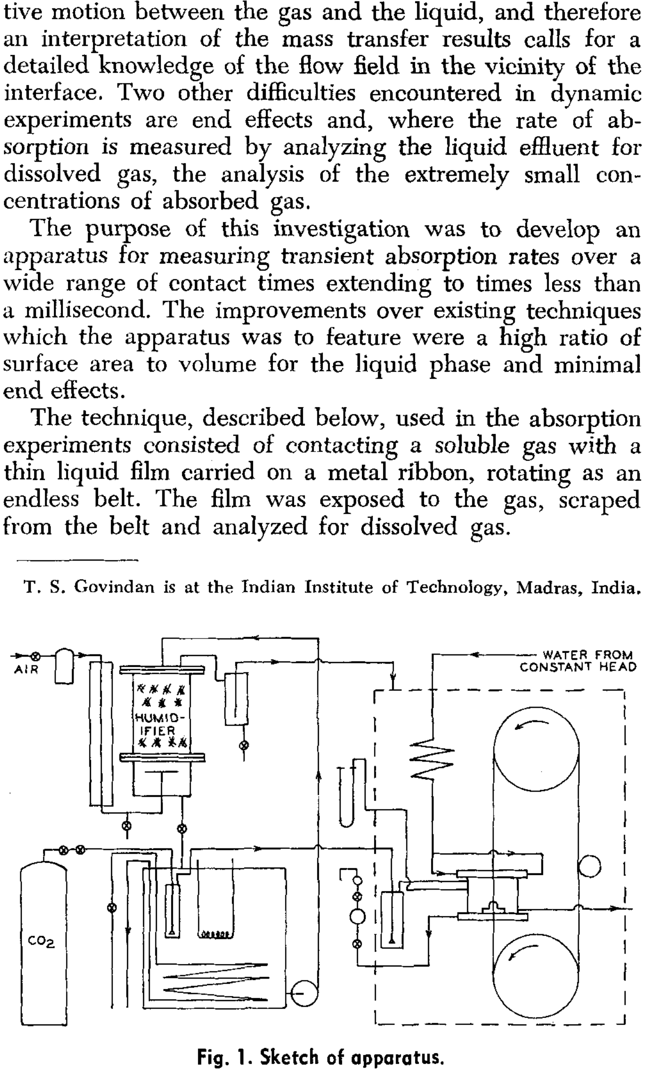

Fig. 1. Sketch of apparatus.

EXPERIMENTAL

A diagram of the apparatus is shown in Figure 1. Liquid was carried through the solute gas on a rotating band fabricated from nichrome ribbon (0.004 × 0.125 in.). The endless belt ran between two 6-in. diameter steel pulleys. Deionized, degassed water from a constant head source was injected onto the moving belt, carried through the gas and a receiver, and removed by a scraping device. The outlet liquid discharged through a sampling pipette.

Absorption Chamber

The absorption chamber consisted of a length of Plexiglas tubing, 3-in. diameter, clamped between two stainless steel plates. Both plates were made from two semicircular sections fastened together with screws. On the upper plate the bearing surfaces of the two sections were ground to a highly polished finish making a gas tight seal when the two halves of the plate were connected. Grooves 0.004 × 0.130 in. were milled at the center of the polished surface of both sections providing a rectangular slit 0.008 by 0.130 in. through which the metal band entered the chamber. On the underside of the upper plate rectangular channels 0.130 in. wide and 0.004 in. deep extended from the center to the edge of the plate. The channels were covered with thin strips of stainless steel forming closed slits through which water was injected onto the moving belt. A set of bearings mounted on the top of the plate aided in aligning the belt with the water feed slots.

The belt carrying the water film entered a Plexiglas receiver at the base of the chamber. The receiver was made from two L shaped sections with slots 0.015 × 0.130 in. cut in the center of both vertical faces with the two sections glued together along the vertical plane. The top of the receiver was cut in a roof-top shape at an angle of 10 deg. so that any spill over from the receiver would flow into the chamber.

In the base plate the belt passed between two rubber scrapers which were mounted on the bearing surfaces of the two semicircular sections of the plate. The pressure on the scrapers was adjustable. Water scraped from the belt flowed out of the base plate into the sampling pipette.

A small amount of water invariably remained on the belt after it had passed between the scrapers. Because the mass of the belt was small, evaporation of this water would cause cooling of the belt and introduce uncertainty in the actual temperature at which absorption occurred. To prevent evaporation from the belt the apparatus was enclosed in a Plexiglas chamber with a continuous circulation of saturated air.

Operation

A selected length of Chromel A nichrome ribbon was threaded through the absorption chamber. The ends of the ribbon were overlapped 0.03 in. and welded together with a spot welder. The joint was then heat treated, and the thickness of the joint was reduced to that of the ribbon. If welded properly the belts would perform satisfactorily for several hours continuous operation. In some cases belts lasted through more than one million revolutions.

After a belt was installed, great care was taken to properly align the belt with the feed slots, receiver, and scraper. Also to minimize vibration the tension in the belt had to be properly adjusted. Belt tension was adjusted by raising or lowering the upper pulley. To insure that the ribbon was wetted uniformly the belt was periodically cleaned with a fine emery paper.

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In starting a run the water inlet was opened, the belt speed adjusted to the proper value, and the outlet from the receiver gradually closed until the water level was maintained exactly at the top of the receiver. Presaturated carbon dioxide was flushed through the chamber to prevent accumulation of inerts, and a positive pressure of 1 to 2 mm. of mercury was maintained within the chamber.

The speed of revolution was measured with a tachometer and a Strobotac. Temperatures of the inlet and outlet liquid and of the gas were measured to 0.1°C. with thermocouples, and in all runs the three temperatures were within 0.2 to 0.5°C.

Samples of the outlet liquid were taken through a sampling pipette connected to the discharge line. Carbon dioxide in the samples was measured by precipitating the carbonate ion as barium carbonate from a solution of standard sodium hydroxide and barium chloride and back titrating with hydrochloric acid. A carbon dioxide-free atmosphere was maintained above the solution while sampling and during titration. The average concentration of the samples ranged from 10 to 30% of saturation, and the precision of the analysis was approximately 1%.

DIFFUSION CALCULATIONS

If it is assumed that the velocity in the liquid film is everywhere constant and equal to that of the rotating band, and that absorption at the edges of the film is negligible, then the diffusion problem is identical to that of diffusion into a finite slab. The appropriate equations are

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2},\ 0 < x < \delta \tag{1}$$

$$C(x, 0) = C_o,\ \frac{\partial C}{\partial x}(\delta, t) = 0 \tag{2}$$

with the flux at the gas-liquid interface expressed as

$$-D\frac{\partial C}{\partial x}(0, t) = k_s\,[C^* - C(0, t)] \tag{3}$$

where k_s is the interfacial mass transfer coefficient, the reciprocal of which $(1/k_s)$ is a measure of the mass transfer resistance of the interface. The finite thickness of the film δ does not affect the amount of gas absorbed in time t by more than ½% providing $\delta/\sqrt{Dt} > 2$, (1). This inequality is satisfied for all the measurements reported here.

Subject to these assumptions the average concentration in the film is

$$\frac{\bar{C} - C_o}{C^* - C_o} = \frac{2}{\delta}\sqrt{\frac{Dt}{\pi}} + \frac{D}{k_s\delta}\left\{\exp\left[\frac{k_s^2 t}{D}\right]\operatorname{erfc}\left[k_s\sqrt{\frac{t}{D}}\right] - 1\right\} \tag{4}$$

The first term in Equation (4) is the usual penetration theory expression for absorption with interfacial equilibrium. The second term, which approaches zero as t or k_s becomes large, shows the effect of an interfacial resistance.

For comparison with experiment Equation (4) can be expressed in a simplified form if $k_s\sqrt{t/D}$ is greater than 3:

$$\frac{\bar{C} - C_o}{C^* - C_o} = \frac{2}{\delta}\sqrt{\frac{Dt}{\pi}} + \frac{D}{k_s\delta}\left\{\frac{1}{k_s}\sqrt{\frac{D}{\pi t}} - 1\right\},\ k_s\sqrt{\frac{t}{D}} > 3 \tag{5}$$

In terms of experimentally measured quantities Equation (5) becomes

$$\frac{\bar{C} - C_o}{C^* - C_o} = \frac{4wu}{Q}\sqrt{\frac{DL}{\pi u}} + \frac{2Dwu}{Qk_s}\left\{\frac{1}{k_s}\sqrt{\frac{Du}{\pi L}} - 1\right\} \tag{6}$$

where δ and t have been replaced by

$$\delta = \frac{Q}{2wu},\ t = \frac{L}{u} \tag{7}$$

Throughout tthe course of the experimental work runs were made in the temperature range of 23° to 30°C. However the majority of the data were obtained at temperatures of 24° to 26°C. Solubility data for carbon dioxide in water were taken from Seidell (8). These values were checked experimentally, and they agreed within the precision of the chemical analysis. The diffusivity of carbon dioxide in water was taken as 1.97×10^{-5} sq.cm./sec. at 25°C. (7). Values of the diffusivity at other temperatures were calculated from the 25°C. value by extrapolation with the Nernst-Einstein equation.

In comparing the experimental results with Equation (6) four minor adjustments were made in the calculations:

1. The saturation values C^* reported for a carbon dioxide pressure of 760 mm. Hg were adjusted to the partial pressure existing in the chamber, that is total pressure minus water vapor pressure at the temperature of the experiment.
2. The concentration of carbon dioxide in the feed water was measured, and typically it was found to be 0.1% of saturation. The concentration values reported below represent net transfer, that is relative to C_o.
3. Since the cross section of the receiver was larger than that of the belt there was a small but measurable area of liquid exposed at the surface of the receiver. In all runs the exposed area at the receiver was less than 4% of the area of the belt, and for a length of 3 cm. the exposed area was approximately 1%. In the calculations this exposed area was treated as an equivalent length of belt. Thus the term L in the results represents the distance from the feed point to the top of the receiver plus a length equivalent to the exposed area of the receiver. At a maximum this modification increased the predicted average concentration by no more than 2%.
4. Data for the various belt lengths were normalized to integral values of L. Again, this was a minor adjustment; for example data reported for L equal to 3 cm. were obtained on exposed belt lengths of 2.955 to 3.130 cm.

RESULTS AND DISCUSSION

The results for exposed belt lengths of 1 and 3 cm. are shown in Figure 2, where the product of average concen-

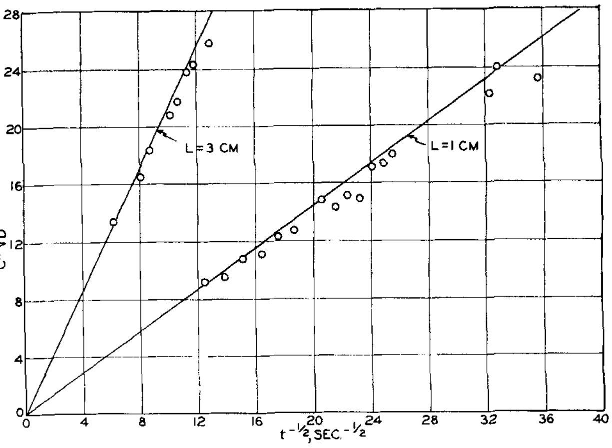

Fig. 2. Absorption of carbon dioxide in water, results on 1 and 3 cm. exposed lengths.

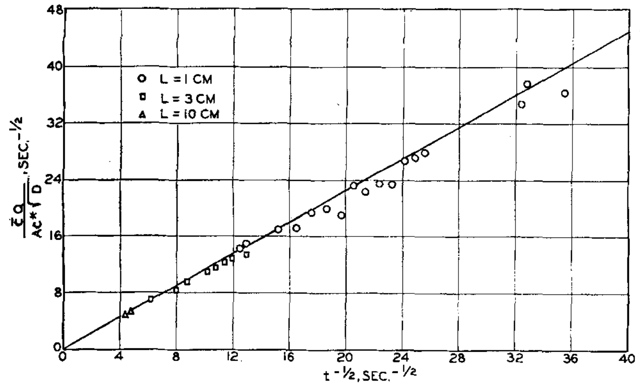

Fig. 3. Absorption of carbon dioxide in water, results on 1, 3, and 10 cm. exposed lengths.

tration and flow rate, divided by $C^*\sqrt{D}$ to remove the temperature dependence, is shown as a function of $1/\sqrt{t}$. The data were obtained with liquid flow rates of 20 to 50 cc./min. resulting in film thicknesses of 10 to 50μ. Each of the circled points represents the average of several samples. The straight lines in Figure 2 were calculated from Equation (6) with the assumption of interfacial equilibrium. The data are replotted in Figure 3 along with the results on an exposed belt length of 10 cm. Here the ordinate has been divided by the exposed area 2 w L, and the straight line with slope of $2/\sqrt{\pi}$ represents the predicted values with no interfacial resistance, that is infinite k_s. Approximately 90% of the results are within 5% of the predicted values, and all of the results are within 10%.

In the calculations above it is assumed that the velocity in the liquid film is everywhere constant. Obviously this is not correct, since the free surface of the film has zero velocity at the entry and a small but finite distance is required to accelerate the liquid to the belt velocity. In the range of film thicknesses used here the distance over which the film accelerates is small, and it is unlikely that the nonuniform velocity would lower the predicted absorption rate by more than a few percent. The relative agreement of the 1 and 3 cm. data support this conclusion.

The scatter of the experimental points, though small, is consistently below the line predicted with interfacial equilibrium assumed. If it is assumed that the deviation between the experimental points and the predicted values is due solely to an interfacial resistance, that is there is no systematic experimental error such as an acceleration correction or end effect, then a maximum value for the surface resistance can be calculated with Equation (6). A statistical analysis of the deviation between the experimental points and the equilibrium prediction indicates that the most probable value of k_s is approximately 2 cm./sec.

In light of experimental uncertainties and of overall agreement between measured and predicted results (with equilibrium assumed) it may be concluded that if there is an interfacial resistance at the carbon dioxide-water interface it is no larger than 0.5 sec./cm. and it is quite possible that it is considerably smaller. The magnitude of the interfacial resistance establishes an induction time for the absorption process. If, following Vignes (9), one defines an induction time as the time required to realize a state indiscernible from equilibrium, one in which the actual and equilibrium rates differ by less than 5%, the extremely small resistance of 0.5 sec./cm. yields an induction time of less than 10^{-4} sec.

These results are in substantial agreement with previous investigations on the carbon dioxide-water system. Scriven and Pigford (7) using a laminar jet technique, and properly allowing for the nonuniform velocity profile within the jet, obtained excellent agreement between measured and predicted results (assuming interfacial equilibrium) at contact times as small as 0.003 sec. Raimondi and Toor (6), also using a laminar jet, report measurements 1 to 4% lower than the equilibrium prediction over contact times of 0.001 to 0.020 sec. If the deviation between measured and predicted results in the work of Raimondi and Toor is ascribed to an interfacial resistance, then their results yield k_s in the range of 2.6 to 11.8 cm./sec. Harvey and Smith (5) measured transient absorption rates into a stationary liquid at times as small as 0.02 sec. They concluded that k_s for the carbon dioxide-water interface must be at least 4 cm./sec., the highest value which they could detect with certainty.

END EFFECTS

End effects are a source of error in all dynamic experiments. Some of the end effects encountered with wetted-wall columns and laminar jets can be eliminated with a properly designed moving-band absorber. For example acceleration corrections are reduced through the use of very thin films. Observations on end effects in this work are discussed below.

It is important that the exposed length of belt be between sharply defined boundaries. For this reason the cover strips for the feed slots were sharp edged, as shown in Figure 4. During normal operation there was little wear on the grooves in the feed plate, and the distance between the feed slot and belt remained constant. The clearance between the belt and the plate was kept less than 0.005 in. While operating the gap between the belt and the feed plate was filled with liquid drawn in by capillarity. This provided an excellent seal to prevent air from being drawn into the chamber.

At the exit of the chamber the exposed liquid surface was decelerated by a pool of liquid rather than a knife edge or solid barrier as in most absorption apparatus. Also the drag of the moving belt kept the liquid in the receiver constantly agitated. Under these conditions there was very little chance for impurities present in the water to accumulate at the surface, an end effect reported in several studies (7).

At very low belt speeds with high liquid flow rates a narrow band of ripples, similar to fine capillary waves, were observed at the receiver. The ripples extended over a vertical distance of a few millimeters, and at a flow rate of 20 cc./min. they could not be detected at belt speeds greater than approximately 150 cm./sec.

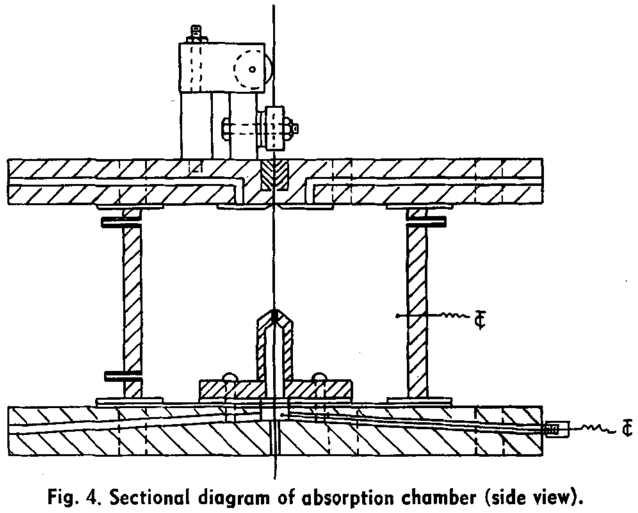

Fig. 4. Sectional diagram of absorption chamber (side view).

Throughout it has been assumed that the surface of the liquid film is flat and that the edges of the film do not significantly effect the exposed area. The ratio of belt width to film thickness in all runs was in the range of 25 to 125. To test the uniformity of the film a movable probe constructed from a hypodermic needle was inserted into the chamber. The tip of the probe touched the moving belt. When viewed through a traveling microscope a pattern of ripples could be seen above the tip of the probe. The probe was moved across the belt, and the resulting ripple pattern gave a qualitative indication of the film thickness across the belt.

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NOTATION

$\bar{C}$ = average liquid concentration, moles/cc.
C_0 = initial liquid concentration, moles/cc.
C^* = equilibrium liquid concentration, moles/cc.
δ = film thickness, cm.
D = diffusivity, sq.cm./sec.
k_s = interfacial mass transfer coefficient, cm./sec.
L = exposed belt length, cm.
Q = volumetric flow rate, cc./sec.
t = contact time, sec.
u = velocity, cm./sec.
w = belt width, cm.
x = distance normal to interface, cm.

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Frictional Pressure Drop in Two-Phase Flow: A. A Comparison of Existing Correlations for Pressure Loss and Holdup

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The current status of knowledge and practice in two-phase flow has been well summarized in the following paragraph (*14*):

"Multiphase flow still suffers when compared on a theoretical basis with other general fields of flow theory as is natural in view of the great complexity of the problem. We may note, however, that the buildup of empirical knowledge in this field is now very impressive. *What is most needed are critical reviews of the various specialized subjects such as pressure drop* in horizontal and vertical pipes, flow regimes, atomization, and the mechanics of fluid particles."

The total number of experimental measurements of two-phase pressure drop is currently well over 20,000, half of which have been obtained since 1959. It is evident that two-phase flow is a timely subject. Furthermore this continued accumulation of data demonstrates that there is not yet even a phenomenological understanding of this type of flow.

The purpose of the first part of this paper is to critically compare the prediction of certain correlations for pressure drop and holdup in horizontal flow with selected experimental data. The second part presents a new analysis of frictional energy loss.

DATA BANK

The first problem one must solve in a comprehensive study using information from various sources is that of data handling. In order to characterize a single two-phase flow measurement it is necessary to specify two flow rates, five fluid properties, a pipe diameter, several measurements of length, a test section orientation as well as an