K = usual equilibrium constant
M = net rate of phase change
n_i = number density at surface
n_i^0 = equilibrium density
P = pressure
Q = nonequilibrium concentration function
R = usual gas constant
T = absolute temperature
V^* = volume/molecule in the liquid
W = molecular weight

Greek Letters

μ_i = chemical potentials of the chemical components or phases undergoing the changes being considered
ν_i = stoichiometric coefficients

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On Phase Equilibrium at the Gas-Liquid Interface During Absorption

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That phase equilibrium exists at the gas-liquid interface during gas absorption is usually assumed in the analysis and design of absorption equipment, but the validity of this assumption has been in doubt since Higbie's pioneering gas-absorption studies. Accurate measurements are reported herein of the absorption rates at 25°C. of carbon dioxide into short water jets in which the liquid was in laminar flow. The jets issued from circular nozzles of about 1.5-mm. diam., flowed intact downward through an atmosphere of carbon dioxide at average velocities of from 75 to 550 cm./sec. over distances of 1 to 15 cm., and were collected in a receiver slightly larger in diameter than the nozzles. The measured absorption rates are in excellent agreement with predictions based on unsteady state diffusion theory, when one assumes interfacial equilibrium. It is concluded from these results and those of other investigators that equilibrium prevails at a freshly formed, relatively clean, carbon dioxide–water interface and that the same statement probably applies to the absorption of other slightly soluble gases in water.

Evidence is discussed which indicates that an accumulation of minute quantities of surface-active materials may seriously reduce the rate of gas absorption, either by affecting the hydrodynamic characteristics of the system or perhaps by offering resistance to the transfer of solute molecules across the interface.

That phase equilibrium exists at the gas-liquid interface has commonly been assumed in applications of the film theory (*21*, *32*) and the more realistic penetration theory (*6*, *15*, *16*, *32*) to gas absorption. In attempting to test the validity of this assumption, various previous investigators have obtained conflicting results (*4*, *7*, *8*, *11*, *16*, *23*, *25*, *35*). It seems likely that this lack of agreement is due principally to inadequate knowledge of the fluid dynamics of the different flow systems employed, although in certain cases it may arise from unknown chemical reaction effects, inaccurate diffusivity values, and so forth. Several careful studies have been published recently. From data obtained with their novel rotating-drum apparatus Danckwerts and Kennedy (*7*) concluded that there may be a small interfacial resistance to mass transfer in the carbon dioxide–water system. Lynn, Straatemeier, and Kramers (*23*) decided on the basis of their wetted-wall column experiments that interfacial equilibrium exists in the sulfur dioxide–water system. Cullen and Davidson (*4*) concluded from jet-absorber experiments that interfacial equilibrium exists in the carbon dioxide–water system, and in a companion study employing a wetted-sphere absorber (*8*) they confirmed this conclusion and found that it is probably also true in the absorption of a number of other slightly soluble gases.

The present investigation was undertaken to resolve the controversy on the basis of careful physical-absorption measurements carried out at short liquid-exposure times and with a relatively simple flow system amenable to mathematical analysis. At the time of its inception laminar liquid jets similar to those described herein had been utilized in surface-tension studies (*27*) and in a few absorption studies (*9*, *24*, *25*); subsequent applications in absorption

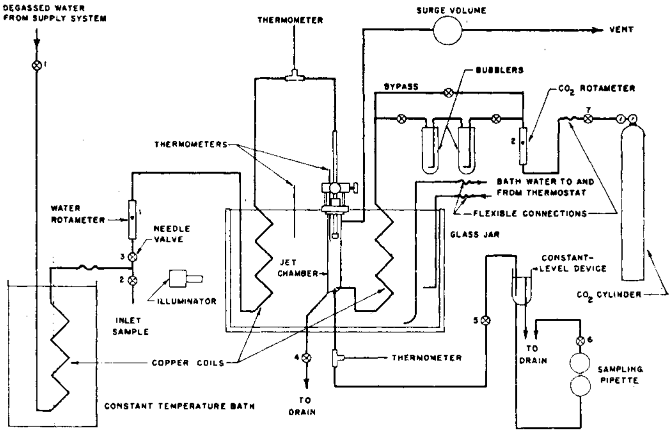

Fig. 1. Flow diagram of jet apparatus.

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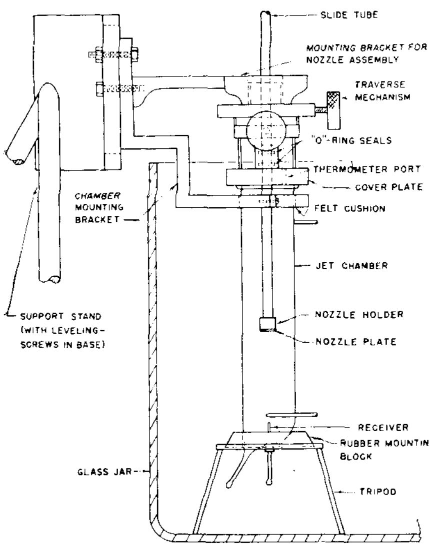

Fig. 2. Jet chamber assembly for gas absorption studies.

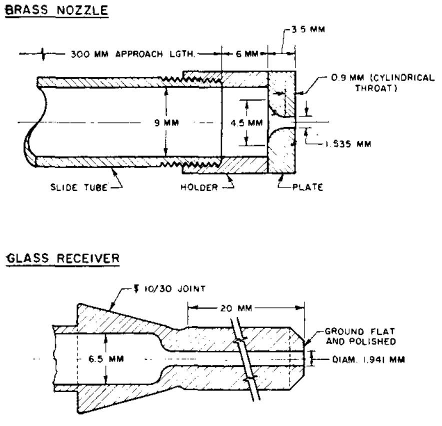

Fig. 3. Jet nozzle and receiver.

studies include those of Edwards et al. (*10*) and Cullen and Davidson (*4*).

APPARATUS AND PROCEDURE

Figure 1 shows a schematic diagram of the apparatus. Gas-free distilled water from a constant-head system and 99.9% pure carbon dioxide, dry or presaturated with water vapor, were fed through various temperature control baths to a jet chamber, within which a jet of water issued from a circular nozzle about 1.5 mm. I.D., flowed intact downward through an atmosphere of carbon dioxide at an average velocity of from 75 to 550 cm./sec. over a distance of 1 to 15 cm., and was collected in a glass capillary receiver of about 2 mm. I.D. The nominal contact time of liquid with gas $t_* = \pi h d_0^2/4q$ varied from 0.003 to 0.05 sec.

Jet Chamber Assembly

The nozzle was mounted on the end of a slide tube which passed through a double *O*-ring seal in the brass cover plate used to seal the top of the glass jet chamber (Figure 2). The open top of the chamber was ground flat, and the surface of the cover plate was polished to a fine finish so that a gas-tight seal allowing sliding motion was possible with the aid of stopcock grease. Jet length was adjusted by raising or lowering the slide tube. A traversing mechanism permitted easy horizontal alignment of the nozzle with the jet receiver. The whole assembly was immersed in a large, glass water bath (Figure 2). The jet chamber, a glass vessel 5 cm. in diam. by 25 cm. in length was provided with a tangential gas entry near the bottom, an overflow port in the bottom, a gas outlet near the top, and a carefully aligned female tapered joint blown into the bottom to hold the receiver. To avoid vibration insofar as possible the main water bath was placed on a massive table, which in turn rested on a vibration-damping mounting. The entire apparatus was located in a basement room relatively free of building vibration. All lines leading to the equipment in the bath were provided with flexible sections of rubber tubing.

Nozzles

Several nozzle designs were considered, two of which were employed for absorption measurements. The first of these was a glass nozzle, prepared by joining a short length of 1.4-mm. I.D. capillary to a piece of 6-mm. tubing, reworking the joint to obtain a smooth transition, and then grinding away most of the capillary section to leave only 1 mm. or so of throat. The jets produced by this nozzle were not entirely satisfactory (*30*); finally a small flow nozzle of brass was carefully turned to the shape shown in Figure 3. The profile of the converging section was made to approach a quadrant of an ellipse as closely as possible, and the throat and face surfaces were polished to a smooth finish. The nozzle face was coated with a very thin film of paraffin wax to prevent wetting.

Receiver

The receiver, shown in Figure 3, was made from a 2-cm. length of select capillary tubing of 1.94 mm. I.D. joined to a standard-taper male joint member. The face of the receiver was ground flat and polished. The downstream end was connected to a constant-level overflow, which was mounted on a vertical slide rod and provided with a fine-adjustment leveling screw.

Operation

The jet was horizontally aligned with the receiver by setting a relatively high feed rate from the constant-head supply system to the nozzle and manipulating the traverse mechanism until the jet striking the receiver formed a symmetrical, mushroom-shaped film about the receiver, as in Figure 4(*a*). During this procedure the outflow line leading from the receiver was closed off. If the film were symmetrical about the receiver, upon opening the outflow line the jet would pass entirely into the receiver.

The operation of the receiver was controlled by varying the elevation of the constant-level overflow in the outlet line. When the overflow level was slightly too high, not all the jet was collected in the receiver; some of the liquid spilled over, as shown in Figure 4(*b*). When the overflow level was too low, the free jet continued several millimeters down into the receiver before reaching a point (labeled *i*) at which liquid completely filled the tube, as in Figure 4(*c*). With this condition small gas bubbles were entrained in the rapidly moving liquid at *i*. For absorption measurements the overflow was adjusted to give the condition shown in Figure 4(*d*), in which there was neither spillover of liquid nor entrainment of gas (*30*). Figure 5 is a photograph of a laminar water jet in flight.

In the absence of sudden jars and strong vibration, steady operation of the jet with condition (*d*) at the receiver was possible for extended periods; operating troubles, when they occurred, seemed to arise from occasional small fluctuations in the liquid feed rate. The maximum operable jet length depended upon the liquid feed rate and was limited by the instability of the moving liquid column with respect to breakup.

Jet length was measured by a cathetometer with an accuracy of 0.005 cm. Flow rate was determined by weighing the liquid discharged in a timed interval during each experiment. Temperatures of the liquid entering and leaving and of the gas entering the jet chamber were measured to an accuracy of 0.02°C. Sampling was commenced only after these temperatures ceased varying. In all cases the three temperatures fell within a 0.1°C. range.

Sampling

Outflow from the receiver entered the constant-level overflow well beneath the liquid surface. The point of discharge was immediately above the entrance to another line, through which part of the effluent flowed continuously to a special sampling pipette, from which samples were periodically withdrawn with precaution to ensure adequate purging of the sampling system. With this arrangement it was possible to draw several samples without disturbing the operation of the jet. The sampling pipette consisted, in essence, of two glass bulbs

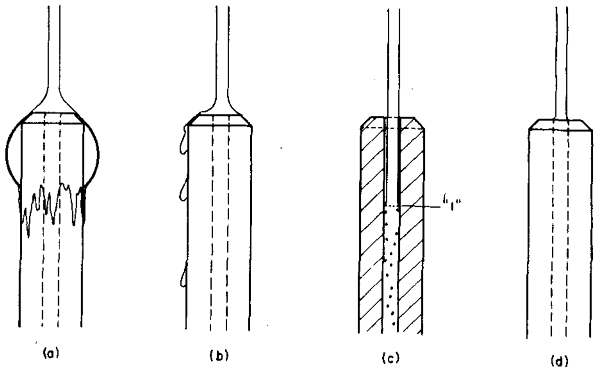

Fig. 4. Operation of jet receiver.

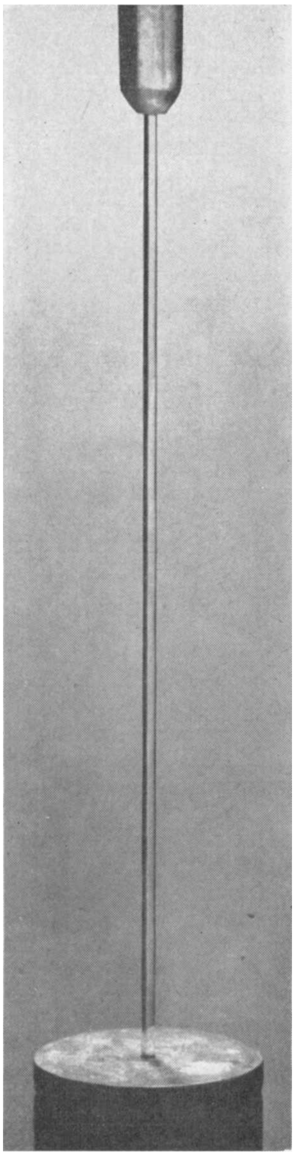

Fig. 5. Laminar liquid jet, nozzle above and receiver below.

connected in series. In discharging a sample the volume withdrawn was measured between reference marks on the upper bulb, but the liquid actually withdrawn came chiefly from the lower bulb, which remained full of liquid, thus minimizing the possibility of desorption of carbon dioxide during sampling. Samples of the feed water were taken before and after every set of runs at each jet length.

Chemical Analysis

Liquid samples were discharged from the sampling pipette into flasks containing reagent solution beneath an inert nitrogen atmosphere. The analytical scheme consisted of precipitation of carbon dioxide as barium carbonate from a solution of dilute, standard sodium hydroxide and excess barium chloride (to suppress ionization of the carbonate at the endpoint), followed by slow back-titration under nitrogen blanketing of the residual hydroxide to a *p*H 8.8 end point with dilute, standard hydrochloric acid. This method is well known, but certain precautions, often overlooked, must be taken to obtain accurate results at low carbon dioxide concentrations (*19*, *20*, *30*). In the present case the range of concentrations analyzed in the effluent water was 10 to 44 p.p.m.; both the precision and accuracy of analysis were found to be about 0.4 p.p.m.

TREATMENT OF DATA

The experimental absorption rate was calculated from the measured change in average concentration experienced by the liquid in passing through the jet. Very small adjustments were made in the experimental absorption rates in order to reduce them all to the same bases of 25°C., 760 mm. Hg total pressure, and standard flow rates. This was done by means of the equation for absorption (when one assumes interfacial equilibrium) into an *ideal* jet, that is, a jet throughout which the velocity is constant and equal to the average velocity at the point of emergence; for an ideal jet it follows from the penetration theory (*4*, *30*, *32*), that

$$\begin{aligned}\phi_* &= \frac{2}{\sqrt{\pi}}(C_e - C_0)(\pi d_0 h)\sqrt{\frac{D}{t_*}} \\ &= 4(C_e - C_0)\sqrt{Dqh} \qquad (1)\end{aligned}$$

Thus the adjusted absorption rate is given by

$$\phi = q(C_{av} - C_0)(1 + \delta) \qquad (2)$$

$$\begin{aligned}1 + \delta &= \frac{\phi}{\phi'} \simeq \frac{\phi_*}{\phi_*'} \\ &= \frac{C_e - C_0}{C_e' - C_0'}\sqrt{\frac{Dq}{D'q'}} \qquad (3)\end{aligned}$$

where primes denote values at experimental conditions and unprimed symbols represent values at the standard conditions selected. In no case did the quantity δ exceed 0.01.

The solubility of carbon dioxide in water at 25°C. and 760 mm. Hg partial pressure was taken as 3.39×10^{-5} g.-moles/cc., a value based on the results of numerous investigators, all in substantial agreement (*30*). The diffusivity of carbon dioxide in water at 25°C. has not been so well established, although from the data shown in Figure 6 it is apparent that the best estimate lies between 1.9 and 2.0×10^{-5} sq. cm./sec. The value 1.97×10^{-5} sq. cm./sec. was adopted in this work.

RESULTS

Experimentally determined absorption rates at 25°C. and 760 mm. Hg total pressure are shown in Figures 7 and 8. The agreement of replicate measurements is, with few exceptions, excellent over the twelvefold range of jet length and the twofold variation of liquid velocity reported.

While the jets produced with the glass nozzle are not subject to the theoretical analysis discussed below because of serious wetting of the nozzle face and periodic variation of cross sectional shape with length, the data obtained with them (Figure 8) are nevertheless of interest. They indicate that there is no significant effect of presaturating with water vapor the carbon dioxide fed to the jet chamber. Thus the gas immediately adjacent to the jet surface is very nearly saturated with water vapor, even if the feed gas is dry, and therefore the proper partial pressure of carbon dioxide to use in

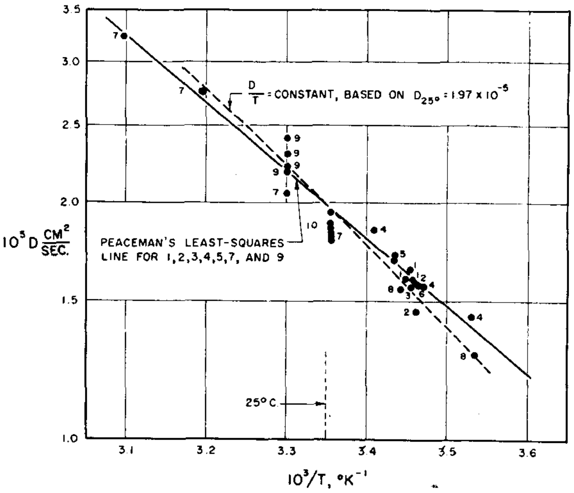

Fig. 6. Diffusivity of carbon dioxide in water.

1. Steady state capillary (*33*).
2. Unsteady state capillary (*33*).
3. Hydrophane plate (*17*).
4. Agar-agar solution (*18*).
5. Counterdiffusion of potassium chloride (*1*).
6. Counterdiffusion of potassium chloride (*3*).
7. Unsteady state capillary (*20*).
8. Agar-agar solution (*34*).
9. Diaphragm cell (*26*).
10. Diaphragm cell (*30*).

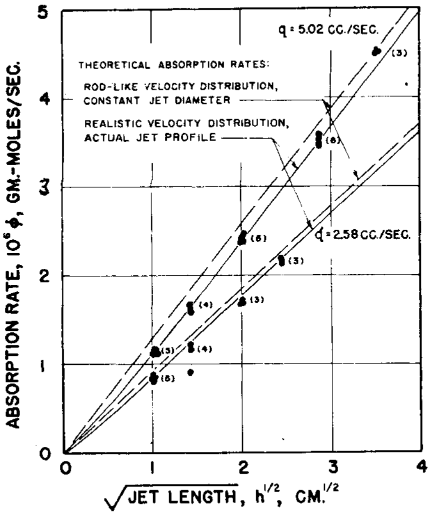

Fig. 7. Absorption of carbon dioxide in water jets issuing from 1.535-mm. I.D. paraffin-coated brass nozzle. The number of measurements in each group is shown in parenthesis.

calculating predictions of the absorption rate is nearly equal to the total pressure less the vapor pressure of water at the temperature of the experiment.

The dashed lines in Figures 7 and 8 were calculated from Equation (1). As far as absorption rates are concerned, the jets employed in this work were evidently similar to ideal jets. However, viscous effects close to the wall in the throat of the nozzle produce a nonuniform velocity distribution in a real jet. Owing to momentum interchange between the surface layers and the more rapidly moving core, a flat velocity profile is approached downstream. Gravitational acceleration further complicates the velocity distribution in a vertical jet. Both agencies result in contraction of the jet as it flows downward.

A quantitative understanding of the fluid dynamics is necessary for the accurate prediction of absorption rates into the jets of interest here. A method of deducing equations describing the liquid flow near the jet surface from measurements of jet diameter *vs.* length and by analogy with closely related flow situations, viz. the laminar wake behind a thin flat plate oriented parallel to the flow and the fall of a nonviscid liquid jet in a gravitational field, has been presented elsewhere (*30, 31*).

Because the penetration depth of the diffusing carbon dioxide molecules is small compared with the jet diameter under the conditions of the experiments reported here, the absorption can be described in terms of a two-dimensional model by using Cartesian coordinates. The differential equation governing the diffusion of carbon dioxide within the jet is

$$U\frac{\partial C}{\partial X} + V\frac{\partial C}{\partial Y} = D\frac{\partial^2 C}{\partial Y^2} \qquad (4)$$

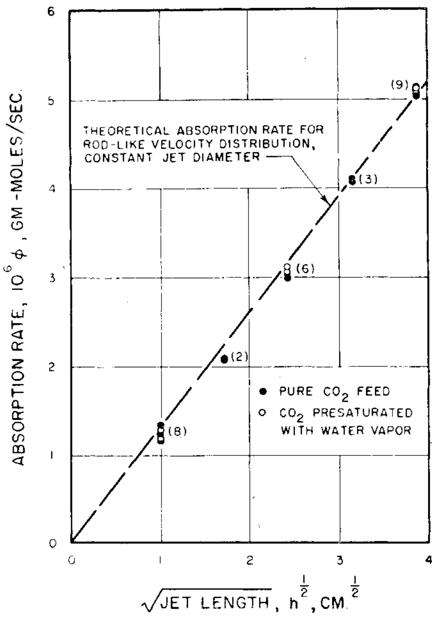

Fig. 8. Effect of presaturating carbon dioxide feed with water vapor. Absorption of carbon dioxide in water jet issuing from 1.414-mm. I.D. glass nozzle at 5 cc./sec.

Two of the boundary conditions are

$$C = C_0 \quad \text{for} \quad X < 0, \quad Y \geq 0 \qquad (5)$$

$$C = C_0 \quad \text{for} \quad X > 0, \quad Y = \infty \qquad (6)$$

If interfacial equilibrium is assumed, the third boundary condition is

$$C = C_e \quad \text{for} \quad X \geq 0, \quad Y = 0 \qquad (7)$$

An approximate but nevertheless quite accurate solution of this boundary-value problem for rates of absorption into the jets employed in this work has been given elsewhere (*30, 31*). The solution was obtained through a kind of perturbation technique in which the ideal jet (previously mentioned) was taken as the undisturbed system, and deviations in absorption rate caused by nonuniform velocity profiles at the nozzle and gravitational acceleration were derived. The computed deviation never exceeded 10% of the ideal-jet absorption rate. Predicted absorption rates, which are plotted as solid lines in Figure 7, are subject to no more than a few percent uncertainty arising from the approximation.

Agreement of the data with the theoretical predictions at the higher flow rate, 5 cc./sec., is outstanding; agreement at the lower flow rate, 2.6 cc./sec., though not as striking is quite good. It is felt that the agreement establishes the validity of the assumption of phase equilibrium at the freshly formed carbon dioxide–water interfaces obtained in the jet apparatus.

DISCUSSION

End Effects in Absorption Experiments

Matsuyama (*25*) reported that the carbon dioxide absorption rate which he measured with a laminar water jet 0.3 cm. long was only about 40% of the predicted value for an ideal jet according to Equation (1). Noting that the longer the jet the better the agreement with ideal-jet predictions, he presumed that because of the high surface tension of water there existed a very short surface film which covered the liquid column attached to the end of his glass nozzle. Absorption rates lower than ideal-jet predictions are to be expected in the case of very short jets, for the surface layers immediately after emerging from the nozzle are moving much more slowly than the average velocity of the liquid, absorption proceeds farther in a given distance traveled, and absorption rate falls off. Unfortunately, as Matsuyama described neither the design of his nozzle nor the downstream contraction of his jet, it is impossible to determine the extent to which the velocity profiles of his jet deviated from the flat profile he tacitly assumed.

If the face of his nozzle was wetted with water, which is likely, a more or less stagnant ring of liquid undoubtedly surrounded the jet for a short distance below the nozzle. The notion of a surface film, however, was based on experiments in which carbon dioxide was absorbed into concentrated barium hydroxide solutions with the formation of easily visible barium carbonate precipitate which accumulated at the face of the nozzle and at the horizontal surface of the receiver. Under certain conditions a film of precipitate surrounding the jet column grew up from the receiver all the way to the nozzle, and absorption of carbon dioxide ceased even though the flow of liquid continued. The same sort of film was produced by Cullen and Davidson (*4*) by sprinkling talc onto the surface of their jet. It seems reasonable that, as they have perceptively suggested, the stability of such films derives from the force with which the particles adhere to the water surface and the strength in compression of their structures, which are supported by solid surfaces at the nozzle and receiver. The stability of such a film does not necessarily indicate that any part of the surface of the jet is stagnant in the absence of the film.

Similar stable films, composed of fine solid particles and extending upstream as much as 2 cm. from a solid obstacle touching the liquid surface, can be produced on the surface of the falling liquid film in a short wetted-wall column (*23, 36*) and on the surface of the moving liquid in a rotating-drum apparatus (*20*). It is highly unlikely that a free liquid surface can assume a rigid structure over such distances in the absence of solid particles or other surface-active impurities capable of forming a rigid surface film.

During the normal operation of a wetted-wall, rotating-drum, or jet absorber a family of standing, capillary waves exists on the free surface of the moving liquid at a greater or lesser distance upstream from the exit slot, outlet knife edge, or receiver, respectively. Tests with powder blown onto, and dye injected into, the surface indicate that it is nearly stagnant between the standing waves and the exit aperture (*20*, *23*, *36*). From careful measurements of absorption rates of carbon dioxide and sulfur dioxide in water in short wetted-wall columns the presence of an exit end effect has been established; this end effect is very well accounted for by supposing that the surface between standing waves and exit is inactive in absorption (*23*, *36*). The most striking feature of the wave disturbance is that following a sudden surge in liquid flow which carries it downstream over the solid obstacle at the exit it is immediately reestablished at that obstacle, and thereupon it very slowly climbs upstream until it has reached its original position. Wendel (*36*) found that the exit end effect in a short wetted-wall absorber can be eliminated almost completely by deliberately causing momentary spill over at the outlet slot at regular, widely spaced intervals.

Capillary waves were observed on the surfaces of the jets employed in this work. At a low flow rate (1.25 cc./sec.) a family of waves was clearly visible, extending about 1 mm. upstream of the receiver. (See *w* in Figure 4(*d*).) As the flow rate was increased, the height to which the waves extended decreased; at 5 cc./sec. (the higher of the two flow rates reported in Figure 7) a single standing wave was barely discernible about 0.1 mm. above the face of the receiver. It is concluded that the absorption measurements reported in this paper were ***not*** significantly affected by an exit end effect similar to that which exists in wetted-wall–column and rotating-drum apparatus.

Effects of Surface-Active Contaminants

The conclusion seems inescapable that surface-active contaminants, initially present within the apparatus or in the feed streams, accumulate on the surface of the liquid film at the downstream end of both wetted-wall–column and rotating-drum apparatus, and there they form a rigid or semirigid surface structure which drastically impedes liquid flow close to the surface. The presence of this structure explains the observed behavior of the capillary-wave disturbance. Stagnation of the liquid adjacent to the surface is sufficient to account for the relative inactivity in absorption of the region associated with the exit end effect, but a highly compressed film of surface-active material may itself offer appreciable resistance to the passage of solute molecules.

Hammerton and Garner (*12*) reached a similar conclusion with regard to a comparable situation. Their studies of gas absorption from single bubbles demonstrated clearly that contamination of the surface of a rising bubble by surface-active material initially present in trace amount can convert a mobile, free liquid surface into a rigid structure and that such a conversion is accompanied by a marked reduction in absorption rate.

Table 1. Summary of Recent Investigations

Physical Absorption of Slightly Soluble Gases in Water

Investigator(s)	Type of absorber	Nominal liquid exposure time, sec.	Solute gas	Value of D used, 10^5 sq. cm./sec.	Departure of absorption rates from interfacial equilibrium theory
Kennedy (*20*)	Rotating drum	0.008–0.22	CO_2	2.02(25°C.)	5 to 20% below theory
Lynn *et al.* (*23*)	Wetted-wall columns	0.01 –0.98	SO_2	1.46(20°C.)	None (see text)
	Single wetted spheres	0.05 –1.78	SO_2	1.46(20°C.)	None (theory according to reference *8*)
Wendel (*36*)	Short wetted-wall column	0.02 –0.20	CO_2	1.97(25°C.)	None
Cullen and Davidson (*4*)	Orifice jet	0.01 –0.34	CO_2	1.92(25°C.)	None
Davidson and Cullen (*8*)	Wetted sphere	0.12 –0.57	CO_2	1.92(25°C.)	None
			O_2	2.44(25°C.)	None (see text)
			H_2	6.85(25°C.)	
			N_2O	2.12(25°C.)	
Authors	Jet	0.003–0.05	CO_2	1.97(25°C.)	None

There is ample evidence of the presence of minute amounts of surface-active materials in all but the most extraordinarily carefully purified water (*13*, *14*). The effect upon absorption of adding to water measurable quantities of surfactants, such as Teepol and Petrowet, has been investigated by a number of workers (*3*, *11*, *20*, *23*). In long wetted-wall columns the addition of a wetting agent markedly affects both the liquid-flow regime, causing the disappearance of rippling in the falling film under certain conditions, and the rate of absorption, which is much reduced in the absence of rippling. In shorter columns the wetting agent does not noticeably affect the rate of absorption, although it does influence the amplitude and position of the capillary waves described. The wetting agent likewise affects the position of the capillary waves above the receiver of a jet absorber. Cullen and Davidson (*4*) showed convincingly that this effect is a free-energy phenomenon. The same investigators found that the influence of commercial wetting agents on absorption is apparently related to the small amounts of impurities which they contain (*3*). Apart from a reduction of mixing in a liquid film when rippling is suppressed the action of surface-active agents on absorption is not yet understood. The action probably depends upon the rate at which they diffuse from the bulk liquid to freshly formed surface, the properties of the adsorbed film they form on the surface, and possibly interaction between them and the solute molecules.

Phase Equilibrium at the Interface

The principal conclusion drawn from the present work, that phase equilibrium prevails at freshly formed, relatively clean interfaces between water and slightly soluble gases, answers the question of interfacial resistance in gas absorption, first posed on the basis of Higbie's data (*5*, *15*, *16*). It is corroborated by recent, careful studies of several investigators, whose results are summarized in Table 1. Only Kennedy's data give any significant indication of an interfacial resistance. However his theoretical predictions are based on the assumption that his liquid films accelerated *instantaneously* to the drum velocity. The data fall farthest below the predictions at the shortest liquid exposure times, that is, at conditions under which the undetermined acceleration entrance effect was greatest (*20*). At the longest contact times he achieved, the departure of his data is scarcely significant because of the uncertainty regarding the value of diffusivity which he used. Wendel (*36*) evidently was successful in allowing for the acceleration entrance effect in his short wetted-wall column by means of an equation derived by Scriven (*30*) and in eliminating the stagnation end effect (already discussed) by deliberately causing momentary spill over at the outlet slot at regular widely spaced intervals.

Predicted absorption rates are proportional to the square root of diffusivity [Equation (1)], the values of which are subject to greater uncertainty in the cases of sulfur dioxide and oxygen and much greater uncertainty in the cases of nitrous oxide and hydrogen than in the case of carbon dioxide. Nevertheless the agreement of the data for gases other than carbon dioxide with predicted absorption rates based on reasonable diffusivity values is impressive. There remains the task of confirming the diffusivity values of these gases, and it would perhaps be desirable to extend downward the liquid exposure times in absorption measurements made with them.

The absorption measurements of earlier workers (*11*, *15*, *16*, *24*, *25*, *26*, *35*) are subject to rather more experimental error than those included in Table 1. Generally they do not differ by more than 20 or 30% from predictions (which are in every case open to question because of undetermined hydrodynamic and surface effects) based on unsteady state diffusion theory and the assumption of interfacial equilibrium, and this is not, in the writers' opinion, sufficient to invalidate the conclusion already drawn. Higbie (*15*, *16*) took no account of the intricate flow regime surrounding his bubbles, and his reported absorption rates represent relatively small differences between two sets of values, those obtained from *absorption runs* and a *parallel series of blank runs*. Thus his results are of doubtful significance. Vivian and Peaceman (*26*, *35*) were unable to give an adequate accounting, and Emmert and Pigford (*11*) did not recognize the importance of end effects in their short wetted-wall columns. The latter also reported absorption and desorption rates, measured in long wetted-wall columns with a wetting agent present, which fell below their theoretical predictions. Their results may reflect interference of an accumulation of surface-active material with the passage of solute molecules through the interface.

Phase equilibrium is probably established as rapidly as sufficient solute molecules arrive at the liquid surface to saturate the first few molecular layers of liquid. According to estimates based on the Knudsen equation of gas kinetic theory,

$$\Gamma = \frac{p}{\sqrt{2\pi MRT}} \qquad (8)$$

the time required for this to occur, with the exception of very low partial pressures of solute gas, is many orders-of-magnitude less than the shortest time of contact of liquid with gas yet studied, 0.003 sec. Schrage (*29*) has treated the case in which the rate of incidence of gas molecules on the liquid surface becomes a controlling factor in absorption. The apparent interfacial resistance to mass transfer in earlier absorption studies was explained in terms of an *accommodation coefficient* (*5*, *7*, *11*). It now seems certain that the accommodation coefficient of a clean water surface absorbing a slightly soluble gas, in particular carbon dioxide, is no smaller than 0.001, and it is quite possible that it approaches unity. It is worthy of mention that the evaporation coefficients (equivalent to the accommodation coefficient in gas absorption) of pure substances have been found to be unity when proper allowance was made for thermal effects in the experimental determinations (*22*).

There is mounting evidence that small, possibly infinitesimal, amounts of surface-active materials may bring about a much reduced rate of absorption into a flowing liquid or from a rising bubble. It is important to determine whether this reduction is the result of hydrodynamic effects or of an interfacial resistance to mass transfer. The need for additional data is great, for the implications of the available evidence are obvious in commercial mass transfer operations, where high-purity process streams and apparatus free of possible surface contaminants are rare indeed. Hickman several years ago expressed surprise that chemical engineers and physical chemists continue to treat water as though its surface were H_2O (*14*). Drawing upon his experience in high-vacuum distillation he stated that liquids are inherently self-soiling: "It is axiomatic that an ordinary liquid is contaminated (*13*)."

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NOTATION

C = liquid concentration, moles/cc.
C_e = equilibrium liquid concentration, moles/cc.
C_0 = initial liquid concentration, moles/cc.
C_{av} = average (outlet) liquid concentration, moles/cc.
d_0 = nozzle diameter, cm.
D = diffusivity, sq. cm./sec.
h = jet length, cm.
M = molecular weight, g./mole
p = partial pressure, dyne/sq. cm.
q = volumetric flow rate, cc./sec.
R = gas constant, 8.316×10^7 (dyne)(cm.)/(mole)(°K.)
t_* = nominal exposure time, sec.
T = absolute temperature, °K.
U = velocity parallel to jet surface, cm./sec.
V = velocity normal to jet surface, cm./sec.
X = distance parallel to jet surface, cm.
Y = distance normal to jet surface, cm.

Greek Letters

Γ = molecular flux in gas phase, moles/(sq. cm.)(sec.)
δ = dimensionless quantity defined in Equation (3)
μ = liquid viscosity, g./(cm.)(sec.)
ϕ = absorption rate, moles/sec.
ϕ_* = absorption rate into ideal jet, moles/sec.

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