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Gas Absorption by Drops Traveling on a Vertical Wire

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In the measurement of the absorption of carbon dioxide gas by a series of oil drops moving down a vertical wire the variables studied are drop frequency, oil viscosity, wire size, and column length. A model is proposed which assumes that the gas is absorbed by almost stagnant liquid film between and covering the drops, that the film is subsequently mixed with a drop as it moves past, and that the dissolved gas is carried from the column in circulating loops of liquid within the drops. The model leads to an equation which correlates the data and gives a good approximation to the slope of the line.

This study is concerned with the liquid-side controlled absorption of carbon dioxide gas by a series of white oil drops moving down a vertical wire. Adjacent drops are connected to each other by a thin liquid film, and both the drops and film are axisymmetric about the wire. Inside each drop is a circulating loop of liquid roughly in the

shape of a torus. Throughout this paper, drop is used to denote the combination of the circulating torus with the region surrounding it to form the observed bulge; torus refers to the circulating loop only.

Figure 1 gives the geometry of the flow and also defines the nomenclature used. Figure 2c is a schematic representation of the streamlines for the flow of the liquid in a coordinate system moving with the drops. It may further help the reader to visualize the flow if we give some typical dimensions. For the No. 7 white oil (density, $\rho =$ 0.87 g./cc.; surface tension, $\sigma = 35$ dynes/cm.; viscosity, $\mu = 0.57$ poise) flowing down a wire of 0.079-cm. diameter at a frequency of 2 drops/sec., the volumetric flow rate is 9.3×10^{-3} cc./sec. This value and the others to be cited depend on the size of the drop, which can be controlled by the geometry of the apparatus at the point of drop formation. The drops travel down the wire with a wave velocity of 1.9 cm./sec. The maximum drop diameter is 0.19 cm., the diameter of the film is 0.11 cm., the film thickness is 1.5×10^{-2} cm., the drop length is 0.35 cm., and the wavelength is 0.74 cm. The velocity at the free surface of the film, which connects two drops, was calculated by assuming a fully developed parabolic flow with the measured film thickness. This velocity was found to be 0.17 cm./sec., an indication that the liquid in the film moves much more slowly than the liquid in the circulating torus.

The flow just outlined provides a novel method of gasliquid contacting. The study was undertaken because we saw a need for a continuous gas-liquid contacting process which could be operated at very low liquid rates with large interfacial areas and widely varying contact times in a small simple apparatus. The work to be described might thus find use in the treatment of certain biological or radiological liquids which are available only in small quantities. In addition the contacting process is of some

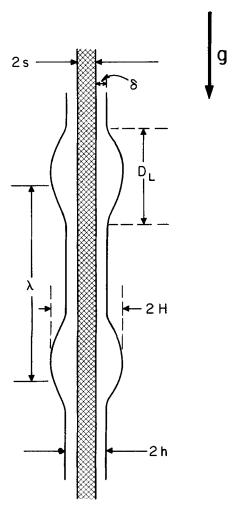


Fig. 1. Geometry of the flow of drops traveling on a vertical wire.

interest in that it is a hybrid of three conventional methods of gas-liquid contacting: liquid jets, falling liquid films, and falling drops.

APPARATUS AND PROCEDURE

The liquids used in this study were Standard Oil Company of California's white oils No. 7, 9, and 15. The pertinent physical properties of the oils used are shown in Table 1. The densities and surface tensions are catalogue values. The saturation concentrations and diffusivities of carbon dioxide in the oils were measured by methods which will be described.

The apparatus used to measure the absorption is shown in Figure 3. The oil supply reservoir is connected to a 13-gauge syringe needle, and the oil flow is controlled by a needle valve. The exit end of the syringe needle was cut perpendicular to the needle axis and machined to a smooth surface. The needle enters the absorption chamber through a three-hole rubber stopper at the top of the column with a gas outlet and a thermometer. The absorption chamber is a 2.5-in. O.D., heavy-wall glass tubing of lengths varying from 40 to 3 cm. At the bottom of the chamber is another three-hole rubber stopper which contains a take-off tube, the gas inlet, and a tube leading to a manometer. The take-off tube is a 3-in. long, ¼-in. I.D. plastic tube connected directly to a Van Slyke manometric gas analyzer. All connections in the apparatus are made with Tygon tubing. A piano wire down which the drops of oil move is stretched taut through the syringe and take-off tube. The wire is vertical and centered at the syringe exit so that the oil drops form and move with angular symmetry about the wire; 0.079- and 0.051-cm. diameter wires are used.

Dissolved gases are removed from the oils by heating the oils under vacuum. When a sample of oil is transferred from the vessel in which it was degassed to the reservoir of the absorption apparatus, the oil is exposed briefly to the air, permitting some gas pick up. Precautions are taken to avoid transed air hubbles in the oil.

trapped air bubbles in the oil.

To ensure negligible gas phase resistance to the transfer, the oil is contacted with pure carbon dioxide gas, which, because of its high solubility, facilitated concentration measurements. The partial pressure of carbon dioxide gas in the absorption chamber is maintained at 1 atm. A constant level of oil is maintained in the take-off tube so that the column length for absorption is constant during the run. The oil is allowed to flow through the take-off section for at least one complete residence time before a sample was taken, after which a sample is drawn into the Van Slyke apparatus for analysis.

The amount of carbon dioxide absorbed was measured for each oil flowing down the 0.079-cm. diameter wire for a series of lengths and flow rates. Absorption into the No. 15 oil flowing down the 0.051-cm. diameter wire was also measured. Two separate samples were analyzed for each run. If the measured concentrations agreed to within 5%, the average value of the two readings was used as the concentration. If the two values did not agree, a third sample was analyzed and the three values were averaged.

The frequency of the drop flow was measured by counting, the flow rate by collecting the oil in a graduated cylinder for a known period of time, and the wave velocity by timing a drop traveling a known length of column. Reported values are the averages of three measurements.

The saturation concentration of carbon dioxide in the No. 7 oil was measured by bubbling carbon dioxide in the oil for several hours and analyzing the sample in the Van Slyke apparatus. A mass transfer run with the 30-cm. column with a drop frequency of 1 drop/4 sec. indicated that over 95% of saturation was achieved. A run with the 40-cm. column reproduced the saturation value to within 1%. Hence mass transfer runs with the 40-cm. columns were used to measure saturation concentrations of carbon dioxide in all three oils and these data are used in the subsequent calculations.

The only known data on diffusivity in white oils are those of Reamer, Duffy, and Sage (2) and of Reamer and Sage (3), who have worked at elevated pressures. An extrapolation can be made for atmospheric pressure but only at the risk of a large error. After several methods of absolute diffusivity measurements were investigated, the following was

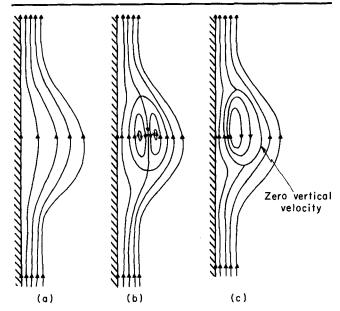


Fig. 2. Possible streamlines in the liquid in a coordinate system moving with the wave velocity. The arrows indicate the direction of flow in this coordinate system. (a) No circulating loop. (b) Double circulating loop. (c) Single circulating loop.

adopted. A sample of the oil saturated with carbon dioxide was injected under an atmosphere of carbon dioxide into a cell whose bottom is an optically flat surface. After the oil had spread out into a thin film (approximately 0.15 cm. thick) the carbon dioxide above the oil was evacuated by pulling a vacuum for 1 min. The carbon dioxide in the oil was then allowed to desorb into air for 30 min. Then a vacuum was again pulled for 1 min. in order to evacuate the desorbed carbon dioxide. Next, a known volume of barium hydroxide solution was added to the cell and the mixture vigorously shaken; the excess barium hydroxide was titrated to the phenylphthalein end point with 0.01 molar hydrogen chloride. Because the oils were viscous and the layers were thin, and because the gas above the layer of oil was stagnant, convective currents in the oil layer are thought to be minimized. The diffusivity was then calculated from the analytical solution for the transfer from an initially uniform slab when the surface condition is suddenly changed (4). There was very good reproducibility in the case of the No. 7 and 15 oil but the reproducibility was unaccountably very poor for the No. 9 oil. The calculated values of the diffusivities are:

TABLE 1. PHYSICAL PROPERTIES OF THE OILS AT 25°C.

Property	No. 7	No. 9	No. 15
Density ρ, g./cc.* Surface tension σ, dyne/cm.*	0.870 35	0.878 36	0.868 36
Viscosity μ, poise†	0.566	0.716	1.34
Carbon dioxide saturation concentration P_s , moles/liter‡ when liquid is exposed to carbon dioxide gas at 1 atm. pressure	0.326	0.326	0,0333
Diffusivity of carbon di- oxide D, sq.cm./sec. × 106**	3.9	3.3 ¶	2.4

The diffusivity is unexpectedly low for the No. 9 oil. This has been attributed to the difficulty in the reproduction of the value, which varied from a low value of 0.65×10^{-6} to a high value of 2.8×10^{-6} sq.cm./sec. The diffusivities were plotted as a function of viscosity on log-log paper, with a straight line connecting the No. 7 and 15 oil values. The diffusivity value for the No. 9 oil was obtained by interpolation. The value obtained was 3.3×10^{-6} sq.cm./sec., which has been used in all calculations. It is interesting to note that the extrapolation of Sage and Reamer predicts a value of 1.5 to 3.0×10^{-6} sq.cm./sec. for the carbon dioxide-white oil (56 centipoise) system, depending on how the curves are read.

A Linhof 4×5 camera with f-8, 1/400 sec. settings and with ASA 400 speed sheet films were used to photograph drops for each flow condition. Measurements of the dimensions shown on Figure 1 were made from the negatives on a Vanguard motion analyzer.

THEORETICAL MODEL

Fluid Mechanics

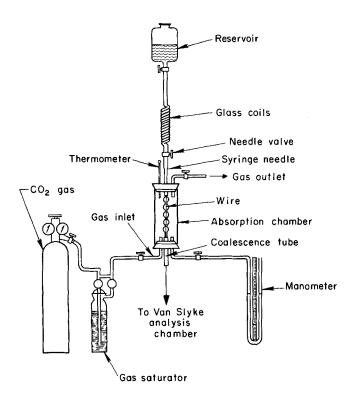
Based on the external geometry of the drop and observations of the motion of small carbon black particles introduced into the oil, a fairly clear picture of the flow pattern emerges. Three conjectured streamline patterns are shown in Figure 2. To reduce the patterns to those for equivalent systems in steady state, the streamlines are drawn in a coordinate system moving with the wave veloc-

For the noncirculating flow represented in Figure 2a all carbon black particles in the oil would move upstream relative to the drop. For flow with a double circulating loop, as represented in Figures 2b, particles outside the loops would move upstream relative to the drop, while those within the circulating loops would travel down the wire with the drop (that is, with the wave velocity). Of those particles moving with the drop, the particles caught in the circulating loop farther from the wire would circulate counterclockwise, as viewed in the drawing, while those caught in the loop nearer the wire would circulate clockwise. For the flow with a single circulating loop as represented in Figure 2c, again those particles outside the circulating loop would move upstream relative to the drop, while those within the loop would travel down the wire with the wave velocity. As shown in the figure these latter particles would rotate in the clockwise direction. It is also possible to imagine a flow with a single counterclockwise circulating loop but this is physically less likely, because then the region of highest liquid velocity would be on the side of the loop nearer the wire.

When carbon black particles were introduced into the flow, some of the particles were observed to move upstream relative to the drop, while others moved down the wire with the drop circulating in a clockwise direction (as viewed in the drawing). No counterclockwise circulation was observed. Since the counterclockwise circulating loop of Figure 2b is closer to the outer surface of the drop, particles would have to circulate counterclockwise when they are introduced near the surface. Several introductions near the surface resulted in only clockwise circulation of particles. Therefore we concluded that in a coordinate system moving with the wave velocity, the drops have a single circulating loop and the circulation is clockwise, as viewed in the drawing. The circulating fluid forms welldefined tori which move down the wire with the wave velocity and retain their identity for long distances.

Carbon black particles in the film between drops or near the surface of a drop were observed to move much more slowly than the wave velocity; that is, velocity of the bulge

<sup>Catalogue value.
Measured in Haake viscometer.
Measured in Van Slyke apparatus.
Measured in diffusion cell.
Interpolated value from measured diffusivities of No. 7 and 15 oils.</sup>



Note: All conections are made with Tygon tubing.

Fig. 3. Schematic diagram of experimental apparatus.

and particles undergoing circulation. This qualitative observation is given some quantitative support by calculating the velocity of the free surface of the film under the assumption of fully developed parabolic flow with the (photographically) measured film thickness. The surface velocity is given by the formula

$$u_s = \rho \ g \ \delta^2/2\mu$$

This calculation shows that the maximum velocity in the film is on the order of a tenth of the measured wave velocity (see Table 2). One should also note that the thickness of the drop, as measured by (H-s), is larger than the film thickness by about a factor of four. These two observations, the smallness of the velocity in the film and the thinness of the film, indicate that the bulk of the liquid is carried down the wire in the drops as circulating tori and the film between drops can be regarded as essentially stagnant.

Table 2. Calculated and Measured Results from Photographic and Flow Measurements (See Figure 1)

No. 7 Oil, 0.079-cm. Wire

Dr

rop frequency, drops/sec.	1	2	3
$q imes 10^3$, cc./sec.	5.6	9.3	14.0
U, cm./sec.	2.0	1.9	1.9
us, cm./sec.	0.16	0.17	0.25
$V \times 10^3$, cc.	5.6	4.7	4.8
2s, cm.	0.079	0.079	0.079
2H, cm.	0.21	0.19	0.19
2h, cm.	0.11	0.11	0.12
ð, cm.	0.015	0.015	0.018
λ, em.	2.0	0.74	0.52
D_{r} , cm.	0.35	0.35	0.34

Mass Transfer

At contact times for which the concentration of absorbed gas in the torus is an appreciable fraction of the saturation concentration, the concentration of the exit stream will be essentially that of the exiting torus. This is because of the much larger flow rate associated with the torus than with the film as pointed out above. The model proposed below is an extreme case, with the assumption of complete mixing within a drop except for the region immediately adjacent to the drop surface. The extent to which the drop can be considered completely mixed is difficult to assess and will be discussed shortly.

In a coordinate system moving with the drop, the volumetric flow rate into and out of the drop is

$$Q = \pi \{(s + \delta)^2 - s^2\} \ U = 2\pi s \delta U \ (1 + \delta/2s) \ \ (1)$$

Inherent in this equation is the assumption that the film is essentially stagnant. If the film becomes saturated before a drop reaches it, a mass balance on the well-mixed drop gives

$$V\frac{dP}{d\Theta} = Q(P_s - P) = -V\frac{d}{d\Theta}(P_s - P)$$
 (2)

Here any gas absorbed through the surface of the drop is counted as being part of the film from the preceding drop. With the boundary condition

$$at \Theta = 0, P = P_i \tag{3}$$

Equation (2) can be integrated to yield

$$(P_s - P)/(P_s - P_i) = \exp(-Q\Theta/V)$$
 (4)

The contact time of the drop Θ is the ratio of the column length L to the drop velocity U. Substitution of this relation and of Equation (1) into Equation (4) results in

$$(P_s - P)/(P_s - P_i) = \exp \left[-2\pi s \delta L(1 + \delta/2s)/V\right]$$
 (5)

Two important questions arise in this model: (1) Does the film become saturated? (2) Is the drop well mixed?

1. The criterion for determining if the film becomes saturated with solute between the passage of successive drops is given by the value of $\mathcal{D}t/\delta^2$. If the value of this group is greater than unity, then the film is essentially saturated. The extreme values for the above quantities in this study are

$$\mathcal{D} = 3.9 \times 10^{-6} \text{ sq.cm./sec.}$$

 $t = \lambda/U = 2.3 \text{ sec.}$
 $\delta = 1.5 \times 10^{-2} \text{ cm.}$

With these values, $\mathfrak{D}\lambda/U\delta^2\approx 6\times 10^{-2}$. This implies that the film is far from saturation; in fact the penetration theory seems to be applicable.

Since the film is not saturated, the differential equation that describes the mass balance becomes

$$V\frac{dP}{d\Theta} = Q(P' - P) \tag{6}$$

where P' represents the average solute concentration in the film before entering the drop and is expected to be given by an equation of the form

$$(P_s - P')/(P_s - P) = f(\mathfrak{D}\lambda/U\delta^2) \tag{7}$$

Equation (6) now becomes

$$-V \frac{d(P_s - P)}{d\Theta} = Q [(P_s - P) - (P_s - P')] = Q(1 - f) (P_s - P)$$
(8)

which, when integrated with the same boundary condition as before, gives

$$(P_s - P)/(P_s - P_i) = \exp[-Q(1 - f)\Theta/V]$$
 (9)

Since the film is essentially stagnant and the penetration theory is applicable, the exact form of f can be determined easily. The well-known result is (5):

$$(1-f) = (4\mathfrak{D}\lambda/\pi U\delta^2)^{1/2} \tag{10}$$

This should be corrected by the factor A, which accounts for the greater area of that part of the film which surrounds the drop. To estimate this correction we have treated the drop as an ellipsoid of revolution that has major diameter D_L and minor diameter 2H. This leads to corrections between 5 and 30% depending on the drop frequency. For the volume of the mixed part of the drop, we have taken V as equal to q/n (see the discussion). The wave velocity U is related to the wavelength λ and the drop frequency n by $U = n\lambda$. When these results and Equation (1) are substituted into Equation (9) we obtain upon simplification

$$\frac{P_s - P}{P_s - P_i} = \exp\left[\frac{2\pi s}{(q/n)} \left(1 + \frac{\delta}{2s}\right) A \left(\frac{4\mathcal{D}}{\pi n}\right)^{1/2} L\right] = e^{-L^*} \quad (11)$$

2. Although good circulation is observed inside the drops, it is difficult to judge whether the drops can be considered well mixed. The flow is certainly laminar. However by mixing we do not mean the drop to be turbulent or stirred or even of uniform concentration; rather, the drop is a region of intensified diffusion. Estimates, after the method of Kronig and Brink (6), of the time characteristic of circulation show it to be very much less than a time characteristic of molecular diffusion. Thus the streamlines within the torus should also be lines of constant concentration. Because it is probable that the streamlines are compressed on the side of the torus near the wire, it is probable that there will be large concentration gradients there accompanied by rapid diffusion. On the other hand, the expansion of the streamlines on the side of the torus far from the wire will facilitate transfer into the torus from the film. When a drop must fall through several drop lengths before occupying the position of the preceding drop, mixing is facilitated so that the assumption should be best at low drop frequencies.

EXPERIMENTAL RESULTS AND DISCUSSION

Typical results of the flow and photographic measurements are listed in Table 2. The complete set of measurements for Tables 2 and 3 may be found in the thesis by Rajan (1). The accuracy of all measurements is about 10%, except for the drop length D_L , which is somewhat less accurate because the gradual merging of the drop with

TABLE 3. MASS TRANSFER DATA

No. 7 Oil; 0.079-cm. wire; $P_s = 0.326$ mole/liter

Drop frequency, drops/sec.

2 3

Volumetric flow rate, cc./sec.

$$5.6 \times 10^{-3}$$
 9.3×10^{-3} 14×10^{-3}

Column length, cm.	Exit concentration, mole/liter			
16.0	0.0281	0.0268	0.0243	
10.5	0.0263	0.0248	0.0220	
6.0	0.0233	0.0208	0.0175	
3.0	0.0174	0.0170	0.0139	

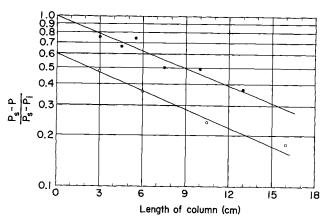


Fig. 4. Gas absorption as a function of column length for No. 7 oil moving down the 0.031-in. diameter wire with a frequency of 2 drops/sec. $\bigcirc = P_i = 0$ as the total length of column. $\bullet = P$ and P_i as the measured concentrations for two column lengths differing by the amount L.

the film made it difficult to pick off a unique length. For a given oil and wire (and entrance geometry) only the wavelength and volumetric flow rate varied significantly with the drop frequency. The wave velocity, the torus volume, and the other geometrical factors were nearly independent of drop frequency. In addition, for the 0.079cm diameter wire, the geometry of the drop itself was roughly the same for all three oils. One should note that the product $n\lambda$ was not precisely equal to U as was assumed above, the deviation being within 15% for all except two cases.

The results of typical mass transfer experiments are listed in Table 3. The reproducibility of the runs was generally about 5% but it was somewhat poorer at the lower flow rates.

The data for each flow condition were plotted as $(P_s P/P_s - P_i$) (where P_i was taken to be zero) vs. column length. A typical plot (for No. 7 oil on the 0.079-cm. wire at a drop frequency of 2 drops/sec.) is shown in Figure 4. This method of plotting gave fairly straight lines and when extrapolated to zero column length indicated end effects ranging from 20 to 60% of saturation. The tendency was for the end effect to increase as the drop frequency decreased, that is, as the time of formation increased. To suppress the end effects the data were replotted as $(P_s - P)/(P_s - P_i)$ vs. L, where P and P_i are the measured concentrations for two column lengths differing by the amount L. This method of plotting also gave straight lines with the same slope as before but with somewhat greater scatter and now passing through $(P_s - P)$ $(P_s - P_i) = 1$ at L = 0 (see Figure 4). The data for all flow conditions studied were then plotted as $(P_s - P)$ / $(P_s - P_i)$ vs. L* is the dimensionless column length suggested by the model [see Equation (11)]. This is shown in Figure 5.

The model does an adequate job in correlating the data and in predicting the slope of the line. In coming to this conclusion one should keep in mind the large tolerance on the ordinate permitted by the 5% accuracy of the concentration measurements. The permissible error is shown in Figure 5 by vertical lines for several arbitrarily chosen points. Although the correlations for most flow conditions individually are somewhat better than the overall correlation presented in Figure 5, there is no significant trend with changing flow rate, oil viscosity, or wire size not already taken into account. The consensus of the data is that the model underestimates the column length required for a given amount of transfer by about 30%. This may be due partially to underestimating the drop (mixing)

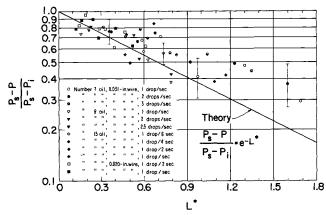


Fig. 5. Overall correlation of gas absorption as a function of dimensionless column length.

volume by using the torus volume. Estimation of the drop volume from the photographic measurements is difficult owing to the uncertainty in D_L . Graphical integration of the measured shapes gave volumes about 20% larger than q/n. However, it is likely that not all of the drop volume, and especially the liquid adjacent to the wire and the free surface, is effectively mixed. There is also a practical advantage in using q/n. In this way everything needed in the final equation can be determined by measurement of the volumetric flow rate and drop frequency alone, except for two minor corrections $(1 + \delta/2s)$ and A. A correlation of these geometrical quantities with the physical properties of the liquid and the operating variables could be established (analogous to the correlation of the thickness of the film left on a tube wall as the liquid drains from the tube) but at present we have insufficient data to do this. Dimensional and physical arguments lead one to expect a correlation for the film thickness of the form $\delta/s = f(\rho g s^2/\sigma, q/n s^3)$

The value of the model proposed here can be judged by comparing it with the data and with alternative reasonable models. We have just seen that the proposed model correlates the data and predicts the right magnitude of column length for a given amount of gas absorption. Other models were considered. These included treating the drops as unconnected volumes with the absorption given the equations developed by Kronig and Brink (6) for circulating drops and treating the system as unrippled flow down a vertical wall as discussed by Emmert and Pigford (7). Both models predicted column lengths more than an order of magnitude larger than the observed column length. The work of Handlos and Baron (8) on mass transfer to unconnected turbulent drops can be arranged to give the following equation:

$$(P_s - P)/(P_s - P_i) = \exp\left\{-\frac{0.00375 \text{ SL}}{(1 + \mu_{\rm in}/\mu_{\rm out})V}\right\}$$
 (12)

The result is that the change in concentration is governed solely by geometrical considerations and is independent of the molecular diffusivity! To compare the equation with the data, the ratio of the viscosity of the drop to the viscosity of the continuous phase was taken as unity, the area available for transfer was estimated as $2\pi HD_L$, and the drop volume was estimated as q/n. A correlation as good as that shown in Figure 5 was obtained and the equation predicted the right slope of the line.

SUMMARY

The liquid-side controlled absorption of a gas by a series of drops moving down a vertical wire has been investigated. Adjacent drops are connected by a thin film and both the drops and the film are symmetric about the wire. Observations of the motion of small particles introduced into the flow indicated that there is a circulating loop of liquid within each drop. A model for the mass transfer has been proposed which assumes that the gas is absorbed by the almost stagnant liquid film between and covering the drops, that the film is subsequently mixed with a drop as it moves past, and that the dissolved gas is carried from the column in the circulating loops of liquid within the drops. Measurements of the absorption of carbon dioxide gas into white oil have been made. The mass transfer was adequately correlated by the model, but it could also be adequately correlated by the model of Handlos and Baron (8) for unconnected turbulent drops.

ACKNOWLEDGMENT

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NOTATION

= correction factor for area A

 D_L = drop length, cm.

= diffusivity, sq.cm./sec. D

= penetration theory solution f

= acceleration of gravity, sq.cm./sec.²

 $_{h}^{g}$ = minimum radius of drop, cm. Η

= maximum radius of drop, cm.

 \boldsymbol{L} = column length, cm.

= dimensionless column length

= drop frequency, sec. -1

= concentration of carbon dioxide in oil, moles/liter

= inlet concentration, moles/liter

= saturation concentration, moles/liter

= average concentration in film before entering drop, moles/liter

= volumetric flow of oil, cc./sec.

= volumetric flow rate into drop, cc./sec.

= wire radius, cm.

= surface area of a drop, sq./cm.

= exposure time of film between successive drops,

= velocity of surface of film, cm./sec.

 \boldsymbol{U} = wave velocity, cm./sec.

V= drop volume, cc.

Greek Letters

= film thickness, cm.

= contact time, sec.

= wavelength, cm.

= viscosity, g./(cm.) (sec.)

= density, g./cc.

= surface tension, dyne/cm.

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