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**GAS ABSORPTION BY DROPS TRAVELING ON A
VERTICAL WIRE**

Berkeley, California

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GAS ABSORPTION BY DROPS TRAVELLING ON
A VERTICAL WIRE

S. M. Rajan

June 1965

M.S. Thesis

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Gas Absorption by Drops Travelling on a Vertical Wire

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ABSTRACT

June 1965

In this work liquid phase controlling mass transfer has been studied for a gas-oil system. Pure CO_2 is absorbed in white oil travelling on a wire in the form of drops interconnected by a thin film. Circulating tori within the drops moving down with the wave velocity have been observed. The effects of drop size, flow rate, diffusivity and column length on the mass transfer have been examined. The results have been plotted by a method suggested in the literature for mass transfer to circulating spherical drops. A model is presented to get a handle on a correlation to coalesce all the obtained data.

The results indicate that there are three stages of mass transfer. First, the gas is transferred to the film and the drop; next the gas in the film is transferred to the circulating tori; finally, the tori carry the dissolved gas out of the column. Any correlation would have to include all three of these contributions. The proposed model coalesces the obtained to within experimental accuracy.

I. INTRODUCTION AND DESCRIPTION OF FLOW

In chemical engineering there are many processes which require the contact of a liquid with another liquid or a gas. Such contact often results in transfer of heat or mass or a combination of both heat and mass. Gas absorption, distillation and extraction are examples of contact processes of wide industrial use and interest. Among systems of simple geometry, gas absorption by a liquid has been studied where the liquid is in the form of a jet, a thin film flowing on a wall, or drops falling through a gaseous phase. This thesis will describe gas absorption by a liquid for a situation which at one and the same time combines features characteristic of each of these geometries.

This study is concerned with the liquid side controlled absorption of CO_2 gas by a series of white oil drops moving down a vertical wire. Adjacent drops are connected by a thin film and both the drops and film are axisymmetric about the wire. There is evidence that inside each drop, as viewed in a coordinate system moving with the drops, is a circulating loop of liquid roughly in the shape of a torus. Throughout this thesis the word drop is used to mean the combination of the circulating torus with the region surrounding it forming the observed bulge or "drop". The term circulating torus (or tori) refers to the circulating loop only. To get a clearer picture of the flow one may examine Fig. 1 which reproduces photographs of the flows for which gas absorption was measured. Figure 2 gives the geometry of the flow and also defines the nomenclature used. In Fig. 6C a schematic representation of the streamlines for the flow (in a coordinate system moving with the drops) is

Fig. 1. Photographs of moving drops.

A. Number 7 oil, 0.031-inch wire

- a. 1 drop/sec
- b. 2 drops/sec
- c. 3 drops/sec

B. Number 9 oil, 0.031-inch wire

- a. 1 drop/sec
- b. 2 drops/sec
- c. 2.5 drops/sec

C. Number 15 oil, 0.031-inch wire

- a. 1 drop/6 sec
- b. 1 drop/4 sec
- c. 1 drop/2 sec
- d. 1 drop/sec

D. Number 15 oil, 0.020-inch wire

- a. 1 drop/2 sec
- b. 1 drop/sec

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Fig. 1 a

ZN-5036

Fig. 1 b

ZN-5035

Fig. 1 c

ZN-5034

Fig. 1 d

Fig. 2 Geometry of the flow of drops down a vertical wire.

Wire radius	= s
Minimum liquid radius	= h
Maximum liquid radius	= H
Wave length	= λ
Drop length	= D_L
Thinnest film	= δ

Other variables

Volumetric flow rate	= q
Drop flow rate	= n
Wave velocity	= U
Film surface velocity	= u
Column length	= L^s
Concentration (Pressure)	= P

P = Saturation concentration

P_i^s = Initial concentration

Diffusivity	= $\mathcal{D}$
Density	= ρ
Viscosity	= μ
Gravity constant	= g
Surface tension	= σ

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Fig. 2

drawn. It may further help the reader in visualizing the flow if, at this point, we give some typical dimensions. For the Number 7 White oil (density, $\rho = .87 \text{ gm/cm}^3$; surface tension, $\sigma = 35 \text{ dyne/cm}$; viscosity, $\mu = .57 \text{ poise}$) flowing down a wire of diameter, $2S$, of $.079 \text{ cm}$ with a frequency, n , of 1 drop/sec . The volumetric flow rate, q , is $0.56 \times 10^{-2} \text{ cm}^3/\text{sec}$. This value and the others to be cited depend on the size of the drop, $V = q/n$, 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, U , of 2.0 cm/sec . The maximum drop diameter, $2H$, is $.21 \text{ cm}$, the diameter of the film, $2h$, is $.11 \text{ cm}$, the film thickness, $\delta = h-s$, is $1.5 \times 10^{-2} \text{ cm}$, the drop length, D_L , is $.35 \text{ cm}$, and the wave length, λ , is 2.0 cm . The velocity at the free surface of the film connecting two drops, u_s , was calculated by assuming a fully developed parabolic flow having the measured film thickness. It was found to be $.16 \text{ cm/sec}$ indicating that the liquid in the film moves much more slowly than the liquid in the circulating torus. The results of the measurements for the other flow conditions investigated are listed in Table II.

II. LITERATURE SURVEY

There is a large amount of literature available on transfer to and from drops and falling films. Here we shall refer briefly to the most pertinent papers only.

A. End Effects

Several papers have discussed the important contributions of the end effects to the total mass transfer to a drop.¹⁻¹⁰ Licht and Conway⁵ have shown that there are three distinct contributions to the total mass transfer: entrance effect (including the time of formation and time to reach constant velocity), free fall period, and the time of coalescence. The end effects, including both the entrance effects and the coalescence effect, have been difficult to separate into distinct categories. Popovich, Jervis, and Trass¹⁰ have studied the contribution to the total mass transfer during the time of formation and have obtained experimental data. They have reviewed the existing theories on mass transfer during the formation of a drop and have concluded that all theories fit the general equation

$$N_A = \text{constant} (C_s - C_o) (\mathcal{D}\pi)^{1/2} d_f^2 t_f^{1/2}$$

where

N_A = total mass transferred across the interface

C_s = saturation or equilibrium concentration of diffusing species

C_o = initial concentration of diffusing species

$\mathcal{D}$ = diffusivity

d_f = diameter of drop after formation (after t_f)

t_f = time of formation

The numerical constant in the equation assumes slightly different values

for the different theoretical calculations. Their data correlated best with the equation proposed by Ilkovic where the numerical constant has the value $\sqrt{12/7}$.

At present one widely accepted method of accounting for the end effects experimentally is the method described by Johnson and Hamielec.³ They have combined the entrance end effect and the coalescence end effect into a single term, E_F ; they have also defined a free fall fractional approach to equilibrium, or efficiency, E_m , and a total fractional approach to equilibrium or efficiency, E_T . They show that

$$E_m = \frac{E_T - E_F}{1 - E_F}$$

Next they have given methods to obtain the combined end effects efficiency, E_F , for two separate conditions. If $E_m < 0.5$ (low efficiency region), they suggest a plot of E_T versus the square root of the drop fall time. The extrapolated value at zero drop fall time can be used to obtain the value of E_F from their semi-empirical equation.

$$E_T = 0.905 (1 - E_F) \sqrt{\frac{R\sqrt{\pi}^2 t}{a^2}} + 0.0189 + 0.981 E_F$$

E_T = overall efficiency

E_F = combined end effects efficiency

R = dimensionless correlation factor

$\mathcal{D}$ = molecular diffusivity

t = free fall contact time

a = drop radius

For $t = 0$, $E_F = (E_T - 0.0189)/0.981$. For higher efficiency runs, i.e.

$E_m > 0.5$, they suggest the use of $\ln(1 - E_T)$ versus time of contact. Once again extrapolating to zero contact time gives a value of E_F obtained

from the equation

$$\ln(1-E_T) = - \frac{\lambda_1^2 R \theta}{a^2} + \ln(6B_1(1-E_F))$$

For zero contact time

$$E_F = 1 - \frac{(1-E_T)}{6B_1}$$

B_1 in the equation is a constant. For zero continuous phase resistance the value for B_1 is 1.29.

Skelland and Wellek¹¹ in their study of mass transfer to drops have pointed out that if the interfacial area of the coalesced layer is made very small (approximately 0.5 cm^2 or less), then the coalescence end effect is reduced to a minimum.

A literature search on the study of total mass transfer to a drop reveals that an extensive amount of work has been carried out on this subject.^{8,11-25} Most studies consider the problem of freely falling or rising drops (or bubbles) in a continuous fluid phase. The important fact to note is that no two drops are in anyway interconnected (except perhaps by the wake they leave behind). The present study deviates sharply from others in that single feature. The oil drops descending the wire are interconnected by a thin film on the wire. Consequently it becomes necessary to study both the film between the oil drops and the drops themselves.

B. Film

In the literature there are several theories describing the mass transfer to a liquid film. Lewis and Whitman²⁷ postulated a stagnant film next to the surface of the liquid layer. They assumed that the concentration gradient existed only in the film and beyond the film the

liquid was well mixed. This led to an equation which showed that the mass transfer coefficient (k_L) was proportional to the first power of the diffusivity. The relation was given by

$$k_L = \frac{D}{x_f}$$

where x_f represents the stagnant film layer thickness. The thickness of the film is accessible through experiments only. Further, several experiments by different groups have revealed that the mass transfer coefficient varies as the square root of the diffusivity in many cases.

Higbie²⁸ advanced a theory in which the mass transfer was proportional to the square root of the diffusivity. He considered a semi-infinite liquid layer, henceforth referred to as the film, in contrast to Lewis and Whitman who considered mass transfer only to a fraction of the liquid layer. The main assumptions made by Higbie were: (1) The surface of the film moves at a uniform velocity, (2) the interfacial concentration is constant, (3) the falling film is in laminar motion, (4) the diffusion in the direction of the flow is negligible and (5) as far as diffusion is concerned the film can be treated as if it were infinitely thick. This last assumption restricts the theory to "short" contact times. These assumptions led Higbie to the following equation

$$(k_L)_{avg} = 2 \sqrt{\frac{D_A}{\pi \Theta}}$$

where $(k_L)_{avg}$ = average mass transfer coefficient

D_A = diffusivity of the solute

Θ = contact time, $(=Z/u_s)$

Z = height of column

u_s = surface velocity.

Emmert and Pigford²⁶ have studied the problem of gas absorption in falling liquid films. They considered a parabolic velocity profile in the falling film with the following boundary conditions: the velocity is maximum at the gas-liquid interface and the velocity is zero at the solid-liquid interface. This situation was mathematically described by Pigford in the following equation:

$$\mathcal{G}_A \frac{\partial^2 A}{\partial x^2} = u_s \left[1 - \left(\frac{x}{B_F} \right)^2 \right] \frac{\partial A}{\partial z}$$

The solution obtained was

$$\frac{A_1 - A_2}{A_1 - A_L} = 0.7858 \exp(-0.5121 p) + 0.1001 \exp(-39.31 p) + \dots$$

where

A_1 = solute concentration at the transfer interface

A_L = average inlet concentration

A_2 = average outlet concentration

$$p = \mathcal{G}_A \Theta / B_F^2$$

B_F = actual film thickness

This solution can be simplified under special conditions. For short contact times the equation reduces to

$$\frac{A_2 - A_L}{A_1 - A_L} = 3 \sqrt{\mathcal{G}_A Z / \pi B_F^2 u_s}$$

or in terms of the mass transfer coefficient

$$(k_L)_{l.m.} = \sqrt{6 \mathcal{G}_A \Gamma / \pi Z B_F \rho}$$

where

ρ = liquid density

Γ = mass flow rate (Mt/L)

$(k_L)_{l.m.}$ = mass transfer coefficient based on log-mean driving force.

The above analysis is equivalent to Higbie's analysis for short contact times. For long contact times the equation becomes

$$(k_L)_{l.m.} = 3.41 \frac{G}{B_F}$$

The film thickness, B_F , for the laminar, ripple free flow down a vertical wall is given by

$$B_F = (4\mu\Gamma/g\rho^2)^{1/3}$$

where μ is the liquid viscosity. Inherent in the derivation of the equation for the film thickness is the assumption that the surface velocity, u_s , is $3/2$ the value of the average film velocity. Although derived for a non-rippling film, the equation for B_F should work well for an average film thickness even in the case where rippling occurs. Emmert and Pigford point out that the derivation for B_F has the implicit assumptions that there is no slip at the wall and $\rho_{gas} \ll \rho_{liq}$. The analysis of Emmert and Pigford is valid only for low Reynolds numbers. Beyond a certain critical Reynolds numbers ripples are apparent on the surface. An extensive amount of study in wetted wall columns has shown that where there is rippling in a falling film the mass transfer is significantly increased and the data are usually correlated in the following form: $Sh = a(Re)^b(Sc)^c$, the constants a , b , and c being obtained empirically.

C. Drops

Turning next to the mass transfer to drops many equations--both semi-empirical and theoretical--have been found in the literature.⁹ The model for rigid drops is an extension of the well-known theory of transfer

to solid spheres. Various studies have been carried out solving diffusion equation stipulating the various boundary conditions. The most widely used correlation for internal transfer is that of Newmann:

$$E = \frac{C_{out} - C_{in}}{C_s - C_{in}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[\frac{-n^2 \pi^2 \theta}{R^2} \right]$$

This equation assumes a constant continuous phase concentration (temperature) and also a negligible continuous phase resistance. Vermeulen has found a simple but accurate representation of the above equation:

$$E = [1 - \exp(-\pi^2 t/R^2)]^{1/2}$$

The transfer to drops is usually more complex than transfer to rigid spheres. There are two main reasons for this complexity. First the frictional drag surrounding a drop may induce circulation of both the interface and the interior of drops. Second, a drop may deform from a spherical shape. A third complication, oscillations, may occur if Reynolds numbers are high. Handlos and Baron¹³ theoretically analyzed the problem using an eddy diffusivity as a function of position in the drop. Their circulation patterns inside a drop deviated markedly from that used by Hadamard.³⁰ Further their model assumes that the circulation in the drop is fully developed. Their final result for the mass transfer to a drop was

$$Nu_i = 0.00375 Pe_i'$$

where

Nu_i = dispersed phase Nusselt number, kd/D

Pe_i' = modified dispersed phase Peclet number

$$= (dV/D)/(1 + \mu_d/\mu_c)$$

k = mass transfer coefficient

d = drop diameter

D = diffusivity

V = drop velocity

μ_d, μ_c = dispersed phase and continuous phase viscosities

In this equation a concentration difference driving force was used. They were able to correlate their data better with an activity difference.

Skelland and Wellek¹¹ performed a dimensional analysis and obtained a semi-empirical equation to describe the mass transfer to drops at Reynolds numbers up to 300.

$$Sh = 0.142 Tm^{-0.141} We^{0.769} P^{0.285}$$

where

Sh = calculated Sherwood number, $k_d d_e / D_L$

Tm = time group, $4D_L t_c / d_e$

We = Weber number, $d_e U^2 \rho_c / \sigma$

P = P group, $\sigma^3 P_c^2 / g \mu_c^4 (\Delta f)$

k_d = calculated dispersed phase mass transfer coefficient

d_e = diameter of a sphere having the same volume as drop

D_L = molecular diffusivity of solute in dispersed phase

t_c = contact time during fall

U = terminal velocity of drop

ρ_c = continuous phase density

σ = interfacial tension

g = acceleration of gravity

μ_c = continuous phase viscosity

Kronig and Brink²⁴ formulate an equation based on the following assumptions: constant continuous phase temperature, negligible continuous phase resistance, Reynolds numbers < 1 , and streamlines are also isothermal lines. Including the effects of internal circulation on diffusion their final result was

$$E = 1 - \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp(-\mu_n \cdot 16 \alpha t / r^2)$$

where

E = fractional approach to equilibrium

μ_n, A_n^2 = eigenvalues and weighting constants

α = thermal diffusivity

t = contact time

r = drop radius

Calderbank and Korchinski²⁵ were able to use the above equation and represent their data by a simplified form of the equation:

$$E = (1 - \exp(-2.25 \pi^2 \alpha t / r^2))^{1/2}$$

Although the above analysis has been carried out for a heat transfer study on drops, it should be equally applicable to a mass transfer problem with appropriate changes in parameters:

$$E = \frac{C_{out} - C_{in}}{C_{sat} - C_{in}} = (1 - \exp(-2.25 \pi^2 D t / r^2))^{1/2}$$

where

C_{out} = average outlet concentration of drop

C_{in} = average inlet concentration of drop

C_{sat} = saturated concentration of drop

D = molecular diffusivity

Comparison of the above equation for circulating drops to that for

rigid spheres reveals that the molecular diffusivity in the rigid spheres equation has been replaced by an effective diffusivity, i.e.

$$D_{\text{effective}} = 2.25 D.$$

III. APPARATUS AND PROCEDURE

In this study the (liquid side controlling) absorption of CO_2 gas by white oil drops moving down a vertical wire was measured. Several different grades of white oil are available from Standard Oil Company of California, and in this study grades Nos. 7, 9, and 15 were used. The pertinent physical properties of the oils used are shown in Table I. The densities and surface tensions are catalogue values. The viscosities were measured in a Haake (Couette type) viscometer and were found to agree with the catalogue values. The saturation concentrations and diffusivities of CO_2 in the oils were measured by methods which will be described shortly.

The apparatus used to measure the absorption is shown in Fig. 3. It consists of a reservoir in which the oil to be tested is stored. The reservoir is connected to a 13-gauge syringe needle and the flow of oil 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 holed rubber stopper at the top of the column. The other two holes on the stopper contain a gas outlet and a thermometer. The absorption chamber is 2.5 inch o.d., heavy wall glass tubing varying in lengths from 40 cm to 3 cm. At the bottom of the chamber is another three holed rubber stopper which contains a take-off tube in the middle flanked by the gas inlet and a tube leading to a manometer. The take-off tube is a 3-inch long, 1/4 inch i.d. plastic tube and is 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

Note: All connections are made with Tygon tubing.

MU-35939

Fig. 3

taut through the syringe and take-off tube. A little adjustment is usually necessary to insure that the wire is vertical and centered at the syringe exit so that the oil drops form and move with angular symmetry about the wire. Wires of 0.031 inch diameter and 0.020 inch diameter were used.

Dissolved gases were 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 were taken to avoid trapping air bubbles in the oil.

Oil flows from the reservoir through the syringe needle onto the wire. The flow rate is maintained and controlled by the needle valve quite accurately. To insure negligible gas phase resistance to the transfer the oil is contacted with pure CO_2 gas. CO_2 was also used because of its relative high solubility thus facilitating easier concentration measurements. Carbon dioxide gas enters at the bottom of the absorption chamber. Before the gas enters the chamber it is bubbled through a column of the test oil. A very low flow rate of CO_2 gas through the absorption chamber is maintained to keep the partial pressure of carbon dioxide gas at 1 atmosphere. A constant level of oil was maintained in the take-off tube so that the column length for absorption was the same during the run. The oil was allowed to flow through the take-off section for at least one complete residence time before a sample was taken. After this period of time a sample is drawn into the Van Slyke apparatus for analysis.

The Van Slyke manometric apparatus (Fig. 4) is an analytic device that works on a simple principle. A sample of the liquid (oil in this

Fig. 4 - Van Slyke Manometric Gas Analyzer

(A) Level 2 for mercury reservoir

(B) Manometer

(C) Mercury reservoir

(D) Level 1 for mercury reservoir

(E) Stopcock 1

(F) Analysis chamber

(G) Stopcock 2

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Fig. 4

study) is taken into a chamber. A vacuum is created in the chamber by controlling the level of a mercury reservoir. At the lower pressure in the chamber gases which dissolved in the liquid sample are boiled off. The boiling is facilitated by stirring the liquid with a magnetic stirrer. After boiling, the gas is compressed to a known volume. The pressure of this compressed volume of gas is read on a connecting manometer. Knowing the pressure, volume, temperature and the sample size it is easy to calculate the concentration of the dissolved gases in the liquid with the aid of the ideal gas law. CO_2 can be considered an ideal gas since the pressure is low (1 atm) and the temperature is 25°C . Even if the vapor pressures of the oils are significant they introduce no error because they are subtracted out when differences are taken as is shown shortly. Etched on the analysis chamber are graduations of 0.5, 1.9 and 50.0 cc. A 1.9 cc sample is drawn into the analysis chamber of the Van Slyke apparatus by opening stopcocks 1 and 2 while the mercury reservoir is at level 1. (Refer to Fig. 4) It is important to draw the liquid into the analysis chamber slowly to prevent immediate boiling and loss of gas.

Stopcock 1 is then closed but stopcock 2 remains open. The mercury reservoir is then lowered below the level 1 in order to lower the level of the sample in the analysis chamber to just above the 50 cc graduation mark. Stopcock 2 is now closed and the mercury reservoir placed at level 2. The oil is now stirred with the aid of the magnetic stirrer and care is taken not to stir the mercury below the oil as well. Stirring times can be varied with the aid of the timer. Times varying from three to six minutes were used by the author. After stirring is complete stopcock 2 is reopened enough to cause the liquid level in the chamber to

slowly rise. It is imperative that the rising of the level be slow to prevent oil adhering to the walls of the chamber being entrained in the mercury. The upper meniscus of the oil is brought up to the 1.9 cc graduation mark and stopcock 2 closed. Thus the gas that has been boiled is now compressed to a volume of 1.9 cc. The corresponding pressure of this compressed gas is now recorded from the manometer. Stopcock 2 is once again reopened and the liquid level allowed to rise until it can no longer rise. (This simultaneously allows the mercury in the manometer to reach its maximum level.) Stopcock 1 is now opened and the gases ejected on the ejection side; the stopcock needs only a slight opening and care must be taken to avoid the ejection of any substantial amount of the liquid. Stopcock 1 is now closed. It is extremely important that stopcock 1 remain closed until the level of mercury in the manometer and the level of the oil in the analysis chamber have reached their maximum. If the levels have not reached their maximum and stopcock 1 is prematurely opened gases and oil in the ejection tube are sucked into the analysis chamber thus contaminating the test sample. After the ejection of the gas the sample is once again lowered in the analysis chamber for further degasification. This procedure is continued until two successive pressure readings are identical. Generally five pressure readings were necessary with the last two being equal. Representing the five pressure readings by $p_1, p_2, p_3, p_4, p_5 = p_4$, one may compute the partial pressure of the dissolved gas as follows:

$$P = (p_1 - p_4) + (p_2 - p_4) + (p_3 - p_4)$$

Knowing the volume, V , of the compressed gas in the chamber, the

temperature, T , one may use the ideal gas law to calculate n , the moles of the dissolved gas:

$$n = (P)(V)/RT$$

The concentration of the gas in the oil is obtained by dividing the volume of the sample into n and converting to appropriate units.

Two separate samples were analyzed for each run. If the P values agreed to within 5%, the average value of the two readings was used for the P value. If the two values were not within 5%, a third sample was analyzed and the P values which agreed within 5% were averaged. If no two values of P were within 5% all three values were averaged.

Throughout the calculations the P values have been used as concentrations since ratios of concentrations are always used. The temperatures of the runs varied from 24°C to 26°C and thus an average of 25°C was used. The vapor pressures of the oils used in this experiment are negligible.

The amount of CO_2 absorbed was measured for each oil flowing down the 0.031 inch diameter wire for a series of lengths and flow rates. Absorption into the No. 15 oil flowing down the 0.020 inch diameter wire was also measured.

The frequency of the drops was measured by counting the number of drops flowing past a fixed point in a given time period. Three measurements were made and the values were averaged. The flow rate was measured by collecting the oil, at a given drop frequency, in a graduated cylinder for a known period of time. The wave velocity was measured by timing a drop travelling a known length of column. Three measured values were averaged for each flow condition.

The saturation concentration of CO_2 in the No. 7 oil was measured

by bubbling CO_2 in the oil for several hours and analyzing the sample in the Van Slyke apparatus. A mass transfer run with the 30 cm column 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 CO_2 in all three oils. The drop frequency was approximately 1 drop/4 sec.

Photographs were taken with a Linhof camera. F-8, 1/400 sec settings with ASA400 speed sheet films were used. Measurements were made from the negatives on the Vanguard analyzer.

The measurement of the diffusivity values needed in this work presented a unique problem. The only known data on diffusivity in white oils are those published by Sage and Reamer.^{31,32} They have worked at elevated pressures. An extrapolation can be made for atmospheric pressure, but only at the risk of a large error. Consequently the established method of the diaphragm cell could not be used because this method does not permit absolute measurements of diffusivities. After several methods of absolute diffusivity measurements were investigated, the following was adopted.

A 10 cc sample of the oil saturated with CO_2 was injected into a special cell under an atmosphere of CO_2 . The cell (Fig. 5) is 9.5 cm in diameter and 5 cm in height. The bottom is an optically flat surface. Openings into the cell for titration, gas entrance and exit are provided at the top surface. The cell was floated on a concentrated cellulose-water solution. This thick, visco-elastic liquid appeared to be very effective in damping out room vibrations. Because the oils were viscous and the layers were thin and because the gas above the layer of oil was

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Fig. 5

stagnant convective currents in the oil layers are thought to be minimized. After the oil had spread out into a thin film (approximately 0.15 cm thick) the CO_2 above the oil was evacuated by pulling a slight vacuum for 1 minute. The CO_2 in the oil was then allowed to desorb into air for 30 minutes. At the end of this time period a slight vacuum was again pulled for 1 minute in order to evacuate the desorbed CO_2 . Next a known volume of .00492M $\text{Ba}(\text{OH})_2$ solution was added to the cell and the oil and caustic mixture vigorously shaken. The excess $\text{Ba}(\text{OH})_2$ was titrated to the phenylphthalien end point with 0.01 M HCl . In order to check the initial concentration the same procedure was followed except for the 30 min desorption period. The diffusivity was then calculated from the analytical solution for the transfer from an initially uniform slab when the surface condition is suddenly changed.³³ There was very good reproducibility in the case of the 7 and 15 oil but the reproducibility was unaccountably very poor for the No. 9 oil. The calculated values of the diffusivities are:

No. 7 oil---56cp-- 3.9×10^{-6} cm^2/sec (average of 3 runs)

No. 9 oil---72cp-- 1.7×10^{-6} cm^2/sec (average of 6 runs)

No. 15 oil---135cp-- 2.4×10^{-6} cm^2/sec (average of 3 runs)

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 $.65 \times 10^{-6}$ cm^2/sec to a high value of 2.8×10^{-6} cm^2/sec . The diffusivities were plotted as a function of viscosity on log-log paper. A straight line was drawn connecting Nos. 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} cm^2/sec and this value has been used in all calculations. The extrapolated

values from Sage and Reamer^{31,32} predicted a value of $1.5-3.0 \times 10^{-6}$ cm²/sec for the CO₂-white oil (56 cp) system depending on how the curves were read. It is assumed in the calculations that the molecular weight of the solute molecule varies to the -0.6 power.

IV. THEORETICAL MODEL

A. Fluid Mechanics

Before proposing a model for the mass transfer one should first understand the fluid mechanics of the system. Based on the external geometry of the drop (see Fig. 1 for photographs) 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 Fig. 6. To reduce the patterns to those for equivalent systems in steady state the streamlines are drawn in a coordinate moving with the wave velocity.

For the noncirculating flow represented in Fig. 6a all carbon black particles in the oil would move upstream relative to the drop. For flow with a double circulating loop, as represented in Fig. 6b, 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 (i.e. with the wave velocity). Of those particles moving with the drop, the particles caught in the circulating loop farther from the wire would circulate counter-clockwise, 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 Fig. 6c, 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 drawn in the figure these latter particles would rotate in the clockwise direction. It is also possible to imagine a flow with a single counter-clockwise 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.

Fig. 6 - Possible streamlines 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

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Fig. 6

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 counter-clockwise circulation was observed. This would lead to the conclusion that there is a single circulating loop within the drop. Since the counter-clockwise circulating loop of Fig. 6b is closer to the outer surface of the drop, particles would have to circulate counter-clockwise when they are introduced near the surface. Several introductions near the surface resulted in only clockwise circulation of particles. It is therefore 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 well defined 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, i.e. the velocity of the bulge 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 having the (photographically) measured film thickness. The surface velocity, u_s , is given by the formula

$$u_s = \frac{\rho g \delta^2}{2\mu}$$

This calculation showed that the maximum velocity in the film was on the order of a tenth of the measured wave velocity (see Table II). 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.

B. Mass Transfer

A model for mass transfer is presented that takes into consideration both the film between the drops and the circulating tori. Consider the following equation which defines the concentration of gas in the oil being carried out of the absorption chamber, P_{out} :

$$P_{out} = \frac{q_F P_F + q_T P_T}{q_F + q_T} \quad (1)$$

where q_F = volumetric flow rate of the film (liquid exclusive of the tori

q_T = volumetric flow rate of the tori

P_F = mixed cup solute concentration in the film at outlet, and

P_T = mixed cup solute concentration in the tori at outlet.

Because the film drains very slowly and is very thin the measured flow rate is mainly that due to the circulating tori. In other words,

$q_F \ll q_T$. Consequently one might also expect that $q_F P_F \ll q_T P_T$, at least for moderate contact times. Equation (1) then becomes

$$P_{out} \approx P_T \quad (2)$$

It is therefore necessary to concentrate mainly on the circulating tori.

The model proposed below is an extreme case, assuming complete "mixing" within a drop.* The extent to which a drop can be considered completely

* (except for the region immediately adjacent to the drop surface)

mixed is difficult to assess and will be discussed shortly. In a coordinate system moving with the drop the volumetric flow rate, Q , into and out of the drop is

$$Q = \pi \left[(s+\delta)^2 - s^2 \right] U = 2\pi s \delta \left(1 + \frac{\delta}{2s} \right) U \quad (3)$$

where s = wire radius
 δ = film thickness, and
 U = wave velocity.

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

$$\frac{dPV}{d\theta} = Q(P_s - P) = -V \frac{d}{d\theta} (P_s - P) \quad (4)$$

where P = concentration of solute in the drop
 P_s = saturation concentration of solute
 and θ = contact time of drop
 V = volume of the drop.

Here any gas absorbed through the surface of the drop is counted as being passed into the film above the drop. With the boundary conditions

$$\begin{aligned} \text{at } \theta = 0 \quad P &= P_i, \text{ and} \\ \text{at } \theta = \theta \quad P &= P_s \end{aligned} \quad (5)$$

Equation (4) can be integrated to yield

$$\frac{P_s - P}{P_s - P_i} = \exp [-Q\theta/V] \quad (6)$$

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 Eq. (3) into Eq. (6) results in the following:

$$\frac{P_s - P}{P_s - P_i} = \exp \left[- \frac{2\pi s \delta}{V} \left(1 + \frac{\delta}{2s}\right) L \right] \quad (7)$$

Several questions arise in this model. A brief answer is given to each of the questions: (1) Does the film become saturated? (2) Is the drop well mixed? (3) How are end effects determined?

(1) Does the film become saturated between the passage of successive drops? The criterion for determining whether or not a film is saturated with the solute is given by determining the value of $\frac{\mathfrak{D} t}{\delta^2}$ where $\mathfrak{D}$ is the molecular diffusivity, t is the exposure time between successive drops and δ the film thickness. If the value of the group is greater than unity, then the film is essentially saturated. The extreme values for the above quantities in this study are:

$$\mathfrak{D} = 3.9 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$t = \frac{\lambda}{U} = \frac{3.5}{1.5} \text{ sec} = 2.3 \text{ sec}$$

$$\delta = 1.5 \times 10^{-2} \text{ cm}$$

With the above values $\frac{\mathfrak{D} \lambda}{U \delta^2} \approx 6 \times 10^{-2}$. This is far below the required value of unity for saturation. This implies that the film is far from saturation and in fact penetration theory seems applicable.

Since the film is not saturated the differential Equation (4) describing the mass balance becomes:

$$\frac{dPV}{d\theta} = Q(P' - P) \quad (8)$$

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

$$\frac{P_s - P'}{P_s - P} \approx f \left(\frac{\mathfrak{D} \lambda}{U \delta^2} \right) = \beta \quad (9)$$

Now:

$$-\frac{Vd(P_s - P)}{d\theta} = Q \left[(P_s - P) - (P_s - P') \right] = Q(1-\beta)(P_s - P). \quad (10)$$

Solving Eq. (10) with the same boundary conditions as in Eq. (5) one obtains the result:

$$\frac{P_s - P}{P_s - P_i} = \exp [-Q(1-\beta)\theta/V] \quad (11)$$

If the neck is stagnant and penetration theory is applicable the exact form of β can be determined. In this study penetration theory is applicable as shown earlier. Thus,

$$\frac{\partial P'}{\partial t} = D \frac{\partial^2 P'}{\partial y^2} \quad (12)$$

where y is the distance from the gas liquid interface. The boundary conditions are

$$\begin{aligned} t &= 0, & P' &= P \\ y &= 0, & P' &= P_s \\ y &= \infty, & P' &= 0 \end{aligned} \quad (13)$$

Equation (13) is easily solved by combination of variables. The result is

$$\frac{P_s - P'}{P_s - P} = \beta = 1 - \left(\frac{4Dt}{\pi \delta^2} \right)^{1/2} = 1 - \left(\frac{4S\lambda}{\pi \delta^2 U} \right)^{1/2} \quad (14)$$

The wave velocity, U , is related to the wave length, λ , and the drop frequency n by

$$U = \lambda n.$$

Also, neglecting the volumetric flow rate of the film, the torus volume, V , is the ratio of the volumetric flow rate, q , to the drop frequency, n . Substituting these results and Eq. (3) into Eq. (12) and simplifying the final result obtained is

$$\frac{P_s - P}{P_s - P_i} = \exp \left[- \frac{2\pi s}{(q/n)} \left(1 + \frac{\delta}{2s} \right) \left(\frac{4.0}{\pi n} \right)^{1/2} L \right] \quad (15)$$

(2) Is the drop well mixed? Although good circulation is observed inside the drops, it is difficult to judge whether the drop is well mixed. The mixing of the drop is also dependent on the wave length or the number of drop lengths the drop falls before occupying the position of the preceding drop. When the drop falls through several drop lengths, i.e. at low drop frequency mixing is facilitated. The assumption is least reliable at high drop frequencies. An indication of the validity of this assumption can best be obtained by noting how well the proposed model of complete mixing correlates the experimental results.

(3) How are end effects determined? It is difficult to determine the separate contributions of the entrance and coalescent end effects to the total mass transfer. The entrance effect consists of the gas absorbed while exposed to air, mass transfer during drop formation, and mass transfer during the time needed to achieve constant velocity. The former and latter parts are difficult to analyze mathematically. A mathematical analysis for the mass transfer during drop formation yields an expression similar to that proposed by Ilkovic as presented by Popovich et al.¹⁰ Hence, Ilkovic's equation will be used to determine the mass transfer during drop formation. The determination of coalescence end effect is also difficult for mathematical analysis. Skelland and Wellek¹¹ have reported that if the area for coalescence is less than 0.5 cm^2 , then the mass transfer occurring coalescence can be considered negligible. This criteria will be used in the analysis of the results. In order to obtain the combined end effects contribution a plot of gas absorbed as a function

of column length will be extrapolated to zero column length. The intercept of such a plot should yield the contributions to the total mass transfer by the end effects.

The model proposed is admittedly crude. Although many improvements can be suggested, the roughness of the model does not warrant these refinements.

V. EXPERIMENTAL RESULTS AND DISCUSSION

The measured and calculated values in this study are presented in Table II. The mass transfer obtained are tabulated in Table III. The results are also plotted in Fig. 7. The vertical lines in these figures represent a 5% allowed error in the measurements. Several methods for plotting the data were tried. Among them were plots of $\ln(1 - \frac{P}{P_s})$ vs L and $\frac{P_s - P}{P_s}$ vs $\sqrt{L}$. However, these curves indicated that there were extremely large end effects. These are contrary to the expected results as discussed below. The latter method of plotting also has the disadvantage that for high efficiency studies, i.e. when mass transfer occurring is beyond about 60% of saturation, the curve becomes asymptotic to the saturation value. The method chosen to plot the data, $\ln[1 - (P/P_s)^2]$ as a function of column length, suggested by Calderbank and Korchinski,²⁵ has the advantage that even for high efficiency studies the line remains linear. Most of the data obtained in this study are situations in which over 50% of saturation value of the solute concentration is achieved. Both methods of plotting results in straight lines for low efficiency studies. The extrapolation of the line to zero column length would give a value for the combined end effects. As seen from the plotted lines, the ordinate intercept is 1 which implies that the contribution to the total mass transfer by the end effects is, to within experimental accuracy, zero.

There are two main contributions to the total end effects: Mass transfer during drop formation and mass transfer during coalescence. As has been mentioned earlier Skelland and Wellek¹¹ have suggested that if the total area for coalescence is less than 0.5 cm^2 then the contribution to the total mass transfer by the mass transfer occurring during

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Fig. 7 a

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Fig. 7 b

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Fig. 7 c

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Fig. 7 d

coalescence is negligible. In this study the coalescence occurred in a tube of 0.65 cm in diameter which presents a coalescence area of approximately 0.3 sq. cm. This is less than the suggested limit of 0.5 sq. cm. Hence the contribution to the total mass transfer by coalescence has been assumed negligible.

Popovich et al.¹⁰ in their study of mass transfer to drops during formation have pointed out that their data is best represented by an equation proposed by Ilkovic. Rearrangement of Ilkovic's equation yields the following:

$$\frac{C \text{ after formation}}{C_s} = \frac{18}{7} \left(\frac{4\pi}{3qt_f} \right)^{1/3} \left(\frac{gt_f}{\pi} \right)^{1/2}$$

For the No.15 oil, 0.031 inch wire and 1 drop/6 sec the case where formation effects should be most prevalent, the values are:

$$t_f = 1/n = 6 \text{ sec}$$

$$qt_f = V = 6.48 \times 10^{-3} \text{ cm}^3$$

$$g = 2.4 \times 10^{-6} \text{ cm}^2/\text{sec}$$

$$\frac{C}{C_s} = \frac{18}{7} \left(\frac{4\pi}{3 \times 6.48 \times 10^{-3}} \right)^{1/3} \left(\frac{2.4 \times 10^{-6} \times 6}{\pi} \right)^{1/2} = 0.015.$$

The total mass transfer observed for the above condition for the lowest column length is 0.79. Therefore the formation effect is negligible.

Other flows yielded values ranging from 3 to 6% of the total mass transfer.

These values are well within the accuracy of the experimental results.

Hence the conclusion is reached that within experimental accuracy the mass transfer during drop formation is negligible. Another possible source of "end effect" is that due to solubility of air before drop formation. The degassed oil is exposed to air while in the reservoir.

Air is absorbed by the oil mainly by diffusion. Air is less soluble than

carbon dioxide in hydrocarbons. It is therefore reasonable to expect that air is less soluble in white oil as well since white oil is a mixture of hydrocarbons. The diffusivity of carbon dioxide in white oil is $3 \times 10^{-6} \text{ cm}^2/\text{sec}$. Therefore the diffusion process is slow and hence mass transfer is small.

Consideration of the above facts leads to the conclusion that the combined coalescence and initial effects (including the drop formation contribution) are small in comparison to the free fall effect during mass transfer. Hence the line resulting in the plot of $\ln[1-(P/P_s)^2]$ as a function of column length should pass through the point (0,1). This is borne out in Fig. 7.

Figure 7 also shows that the gas absorbed is a function of drop frequency. Figure 8 is a plot of the slope of $\ln[1-(P/P_s)^2]$ vs L line as a function of drop frequency. The consensus of the four separate flow conditions seems to be that the slope is inversely proportional to the square root of the drop frequency. The slopes seem relatively independent of the viscosity but depend on the drop size. (Compare No.15 oil, 0.031 inch wire to No. 15 oil, 0.020 inch wire.) These observations are in agreement with the model proposed. Let us take a closer look at the model. Equation (15) for zero inlet concentration reads:

$$\frac{P_s - P}{P_s} = \exp \left[- \frac{4\pi s}{q/n} \left(1 + \frac{\delta}{2s} \right) \left(\frac{D}{\pi n} \right)^{1/2} L \right] \quad (16)$$

It is easily shown that a plot of $\ln[1-(P/P_s)^2]$ vs L would yield a line with a slope that is easily correlated with the following group:

$$\text{slope} = - \frac{4\pi s}{q/n} \left(1 + \frac{\delta}{2s} \right) \left(\frac{D}{\pi n} \right)^{1/2} \quad (17)$$

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Fig. 8

A look at Table II will show that the ratio q/n is relatively independent of drop frequency. The square root dependence on the drop frequency is observed in the relation. There is roughly a first power dependence on the wire size, s . The variation in viscosity enters mainly in the diffusivity; because diffusivity enters the square root power the slopes would not be as sensitive to changes in viscosities. All these effects were observed.

The group of terms in Eq.(17) contains all the variables studied in this work. The variables are drop frequency, diffusivity (via viscosity), drop size, wire size and column length. A plot of $\ln [1-(P/P_s)^2]$ as a function of L^* , where

$$L^* = \frac{4\pi s}{q/n} \left(1 + \frac{\delta}{2s}\right) \left(\frac{\delta}{\pi n}\right)^{1/2} L,$$

should coalesce all the observed data. Such a plot appears in Fig. 9. All the points coalesce if the 5% allowed error in the measurements are plotted. Although there appears to be a large scatter at the bigger values of L^* , 5% vertical lines as drawn in Fig. 7 would include these points in the straight line drawn. A theoretical line is also shown in Fig. 9. Comparison of the two lines indicates that the actual mass transfer is greater by a factor of approximately 1.5. Recall that the model proposed assumes complete circulation. Calderbank and Korchinski²⁵ have shown that for a case of complete circulation in drops the mass transfer is greater by a factor of 1.5 in comparison to mass transfer in rigid drops. They have included this effect in the form of an effective diffusivity that is 2.25 times the molecular diffusivity. An equally probable explanation for the increase in mass transfer can be derived by noting the area term for mass transfer. The area term used is the area

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Fig. 9

as seen by a penetration theory. Because of circulation inside the drops there is effectively an increase in the area into which mass transfer occurs. If an effective area was used, the two lines can be made to coincide. Both these reasons could individually and collectively account for the observed greater mass transfer. The conclusion that can be drawn from Fig. 9 is that the model that concentrates on the three stages of mass transfer--to the film and drop, from the film to the circulating tori and the mass carried out by the tori--is applicable to this study.

The experimental data indicates that for a given wire size and oil the velocity of the drop is approximately independent of the drop frequency. The product of the viscosity and velocity is also a constant for a given wire (and hence drop) size. The volume of the drop is equal to the rates of the flow rate and drop frequency and depends only on the wire size. All these observations are in agreement with theoretical predictions. (See Table II.)

There are few major sources of error in this study. First, the temperature was between 24-26°C. No special equipment, such as a constant temperature bath, was used to achieve this. The room temperature remained between 24 and 26°C as seen on the thermometer in absorption chamber and the Van Slyke analysis chamber. The oil flowing down the coils (see Fig.2) can be surrounded by a tube through which a constant temperature liquid can be circulated. Similarly, the absorption chamber can be jacketed and constant temperature liquid circulated in the shell. Provisions have also been made by the manufacturers to maintain the Van Slyke analysis chamber at constant temperature.

The second major error occurs in the analysis for the absorbed carbon dioxide in the oil sample. The Van Slyke manometric gas analyzer, although

an excellent instrument for gas analysis, has two major drawbacks in the adaptation to this study: (i) the oil coats the wall of the absorption chamber and often a very thin film remains on the wall. This is particularly true for the case for the highest viscosity oil used in this study. (ii) The Van Slyke does not discriminate between the various gases present in the sample. It merely gives a pressure reading for all the gases present in the sample. This could be a cause of major error if the solubility of gases other than CO_2 is large. The alternate method of CO_2 analysis is the titration technique used in diffusivity measurements. Here the CO_2 in the sample was precipitated with $\text{Ba}(\text{OH})_2$ and the excess $\text{Ba}(\text{OH})_2$ was back titrated with HCl . The latter method has two drawbacks: (i) the $\text{Ba}(\text{OH})_2$ should have minimum exposure to atmosphere lest it pick up the CO_2 present in air and (ii) a known volume of oil sample has to be injected in the $\text{Ba}(\text{OH})_2$ solution. The latter is difficult to achieve because of the viscosity of the oils. However, techniques of coalescing the oil under a layer of less dense, immiscible liquids can perhaps be used here. A syringe can be injected in the $\text{Ba}(\text{OH})_2$. Work done by the author in CO_2 - H_2O systems has shown that such a technique allows for a quantitative study of the mass transfer.

The third major error is provided by the diffusivity measurements. The assumption made about negligible convective currents does not permit a quantitative error treatment. The reproducibility of the results, and the observed lack of vibrations in the thin film seem to justify the assumption. Qualitatively, the measured values would be greater than the true values because the use of vacuum to remove the CO_2 present above the oil layer after the desorption process could also facilitate the removal

of some CO_2 from the oil surface. This would indicate a faster desorption thus giving a higher diffusivity value.

VI. CONCLUSIONS

1. A model that takes into account the mass transfer to the circulating tori as well as the film between drops is necessary for a description of the mass transfer for the flow studied here.
2. The end effects, i.e. the entrance and coalescence effects are negligible.
3. The slope of the line $\ln [1-(P/P_s)^2]$ vs L is inversely proportional to the square root of the drop frequency. The slope is also correlated by the group $\frac{2\pi s}{q/\eta} (1 + \delta/2s) (\frac{4D}{\pi\eta})^{1/2}$.
4. The use of the dimensionless column length $L^* = \frac{2\pi s}{q/\eta} (1 + \frac{\delta}{2s}) (\frac{4D}{\pi\eta})^{1/2} L$ suggested by the rough theory proposed coalesces all the experimental data obtained in this work.
5. The volume of the drop is independent of the viscosity of the oil and drop frequency. For given entrance geometry and physical properties the volumetric flow rate is proportional to the drop frequency.
6. For a given drop size and viscosity of oil, the velocity of the drop is independent of the drop frequency. Further the product μU is an approximate constant.

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Table I. Physical properties of the oils at 25°C

Symbol	Property	No.7	No.9	No.15
ρ	Density, gm/cm ³ (A)	0.870	0.878	0.868
σ	Surface tension, dyne/cm (A)	35	36	36
μ	Viscosity, poise (B)	0.566	0.716	1.34
P_s	CO ₂ saturation concentration, cm Hg/1.9 cm ³ (C)	60.57	60.54	61.94
$\mathcal{D}$	Diffusivity of CO ₂ , $\frac{\text{cm}^2}{\text{sec}} \times 10^6$ (D)	3.9	3.3 (E)	2.4

(A) Catalogue value

(B) Measured in Haake viscometer

(C) Measured in Van Slyke apparatus, in equilibrium with CO₂ at 1 atm. pressure

(D) Measured in diffusion cell

(E) Interpolated value from measured diffusivities of No.7 and No.15 oils

Table II. Calculated and measured results from photographs and flow measurements

n→	No.7 oil, 0.031-inch wire			No.9 oil, 0.031-inch wire		
	1 drop/ sec	2 drops/ sec	3 drops/ sec	1 drop/ sec	2 drops/ sec	2.5 drops/ sec
$q \times 10^2$ cm^3/sec	0.556	0.993	1.43	0.528	0.958	1.25
$U, \text{cm/sec}$	2.02	1.87	1.88	1.52	1.57	1.69
$V \equiv q/n$, $\text{cm}^3 \times 10^2$	0.556	0.467	0.477	0.528	0.479	0.500
$u_s, \text{cm/sec}$	0.161	0.165	0.252	0.293	0.221	0.146
$2s, \text{cm}$	0.0787	0.0787	0.0787	0.0787	0.0787	0.0787
$2H, \text{cm}$	0.206	0.192	0.191	0.192	0.213	0.206
$2h, \text{cm}$	0.108	0.108	0.115	0.123	0.117	0.110
$\delta = h - s$, cm	0.0146	0.0148	0.0183	0.0221	0.0192	0.0156
λ, cm	2.03	0.743	0.524	1.70	0.796	0.633
$D_L, \text{cm} \times 10$	3.48	3.52	3.39	4.05	3.90	3.73

n→	No. 15 oil, 0.031-inch wire			No. 15 oil, 0.020-inch wire		
	1 drop/ 6 sec	1 drop/ 4 sec	1 drop/ 2 sec	1 drop/ sec	1 drop/ 2 sec	1 drop/ sec
$q \times 10^2$ cm^3/sec	0.108	0.168	0.268	0.500	0.611	1.23
$U, \text{cm/sec}$	0.670	0.793	0.880	0.852	1.90	2.47
$V \equiv q/n$ $\text{cm}^3 \times 10^2$	0.648	0.669	0.534	0.500	1.22	1.23
$u_s, \text{cm/sec}$	0.051	0.107	0.100	0.066	0.047	0.186
$2s, \text{cm}$	0.0787	0.0787	0.0787	0.0787	0.0508	0.0508

n→	No. 15 oil, 0.031-inch wire				No. 15 oil, 0.020-inch wire	
	1 drop/ 6 sec	1 drop/ 4 sec	1 drop/ 2 sec	1 drop/ sec	1 drop/ 2 sec	1 drop/ sec
2H, cm	0.188	0.204	0.209	0.192	0.228	0.257
2h, cm	0.104	0.115	0.114	0.108	0.075	0.099
$\delta = h - s$ cm	0.0126	0.0183	0.0177	0.0144	0.0121	0.0241
λ , cm	3.08	2.98	1.72	0.61	3.36	2.62
D_L , cm x 10	3.31	3.39	3.55	3.08	3.63	4.34

Table III. Mass-transfer data

(a) No. 7 oil, 0.031-inch wire; $P_s = 60.57$ cm.

1 drop/sec				2 drops/sec		
L (cm)	P (cm)	P/P_s	$1-(P/P_s)^2$	P (cm)	P/P_s	$1-(P/P_s)^2$
16.0	52.30	0.863	0.255	49.84	0.823	0.523
10.5	48.91	0.807	0.349	46.09	0.761	0.421
6.0	43.25	0.714	0.490	38.66	0.638	0.593
3.0	32.29	0.533	0.716	31.67	0.523	0.726

Slope, cm^{-1}

-0.104

-0.082

3 drops/sec			
L (cm)	P (cm)	P/P_s	$1-(P/P_s)^2$
16.0	45.15	0.745	0.445
10.5	40.82	0.674	0.546
6.0	32.59	0.538	0.711
3.0	25.78	0.426	0.819

Slope, cm^{-1}

-0.058

(b) No. 9 oil, 0.031-inch wire; $P_s = 60.54$ cm.

1 drop/sec			
L (cm)	P (cm)	P/P_s	$1-(P/P_s)^2$
10.3	51.91	0.857	0.266
5.5	43.92	0.725	0.474
4.3	37.80	0.624	0.611
Slope, cm^{-1}			-0.134

2 drops/sec				2.5 drops/sec		
L (cm)	P (cm)	P/P_s	$1-(P/P_s)^2$	P (cm)	P/P_s	$1-(P/P_s)^2$
10.3	48.20	0.796	0.366	41.04	0.678	0.540
5.5	36.91	0.610	0.628	33.54	0.554	0.693
3.6	31.42	0.519	0.731	25.84	0.427	0.818
Slope, cm^{-1}			-0.090	-0.060		

(c) No. 15 oil, 0.031-inch wire; $P_s = 61.94$ cm.

1 drop/6 sec				1 drop/4 sec		
L (cm)	P (cm)	P/P _s	1-(P/P _s) ²	P (cm)	P/P _s	1-(P/P _s) ²
10.0	-	-	-	54.05	0.873	0.238
6.0	54.46	0.879	0.227	52.63	0.850	0.277
3.0	49.04	0.792	0.373	43.13	0.696	0.516
Slope, cm ⁻¹			-0.291	-0.190		

1 drop/2 sec				1 drop/sec		
L (cm)	P (cm)	P/P _s	1-(P/P _s) ²	P (cm)	P/P _s	1-(P/P _s) ²
10.0	52.86	0.853	0.272	47.27	0.763	0.418
6.0	48.88	0.789	0.377	41.72	0.674	0.546
3.0	38.36	0.619	0.617	35.34	0.571	0.674
Slope, cm ⁻¹			-0.151	-0.108		

(d) No. 15 oil, 0.020-inch wire; $P_s = 61.94$ cm.

1 drop/2 sec			
L (cm)	P (cm)	P/P_s	$1-(P/P_s)^2$
16.0	39.07	0.631	0.602
10.0	32.88	0.531	0.718
6.0	31.46	0.508	0.742
3.0	25.03	0.404	0.837
Slope, cm^{-1}			-0.039

1 drop/sec			
L (cm)	P (cm)	P/P_s	$1-(P/P_s)^2$
16.0	36.61	0.591	0.651
10.0	33.62	0.543	0.705
6.0	29.91	0.483	0.767
3.0	21.20	0.342	0.883
Slope, cm^{-1}			-0.036

FIGURE CAPTIONS

- Fig. 1 Photographs of moving drops.
- Fig. 2 Geometry of flow of drops travelling on a vertical wire.
- Fig. 3 Schematic diagram of experimental apparatus.
- Fig. 4 Van Slyke manometric gas analyzer.
- Fig. 5 Cell used to measure diffusion coefficient.
- Fig. 6 Possible streamlines in a coordinate system moving with the wave velocity.
- Fig. 7 Gas absorption as a function of column length.
- Fig. 8 Slope as a function of drop frequency.
- Fig. 9 Overall correlation.

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