

# THE BEHAVIOUR OF GAS BUBBLES IN RELATION TO MASS TRANSFER

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## SUMMARY

The equation  $V_B = C \frac{D\gamma}{\rho}$  describes satisfactorily the relation between the size of bubble formed at a circular orifice, the diameter of the orifice, the surface tension and the liquid density so long as the value of  $C$  is related to the rate of bubble formation; an empirical relationship between  $C$  and the rate of bubble production is presented.

The upward velocity of a bubble in water varies with the diameters of both the bubble and the column of liquid in which it moves, and also with the rate of production of bubbles.

The mass transfer coefficient from oxygen to water has been measured, and was found to vary from 0.028–0.055 g. O<sub>2</sub>/sq. cm. sec. g. O<sub>2</sub>/cu. cm. The apparent effect of velocity upon the coefficient was considerable within the range measured. Although a strict comparison with coefficients measured in packed towers is not possible, the values of  $K_L$  for bubbles are slightly higher than those measured in packed towers for the desorption of oxygen.

## Introduction

Emphasis has already been laid on the importance of the study of the behaviour of gas bubbles in liquids, at the Conference arranged by the Institution of Chemical Engineers on 14 February 1950. In this Conference attention was drawn not only to the wide variety of operations in which gas bubbles play a part, but also to the fact that the amount of published information is small in relation to the importance of the subject. In the particular sphere of mass transfer from gas bubbles to liquids, the lack of published information is even more marked. The rate of absorption of carbon dioxide in water has been studied<sup>1, 2</sup> and also the rate of absorption of oxygen,<sup>3, 4, 5, 6</sup> but there is so far no extensive background of experimental work comparable to that, for example, in absorption in packed towers. It is the purpose of the present paper to examine some of the factors influencing the rate of mass transfer from bubbles to the surrounding liquid, and to express the results in a form that will enable comparisons to be made with other unit operations in which mass transfer takes place.

## Mass Transfer from Bubbles

A bubble and its liquid environment may be regarded as a two-phase system in which it is possible for mass transfer to take place across the gas/liquid interface. If both the bubble and the surrounding fluid can be regarded as stationary,

*i.e.*, if there are no eddy currents or other movements of material, transfer of matter from the bubble to the liquid presents the same general problem as transfer from any still gas to a motionless liquid in contact with it. It rarely happens, however, that the bubble and liquid are stationary and, when they are in motion relative to each other, the system becomes quite complex.

If it is assumed that the usual concept of film resistance can be applied to the system, namely, that the resistance to mass transfer is dependent upon the thickness of the liquid or gas film at the gas/liquid interface, it is important to know how, and to what extent, the film thickness varies. This variation, for a system of given materials, will depend largely on the rate of movement of the bubble relative to the liquid.

In the first place, the film thickness will vary from one part of the surface of the bubble to another; a spherical bubble in motion is not a completely symmetrical system, and examination of the stream lines shows there may be considerable variation in what is regarded as film thickness. In practice many bubbles are found to be far from spherical, and the variation in film thickness is probably greater in these cases. It is then possible that the mass transfer coefficient may vary from one part of the surface of the bubble to another; to demonstrate this quantitatively would probably be extremely difficult, and for the purposes of this paper only the average mass transfer rate for the whole surface will be considered.

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In the second place, the effective film thickness may vary according to the rate of movement of the bubble with respect to the surrounding liquid; the mass transfer coefficient may thus be expected to vary with the velocity of the bubble relative to the liquid. In this case, too, a further complication is introduced if the liquid itself is in motion and eddy currents are formed which make the movement of the bubble irregular.

If the case of a single bubble moving freely upwards in a still liquid is considered, it is evident that the volume of the bubble will increase during its ascent owing to the decrease in hydrostatic head. The velocity of the bubble will then vary in proportion to its size. If at the same time mass transfer takes place from the bubble to the liquid, the bubble size will decrease and the velocity and film thickness will vary accordingly. This effect of mass transfer from the bubble opposes the effect of decreasing hydrostatic head. A further complication may exist here if there is simultaneous mass transfer from the liquid to the bubble.

The system of a single bubble is thus fairly complex, and some simplifying assumptions are necessary to make feasible a theoretical treatment of mass transfer from bubbles. First of all, the case of mass transfer in one direction only will be considered, from the bubble to the liquid. Secondly, in a relatively shallow liquid the bubble volume may be regarded as constant, since the effects of decreasing hydrostatic head and loss of gas by mass transfer oppose each other and both effects will be very small; it follows that with constant volume the velocity of ascent and effective film thickness can also be regarded as constant. On the basis of these assumptions, the following equation may be written for a single bubble:

$$dm = -K_L a (c_s - c) dt \quad (1)$$

The  $K_L$  used here is the *overall* mass transfer coefficient; in the experimental work described later the liquid film provided the main resistance and the liquid film controlling coefficient  $K_L$  has been used. It should be noted that this coefficient is not necessarily the same as that determined, for example, in a falling film tower, and that it cannot be said to apply to any particular part of the surface of the bubble since, as has been mentioned, the coefficient may vary from one part of the surface to another. Equation (1), in fact, constitutes a definition of  $K_L$  as used in this paper.

It is not easy directly to measure the rate of

mass transfer from a single bubble to the surrounding liquid; it is much easier to measure the increase in concentration of gas in a solution which is being aerated by a stream of bubbles. Such a system can be expressed as follows:

$$V_L dc = -dm N \frac{h}{v} \quad (2)$$

Combining equations 1 and 2,

$$V_L dc = K_L a N \frac{h}{v} (c_s - c) dt \quad (3)$$

Equation (3) describes mass transfer from bubbles to liquids as long as it can be assumed that:

- (a) the volume of each bubble, and hence its velocity, remains constant during its ascent;
- (b) the bubbles are of uniform size.

It follows from equation (3) that before a determination of  $K_L$  can be made, it is necessary to know how to produce a stream of bubbles of uniform size, to know the velocity of ascent, and to know the number of bubbles passing through the liquid in unit time. The next section describes the experimental methods used and the results obtained in an investigation in these properties of gas bubbles. The system air-water was chosen as being the most convenient for experimental work; in addition it would enable a direct comparison to be made in some cases with the work of previous investigators.

## The Behaviour of Bubbles

### I. Bubble size

Air bubbles were produced in water at circular jets made from glass capillary tubing; glass tanks or vertical columns were used so that the bubbles could be observed easily and the normal laboratory air supply was used.

The size of a bubble formed at a circular orifice has been related to the diameter of the orifice, the surface tension of the liquid and its density, by means of the following equation<sup>1</sup>:

$$V_B = \frac{\pi D \gamma}{g \rho} \quad (4)$$

It was assumed in this equation that the angle of wetting was zero and that the bubble was quite spherical.

It was found experimentally that this equation described adequately the measured sizes of bubbles under certain specified conditions only; otherwise wide deviations from the calculated volume were observed, and it is now proposed to



use the equation in another form,

$$V_B = C \frac{D \gamma}{\rho} \quad (5)$$

and to relate the numerical factor  $C$  to the conditions of the experiment. Investigation of the factors influencing the size of a bubble produced at a circular orifice was carried out on the basis of this equation.

The apparatus which is illustrated in Fig. 7 consisted of a narrow, vertical tank with plate glass sides, into the bottom of which capillary jets fitted. The size of the bubbles generated at the jet was measured by collecting a number of bubbles in an inverted burette; the measured volume was corrected for pressure and temperature to give the volume per bubble at the jet. The jets were made by cutting glass capillary tubing with a glass knife in the usual way, and only those with a clean, regular cut were retained for use. The jets were cleaned thoroughly so as to avoid spreading of the bubble over the surface of the glass. When bubbles were generated rapidly a deflector plate was placed in the rising stream so that any desired proportion could be deflected from the main stream; in this way it was still possible to collect and measure the volume of a known number of bubbles.

#### a. Temperature

Using air at atmospheric temperature, the effect of water temperature was studied over the range 13° to 60° C. The effect of uptake of water vapour by the bubble was ignored. The results are given in Table I.

TABLE I.—Effect of Liquid Temperature on Bubble Size  
0.293 cm. diameter orifice

Water temperature (°C.)	Number of bubbles per minute	Bubble volume (cu. cm.)	C.
13	62	0.0652	0.00303
20	60	0.0652	0.00305
30	61	0.0655	0.00313
40	60	0.0660	0.00321
60	60	0.0655	0.00332

Within the range of the experiment the volume of the bubbles did not change with temperature, any variation being well within possible experimental error. The value of  $C$ , however, showed a tendency to increase with rising temperature, but it is doubtful whether or not this tendency is real.

#### b. Pressure

Results for the effect of pressure confirm previous work<sup>1</sup> that the size of the bubble remains unchanged within the range of pressure investigated. The results are reported in Table II.

Since the physical dimensions of a bubble are independent of pressure within the range studied, it follows that for a given size of orifice the mass of gas within the bubble is proportional to the total pressure at the orifice.

#### c. Orifice diameter

The effect of orifice diameter was studied with six glass jets ranging from 0.061 to 0.293 cm. in diameter. The flow rate of air supply to each jet was also varied.

At low flow rates it was possible to count by eye the number of bubbles produced per minute, and to collect and measure the volume of a suitable number of bubbles. At high flow rates this was not possible, so a deflector plate was placed in the rising stream of bubbles so that any desired proportion of the stream could be deflected without coalescence, counted, collected and the volume measured. The rate of bubble production could then be calculated from the bubble volume and the flow rate of air supplied to the orifice. This method does not reveal lack of uniformity in the size of consecutive bubbles, nor the formation of two distinct bubble sizes at the same jet as described by Pattle.<sup>6</sup>

A typical curve for one orifice is shown in Fig. 1. It will be seen that the bubble size varies considerably as the flow rate to the orifice is varied and at high flow rates the results tend to be

TABLE II.—Effect of Pressure on Bubble Size  
Orifice diameter

Hydrostatic head (cm.)	0.061 cm.		0.142 cm.		0.293 cm.	
	Number per minute	Volume (cu. cm.)	Number per minute	Volume (cu. cm.)	Number per minute	Volume (cu. cm.)
30	63	0.0117	62	0.0281	60	0.0660
60	58	0.0116	58	0.0281	58	0.0651
90	62	0.0133	63	0.0280	62	0.0660
120	58	0.0114	62	0.0286	60	0.0662
150	57	0.0113	59	0.0289	61	0.0671
180	63	0.0113	60	0.0292	62	0.0674



very erratic. At these high flow rates the bubbles are not of uniform size; large and small bubbles are produced and, unless particular care is taken, coalescence may take place in the rising stream of bubbles.

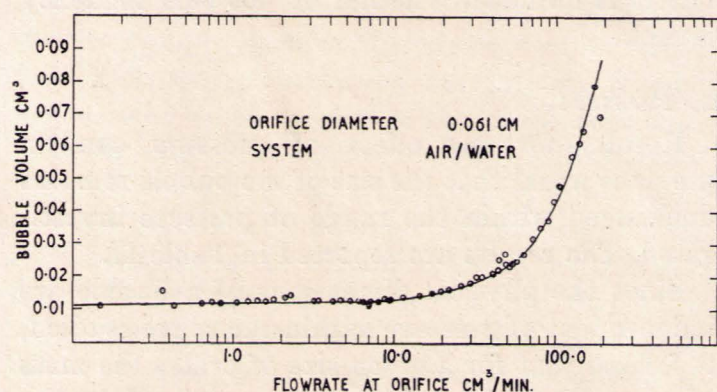


Fig. 1—Effect of flow rate on volume of bubbles formed at a circular orifice

An attempt was made to find a general correlation which would take into account the change in bubble size with change in the rate of air supply to the orifice. This was done by plotting the value of  $C$  in equation (5) against various parameters, such as flow rate, gas velocity at the orifice and rate of bubble formation. In Fig. 2 is shown a plot of  $C$  against gas velocity for three different jets; three distinct curves are found, and the same type of plot is obtained in every case except that of  $C$  against rate of bubble formation. In this last plot, which is illustrated in Fig. 3, the curves for different sizes of orifice coincide, and the correlation was found to hold good for all the jet diameters examined over the range from 10 to  $> 1000$  bubbles per minute.

It is noteworthy that for jets formed from glass capillary tubing, it does not seem possible to generate more than about 2500 bubbles per minute in water. If at this rate more air is supplied to the jet the bubbles merely become larger and not more numerous. This observation agrees with the results reported by Eversole and Wagner,<sup>10</sup> who found that under the conditions employed the bubble rate was constant at 2700–3000 per minute and that the bubble size increased with increasing flow rate at the jet.

The experimental errors in this work were relatively large, and the scatter in Fig. 3 is much greater than one would wish. It is surprisingly difficult, however, to obtain closely reproducible results with simple apparatus in this type of work, and there may have been many factors affecting the size of the bubbles which were not adequately controlled. Nevertheless, the correlation illustrated in Fig. 3 is useful in choosing the proper size of jet for any desired bubble size and flow-rate.

#### d. Liquid density

In equation (5) the density referred to is, strictly, the difference in density between the liquid and the gas; in practice the density of the gas may be neglected. The effect of density was studied by means of zinc chloride solutions of measured density and surface tension, and the results are given in Table III. The value of  $C$  remains constant within the margin of probable error and the bubble size is inversely proportional to the liquid density.

TABLE III.—Effect of Liquid Density on Bubble Size

Liquid density (g./cc.)	Orifice diameter (cm.)											
	0.061		0.091		0.102		0.181		0.188		0.293	
	cc.	C.	cc.	C.	cc.	C.	cc.	C.	cc.	C.	cc.	C.
1.000	0.0121	0.0027	0.0177	0.0027	0.0201	0.0027	0.0322	0.0025	0.0326	0.0024	0.0592	0.0028
1.186	0.0104	0.0028	0.0155	0.0028	0.0177	0.0029	0.0264	0.0024	0.0315	0.0028	0.0481	0.0027
1.280	0.0110	0.0031	0.0147	0.0028	0.0169	0.0029	0.0249	0.0024	0.0303	0.0028	0.0437	0.0026
1.486	0.0101	0.0032	0.0131	0.0028	0.0151	0.0029	0.0237	0.0025	0.0267	0.0027	0.0400	0.0028

The flow-rate to the orifice was maintained at 1 cu. cm./minute.

TABLE IV.—Effect of Surface Tension on Bubble Size

Liquid density (g./cc.)	Surface tension (dy./cm.)	Orifice diameter (cm.)											
		0.061		0.091		0.102		0.135		0.149		0.181	
		cc.	C.	cc.	C.	cc.	C.	cc.	C.	cc.	C.	cc.	C.
0.690	33.4	0.0065	0.0031	0.0095	0.0030	0.0107	0.0031	0.0137	0.0029	0.0156	0.0030	0.0182	0.0029
0.975	42.1	0.0083	0.0032	0.0119	0.0030	0.0136	0.0031	0.0163	0.0028	0.0181	0.0028	0.0210	0.0027
0.989	54.0	0.0100	0.0030	0.0140	0.0028	0.0148	0.0027	0.0219	0.0030	0.0236	0.0029	0.0284	0.0029
1.000	72.0	0.0133	0.0030	0.0185	0.0028	0.0212	0.0029	0.0275	0.0028	0.0281	0.0026	0.0348	0.0027



## e. Surface tension

Of the variables in equation (5), only surface tension remains to be considered. Its effect was studied first by means of alcohol-water mixtures, and the results, set out in Table IV, confirm what has already been reported in the literature.<sup>1</sup>

In these experiments the bubble volume was approximately proportional to the surface tension and, when allowance was made for the change in liquid density with composition of the alcohol/water mixture, the value of  $C$  was found to be fairly constant.

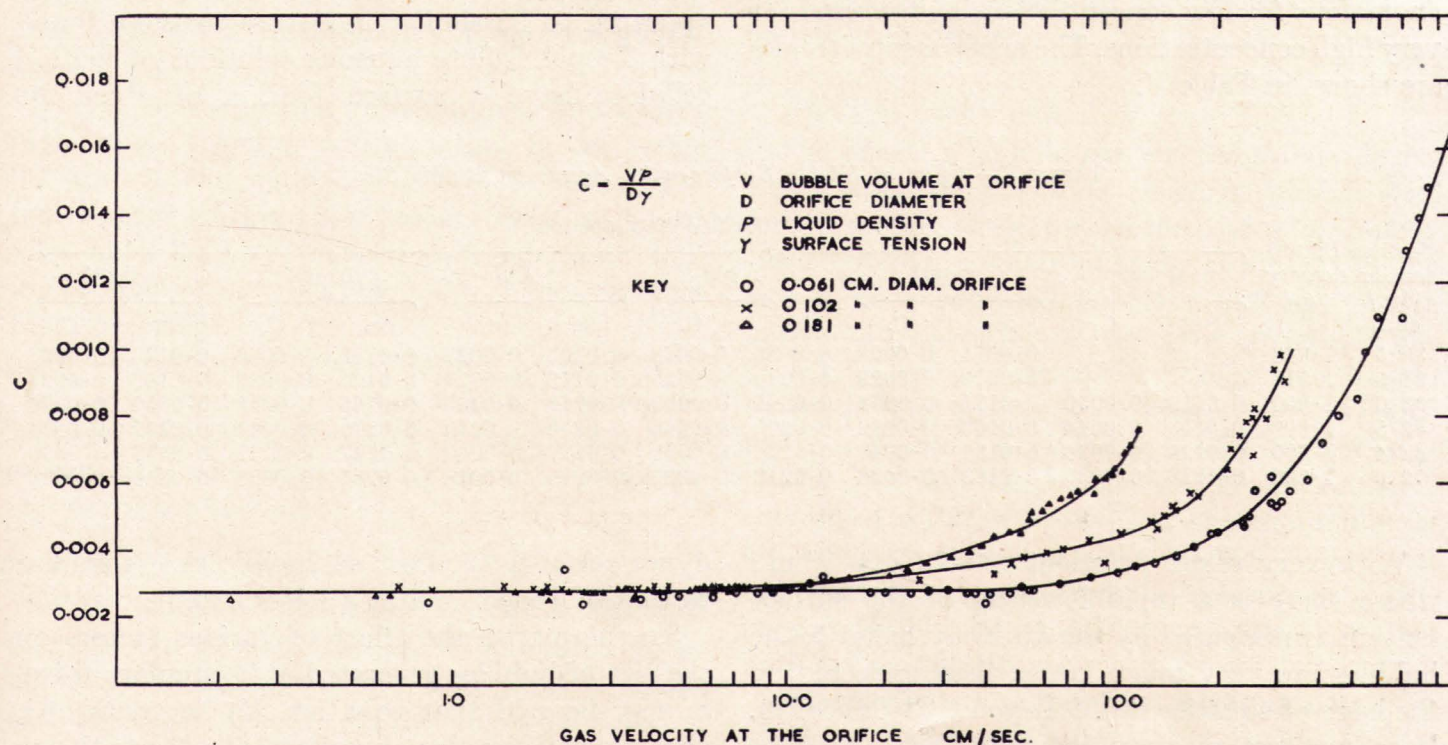


Fig. 2—Relationship between "C" and gas velocity at the orifice

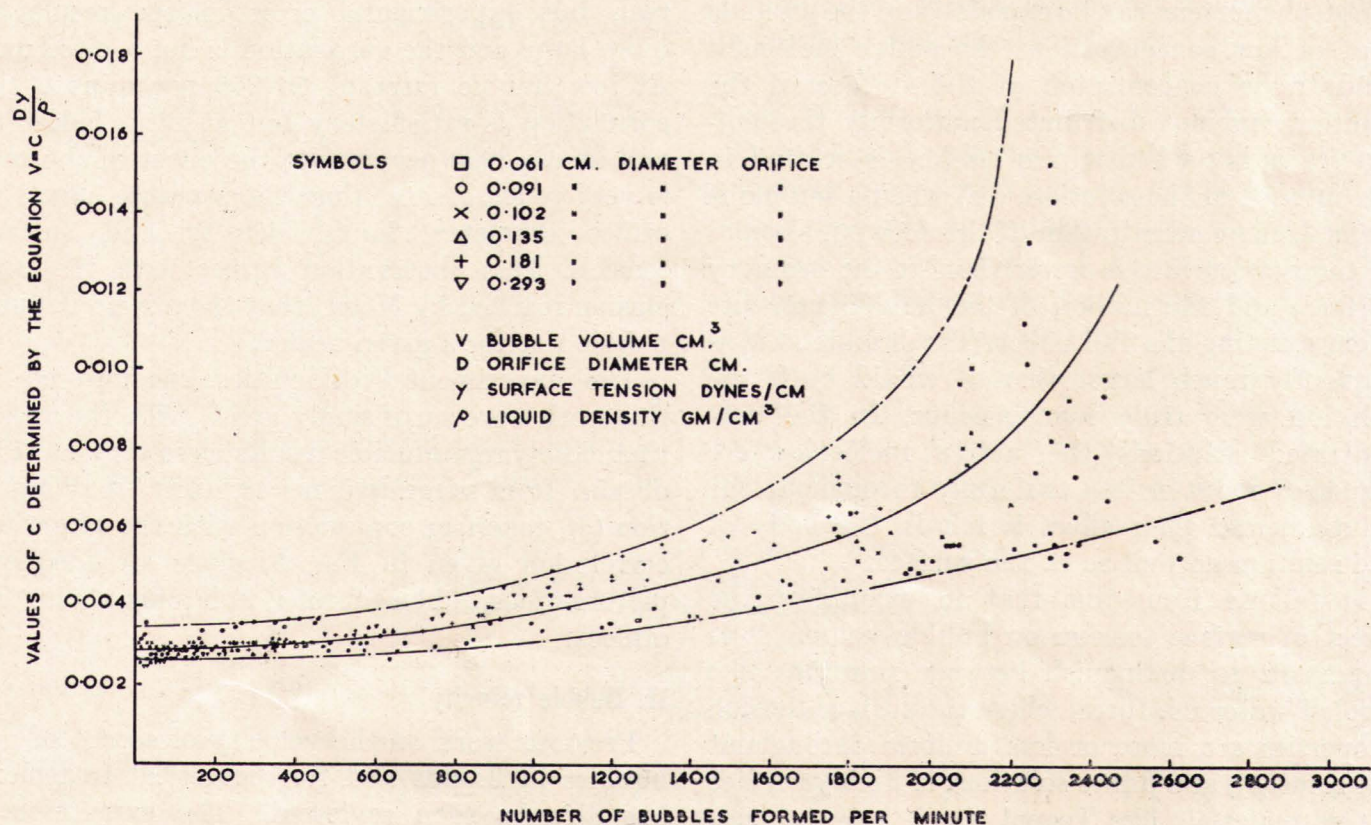


Fig. 3—Correlation between bubble size and rate of bubble formation



It was found, however, that when solutions containing a surface-active agent, such as Teepol, were studied, values of  $C$  calculated from the experimental results were widely different from the usual value of about 0.0028. A systematic study of the effect of concentration of the surface-active agent showed that the value of  $C$  was anomalous for low concentrations and normal for very high concentrations. The experimental results are shown in Table V.

#### f. Viscosity

Previous investigations<sup>1</sup> reported in the literature indicated that viscosity had little or no effect on the bubble size. This has been confirmed, but it may be mentioned in passing that while using dilute solutions of methyl cellulose in water unexpected deviations were found which appeared to be similar in nature to those found with Teepol. Dilute aqueous solutions of methyl cellulose have a surface tension of about 50

TABLE V.—Effect of Highly Surface-active Agents on Bubble Size

Surface tension (dy./cm.)	Liquid density (g./cc.)	Orifice diameter (cm.)											
		0.061		0.091		0.102		0.135		0.149		0.181	
		cc.	C.	cc.	C.	cc.	C.	cc.	C.	cc.	C.	cc.	C.
30.5	1.048			0.0074	0.0028	0.0083	0.0028	0.0108	0.0027	0.0112	0.0026	0.0143	0.0027
31.0	1.018			0.0079	0.0029	0.0089	0.0029	0.0112	0.0027	0.0125	0.0028	0.0149	0.0027
33.0	1.000	0.0113	0.0056	0.0174	0.0058	0.0801	0.0060	0.0252	0.0057	0.0256	0.0052	0.0335	0.0056
42.5	1.000	0.0113	0.0044	0.0163	0.0042	0.0200	0.0046	0.0258	0.0045	0.0279	0.0044	0.0337	0.0044
53.4	1.000	0.0125	0.0038	0.0192	0.0040	0.0224	0.0041	0.0287	0.0040	0.0297	0.0037	0.0346	0.0036
72.0	1.000	0.0133	0.0030	0.0185	0.0028	0.0212	0.0029	0.0275	0.0028	0.0281	0.0026	0.0348	0.0027

With very dilute solutions (33–72 dynes/cm.) where there is a rapid lowering of the surface tension as measured by the du Noüy method, the bubbles are very much larger than expected on the basis of equation (5). Beyond 33 dynes/cm. large increases in concentration of Teepol produce very little further lowering of the surface tension and the bubble volume becomes normal again. These phenomena can be explained on the grounds that at low concentrations the active molecules tend to be concentrated at the surface of the solution and not distributed uniformly throughout its bulk; when a new surface is created in the interior of the solution, *i.e.*, when a bubble is formed, the concentration of the active molecules at the new surface is lower than at the ordinary surface, and the motion of the bubble prevents them exerting the full effect. The bubble is consequently much larger than it would be if the solution were truly homogeneous. In the concentrated solutions the active molecules are dispersed more or less uniformly throughout the solution, and their effect is felt in the body of the solution as well as at the surface.

It follows from this that in examining the effect of surface tension on bubble volume it is important to distinguish between solutions like alcohol/water mixtures, where the surface tension properties are more or less uniform throughout the solution, and dilute solutions of highly surface active materials like Teepol which may be non-isotropic.

dynes/cm.; their effect on bubble size is similar to that of Teepol, but to a lesser extent.

To summarise the effect of various factors on the size of bubbles generated at a circular orifice, it may be said that equation (5) accounts in a general way for the experimental observations; the correlation between the empirical factor  $C$  and the rate of bubble formation appears to be real, but experimental error in the results is quite large and the correlation is not a close one. At low bubble rates of 50–250 per minute the correlation is satisfactory but at rates below 10 and above 2000 per minute the effect of the rate is very much greater than the separate effects of orifice diameter, liquid density and surface tension. This observation agrees with the conclusion reached by Maier<sup>7</sup> that there is no definite bubble size for a given orifice.

The experimental difficulties encountered in this work were surprisingly great, with the result that closely reproducible results were very hard to obtain. It is suggested, nevertheless, that equation (5), taken in conjunction with the empirical correlation given in Fig. 3, gives an adequate picture of air bubbles formed in liquids at circular orifices.

## II. Bubble velocity

Previous work on the velocity of ascent of gas bubbles in liquids and its theoretical treatment has already been reviewed.<sup>1</sup> The experimental difficulties here were also surprisingly great, and



the reproducibility of results was not always as good as might have been expected in what appeared at first sight to be simple experimental measurements.

The velocities measured were the terminal velocities; it should be noted that the term "terminal velocity" applies only to shallow liquids, since the velocity will vary with depth as a result of the variation in volume with hydrostatic head.

It was observed that most bubbles had a very high initial velocity, and also that in the range 0.1 to 0.4 cm. radius the bubbles followed a helical path during their ascent. Very large and very small bubbles followed a straight path and, in the case of large bubbles, the shape was that of a mushroom.

In the case of bubbles following a helical path there was a tendency for the bubble to alternate between a prolate and oblate spheroid. As will be shown later, this change may have an effect on the velocity of ascent.

#### a. Effect of tube diameter

With bubbles of about 0.1 cm. radius, the wall effect of the column of liquid is noticeable up to about 10–15 cm. diameter: the effect is small, but increases greatly as the tube diameter is decreased. The experimental results are given in Table VI: these were obtained by direct timing of the ascent of a bubble, the first 20 cm. of its path being excluded so as to avoid the high initial velocity.

TABLE VI.—Effect of Tube Diameter on Bubble Velocity

Tube diameter (cm.)	$\frac{d}{D}$	Terminal velocity (cm./sec.)
1.40	4.4	24.0
2.54	8.0	24.3
3.74	11.7	25.4
5.15	16.2	26.8
7.40	23	26.9
10.2	32	26.1
16.5	52	28.1

#### b. Effect of liquid viscosity

The effect of viscosity on velocity was measured by direct timing while the effect of viscosity on

bubble size was being studied. The bubble sizes were consequently not exactly constant throughout any one series of experiments; the range of bubble sizes is therefore quoted in Table VII where the velocity measurements are reported.

It is apparent that the liquid viscosity and the terminal velocity of a bubble are not connected by a simple relationship within the range of bubble sizes studied.

#### c. Effect of bubble size

The effect of bubble size on terminal velocity was studied over a wide range of bubble sizes for the system air/water. In the case of extremely small bubbles, a small quantity of air was drawn into a fine calibrated capillary and the length measured by a cathetometer; the air bubble was then released, and its upward velocity measured by taking two photographs with a vertical centimetre scale and a clock in the field. For very large bubbles an inverted bucket at the bottom of a column of water was used; a known amount of air was introduced into the bucket, which was then turned upwards, and the velocity of ascent of the bubble was measured by direct timing with a stop-watch.

Intermediate size bubbles were produced at glass jets and a cine camera was used to follow their ascent; a clock movement and a centimetre scale were included in the field of the camera. The column diameter was 6 in. The apparatus is illustrated in Fig. 8.

#### Single bubbles

It was found that the most convenient way of producing very small or very large bubbles of known size was to produce them singly rather than as a stream from a jet. The velocities of the bubbles were measured in still water and, as far as practicable, several determinations were made for each bubble size. Experiments were conducted in columns of different diameter and shape; it was found that with bubbles of less than 0.10 cm. radius the wall effect was small,

TABLE VII.—Effect of Liquid Viscosity on Bubble Velocity

Tube diameter, 5 cm. Temperature, 20° C.  
Solutions: Aqueous glycerol and methyl cellulose

Bubble size (cm. radius)	Viscosity, poises										
	0.010	0.0285	0.045	0.0685	0.196	0.276	0.485	0.540	1.54	2.23	3.76
	Terminal velocity (cm./sec.)										
0.050 ± 0.005	25.0	—	13.3	—	7.9	—	4.8	3.4	2.6	—	1.6
0.062	25.0	23.9	20.0	19.3	11.1	9.1	7.4	5.7	4.1	1.8	1.9
0.074 ± 0.004	21.1	22.5	20.0	22.0	14.3	11.6	9.5	8.4	5.1	1.8	2.5
0.090 ± 0.010	22.2	22.2	19.1	24.2	18.2	15.0	14.3	10.3	7.0	2.8	3.2



and that towards 0.01 cm. radius it became almost negligible for tubes of 5–15 cm. diameter.

The results for single bubbles are given in Table VIII below, and it is noteworthy that there is no pronounced peak such as described previously.<sup>1, 11</sup>

The curve of velocity against bubble size, illustrated in Fig. 4, resembles the curve obtained from the results of O'Brien and Gosline,<sup>12</sup> but with the important difference that these authors describe velocities measured for streams of bubbles, whereas the results given in Table VIII are for single bubbles. The main difference between the results described here and those reported previously in the literature lies in the transition region between radii of 0.1 and 0.3 cm.

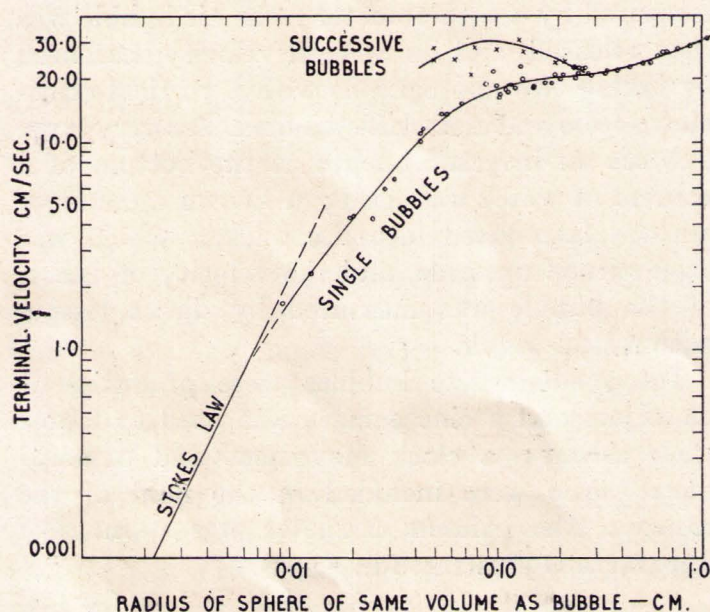


Fig. 4—Variation in terminal velocity with bubble size

TABLE VIII.—Upward Velocity of Single Air Bubbles in Water  
Tube diameters, 5 cm. to 16 cm.

Radius (cm.)	Velocity (cm./sec.)	Radius (cm.)	Velocity (cm./sec.)	Radius (cm.)	Velocity (cm./sec.)
0.0093	1.67	0.107	17.1	0.268	23.2
0.0129	2.31	0.113	18.1	0.278	23.1
0.0197	4.32	0.117	17.6	0.287	21.9
0.0203	4.43	0.120	19.2	0.294	21.2
0.0256	4.30	0.126	18.4	0.346	21.8
0.0290	6.00	0.133	23.6	0.362	22.2
0.0327	6.75	0.136	20.2	0.398	22.4
0.0434	11.1	0.155	18.4	0.457	23.1
0.0438	10.2	0.156	18.9	0.521	24.2
0.0450	11.7	0.178	19.7	0.572	25.2
0.0554	13.8	0.190	19.4	0.622	26.1
0.0582	13.8	0.197	21.4	0.658	27.3
0.0696	15.4	0.210	20.4	0.685	27.3
0.0795	17.0	0.216	21.6	0.780	28.4
0.0911	19.2	0.241	23.3	0.894	29.2
0.0985	22.2	0.249	20.5	0.983	30.8
0.100	18.7	0.251	21.4	1.06	32.0
0.105	16.5	0.258	23.2	—	—

#### Successive bubbles

When the upward velocities of streams of bubbles were measured photographically, it was

found that the results, given in Table IX, agreed with those described by Newitt *et al.*<sup>1</sup> In these results the bubbles were generated at about one per second, so that the distance between successive bubbles was about 25–30 cm. The velocities were significantly higher than those for single bubbles of the same size, particularly in the region of 0.1 cm. radius. Van Krevelen<sup>11</sup> has discussed the effect on upward velocity of the nearness of bubbles in a stream, and has concluded that at high rates of bubble production—the so-called “bubble series”—the velocity of ascent is indeed lower than for “separate bubbles.” These results, however, are not strictly comparable with those described here, since much higher bubble frequencies were used.

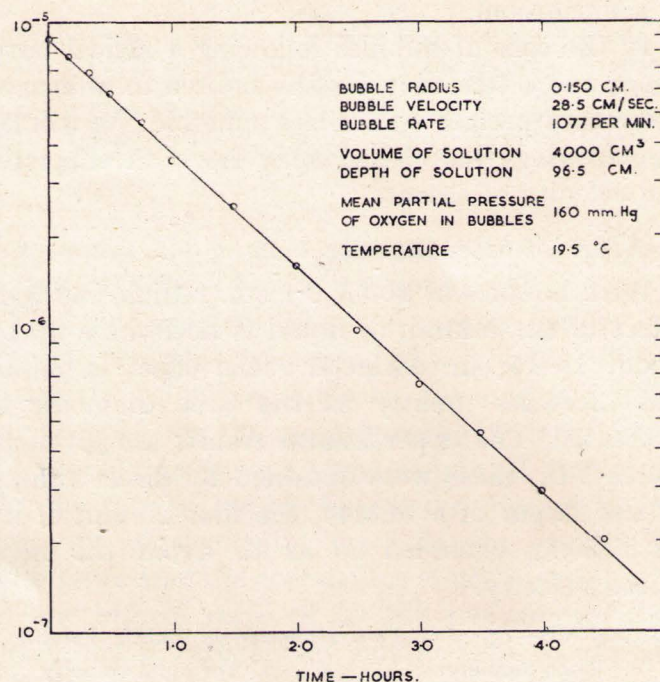


Fig. 5—Uptake of oxygen by water from air bubbles  
Driving force ( $C_s - C$ ) gm. oxygen/cc.

TABLE IX.—Upward Velocity of Successive Air Bubbles in Water

Tube diameter, 16 cm.	
Bubble radius (cm.)	Upward velocity (cm./sec.)
0.103	27.9
0.107	30.8
0.134	31.2
0.140	27.3
0.159	28.1
0.160	27.2
0.200	24.3
0.222	24.8
0.259	22.5

The results described in Tables VIII and IX raise the problem of the actual relation between terminal velocity and proximity of bubbles, and it is possible that some of the differences in the results obtained by different observers are in



fact the result of using different bubble frequencies.

#### d. Variation in terminal velocity

In measuring the terminal velocity of successive bubbles in water by direct timing with a stop-watch, it was observed that over short distances there were apparent variations which were independent of the observer. When cine camera records of the upward journey of a bubble were examined it was found that the velocity of ascent showed considerable variation over fairly short

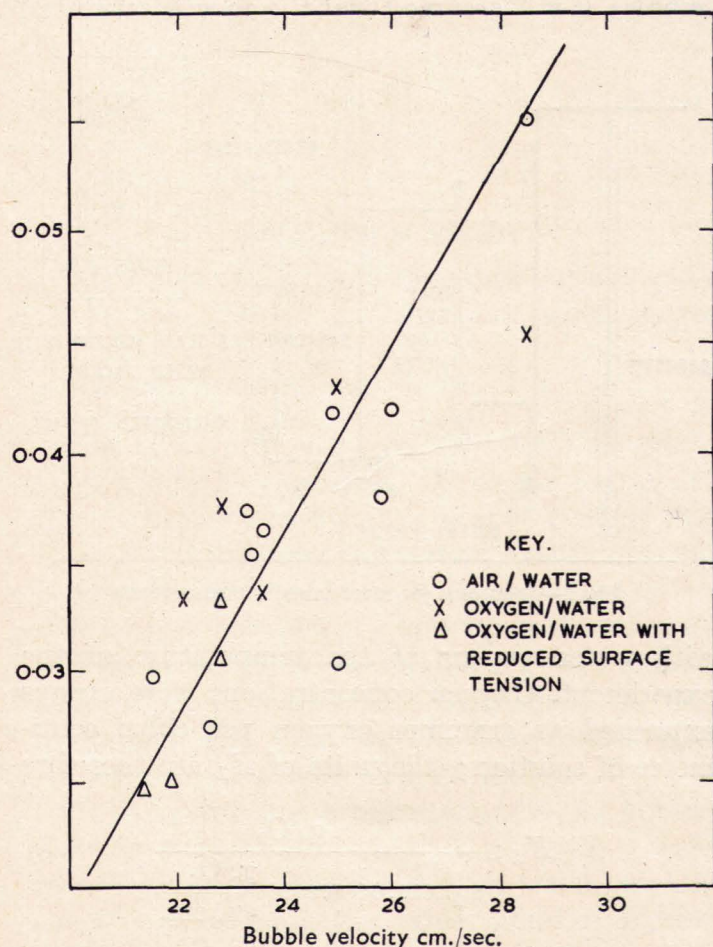


Fig. 6—Variation in mass transfer coefficient with bubble velocity  
Mass transfer coefficient  $\frac{\text{gm. oxygen}}{\text{sq. cm. sec. gm. oxygen. cc.}}$

distances. The timing mechanism in this case was a small electric movement, taking 3.75 seconds per revolution, which had been standardised photographically against a pendulum. The method adopted was to measure the average velocity over intervals of 10 cm.; it was found that the velocities so determined varied by as much as  $\pm 20\%$  from the terminal velocity measured over the whole distance of between 100 and 200 cm. The variations determined in this way appeared to be quite haphazard, but this may be merely the result of choosing an interval of

10 cm., which did not fit the cycle of acceleration and deceleration.

It was not possible to obtain a clear-cut record of the cycle of increasing and decreasing velocity, nor to decide whether or not the cycle was repeated regularly or at random. The observed variation of  $\pm 20\%$ , however, is much greater than the probable experimental error.

The reason for such variation is not at all clear. It might, for example, be the result of eddy currents produced by the passage of previous bubbles, since the cine camera records were taken while bubbles were being generated at about one per second, so that the interval in space between bubbles was approximately 25–30 centimetres. On the other hand, it might be the result of the helical path and the alteration in shape as described by Miyagi.<sup>8</sup>

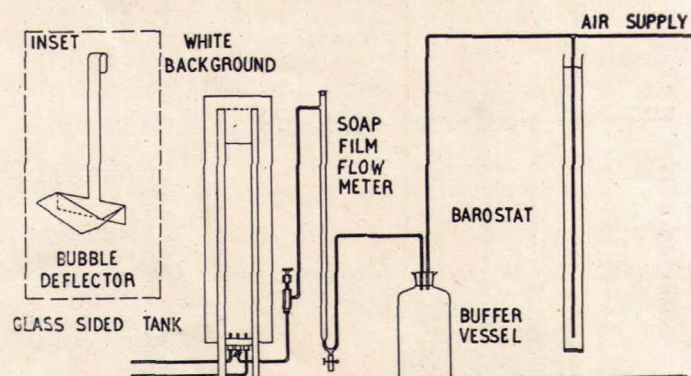


Fig. 7—Apparatus for bubble size measurement

For the purpose of mass transfer measurement the variations in upward velocity were neglected; the average velocity of ascent of the bubbles was used in calculating the time of contact with the liquid, and the results for successive bubbles were used, not those for single bubbles.

### III. Mass transfer coefficient

Integration of the equation developed for mass transfer from gas bubbles to the surrounding liquid (*i.e.*, equation 3) gives the following equation:

$$\ln \frac{c_s - c_1}{c_s - c_2} = K_L a N \frac{h}{v} (t_2 - t_1) \quad (6)$$

in which  $K_L$  is defined by means of equation (4).

Using the information already described on the size and velocity of air bubbles in water, the rate of uptake of oxygen from both air and oxygen bubbles was measured. In these experiments the effect of simultaneous transfer of nitrogen and water vapour was ignored. In the case of air bubbles thoroughly de-gassed water was used.



The apparatus for measuring the rate of uptake of oxygen (which is illustrated in Fig. 9), consisted of a vertical glass tube, 4 ft. long and 3 in. in diameter, fitted with a water jacket. Calibrated jets were fitted as required to the bottom end of the column. Samples were withdrawn through a sampling tube, which entered at the bottom and projected about half-way up the column. The upper surface of the water in the column was protected from the atmosphere by a hollow brass float, conical in shape, which reduced the exposed surface. A small glass ball rested on the upper side of the cone; this allowed gas bubbles to

method was of the same order as  $(c_s - c)$  or  $c$ . A typical graph is shown in Fig. 5.

In every case the surface areas and volumes of the bubbles referred to the size of the bubbles at the moment of release from the jet. In calculating the equilibrium concentration of oxygen in the liquid film, the partial pressure of oxygen was taken as that at the half-way point in the column of liquid. With oxygen bubbles (from cylinder oxygen) the oxygen concentration was taken as 100%, and no allowance was made for uptake of water vapour by the bubbles; in the case of air bubbles, it was assumed that the air was saturated

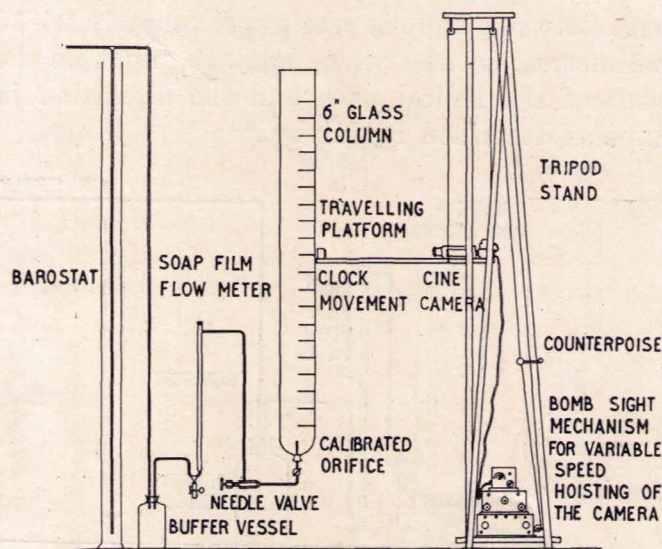


Fig. 8—Apparatus for bubble velocity measurement

escape easily, without allowing any significant uptake of oxygen from the atmosphere even after standing overnight. The rate of air supply to the jet was measured in a soap-film flow-meter, the pressure being controlled at this point by a barostat, and the rate was controlled by means of a fine needle valve. Air or oxygen was passed into the absorption column, and samples were withdrawn from time to time for analysis by the Winkler method or by the polarigraph.

It follows from equation (6) that during the aeration of water by a stream of bubbles, the logarithm of the driving force is proportional to the time of aeration for any given experiment:

$$\ln(c_s - c) \propto t.$$

The experimental results were therefore checked in each case by plotting  $(c_s - c)$  against time on semi-logarithmic paper. In this way it was possible to establish the slope of the curve, and to exclude those results at the beginning and end of the experiment where the error of the analytical

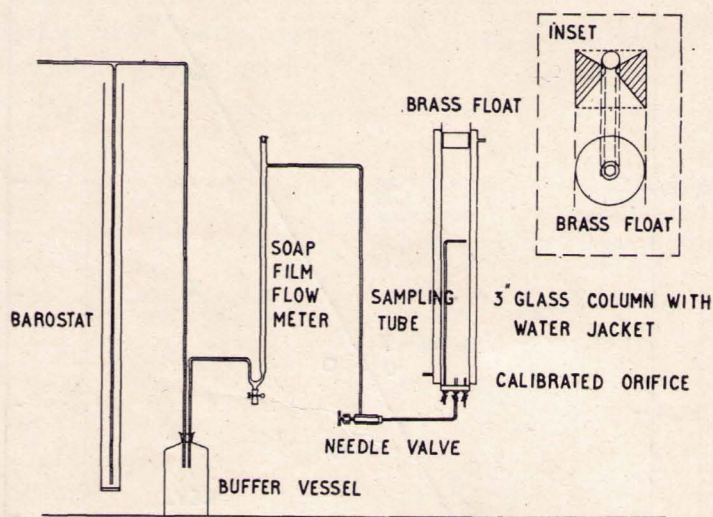


Fig. 9—Apparatus for mass transfer measurement

with water vapour at the temperature of the experiment. Oxygen concentrations were always expressed as grammes oxygen per cubic centimetre of solution; the units of  $K_L$  are therefore

$$K_L; \frac{\text{g. O}_2}{\text{sq. cm.} \times \text{sec.} \times \frac{\text{g. O}_2}{\text{cu. cm.}}}$$

The experimental results, which are set out briefly in Table X, fall into three groups. In the first group air bubbles were used along with de-gassed water. In the second group oxygen bubbles were used; the distilled water was not de-gassed in these experiments. In the last group an attempt was made to examine the effect of surface tension on the value of  $K_L$ , and oxygen bubbles were used in conjunction with distilled water to which small amounts of isopropyl alcohol had been added. Further experiments on the effect of viscosity on the value of  $K_L$  have so far proved unsuccessful, owing to the difficulty of raising the viscosity of water without interfering with the subsequent analyses for oxygen.



TABLE X.—Mass Transfer Coefficients; Oxygen/Water

Surface tension (dynes/cm.)	Bubble radius (cm.)	Upward velocity (cm./sec.)	Temperature (°C.)	$K_L$
—	0.150	28.5	19.5	0.0550
—	0.185	26.0	19.1	0.0420
—	0.188	25.8	18.3	0.0378
—	0.202	25.0	8.5	0.0303
—	0.206	24.9	20.1	0.0433
—	0.237	23.6	22.0	0.0364
—	0.240	23.4	20.8	0.0353
—	0.242	23.3	20.8	0.0372
—	0.278	22.6	20.0	0.0272
—	0.292	22.3	21.5	0.0297
—	0.150	28.5	20.0	0.0453
—	0.203	25.0	20.0	0.0430
—	0.237	23.6	20.0	0.0336
—	0.275	22.8	20.0	0.0375
—	0.330	22.1	20.0	0.0344
44.5	0.200	21.4	20.0	0.0245
50.2	0.201	21.9	20.0	0.0250
59.9	0.203	22.8	20.0	0.0306
64.5	0.204	22.8	20.0	0.0331

### Discussion of Results

The value of  $K_L$  lies in the range 0.028–0.055 g. O<sub>2</sub>/sq. cm. × sec. × g. O<sub>2</sub>/cu. cm., which corresponds to 3.0–6.0 lb. mol./sq. ft. × hr. ×  $\frac{\text{lb. mol.}}{\text{cu. ft.}}$

The effect of upward velocity is rather greater than would be expected;  $K_L$  is plotted against bubble velocity in Fig. 6, and it is evident that, in so far as any real correlation exists, the slope is very great. To obtain a clear picture of the relationship between  $K_L$  and upward velocity it will be necessary to determine  $K_L$  over a much wider range of bubble sizes than has so far been attempted. There are considerable practical difficulties associated with such an attempt.

No other direct determinations of  $K_L$  for bubbles have been reported in the literature, but transfer rates have been determined from which, making some assumptions, comparable values of  $K_L$  may be calculated.

The absorption of carbon dioxide by water has been studied by Newitt *et al.*,<sup>1</sup> and by Guyer and Pfister<sup>2</sup>; the results are expressed in each case as

$$\frac{\text{c.c. CO}_2}{\text{sq. cm.} \times \text{sec.}}$$

and the driving force term is omitted. Assuming that the driving force is equivalent to the solubility of carbon dioxide in water at room temperature and atmospheric pressure, the results are equivalent to a  $K_L$  value of 0.017 to 0.033, which is of the same order as that for oxygen. It might be expected that  $K_L$  for carbon dioxide/water would be somewhat higher than that for

oxygen owing to its higher solubility, but in determining  $K_L$  for both carbon dioxide and oxygen desorption from water in packed towers, Sherwood and Holloway<sup>9</sup> found that the two gases gave closely similar values, with oxygen slightly higher than carbon dioxide. These workers reported  $K_L a$  values of about 30 to 120 lb. mol./sq. ft. × hr. × lb. mol./cu. ft.; making allowance for the various packings used,  $K_L$  varied from about 0.5 to 4.0, depending on the liquor rate. Converting to C.G.S. units, the corresponding range of  $K_L$  for oxygen in packed towers is 0.004 to 0.033. It is interesting to note here that for oxygen/water the value of  $K_L$  is apparently lower for packed towers than for bubbles.

The efficiency of oxygen absorption from air bubbles has also been studied by Pattle<sup>6</sup>; the results given in this case can only be recalculated to give a  $K_L$  value if assumptions are made about the upward velocity of the bubbles and the equilibrium concentration of oxygen at full saturation. In any case the results are not strictly comparable with those described here, since Pattle's experiments were carried out with 0.2% acetic acid, but a tentative calculation showed that over the same range of bubble sizes as described here, the value of  $K_L$  was of the order 0.080–0.220 in C.G.S. units. This is about 5 times greater than found in the experiments described here.

Although the mass transfer coefficient for oxygen to water has been determined over the range of bubble sizes 0.15 to 0.3 cm. radius, much remains to be done to clarify several points which became evident during the course of the experimental work. The effect of velocity, surface active agents and viscosity all require further investigation, and even the apparently simple matter of upward velocity would repay further study in view of the difference noted by various observers.

### Acknowledgment

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### Symbols

- $a$  = area of bubble surface—sq. cm.
- $c$  = concentration of gas in solution—g./cu. cm.
- $c_s$  = equilibrium concentration of gas in solution—g./cc.
- $C$  = empirical constant.
- $D$  = diameter of orifice—cm.



- $d$  = tube or column diameter—cm.  
 $g$  = gravitational constant—cm./sec.<sup>2</sup>  
 $h$  = depth of orifice below surface of liquid—cm.  
 $K_L$  = overall mass transfer coefficient for gas from bubble to liquid—  
 $\frac{\text{g.}}{\text{sq. cm.} \times \text{sec.} \times \text{g./cc.}}$   
 $m$  = mass of gas in a single bubble—g.  
 $N$  = number of bubbles released in unit time—sec.<sup>-1</sup>  
 $t$  = time—sec.<sup>-1</sup>  
 $v$  = upward velocity of a bubble—cm./sec.  
 $V_B$  = volume of bubble—cu. cm.  
 $V_L$  = volume of liquid being aerated—cc.  
 $\rho$  = density—g./cc.  
 $\gamma$  = surface tension—dyne/cm.

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