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THE ROLE OF THE LIQUID STATIONARY FILM IN BATCH ABSORPTIONS OF GASES. I. ABSORPTIONS INVOLVING NO IRREVERSIBLE CHEMICAL REACTIONS[1]

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In the studies on the rates of absorption of olefinic gases by sulfuric acid which were reported in a previous communication[4] it was noted that the specific absorption coefficient (cc. of gas absorbed per sec. per sq. cm. of surface) was not appreciably affected by agitation of the acid. However, in the absorption chamber used (a horizontal cylinder) stirring was obtained by rotation, which also changed the area of the liquid surface exposed. Accordingly a new apparatus (described below) has been devised in which gases can be absorbed at various pressures by liquids with a constant area of surface exposed, while a stirrer is operating at a controllable speed beneath the liquid surface.

The results with the new apparatus have confirmed and extended the generalizations made from the former measurements with the rotating absorber. Some of the facts are at first sight surprising, *e. g.*, that ethylene was absorbed by concentrated sulfuric acid as rapidly when the acid was quiescent as when it was stirred (without breaking the surface or changing its area) at 400 r. p. m. The writers have found that the various phenomena encountered are best explained in terms of the so-called "two film theory" of gas absorption. For this purpose it has been necessary to study and extend further by experimental tests this important hypothesis.

"It is now becoming generally recognized that whenever a liquid and a gas come in contact there exists on the gas side of the interface a layer of gas in which motion by convection is slight compared to that in the main body of the gas and that similarly on the liquid side of the interface there is a surface layer of liquid which is practically free from mixing by convection. This phenomenon is frequently expressed by assuming the existence of stationary films of gas and liquid on the two sides of the interface."[5]

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[1] This paper contains results obtained in an investigation on the "Relative Rates of Reaction of the Olefins," listed as Project No. 19 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] Davis and Schuler, THIS JOURNAL, **52**, 721 (1930).

[5] Lewis and Whitman, *Ind. Eng. Chem.*, **16**, 1215 (1924).

There is good evidence that a similar liquid stationary film exists at a liquid–solid interface. Noyes and Whitney[6] showed that the rate of solution of a solid in water is proportional to the difference between the saturation concentration and its concentration in the water. They assumed that at the interface between the crystals and the liquid the solution is at each moment saturated. The velocity of solution according to this is conditioned only by the rate of diffusion through an unstirred layer close to the solid. Brunner[7] in a very important research extended this work and measured rates of solution per unit area of interface. Nernst[8] suggested that this hypothesis can be so generalized as to apply to all reactions in heterogeneous systems. The similarity of the phenomena caused by the liquid stationary films at various types of interfaces (liquid–gas, liquid–liquid and liquid–solid) should be emphasized.

This paper will be limited to consideration of the role of the liquid stationary film in determining the rates of gas absorption where no irreversible reactions are involved. When dealing with a pure gas of moderate solubility, the effect of the gas film is negligible.

Lewis and Whitman[5] state, "Resistance to diffusion due to the gas film is, of course, non-existent in the special case where an absolutely pure gas is being absorbed. This problem is very rarely encountered in practice, however, since the presence of very small amounts of inert gas which will concentrate at the liquid surface is sufficient to create an effective gas film." This statement might imply that the inert gas is adsorbed on the surface of the liquid and forms a gas film, even at equilibrium conditions, in which its concentration is greater than in the main body of the gas. To such a conception H. S. Taylor[9] has objected that, "It is not in harmony with so much of the treatment found valid by Langmuir in the case of reactions at solid surfaces. On Langmuir's method of treatment there should be no gas film of the nature postulated by Whitman. A unimolecular layer of adsorbed molecules would represent the maximum film which could be formed."

However, it would appear that the fundamental assumption made by Whitman is that on either side of the liquid–gas interface there exists a film of relatively quiet fluid and the gas being absorbed must pass through these films by diffusion. From these postulates Hanks and McAdams[10] have shown that a gas film of the inert gas must exist at the interface when the solute gas is being absorbed from the main body of the gas into the liquid. For, since the solute gas passes inward through the stationary gas layer, by diffusion, it must form a gradient of decreasing concentration to the liquid surface, and since the total gas pressure of inert and solute gas remains constant, there must exist a similar gradient of the inert gas outward.

The stationary films are by no means monomolecular in thickness, nor must they be confused with adsorbed layers. They are much thicker. Thus for water stirred underneath at 1000 r. p. m. the effective thickness is about 0.0045 cm.,[5] which is over a hundred thousand times the diameter of the water molecule.

The reality of the liquid stationary film is confirmed by common-place observations. Thus, dust particles often remain motionless on the surface of water in a well-stirred thermostat. The phenomena stand out still more

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[6] Noyes and Whitney, *Z. physik. Chem.*, **23**, 689 (1897).

[7] Brunner, *ibid.*, **47**, 56 (1904).

[8] Nernst, *ibid.*, **47**, 52 (1904).

[9] Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1926**, p. 1001.

[10] Hanks and McAdams, *Ind. Eng. Chem.*, **21**, 1034 (1929).

plainly under the microscope in water containing fine particles, *e. g.*, freshly precipitated barium sulfate. The solid particles at the surface *and also for a short distance beneath it* appear to be in a separate medium of their own which slips along the water like a thin skin. A little deeper down, the particles are carried here and there by currents and move past the outlines of those at the surface like low-lying storm clouds against those high in the sky.

The writers determined the distance between the quiet particles on the surface and those moving freely beneath it, under a microscope at about 50 diameters magnification. The value obtained for quiescent water at room temperature, 0.04 cm., was checked with surprising closeness by different observers.

What causes the liquid "stationary" film? Some of the contributory factors can be pictured. Thus the upward motion of water in currents must cease before the surface is reached. Again, local currents across the surface are opposed by some force, perhaps that of surface tension. This is indicated by the tendency to preserve their relative spacing shown by particles lying on the surface. It is significant that the effective thickness of the liquid stationary film at the gas–liquid interface is of the same order as that of the liquid film at a liquid-solid interface (see Table I, Note b).

Whatever the causes of its existence, the liquid stationary film plays a major role in the absorption into or the evolution of gases from liquids. With moderate stirring, the main body of the liquid and the main body of the gas are each practically uniform in composition and the gas must pass from one phase to the other through the unstirred layers at the interface mainly by diffusion. In another communication it will be shown that where irreversible chemical reactions are involved, the whole reaction often takes place in the liquid stationary film and the gas never reaches the main body of the liquid at all.

When a pure gas, oxygen for example, is suddenly admitted at atmospheric pressure into contact with pure water from which all gases have been removed, the very surface layer, perhaps monomolecular in thickness, instantaneously becomes very nearly saturated with oxygen.[8] This must be true, because an oxygen pressure is at once exerted from the surface equal to the partial pressure against it, which is the condition necessary for a saturated solution.

The oxygen now begins to diffuse into the film at a tremendous rate, for although the solubility of oxygen in water is small, 0.0012 M, the gradient from the surface is very steep. We wish to stress this point because of its bearing on the rapid rates at which some olefinic gases are absorbed by sulfuric acid, although they are quite insoluble therein.

As diffusion proceeds the magnitude of this gradient quickly grows less and the absorption slows down, soon reaching a constant value (*initial absorption rate*). At this stage the gradient is uniform and the same quantity of oxygen is passed from the surface through each unit cross section of the film into the main body of the liquid which is still practically free from dissolved oxygen.

The Time Required to Build up an Oxygen Gradient through the Film of Water.—Table I shows that the time necessary to establish a uniform gradient through the stationary liquid film depends on the degree of agitation in the water. It can be practically established (98%) through the sides of bubbles in one-tenth of a second, whereas five seconds are required in the case of moderately stirred (60 r. p. m.) water and in the case of quiescent water a still longer period is needed since here an effective film thickness of several millimeters is sometimes encountered.

These conclusions are substantiated by the measurements of Monaweck and Baker[11] on the rates of absorption of pure ammonia gas by water. With stirring at 324 r. p. m., no high initial absorption was noted (readings being taken every ten seconds) and the rate remained constant for 110 sec. Evidently a uniform concentration gradient was very rapidly established through the film. Further, calculation shows that $k_L = 1.3 \times 10^{-6}$ for these experiments, which is in good agreement with a value 2.2×10^{-6} found by the writers from measurements of the absorption rate of carbon dioxide, a much less soluble gas, by water under similar conditions.

On the other hand they found that the absorption rate of pure ammonia by quiescent water fell off over a period of 100 seconds to less than one-sixth of its initial value.

TABLE I

SHOWING THE RISE OF THE CONCENTRATION WITH TIME IN THE CENTER OF THE LIQUID STATIONARY FILM DURING THE ABSORPTION OF OXYGEN BY WATER EXPRESSED AS PERCENTAGE OF THE VALUE AT UNIFORM ABSORPTION (= 0.5 SURFACE CONCENTRATION)[a]

Absorption conditions	Thickness of film,[b] cm.	Seconds					
		0.01	0.1	0.2	0.5	1.0	5
Water stirred at 60 r. p. m.	0.020	..	..	..	..	20%	88%
Water stirred at 1000 r. p. m.	.0045	..	50%	80%	99%	..	..
Bubbles in water	.0021	18%	98%	..	..	..	..

[a] In these calculations it has been assumed that the inner limit of the stationary film is sharply defined and that the concentration of dissolved oxygen at the interface, C_i, remains constant (saturation value), while that at the inner edge and in the main body of the solution can be regarded as zero.

It is further assumed that the course of the oxygen diffusion at all times satisfies the equation $\partial c/\partial t = \Delta(\partial^2 c/\partial x^2)$, (see, however, Lewis and Chang, *Trans. Am. Inst. Chem. Eng.*, **21**, 135 (1928)), where c is concn. of dissolved oxygen, moles per liter; t is time in seconds after oxygen comes into contact with the deoxygenated water; x is distance in cm. from the surface; Δ is diffusion coefficient for oxygen through water.

The writers are indebted to Professor F. C. Hitchcock for a solution of the differential equation for these conditions in terms of a Fourier series.

[b] These values are taken from the calculations of Lewis and Whitman except for

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[11] Monaweck and Baker, *Trans. Am. Inst. Chem. Eng.*, **22**, 165 (1929).

that for bubbles in water, which was calculated by the writers from the data of Adeney and Becker discussed below.

It is interesting to compare these values for the thickness of the liquid stationary film at a gas–liquid (water) interface with those obtained by Brunner, *Z. physik. Chem.*, **47**, 99 (1904), for the liquid stationary films at the surface of solids in well-stirred liquids—0.0030 cm. for pure water and 0.0028 to 0.005 cm. for various solutions.

Experimental

The absorption apparatus was designed to operate at atmospheric pressure or at any desired reduced pressure. Accordingly it was necessary that the seal around the stirrer should stand high vacua, so that an ordinary mercury ring seal could not be used.

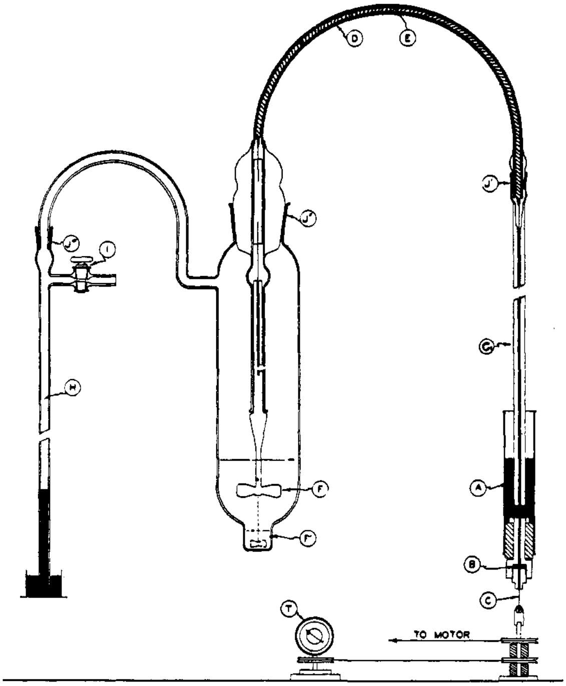

Fig. 1.—Diagram of apparatus for gas absorptions by liquids at atmospheric or at reduced pressures. A, mercury seal; B, packed joint through which drive shaft (C) passes upward through capillary tube (C_1); D, semicircular arc of glass tubing containing a flexible rope pattern watch chain; E, which transmits power to stirrer, F; $J^1J^2J^3$, ground-glass joints; H, manometer tube; T, tachometer calibrated to register r. p. m. of stirrer.

The main outline of the apparatus will be plain from the figure. Its unique feature is the manner in which the stirrer is operated. The mercury seal (A) is outside the apparatus at the bottom of the vertical capillary tube (C) which is longer than barometric height. The drive shaft (C) passes through a packed joint (B) in the bottom of the mercury cup, and extends to the top of the capillary tube. Thence the power is transmitted around the semicircular arc (D) by means of the flexible gold-filled, rope-pattern chain (E) to the stirrer proper (F) in the reaction chamber. The latter is suspended in a constant temperature bath.

Experiments at Constant Volume.—In the experiments a measured volume of the liquid was introduced into the bottom of the chamber by means of a long-stemmed funnel. The apparatus was then closed and evacuated through the side tube I. Next the gas was drawn in. The rate of absorption was followed by the change of pressure with time.

Suitable corrections were made for the changes in volume due to the rise of the mercury level in the drive tube and in the manometer tube.[12]

Experiments at Constant Pressures.—These were carried out with mercury-filled gas burets connected to the reaction chamber at I. In order to keep the gas pressure constant, the leveling bulb was slowly raised by means of a windlass and reducing gears whose speed could be suitably varied to correspond to the rate of absorption. Readings of the buret were taken with time. In the absorptions of olefins by sulfuric acid, in order to observe the rate when the quantity of olefin absorbed was 10% or more equivalent to the acid, two micro experiments were performed, using 1 cc. of acid. The regular stirrer was replaced by a smaller one which stirred the liquid in the small chamber without changing its surface.

The characteristics of the absorption chamber were as follows

Volume including connecting tubes[a] = 340.4 cc.

Area of liquid surface with 30–100 cc. of liquid[b] = 17 sq. cm.

Area of liquid surface in lower cup used for micro experiments (1 to 3 cc. of liquid)[c] = 1.41 sq. cm.

[a] Determined by change of pressure caused by addition of known volumes of air.

[b] Determined by adding known volumes of liquid and noting the rise in liquid level.

[c] Determined as in (b) except that the curvature of the meniscus had to be taken into account.

TABLE OF NOMENCLATURE

N = gram moles of gas
t = time in seconds
dN/Adt = rate of gas absorption per unit area of liquid surface—moles per sec. per sq. cm.

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[12] $P = (I - R) - \Theta$, where $\Theta = (B - R)AR/V_0$
P = Pressure of gas at time t corrected to V_0
I = Initial manometer reading before introduction of gas
R = Manometer reading at time t
B = Barometric pressure (uncorrected)
A = Sum of the cross sectional areas of the mercury in the manometer and drive-shaft tubes
V_0 = Volume of gas space in apparatus at atmospheric pressure

$(dN)/(A\,dt)$Init. = initial rate of absorption after practically stationary concentration gradients have been established in the liquid film, moles per square centimeter per second

A = area of liquid–gas interface in sq. cm.

k_L = a constant which, according to the theory outlined above, is equal to the diffusion coefficient of the dissolved gas through the liquid stationary film, that is, the number of moles which would diffuse through 1 sq. cm. of cross section in one second if the difference in the concentrations of the dissolved gas at the interface and in the main body of the solution were molar

C_i = saturation concentration of the dissolved gas in moles per liter at its partial pressure during the absorption

C_L = molal concentration of dissolved gas in the main body of the liquid at time t

C_B = concentration, moles per liter, of the reacting solute in the main body of the solution. (See paper II in this series)

Cof. = cc. of gas absorbed per sec. per sq. cm. of surface, measured at its own partial pressure.

To avoid confusion the C used in a former communication to denote gas absorption rate is here replaced by *Cof.* The other symbols are similar to those of Lewis and Whitman except that gas quantities and concentrations are expressed in gram moles rather than in grams.

Table II gives collected data on the initial rates of solution of oxygen and a few other gases by liquids under different absorption conditions. Direct comparisons are possible because in each case the investigators have measured the area of the gas–liquid interface so that the absorption rate per unit area could be calculated. The absorption methods were as follows.

I. Liquids at Rest and Liquids Stirred without their Surfaces Being Broken.—The writers have measured the rates of solution of oxygen and of carbon dioxide by water and of oxygen by tetrachloroethane in the apparatus which is described above. Measurements were carried out both at constant volume and at constant pressure (area of gas–liquid interface 17 sq. cm.).

Becker measured the absorption rate of oxygen from air[13] at constant volume by water containing suspensions of ferrous hydroxide precipitated directly therein from ferrous sulfate and potassium hydroxide; volume of liquid, 100 cc.; Area of surface except at high stirring, 11 sq. cm.

II. Gas Bubbles in Liquids.—Adeney and Becker[14] measured the

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[13] Becker, *Phil. Mag.*, **45**, 581 (1923).

[14] Adeney and Becker, *ibid.*, **38**, 317–337 (1919); **39**, 385–404 (1920). The mathematical calculations of these investigators appear to contain certain errors which are confusing to the reader although they do not vitiate the important experimental data or the main conclusions. Thus they define "ω" as the "weight of gas per cc. in the upper layer" of liquid (cc. of gas instead of g. are given in their tables). However, they multiply its rate of change with time $d\omega/dt$ by V, the total volume of the liquid, in order to obtain the total rate of gas absorption. Evidently this latter relationship can only be true if ω represents the average concentration of the gas in the whole liquid. In Tables 1, 2, 3 and 4 of the first paper and Table 6 of the second, "ω" and "a" should be "ωV" and "aV," respectively.

TABLE II

EXPERIMENTAL DATA

No.	Observer	Method of absorption	Gas	Temp., °C.	C_i, M	$\frac{(dN)}{(A dt)}$ Init.	k_L
		I. Stirred liquids					
1	Davis and Crandall	30 cc. water. Stirring 200 r. p. m.	O_2	25	0.0012	4.5×10^{-9}	3.7×10^{-6}
2	Davis and Crandall	30 cc. *sym.*-tetrachloro-ethane 200 r. p. m.	O_2	25	.006	50×10^{-9}	8.3×10^{-6}
3	Davis and Crandall	100 cc. water. Stirring 400 r. p. m.	O_2	25	.0012	2.6×10^{-9}	2.2×10^{-6}
4	Davis and Crandall	100 cc. 1 N $K_2SO_4 + Fe(OH)_2$. Stirring 400 r. p. m.	O_2	25	.0008	1.0×10^{-9}	1.3×10^{-6}
5	Davis and Crandall	100 cc. water. Stirring 400 r. p. m.	CO_2	25	.032	94×10^{-9}	2.9×10^{-6}
6	Becker	100 cc. water containing $FeSO_4$ and KOH. Stirring 1000 r. p. m.	O_2 +			5.2×10^{-9}	
7	Becker	590 r. p. m.				4.2×10^{-9}	
8	Becker	340 r. p. m.				2.9×10^{-9}	
9	Becker	140 r. p. m.				1.6×10^{-9}	
10	Becker	80 r. p. m.				1.3×10^{-9}	
11	Becker	60 r. p. m.				0.8×10^{-9}	
12	Becker	0 r. p. m.				0.03×10^{-9}	
		II. Gas Bubbled in Liquids					
13	Adeney and Becker	Tip of 15 cc. bubbles	Air	25	0.00079	50×10^{-9}	63×10^{-6}
14	Adeney and Becker	Sides of 15 cc. bubbles	Air	25	.00079	7×10^{-9}	8.9×10^{-6}
15	Adeney and Becker	Sides of 15 cc. bubbles	O_2	35.1	.00093	10.6×10^{-9}	11.4×10^{-6}
16	Adeney and Becker	Sides of 15 cc. bubbles	O_2	25.2	.0011	11×10^{-9}	10×10^{-6}
17	Adeney and Becker	Sides of 15 cc. bubbles	O_2	15.5	.0013	11×10^{-9}	8.5×10^{-6}
18	Adeney and Becker	Sides of 15 cc. bubbles	O_2	2.5	.0018	11.3×10^{-9}	6.2×10^{-6}
19	Ledig and Weaver	Small bubbles	CO_2	25	.033	680×10^{-9}	20×10^{-6}
		III. Shaken Liquids (400 times per min.)					
20	Conant and Scherp	15 cc. water	O_2	25	0.0012	28×10^{-9}	23×10^{-6}
21	Conant and Scherp	15 cc. water satd. with oleic acid	O_2	25	.0012	24×10^{-9}	20×10^{-6}
22	Conant and Scherp	15 cc. water	H_2	25	.0007	25×10^{-9}	36×10^{-6}
23	Conant and Scherp	15 cc. water satd. with oleic acid	H_2	25	.0007	19×10^{-9}	27×10^{-6}
24	Conant and Scherp	5 cc. tetrachloro-ethane	O_2	25	.0076	160×10^{-9}	21×10^{-6}
25	Conant and Scherp	5 cc. tetrachloro-ethane	H_2	25	.0031	86×10^{-9}	28×10^{-6}
26	Conant and Scherp	5 cc. bromobenzene	O_2	25	.008	210×10^{-9}	26×10^{-6}

+ Calculated from the results obtained with air.

rates of absorption of oxygen and nitrogen at practically constant pressure from bubbles (vol., 15 cc.) moving upward through 94 cc. of water in a cylindrical tube 1 cm. in diameter; velocity of bubble upward, 10 cm. per sec.; velocity of water past cylindrical part of bubble through an annular space 0.05 cm. thick, 65 cm. per sec.

IIB.—Ledig and Weaver[15] measured the rate of carbon dioxide absorption at atmospheric pressure from bubbles, vol. 0.036 cc., suspended in downflowing water.

III. Liquids in a Shaken Absorption Chamber.—Conant and Scherp[16] have measured the rates of absorption of gases by 5–15 cc. of liquids when shaken in a 70-cc. flask 400 times a minute. Direct measurements showed the area of the liquid and wetted glass surfaces exposed during the shakings to be 50–75 sq. cm. A closer estimate was then made by determining the ratio of the over-all rate of ethylene absorption by concentrated sulfuric acid during shaking, to that at rest. This ratio was 5.6 and the area of the liquid surface at rest 11.5 sq. cm. On the assumption that the over-all rate of this particular absorption is proportional to the area of the acid surface and unaffected by the degree of its agitation,[4] the area during shaking was calculated to be 64 sq. cm.

Measurements carried out with the dissolved gases in the liquids at different degrees of saturation showed that the absorption rates satisfy fairly well the equation of Lewis and Whitman

$$\frac{\mathrm{d}N}{A\,\mathrm{d}t} = k_{\mathrm{L}}(C_{\mathrm{i}} - C_{\mathrm{l}})$$

Discussion

The Speed of Stirring and the Absorption Rate.—Becker measured the rates of oxygen absorption per unit area from air by suspensions of ferrous hydroxide stirred at various speeds (Expts. 6–12). He found the rate to be constant at any one speed, a result which has been confirmed by the writers, and he assumed it to be the same as the initial absorption rate by pure water (compare Expts. 3 and 8).

It will be seen that in Becker's experiments the absorption rate increased enormously with the stirring at first but tended to a maximum independent of further increases in the stirring speed. The value at 1000 r. p. m. was 5.2×10^{-9} mole per sq. cm. per sec., which is undoubtedly lower than the initial rate for pure water as pointed out below. (Unfortunately Becker did not record the quantities of ferrous sulfate and potassium hydroxide used.) Now Adeney and Becker (Expt. 16) found the value 11×10^{-9} mole per sq. cm. per sec. for the absorption rate of oxygen from the sides of bubbles. Considering the fact that in their experiments

[15] Ledig and Weaver, This Journal, **46**, 650 (1924).

[16] Conant and Scherp, unpublished data from the Converse Chemical Laboratory, Harvard University.

the water was streaming past the sides through an annular space 0.05 cm. thick at the rate of 65 cm. per sec. it appears that this value represents about the maximum oxygen absorption rate that could be obtained into pure water stirred without breaking or enlarging the surface.

If currents brought fresh liquid continually to the very surface, the absorption rate per unit area should increase almost proportionally with the degree of agitation nor would it tend to a maximum. Thoughtful consideration of these facts impresses one with the reality of the liquid stationary film.

The Effect of Renewing the Surface.—Adeney and Becker found oxygen to be absorbed at a faster rate (about 7.5 times) from the tip of bubbles than from the cylindrical portion and they offered the following explanation. "The rate at which the water streams past the head of the bubble is much less than that at which it passes down the cylindrical portion of it; hence the absorption due to the head of the bubble is much greater than might be expected from its area." But this would mean that agitation below the liquid surface decreases the rate of oxygen absorption whereas Becker has shown that exactly the reverse is true. The writers suggest that the greater absorbing power of the head of a bubble is caused by a continual pulling out laterally of the surface in front, which brings fresh water into the stationary film. On the other hand, the surface slides down the cylindrical portion without changing in area. The fact that the average absorption rate per unit area was found to be the same from this portion in bubbles of different sizes proves that a uniform oxygen gradient was very rapidly established through the film, in agreement with the calculations in the last section.

Ledig and Weaver's value for the absorption rate of carbon dioxide by water represents the average for the whole surface of small bubbles and their value for $k_L \times 10^6 = 20$ (Expt. 19) lies between those of Adeney and Becker for the head and for the sides of large bubbles.

The film coefficients calculated from Conant and Scherp's experiments (20–26) $k_L \times 10^6 = 20\text{–}36$ are almost half that for the head of bubbles in water. It appears that if the volume of the containing vessel is much greater than that of the liquid, then tossing it back and forth, continually spreads out new liquid surfaces on the walls and is an excellent way to secure high absorption rates. Under these conditions, diffusion no longer plays the dominating role in limiting the absorption. Currents in the film have become an important factor also.

A Comparison of the Rates of Solution of Gases by Water and by Organic Solvents.—In the experiments with stirred liquids the film diffusion coefficient k_L of tetrachloro-ethane was over twice that for water under the same conditions. On the other hand, in Conant and Scherp's experiments with shaken liquids, the coefficients were practically the same for absorption of oxygen and hydrogen into water, tetrachloroethane and bromobenzene. The magnitude of the absorption rate depended almost entirely on the solubility of the gas.

Hydrogen and Oxygen.—The film coefficients for hydrogen in Conant and Scherp's experiments are 1.3 to 1.4 times those for oxygen under the same conditions; but data in "International Critical Tables" show that hydrogen diffuses about 2.4 times faster than oxygen in liquids. Perhaps this bears out the assumption of Lewis and Whitman that the liquid film diffusion coefficients for all solutes are of about the same magnitude.

Absorption Rate and Reaction Rate.—When a gas, oxygen for example, is absorbed by a solution and reacts irreversibly with some substance dissolved therein, steady conditions are often reached where the rate of oxygen absorption is just equal to the rate at which it is consumed in the solution. What is the concentration of the dissolved oxygen? Evidently not the saturation value, for oxygen could not then be absorbed at all. If the absorption rate at the steady state is less than the initial physical absorption rate into the pure solvent, then an estimate of its fractional saturation in the solution will be obtained from the ratio of these rates. Hence the importance of determining the initial absorption rate.

Suspensions of ferrous hydroxide in dilute solutions can be used conveniently for finding the order of the value for the initial rate of oxygen absorption by water in an apparatus. However, experiments 3 and 4, Table II, show that the rate for a suspension in 1 *N* potassium sulfate is less than half that for pure water and the fact that the film diffusion coefficient is also lower shows that the effect is not entirely due to the lowering of the oxygen solubility by the potassium sulfate.

Miyamoto[17] has shown that when air is bubbled through suspensions of ferrous hydroxide in sodium hydroxide solution, the over-all absorption rate is independent of the quantity of the precipitate but is reduced by the addition of more alkali. It is to be regretted that absorption rates per unit area of surface cannot be calculated from the extensive data of this investigator.

If the oxygen absorption rate is greater than the initial rate it means that the main body of the solution contains little or no dissolved oxygen and that part or all of the reaction takes place in the liquid stationary film. This will be treated further in another communication.

Summary

1. The reality of the liquid stationary film, the thin unstirred layer, on the surface of liquids is emphasized. The important role of this film in gas absorptions, though known to engineers, has not perhaps been generally recognized. Its effective thickness depends on the absorption conditions.

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[17] Miyamoto, *Bull. Chem. Soc., Japan*, **2**, 40 (1927); **3**, 137 (1928); **4**, 65 (1929); *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **7**, 35 (1927); **9**, 203 (1928).

2. When a pure gas is suddenly brought into contact with a liquid, a gradient of dissolved gas, tending to uniformity, is rapidly built up through the film. The rates at which the gradients are established in oxygen absorption by water have been calculated for different effective thicknesses of the stationary film corresponding to various conditions of liquid agitation. In well-stirred water the gradient becomes practically uniform in a fraction of a second.

3. The absorption rate after stationary gradient conditions have been established in the film (initial absorption rate) is the maximum at which dissolved gas can reach the main body of the solution. At any time, for a moderately soluble gas, the rate is proportional to the fractional unsaturation of the liquid with dissolved gas.

4. The initial absorption rates per unit area of surface and the liquid film diffusion coefficients have been calculated from data on gas absorptions by water and a few organic liquids for (a) stirred liquids, (b) gas bubbles and (c) shaken liquids.

5. The absorption rate for liquids stirred without breaking the surface increases with the stirring but tends to a maximum. For oxygen absorption by water, this maximum appears to be about the same as the rate from the sides of cylindrical bubbles moving rapidly through deoxygenated water, 11×10^{-9} mole per sq. cm. per sec. at 25°.

6. Adeney and Becker showed that air is absorbed faster, per unit area of surface, from the head of a cylindrical bubble than from the sides. It is suggested that this phenomenon is caused by film renewal at the head where the surface is continually pulled out laterally. The absorption rate per unit area for shaken liquids can become greater than the maximum with stirring, due apparently to the continual spreading out of the surface layer.

7. With stirring, the liquid film diffusion coefficients of water were less than, but of the same order as, those of organic liquids under the same conditions. With shaking the coefficients were practically identical for all the liquids. The absorption rates were then simply proportional to the solubilities of the gases.

8. It is suggested that the ratio of absorption rate of a pure moderately soluble gas by a liquid under any one set of conditions, to the initial absorption rate under the same conditions, affords a measure of the fractional unsaturation of the liquid with gas. If the gas reacts with the solvent itself, an inert gas of similar solubility could be used.

9. Where the effects of foreign substances on rates of reaction in solution are being measured by the rates of absorption or evolution of gases, the importance of also checking up their effects on the initial absorption rate of the gas is suggested.

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