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THE ROLE OF THE LIQUID STATIONARY FILM IN BATCH ABSORPTIONS OF GASES. II. ABSORPTIONS INVOLVING IRREVERSIBLE CHEMICAL REACTIONS¹

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In the preceding communication⁴ it was pointed out that under fixed absorption conditions (agitation, temperature, gas pressure, etc.), the *initial* absorption rate is the highest at which a gas can pass by physical dissolution into the main body of a liquid.

The present paper deals with the relationships between the absorption rate and other factors when the gas reacts irreversibly in the solution. With rapid reactions the rate of absorption can be much greater than the initial speed of pure physical solution.

Let us consider the absorption of a pure gas through an unbroken surface into a well-stirred liquid, when any irreversible chemical reactions taking place are instantaneous compared to the rate of absorption. The following postulates will be made for these conditions.

1. The effect of the gas film is negligible and the surface of the liquid is kept saturated with gas.
2. The main body of the liquid is homogeneous right up to a sharply defined surface that marks the inner limit of the stationary liquid film.
3. The specific diffusivity of each solute through the liquid stationary film is the same.⁵

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 cooperation of the Central Petroleum Committee of the National Research Council.

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⁴ Davis and Crandall, *THIS JOURNAL*, 52, 3757 (1930).

⁵ This is the assumption originally made by Lewis and Whitman, *Ind. Eng. Chem.*, 16, 1215 (1924), and there is indeed a surprising similarity in the values which have been found for the coefficients of diffusion of solutes in aqueous solution under similar conditions (see "International Critical Tables," Vol. V, pp. 63-72). On the other hand, Schwab and Beringer, *Z. physik. Chem.*, 138A, 55-74 (1928), concluded that the liquid film diffusion coefficients for five permanent gases in water were practically the same at 20° but changed relatively to each other as the temperature was raised. The results of these investigations are somewhat puzzling. Although they claim an accuracy of 10% for their experiments (bubble method of Adeney and Becker, *Phil. Mag.*, 39, 385 (1920)), yet values for the solubilities of the gases calculated from their data show large deviations from those obtained by other investigators, as the table shows.

The concentration gradients which will now be examined are those existing in the film after a uniform absorption (initial absorption rate) has been reached but while the concentration of the reaction products in the main body of the liquid is still negligible.

Case A. The Absorption of a Pure Gas by a Liquid with which it Does not React Irreversibly.—This case has been considered in our previous communication; however, for the purpose of comparison, the conditions in the film are shown diagrammatically in Fig. 1, Case A. The sloping line denotes the gradient of decreasing concentration of the dissolved gas inward from the surface. It is uniform because the same quantity of solute passes per second through each unit cross section of the film made parallel to the surface.

$(dN)/(A dt)_{\text{Init.}} = k_L C_i$ or in general as the gas builds up in the main body of the solution $dN/A dt = k_L(C_i - C_L)$. The same nomenclature is used as in the preceding article.

Case B. The Absorption of a Pure Gas by a Solution of a Substance with which it Reacts Irreversibly in One Stage and Mole for Mole.—The position of the Zone A, Fig. 1, Case B, at which the reaction takes place will depend on the relative magnitudes of C_i and C_s , the concentrations of the gas at the interface and of the solute in the main body of the solution, respectively.⁵

COMPARISON OF DATA ON SOLUBILITIES OF GASES IN WATER

a = cc. gas (at 760 mm. and 0°) dissolved by 1 cc. liquid when partial pressure of gas is 760 mm.

	O ₂				H ₂	
	20°	30°	60°	80°	20°	30°
Schwab and Beringer	0.020	0.021	0.016	0.016	0.018	0.016
Landolt-Börnstein-Roth "Tabellen"	0.031	0.026	0.019	0.017	0.018	0.017
Adeney and Becker	0.029	0.025

	CO ₂			C ₂ H ₄		C ₂ H ₂	
	20°	30°	60°	20°	30°	20°	30°
Schwab and Beringer	0.68	0.50	0.34	0.10	0.08	0.67	0.63
Landolt-Börnstein-Roth "Tabellen"	0.88	0.67	0.36	0.12	0.10	1.0	0.84
Adeney and Becker

Further, it would appear from their data that the initial absorption rate of oxygen by water at 30° is almost twice that at 20°, whereas Adeney and Becker found it less. Until these discrepancies have been explained, some hesitation must be felt in accepting the conclusions of Schwab and Beringer that the differences in the diffusivities, calculated from their data, indicate the degrees of hydration of the dissolved gases.

⁵ Similar diagrams of the concentration gradients of the reactants and of the reaction zone for the dissolution of a solid in a solution of a substance with which it reacts have been given by Brunner [*Z. physik. Chem.*, **47**, 67, *et seq.* (1904)]. The similarity of the liquid stationary film at the two types of interfaces should be emphasized. Weber and Nillson, *Ind. Eng. Chem.*, **18**, 1070 (1926), and Hatta, *Tech. Reports Tohoku Imp. Univ.*, **8**, 1 (1928), have also given diagrams of concentration gradients in films.

The quantities of dissolved gas and solute diffusing to the reaction zone in unit time and of the reaction product diffusing away are equal and it is evident that

$$\frac{(dN)}{(A dt)_{\text{Init.}}} = k_L(C_1 + C_s)$$

The molar concentration of the reaction product between the surface and the reaction zone is uniform and equivalent to that of the solute in the main body of the solution. If the solubility of the reaction product

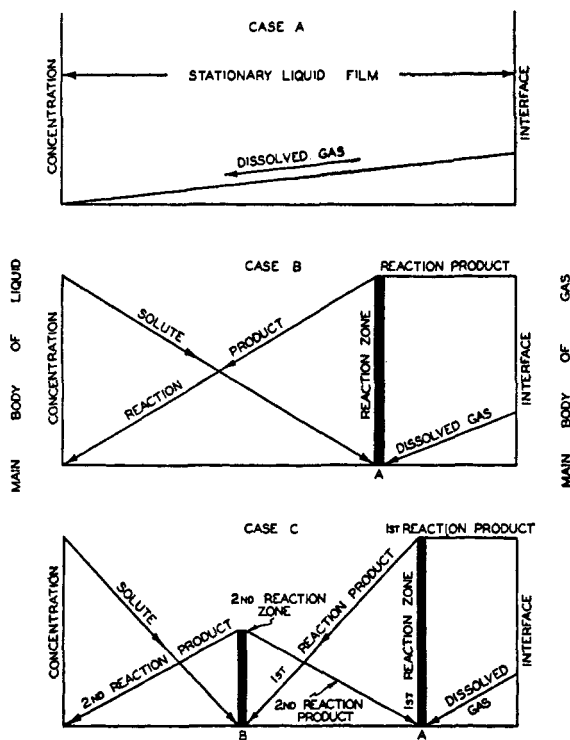


Fig. 1.

is low and its metastable limits are exceeded, it may precipitate as a solid or liquid (the case of a gas is not considered here) which tends to fall into the main body of the liquid or rise to the surface. In any case the presence of the precipitated reaction product will cut down the absorption and may almost stop it.

Case C. The Absorption of a Pure Gas by a Solution of a Substance with which it Reacts in Two Stages in Instantaneous Irreversible Reactions (Fig. 1, Case C).—As in Case B the primary reaction product exists in uniform concentration between the first reaction zone and the

surface. The secondary reaction product diffuses in both directions from the second zone but never reaches the surface.

$$\frac{(dN)}{(A dt)_{\text{Init}}} = k_1(C_1 + C_s)$$

The following factors have not been considered in these pictures: (1) the time required for the completion of the reactions (they are assumed to be instantaneous with respect to the diffusion rates); (2) the effects of the reaction products on the solubility of the gas; (3) the effects of the reaction products on the effective thickness of the stationary film and on the diffusivities of the solutes; (4) the heat produced in the film by the reactions. (It must also flow away by diffusion since it is assumed convection plays a minor part in the film.)

Keeping in mind these limitations, which will be considered later, the main conclusions from these pictures will now be tested by experimental data of the authors and other investigators.

Experimental Part.—The apparatus used was that described in the preceding paper in which gas absorptions can be carried out at constant volume or at constant pressures into a known area of liquid surface while the liquid is being stirred beneath the surface.

General Relationship.—According to these postulates the rate of absorption of a pure moderately soluble gas by a concentrated solution should be largely independent of the gas pressures (since C_1 is negligible compared to C_s) and the experiments at constant volume showed this to be indeed the case. Even in the absorption of sulfur dioxide by 1.8 *M* potassium hydroxide, Expt. 13, Table I, the pressures decreased almost uniformly with time, about four-fifths as much gas being absorbed per second at one-fifth as at one atmosphere. It may be seen from Table I that under similar conditions there is a qualitative agreement between the ratios of the rates of absorption determined experimentally (Col. 9) and the ratios calculated on the simple assumption that the rate is proportional to $(C + C_s)$ (Col. 10). The relationship appears to be valid in the absorption of carbon dioxide by water and by very dilute alkaline solutions (Expts. 2, 4, 5) but falls down as the concentration of the solute is increased (Expts. 6, 7, 8 and Table II). Even when the gaseous solubilities are quite different, the relationship still holds, *e. g.*, Expts. 12, 13, and a remarkable agreement is found in the absorption of ethylene by bromine water (Expt. 11), even though the reaction is quite different. Detailed treatment of the absorption of ammonia by water and by hydrochloric acid is given later. Nevertheless, the relationship is only qualitative and a more exact one must include the four neglected factors noted above. For this purpose the following studies of the absorption of carbon dioxide by water and by alkaline solutions are presented.

TABLE I
EXPERIMENTAL DATA

No.	Gas	Liquid	R. p. m.	C_i	C_s	$\frac{(dN)}{(Ad)} \text{Init.} \times 10^9$	$k_L \times 10^6$ (exptl.)	Ratios of absorption rates		
								Exptl.	assuming $k_L = \text{const.}$	Calcd. corrected for change of k_L
Authors' experiments										
1	O ₂	100 cc. water	400	0.0012	..	2.57	2.15	0.028	0.036	..
2	CO ₂	100 cc. water	400	.033	..	94	2.85	1	(1)	(1)
3	CO ₂	100 cc. 0.1 M NaHCO ₃	400	.030	..	60	2.0	0.64	0.9	..
4	CO ₂	100 cc. 0.1 M NaOH	400	.030	0.1	218	..	2.3	3.9	2.9
5	CO ₂	100 cc. 0.1 M Na ₂ CO ₃	400	.030	.1	235	..	2.5	3.9	2.9
6	CO ₂	100 cc. 1.2 M Na ₂ CO ₃	400	.03 ^a	1.2	170	..	1.8	37	15
7	CO ₂	100 cc. 2.3 M KOH	400	.03 ^a	2.3	1850	..	19.7	71	21
8	CO ₂	100 cc. 2.6 M NaOH	400	.03 ^a	2.6	1300	..	13.8	80	22
9	CO ₂	100 cc. 12 M KOH	400	...	12	1600
10	CO ₂	100 cc. 12 M KOH	0	...	12	5100
11	C ₂ H ₄	100 cc. 0.85 M Br ₂ in 2 M KBr	400	.04 ^a	0.85	1560	..	16.6	27	..
12	CO ₂ (0.5 atm.)	100 cc. 1.7 M KOH	600	.016 ^a	1.74	1800	..	1	(1)	..
13	SO ₂ (0.5 atm.)	100 cc. 1.8 M KOH	600	.73 ^a	1.80	4300	..	2.4	1.5	..
Whitman and D. S. Davis experiments										
16	NH ₃	Water	60	0.62	..	580	..	1	(1)	..
17	NH ₃	2.3 M HCl	60	...	2.3	1100	..	2	3.7	..

^a Approximate values.

TABLE II

LEDIG AND WEAVER'S DATA ON THE ABSORPTION OF CARBON DIOXIDE FROM BUBBLES

No.	Concn., <i>M</i>	Ratios of absorption rates		Calcd.
		NaOH Experimental	KOH	
1	0	1.0	1.0	(1.0)
2	0.2	2.8		4.3
3	.5	5.6	7.5	8.8
4	1.0	9.0	11.0	13.7
	1.27	Saturation concn. of NaHCO ₃		
5	1.5	10.5		16
6	2.0	11.0	16.0	20
7	2.5	11.5		21
	2.7	Saturation concn. of Na ₂ CO ₃		
8	3.0		18.0	23
	3.25	Saturation concn. of KHCO ₃		
9	3.3	11.0		
10	4.5		19.0	
	5.9	Saturation concn. of K ₂ CO ₃		
12	6.0		19.0	
13	6.6	5.0		
14	7.0			
15	7.5		19.0	

TABLE III

ABSORPTION RATES OF THE OLEFINS INTO QUIESCENT AND INTO STIRRED SULFURIC ACID AT 25°

Expt.	Olefin	Concn. of H ₂ SO ₄ , %	R. p. m.	$\frac{(dN)}{(Ad)_{\text{Init}}} \times 10^3$	Cof. $\times 10^4$	Cof. $\times 10^4$ (Davis and Schuler)
(A) Experiments at constant volume						
E 1	Ethylene	95.8	0	6.04	1.48 ^a	1.4
			90	6.04	1.48	1.8 (28) ^b
			480	6.04	1.48	
			1000 ^c	61.2	15	
E 2	Propene	80	0, 200,			
			250-360	12.5	3.07	3.99 (28) ^b
E 3	Isobutene	70	0	204	50.1	58.9
			120-240	317	77.5	57.8 (28) ^b
E 4	Isobutene	70	0	243	59.4	
			88	287	70.4	
E 5 (a)	Isobutene	60	0	66.3	16.25	14.7
			120-240	53.9	13.20	9.7 (28) ^b
				63.9	15.65	
			(c)	120-240	55.8	13.65
0	60.8	14.85				
(B) Experiments at constant pressure						
E 6	Isobutene	60	0	53.2	15.5	14.7
			220	59.2	14.5	9.7 (28) ^b
E 9 ^d	Isobutene	60	200	47.4	11.6 at 0% ^e	
			200	50.2	12.3 at 10%	
			200	55.5	13.6 at 20%	

TABLE III (Concluded)

Expt.	Olefin	Concn. of H ₂ SO ₄ , %	R. p. m.	$\frac{(dN)}{(Ad) \text{Init.}} \times 10^3$	Cof. $\times 10^4$	Cof. $\times 10^4$ (Davis and Schuler)
			200	57.8	14.1 at 30%	
			200	57.8	14.1 at 40%	
			200	42.0	10.3 at 50%	
E 10 ^d	Propene	87	600	150	36.6 at 0%	36.2 (28) ^b
			600	122	29.8 at 10%	
			600	106	26.0 at 20%	
			600	92	22.5 at 30%	

^a Mr. H. W. Scherp, working at the Harvard Chemical Laboratory, obtained the value $Cof. = 1.8 \times 10^{-4}$, using the very same acid and ethylene that was used in our experiments. He used an apparatus with a sensitive manometer filled with tetrachloro-ethane (sp. gr. 1.6) and a compensator to avoid the necessity of correcting for changes in barometric pressure. ^b Revolutions per minute of rotating absorption chamber. ^c The surface of the liquid was drawn down in the center and thrown up on the sides by the rapid stirring so that its area was greatly increased. ^d These experiments were performed in the small chamber with 1 cc. of acid. ^e Quantity of isobutene absorbed. 100% = 1 mole isobutene per 1 mole sulfuric acid.

Hatta⁷ has investigated the rates of absorption of carbon dioxide by stirred solutions of potassium hydroxide. He concluded that the reaction to bicarbonate is slow, being negligible in the film, while the reaction to normal carbonate is instantaneous at a zone inside the film. Accordingly the concentration gradients at the stationary state should be of the type shown in Case B of Fig. 1 (except that two moles of hydroxide unites with one of the dissolved gas).

However the writers submit for consideration the following evidence that the reaction to bicarbonate is rapid, taking place principally in the film, and that the concentration gradients are of the type shown in Case C of Fig. 1.

1. The initial rate of absorption of carbon dioxide by 0.1 *M* sodium carbonate is considerably higher than the initial rate of physical dissolution into pure water (Expts. 2 and 5, Table I). Indeed it is practically the same as that of 0.1 *M* sodium hydroxide. This was proved not only by experiments with prepared solutions of the two but also by following the absorption rate at constant pressure into 0.1 *M* sodium hydroxide until no more gas was absorbed. The rate at the stage represented by complete transformation to normal carbonate was almost exactly half the initial rate, and the total quantity absorbed corresponded to that necessary to form bicarbonate and physically to saturate the solution.

2. There is strong evidence that sodium bicarbonate precipitates in the stationary film when carbon dioxide is absorbed by solutions of sodium hydroxide or sodium carbonate stronger than approximately 1.5 *M*. When carbon dioxide is brought into contact with quiescent 2.5 *M* sodium

⁷ Hatta, *Tech. Reports Tohoku Imp. Univ.*, 8, 1 (1928).

hydroxide, the whole surface is soon covered with a mat of crystals. These cannot be the normal carbonate because sodium hydroxide of this concentration will readily dissolve an equal molecular quantity of sodium carbonate and it is difficult to conceive how in a closed space the concentration of carbonate in the surface layer could ever exceed by very much, that of the hydroxide in the main body of the solution. Hence the crystals must be sodium bicarbonate. This conclusion is confirmed by the observation that crystals can be seen to form on the quiescent surface of sodium carbonate about three-quarters saturated, when allowed to stand in contact with carbon dioxide.

The phenomena stood out still more clearly under the microscope at about fifty diameters magnification. The solution to be examined was placed in a small cell 12 mm. wide and 2 mm. deep made by cementing a glass ring upon a slide. The cell and the objective of the microscope were surrounded by a glass cylinder 22 mm. wide and 25 mm. deep pressed tightly against the slide. The carbon dioxide was introduced through a side tube in the cylinder so that the whole solution was covered with the gas at substantially atmospheric pressure. To facilitate observations some particles from a lead pencil were rubbed into the solution. As soon as the gas entered, the particles below the surface of the solution became agitated by thermal currents while those at the surface remained practically stationary. Precipitation in the film showed as a cloud which sometimes gradually and sometimes quickly (after a lapse of a few minutes) obscured the field of vision. The results were as follows

Solution	Observations
0.5 <i>M</i> NaOH	No cloud
1.3 <i>M</i> NaOH	Gradual dimming of field
2.6 <i>M</i> NaOH	Distinct cloud suddenly appearing after one to three minutes
2.6 <i>M</i> KOH	Field actually brightened, no cloud. Thermal currents rapid until alkali was neutralized by carbon dioxide
9 <i>M</i> KOH	Thick cloud in a little over one minute

These results should be studied in relation to Tables I and II and leave no doubt but that actual precipitation of either primary or secondary reaction product occurs in the liquid stationary film at approximately the concentration of alkali at which it would be predicted from our postulates. Visual observations, especially with the aid of a microscope, can be of great service in studies of these reactions which take place in the film.

The Effects of the Reaction Products on the Liquid Film Diffusion Coefficient.—Experiments 2 and 3, Table I, show that the absorption rate of carbon dioxide by 0.1 *M* sodium bicarbonate was 36% less than by pure water, although the solubility was only decreased 8%. This indicates that the liquid film diffusion coefficient of the 0.1 *M* salt solution is only 0.7 times that for pure water. Figure 2 shows the general rela-

tionship (determined by separate experiments similar to 2 and 3) between the values for k_L , relative to that for pure water, and the concentration of bicarbonate. It is important, however, to note that this is not simply a salt effect because k_L for 1 *M* potassium chloride was found to be practically identical with that for pure water.

Using the corrected value for the film coefficient, the ratio of the absorption rates of either 0.1 *M* sodium hydroxide or 0.1 *M* sodium carbonate to that of pure water should be 0.7 $(0.1 + 0.030)/(0.033) = 2.8$, whereas the values actually found were 2.5 and 2.3. In a similar way the values in Col. 11, Table I, and in Col. 5, Table II, have been calculated.

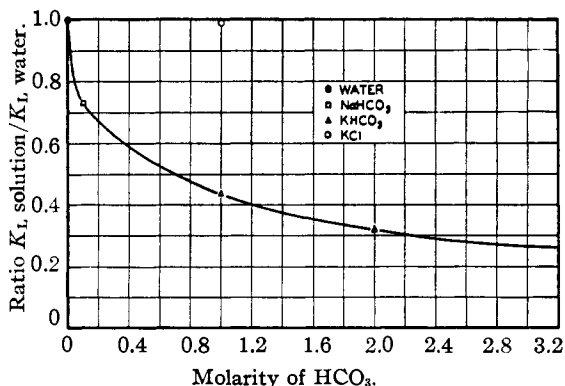


Fig. 2.

The legitimate objection will be raised that these modified values of k_L determined for bicarbonate solutions have been applied to the calculations in the absorption of carbon dioxide by solutions of caustic alkalis whereas bicarbonate exists only in the outer portion of the film. The writers can only suggest that the secondary product (normal carbonate) which exists in the inner portion may have a similar effect. At any rate, the agreements between the calculated and the experimental ratios is rather striking up to the point where the reaction product begins to precipitate. The effects of reaction products and of other substances on the liquid film diffusion coefficient offer a field worthy of further study.

Ledig and Weaver⁸ measured the rates of absorption, per unit area, of carbon dioxide from bubbles into water, and into solutions of sodium and potassium hydroxides. By an ingenious device the bubble (vol. 0.036 cc.) was held stationary in the solution in a closed system by running the liquid downward at a rate sufficient to compensate for the tendency of the bubble to rise. The changes in volume were followed by the movement of the surface of the liquid in a capillary tube open to the atmosphere.

⁸ Ledig and Weaver, *THIS JOURNAL*, 46, 650 (1924); Ledig, *Ind. Eng. Chem.*, 16, 1251 (1924).

They state that "the rate is not constant during the whole period of absorption from a bubble (at constant pressure) but follows a three-stage cycle. This can best be seen in the absorption curves for very dilute solutions (see Fig. 3 reproduced from their article) and the higher concentrations undoubtedly follow the same course though this is not entirely evident if a curve is studied by itself. The cycle is begun by a very high absorption rate at the newly formed liquid-gas interface but as absorption goes on it falls again very quickly to a rate where an equilibrium condition exists, the rate being controlled by the diffusion of the reagent to the surface and of the reaction product away from the surface. The third stage in the cycle begins when the diluting gas starts to retard diffusion of gas to the surface. This latter state is undoubtedly affected by the diminished buoyancy or rate of rising as the bubble becomes smaller and there is a decrease in the stirring action which renews the absorbing liquid at the surface."

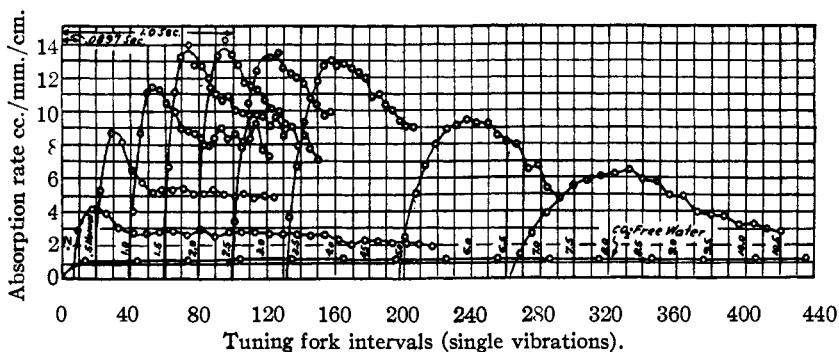


Fig. 3.—Effect of concentration upon rate of absorption in NaOH solutions. (After Ledig and Weaver.)

Examination of the curves shows that no initial high absorption rate was detected in the case of absorption into pure water. This suggests that the high initial values clearly shown for absorption into sodium hydroxide solutions are caused by the hydroxide already in the freshly formed film. This diffuses outward to meet the carbon dioxide diffusing inward and the extension of the gradient of the latter into the film will increase, that is, the rate of gas absorption will decrease until the sodium hydroxide is diffusing uniformly from the main body of the solution into the film. The greater the initial concentration of the hydroxide in the film, the longer the time required to reach the conditions for constant absorption which might finally not appear at all. And this is exactly what the absorption curves show.

The initial absorption rate, by pure water, of carbon dioxide from the bubbles of Ledig and Weaver was $dn/(Adt)_{\text{Init.}} = 680 \times 10^{-9}$. This

is over seventy times the value found by the writers (Table I) for water stirred underneath at 400 r. p. m. Nevertheless, the ratios of the rates into caustic solutions to that into pure water are very much the same in both cases. See, for example, 2.3 potassium hydroxide 19.1, Table I, and 3.0 potassium hydroxide 18, Table II. Apparently our generalizations hold for widely different absorption conditions.

Columns 3 and 4, Table II, give the ratios of the absorption rates at the stationary state found by Ledig and Weaver. Column 5 gives the ratios calculated on the assumption that they are proportional to $k_L(C_i + C_s)$. The results are striking. The calculated ratios for sodium hydroxide agree fairly well with the experimental up to the concentration where bicarbonate would be expected to precipitate, the experimental rates then remain constant up to a concentration somewhat beyond that of saturated sodium carbonate and finally steadily decrease. For potassium hydroxide the experimental and calculated ratios agree even better up to a point where potassium bicarbonate should precipitate, after which the former remain fairly constant for the range given in the table.

Ledig and Weaver found, however, no decrease in the rate for potassium hydroxide beyond a concentration corresponding to saturation of normal carbonate but on the contrary a rapid rise for concentrations somewhere above 9 *M*. They state "an attempt has been made to link this rapid rise of rate with the known properties of the solutions—solubility of the carbonates, viscosity of the solution and ionization of the hydroxide and carbonate solutions—but no quantitative relation has yet been found." The writers suggest that this phenomenon is caused by the large quantity of hydroxide brought into the film in the case of concentrated potash, by its renewal at the head⁹ of the bubble. It has been pointed out that the period of persistence of the high preliminary rate increased with the concentration of the hydroxide. The quantity initially in the film for 0.1 *M* hydroxide was calculated to be about 1×10^{-7} mole. This is negligible compared to the amount of gas in the bubble, 1.3×10^{-5} mole, but the quantity for 6 *M* hydroxide, 0.6×10^{-5} mole, must play an important part in the absorption when the film is being renewed at the head. The conclusion is confirmed by the fact that in our experiments where the liquid was stirred without renewing the film, 12 *M* potassium hydroxide actually absorbed at a slower rate than 2.3 *M* solution.

Temperature Changes in the Film.—Adeney and Becker¹⁰ found that the rate of oxygen absorption by water decreased slightly over the range 2.5 to 35.1°. The film coefficient increased almost 100% but was compensated for by a corresponding decrease in gaseous solubility.

⁹ For a discussion of the renewal at the head see Davis and Crandall, Ref. 4.

¹⁰ Adeney and Becker, *Phil. Mag.*, 39, 391–402 (1920).

Nevertheless, these same investigators¹¹ have shown that oxygen is absorbed by water considerably faster from dry air than from air saturated with water vapor and have attributed this in part to local cooling of the surface layer by evaporation into the dry air. This indicates that considerable local temperature changes in the film may take place even for simple physical absorption of gases.

All the heat produced in the film by chemical reactions must flow away by diffusion to the surface or to the inner boundary, if convection plays only a minor part, so that the temperatures in the film will always be higher than in the main body of the solution. The writers found the rate of carbon dioxide absorption by unstirred 12 *M* potassium hydroxide to be three times that into the solution stirred at 400 r. p. m. Evidently a great rise in temperature takes place in the film of the liquid at rest and the absorption rate is high because of the increased solubilities of the reaction products and the increased film diffusion coefficient. Stirring helps to dissipate the heat into the main body of the liquid.

The Relative Rates of Carbon Dioxide Absorption by Solutions of Sodium Hydroxide and of Potassium Hydroxide.—The assumption of equal diffusivities for all solutes in the film appears to be only an approximation. Ledig and Weaver state that "potassium hydroxide solutions absorb carbon dioxide more than twice as fast as sodium hydroxide solutions at the lower concentrations." However, they compared the averages of the rates over the whole period of the absorption, including the high initial speeds. The ratio of the rates at the steady state (when uniform concentration gradients had been established) was about 1.5. This accords with the fact that the specific diffusivity of potassium hydroxide in dilute solutions is about 1.5 times that of sodium hydroxide. It seems clear that the differences in the absorption rates of carbon dioxide by the two is related to diffusivities and not to actual differences in the reaction rates as assumed by Hatta.¹²

The Experiments of Whitman and D. S. Davis.¹³—These investigators determined the rates of absorption where a gas was passed over 4 liters of liquid with 405 sq. cm. of surface exposed. Both gas and liquid were stirred by separate blades at 60 r. p. m. The following table has been prepared from their data.

Oxygen was absorbed so slowly that the over-all liquid film diffusion coefficient for this case was assumed to be identical with the true liquid film diffusion coefficient. However, in the fast ammonia absorption the surface could not become saturated because of the resistance of the gas film through which a considerable gradient had to be established in order

¹¹ Adeney and Becker, *Phil. Mag.*, 42, 92-93 (1921).

¹² Hatta, *C. A.*, 24, 763 (1930).

¹³ Whitman and D. S. Davis, *Ind. Eng. Chem.*, 16, 1233 (1924).

TABLE IV
DATA OF WHITMAN AND DAVIS

Solute	Average partial pressure of solute in air mixture, mm.	Liquid	$\frac{(dn)}{(Adt)}$ Init.	K_L (Over-all)
Oxygen	746	Water	0.87×10^{-9}	0.92×10^{-6}
Ammonia	2.3	Water	580×10^{-9}	0.29×10^{-6}
Ammonia	19.09	2.3 <i>N</i> HCl	1100×10^{-9}

to convey the ammonia to the liquid surface at such a rapid rate. It will be assumed here that the fractional saturation of the surface layer is shown by the ratio of the over-all coefficient to the true coefficient $0.29/0.92 = 0.31$ (which is true if the gas follows Henry's law). Water at 30° saturated with ammonia at 21.3 mm. is about $2 M$,¹⁴ so that the surface concentration for the absorptions into water was $0.62 M$.¹⁵ Whitman and Davis assumed that during the absorption into 2.3 *N* hydrochloric acid the concentration of the ammonia in the surface layer was negligible. These values were used in calculating the ratios given in Table III (1 to 2.0 experimental and 1 to 3.7 calculated, the divergence may be due to changes in k_L).

Absorptions of Gaseous Olefins by Sulfuric Acid.—In a former communication¹⁶ it was pointed out that the values of the absorption coefficient in a rotating chamber were characteristic for the separate olefins. It will be noted that values obtained in the new apparatus agree very well with the former ones (see Cols. 6 and 7, Table III). The absorption rates are expressed both as *Cof.* and as dN/AdT to facilitate comparisons of the latter values with the former. This agreement holds even where the ratio of liquid surface to liquid volume is changed over a large range (from 12.2 rotating and 2.45 sq. cm./cc. at rest in the former to 0.57 sq. cm./cc. in the new apparatus). As has been shown in that communication, the absorption coefficient *Cof.* calculated from the constant volume experiments should equal the rate at which the olefin would be absorbed at constant pressure, the gas being measured at that pressure. It will be noted that the initial rates of absorption at constant pressure agree well with the values of *Cof.* calculated from the constant volume experiments.

In the experiments with ethylene and propene using concentrated sulfuric acid, the absorption rate per unit area was not affected by stirring.¹⁷

¹⁴ Haslam, Hershey and Keen, *Ind. Eng. Chem.*, 16, 1224 (1924).

¹⁵ Whether or not the gas film is controlling in the absorption of a very soluble gas such as ammonia in water can be conveniently tested by measurements of the absorption under similar conditions by a solution (*e. g.*, hydrochloric acid), with which the dissolved gas reacts instantaneously.¹³

¹⁶ Davis and Schuler, *THIS JOURNAL*, 52, 721 (1930). *Cof.* instead of *C* is used in the present paper for The Coefficient, because here *C* denotes concentration.

¹⁷ The statement of Damiens, *Compt. rend.*, 175, 585 (1922), that stirring at 200

However, in the absorption of isobutene into 70% acid the rate of absorption was greater into the stirred acid than into acid at rest but within the range investigated was independent of the rate of stirring. Further, the rate at rest was irregular, falling off quite rapidly toward the end. In this experiment a layer of polymer insoluble in the acid was found on top of the acid at the end. For isobutene and 60% acid the absorption rate was less when the acid was stirred but independent of the rate of stirring (within the range investigated). The absorption curves for this experiment (Fig. 4, Nos. E5A and E5B) merit careful study. That of

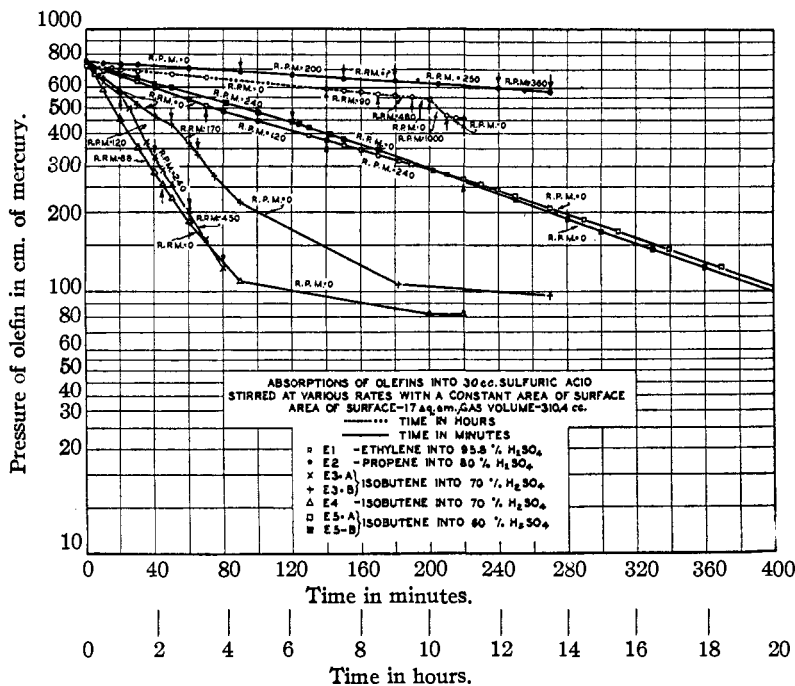


Fig. 4.

5A (r. p. m. = 0) starts at a faster rate than that of 5B (r. p. m. = 240). When the stirring conditions were reversed the two curves cross. Finally, at the end for the same stirring conditions (r. p. m. = 0) the curves are parallel. All the reaction products in this case were soluble. r. p. m. increases the absorption rate of ethylene by concentrated sulfuric acid 20–27 times has been frequently misinterpreted. Unfortunately the full experimental details are not given. He found the absorption rate to be proportional to the partial pressure of the gas and to the surface of contact.

The writers suggest that a method for determining the effective area of a liquid when stirred or shaken can be based on these facts. The over-all absorption rate of ethylene by concd. sulfuric acid under the same conditions of agitation should be divided by its absorption rate per unit area into the acid at rest.

in the acid. Further, *tert.*-butyl alcohol was salted out when the acid was neutralized in the cold with sodium hydroxide. The rate of absorption of isobutene at constant pressure by 60% acid increased as more olefin was absorbed up to 0.4 mole of isobutene per mole of acid and then fell off. However, in the absorption of propene by 87% acid the rate steadily decreased from the first.

It has been shown¹⁶ that the physical solubilities of the olefinic gases in sulfuric acid are very low, and yet enormous rates of absorption are observed in some cases. It is inconceivable that under these conditions the dissolved olefin could penetrate to and react in the main body of the liquid. The entire reaction must take place either at the surface or in the stationary film. In the latter case it can only penetrate a short distance because the concentration gradients from the surface must be very steep. For instance, 500×10^{-4} cc. of propene was absorbed per sec. per sq. cm. by 97% sulfuric acid and a uniform gradient carrying oxygen under atmospheric pressure into water at that rate could only extend in from the surface about 0.00001 cm.

The conclusion that the olefin never reached the main body of the liquid in our experiments is confirmed by the facts that the absorption rates were in the majority of cases unaffected by stirring underneath the surface or by changing the acid volume.¹⁸

The conclusion that the reaction does take place inside the film rather than at the interface is confirmed by the experiments with isobutene. As pointed out above, the absorption rate of isobutene into an excess of 60% sulfuric acid at rest rises slightly as the absorption proceeds. The rate is brought back to normal if the solution is stirred. At constant pressure, with stirring, the rate per unit area increases slowly to a total absorption of 0.4 mole per mole of sulfuric acid and then slowly decreases. When isobutene is absorbed by acid of this concentration, *tert.*-butyl alcohol is formed directly¹⁹ and is only slowly polymerized at 25°. The sulfuric acid functions as a catalyst for the union of water with the olefin. The intermediate sulfate has never been isolated. It seems reasonable to attribute the "abnormal" effects just cited to the *tert.*-butyl alcohol. This accumulates in the film of the unstirred liquid until its rate of diffusion into the main body of the acid equals the rate of formation. Its presence increases the solubility of the isobutene and hence the absorption rate is higher. This illustrates again how much the presence of reaction products may affect an absorption rate. It has actually given rise to a maximum in the rate of absorption in this case.

¹⁸ Plant and Sidgwick, *J. Soc. Chem. Ind.*, 40, 14-18T (1921), absorbed ethylene into concentrated sulfuric acid by bubbling the gas through the liquid. Their assumption that "the liquid phase must be regarded as saturated with ethylene" appears to be unjustified.

¹⁹ Michael, *Am. Chem. J.*, 38, 267-279 (1912).

On the other hand, the absorption of propene at constant pressure into stirred 87% acid decreases continuously with the quantity taken in. Here isopropyl sulfate is formed, which decreases the concentration of the acid. The separate olefins are absorbed at widely different rates by the same concentration of acid. It is concluded that the reaction rates of the dissolved olefins are different. However, the absorption rates cannot be directly proportional to the reaction rates. For, consider the case of two olefins of equal solubility but with reaction rates in the ratio 1:2; evidently, at any time, there is more of the slower reacting one in the solution, so that the quantity which reacts in unit time, and therefore its absorption rate, is more than half that of the other. The slower reacting one has an unfair advantage.

Summary

1. The two-film theory of gas absorption proposed by Lewis and Whitman has been extended to cases where rapid chemical reactions take place in the solution.

2. The reactions between the dissolved gas and a solute, for the cases studied, appear to occur inside the liquid. If the reaction rates are very fast compared to the rates of diffusion through the liquid film, then the reactions take place at zones in this film parallel to the liquid surface.

3. Diagrams are given of the concentration gradients in the film at the initial state of uniform gas absorption for instantaneous reactions taking place in one stage and in two. The primary reaction product exists between the surface and the first reaction zone, in concentration equal to that of the solute in the main body of the solution. If the metastable limit of its solubility is exceeded, it will precipitate.

4. A general equation is proposed for calculating the rate of absorption of a pure gas by a liquid (physical solution, or when reacting instantaneously with a solute) from its solubility, the concentration of the solute and the liquid film diffusion coefficient. The validity of this relationship is supported by calculations from gas absorption rate data of the authors and of other investigators for gases of widely different solubilities and for reactions of very different types.

5. A study is given of the rates of absorption of carbon dioxide by water and by solutions of sodium and potassium hydroxides. Conditions are described under which the precipitation in the film of a reaction product, sodium bicarbonate, can be seen during the absorption. Explanations are offered for the various phenomena observed by Ledig and Weaver regarding the absorption of carbon dioxide from minute bubbles by alkalies.

6. A study has been made of the effects of the reaction products on the magnitude of the liquid film diffusion coefficient. Some observations are given on the effects of the heat produced by reactions in the film.

7. The absorption rates of several olefin gases by sulfuric acid both at rest and stirred beneath its surface have been measured. The values for the absorption coefficients agree well with those obtained in a previous investigation using a rotating absorbing chamber.

8. The reactions between the olefins and sulfuric acid take place mainly in the liquid stationary film itself. This is indicated (a) by the enormous rates of absorption obtained in some cases, although the physical solubilities of the gases in the acid appear to be very low and (b) by the fact that stirring the acid underneath the surface or changing its volume, in most cases, did not change the absorption rate. The reaction rates of the dissolved olefins are quite fast and are not proportional to the absorption rates as is often assumed.

9. The fact that isobutene is absorbed by 60% sulfuric acid faster when the acid is at rest than when it is stirred is attributed to a greater accumulation of the reaction product, *tert.*-butyl alcohol, in the liquid stationary film of the quiescent acid.

10. It is suggested that the over-all rate of absorption of ethylene by concentrated sulfuric acid (the rate per unit area being independent of the agitation) may be used to determine the area of the surface of a liquid when stirred or shaken in an apparatus.

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STUDIES IN GASEOUS OXIDATIONS. I. THE HOMOGENEOUS UNCATALYZED REACTION BETWEEN OXYGEN AND ACETYLENE

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The problem of the oxidation of hydrocarbons has been of great scientific and technical interest for many years. The present work was undertaken to study in detail the features of a simple hydrocarbon oxidation in the hope that it would contribute to the general knowledge of the mechanism of gaseous oxidations. Acetylene was chosen because it reacts with oxygen at lower temperatures than other hydrocarbons; this made it possible to isolate intermediate reaction products.

A systematic study of the slow reaction of simple hydrocarbons was initiated by Bone¹ about thirty years ago. More recently Pease² and also

¹ Bone and Townend, "Flame and Combustion in Gases," Longmans, Green and Co., London, 1927.

² Pease and Chesbro, *Proc. Nat. Acad. Sci.*, 14, 472 (1928).