The Kinetics of the Absorption of Phosgene into Water and Aqueous Solutions

W. H. MANOGUE and R. L. PIGFORD
University of Delaware, Newark, Delaware

Pure phosgene gas was dissolved in short laminar jets of aqueous solution, and the results were interpreted with an unsteady state absorption-plus-reaction theory. Absorption rates of sulfur dioxide and carbon dioxide into water in the same equipment support this interpretation. The solubility of phosgene in water at 25°C. has been estimated from the absorption rates as 0.069 g.mole/(liter) (atm.). The estimated heat of solution is 6,800 cal./g.mole. At 16° and 25°C. the effect of a chemical reaction between phosgene and water on the absorption rate in a jet appears to be almost negligible, but at 45°C. a first-order reaction rate constant of 75 sec.$^{-1}$ can be derived from the absorption rates.

From absorption measurements with short jets and sodium hydroxide solutions so strong that a pseudo-first-order reaction accompanied absorption, the reaction rate constant for the bimolecular reaction between dissolved phosgene and the hydroxyl ion was estimated. A value of 1.6 x 10^4 liters/(g. mole) (sec.) was obtained at 25°C. in 1-*N* sodium hydroxide; at 35°C. in the same solution the estimated value was 2.9 x 10^4. There appears to be a slight increase in the reaction-rate constant with the ionic strength of the solution.

In chemical operations involving gaseous phosgene it is frequently desirable to remove phosgene from air, owing to its high toxicity. Scrubbing the air-phosgene mixture with a liquid absorbent is a useful technique but one for which it is difficult to design absorption equipment owing to the lack of necessary physicochemical data. It is well known that phosgene hydrolyzes in water to form carbon dioxide and hydrogen chloride in solution, but the rate constant for the reaction and concentration of dissolved phosgene at the reaction site are not known. Solubilities of unreacted phosgene in reactive solvents are of course impossible to measure by conventional methods because equilibrium cannot be established experimentally between finite quantities of gas and liquid phases. For similar reasons homogenous reaction rates cannot be observed in conventional ways. Such data are required however if the theory of diffusion and chemical reaction that has been developed in recent years (*2*, *3*, *22*) is to be employed for computing the effect of the irreversible reaction on the resistance to mass transfer through the liquid.

Because of the complex flow phenomena that doubtless exist in conventional gas absorption process equipment and because fluid motion has to be represented accurately in mass transport equations if valid physical constants are to be obtained from the solutions of the equations, measurements of absorption rates in large equipment are much more difficult to interpret than measurements in specially designed laboratory absorbers. If the fractional increase in the absorption rate per unit of surface can be determined in idealized apparatus, the corresponding increase in the rate per unit volume of the conventional absorber should be predictable with at least fair accuracy because the results of the laboratory experiments permit the well-established principles of physical chemistry to be employed quantitatively on the larger scale.

The most popular types of idealized absorbers employed for laboratory studies of this kind have been the short wetted-wall column (*16*), the rotating drum absorber (*4*), and the laminar liquid jet apparatus (*1*, *5*, *4*, *14*, *15*, *24*). Although the first of these has been used successfully (*27*), it has been recognized recently that the end effects associated with the establishment of the parabolic velocity distribution in the liquid layer and with its disengagement from the gas introduce uncertainties. The jet apparatus seems to be more nearly free from these objections. In the thin, laminar jet the fluid velocities are everywhere nearly parallel to the axis, so that the flow pattern is very nearly rodlike. The small corrections that are required to account for the boundary-layer flow near the surface and near the nozzle and for the gradual acceleration due to gravity can be computed with accuracy, as shown by Scriven (*19*). Although the shape of the liquid surface in such apparatus is wholly different from that employed in large equipment, the possibility of giving quantitative interpretation to absorption-rate data make it ideal for laboratory investigations of mechanisms.

THEORY OF DIFFUSION COMBINED WITH FIRST-ORDER, IRREVERSIBLE REACTION

When phosgene is absorbed into a chemically reactive solvent the diffusion equation is

$$\mathcal{D} \frac{\partial^2 A}{\partial x^2} = \frac{\partial A}{\partial t} + k_I A \qquad (1)$$

in which the last term on the right represents the effect of a first-order reaction. If the solvent is water, the reaction that destroys phosgene is the hydrolysis reaction

$$COCl_2 + H_2O \rightarrow CO_2 + 2H^+ + 2Cl^-$$

the rate of which is probably proportional to the phosgene conentration,

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W. H. Manogue is with E. I. du Pont de Nemours and Company, Inc., Eastern Laboratory, Gibbstown, New Jersey.

water being in very large excess. If the solvent is an aqueous solution of an alkali like sodium hydroxide, the reaction very likely involves the direct attack of a hydroxyl ion on the dissolved phosgene molecule

$$COCl_2 + 3OH^- \rightarrow HCO_3^- + 2Cl^- + H_2O$$

and is pseudo first-order only if there is a large excess of hydroxyl ion which is essentially not depleted by reaction with phosgene in the important reaction region near the interface. (Otherwise, a second diffusion equation representing the concentration of OH^- has to be included.) The boundary conditions are

$$A(0, t) = A_i;\ A(\infty, t) = A(x, 0) = 0 \qquad (2)$$

which assume phase equilibrium at the interface and an effectively infinite depth of liquid in the direction perpendicular to the interface.

The solution of this boundary value problem has been obtained (*2, 22*) as

$$N_A = A_i \sqrt{k_l \mathfrak{D}} \left[\frac{\exp(-k_l t)}{\sqrt{\pi k_l t}} + \text{erf}\,(\sqrt{k_l t}) \right] \qquad (3)$$

The approximate form of this result when $k_l t$ is small is of special interest in the present work. It is

$$N_A \sim A_i \sqrt{\frac{\mathfrak{D}}{\pi t}}\,(1 + k_l t + \ldots) \qquad (4)$$

Furthermore when $k_l t$ is very large

$$N_A \sim A_i \sqrt{k_l \mathfrak{D}} \qquad (5)$$

Owing to slight variations in the fluid velocity near the surface of the jet, t is not precisely the same for the fluid particles that flow near the surface and near the jet's axis. The differences are slight for jets moving at high speed however, as shown by Scriven's calculations (*19, 20*) for absorption without reaction. As a result,

$$t = h/U_o = \pi \overline{D}^2 h/4Q \qquad (6)$$

with good accuracy for long, slender jets.

The total rate in moles of gas per unit of time, ϕ, is obtained by summing N_A over the surface of the jet:

$$\phi = \pi \int_0^h D(h) N_A(h)\, dh$$

$$\sim \pi \overline{D} \int_0^h N_A(h) dh \qquad (7)$$

When $k_l t = 0$, that is for purely physical absorption

$$\phi = 4\, A_i \sqrt{\mathfrak{D}\, Q h} + \epsilon(h) \qquad (8)$$

where $\epsilon(h)$ is a small correction factor calculated by Scriven and Pigford (21). Similarly when $k_l t$ is small but not zero

$$\phi = 4\, A_i \sqrt{\mathfrak{D}\, Q h}\,\left(1 + \frac{\pi \overline{D}^2 k_l h}{12\, Q} + \ldots\right) \qquad (9)$$

and when $k_l t >> 0$

$$\phi \sim \pi\, A_i\, \overline{D} \sqrt{\mathfrak{D}\, k_l} \cdot h \qquad (10)$$

The correction term in Equation (9), accounting for deviations from rodlike flow, has not been evaluated when $k_l t \neq 0$, but it is probably smaller than the already small correction in Equation (8). The local absorption rate tends toward a constant value when $k_l t$ increases, and variations in t from one streamline to another should have decreasingly small influences on N_A.

When $k_l t$ exceeds 20, the average rate of absorption $\overline{N}_A = \phi/(\pi \overline{D} h)$ becomes independent of the jet length with an error not exceeding 2.5%. For an ideal jet having the same surface area and length as the actul jet but having a rodlike uniform velocity and a cylindrical shape it is

$$\overline{N}_A = A_i \sqrt{\mathfrak{D} k_l} \qquad (11)$$

By operating experimental gas-absorption apparatus under conditions such that Equation (11) is applicable, estimates of both reaction-rate constant and equilibrium solubility can be derived from observed rates per unit surface $\overline{N}_A$, and the results can be expected to be independent of the fluid mechanical situation in the jet.

EQUIPMENT

The apparatus consisted of an absorption chamber, a jet nozzle and receiver, liquid and gas feed systems, constant-temperature baths, supporting structure and fume hood. The equipment is shown schematically in Figure 1.

The jet was produced by a piece of 6-mm. glass tubing drawn to a capillary tip (I. D. = 0.63 mm.). The capillary was slightly elliptical, the maximum range in measured diameter being about 4%. The nozzle holder was a cylindrical piece of iron which had two small packing glands for the nozzle and a thermometer. A rubber gasket permitted easy adjustment of the jet position relative to the receiver. The jet collector was a short, pointed piece of capillary tubing with an 0.78-mm. bore, a size chosen to reduce the possibility of entraining gas bubbles. Jet lengths were taken as the distance between the end of the nozzle and the top of the collector since the liquid level was maintained without fluctuation at the top of the collector during a run in order to avoid entrainment. The jet lengths were measured with a cathetometer.

The absorption chamber was a piece of 64-mm. glass tubing 180 mm. long and closed at the bottom. It was located in a constant-temperature bath. Gas entered near the bottom of the chamber through a short section of glass tubing sealed tangentially into the side. The bottom of the chamber sloped to a trapped drain line to remove any liquid spilled during start-up of the jet.

Absorbent liquid passed from the storage bottles through a constant-temperature bath into a constant-head tank. It then flowed through a rotameter and into the absorption chamber. Effluent liquid from the chamber went through the bottom of the water jacket into an overflow device that permitted adjustment of the liquid level in the capillary receiver. From there it went either to a sample bottle or to the drain.

All solutions were made with deionized water and were stored in 5-gal. Pyrex bottles, which normally held enough solution for several runs. Reagent-grade sodium hydroxide and sodium nitrate were used to prepare the salt solutions. The sodium hydroxide solutions were prepared by diluting 50% caustic, which had been decanted from the insoluble carbonate. They were stored in Pyrex bottles provided with a vent line containing Ascarite.

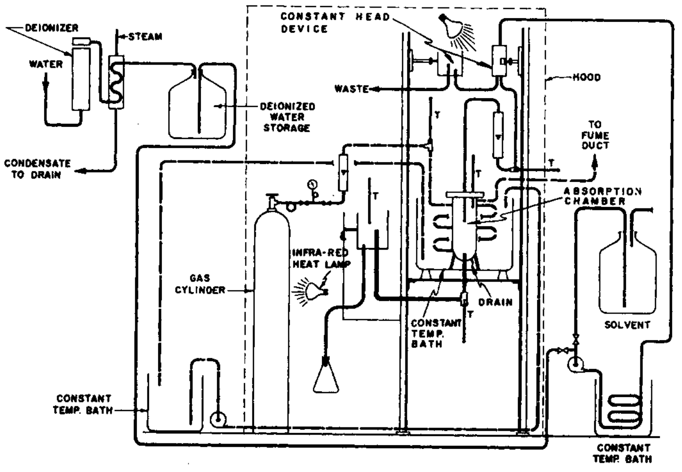

Fig. 1. Schematic drawing of apparatus.

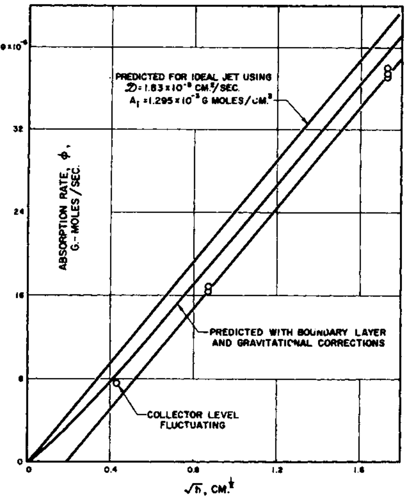

Fig. 2. Sulfur dioxide absorption into water at 25°C., corrected to 1.182 cc./sec. and 736 mm. Hg.

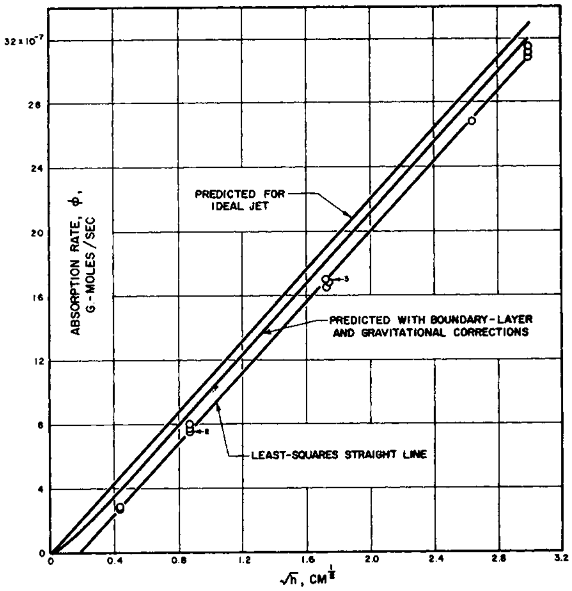

Fig. 4. Rates of phosgene absorption into water at 25°C. with 0.0628 cm. I.D. nozzle (data corrected to 1.182 cc./sec. and 736 mm. Hg).

The densities and viscosities of all solvents were obtained from the International Critical Tables.

The alkaline solutions fed to the absorber were titrated with standard hydrochloric acid to consecutive end points of 8.4 and 4.0 pH to determine both the hydroxyl ion and the amount of carbonate present. The sodium carbonate was generally less than 1% of the total alkalinity.

Special techniques were required for collecting exit liquid samples during the absorption of sulfur dioxide and carbon dioxide to minimize desorption of dissolved gas. The vapor space in the overflow chamber was made as small as possible, and the absorber effluent was fed into the bottom of a bottle containing sodium hydroxide solution. The sample bottles were purged with nitrogen prior to filling them with base. For sulfur dioxide an excess of hydrogen peroxide was added to the base. Carbon dioxide was determined by titration of the excess sodium hydroxide with standard hydrochloric acid in the presence of excess barium chloride to an end point at pH = 8.8. Sulfur dioxide was determined by titration with hydrochloric acid in the presence of an excess of hydrogen peroxide.

The absorber solutions were analyzed for chloride ion by titrating with 0.03-N silver nitrate solution. The end point was indicated by a potentiometric method which used a billet type of silver electrode with a sleeve type of mercury-mercuric sulfate reference electrode containing saturated potassium sulfate bridge solution. One ml. of concentrated nitric acid was added per 100 ml. of sample before titrating. Solutions containing sodium hydroxide were first neutralized with acetic acid. The method of analysis was checked by analyzing standard sodium chloride solutions.

Thermometers reading to 0.1°C. indicated the inlet and effluent liquid temperatures. For physical absorption the exit liquid temperature normally was maintained within 0.1°C. of the desired value. In runs where the bulk temperature of the liquid increased as a result of a chemical reaction, the average of the inlet and exit liquid bulk temperatures normally was maintained within 0.2°C. of the desired value.

Gas was taken from the top of the cylinders, fed through a rotameter into a copper coil in the constant-temperature bath surrounding the absorption chamber,

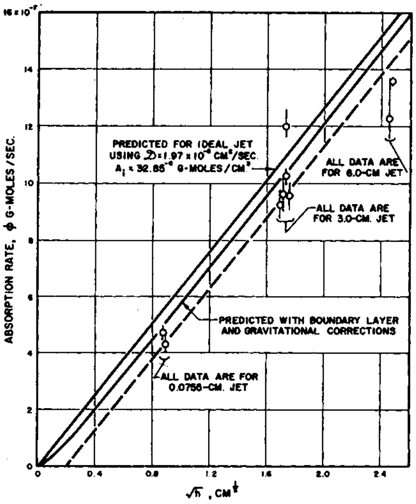

Fig. 3. Carbon dioxide absorption into water at 25°C., corrected to 1.182 cc./sec. and 736 mm. Hg.

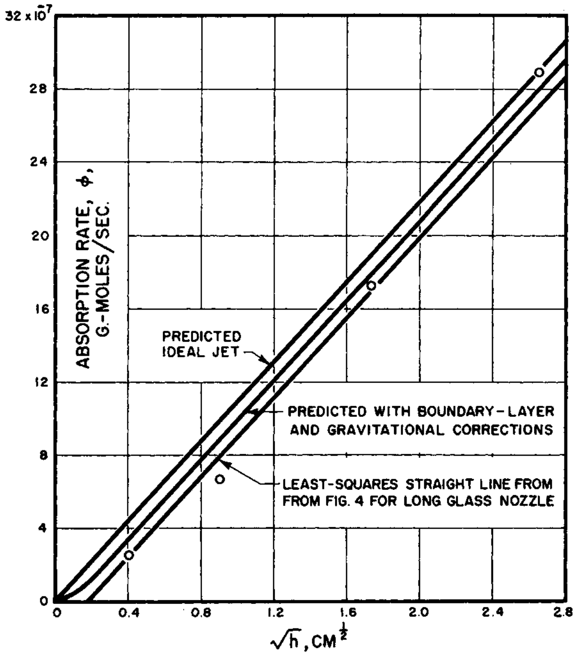

Fig. 5. Rates of phosgene absorption into water at 25°C., with 0.0609 cm. I.D. short glass nozzle (data corrected to 1.182 cc./sec. and 736 mm. Hg).

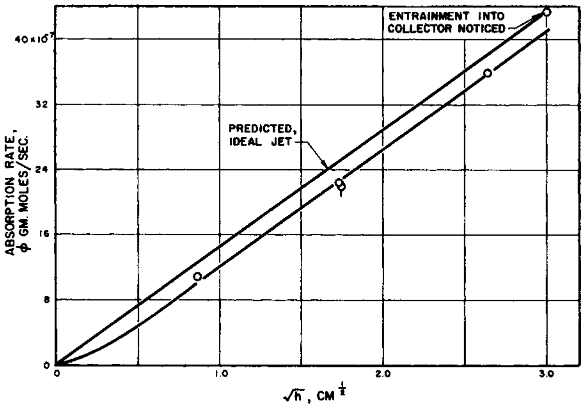

Fig. 6. Rates of phosgene absorption into water at 15°C., (corrected to 1.182 cc./sec. and 747 mm. Hg).

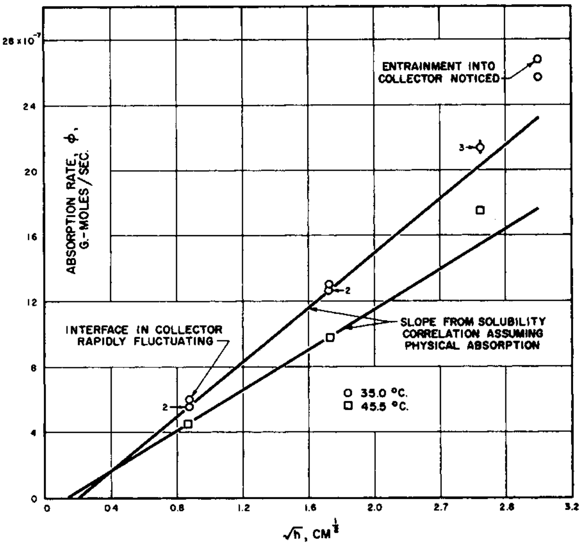

Fig. 7. Rates of phosgene absorption into water at 35° and 45.5°C. (data corrected to 1.182 cc./sec. and 760 mm. total pressure).

and then into the chamber. The stream flowed out a side arm at the top of the chamber and was vented into the exhaust duct of the hood.

Phosgene was purchased in a 150-lb. cylinder as better than 99.5% pure. After approximately 20% of the cylinder contents were bled off, the residue gas gave constant absorption rates on check runs. An infrared analysis of this material showed no detectable hydrochloric acid, carbon monoxide, or carbon dioxide.

RESULTS

Absorption in water

Absorption rates of sulfur dioxide into water at 25°C. for several jet lengths are shown in Figure 2. Previous workers (*9*, *15*) have shown that this absorption may be treated as purely physical. The data were corrected slightly by means of Equation (8) to a constant partial pressure of sulfur dioxide of 736 mm. Hg and to a constant liquid rate of 71 cc./min. Although pure gas was fed to the apparatus, it was assumed that the gas phase at the interface was saturated with water. This assumption is supported by some preliminary work in this equipment and by the more extensive work of Scriven (*19*) with carbon dioxide, which showed that presaturating the gas with water had no detectable effect on the absorption rate.

The data in Figure 2 result from five runs in which sixteen samples were taken. They are correlated by a straight line falling below the curve predicted by Equation (8), in which the correction term ϵ (h) allowing for boundary layer and gravitational corrections has been evaluated by the methods given by Scriven and Pigford (*21*). These methods require that the thickness of the boundary layer in the jet emerging from the nozzle be known; it was estimated in this work from measurements of the profile of the liquid jet actually employed. Including the correction term in Equation (8) causes the theoretical line to be displaced parallel to the line for an ideal jet, that is one having constant velocity and constant diameter. In accordance with the data the displacement from the ideal jet line should be still greater than that expected from the fluid mechanical theory. This may be due to the fact that the tip of the glass nozzle used to form the jet was wetted by the liquid, forming a stagnant pool through which dissolving gas would diffuse slowly. Alternately the lower rate of absorption may have been due to the presence of a surface-active contaminant that was present on the whole surface of the liquid, contributing an extra, constant resistance to passages of molecules through the interface.

Other authors, notably Lynn, Straatemeier, and Kramers (*10*) and Wendel (*27*) using wetted-wall columns and Cullen and Davidson (*1*) using a jet apparatus, have found that portions of their interfaces were inactive for gas absorption, evidently because of the accumulation of film at the bottom of the surfaces. Lynn et al. have shown that the subtraction of a constant area from the total interfacial area helps greatly in the correlation of data from such experiments. Scriven and Pigford (*20*) on the other hand found that the entire surface of their water jets apparently was effective in the absorption of carbon dioxide. This was probably due to the greater velocity of their interfaces. The jet design employed in this work was similar to that of Scriven, and furthermore the subtraction of a constant amount of supposedly inactive surface causes the experimental data in this work to deviate from a straight line even when conformity to a straight line would be expected. It is concluded therefore that this sort of correction is not likely to be the proper one under the experimental conditions employed. In any case however the deviations from the theoretical lines are not large. Although the magnitude of the fluid mechanical corrections is subject to some uncertainty, it is the slope of the experimental line that is most significant for the computation of the gas

TABLE 1. SOLUBILITY OF PHOSGENE IN WATER AND AQUEOUS SOLUTIONS

Solvent	Temp., °C.	Solubility, A_i, g.-moles (liter)(atm.)	$\mathfrak{D}$, diffusion coefficient used to calculate solubility, sq. cm./sec.	k_1, pseudo-first-order reaction rate constant, sec.$^{-1}$
Water	15	0.109	9.6×10^{-6}	3*
Water	25	0.069	12.7	6*
Water	35	0.046	16.1	22
Water	45.5	0.027	20.4	75
0.522-Molal $NaNO_3$	25	0.060	12.4	—
1.092	25	0.052	11.9	—
2.0	25	0.046	10.9	—
SO_2 in water	25	1.295 (*17*)	18.3 (*16*)	—
CO_2 in water	25	0.03285 (*17*)	19.7 (*20*)	—

* Obtained by extrapolation from the two higher temperatures.

solubility from the results, and it is believed that the properties of unstable, dissolved phosgene to be reported are reliable. The slopes of lines such as those on Figure 2 can be determined accurately from the data and are very nearly independent of any minor errors in the calculation of the true velocity of the surface.

Corrected rates of absorption of carbon dioxide into water at 25°C. for several jets are shown in Figure 3. These data result from nine runs in which twenty-nine samples were taken. The range of the observed rates as well as the average for each run are shown on the graph. Although they show considerable scatter, the data for all but one run are below the ideal-jet curve; they are also generally below the predicted curve for a real jet and may be correlated by a line parallel to the line for an ideal jet, as were the sulfur dioxide data.

The measured rates for the 6-cm. jet are farther from the predicted values than are those for other jet lengths. These data were the first taken in this investigation, when the absorption chamber was a 5-gal. battery jar which may not have been completely purged of air. Some difficulty in purging this chamber had been experienced previously, so that the presence of air may have led to the low results. The scatter of the data may be caused largely by variations in the analysis of carbon dioxide. In runs at the shorter jet lengths the blank corrections for carbon dioxide in the feed water and in the sodium hydroxide used for titration were about 20% of the titres, and these blanks showed considerable scatter from run to run.

TABLE 2

Gas	Solvent	Temperature range, °C.	Average heat of solution, cal./g.-mole
Phosgene	Water	15-45.5	6,800
Carbon dioxide	Water	15-35	4,600
Nitrous oxide	Water	15-35	5,400

The results for sulfur dioxide and carbon dioxide indicate that the method chosen to correlate the data is valid for absorption without reaction. They also show that the equations resulting from Scriven's analysis of the jet flow pattern predict the order of magnitude of deviations, ϵ, of the absorption rate in a real jet from the rates predicted for a constant-velocity jet. (The solubilities and diffusivity used in calculating the predicted rates are listed in Table 1.)

Adjusted rates of phosgene absorption in water at 25°C. are shown in Figure 4. The data result from sixteen runs in which seventy-seven samples were taken. (A run is a series of several repetitive but independent samples leading to a mean.) The results from five samples in five runs were discarded because they varied from the mean of that run by more than four times the standard deviation for the run. The standard deviations ranged from 0.2 to 2.6% of the respective means.

The absorption rate increased linearly with the square root of the jet length. This is the same dependence on the jet length which is predicted for physical absorption by Equation (8), so that the rate-determining process is probably molecular diffusion of dissolved and unreacted phosgene into water.

To compare absorption rates for different nozzles phosgene was also absorbed into water at 25°C. in a jet formed by a short 0.0609-cm. I.D. nozzle. This nozzle was constructed by sealing a piece of capillary tubing on the end of a length of 6-mm. tubing and then cutting off the capillary tubing so that only about 1.5 mm. of length remained. The data are shown in Figure 5 and are more scattered than those taken with the long nozzle. In these runs a 0.09-cm. I.D. collector was used instead of the 0.08-cm. I.D. one used with the larger nozzle. This larger collector probably is responsible for most of the scatter. However there is no apparent difference in the results obtained with the two different nozzles. The least-squares straight line through the data of Figure 4 represents the data in Figure 5 equally well.

Absorption rates of phosgene into water at 15°, 35°, and 45.5°C. are represented in Figures 6 and 7. The data scatter somewhat more than in Figure 4. The solubility of phosgene in water was calculated from the slopes of the lines in Figure 4, 6, and 7 with Equation (8) used. The term $A_i\sqrt{\mathfrak{D}}$ was determined from the data, and the diffusivity was calculated by the use of the correlation of Wilke (*28*). This correlation predicts the diffusivity of carbon dioxide in water within 5% of the value selected by Scriven (*19*) after a careful study of data from several sources; it predicts the diffusivity of sulfur dioxide within 15% of Peaceman's (*16*) measured value. The phos-

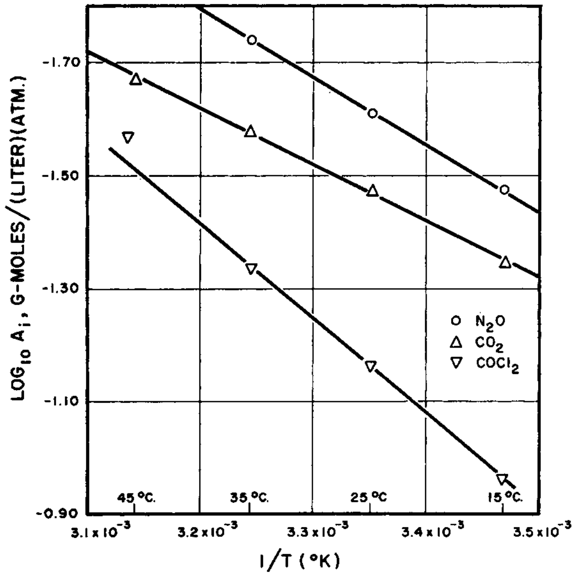

Fig. 8. Effect of temperature on the solubility of phosgene in water.

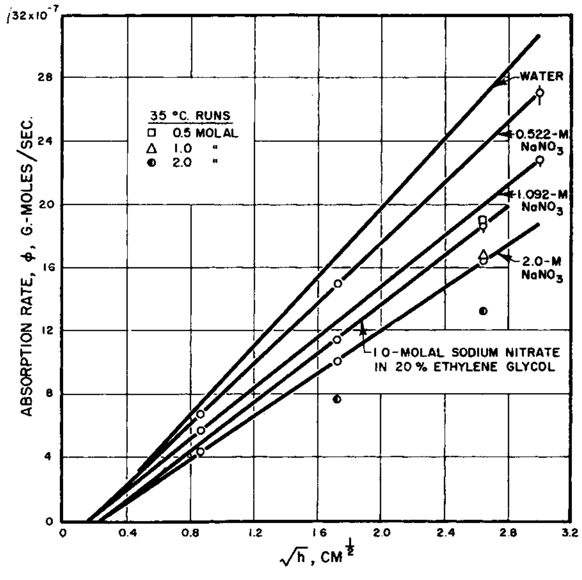

Fig. 9. Phosgene absorption into aqueous solutions of sodium nitrate at 25°C. (data corrected to 1.182 cc./sec. and 736 mm. Hg).

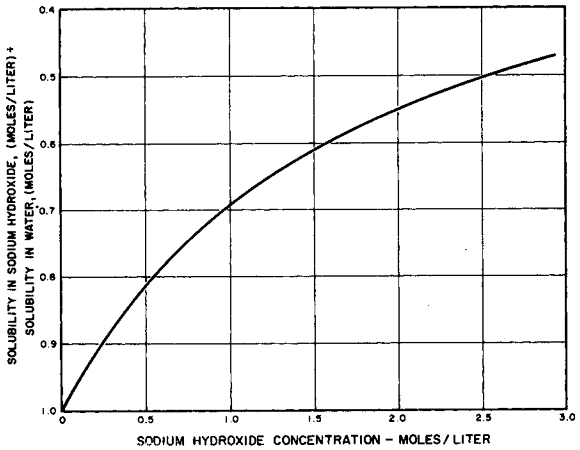

Fig. 10. Predicted solubility of phosgene in aqueous sodium hydroxide at 25°C. (corrected to 736 mm. Hg).

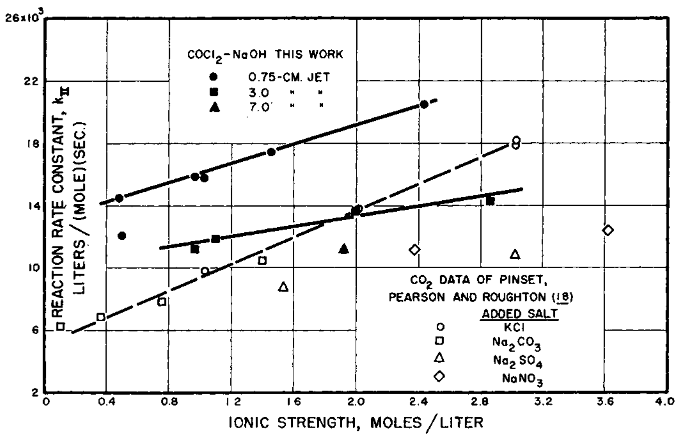

Fig. 11. Effect of ionic strength on reaction-rate constant for reaction with hydroxide ion (all measurements at 25°C.).

gene solubilities are listed in Table 1 with the estimated diffusion coefficients that were used to calculate them.

At 35° and 45.5°C. the rate of absorption into water is affected by the reaction of the dissolved phosgene, so that the second term in the parentheses of Equation (9) cannot be neglected. Its effect is greatest at the highest temperature and the largest value of jet length. On the other hand the slope of the line relating absorption rate and $h^{1/2}$ in the range where h is small is hardly affected by the reaction and gives an approximate value of $A_i\sqrt{\mathfrak{D}}$. By successive trial of various values of $A_i\sqrt{\mathfrak{D}}$ and k_I a pair of values can finally be computed for which the data for both short and long jets can be brought together. The values of solubility and rate constant listed in Table 1 at the two higher temperatures have been obtained by this procedure.

The logarithm of the saturation concentration of phosgene in water at equilibrium with pure phosgene gas at 1 atm. is plotted against the reciprocal of the absolute temperature in Figure 8. For comparison, data for carbon dioxide and nitrous oxide (*17*) are also shown in Figure 8. The calculated heats of solution are given in Table 2.

Figure 9 represents absorption rates of phosgene into aqueous solutions of sodium nitrate. Here again physical absorption theory correlates the data. Sodium nitrate was used for these measurements because it produced the same cation as sodium hydroxide, it was composed of monovalent ions, and its use did not interfere with the determination of absorbed phosgene by chloride ion titration.

The solubility data for the inert salt solutions are shown in Table 1. They are correlated and extrapolated with an equation similar to one proposed by Markham and Kobe (*12*):

$$\frac{S_m}{S_o} = am + \frac{1}{1 + bm} \qquad (12)$$

This equation appears to be the best one available for solution strengths above 1 molal. Neither the Setschenow (*13*) equation nor the equation proposed by van Krevelan and Hoftijzer (*25*) seems to be as accurate for concentrated solutions.

Absorption in Alkaline Solutions

In order to calculate mass transfer coefficients from rates of absorption into sodium hydroxide solutions the solubility of unhydrolyzed phosgene in these solutions is required. This may be estimated from the solubility of phosgene in aqueous sodium nitrate solutions by a method similar to that used by Markham and Kobe (*12*) which has been described in detail by Wendel (*26*). Briefly it used the fact that the salting out of gases by strong electrolytes in water has been found to depend additively on the effects of the ions present. The increased effectiveness of the hydroxyl radical over nitrate in salting out phosgene is obtained by comparing the solubilities of nitrous oxide in potassium nitrate and potassium hydroxide (*13*). Nitrous oxide is used as a reference gas because data for hydroxide solutions are available and the solubility of nitrous oxide in water is of the same magnitude as that of phosgene, so that salting out effects can be expected to be similar for the two gases. Figure 10 shows the estimated solubility of phosgene in sodium hydroxide.

A number of experiments were carried out at 25°C. in which phosgene was dissolved in sodium hydroxide solutions of varying strength up to about 3 moles/liter, with a 7.5-mm. jet used. The data are given in Table 3. It seemed probable that the change in the sodium hydroxide concentration in the reaction zone would be small enough in some of these experiments that the reaction would be pseudo-first-order; it also seemed that the rate con-

TABLE 3. RATES OF PHOSGENE ABSORPTION INTO AQUEOUS SODIUM HYDROXIDE SOLUTIONS AT 25°C.

Normality of NaOH solution	Phosgene absorption rate, g.-moles/sec. × 10^6 (corr. to 760 mm. Hg total pressure)	Contact time, sec. × 10^3 (with rodlike flow assumed)	k_{II} from Equation 11, liters / (g.-mole)(sec.)
Jet length 0.75 cm., interfacial area 0.144 sq. cm.			
2.43	3.08	1.85	20,500
1.44	3.06	1.81	17,500
1.02	2.86	1.80	15,800
0.96	2.84	1.80	15,900
0.49	2.17	1.87	12,000
0.47	2.33	1.78	14,500
Jet length 3.0 cm., interfacial area 0.575 sq. cm.			
2.86	9.74	7.78	14,200
1.99	10.4	7.57	13,600
1.09	9.94	7.40	11,800
0.96	9.48	7.20	11,200
Jet length 7.0 cm., interfacial area 1.325 sq. cm.			
1.92	22.0	16.9	11,100

stant for this reaction might be sufficiently large that Equation (11) would represent the absorption rate. This speculation was encouraged by the high numerical values of B_o/A_i, the short contact times of the experiments, and the marked effectiveness of sodium hydroxide in increasing the phosgene absorption rate. Rate constants have been calculated from the data by means of Equation (11) and are shown as a function of sodium hydroxide normality in Figure 11.

The rate constants increase linearly with sodium hydroxide concentration. This may be interpreted in several ways: either phosgene was not hydrolyzed by a first-order reaction, or the trend in rate constants is caused by a defect in the solubility predictions or an effect of the ionic strength of the solution on the rate constant itself.

It is believed that the reaction in the short jet did not deplete the hydroxyl radical concentration appreciably and that the chemical rate is therefore pseudo-first-order. The solubility prediction is also believed satisfactory. It was assumed in the calculations that the diffusivity in Equation (11) varies inversely with the solution viscosity. Any error in this approximation is believed to be slight. A maximum error of about 2% in the estimated rate constants arises from neglecting the increase in interfacial area caused by wetting of the nozzle. This is well within the experimental error of the estimates.

The increase in the rate constants with the sodium hydroxide concentration probably results from the changing ionic strength of the solution. A similar variation in the second-order rate constant for the reaction between carbon dioxide and hydroxyl ion has been reported by Pinset, Pearson, and Roughton (*18*) and Nijsing (*15*). The data from (*18*) are reproduced in Figure 11. For ionic strengths greater than 0.3 moles/liter their data show that the rate constant increases about linearly with the ionic strength, although some ions are less effective than others. Replacing concentration with activity does not cause the results with the different salts to fall on the same line. The observed variation in the rate constant with the ionic strength is relatively slight and is about what would be expected for the reaction between a neutral molecule and an ion (*7*).

Rate constants from jets longer than 0.75 cm. are also shown in Figure 11 for comparison, although the reaction in these jets is slowed appreciably by the reduction of the hydroxyl radical concentration near the interface. Equation (11) does not apply accurately to these experiments and gives rate constants that are too small, as seen on the figure.

A value of 1.6×10^4 liters/(g.-mole)(sec.) is selected as the best estimate of the second-order rate constant in 1-*N* sodium hydroxide at 25°C. At 35°C. the only measurement which was made under pseudo-first-order conditions is in 1-*N* sodium hydroxide and gives a rate constant of 2.9×10^4.

The ratio $k_{II}(\mathrm{OH^-})/k_{II}(\mathrm{H_2O})$ at 25°C. for phosgene is 9.14×10^6. This is consistent with the values for other compounds hydrolyzing by the same mechanism (*23*), although it is lower than the value of the corresponding ratio of reaction rates for carbon dioxide, 18×10^6 (*18*).

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NOTATION

a = constant in Equation (12), 0.01 for phosgene

A = concentration of dissolved but unreacted gas molecules; subscript i refers to the concentration at the gas-liquid interface

b = constant in Equation (12), 0.232 for phosgene

B_o = concentration of sodium hydroxide in the liquid fed to the absorber

$\mathcal{D}$ = diffusivity, sq. cm./sec.

D = jet diameter, cm.

$\overline{D}$ = average jet diameter, cm.

$\overline{D^2}$ = mean squared jet diameter, sq. cm.

h = jet length, cm.

k_I = pseudo-first-order reaction rate constant, sec.$^{-1}$.

k_{II} = second-order reaction rate constant, liters/(mole)(sec.)

m = molality of solution

N_A = instantaneous absorption rate of component A, g.-moles/(sq. cm.)(sec.)

$\overline{N_A}$ = average absorption rate of component A, g.-moles/(sq. cm.)(sec.)

Q = volumetric flow rate, cc./sec.

Sm = volume of gas at standard temperature and pressure dissolved by the quantity of solution of molality m containing 1 g. of water

So = volume of gas at standard temperature and pressure dissolved by 1 g. of water

t = elapsed time of exposure of an element of liquid surface to the gas

Uo = average velocity parallel to jet surface, defined by Equation (6)

x = distance into the liquid phase measured from the interface

ϵ = small correction factor which accounts for the effect of nozzle drag and gravitational acceleration on the absorption rate

ϕ = total absorption rate at 760 mm. Hg. pressure, moles/sec.

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