Subscripts

i = component i
j = component j
P = evaluated at total pressure, P
P_i° = evaluated at vapor pressure, P_i°

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Reaction Kinetics in the Absorption of Chlorine into Aqueous Media

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It was established that chlorine reacts with both water and hydroxyl ions. At a short reaction time when the pH was less than 3 the reversible reaction of chlorine and water controlled the absorption rate. From pH 3 to 10.5 the forward reaction predominated and yielded an apparent first-order rate constant of 20.9 sec.$^{-1}$ at 25°C. Between pH 10.5 and 12.5 the reaction of chlorine with hydroxyl ions occurred simultaneously with the chlorine-water reaction. Above pH 12.5 the second-order reaction between chlorine and hydroxyl ions became controlling and the reaction-rate constant was evaluated to be in the order of 10^6 liters/(mole)(sec.) at 25°C.

These ionic reactions of chlorine were further interpreted through the collision and transition state theories. Certain important quantities with regard to the reaction characteristics were derived from the experimental data.

When chlorine is dissolved in aqueous solutions, certain ionic reactions are known to occur. The kinetics of these reactions however are not yet clear, and the important reaction characteristics have never been quantitatively determined. Shilov and Solodushenkov (*1*) investigated the kinetics of the reaction of chlorine in water by the conductivity technique. They assumed that the reaction

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl \quad (1)$$

was the rate-controlling mechanism and evaluated the apparent first-order rate constants which indicated a decreasing tendency as the reaction proceeded.

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Commenting on the results of Shilov and Solodushenkov, Morris (*2*) suggested the rate-determining reaction to be between chlorine and the hydroxyl ion as follows:

$$Cl_2 + OH^- \rightleftharpoons HOCl + Cl^- \qquad (2)$$

He interpreted that the apparent decrease in rate constant could be due to the continuous decrease in the hydroxyl-ion concentration during the reaction.

In view of Morris' interpretation Shilov and Solodushenkov (*3*) reinvestigated the reaction more carefully and obtained data that did not repeat the decreasing trend in rate constant. Thus they attributed their previously observed results to a systematic experimental error.

Recently Liftschitz and Perlmutter-Haymen (*4*) attempted to clarify the question of the rate-controlling mechanism in the chlorine-water system by another technique. They measured the rise in temperature of the reacting solution as a function of time. By assuming the temperature change to be proportional to the concentration change, they evaluated the rate constants in accordance with both Equations (1) and (2). They found that in the first case the calculated rate constant remained practically constant with the reaction time, while in the second case it displayed a slightly increasing tendency with time. From this analysis they concluded that reaction (1) was the appropriate mechanism of chlorine hydrolysis.

Pozin (*5*) absorbed chlorine gas into strong sodium hydroxide solutions in a wetted-wall column and analyzed his results under the assumption that a very rapid reaction occurred between chlorine and the hydroxyl ion. He was able to correlate the absorption rate with the hydroxyl ion concentration as an evidence for the validity of his assumption.

These previous studies suggest that chlorine probably reacts with both water molecules and hydroxyl ions and that either or both of these reactions are rate-controlling, depending upon the pH of the solution. Under what exact conditions and to what precise extents these reactions occur during absorption are questions which remain unanswered.

THEORY

In this work the kinetics of the chlorine-water reaction were studied by absorbing chlorine gas into aqueous solutions of varying pH. The absorption rates were compared with the absorption rates that would have occurred if no chemical reaction had taken place, in conjunction with the penetration theory of absorption with simultaneous chemical reaction.

The concepts, assumptions, and limitations of this theory have been discussed in several papers (*6* to *8*) and are now quite well known. Briefly the theory states that the rate of absorption of a gas into a liquid is equal to the penetration of the gaseous solute by molecular diffusion from the gas-liquid interface into a stagnant liquid. This diffusion process is mathematically described by Fick's laws of transient diffusion solved under appropriate boundary conditions. If no chemical reaction occurs, the average absorption rate over a given contact time θ is given by

$$\overline{N}_A^* = 2(A_i - A_o)\sqrt{D_A/\pi\theta} \qquad (3)$$

If the gaseous solute undergoes a chemical reaction, its concentration at any given plane within the liquid (except at the interface) will be less than if no chemical reaction occurred. This will cause the solute concentration gradients to be larger and thus increase the rate of diffusion away from the interface or, in other words, increase the rate of absorption. The average rate of absorption with chemical reaction is usually expressed in the general form

$$\overline{N}_A = 2(A_i - A_o)\sqrt{D_A/\pi\theta}\cdot\Phi \qquad (4)$$

where the function Φ represents the effect of a chemical reaction on the rate of absorption.

Expressions for the factor Φ have been determined for the simpler types of chemical reactions such as first-order irreversible (*7*) and second-order infinitely rapid (*8*) reactions. In the first case the solution is

$$\Phi = 1/2\,[\sqrt{\pi/k_1\theta}\,(1/2 + k_1\theta)\ \mathrm{erf}\,\sqrt{k_1\theta} + \exp\,(-k_1\theta)]\ (A_o = 0) \qquad (5)$$

and in the second case

$$\Phi = 1/\mathrm{erf}\,(\alpha/\sqrt{D_A})\ (A_o = 0) \qquad (6)$$

where α is given by

$$A_i\sqrt{D_A}\exp(-\alpha^2/D_A)\,\mathrm{erfc}(\alpha/\sqrt{D_B}) = B_o\sqrt{D_B}\exp(-\alpha^2/D_B)\ \mathrm{erf}(\alpha/\sqrt{D_A}) \qquad (7)$$

It is convenient to express absorption rates in the form of Equation (4) because then the factor Φ becomes simply the ratio of the average rate of absorption with chemical reaction $\overline{N}_A$ to the average rate of absorption that would occur if there were no chemical reaction $\overline{N}_A^*$. By comparing these absorption rates the kinetics of the chemical reaction may be analyzed.

APPARATUS AND PROCEDURES

Absorption in a laminar liquid jet has been shown to conform with the penetration theory far better than other types of absorption equipment (*9* to *11*). For this reason the jet method was used in this work.

The jet nozzle, jet receiver, absorption chamber, and sampling systems (Figure 1) were very similar to those used by Scriven and Pigford (*12*). The apparatus description and procedures given by these authors also apply in this work.

The absorption runs were made with jet lengths varying from 2.5 to 9 cm. and at liquor flow rates varying from 3 to 6 cc./sec. The liquor issued from a lucite bell-shaped nozzle with an exit diameter of 1.645 mm. The jet terminated in the receiver in such a way that there was no overflow of liquor and no entrainment of gas.

The liquor ran through a sampling pipet to the drain. It was sampled by simply removing the pipet and delivering the sample.

The chlorine issued from a small cylinder; it was filtered, brought to temperature, saturated with water vapor, and delivered to the absorption chamber. From the chamber it was exhausted by bubbling it through 25% sodium hydroxide.

All experiments were conducted at a constant temperature of 25.0° ± 0.1°C.

The solutions were analyzed iodometrically for total chlorine. The samples were introduced beneath the surface of a 10% potassium iodide solution which was then made acidic with acetic acid and finally titrated with standard sodium thiosulfate to a starch end point under a blanket of nitrogen to prevent oxidation of the iodide to iodine.

TREATMENT OF DATA

The average rate of absorption per unit area was calculated from the sample concentration, the liquor flow rate, and the interfacial area. The interfacial area was taken to be $\pi\overline{D}H$. The diameter of the jet at various flow rates and jet lengths (H) was measured by a simple optical technique, and from these measurements the proper average diameter was calculated. The absorption rates were reduced to the common basis of a chlorine pressure of 760 mm. Hg in accordance with the penetration theory.

The time that the absorbent was exposed to the gas was calculated by the following integral equation:

$$\theta = \int_0^H \frac{dh}{U_s} \qquad (8)$$

The jet surface velocity close to the nozzle opening was estimated by considering the velocity gradient in this region to be analogous to that in the wake behind a flat plate as done by Scriven and Pigford (*10*) and Rideal and Sutherland (*13*). The effect of gravitational acceleration on the jet velocities was accounted for by the use of the mean of the diameter squared to calculate the average velocity of the jet.

TABLE 1. THE EFFECT OF THE CHLORINE HYDROLYSIS REACTION ON ABSORPTION RATES AT 25°C. ($\theta = 0.03$ SEC.)

Absorbent	pH	Absorption rate with chemical reaction, $\bar{N}_A$ g./(sq. cm.) (sec.) × 10^4	Absorption rate without chemical reaction, $\bar{N}_A^*$ g./(sq. cm.) (sec.) × 10^4	$\Phi = \bar{N}_A/\bar{N}_A^*$
1.733*N* NaOH	14.2	27.3	0.647	42.2
1.166	14.1	21.0	0.777	27.0
0.500	13.7	10.5	0.915	11.5
0.244	13.4	6.07	0.979	6.22
0.1268	13.1	3.60	1.023	3.51
0.0603	12.8	2.19	1.056	2.07
0.00610	11.8	1.365	1.059	1.29
Dil. NaOH	10.3	1.275	1.059	1.21
Dil. NaOH	9.7	1.260	1.059	1.19
Dil. NaOH	8.8	1.261	1.059	1.20
H_2O	6.8	1.278	1.059	1.21
Dil. H_2SO_4	4.2	1.267	1.059	1.20
Dil. H_2SO_4	2.7	1.250	1.059	1.17
Dil. H_2SO_4	1.6	1.186	1.058	1.12
0.1*N* H_2SO_4	1.0	1.152	1.055	1.09

RESULTS AND DISCUSSION

Chlorine was absorbed into 0.1N hydrochloric acid to ascertain how well the experimental system agreed with the penetration theory for physical absorption. The average rate of absorption is plotted against $1/\sqrt{\theta}$ in Figure 2, from which it is seen that a straight line with a 0-0 intercept can be readily obtained, as predicted by Equation (3).

The equilibrium solubility of chlorine in 0.1N hydrochloric acid was measured by a static method and found to be 4.22 g./liter at a chlorine pressure of 760 mm. Hg and 25°C. in agreement with that of molecular chlorine in water as calculated from the equilibrium data of Connick and Chia (*23*) and total solubility measurements made in connection with this work (*14*). The diffusion coefficient of molecular chlorine through 0.1N hydrochloric acid was measured on an electrophoresis-diffusion apparatus and found to be 1.48 by 10^{-5} sq. cm./sec. at 25°C. This value agrees very well with that obtained by Peaceman (*15*) by the diaphragm method. These values were used to evaluate Equation (3) for the chlorine-0.1N hydrochloric acid system, which is plotted in Figure 2. It is seen that the measured absorption rates agree very well with the penetration theory, lending strong support to the reliability of the results of subsequent experiments with chemical reactions.

Chlorine was then absorbed into aqueous solutions having initial pH values from 1 to 14. The water was acidified with sulfuric acid and made basic with sodium hydroxide. Runs were made at exposure times ranging from 0.018 to 0.039 sec. for each solution.

At each pH value the absorption rates were plotted against $1/\sqrt{\theta}$. The values of the absorption rates at 0.03 sec. were then determined by interpolation and used in comparison on a common basis. This rate was then divided by the rate of absorption without chemical reaction to obtain the factor Φ at 0.03 sec.

The rates of absorption without chemical reaction were calculated from Equation (3). With the exception of the concentrated caustic solutions the absorbents were dilute enough to use the equilibrium solubility and the diffusion coefficient previously mentioned. When the ionic strength of the caustic solutions was quite high, the equilibrium solubility and diffusion coefficient were corrected for the effect of the salt ions. The effect on the diffusion coefficient was estimated from chlorine absorption data taken on concentrated sodium chloride solutions with the same apparatus (*14*). The effect on the equilibrium solubility was accounted for by a comparison of solubility data of oxygen in sodium chloride and sodium hydroxide solutions in accordance with the theory of Debye and McAuley on the salting out of neutral molecules (*16*).

The values of $\Phi - 1$ at 0.03 sec. are shown as a function of initial absorbent pH in Table 1 and Figure 3. These values rather than Φ itself are used in the plot merely to make the log scale more sensitive at Φ values close to 1.

The penetration theory for absorption with chemical reaction shows that the factor Φ increases as the rate of the chemical reaction increases.[7] Thus Φ is an indirect measure of the reaction rate. With this in mind the rate-

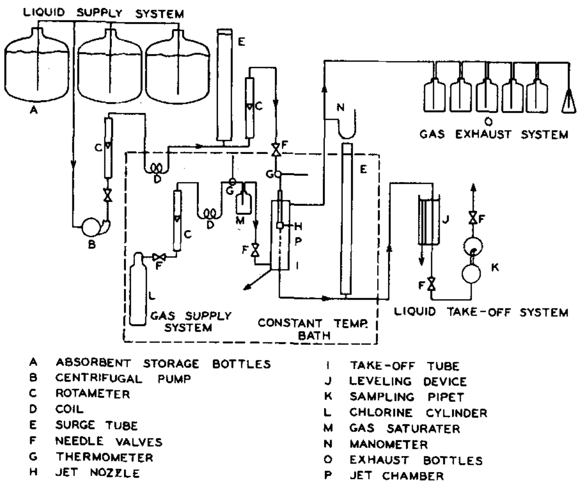

Fig. 1. The absorption apparatus.

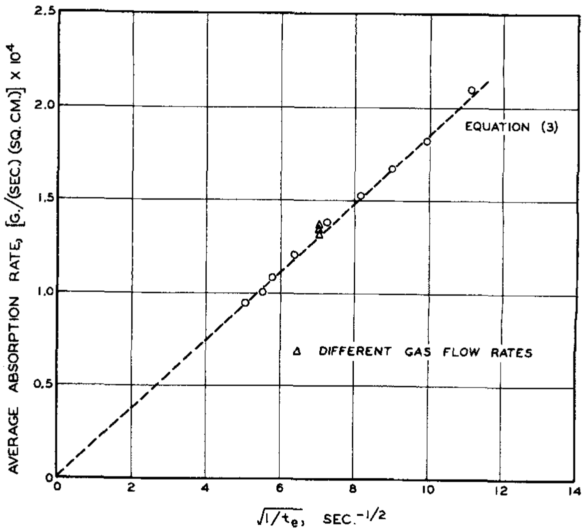

Fig. 2. Absorption in 0.1N hydrochloric acid.

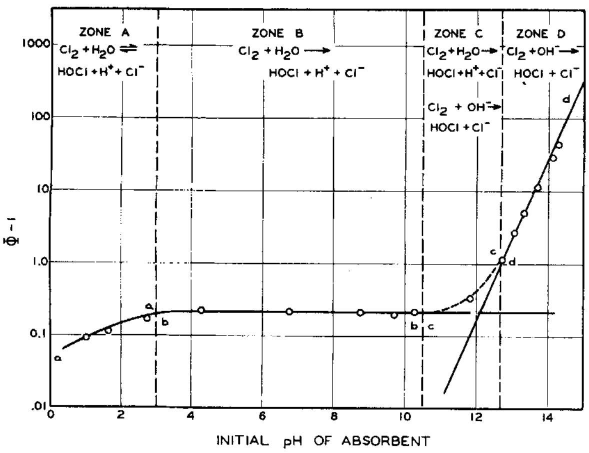

Fig. 3. The effect of chlorine hydrolysis on the chlorine absorption rate at 25°C. ($\theta = 0.03$ sec.).

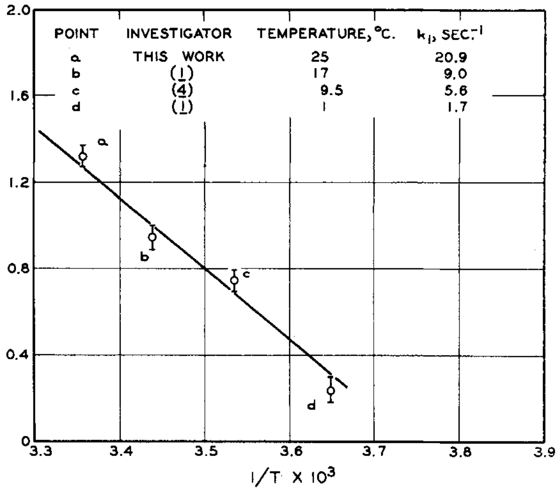

Fig. 4. Rate constant vs. temperature for chlorine hydrolysis reaction.

determining mechanism for the chlorine-water reaction can be deduced from the shape of the curve in Figure 3.

Upon examination of the initial portion of the curve labeled aa in Zone A of Figure 3 it is at once seen that the reaction rate increases as the hydrogen ion concentration decreases. If reaction (2) were the controlling mechanism in this pH region, an increase in the reaction rate would be expected because of the increase in hydroxyl ion concentration. However the increase in reaction rate would be expected to become more and more pronounced at higher pH values because the hydroxyl ion concentration is building up faster than the product concentrations. Such an interpretation contradicts the experimental evidence shown by the next portion of the curve bb in Zone B which indicates that the reaction rate is independent of the hydroxyl ion concentration for quite a wide range. Thus reaction (2) does not consistently explain these facts.

The experimental facts up to a pH of 10.5 can be explained in a satisfactory manner if reaction (1) is considered to be the controlling mechanism. The reaction rate increases initially and then levels off with decreasing hydrogen ion concentration because the rate of the reverse reaction of reaction (1) assumes less and less importance until its influence on the overall reaction rate is negligible (portion bb). During this range the hydrolysis reaction is kinetically first order with respect to chlorine and irreversible.

The reaction rate remains constant with pH until it suddenly begins to rise again. The plausible reason for this behavior could be that now the hydroxyl ion concentration is great enough for reaction (2) to influence the overall reaction rate. In Zone C both reactions show their influence. As pH further increases, the influence of reaction (1) continuously diminishes until finally in Zone D only reaction (2) affects the overall rate.

These results definitely show that when chlorine is dissolved in water it reacts with both hydroxyl ions and water molecules. The rate at which the chlorine reacts is controlled by one, the other, or both of the reactions depending upon the pH of the solution.

The apparent first-order forward reaction rate constant for reaction (1) was calculated from Equation (5) based on the Φ value represented by the horizontal portion of the curve in Figure 3. The value obtained was 20.9 ± 1.2 sec.$^{-1}$. This value was compared with those of Shilov and Solodushenkov (*1*) and Liftshitz and Perlmutter-Haymen (*4*) at other temperatures on the basis of the Arrhenius equation:

$$k_1 = F \exp(-E_a/RT) \qquad (9)$$

in which it is tacitly assumed that the activation energy is independent of temperature. Thus a plot of log k_1 vs. $1/T$ should yield a straight line. Such a plot is shown in Figure 4. It is seen that the points are nearly on a straight line. When one considers that the data come from three independent sources and were obtained by three widely different methods, the Arrhenius representation is satisfactory.

The activation energy value was then calculated from the slope of the line in Figure 4 to be 15,100 cal./mole, and the value of F in the Arrhenius equation was determined to be 2.58×10^{12} sec.$^{-1}$. If the reaction is considered to be bimolecular, the frequency factor of the Arrhenius equation becomes 4.65×10^{10} liters/(mole)(sec.). This value was obtained by dividing the apparent first-order value by the molecular concentration of water, that is 55.5 moles/liter.

In terms of the collision theory of bimolecular reactions Equation (9) is sometimes written as

$$k_1 = pZ \exp(-E_a/RT) \qquad (10)$$

where Z is the number of collisions between the reacting molecules per second at unit concentration. The terms $p \exp(-E_a/RT)$ then represent the fraction of collisions that result in actual chemical combination. The factor $\exp(-E_a/RT)$ represents the fraction of colliding molecules which possess the required energy for combination, and p represents a steric factor which describes the fraction of colliding molecules which are oriented in the proper manner for chemical combination. It is interesting to estimate the order of magnitude of each of these factors for the hydrolysis reaction. The factor $\exp(-E_a/RT)$ is in the order of 10^{-11}. The frequency of collision of ions in solution is estimated from kinetic theory to be about 10^{11} liters/(mole)(sec.) (*17*). Thus p is in the order of unity.

The steric factor can be much less than unity even for small inorganic molecules. This arises from the polarity of the molecules or interference from the solvent. These factors are evidently not very prominent for the reaction between chlorine and water.

In terms of the transition theory of reaction rates the rate constant is given by

$$k_1 = \epsilon/T \cdot e^{\Delta S\ddagger/R} \cdot e^{-\Delta H\ddagger/RT} \qquad (11)$$

where $H\ddagger = (E_a - RT)$ in solution. The entropy of activation for the hydrolysis reaction was calculated to be -14 entropy units (standard state of 1 mole/liter). The negative value of entropy arises because of the standard state chosen. This value and the value of the activation energy 15.1 kcal./mole are both in the range listed by Frost and Pearson (*18*) for ionization of neutral molecules in water solvent reactions.

Thus the chlorine hydrolysis reaction proceeds at a normal rate and has a normal temperature dependence when compared to similar reactions.

Line dd in Figure 3 represents the results of calculation according to Equations (6) and (7) for absorption with infinitely rapid irreversible reaction. B in Equation (7) denotes the concentration of the hydroxyl ion. The diffusion coefficient of the hydroxyl ion was taken to be that of sodium hydroxide which was obtained from data in the "International Critical Tables" (*19*). The data points fall very close to line dd indicating that the reaction between chlorine and hydroxyl ions is very rapid.

Recently Brian, Hurley, and Hasseltine (*20*) presented a numerical solution to the penetration theory equations for absorption with a second-order irreversible chemical reaction. An attempt was made to estimate the reaction rate constant for the reaction between chlorine and hydroxyl ion by means of these data and their solution. However for values of Φ determined in this work that were within the range of values presented in the solution of Brian, Hurley, and Hasseltine the difference between the data and the case of an infinitely rapid reaction was not great enough to estimate the reaction rate constant. Where an appreciable difference did occur (at the two points above pH 14), the resulting Φ values were beyond the range of the solution.

A crude estimate of the rate constant was made however from the equations of VanKrevelen and Hoftijzen (*21*) who present an approximate solution for absorption with second-order irreversible chemical reaction in accordance with the familiar film theory of absorption. The reaction rate constant was thus estimated to be in the order of 10^6 liter/(mole)(sec.). Dankwerts and Kennedy (*22*) have shown that when the absorption is accompanied by simpler chemical reactions, the penetration theory and the film theory predict absorption rates which are fairly close. For this reason it is believed that the order of magnitude of the calculated rate constant is correct even though the actual value cannot be firmly established.

CONCLUSIONS

It has been shown that when chlorine comes in contact with water it reacts with both hydroxyl ions and water. Either or both of these reactions control the rate of chlorine consumption depending upon the pH of the solution.

Analysis of the absorption data in terms of the penetration theory established that the forward reaction between chlorine and water had an apparent first-order rate constant of 20.9 sec.$^{-1}$ at 25°C. These data and the data of others at different temperatures show that the reaction proceeds at a normal rate and has a normal temperature dependence as interpreted through the collision and transition state theories of reaction rates.

The absorption data in conjunction with the penetration theory further show that the reaction between chlorine and hydroxyl ions is very rapid. At hydroxyl ion concentrations less than 0.1N, the effect of this reaction on the rate of chlorine absorption may be predicted by the penetration theory for absorption with simultaneous infinitely rapid chemical reaction. The reaction rate constant for this reaction was estimated to be on the order of 10^6 liters/(mole)(sec.).

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NOTATION

A_i = concentration of gaseous solute at liquid interface, moles/cc.
A_o = concentration of gaseous solute in bulk of liquid, moles/cc.
B_o = concentration of reactant in bulk of liquid, moles/cc.
D_A = diffusion coefficient of gaseous solute in liquid, sq. cm./sec.
D_B = diffusion coefficient of reactant in liquid, sq. cm./sec.
$\overline{D}$ = mean diameter of jet, cm.
$\overline{D^2}$ = mean of diameter of jet squared, sq. cm.
E_a = activation energy defined in Equation (9), cal./mole
F = frequency factor defined in Equation (9), liter/(mole)(sec.) for a second-order reaction
h = intermediate jet length, cm.
H = total jet length, cm.
$\Delta H^\ddagger$ = enthalpy of activation, cal./mole
k_2 = reaction rate constant, liter/(mole)(sec.) for a second-order reaction
$\overline{N}_A{}^*$ = average rate of absorption without chemical reaction, mole/(sq. cm.)(sec.)
$\overline{N}_A$ = average rate of absorption with chemical reaction, mole/(sq. cm.)(sec.)
p = steric factor in collision theory
R = unusual gas constant, cal./mole °K.
$\Delta S^\ddagger$ = entropy of activation, cal./mole °K.
T = absolute temperature, °K.
U_s = velocity of jet at its surface, cm./sec.
Z = frequency of collision, liter/(mole)(sec.) for a second-order reaction
α = function defined by Equations (6) and (7)
ϵ = constant in Equation (11)
Φ = ratio of average rate of absorption with chemical reaction to average rate of absorption without chemical reaction
θ = time of exposure of gas to liquid interface

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