ABSORPTION OF CHLORINE
IN WATER AND CAUSTIC

By

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Signature of Author

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Watertown, Mass.
May 18, 1945

Professor George W. Swett,
Secretary of the Faculty,
Massachusetts Institute of Technology,
Cambridge, Mass.

Dear Sir:

In accordance with the regulations of the Faculty, I hereby submit a thesis, entitled "The Absorption of Chlorine in Water and Caustic", in partial fulfillment of the requirements for the degree of Doctor of Science in Chemical Engineering from the Massachusetts Institute of Technology.

Yours very truly,

Edward Vivian
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I SUMMARY

The role of gas absorption in chemical engineering has become increasingly important in recent years, and the subject has attracted the attention of a large number of research engineers. Most of the effort has been directed toward the development of correlations of experimental data to provide a basis for design of absorption equipment in a wide variety of industrial applications. With the collection of more and more data, exceptions to these general correlations began to appear, the system involving chlorine and water being one such exception.

Because of the increasing interest in chlorine bleaching solutions in pulp mill operations, it was the purpose of this thesis to obtain design data for the absorption of chlorine in water and in caustic solutions, and to explain the apparent difference between the chlorine-water system and similar absorption systems.

Two experimental absorption towers, a four-inch tower and a semi-commercial fourteen-inch tower, together with the necessary auxiliary equipment were designed and constructed. From the data obtained with these experimental towers, a commercial tower was designed to meet the chlorine-water requirements of a 110-ton per day sulfite pulp mill. This tower was put into operation at the South Brewer Plant of the Eastern Corporation.
From the small amount of data on the chlorine water system which was available prior to this research, it was indicated that absorption in this system would be controlled primarily by the resistance of the liquid film. It was not possible, however, to correlate these data for chlorine with those for other liquid film phenomena such as the absorption of oxygen or carbon dioxide in water.

The results of this thesis show conclusively that while chlorine absorption in water is a liquid film phenomenon, it differs in many respects from oxygen absorption in water. It was found that the liquid film coefficient, \( k_{La} \), for chlorine and for oxygen in the same equipment is a function of the 0.6 and the 0.75 power of the liquor rate respectively. Absolute values of the coefficient vary from 13 to 80 lb.mols/(hr.)(cu.ft.)(lb.mols per cu.ft.) for chlorine and from 19 to 190 lb.mols/(hr.)(cu.ft.)(lb.mols per cu.ft.) for oxygen for liquor rates from 900 to 20,000 lbs./(hr.)(sq.ft.). Thus the coefficients for chlorine are only 40 to 70 per cent of those for oxygen in the same equipment. The chlorine coefficient was found to be independent of gas rate and a function of the sixth power of the absolute temperature, in agreement with the data on the oxygen system.

The equilibrium solubility data for chlorine in water were determined experimentally and the shape of the equilibrium solubility curve was explained satisfactorily by assuming that chlorine in solution hydrolyses to form hypochlorous acid and hydrogen and chloride ions, and that the
partial pressure of chlorine in the gas phase is proportional to the molecular or unhydrolysed chlorine in the liquid phase. Over the range of concentrations used in the absorption studies, the molecular chlorine varied from 0 to 40 per cent of the total chlorine in solution. This contrasts with the oxygen system where the partial pressure of oxygen in the gas phase is proportional to the total oxygen concentration in the liquid phase.

In an attempt to bring the chlorine system into line with other liquid film systems, a pseudo-coefficient based on the total chlorine absorbed and the molecular chlorine concentration difference across the film was developed. These coefficients vary as the 0.6 power of the liquor rate, and range from 25 to 150 lb.mols/(hr.)(cu.ft.)(lb.mols per cu.ft.) for liquor rates from 900 to 20,000 lbs./(hr.)(sq.ft.) At high liquor rates, the agreement between pseudo-coefficients and those predicted from the oxygen data is excellent, while at low rates, the pseudo-coefficients are considerably greater than predicted values.

On the basis of these results, it is concluded that the rate of absorption of chlorine in water is governed by the rate of removal of molecular chlorine from the gas-liquid interface. This, in turn, is governed by two sets of conditions: first, those conditions controlling the rate of diffusion across the film, and second, those conditions controlling the rate of the hydrolysis reaction in the film. Depending on the relative magnitude of these rates, one or
both may control the rate of absorption of chlorine. At high liquor rates, the rate of diffusion is controlling. Only slight reaction occurs within the film, and the conditions of absorption without chemical reaction are approximated, with the result that pseudo-coefficients agree with values predicted from the oxygen data. At low liquor rates, the rate of diffusion decreases relative to the rate of reaction. In this case, the rate of reaction is an added effect in removing molecular chlorine from the interface, and is equivalent to an abnormally low film thickness for a given liquor rate. As a result, the calculated pseudo-coefficient corresponds to that for a higher liquor rate, and is greater than predicted from oxygen data.

This picture of the mechanism is substantiated by a qualitative analytical treatment involving the ratio of the rate of reaction to diffusivity, and explains the 0.6 power function of the liquor rate in place of the usual 0.75 power. The analytical treatment also indicates that, at high liquor rates, over 95 per cent of the molecules diffusing traverse the film without reacting, while at low rates practically complete reaction equilibrium prevails in the film. Hence, the total chlorine concentration at the interface is evidently less than the total chlorine concentration in equilibrium with the gas, and the use of total chlorine concentrations obtained from equilibrium solubility data gives a concentration gradient far in excess of that actually existing across the film, with the result that the ordinary coefficients based on total chlorine concentrations are abnormally low.
This may be expected to be most noticeable at high liquor rates, corresponding to thin films. At low liquor rates, this effect is not so serious, and the discrepancy between the experimental values and those predicted on the basis of oxygen absorption data is much less.

Furthermore, independent of the effect of the specific rate of reaction, the adjustment of reaction equilibrium within the film because of the existing concentration gradient tends to change the shape of the molecular chlorine concentration gradient. As a result, actual rates will differ from predicted rates.

It is concluded that when the system involves chemical reaction together with absorption, extreme care must be exercised in the use of the proper equilibrium values if reliable results are to be obtained with the use of coefficients predicted from data on systems where chemical reaction does not occur. It has been shown experimentally that the data collected for the chlorine water system and expressed as values of $k_{L}a$ based on total chlorine can be used for design purposes for that system, but, at the present state of development, such data cannot always be correlated with systems involving only pure physical absorption.

In order to substantiate the conclusions drawn with regard to the chlorine water system, it is recommended that the absorption of chlorine in hydrochloric acid solutions be studied with a view to obtaining liquid film data under conditions where the hydrolysis reaction is suppressed
to a large degree. Furthermore, on the basis of the mechanism advanced, desorption coefficients would be expected to differ from absorption coefficients in such systems, and it is recommended that experimental work to investigate the desorption of chlorine from chlorine water be carried out.

In the work on the absorption of chlorine in caustic, the attempt was made to determine experimental data in the high caustic concentration range, where it was expected the resistance of the gas film is controlling. Inherent experimental difficulties gave rather poor precision to the data, and, to overcome some of these difficulties, a special calculation technique was developed to obtain coefficients from the observed data. The results indicate that, at high caustic normalities, the coefficient, $k_g a$, becomes independent of caustic concentration, and that, in this range, it can be assumed that all the resistance to diffusion is in the gas film. These gas film coefficients vary as the 0.7 power of the gas rate, and correlate reasonably well with data for other gas film systems in which $k_g a$ varies as the 0.63 to 0.8 power of the gas rate, the 0.67 power of the diffusivity, and the 0.33 power of the liquor rate. Some data were obtained on the effect of liquor rate, but, because of the extremely poor precision, these are not considered reliable.

It is concluded that systems such as chlorine in caustic leave much to be desired with respect to experimental technique for procuring reliable gas film data, and that the results support the use of the Sherwood and Holloway gas film
correlation for predicting coefficients for this system, providing sufficiently strong caustic solutions are to be used.
II INTRODUCTION

The role of gas absorption in chemical engineering in recent years has become relatively important, and has attracted the attention of a large number of research engineers. Contribution to this field of knowledge through the literature has been considerable, and the state of the science has reached an advanced stage. Most of the effort, however, has been directed toward the development of generalizations which would be suitable for design purposes in a wide variety of industrial applications, such as are found in the petroleum industry, chemical manufacturing, by-product recovery in the coke industry, and reagent manufacture in the pulp and paper industry.

As the field of knowledge of gas absorption widened, exceptions to the general correlations began to appear. One such case was the absorption of chlorine in water. Because of the importance that this operation was assuming in the preparation of chlorine water bleaching solutions in the pulp and paper industry, it was the purpose of this research, first, to obtain data on the absorption of chlorine in water to aid in the design and operation of equipment for the production of this bleaching agent, and, second, to explain the apparent exception of chlorine-water absorption to the general absorption correlation.

Although the theoretical basis for the gas absorption equations has been published in complete form, it seems advisable at this point to present a brief résumé in order
that the argument of this thesis may be followed more easily.

The operation is usually performed in some form of tower in which a solvent liquid passes downward, coming in contact with an inert gas carrying the solute gas passing upward. The rate at which mass transfer of solute gas across the liquid interface to the liquid takes place is subject to a number of conditions, and it is this rate of mass transfer that is of industrial importance. The current picture of this mass transfer, which has been substantiated by a large amount of data in the field of heat transfer as well as absorption, is that adjacent to the gas-liquid interface there are relatively stagnant gas and liquid films. As a result of concentration gradients, mass transfer occurs by molecular diffusion of the solute through these films which act as resistances in series. In the main body of the liquid, mass transfer occurs by eddy diffusion. Relative to molecular diffusion, eddy diffusion offers very much less resistance to mass transfer, with the result that concentration gradients in the main body of the gas and the liquid may be neglected in most cases. Hence, factors which affect the properties of the films, in general, control the rate of mass transfer.

The resistance of the film is usually measured by its reciprocal, the conductivity, and is called the absorption coefficient, represented by \( k_L \) or \( k_g \), depending on whether the coefficient refers to the liquid or
gas film. Equations representing the rate of absorption have been developed (27) and may be stated as follows.

\[ N_A = k_g (P_g - P_i) \] ............................(1)
\[ = k_L (C_i - C_L) \] ............................(2)
\[ = \text{Mols solute transferred per hour per sq.ft.} \]
\[ P_g - P_i = \text{concentration gradient across gas film, atm.} \]
\[ C_i - C_L = \text{concentration gradient across liquid film, lb. mols/ cu.ft.} \]

In the usual form of absorption equipment, it is not possible to evaluate the amount of surface of the interface with any degree of precision. To overcome this difficulty, the rate of solute transfer is evaluated on a volume basis.

Thus

\[ N_A a = k_g a (P_g - P_i) \] ............................(3)
\[ = k_L a (C_i - C_L) \] ............................(4)
\[ = \text{mols solute per hour per cu. ft.} \]

where \( a = \text{surface area per cu. ft.} \)

Since experimental techniques have not been sufficiently developed to permit measurement of solute partial pressures and concentrations at the interface, it is customary to evaluate absorption in terms of an overall coefficient as defined in the following equation,

\[ N_A a = K_a (P_g - P_L) \] ............................(5)
\[ = K_L a (C_g - C_L) \] ............................(6)
\[ = \text{mols solute transferred per hour per cu.ft.} \]

where \( P_g - P_L = \text{overall concentration gradient across both} \)
\[ \text{films expressed in terms of partial pressures (atm).} \]
and \( C_g - C_L = \) overall concentration gradient across both films expressed in concentration units. (lb. mols/cu. ft.)

The values of \( P_L \) and \( C_g \) are obtained from the corresponding values of \( C_L \) and \( P_g \) and the equilibrium solubility relationship for the particular solute-solvent system. If the system is such that the relationship follows Henry's solubility law, viz

\[
C = H P \quad \text{..............................}(7)
\]

where \( H \) = Henry's law constant, an expression may be obtained for the overall coefficients in terms of the individual film coefficients. Thus, for the overall coefficient expressed as a gas film coefficient, by remembering that

\[
P_g - P_L = (P_g - P_i) + (P_i - P_L) \quad \text{.........}(8)
\]

and combining equations (3), (4), (5), (7) and (8)

\[
\frac{1}{K_{ga}} = \frac{1}{k_a} + \frac{1}{Hk_L a} \quad \text{............................}(9)
\]

A similar equation for the overall coefficient expressed as a liquid film coefficient is

\[
\frac{1}{K_{La}} = \frac{H}{k_g a} + \frac{1}{k_L a} \quad \text{..........................}(10)
\]

It must be remembered that equations (9) and (10) apply only when the solubility follows Henry's law or when the concentration can be assumed proportional to the partial pressure over the range of concentrations involved.

Overall coefficients, because of their composite nature, have little meaning unless they can be interpreted
in terms of the individual film coefficients. Hence, in obtaining absorption data, unless one of the individual film coefficients is known, the effect of one of the films must be subordinated. This may be accomplished by one or both of two ways. From equation (10), it is seen that if the solute gas is only slightly soluble the term $H/k_g a$ becomes small in comparison with the term $1/k_{La}$, and the overall coefficient $K_{La}$ approximates $k_{La}$ in value. Similarly from equation (9) if the solute is readily soluble, the value of $k_{La}$ is essentially that of $k_g a$.

Furthermore, as it will be pointed out, the values of the individual film coefficients are functions of those factors which affect the film thicknesses, such as velocity of gas and liquid and the diffusivity of the solute. By suitable choice of operating conditions, it is possible to subordinate or accentuate the effect of one or the other of the films to some extent. However, it is generally the solubility relation which determines the relative effect of the two films.

On this basis, it is possible to classify types of absorption in three categories. First, so-called gas film absorption in which the gas film offers the major resistance; secondly, liquid film absorption in which the liquid film is the major resistance; and thirdly, an intermediate group in which both films offer appreciable resistance. The first group includes those systems in which the gas is very soluble, such as the absorption of
chlorine in strong caustic, the absorption of ammonia in strong sulfuric acid and, under certain conditions, the absorption of ammonia in water. Systems in which the solute is relatively insoluble comprise the second group, such as the absorption of chlorine, carbon dioxide and oxygen in water. The majority of industrial systems fall in the third group, where the gas is moderately soluble, and both films add to the resistance to mass transfer. Examples are the absorption of sulfur dioxide in water and bisulfite solutions, of ammonia in water under most conditions, of light oil in straw oil.

A comprehensive review of the data on absorption published prior to 1939 has been presented by Holloway\(^{(14)}\). The conclusions emanating from that review were:

1. The only published liquid film data were those of Sherwood, Draemel and Ruckman\(^{(28)}\) on the absorption of carbon dioxide, Johnstone\(^{(13)}\) on the absorption of sulfur dioxide and oxygen where the oxygen was the controlling factor, and Adams and Edmonds\(^{(1)}\) on the absorption of chlorine in water.

2. In the light of thesis work by Cornforth and Skaperdas\(^{(7)}\), the data of Sherwood, Draemel and Ruckman\(^{(28)}\) were believed to be in error because of misinterpretation of the analytical results.

3. Sherwood\(^{(27)}\) pointed out that the data of Johnstone\(^{(13)}\) would be expected to be high because of reaction of the sulfur dioxide and oxygen within the film, and hence, part of
the true film resistance would be omitted.

(4) The data of Adams and Edmonds\(^{(1)}\), based on equilibrium data calculated from hydrolysis constants, appeared to be abnormally low.

This situation in which the scarcity and disagreement of liquid film data were critical was remedied to a large extent by Holloway\(^{(14)}\) in presenting data on the desorption of oxygen, carbon dioxide, and hydrogen from water in a twenty-inch diameter tower, packed with various sizes of Raschig rings and Berl saddles. It was found that the value of the coefficient \(k_{la}\) varied approximately as the 0.75 power of the liquor rate depending on the type of packing, was independent of the gas rate, and varied as the 0.5 power of the molecular diffusivity. The coefficient was found to be an exponential function of the temperature. However, this is merely an empirical method for correcting for the effect of temperature on such variables as diffusivity, density and viscosity in the liquid film. In the range from 50\(^{\circ}\) to 400\(^{\circ}\)C, this relation indicates that \(k_{la}\) is proportional to \(e^{0.023t}\), where \(t\) is the liquor temperature in degrees C.

The recommended basis of correlation as derived by Holloway\(^{(14)}\) from dimensional analysis and with exponents based on his data is

\[
\frac{k_{la}}{D} = \text{constant} \left( \frac{L}{\mu} \right)^{0.75} \left( \frac{\mu}{D} \right)^{0.5} \quad \ldots \ldots \ldots \ldots (11)
\]

where \(\mu\) = viscosity of the liquid,
\[ \varrho = \text{density of the liquid}, \]
\[ D = \text{liquid diffusivity}, \]
\[ L = \text{liquid rate}. \]

Combining the various terms, a somewhat more usable expression may be obtained for purposes of discussion. Thus \( K_L \alpha \) is proportional to \( (L)^{0.75} (\mu)^{-0.25} (D)^{0.5} \).

Since the density, \( \varrho \), changes very little over the range of temperature involved, it may be neglected. A plot of \[ \frac{K_L \alpha}{(D)^{0.5}} \frac{\mu}{(D)^{0.5}} \text{ vs. } L \]
should give a straight line of slope 0.75 on log coordinates. As pointed out by Holloway\(^{14}\) the value of this slope is a function of the packing, and may vary from 0.65 for small Raschig rings to 0.6 for large rings. For purposes of clarity and for comparison with the work of this thesis, the discussion will be limited to 1-inch Raschig rings for which the value of the slope as given by Holloway is 0.75.

Prior to the work of Holloway\(^{14}\), some of the least questionable data from a technical point of view on liquid film absorption had been published by Adams and Edmonds\(^{1}\) on the absorption of chlorine in water using one-inch coke as packing material. These data were recalculated from a Practice School report\(^{11}\) using equilibrium data calculated by Adams and Edmonds\(^{1}\) from hydrolysis constants.
for chlorine in water.

However, these absorption data were obtained at three different temperatures (39°, 42-43°, 50°F.), and the effect of temperature was not appreciated at the time of their publication. Because of considerable scattering of the data and the range of variables used, the effect of temperature could not readily be observed, and it was concluded that the $K_La$ for chlorine in water was independent of temperature. With the different ranges of liquor rates used at the different temperatures (the high range at the high temperature), the indications were that the $K_La$ varied as the 0.8 power of the liquor rate. This was the result of the combined effect of temperature, liquor rate and range of liquor rates used. Actually, if the data at 42°-43°F. which are widely scattered are omitted, there are definite indications of the effect of temperature, as shown in Fig. 1. Furthermore, at both 39° and 50°, the coefficient varies as approximately the 0.6 power of the liquor rate instead of the 0.8 power as reported. The effect of temperature indicated is much greater than would be expected, $K_La$ being proportional to about the 9th power of the absolute temperature. However, the data cover a very narrow range of temperature, and, because of scattering, cannot be considered reliable with respect to the effect of temperature.

Adams and Edmonds data for chlorine absorption at 50°F. are compared with those of Sherwood and Holloway(29)
FIG. 1

DATA OF ADAMS & EDMONDS
O - RUNS AT 39°F
□ - RUNS AT 42 - 43°F
▽ - RUNS AT 50°F

SLOPE = 0.8
SLOPE = 0.6

K_L A - LB MOLS/HR - CUFT - LB MOLS/CU FT
LBS/HR - SQ FT
for oxygen absorption at 25°C in Fig. 2. From this comparison it is seen that the coefficient for chlorine absorption is approximately one third that for oxygen.

If absorption coefficients for the absorption of chlorine in water at 25°C are calculated from the oxygen absorption data using the correlation given by equation (11), curve A-A in Fig. 2 is obtained. Curve B-B in Fig. 2 represents absorption coefficients for the absorption of chlorine in water at 25°C calculated by correcting the chlorine absorption data of Adams and Edmonds for difference in temperature. The Adams and Edmonds data were obtained in a tower packed with one-inch coke, and it would be expected that the absorption coefficients would be about 20 per cent lower than those for one-inch rings. Early work(37) associated with this investigation indicated that 1½-inch coke gave coefficients approximately 25 per cent lower than one-inch rings, and one-inch coke would be expected to give coefficients slightly higher than 1½-inch coke. Curve C-C would be expected to represent absorption coefficients for chlorine in water at 25°C and for one-inch rings based on the Adams and Edmonds data. The discrepancy between the two sets of data is still considerable, and it seems evident that this difference in values cannot be attributed to the different packings and operating conditions.

In view of this, an investigation of the absorption of chlorine in water was carried out in conjunction with the work of the Bangor Station of the Practice School. A 14-inch
LIQUID FILM ABSORPTION

Q DATA OF HOLLOWAY
● DATA OF ADAMS AND EDMONDS

A - AK_{L A} FOR Cl_{2} CALCULATED FROM O_{2} DATA AT 25°C
B - BK_{L A} FOR Cl_{2} CALCULATED FROM ADAMS & EDMONDS DATA FOR 25°C & 1" COKE
C - CK_{L A} FOR Cl_{2} ESTIMATED FROM ADAMS & EDMONDS DATA FOR 25°C & 1" RINGS

O_{2}
G = 100 LBS
T = 25°C
1" RINGS

CL_{2}
G = 68 LBS
T = 10°C
1" COKE

K_{L A} - LB MOLLS/HR - FT^3 MOLLS/FT^3
L - LBS/HR - SQ.F.T.
tower packed to a height of eight feet with one-inch Raschig rings was used. A summary of this work has been presented by the author\(^{(32)}\), and published by Whitney and Vivian\(^{(37)}\). The results are shown in Fig. 3 where they are compared with the Adams and Edmonds data. The value of these data was chiefly in indicating the direction and conditions for the successful conduction of the work of this thesis. The results substantiated the effect of liquor rate as found by Holloway, agreed approximately with the data of Adams and Edmonds, and because of rather wide scattering, were inconclusive as to the effect of gas rate and temperature on the value of \(K_La\). The chief difficulties responsible for the poor results were the unsatisfactory analytical techniques used, and the highly corrosive action of the wet chlorine on the materials of construction.

One other doubtful question in connection with the data on chlorine absorption was the validity of the equilibrium data. As has been mentioned above, the best data available were those of Adams and Edmonds\(^{(1)}\), who calculated the equilibria from the hydrolysis constants for chlorine as published by Yakovkin\(^{(41)}\). Chlorine dissolved in water hydrolyses to form hypochlorous acid, hydrogen ions, and chlorine ions. At equilibrium, some of the chlorine exists as molecular chlorine in solution.

The hydrolysis equation is
DATA OF WHITNEY
AND VIVIAN - 1935
SOLUTE - CL₂ 37-70°C

DATA OF ADAMS
AND EDMONDS-----39 - 50°C

FIG. 3
Cl₂ + H₂O ⇌ HOCl + H⁺ + Cl⁻ (12)

By assuming that Henry's law applies to the molecular chlorine in solution, and knowing the hydrolysis constant, the partial pressure in equilibrium with a given concentration of total chlorine in solution can be calculated. Further development of this calculation is given in the Appendix. The few experimental data available at chlorine pressures of one atmosphere agreed well with the calculated values, but otherwise the equilibrium calculations were without experimental confirmation.

In order to operate chlorine absorption equipment over a desirable range of operating variables and still maintain a fair degree of precision in the analytical work, it was frequently necessary to operate with the lower part of the tower close to equilibrium conditions. This, of necessity, greatly augmented any small error which might exist in the equilibrium data. In view of this, it was felt necessary to determine the equilibrium data experimentally in this investigation.

It was also suggested that the low value of the overall coefficient (as compared with oxygen desorption) might be due to an appreciable resistance of the gas film. Although chlorine is very much more insoluble than ammonia, it is somewhat more soluble than carbon dioxide and oxygen. However, assuming that the data of Johnson and Doherty (8) on the absorption of ammonia in acid give the magnitude of the gas film coefficient, and taking an average value for
Henry's law constant over the range of concentrations involved, it is possible to estimate the fraction of the total resistance which is due to the gas film. If this calculation is applied to the data of Whitney and Vivian(37), the effect of the gas film is found to be from 1% to 3% of the total resistance depending on operating conditions. Thus the gas film, in itself, cannot account for the discrepancy between the coefficients for chlorine and other liquid film cases. For all practical purposes, chlorine absorption in water would be expected to be a case of liquid film controlling.

As pointed out previously, a solution of chlorine in water is in reality a solution of molecular chlorine, hypochlorous acid, hydrogen and chlorine ions all in equilibrium. The vapor pressure of chlorine at the liquid-gas interface will be due to the concentration of molecular chlorine at the interface. If equilibrium conditions exist within the liquid phase, then a statement of either the total amount of chlorine in solution or of the molecular chlorine will serve equally well in defining the vapor pressure of chlorine from the solution. However, if chlorine can diffuse from the interface, and so reduce the molecular chlorine, faster than equilibrium in the solution can adjust itself, then the total chlorine concentration no longer defines the vapor pressure of chlorine exerted by the solution. It is the molecular chlorine concentration which determines the vapor pressure of chlorine; total
chlorine is indicative of the vapor pressure only if equilibrium exists between hydrolyzed and unhydrolyzed chlorine. Applying this to the absorption of chlorine in water it would be possible to have a molecular chlorine concentration built up at the interface in excess of that demanded by equilibrium conditions unless the rate of hydrolysis was very rapid in comparison with the rate of diffusion. Unless the hydrolysis were relatively very rapid, it would be impossible to determine from the equilibrium data the actual driving force for the diffusion across the liquid film, and the best that could be obtained would be a coefficient representative for chlorine but not permitting its correlation with true liquid film diffusion phenomena. Further discussion of this complicating factor will be presented in the Discussion of Results of this thesis.

During recent years, the use of chlorine water as a bleaching agent has developed to a large extent. The chlorine is produced by the electrolysis of brine, and may be supplied to the pulp mill as liquid in tank cars, or may be produced at the mill from electrolytic cells. In the former case, the liquid is passed through a vaporizer, and in the latter case, the chlorine comes off the cells as a gas usually mixed with air. In either case, this chlorine gas mixed with more or less air is absorbed in some form of contacting equipment. At present the trend is toward regular packed absorption towers for
this operation. Construction must necessarily be tile and acid resisting cement because of the highly corrosive nature of this bleach.

Although the extensive use of chlorine water bleach is relatively recent, bleaching agents of alkaline chlorine solutions such as sodium and calcium hypochlorite have been applied extensively from the early days of the wood pulp industry. At first, ordinary bleaching powder was used, but with the development of the simple types of electrolytic cells, pulp mills began making their own bleach by absorbing chlorine from cell gas in lime slurry. The equipment used was generally crude and seldom well designed. With the need for greater control in bleach manufacture, the use of spray towers developed. For the production of certain types of pulps, it was found advantageous to use caustic in place of the lime. Although a packed tower is not suitable for the production of lime bleach because of the suspended solids in the liquor, it can be used to advantage in the production of caustic or soda bleach. But here, as is the case with many absorption operations, suitable data for design were non-existent. It was partly to satisfy this need that a study of the absorption of chlorine in caustic solutions was included in the work of this thesis.

It is evident immediately that the absorption of chlorine in caustic is a case where the diffusion is complicated by chemical reaction in the liquid film. In the
liquid film, as chlorine diffuses from the liquid interface, caustic diffuses from the main body of the liquid, and the result is a reaction interface or zone. The position of this interface will depend primarily on the relative rates of diffusion of caustic and chlorine, and these rates are in turn dependent on the respective concentrations. By maintaining a sufficiently high caustic concentration, it should be possible to maintain the reaction interface at or very near the gas-liquid interface. Under this condition, the only important resistance to the diffusion of chlorine from gas to liquid is the gas film. Thus a study of this system should yield valuable data on gas film absorption. The work and discussion of this thesis on the absorption of chlorine in caustic will be limited to the case of true gas film absorption.

Holloway\(^{(14)}\) has pointed out that much of the data published on the gas film may not be true gas film absorption. This is the case with data on the absorption of ammonia in water where the resistance of the liquid film may be as high as 20 per cent depending on operating conditions. Assuming that vaporization and condensation of water and solvents in packed towers can be considered as absorption, the best correlation for the gas film can be expressed as follows\(^{(14)}\).

\[
k_g a = \text{constant} \left( G \right)^{0.63} \left( L \right)^{0.33} \]

This correlation checks fairly well with a number of
investigations. Doherty and Johnson\(^{(8)}\) absorbing ammonia in 3.5 \(N\) sulfuric acid solution found \(k_g a\) to vary as the 0.63 power of \(G\). The data on the absorption of \(NH_3\) in water by Kowalke, Hougen and Watson\(^{(19)}\) also fit this correlation well with \(k_g a\) proportional to the 0.7 power of the gas rate. Rennolds\(^{(25)}\) and Kowalke, Hougen and Watson\(^{(19)}\) also agree reasonably well with the exponent of 0.33 for the effect of liquor rate.

Although the use of chemical reaction has been used recently by a number of investigators to suppress the effect of the liquid film, failure to appreciate the many factors involved has lead to inconclusive and conflicting results. Extensive work has been carried out continuing the work of Doherty and Johnson by Fellinger\(^{(10)}\) using a packed stoneware tower. His results were entirely out of line, a matter which has not been satisfactorily explained as yet. Failure to appreciate the full significance of the so-called critical concentration of the absorbing solution can lead to misleading results which are incapable of being properly interpreted. Further discussion of this subject is given in the Appendix.

In the study of absorption of chlorine as with many of the industrial gases which are highly corrosive and poisonous, difficulties are encountered which render its use on a semi-industrial scale impractical in the ordinary chemical engineering laboratory. First, there is the problem of an adequate supply of the gas, and second, and more
critical, the problem of the disposal of the highly corrosive chlorine water and toxic exhaust. Fortuitously, the arrangement of the Bangor Practice School Station with the South Brewer plant of the Eastern Corporation provided a satisfactory solution to both of these serious difficulties. Throughout this investigation, it was possible to withdraw chlorine from the cell gas lines in the Chemical Plant, and after its use in the experimental equipment, both the liquor and exhaust gas were returned to the Company's bleach manufacturing process. In the study of the absorption of chlorine in caustic, the caustic was supplied by the Company and later returned to the bleach process.

With these facilities available, it was the main purpose of this thesis to study the absorption of chlorine in water and the factors affecting it in semi-commercial packed towers; to obtain data suitable for the design and control of a commercial absorption tower for the preparation of chlorine water bleaching solution; and to compare and, if possible, correlate data on the absorption of chlorine with absorption theory in general. Second, it was proposed to study the absorption of chlorine in caustic solutions insofar as time would permit to obtain data for the design and control of equipment for the production of soda bleach, and to further the study of absorption for the case of gas film controlling. Third, after design (32) and construction of a commercial tower by the Company, it was proposed to present data representative of absorption in the commercial tower.
III PROCEDURE

General Design of Experimental Equipment.

The apparatus and procedure used in this research developed as the result of attempts to satisfy several conflicting factors. Materials of construction were definitely limited by the corrosive nature of wet chlorine, and some of the materials, which were sufficiently resistant to the action of the chlorine, were prohibited on the basis of their cost. The corrosion and toxicity factors imposed the necessity of operating the proposed system under a slight vacuum, since the suitable materials were more or less gas porous.

It was desirable to design the equipment large enough to be representative of industrial absorption, and yet, within the range where the quantities of chlorine and liquor could be handled conveniently. This consideration determined the allowable cross-section of the tower, and in turn, the packing material. If the ratio of the cross-section of the tower to the size of the packing is below a value of about eight, it is reported that there is a tendency for the wall effect to become appreciable, and the resulting data may not be representative of the packing material.

The minimum height of packing in the tower was governed by the height necessary for its precise measurement, and by the desirability of reducing to a minimum the percentage of mass transfer taking place in
the sections of the tower above and below the packing. The upper limit of the height of packing was governed by the amount of absorption occurring in the tower. If this were too great, near equilibrium conditions would be established between the gas and the liquor, and the data would lack precision because of small errors in concentration determinations being magnified by taking the small difference between them as the driving force.

During the course of this investigation three towers were designed and constructed, - two for the experimental work based on the factors already discussed, and one for the commercial production of chlorine water bleach for use in a 110-ton sulfite pulp mill. The first experimental tower designed and constructed was 14-inches in diameter, and could accommodate up to eight feet of packing. With the exception of a few preliminary runs using one-and-a-half-inch graded coke as a packing material, one-inch tile Raschig rings were used throughout the investigation. On the basis of the experience gained with this tower, and the difficulty encountered in handling the relatively large amount of materials, a second tower four inches in diameter was constructed, and operated with two feet of packing. The major part of the work was performed by the use of the four-inch tower, and the data compared with the fourteen-inch tower. Since the data obtained with the four-inch tower are the most significant, it will be described first.
Four-Inch Tower.

The experimental setup including auxiliary equipment is shown diagramatically in Fig. 4 and the detail of the four-inch tower is shown in Fig. 5. The tower was constructed from two sections of four-inch "transite" pipe, fitted together with hardwood flanges, and the assembly held together with tie-rods. A wooden grid to support the packing was built into one of the wooden flanges, and inserted between the two sections of transit pipe. About six inches of free space was provided above the packing to permit separation of the gas and liquor. Below the packing support, a one-foot length of pipe provided a liquid seal for the tower. Rich chlorine gas entered the tower immediately below the packing support. A liquor distributing system was built into the top flange. This consisted of a circular weir, and a series of down-comers to conduct the liquor to the surface of the packing before it could come in contact with solute bearing gas. These down-comers were specially located to insure good distribution throughout the cross-section of the packing. The down-comers were constructed of glass, and the weir and an inverted cup which formed a water seal at the top of the tower were of sheet copper.

This tower was packed with one-inch tile Raschig rings to a height of two feet. Although the ratio of tower diameter to packing size was only four in this
FIG. 4
FLOW DIAGRAM OF EXPERIMENTAL APPARATUS

P - STATIC PRESSURE GAGES
S - SAMPLING POINTS
T - THERMOMETERS
FIG. 5
DETAIL OF EXPERIMENTAL TOWER

LIQUOR FEED LINE
LIQUOR SEAL
LIQUOR DISTRIBUTING PLATE
MANOMETER
EXHAUST GAS LINE
4" I.D. TRANSITE PIPE
BASE PLATE
SAMPLING TUBES
MANOMETER
GAS FEED LINE
LIQUOR LINE
VENT
TRAP
set-up, it was found from operation of the fourteen-inch tower to be advantageous to compromise in this respect to obtain more consistent data as to the effect of operating variables on the rate of absorption. With good liquor distribution, it was expected that the relative values of the coefficients under varying operating conditions would not be seriously affected, although the absolute values might be in error. Actually, as will be shown later, the small diameter has practically no effect on the values of the coefficients in this case.

The liquor used throughout the study of the liquid film absorption of chlorine was water taken from the plant mains. This water had been treated by chlorination and, after lime and alum additions by settling and sand filtering. It was found that impurities remaining in this water were inert to the action of chlorine. Furthermore, the presence of free chlorine in the water could not be detected.

The liquor was fed to the tower through a constant-head tank and a calibrated orifice. A series of orifices was constructed to cover the desired range of liquor rate, and these could be inserted in the liquor line interchangeably. The liquor from the tower passed through a U-tube seal and vent, and was then introduced below the surface of a tank of strong caustic. This provided an effective means of fixing the free chlorine in the liquor.
The caustic and dissolved chlorine were then turned into
the plant soda bleach preparation system. The feed to
the tower was constructed of iron pipe, the liquor dis-
charge line was of one-and-a-quarter-inch glass tubing.
Means were provided in the feed line for checking the
calibration of the orifices frequently.

The gas lines to and from the towers were constructed
entirely of one-and-a-quarter-inch glass tubing. Rich
chlorine gas was drawn from the plant mains, and diluted
with air. The cell gas was saturated and at relatively
high temperature (150°F) and, although a saturator was
used in some of the early runs, it was found to be un-
necessary, since after cooling essentially to room
temperature in the long glass line the gas mixture was
close to saturation. An Orsat apparatus was used as a
control over the ratio of cell gas to air.

From the top of the tower, the exhaust gas passed
through a calibrated glass venturi-meter. Two of these
venturi-meters were constructed to cover the desired
range of gas rates. The gas flow was maintained by a
compressed-air ejector which was constructed of glass,
and the discharge from this ejector was introduced into
one of the plant bleach towers. Since the characteristics
of the ejector were such that it operated most satis-
factory at more or less constant rate, the gas rate was
controlled by an air bleed downstream from the tower and
venturi-meter.
Sampling points were provided in all lines in order to determine the concentration of chlorine in the gas and liquor to and from the tower. The gas stream could be sampled just before it entered the tower. This was used, however, only in those runs where a material balance was to be calculated. In the majority of the runs, since the difference between inlet and outlet gas concentrations was so small, accurate material balances were not determined experimentally and hence, only the exit gas analysis was obtained. Sampling and analysis were performed by means of evacuated gas-weighing bulbs.

Liquor samples could be taken at four points, one sample from the trap and three from sample cups immediately below the packing material. A number of runs was made using these four sample points, and in this way it was possible to evaluate the effect of absorption below the packing. Since use of the three sampling points was extremely difficult and time consuming, only the trap sample was used in the latter part of the work after the end effect had been determined. Samples of the water fed to the tower were also taken at intervals, and in no case was free chlorine found. Details of the analytical procedure will be found in the Appendix.

The temperature of the gas entering and leaving the tower was measured. The liquor temperature was controlled by injection of steam into the water line to the constant head tank. In all runs except where the effect of
temperature was being investigated, the water temperature was held at 70\(^{\circ}\text{F.}\)

The general procedure followed in making a run consisted of, first, setting the water rate and adjusting the water temperature. Then the ejector was turned on, and the gas rate and composition were adjusted. After running about ten minutes to allow the system to reach steady state operation, a liquor sample was taken and analysed for free chlorine. Ten minutes later, a second liquor sample was taken and analysed. If the analyses checked, the exit gas sample was taken in an evacuated bulb, the water and gas-rate manometer readings, temperatures and static pressure of the gas recorded. If the liquor analyses did not check, a third sample was taken after an interval of ten minutes. This procedure was followed until check analysis showed the system to be in equilibrium. Except when the system was first started up after being shut down overnight, it was found that ten minutes was sufficient time for establishing equilibrium operation.

**Semi-commercial (14-inch) Tower.**

In the use of the fourteen-inch tower, the system and procedure were identical with the above description except that larger liquor lines were used. Unfortunately larger gas supply lines were not available, and hence, this phase of the investigation was limited to the use of relatively low gas rates. The tower was constructed of a ten-foot section of fourteen-inch redwood pipe, capped at
each end by wooden flanges. As originally designed and constructed, a support for the packing was built into the tower one foot from the bottom and a liquor distributing plate was installed at the top. Eight feet of one-inch Raschig rings were dumped into the tower. All wooden and metal surfaces exposed to the chlorine gas were coated with chlorine-resistant plastic gum.

After the completion of the preliminary work on this tower, a more satisfactory support for the packing and a liquid distributing plate with sixteen downcomers were designed similar to those used in the four-inch tower. Only four feet of packing was installed. The data reported on the fourteen-inch tower in this thesis were obtained with the redesigned tower.

**Commercial Tower.**

Using the data obtained in the preliminary work of this thesis, a commercial tower for the production of chlorine-water bleaching solution was designed and constructed by the plant. It consisted of a 1.6 x 3.7 ft. rectangular tower (Fig. 6), packed to a height of 10.25 ft. with two-inch tile Raschig rings. The tower was built of concrete with acid-resisting tile lining. In testing this tower, water was fed to the top of the tower through a calibrated orifice, and the chlorine fed to the tower was determined by the caustic output of the electrolytic cell room. Concentrations of the effluent liquor and inlet gas composition were determined. The temperature of
Fig. 6.
CHLORINE-WATER TOWER

Cross-section area of packing - 5.92 sq.ft.
Height of packing - 10.25 ft.
Packing - 2 inch Raschig rings
the feed water was automatically controlled at approximately 65°F. Because of the inflexibility of the system, it was possible to obtain data at one gas rate only and over a relatively narrow range of liquor rates.

Desorption of Oxygen.

In order to insure a satisfactory basis for the comparison of the absorption of chlorine with other liquid film phenomena, it was desirable to have a means of comparing the equipment used in this research with that of other investigators. To do this, the extremely simple procedure developed by Holloway\(^{(14)}\) for the desorption of oxygen from water was used. The water fed to the tower was enriched with pure oxygen, analysed for dissolved oxygen before and after passing over the packing, and the temperature and water rate recorded. The equilibrium solubility relationship was determined for the particular water used. Coefficients over the range of liquor rates used in this thesis were calculated from the data on both experimental towers.

Solubility of Chlorine in Water.

As has been pointed out, previous experimental data on equilibrium solubility for chlorine and water were somewhat scarce and in poor agreement. Up to the time of this investigation, the most reliable data were those of Adams and Edmonds\(^{(1)}\) calculated from the hydrolysis constants of Yakovkin\(^{(41)}\). To remedy this situation, the solubility relationships for chlorine and
water were determined experimentally in this research. The apparatus was essentially that used by White$^{(34)}$ with minor modifications. It consisted of a double flowmeter (Fig. 7), which proportioned the relative amounts of chlorine and nitrogen necessary to produce the desired concentration of chlorine; a heating or cooling coil through which the prepared mixed gas passed; a gas bubbler to saturate the mixture; the equilibrium cell which contained about 150 ml of liquid through which the saturated gas mixture passed; a manometer to determine the total pressure in the equilibrium cell; a 250 ml or 500 ml gas weighing bulb to determine the exact mole fraction of chlorine in the gas mixture at equilibrium; a 250 ml weighing bulb into which 5 to 10 ml of the liquid in the cell could be withdrawn and analysed; and a thermostat bath capable of maintaining a constant temperature within 0.05°C in which all of the equipment except the flowmeters was immersed.

All of the equipment which came in contact with chlorine was constructed of glass. The chlorine and nitrogen gases were obtained from cylinders; the chlorine analysed 98.5% chlorine and 1.5% air; and the nitrogen contained less than 1.0% oxygen. Since oxygen has no effect on the equilibrium, these gases were not purified.

A typical run was carried out as follows: after adjusting the thermostat to maintain the desired temperature, distilled water was admitted to the equilibrium cell to bring the level to the desired point. The cylinder gases
FIG. 7

EQUILIBRIUM APPARATUS

FLOWMETERS

CL₂

N₂

EXHAUST

TO MANOMETER

GAS SAMPLING POINT

EQUILIBRIUM CELL

COOLING COIL

GAS SATURATOR

THERMOSTAT

LIQUOR SAMPLING POINT
were turned on and the ratio of chlorine to nitrogen adjusted approximately to the desired value. The total rate of gas flow was about 200 ml per minute. The flowmeters were used only to proportion the gas approximately and to maintain this proportioning constant during a run.

After the apparatus had been allowed to run for an hour, samples of the exhaust gas and of the liquor in the equilibrium cell were taken and analysed. At the end of another half-hour, a second set of samples was taken. If the two sets checked, the system was assumed to be in equilibrium, and the temperature of the bath and pressure in the cell were recorded. If they did not check, a third set was taken a half-hour later. In very few cases did it take longer than an hour for equilibrium to be attained. The proportion of chlorine in the gas was then changed and the apparatus was ready for another run. In this way, it was possible to approach equilibrium in two ways - that is, by increasing or decreasing the liquor concentration.

The methods of analysis for the gas and the liquor were the same as those used throughout this investigation, and are described in the Appendix.

Absorption of Chlorine in Caustic.

For the work on the absorption of chlorine in caustic, the four-inch tower was used exclusively. A caustic feed tank with cooling coil and pump were installed. The gas lines were the same as used in the work on chlorine water. The liquor effluent from the tower was discharged to the
plant system.

To make a run, $50^\circ$ Be caustic was diluted with water to the desired normality and cooled. Then the gas rate and composition were adjusted. The caustic solution was then pumped through the tower, and after a 15 - 20 minute interval, a sample of the caustic feed, gas samples at inlet and outlet were taken, temperatures and rate manometer readings were recorded. Outlet liquor samples were titrated for caustic normality.

**Equations.**

The equations used in calculating coefficients from the data of this research are developed in the Appendix and summarized here.

For the absorption of chlorine in water, $K_{La}$ is defined as follows.

$$K_{La} = \frac{L}{\varrho h} \int_{C_1}^{C_2} \frac{dC}{Q-C} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (14)$$

where $K_{La} = \text{overall coefficient, lb.moles/(hr.)(cu.ft.)}$

(lb.moles per cu.ft.),

$L = \text{liquor rate, lbs./(hr.)(sq.ft.)},$

$h = \text{height of packing, feet},$

$C = \text{concentration of total chlorine, lb.moles/cu.ft.}$

$\varrho = \text{density of the liquor, lbs. per cu. ft.}$

subscripts $1 = \text{conditions at the top of the tower,}$

$2 = \text{conditions at the bottom of the tower,}$
\( c \) = concentration of total chlorine in the liquid in equilibrium with the partial pressure of chlorine in the gas phase.

In most of the runs, it was permissible to assume a straight line relationship for the equilibrium solubility of chlorine in water for the range covered in a single run. On this assumption, the equation defining the coefficient was integrated, and used in the following form.

\[
K_{L_a} = \frac{L (C_2 - C_1)}{\varphi h \Delta C_{1m}} \quad \text{(14a)}
\]

where \( \Delta C_{1m} = \log \text{mean of the driving force at the top and bottom of the tower,} \)

\[
= \frac{(C_1 - C_0) - (C_2 - C_0)}{\ln \frac{(C_1 - C_0)}{(C_0 - C_2)}} \quad \text{(15)}
\]

In those cases where the range of partial pressures and concentrations involved was sufficiently large to introduce an error of about 3\% by the use of \( \Delta C_{1m} \), equation (14) was graphically integrated.

While the absorption coefficient is inversely proportional to the resistance to diffusion, a related quantity, called the height of a transfer unit (H.T.U.) is proportional to the resistance. The quantity has the units of feet, and is preferred by some. The H.T.U. for the liquid film and its relation to the absorption coefficient may be defined as follows.
\[
(H.T.U.)_L = \frac{L}{q_{K_{La}}} = \frac{hC}{(C_2-C_1)} \quad \ldots \ldots \ldots \ldots (14b)
\]

Where gas-film coefficients were calculated from the data on chlorine absorption in caustic, an attempt was made to allow for the wide variation in gas rate which occurred within the tower due to the large amount of absorption taking place. The coefficient was assumed to be a power function of the total mass gas rate, that is, \( \dot{G}_1^n \). This function was incorporated in the differential equation, and the coefficient calculated for a particular gas rate. When \( n = 0.8 \), the equation defining the coefficient is as follows.

\[
K_{g,a}(P_{Bm})_1 = \frac{Gn(42P_1+29\pi)^{0.8}}{n(\pi-P_1)^{0.8}} \int_{P_1}^{P_2} \frac{dP}{\left(42P+29\pi\right)^{0.8}(\pi-P)^{1.2/n}} \quad \ldots (16)
\]

where \( K_{g,a} = \) overall coefficient, lb. moles/(hr.) (cu.ft.)(atm.),

\( P_{Bm} = \) log mean inert gas pressure at the gas inlet, atm.,

\( G = \) inert gas rate, moles/(hr.) (sq.ft.),

\( \dot{G}_1 = \) total mass gas rate, lbs/(hr.) (sq.ft.),

\( \Pi = \) total pressure, atm.,

\( P = \) partial pressure of chlorine, atm.,

\( n = \) power of the function relating \( K_{g,a} \) and \( \dot{G}_1 \).

The usual equation used to define the gas-film coefficient, as given below, represents an average coefficient for the range of gas rates existing in the tower. With dilute gases, the variation in gas rate through the
tower becomes insignificant, but where the use of concentrated gases is imperative, as in most cases of true gas film absorption (vaporization excepted), it must be taken into consideration.

\[
K_g a(P_{Bm}) = \frac{G \pi}{n} \int_{P_1}^{P_2} \frac{P_{Bm} \, dP}{(\pi-P)^2(P-P_e)} \tag{17}
\]

For the case of the absorption of chlorine in strong caustic \( P_e \) is equal to zero.
IV RESULTS

The results of this thesis are presented in graphical form, and are divided into five sections as follows:

(1) Results obtained with the tower four inches in diameter, showing the effect of operating variables on the absorption of chlorine in water. Fig. 8, 9, 10, 11, and 12.

(2) Results obtained with the semi-commercial fourteen-inch tower and the commercial tower producing chlorine-water bleach. Fig. 13 and 14.

(3) Experimentally-determined data on the solubility of chlorine in water. Fig. 15, 16, and 17.

(4) Comparison of the experimental towers used in this research with that of Holloway. Absorption of oxygen in water. Fig 18.

(5) Results obtained with the four-inch tower in the study of the absorption of chlorine in caustic. Fig. 19, 20, and 21.
FIG. 10

SOLUTE - CL₂
G - 127 LBS/HR-FT²
L - 9000 LBS/HR-FT²
PACKING - 1" RINGS
TOWER DIA. - 4"

Kₘ₀ = LB, MOLS/HR·FT³ - MOLS/FT³

TEMPERATURE - °F
SOLUTE - CL₂
G - 127 LBS/HR.- FT.
TEMPERATURE - 70° F
PACKING - 1 INCH RINGS
TOWER DIA. - 4 INCHES

END FACTOR = \( \frac{K_{LA \ [\text{PACKING}]} }{K_{LA \ [\text{OVERALL}]} } \)

L - LBS/HR. - SQ. FT.
Fig. 14

Solute - Cl\(_2\)
Temperature - 70°F
FIG. 15

SOLUBILITY OF CHLORINE IN WATER

○ - Solubility at 25°C
△ - " " 20°C
□ - " " 15°C
● - " " 10°C

Pressure (atmospheres) vs. Concentration (gms. C<sub>2</sub>/100 gms. H<sub>2</sub>O)
FIG. 16

SOLUBILITY OF CHLORINE IN WATER

CONCENTRATION - MOLS/CU. FT

PRESSURE - ATMOSPHERES

TEMPERATURE - °F

0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001

50 55 60 65 70 75 80
FIG. 17

SOLUBILITY OF CHLORINE IN WATER

CONCENTRATION - MOLS/CU FT

PRESSURE - ATMOSPHERES

TEMPERATURE - °F

0.0040

0.0035

0.0030

0.0025

0.0020

0.0015

0.0010

0.0005

0.0000

0

50 55 60 65 70 75 80

9-16-40
FIG. 20

$K_{GA}(p_{BM}) - \text{lb mol/s} / \text{hr-ft}^3$

LIQUOR RATE - 12,300 LBS. PER HR. - SQ. FT.
Packing - 1" RINGS
TEMP - 70-80°F

G - LBS. / HR.-SQ.FT
V. DISCUSSION OF RESULTS

The results of this thesis have been presented in the order of their significance, and this order will be followed in their discussion.

The effect of operating variables, such as liquor rate, gas rate, temperature and concentration of chlorine in the gas, has been determined for the absorption of chlorine in water. A tower of relatively small cross-section was used, and packed with one-inch rings. It will be pointed out later that, although the ratio of tower diameter to packing size was only 4, liquor distribution was sufficiently satisfactory so that the results may be considered representative for one-inch ring packing.

Liquor Rate.

The variation of the liquid film coefficient, $K_{La}$, with liquor rate is shown in Fig. 8. Thirty four runs were made at a constant gas rate of 127 lbs./(hr.)(sq.ft.) and temperature of 70°F. Over the range of liquor rates from 900 to 18,000 lbs./(hr.)(sq.ft.) the data define a relationship such that $K_{La}$ is proportional to the 0.6 power of the liquor rate L. The maximum deviation from the correlation is 15 per cent, and the average deviation 5 per cent. Above a liquor rate of 18,000 lbs/hr, there are indications that the rate of increase of $K_{La}$ with liquor rate is dropping off. This has been found to be the case by other investigators\(^{(14)(29)}\). The loading point for this particular packing is about 20,000 lbs./(hr.)(sq.ft.)
Since it has been shown\(^{14}\) that it is not economical to operate absorption equipment at liquor rates much above the loading point, liquor rates above 27,000 lbs./(hr.)(sq.ft.) where loading was definitely in evidence were not used in this research.

In the correlation of \(K_L a\) with the 0.6 power of \(L\), the exponent 0.6 is somewhat lower than has been previously reported for liquid film absorption with one-inch ring packing.

Adams and Edmonds\(^{1}\) reported a value of 0.8 for the absorption of chlorine in water, using one-inch coke as packing. As discussed in the Introduction, it would be expected that the coefficient for one-inch coke would be approximately 20 per cent lower than that for one-inch rings, but that about the same function of liquor rate would exist for both packings. It was also pointed out in the Introduction that Adams and Edmonds data were obtained at three different temperatures (39\(^{0}\), 42-43\(^{0}\), 50\(^{0}\)), and that different ranges of liquor rates were used at the different temperatures: the highest liquor range at the highest temperature. Since the data were scattered, and the effect of temperature was not fully appreciated, all the data were considered together, with the result that \(K_L a\) appeared to vary as the 0.8 power of the liquor rate. Actually, this conclusion is due to the combined effect of liquor rate, temperature and the range of liquor rates used. When the widely scattered
data at 42-43°F. are omitted, a definite temperature effect is observed (see Fig. 1), and furthermore, the $K_La$ is then found to vary as the 0.6 power of the liquor rate, in agreement with this thesis. Converting the Adams data at 50° and 39° to 70° according to the temperature correlation found in this thesis and discussed below, coefficients about 10 to 15 per cent lower than those shown in Fig. 8 are obtained. This is good agreement considering the different systems used.

Sherwood and Holloway\(^{(29)}\) correlated their data on oxygen, carbon dioxide and hydrogen with the 0.75 power of liquor rate. Data on chlorine have been published by Whitney and Vivian\(^{(37)}\) where $K_La$ was correlated by the 0.7 power of the liquor rate. These latter data were subject to rather large experimental error, and at the time of the publication, the importance of temperature on the value of the coefficient was not appreciated.

In this thesis, however, the lower power function cannot be attributed to experimental error, and it is concluded that the effect of liquor rate on the overall coefficient is less than for other liquid film phenomena, such as oxygen and carbon dioxide absorption. This will be further discussed in a later section.

**Gas Rate.**

Gas rate was found to have no appreciable effect on the value of the coefficient, as shown in Fig. 9. This is in agreement with Sherwood and Holloway\(^{(29)}\) for liquid
film absorption of oxygen and carbon dioxide. The average deviation of the data is about 7 per cent. Any effect which the gas rate may have is therefore less than this over the tenfold range of gas rates investigated, and is for all practical purposes negligible. Nineteen runs were made at a constant temperature of 70°F and at liquor rates of 2000, 5000 and 9000 lbs./(hr.) (sq.ft.), and the range of gas rates investigated was from 60 to 600 lbs./(hr.) (sq.ft.).

**Temperature.**

The effect of temperature of the liquor on $K_La$ is shown in Fig. 10, where the log of $K_La$ is plotted against the liquor temperature in degrees F. The straight line correlation leads to a function of the following form.

$$K_La = C_{\text{nt}}^{-m}$$

Where $C$, $n$ and $m$ are constants. If $t$ is in degrees F., $n$ has the value 0.0115, and if $t$ is in degrees C., $n$ has the value 0.021. The range of temperature covered was 37° to 90°F. Holloway(14) reports a similar correlation for the effect of temperature on the absorption of carbon dioxide and oxygen in which the value of $n$ is 0.023, where the water temperature is expressed in degrees C. This agreement is surprisingly close when it is considered that the correlation for oxygen and carbon dioxide is based on relatively few data which could
easily be correlated to give a slightly lower effect of temperature.

A more effective and useful correlation for the effect of temperature can be obtained by considering the temperature scale in Fig. 10 to be an expanded log scale in which absolute temperatures are plotted. This leads to the conclusion that the liquid film coefficient is proportional to the 6th power of the absolute temperature. Haslam, Hershey and Kean(12) have reported $K_La$ for SO$_2$ in water as being proportional to the 4th power of the absolute temperature. In view of the agreement between the effect of temperature on the liquid film coefficient for oxygen, hydrogen, carbon dioxide and chlorine, it seems that the 6th power of the absolute temperature is more representative. A comparison of the effect of temperature on the absorption coefficient for these four gases is given in Fig. 22, values being relative only.

It should be pointed out, however, that the precision in determining this power function is extremely poor since the absolute temperature range is small, and as can be seen from Fig. 22, the difference in slope between the Haslam SO$_2$ data and the Cl$_2$ data is very slight.

As mentioned previously, a temperature effect can be found in the chlorine data of Adams and Edmonds(1), but this effect is somewhat greater than that reported
FIG. 22

EFFECT OF TEMPERATURE ON $K_{L_{A}}$
RELATIVE VALUES ONLY

$K_{L_{A}}$: LB MOLS/HR + FT: CUF = MOLY/CUF

$H_{2}$
$O_{2}$
$CO_{2}$
$Cl_{2}$

$SO_{2}$

TEMPERATURE °F

50  60  70  80  90
here. Over the short temperature range of data, it is estimated that $K_La$ varies as the 9th power of the absolute temperature. This discrepancy is not serious, however, since their data are not considered reliable with respect to the effect of temperature because of scattering of the data and the short temperature range covered.

**Chlorine Pressure.**

It has been generally considered that one of the most effective means of checking the accuracy of the equilibrium data used in work on absorption is a determination of the constancy of the coefficient with variation in the solute gas pressure in the tower. By varying this solute pressure with other operating variables held constant, the magnitude of the driving force giving rise to the absorption is varied, and this, in turn, changes the relative effect of constant errors which might exist because of inaccuracy in equilibrium data.

A series of runs were made at a liquor rate of 9,000 lbs./(hr.)(sq.ft.) and 70$^\circ$ F with the chlorine pressure in the entering gas ranging from 0.11 to 0.35 atmospheres. In addition to this, the data obtained in the investigation of the effect of liquor rate were converted to a liquor rate of 9,000 lbs./(hr.)(sq.ft.) by the function of $L$ to the 0.6 power. These values were then plotted against the chlorine pressure in the
entering gas, as in Fig. 11. Although there is considerable scattering of the data, the average deviation from a horizontal line is well within the experimental error. Thus, it may be concluded, on the basis of this criterion, that with the equilibrium data used, the chlorine pressure in the entering gas had negligible effect on the value of $K_{La}$. That this criterion may not always lead to a reliable conclusion will be discussed in a later section.

End Factor.

A factor which interferes with the interpretation and analysis of absorption data obtained in relatively short towers is the amount of mass transfer which takes place in the free space necessary for separation of the countercurrent gas and liquor streams above and below the packing. To be of use in commercial tower design, the data must be representative of the absorption taking place within the packing. As was pointed out in the section on Procedure, the end effect due to absorption above the packing was effectively removed by the suitable design of a liquor distributing system which conducted the entering liquor to the surface of the packing without permitting it to come in contact with solute-bearing gas.

At the base of the tower, the system was not sufficiently well designed to overcome this difficulty. It was originally planned to use a series of sampling
cups installed immediately below the packing support. In general, this method proved unsatisfactory, chiefly because of the difficulty in keeping gas from being trapped in these liquor sampling lines, and also because of the effect that any variations in concentration across the tower from time to time are greatly magnified.

A series of runs were made in which samples, considered to be satisfactory, were obtained from these sampling cups. At the same time, the liquor flowing from the bottom of the tower was sampled at the trap. Coefficients based on the analysis of these samples were calculated, and the ratio of \( K_{L}^{a} \text{(packing)} \) based on the cup samples to \( K_{L}^{a} \text{(overall)} \) based on the trap sample was determined as a function of the liquor rate. This ratio, referred to as the "end factor", is plotted against the liquor rate in Fig. 12.

It is seen that approximately 88 per cent of the total absorption capacity is in the packing. Since the height of the packing was 2.0 feet, the bottom section of the tower was equivalent to approximately 0.25 feet of one-inch rings. This end factor is for all practical purposes independent of liquor rate, and hence, the effective packed height of the tower was taken as 2.25 feet.

In all the data of this investigation in which the four-inch tower was used, calculations were based on the so-called trap sample and an effective height of 2.25
feet of packing. Thus the data of this thesis can be considered as being representative for the absorption of chlorine in water in a tower packed with one-inch rings as far as end effects are concerned. The values of $K_La$ reported may also be considered as having been obtained by calculating the coefficient for a packed height of 2.0 feet and multiplying the result by 1.125.

**Semi-Commercial Tower.**

In general, the work performed on the semi-commercial fourteen-inch diameter tower was more or less unsatisfactory because of inadequate design of auxiliary equipment\(^{(32)}\). The operation of the tower was limited to extremely low gas and low liquor rates, and many of the irregularities encountered can be attributed to poor gas distribution due to faulty design of the gas feed system. The most reliable of these data are presented in Fig. 13. It is seen that there is a spread of about 20 per cent. The coefficient is found to increase as the 0.6 power of the liquor rate, in agreement with the work already reported here. In absolute value, however, these coefficients are about 20 per cent lower than those obtained with the small tower. This cannot be attributed to the fact that the two towers differed because of size, as will be shown in the section discussing the absorption of oxygen.

Some of the early work on this tower was reported by Vivian\(^{(32)}\), and published by Whitney and Vivian\(^{(37)}\) because
of immediate need for data by the pulp industry for the design of commercial bleach towers. It was reported that $K_La$ was proportional to the 0.75 power of the liquor rate and independent of temperature. The data lacked sufficient precision to distinguish the effect of temperature, and were based on equilibrium data calculated by Adams and Edmonds\(^1\). In a later paper published by Whitney and Vivian\(^{39}\) it was reported that these data were low by 10 to 40 per cent depending on the liquor rate, because of errors in the equilibrium data of Adams and Edmonds. The recalculated data using the equilibrium data of this investigation correlate with the 0.6 power of the liquor rate, and are in reasonable agreement with the data of Fig. 13.

The fact that these data are about 20 per cent lower than the data obtained with the small tower is not well understood. These two sets of data are compared in Fig. 14. The semi-commercial tower was packed to a height of four, while the experimental tower operated with an effective height of 2.25 feet, with the result that, at corresponding liquor rates, equilibrium conditions were more nearly approached in the case of the larger tower. However, the fact that the initial chlorine pressure in the gas was not found to have an effect on the $K_La$ tends to substantiate the equilibrium data, and the value of $K_La$ would be expected to be independent of the height of packing. The possibility of channelling of the
be pointed out that the selection of two-inch rings over one-inch rings is a result of an economic balance which, in general, is the governing factor in choice of the packing size for commercial equipment.

Only a small range of variables could be investigated, but over the range of liquor rates from 3,500 to 6,000 lbs./(Hr.)(sq.ft.), the values of $K_L$ are approximately 65 per cent of those for the four-inch tower, and 35 per cent of those for the fourteen-inch tower. From the limited data, the indications are that the same correlation with liquor rate applies as for the experimental towers. Although these coefficients are about 10 per cent lower than would be expected, it was realized that the possibility of experimental error in these tests was rather large, since in producing the strong commercial bleach, the lower part of the tower must necessarily have operated close to equilibrium conditions. In view of this and other peculiarities in the absorption of chlorine, the agreement between the design and the performance of the commercial tower is considered satisfactory, and it may be concluded that the data presented are sufficiently representative of the absorption of chlorine to be used for design purposes.

**Solubility of Chlorine in Water.**

Chlorine would be expected to be irregular in its solubility relation with water, since a large part of the dissolved chlorine hydrolyses to form hydrochloric acid
and hypochlorous acid. The equilibrium existing in the solution may be represented as follows.

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOC}l + \text{H}^+ + \text{Cl}^- \]

Since the solutions are relatively dilute, the hydrochloric acid may be considered as being completely ionized, whereas the hypochlorous acid is probably only very slightly ionized.

The two-phase system (gas and liquid) involving chlorine and water may be visualized physically as consisting of chlorine gas at such a pressure that it is in equilibrium with the molecular chlorine in solution. This equilibrium may be assumed to follow Henry's law. The molecular chlorine, in turn, will be in equilibrium with the hypochlorous acid and the chloride ions, governed by the hydrolysis constant. The hypochlorous acid and chloride ions do not exert vapor pressures. Thus the total amount of chlorine dissolving in water would be expected to be considerably in excess of that expected from pure physical solution.

Previous to this investigation, the experimental data on this solubility relation were extremely meager\(^{(15)}\), and in poor agreement. The experimental data of this thesis have been published by Whitney and Vivian\(^{(38)}\), and are shown in Fig. 15. The range of pressures of chlorine in the gas phase was from 0.06 to 1.0 atmospheres for temperatures of 10°, 15°, 20° and 25°C. The data have been interpolated and replotted in more
convenient form in Fig 16, 17, and 37.

The method employed to determine these data may be
called a flow method as compared with the static or
closed system generally used. This flow method has sev-
eral distinct advantages. It permits easy sampling of
the gas and liquid phases at equilibrium without distur-
bishing that equilibrium. The apparatus can be operated at
atmospheric pressure. It provides a convenient method
for preventing or checking supersaturation effects fre-
quently encountered in determining solubility equilib-
rium, since the final equilibrium can be approached from
both directions. In this investigation, such effects
were found to be entirely absent. Although equilibrium
was not approached from both sides in every run, suffi-
cient runs were made by this procedure to demonstrate
that the time taken for a run was sufficient to establish
true equilibrium.

Sensitive flow meters were used to proportion the
amount of chlorine and inert gases for the desired gas
mixture. These flow meters were watched constantly
throughout a run, since the accuracy and usefulness of
the run depended on the maintenance of a gas mixture of
constant composition.

The temperature of the thermostat was controlled by
a combination of heating and refrigerating units at the
desired temperature within ± 0.05°C. This overall vari-
ation of 0.1°C is well within the desired precision, and
the bath was so constructed that a uniform temperature
was maintained throughout. The absolute temperature was
determined by a calibrated thermometer graduated in 0.1°C.
At all temperatures used (10°C to 25°C), the capacity of the
heating and cooling coil was found to be adequate. It is
estimated that the results give the partial pressure of
chlorine above a solution of chlorine water at a given
temperature within 2 per cent.

This apparatus was first used by White (34) to deter-
mine the solubility of sulfur dioxide in water and in lime
slurries. The sulfur dioxide in water data were compared
with those accepted in the literature (23), for this
equilibrium, and although the methods differed distinctly,
the results obtained were in excellent agreement.

In Table I, data from the International Critical
Tables (16) are compared with the data of this thesis, and
at the four temperatures investigated the maximum deviation
is 1.1 per cent.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Cl₂ Pressure Atm.</th>
<th>Solubility (Moles/Cu.Ft.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I.C.T. data</td>
</tr>
<tr>
<td>10</td>
<td>0.989</td>
<td>0.00874</td>
</tr>
<tr>
<td>15</td>
<td>0.983</td>
<td>0.00745</td>
</tr>
<tr>
<td>20</td>
<td>0.978</td>
<td>0.00640</td>
</tr>
<tr>
<td>25</td>
<td>0.973</td>
<td>0.00562</td>
</tr>
</tbody>
</table>

The agreement between these experimental data and the
calculated data of Adams and Edmonds (1) is close except at
low partial pressures of chlorine (see Fig. 23.). Since it
is in the low range of partial pressures that most of the
absorption work of this thesis was performed, the effect of the experimental data was to give values of $K_{La}$ 10 to 40 per cent higher than those based on Adams and Edmonds data. In spite of this, the close agreement is evidence of the validity of the physical set up involved in the equilibrium as described above, since the calculated data were based on independently-determined hydrolysis constants and the assumption of Henry's law for the relation between molecular chlorine concentration and vapor pressure of chlorine.

The quantitative aspects of this equilibrium have been treated in detail in the Appendix where it is shown that the total chlorine concentration, $c$, can be expressed as a function of the partial pressure of chlorine, $P$, over the solution, and the hydrolysis and Henry's law constants, $K$ and $H$ respectively. The relationship is

$$c = HP + \frac{3}{\sqrt{KH}} \quad \text{(18)}$$

Where the term $HP$ represents the molecular chlorine in solution and the term $\frac{3}{\sqrt{KH}}$ the hydrolysed chlorine. By rearranging equation (18) and plotting $c/P^{1/3}$ vs $P^{2/3}$, it can be shown that the equilibrium data can be represented by a number of isotherms, each having a slope equal to $H$ and an intercept equal to $\frac{3}{\sqrt{KH}}$. The experimental equilibrium data have been plotted in this way in Fig. 24, and the values of $H$ and $K$ calculated from the slopes and intercepts are given in Table II. In addition to its usefulness in extrapolating the data, equation (18) is particularly
SOLUBILITY OF CHLORINE IN WATER

\[ C = H_p + (K_H p)^{1/3} \]
helpful in determining the fraction of the total chlorine existing in solution as molecular chlorine at a given partial pressure of chlorine in the gas phase.

**TABLE II**

<table>
<thead>
<tr>
<th>Tempº C</th>
<th>H (lb.mols/cu.ft.atm.)</th>
<th>K x 10⁷ (lb.mols/cu.ft.)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.00707</td>
<td>7.10</td>
</tr>
<tr>
<td>15</td>
<td>0.00584</td>
<td>8.55</td>
</tr>
<tr>
<td>20</td>
<td>0.00469</td>
<td>10.7</td>
</tr>
<tr>
<td>25</td>
<td>0.00390</td>
<td>12.8</td>
</tr>
</tbody>
</table>

The hydrolysis constants obtained above are presented in Fig. 24A, where it is seen that log K is inversely proportional to the absolute temperature. Values of K for this system have been determined directly by Yakovkin⁴¹ and are compared with the results of this investigation in Table III.

**TABLE III**

<table>
<thead>
<tr>
<th>Tempº C</th>
<th>K x 10⁷ (Data of Yakovkin)</th>
<th>K x 10⁷ (This Thesis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10.0</td>
<td>7.10</td>
</tr>
<tr>
<td>15</td>
<td>12.3</td>
<td>8.55</td>
</tr>
<tr>
<td>20</td>
<td>15.0</td>
<td>10.7</td>
</tr>
<tr>
<td>25</td>
<td>17.3</td>
<td>12.8</td>
</tr>
</tbody>
</table>

It is seen that the hydrolysis constants of Yakovkin are about 50 per cent greater than those calculated from the equilibrium solubility data. At this time, it is not possible to offer a satisfactory explanation for the discrepancy, which is not considered serious in this work. It will be noted from equation (18) that the calculation of c for a given P, or the calculation of the fraction hydrolysed, is relatively insensitive to the value of K.
EFFECT OF TEMPERATURE ON HYDROLYSIS
CONSTANT - CHLORINE IN WATER

\[ K = \left( \frac{\text{lb. mols}}{\text{cu. ft}} \right)^2 \]
Absorption of Oxygen.

In order to determine whether the data of this thesis were comparable with other liquid film data, a series of runs was made, duplicating the work of Holloway\(^{(14)}\) on the desorption of oxygen from water in a 20-inch tower. Both the experimental towers were used, and the results are shown in Fig. 18. The dotted line is representative of holloway's data for the desorption of oxygen with one-inch rings as packing at 25\(^{\circ}\)C or 77\(^{\circ}\)F, while the O\(_2\) data on the four-inch tower are at 70\(^{\circ}\)F. After converting the data of Holloway to 70\(^{\circ}\)F., which lowers those coefficients about 8 per cent, it is evident that the agreement between the data for the two experimental towers and Holloway's data is surprisingly close. The four-inch tower gave essentially the same values for K\(_L\)a as Holloway's apparatus. The fourteen-inch tower gave values of K\(_L\)a at 66\(^{\circ}\)F about 5 per cent lower than the four-inch tower, and when these are adjusted for difference in temperature, they are in good agreement with those for the four-inch tower. Hence, if Holloway's data are accepted, then for all practical purposes, the two experimental towers used in this work may be considered to be representative of large-diameter towers, and in design, the use of the data obtained with the four-inch tower is justified. Further, it may be concluded that the liquor distribution was essentially the same in all cases, since oxygen desorption is a liquid film phenomenon, and the value of K\(_L\)a would
be affected by any factor affecting the liquid film.

However, this agreement in the case of the desorption of oxygen does not preclude the possibility that gas channelling existed in the towers in the chlorine tests. Since, with oxygen, the gas rate has no effect on the value of $K_La$, and the concentration of oxygen in the gas in the tower is virtually constant regardless of gas and liquor rates because of the small amount of oxygen stripped from the water, the amount of oxygen desorbed becomes practically independent of the gas rate, and hence, independent of any gas channelling that might exist. This is not the case with chlorine in the gas, since its concentration may vary over wide ranges, and thus affect the amount of chlorine absorbed.

The results for oxygen desorption on the four-inch tower were calculated on the basis of an effective height of packing as found in the study of chlorine absorption in water, and already discussed. The close agreement between Holloway's data, which were obtained by sampling the liquor immediately above and below the packing, and these results, justifies the use of the end factor in the calculations to allow for the end effect.

Summary of Experimental Results on Chlorine Water.

Before attempting to correlate the absorption of chlorine in water with other liquid film absorption phenomena, it seems advisable to review the facts as determined from the results of this investigation.
1. The solubility of chlorine in water is such that even with the added effect of partial hydrolysis, at least 97 per cent of the resistance to absorption is expected to be in the liquid film. Hence, overall coefficients would be expected to approximate the liquid film coefficients.

2. The overall coefficient, $K_{L_a}$, is a function of the 0.6 power of the liquor rate for chlorine as compared with the 0.75 power of the liquor rate for oxygen in the same tower and packing.

3. The coefficient, $K_{L_a}$, is independent, or nearly so, of the gas rate, in agreement with the oxygen data.

4. The coefficient varies as the sixth power of the absolute temperature, in agreement with other cases of liquid film absorption.

5. The absolute values of the $K_{L_a}$ for chlorine vary from $\frac{1}{3}$ to $\frac{2}{3}$ the values for oxygen at corresponding liquor rates. According to the Sherwood and Holloway correlation they would be expected to be only about 15 per cent lower.

6. Within the precision of the data, the coefficient is independent of the partial pressure of chlorine in the gas phase.

7. Chlorine dissolved in water hydrolyses to establish an equilibrium in the liquid phase between hydrogen and chloride ions, hypochlorous acid and molecular chlorine. Only the molecular chlorine exerts a chlorine vapor pressure, and the equilibrium chlorine pressure is
related to the molecular chlorine concentration in the solution by Henry’s law.

Thus it is seen that, although chlorine absorption in water is a liquid-film case, there are many facts which distinguish it from the general case, and any attempt to explain the apparent deviation from the general case must take the above facts into consideration. The discrepancies cannot be dismissed as experimental error, since they are several times as large as the maximum possible error that could be assigned.

**Correlation and Interpretation of Results.**

The chief physical difference between the chlorine-water and the oxygen-water system is the fact that chlorine reacts with the water according to a reversible hydrolysis reaction, while oxygen is inert toward water. It is in this direction that the system is to be analysed in an effort to find a suitable explanation for the lack of correlation. Until the facts summarized above had been established, it had been tacitly assumed that the rate of hydrolysis was so rapid, compared to the rate of absorption, that it would not have an appreciable effect on the absorption. However, it must be realized that all of the chlorine crossing the gas-liquid interface must enter the liquid as molecular chlorine. This chlorine begins to react with the water, and along with the reaction products, diffuses across the liquid film to the main body of the liquid. Subject to the relative rates of
reaction and absorption, equilibrium of the hydrolysis reaction may be established at some point within the film or in the main body of the liquid.

If the rate of reaction is sufficiently slow, the molecular chlorine entering the liquid phase will have time to diffuse across the liquid film before an appreciable amount has been hydrolysed. This case would closely approximate the conditions of pure physical absorption. However, it would be necessary to use care in the selection of the driving force to be used in the calculation of the liquid film coefficient. At the boundary of the liquid film adjacent to the main body of liquid, the chlorine concentration contributing to the driving force would be the molecular chlorine concentration in equilibrium with the total chlorine concentration in the main body of the liquid. At the interface between gas and liquid, the chlorine diffusing would be in the form of molecular chlorine. The concentration at the interface is ordinarily determined from the solubility equilibrium relationship and the partial pressure of chlorine in the gas phase. In this case, the concentration determined directly from the solubility data would include hydrolysed chlorine in equilibrium with that concentration of molecular chlorine which, in turn, would be in equilibrium with the partial pressure in the gas phase. Actually, the concentration at the interface contributing to the driving force would be only the molecular chlorine in equilibrium with the partial
pressure. Thus the actual concentration at the interface contributing to the driving force would be about 10 to 40 per cent of the concentration determined directly from the equilibrium data for the range of partial pressures used in most of this investigation. The actual concentration of molecular chlorine at the interface can be calculated from the equilibrium data, and for 70°F is shown in Fig. 25. Similarly, at every point in the liquid in the tower, the equilibrium concentration of unhydrolysed molecular chlorine can be determined, and a pseudo-operating line constructed from which the driving force can be calculated in terms of molecular chlorine concentration. This has been done for the runs used to determine the effect of liquor rate on $K_La$, and is shown in Fig. 26, where the results of this calculation are compared with values for chlorine calculated from the data on oxygen and the data for chlorine as presented in the RESULTS of this thesis. It is seen that the values of $K_La$ based only on molecular chlorine diffusion are about the same as the values for oxygen at corresponding liquor rates.

As mentioned above, the chlorine from the gas crossing the interface must first dissolve as molecular chloride. The rate at which chlorine will cross the interface is governed by the rate of removal of molecular chlorine from the interface, assuming a constant concentration of chlorine in the gas phase. In the case of pure physical absorption, removal of the solute across the film is effected by diffusion only, and the resultant concentration
MOLECULAR \( \text{Cl}_2 \) SOLUBILITY

AT 70° F
PSEUDO-COEFFICIENT
CL₂ IN H₂O

A-A: PSEUDO-κₐ FOR CL₂
B-B: κₐ FOR O₂ IN H₂O
C-C: κₐ FOR CL₂ CALCULATED FROM O₂ DATA
D-D: NORMAL κₐ FOR CL₂

FIG. 26
gradient is linear with respect to film thickness. With chlorine, however, the removal of molecular chlorine from the interface is effected not only by diffusion but also by the depleting effect of a chemical reaction.

It seems obvious that the initial rate at which molecular chlorine enters the liquid film at the interface must equal the rate of total chlorine diffusion into the main body of the liquid, since there can be no accumulation or depletion within the film under steady state conditions. Hence, the rate at which molecular chlorine enters the main body of the liquid must be less than the rate at which it enters the interface. In other words, the concentration gradient for the molecular chlorine must be concave upward. The degree of curvature will depend on the relative rates of reaction and diffusion.

An additional factor which deals with the nature of the equilibrium between molecular and hydrolysed chlorine must also be taken into consideration, since the concentration of molecular chlorine at equilibrium is a function of the total chlorine concentration. The lower the total chlorine concentration, the greater the fraction is which exists as hydrolysed chlorine at equilibrium. Thus, even if the rate of reaction is extremely rapid, the concentration gradient will be concave upward because of the adjustment to equilibrium in the liquid film as the total chlorine concentration decreases linearly across the film. (Note: For desorption, the reverse would be the
case, and the concentration gradient would be concave downward.) In the case of pure physical absorption, mass transfer takes place under the influence of one set of equilibrium conditions, but with chlorine, two such sets of conditions must be met.

In the calculation of the pseudo-coefficients described above, the usual absorption equations were used in which it is assumed that the driving force is based on a linear concentration gradient across the film. If a concentration gradient is used which is concave upward, the effect is the same as the use of a film thickness less than is actually the case, and the coefficients will be greater than would be expected for the actual film thickness. This follows from the fact that the \(-dc/dx\) used in the calculations is in effect the initial value for molecular chlorine at the interface, and the concentration differences are molecular chlorine differences. As the liquor rate increases, the film thickness decreases, and the rate of diffusion increases, but the rate of reaction remains constant, since a constant temperature is assumed. Thus the effect of the reaction in removing molecular chlorine from the film decreases relative to the effect of diffusion, and at high liquor rates, the conditions on which the absorption equations are based are more nearly approached. This allows the calculation of values of \(K_{a}\), based on a molecular chlorine driving force, in agreement with absorption theory. The data presented
in Fig. 26 in which the $K_{L}a$ varies as the 0.6 power of the liquor rate are entirely in agreement with the interpretation given above.

Hatta(13) has developed a mathematical analysis of diffusion together with chemical reaction. This analysis is discussed, and further developed by Sherwood(27) for the simplified case of a first order reaction. This treatment serves to define the boundary line cases, but is not suitable for general application. The equations governing the diffusion and hydrolysis of chlorine in water are developed in the Appendix, but the attempt to integrate them has not been made, since the time required for their manipulation would far exceed their usefulness at this time.

Shilox(30) has presented data on the rate of hydrolysis of chlorine in water. It is difficult to estimate the reliability of the data, since there is some question as to whether his data are governed by the rate of mixing in his apparatus or by the rate of reaction. If it is assumed that they are at least representative of the order of magnitude of the rate of reaction, it is possible to compare the relative effects of diffusion and rate of reaction. Sherwood has calculated the fraction of the diffusing molecules which should get through the liquid film unreacted in terms of the diffusivity, the rate of reaction and the film thickness. The conditions for which the calculations apply are not in agreement with those
encountered in the chlorine system, since a first order reaction and zero concentration of solute in the main body of the liquid are assumed. The calculations can be used qualitatively, however, to show the magnitude of the effect of the relative rates of reaction and diffusion.

The indications are that, although the rate of hydrolysis is rapid, over the range of liquor rates investigated conditions vary from that, at low rates, where complete reaction within the film occurs to that, at high rates, where over 95 per cent of the chlorine diffuses across the film without reacting. Thus, at low rates, the use of a total chlorine driving force, based on the equilibrium data, is partially justified, and the calculated $K_{La}$ is approximately in agreement with that expected. At high rates, however, the molecular chlorine diffuses across the film without reacting to any great extent, and the total chlorine concentration at the interface is practically equal to the molecular chlorine concentration at that point, even though the equilibrium total chlorine is much greater. Thus a total chlorine driving force based on the equilibrium data is very much greater than actually exists across the film, with the result that the calculated $K_{La}$ is abnormally low. This is in agreement with the experimental results where, it will be remembered, the deviation from expected values of the coefficients calculated on the basis of total chlorine is much greater at the high liquor rates than at low rates. It is also in
agreement with the results expressed as the so-called pseudo-coefficients based on the molecular chlorine concentration difference where excellent agreement with expected values is found at high liquor rates.

Sulfur dioxide also hydrolyses in water, although to a lesser degree than chlorine. Whitney(36) in studying the absorption of sulfur dioxide in water has found similar effects in the liquid film due to the hydrolysis. From a considerable amount of data, the liquid film coefficient for $\text{SO}_2$ was found to be about 20 per cent lower than values predicted on the basis of data for the absorption of oxygen in water. Recalculating some of these data to obtain pseudo-coefficients as described above, Whitney obtained values which agree very closely with predicted values. This agreement is shown in Fig. 27. Furthermore, it will be seen that the pseudo-coefficient varies with the same power of the liquor rate as in the case of oxygen absorption in his tower.

These data and calculations lead to the conclusions that practically all the sulfur dioxide diffuses through the film without hydrolysing, and that the rate of hydrolysis is sufficiently slow, relative to the rate of diffusion, so that its effect in increasing the rate of absorption above that expected for pure physical absorption is not observed, even at the lowest liquor rates used.

The fact that the data of Whitney give coefficients only 20 per cent low, while the chlorine data give
PSEUDO-COEFFICIENT

SO₂ IN H₂O

○ PSEUDO-Kₐ FOR SO₂
- Kₐ FOR SO₂ CALC.
FROM O₂ DATA
DATA OF WHITNEY [36]

L - LBS./HR - SQ FT
Kₐ - LB.MOLS./HR·FT³ - MOLS./FT³
coefficients averaging 50 per cent low, is due chiefly
to the different degree of hydrolysis in the two systems.
The equilibrium data indicate that for SO₂ in the range
of concentrations used by Whitney, about 70 per cent of
the SO₂ existed as molecular SO₂, whereas in the case of
chlorine, only about 10 to 40 per cent existed as molecular
chlorine. The relatively small amount of SO₂ hydrolysing
would also obscure the effect of reaction rate relative to
the rate of diffusion over the range of liquor rates used,
with the result that the same function of liquor rate
would exist as for pure physical absorption.

In the light of the foregoing discussion of the
mechanics of absorption and chemical reaction it will be
well to discuss what the values for \( K_La \) calculated on the
basis of total solute concentration represent. This \( K_La \) is
based on a driving force which, in the case of chlorine, is
the result of two equilibria. Only the molecular chlorine
contributes to the back pressure, and the rate at which
chlorine enters the liquid phase is governed only by its
rate of removal as molecular chlorine from the interface.
Even if the rate of reaction is infinite, the rate of re-
moval of molecular chlorine is a function of the total
chlorine concentration as well as the rate of diffusion,
since the fraction of the total chlorine which is present
as molecular chlorine is a function of the total concen-
tration. It might be expected that with infinite reaction
rate, the \( K_La \) calculated on the basis of total chlorine
concentration should have the same value as that expected for pure physical absorption. Study of the geometry involved in determining the driving force from the operating diagram (Fig. 28) will show that this could not be the case. The pseudo-operating line representing the molecular chlorine concentration at any point in the tower does not bear the same relation to the molecular chlorine equilibrium line as does the operating line to the equilibrium line for total chlorine. The pseudo-operating line is influenced by the equilibrium between molecular and hydrolysed chlorine in solution corresponding to equilibrium at partial pressures other than those at the particular point in the tower. If the equilibrium lines for molecular chlorine and total chlorine were straight and parallel, then the two coefficients would have the same value, provided the total concentration in the liquid at every point on the operating line was greater than a critical value corresponding to the value of the hydrolysed chlorine. The hydrolysed chlorine concentration would have to be constant, and independent of chlorine partial pressure. However, the equilibrium hydrolysed chlorine concentration varies as the cube root of the partial pressure, with the result that the equilibrium lines are not parallel. Hence, $K_{L,a}$ calculated on the basis of total chlorine concentration differences cannot be expected to correlate with pure physical absorption, even though the hydrolysis reaction may be extremely rapid. This normal $K_{L,a}$ is, in reality, a coefficient
PSEUDO-OPERATING DIAGRAM

FOR RUN No. 12. - L = 13,600 LBS.

FOR RUN No. 70. - L = 910 LBS.

A - B NORMAL OPERATING LINES
A - C PSEUDO-OPERATING LINES
governed by the limitations imposed by two equilibria which must be met.

From the considerations in the case of chlorine absorption in water and the similar situation found by Whitney (36) for sulfur dioxide absorption in water, it is evident that extreme caution must be exercised in the use of any generalized correlation for the prediction of liquid film coefficients for those cases where there is interaction of the solute with the absorbing medium. In such cases, the coefficients are functions not only of factors affecting the liquid film but also those factors affecting the ratio of reacted to unreacted solute in the liquid phase; viz., nature of the liquid phase equilibrium, solute concentration, and rate of reaction.

It has been pointed out that the value of the $K_{La}$ is independent of the partial pressure of the chlorine in the gas. It is generally accepted that this is the criterion indicating the validity of the equilibrium data. However, care must be exercised in the use of this criterion. When the partial pressure alone is varied, the effect is to move the operating line in a vertical direction on the usual operating diagram. If the equilibrium line is steep and the absorption is a case of liquid film controlling, the driving force which is measured by the distance from the operating line to the equilibrium line in a horizontal direction changes only slightly for a large change in partial pressure. The steeper the
equilibrium line the less the change in $\Delta C$.

In the case of chlorine absorbed in water, the equilibrium line is relatively steep, and the value of $\Delta C$ changes only slightly with considerable change in the position of the operating line due to change in partial pressure of chlorine. Thus unknown factors included in the calculated $\Delta C$ would not change significantly with respect to the $\Delta C$ at different partial pressures of chlorine, with the result that $K_L$ appears to be independent of partial pressure. A much more significant method would have been to vary the position of the operating line by using various concentrations of chlorine water, instead of feeding the tower with fresh water in all runs. If this had been done, the effect of the equilibrium between molecular and hydrolysed chlorine discussed above would have been much more in evidence, since different sections of the total chlorine equilibrium curve would have been used.

While it is uncertain to what extent the effect of rate of reaction is subordinated at high liquor rates when absorbing chlorine in water, this subordination could be accomplished with certainty by the use of a hydrochloric acid solution or of a combination of hydrochloric acid and a chloride solution which would suppress the hydrolysis reaction. Calculating from the hydrolysis constant at 70°F, it is found that using a 0.2 N HCl solution, about 1 per cent of the chlorine dissolving
would be hydrolysed, while with a 1 N solution less than 0.04 per cent of the chlorine dissolving would be hydrolysed. It is recommended that this phase of the work be made the subject of a future Master's thesis.

In the preceding discussion, the absorption of chlorine in water has been considered from the point of view of a chemical reaction occurring simultaneously with diffusion. Although this is the most satisfactory method to consider the data for purposes of comparing and correlating chlorine absorption with general liquid film phenomena, it is not readily applicable to the design of commercial chlorine absorption equipment. To this end, the liquid film coefficient has been based on a driving force calculated from the total chlorine concentration at the boundaries of the liquid film as determined from the equilibrium data and liquor analysis. This is the calculational procedure used in presenting the results of this investigation, and has been shown to be suitable for the design of commercial chlorine towers.

Thus it may be concluded that as a result of the rate of reaction and the nature of the equilibrium established in the liquid phase, the rate of absorption of chlorine in water from a purely physical absorption point of view is greater than or equal to the rate of absorption expected on the basis of oxygen absorption, but that the coefficients presented in the RESULTS are low because of the use of an empirical concentration difference as driving force. At
the present state of the data on chlorine, it is not feasible to correlate chlorine data quantitatively with other liquid film data.

It may also be concluded that extreme care must be exercised in the use of the correlation developed by Holloway for liquid film absorption. While his treatment is general, it is applicable only to those cases where pure physical absorption is taking place, free from complicating effects, such as exist in the case of the absorption of chlorine in water. Many of the common industrial gases react in some way with the absorbents, and the amount by which their performance will differ from the general case is not only a function of the ratio of rate of reaction to diffusivity but also the position of the final equilibrium. The latter is probably the significant factor in the absorption of carbon dioxide in water, where ordinarily an extremely small fraction of the total gas in solution hydrolyses, and its effect on the rate of absorption is not distinguishable.

**Absorption of Chlorine in Caustic**

As an attempt to contribute to the field of knowledge of gas film absorption and to obtain design data for use in the pulp industry, a brief study of the absorption of chlorine in caustic was included in this investigation. The work was carried out in conjunction with student assignments at the Bangor Station of the Practice School\(^{(3),(9),(17)}\).
Chlorine is very soluble in caustic, reacting according to the equation

\[ 2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl} + \text{NaCl}. \]

As long as excess caustic is present in solution, the equilibrium vapor pressure of chlorine over the solution is essentially zero. If, in gas-liquid absorption operations, the caustic concentration in the main body of the liquid is high enough so that excess caustic is maintained at the interface, the total resistance to mass transfer will be across the gas film, and overall coefficients determined under such conditions will be representative of gas-film absorption. The highest concentration of caustic in the main liquid at which the excess caustic at the interface is zero, under a particular set of conditions, is loosely spoken of as the "critical concentration". At concentrations below this "critical" value, the vapor pressure in equilibrium with the liquid at the interface is finite, and some of the resistance to mass transfer occurs in the liquid film. It is in concentration ranges above the "critical" that the main interest of this investigation was placed.

It should be pointed out that the so-called "critical" concentration is not a unique function of the particular solute-solvent system, but rather a result of a combination of values of several operating variables occurring simultaneously. The partial pressure of the solute in the gas phase, the gas and liquor rates in so far as they affect
film thickness, and the caustic concentration are determining factors in establishing the "critical" condition. Furthermore, the conditions implied by the use of the term "critical" concentration are point conditions. Thus, in an absorption tower, the critical condition may be developed at any point in the tower by a suitable choice of operating variables, and the position of this point may be varied by varying one or more of the operating conditions. Unless the tower is operated under conditions, such that the critical caustic concentration is not developed, the calculated coefficients are not representative of gas-film absorption, and are low because of additional resistance from the liquid film in part or all of the tower. This resistance of the liquid film for the chlorine-caustic system varies from zero at the "critical" caustic concentration to practically the total resistance at zero caustic concentration. For a given set of operating conditions, varying caustic concentration, within limits, above the critical value does not affect the resistance to chlorine transfer, and the calculated coefficients are independent of caustic concentration.

Since the calculated coefficient is the result of an integration of mass transfer rates over the height of the tower, the transition, as caustic concentration is decreased, from a condition where gas film resistance controls to one where there is appreciable liquid film resistance is gradual, and no sharp break in the $K_La$ vs
N curve is found.

The experimental results are entirely in agreement with the mechanism presented above. Fig. 19 shows the variation of $K_ga(P_{BM})$ with caustic concentration, $N$. For the particular conditions of partial pressure of chlorine in the gas and the gas and liquor rates used in this series of runs, liquid film resistance is in evidence up to an average caustic concentration of 2 (normality). Above this normality the curve is flat, and the coefficient may be assumed representative of gas-film controlled absorption. It should be kept in mind that this curve is the result of a calculation procedure in which the $K_ga$ is determined on the assumption that there is no back pressure of chlorine at the gas-liquid interface. When there is no excess caustic at the interface this assumption is in error, the assumed driving force across the gas film being too high, and the resulting calculated coefficients for the gas film are correspondingly low.

By making a series of runs at high caustic normalities with various gas rates, data to observe the effect of gas rate on $K_ga$ were obtained as shown in Fig. 20. In practically all cases, at least two caustic normalities were used with each gas rate in order to check the absence of liquid film resistance. Only those runs which gave coefficients on the flat part of the $K_ga$ vs $N$ curve have been plotted in Fig. 20. Although the data are scattered, the indications are that the $K_ga$ varies as the 0.7 power of
the gas rate. This is in close agreement with other investigators who generally report $K_{ga}$ as a function of the 0.63 to 0.8 power of the gas rate. Several runs were made at gas rates above 600 lbs./(hr.)(sq.ft.), but with the caustic concentrations used it was not possible to eliminate the effect of the liquid film resistance with the result that the calculated coefficients were low.

The precision of the data leaves much to be desired. This condition arises from the extreme solubility of chlorine in caustic and the resulting high rates of absorption obtained. Chlorine is so completely scrubbed from the carrier gas that in order to have a measurable concentration of chlorine in the exhaust gas from the tower, high concentrations of chlorine in the entering gas must be used. This situation leads to uncertainty in determining the driving force in the upper part of the tower. Furthermore, the reaction between chlorine and caustic is strongly exothermic, with the result that the liquor temperature increases appreciably through the tower. This latter effect is a function of the amount absorbed, and hence, is affected by the gas rate and partial pressure of chlorine in the inlet gas, when the liquor rate is kept constant. The use of solute-rich gas in the tower presents the further complication that the gas rate charges materially through the tower, with the result that for a given set of operating conditions the $K_{ga}$ is not constant through the tower, since the coefficient is a function of the gas
rate.

An attempt to allow for this variation in $K_{ga}$ because of varying gas rate through the tower was made in the integration of the differential equation defining the value of the $K_{ga}$. It was assumed that the $K_{ga}$ was a function of the mass rate to some power $n$, to be found by trial, and a coefficient calculated based on the mass rate at the bottom of the tower. The details of this calculation are given in the Appendix, and the data presented in Fig. 19 and Fig. 20 were calculated in this way. Because of the extreme operating conditions, this method of handling the data was preferred to the use of an average coefficient with an average gas rate. For comparison, the data have been calculated in the usual manner, and the resulting coefficients assigned an average gas rate. The results of these calculations are shown in Fig. 29 where it is seen that the correlation is poor, as would be expected from the difficulty of determining proper average values.

In the calculations, $n$ was assumed to be 0.8, that is, $K_{ga}$ was assumed proportional to $G$ to the 0.8 power. The resulting values of $K_{ga}$ were found to be proportional to $G$ to the 0.7 power. This agreement is well within the precision of the data and the method of calculation, and the data have not been recalculated using $G$ to the 0.7 power.

Because of the use of solute-rich gas and the wide variation in solute concentration through the tower, the results have been expressed as $K_{ga}(P_{Bm})$ rather than as $K_{ga}$. 
FIG. 29

DATA FROM FIG. 20.
Several investigators have reported correlations for predicting gas film coefficients, and the agreement between these correlations leaves much to be desired. Sherwood and Holloway\(^{(29)}\) in reviewing the literature up to 1940, together with their own data on ammonia and water vapor, concluded that gas film coefficients could best be correlated as a function of the one-third power of the liquor rate, the two-thirds power of the diffusivity, and the 0.7 power of the gas rate. It was concluded that the values given by curve A in Fig. 30 were representative of gas film absorption for ammonia and water vapor.

If the Sherwood and Holloway correlation is used to predict \(K_{g,a}(P_{Dm})\) for chlorine by applying the ratio of the diffusivities of chlorine and ammonia to the two-thirds power, curve B in Fig. 30 is obtained. The experimental data taken from Fig. 20 are also given for purposes of comparison. It is seen that the agreement between experimental and predicted values is remarkably close.

Whitney\(^{(36)}\) in presenting data on the absorption of sulfur dioxide in water has also reviewed the literature (to 1945), and in the light of recent data on ammonia absorption in water, together with his \(SO_2\) data, has concluded that the values given by curve C in Fig. 30 are more representative for ammonia absorption, while curve D gives values for \(SO_2\). The diffusivity of \(SO_2\) and
SHERWOOD & HOLLOWAY
CORRELATION
A - A FOR NH₃ & H₂O
B - B FOR CL₂
WHITNEY CORRELATION
C - C FOR NH₃ & H₂O
D - D FOR CL₂ & SO₂
O - CL₂ DATA - THIS
THESIS

FIG. 30
Cl₂ in air are practically identical, and hence, curve D should predict values for chlorine gas film coefficients. It is seen that these predicted values are, on the average, about 30 per cent below the experimental values. Whitney has concluded that, in view of the wide disagreement between the available gas film data as well as the uncertainties associated with many, gas film data cannot be satisfactorily correlated at this time. Because of the inconclusive nature of the chlorine coefficients presented in this work, it is felt that further conclusions regarding the correlation of gas film data cannot be justified on the basis of these data.

A few runs were made at liquor rates ranging from 6,000 to 12,000 lbs./(hr.)(sq.ft) at a fixed gas rate. Unfortunately the short time available for this part of the work because of the general disintegration of the equipment from corrosion, and the lack of appreciation of the full significance of the critical caustic concentration, combined to render the small amount of data collected somewhat inconclusive. The results are shown in Fig. 21, and indicate that $K_{g\alpha}(P_{Bm})$ varies as the 0.4 to 0.5 power of the liquor rate. Sherwood and Holloway(29) have reported that the coefficient of ammonia and water is a function of the one-third power of the liquor rate, and considering the scarcity of these chlorine data and their limitations, the disagreement is not significant. Until further data can be obtained, it is recommended that
$K_{ga}(P_{Bm})$ for chlorine be considered to vary as the one-third power of the liquor rate.

From the foregoing discussion, it is evident that the data on the absorption of chlorine in caustic is not entirely conclusive, and it is suggested as a subject for future thesis work. In this connection, the development of an analytical technique having sufficient precision to permit the determination of chlorine in very low gas concentration would be of considerable value. Such a technique would allow the use of dilute caustic solutions as absorbing medium and the use of low chlorine concentration in the feed gas, and in this way remove the uncertainty introduced by variation in gas rate through the tower as well as the large heat effect encountered in the use of concentrated solutions.
VI CONCLUSIONS and RECOMMENDATIONS

From the results of this thesis, it is concluded that:

1. The absorption of chlorine in water is governed by the resistance of the liquid film. Even with the added effect of partial hydrolysis in the liquid phase, at least 97 percent of the resistance is in that film.

2. The overall coefficient $K_La$ calculated on the basis of the total chlorine equilibrium solubility data is proportional to the 0.6 power of the liquor rate from 900 to 20,000 lbs./(hr.)(sq.ft.) using one-inch rings as packing.

3. The overall coefficient $K_La$ for oxygen obtained in the same equipment varies as the 0.75 power of the liquor rate over the same range of liquor rates using the same packing.

4. The overall coefficient for chlorine is essentially independent of gas rate.

5. The overall coefficient for chlorine varies as the sixth power of the absolute temperature.

6. The overall coefficient for chlorine in water calculated on the basis of the total chlorine equilibrium solubility data varies from 2/3 to 1/3 the coefficient for oxygen at corresponding liquor rates.

7. In the liquid phase equilibrium between hydrogen and chloride ions, hypochlorous acid and molecular chlorine, only the molecular chlorine exerts a vapor pressure, and the equilibrium chlorine pressure is proportional to the molecular chlorine concentration in solution.
8. The rate of chlorine absorption in water is governed by a reaction equilibrium as well as a solubility equilibrium.

9. The ratio of rate of hydrolysis reaction to the rate of diffusion is such that, over the range of liquor rates investigated, conditions vary from that where essentially complete reaction occurs within the liquid film to that where essentially all of the diffusing molecules traverse the film without reacting.

10. Use of the equilibrium solubility data to determine driving forces across the film may not give the actual driving force in systems where there is interaction between solute and solvent, with the result that coefficients calculated from experimental data are lower than expected.

11. Based on the molecular chlorine concentration difference, the rate of absorption of chlorine in water is equal to or greater than that expected from other liquid film absorption data.

12. In the chlorine-water system, the driving force, 
$-dc/dx$, causing absorption (concentration gradient for molecular chlorine) is affected by, (1) the specific hydrolysis reaction rate, and (2) the total chlorine concentration difference across the film.

13. Until a solution of the equations governing chlorine diffusion in the liquid film is obtained, it is not feasible to correlate chlorine absorption coefficients with those for cases of pure physical absorption.
14. In liquid film systems, independence of \( K_{L}a \) on solute gas concentration may not be a satisfactory test for the validity of the equilibrium data. Consideration should be given the relative positions of operating and equilibrium lines, and the manner in which these vary with gas concentration.

15. Care should be exercised in using a generalized correlation for the prediction of coefficients where there is interaction of solute and solvent.

16. In the chlorine-water system, use of the normal empirically calculated \( K_{L}a \) (based on total chlorine) is satisfactory for the design of commercial chlorine towers. This \( K_{L}a \), however, cannot be correlated by generalizations known at this time.

17. The \( K_{g}a \) for the absorption of chlorine in caustic varies as the 0.7 power of the gas rate.

18. The so-called "critical" concentration, as applied to gas absorption systems, is a point condition influenced by many operating variables, and has little significance in the operation of a tower of finite height.

19. At sufficiently high caustic concentrations, the overall \( K_{g}a \) becomes independent of caustic concentration.

20. A method for calculating coefficients from data obtained under conditions where the gas rate changes appreciably through the tower has been developed.

21. The \( K_{g}a \) for the chlorine-caustic system correlates well with other gas-film controlled absorption data, as
represented by the Sherwood and Holloway correlation.
22. Systems similar to the chlorine-caustic system are not entirely satisfactory for the determination of gas film data because of inherent experimental difficulties.

On the basis of the results of this thesis, it is recommended that:
1. The explanation advanced in this thesis for the apparent peculiarity of the chlorine-water system be investigated (a) by the desorption of chlorine-water of various concentrations, and (b) by the absorption of chlorine in HCl solutions of such concentrations that the hydrolysis reaction is suppressed to a large degree.
2. Coefficients for the absorption of chlorine in water, calculated in the usual manner and presented in this thesis, be used for the design of commercial towers for the manufacture of chlorine-water bleach.
3. An attempt be made to solve the equations governing the diffusion across the film for the chlorine-water system, since this system can be considered representative of those involving reaction equilibrium as well as solubility equilibrium.
4. The chlorine-caustic system be investigated further, particularly to develop improved analytical experimental techniques, with a view to checking the data and methods of computation of this part of the work.
5. That the Sherwood and Holloway gas-film correlation
be used in the design of commercial soda bleach towers, due allowance being made for those sections of the tower where the residual caustic is below the "critical" concentration.
VII APPENDIX
A. SUPPLEMENTARY INTRODUCTION

Absorption Theory

The theoretical basis upon which the results of this thesis are presented is that developed from the two-film concept of Whitman (35), and discussed in detail by Sherwood (27).

At the phase boundary between two streams of gas and liquid moving relative to one another, it is assumed that there are two adjacent films, one in the gas phase and one in the liquid phase. These films are relatively stagnant and move in streamline flow. Hence, material transfer across these films can take place only by means of molecular diffusion under the influence of a driving force. This picture of mass transfer is analogous to that of heat transfer across films at phase boundaries where the heat transfer takes place by conduction and not convection, as in the main body of the fluid phase. The counterpart of convection in the case of mass transfer is referred to as "eddy" diffusion. Just as the rate of heat transfer by convection is rapid compared with that by conduction, the rate of molecular diffusion is generally the controlling factor in the rate of mass transfer. The evidence accumulated supporting this theory in both heat transfer and absorption is so conclusive, that it is accepted
without reservation at the present time, and systems that do not fit into this general picture may be considered to be influenced by other factors that have not been taken into account.

Since the rate of diffusion across these films is slow compared with the rate of eddy diffusion, the process may be considered as controlled by the resistance of the two films in series. The evidence supporting the film theory indicates that the interface itself offers no resistance to diffusion, that is to say, the gas and liquid are in equilibrium according to the solubility relationship.

**Equations for Liquid Film Absorption**

Considering, first, the liquid film, where the solute being absorbed has a diffusivity, D, the diffusion across the film will be governed by the film thickness, \( x_L \), the diffusivity, and the magnitude of driving force causing diffusion. This driving force is the solute concentration gradient across the film. If a small area, \( dA \), of the gas liquid interface is considered, the rate of mass transfer, \( dN \), across the film can be written as

\[
dN = \frac{D}{x_L} \Delta C \, dA \quad . . . . . . . . . . . (19)
\]

There are other complicating factors such as the solute and solvent concentration which should be included in the general differential equation. However, for most
engineering purposes and especially where only relatively dilute solutions are to be considered, the foresaid differential equation is adequate.

Since the interface area in a packed tower is difficult to ascertain with any degree of accuracy, it has been found convenient to use a factor, \( a \), which expresses the area of the liquid-gas interface per unit volume of packing, and is unique for a given type of packing. Thus \( dA = adV \). Substituting, the following equation is obtained.

\[
dN = \frac{dA}{x_L} \Delta C dV 
\]

(20)

The combination of physical constants is combined to define an absorption coefficient as follows.

\[
\frac{D_a}{x_L} = k_{La} 
\]

(21)

Assuming that \( D \) is relatively constant, \( k_{La} \) will be expected to vary with the factors that affect the film thickness. The value of \( a \) may also change with certain factors, and is closely related to the amount of liquid hold-up in the tower.

Since equation (20) expresses the rate of mass transfer at a particular point, it must necessarily be integrated over a finite height of the tower. To do this, it may be combined with a material balance written over the small volume, \( dV \). Absorption towers in general operate in countercurrent flow, and each point at a
given cross-section will be the same as any other point. Hence in place of \( dV \), \( Sdh \) may be written where \( S \) is the cross-section area, and \( dh \) is the height of packing considered. Thus the material balance is written over the differential height of tower, \( dh \).

For the finite height of tower, the material balance is given as

\[
G \left[ \frac{P_1 - P_2}{P_1 - P_2} \right] = \frac{L}{\varrho} (C_2 - C_1) \ldots \ldots \ldots \ldots \ldots (22)
\]

Differentiating this equation gives

\[
- \frac{G \pi dP}{(\pi - P)^2} = \frac{L dC}{\varrho} \ldots \ldots \ldots \ldots \ldots (23)
\]

where \( G \) = inert gas rate, (mols)

\( L \) = liquor rate

\( P \) = partial pressure of solute in gas phase

\( C \) = concentration of solute in liquid phase

\( \pi \) = total pressure in gas phase

\( \varrho \) = density of liquid phase

Combining equations (20), (21) and (23), an equation that can be integrated and used to evaluate the absorption coefficient is obtained

\[
\frac{L}{\varrho} dC = k_L a \Delta C Sdh \ldots \ldots \ldots \ldots \ldots (24)
\]

If the gas and liquor rates are expressed as mass velocities, and a unit cross section of the tower considered, equation (24) can be simplified, and re-arranged, after integrating over the height of the
tower, as follows.

\[ kLa = \frac{L}{\gamma h} \int \frac{dC}{\Delta C} \quad \cdots \quad (25) \]

This is the equation used to define and calculate the coefficients for the absorption of chlorine in water, as presented in this thesis.

The term \( \Delta C \) requires some consideration in its evaluation. In its simpliest form, it is the difference between the solute concentration in the liquid film at the interface and at the boundary adjacent to the main body of the liquid. This definition applies only when the rate of change of concentration of solute across the liquid film is constant, that is, when \( dC/dx \) is independent of \( x \). This is the case when the solute is at low concentration, and when there is no reaction between the solute and solvent. In such cases, the value of \( \Delta C \) is calculated by obtaining the partial pressure of solute in the gas at the interface from gas film data, or by assuming that the gas film has negligible effect, and that the interface liquid concentration is in equilibrium with the solute partial pressure in the gas phase. This partial pressure is then converted to solubility units by the equilibrium data. The difference between this calculated concentration and that in the main body of the liquid is the desired driving force.

Since the partial pressure in the gas and also the liquid concentration vary at every point in the tower,
the value of \( \Delta C \) must be obtained for every point in the tower. This is achieved by a graphical construction in which the operating line, equation (22), and the solubility data are plotted on the same coordinates, and the values of \( \Delta C \) for corresponding values of \( C \) obtained. When the operating line and solubility curve are essentially straight over the range of concentrations involved, it can be shown that the mean value of \( \Delta C \) is given by the logarithmic mean, defined as follows.

\[
\frac{\Delta C_2 - \Delta C_1}{\ln \frac{\Delta C_2}{\Delta C_1}} = \Delta C_{1\text{m}} \ldots \ldots \ldots . \text{(26)}
\]

In much of the work of this thesis, the use of the log mean driving force was permissible. However, where the range of concentration was great enough to give a curved operating line, equation (25) was graphically integrated.

**Equations for Gas Film Absorption**

In the gas phase, the resistance to diffusion will be proportional to the number of molecules of gas A, the number of molecules of B, the relative velocities in the direction of diffusion, and the length of the path. The driving force overcoming this resistance will be the pressure differential across the distance, \( x \). With these factors in mind, the rate of diffusion of gas A into gas B may be expressed by the following


\[-\frac{dP_A}{dx} = \frac{\rho_A}{M_A} \left( \frac{\rho_B}{M_B} \right) (U_A - U_B) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (27)\]

\[N_A = \text{mols diffusing per unit time per unit area} = \frac{U_A \rho_A}{M_A} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (28)\]

In the case of diffusion across the gas film, the solute gas A has a velocity, \(U_A\), but the inert gas is stagnant and \(U_B = 0\). Combining this restriction with equations (27) and (28), an equation for the rate of diffusion across the film is obtained.

\[N_A = \frac{M_B}{\rho_B} \left( \frac{-dP_A}{dx} \right) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (29)\]

From the gas law, it is known that

\[\frac{M_B}{\rho_B} = \frac{RT}{P_B} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (30)\]

At any point in the film, the total pressure, \(\pi\), is constant. Therefore \(-dP_A = dP_B\) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (31)\)

Substituting in equation (29) gives

\[N_A = \frac{RT}{xP_B} \left( -\frac{dP_B}{dx} \right) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (32)\]

It is customary to use the term gas diffusivity, \(D\), which is defined as equal to \((RT)^2/\pi x\), which may be assumed to be constant for any one system. Substituting in equation (32), and integrating over the thickness of the film \(x\), the usual form of the rate equation is obtained.

\[N_A = \frac{D\pi}{RTx} \ln \frac{P_{B1}}{P_{B2}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (33)\]
It has been found convenient to make use of a function called the "logarithmic mean" inert pressure in the gas film. This is defined as

$$P_{Rm} = \frac{P_{B1} - P_{B2}}{\ln \frac{P_{B1}}{P_{B2}}}$$

Substituting in equation (33), and remembering that

$$\left( P_{A2} - P_{Al} \right) = \left( P_{B1} - P_{B2} \right)$$

the rate may be expressed by

$$N_A = \frac{D \pi}{RTx} \left( P_{A2} - P_{Al} \right) \left( \frac{P_{A2} - P_{Al}}{P_{Rm}} \right)$$

The gas film coefficient, $k_g$, is defined as

$$k_g = \frac{D \pi}{RTxP_{Rm}}$$

This coefficient will only be a constant provided $x$ and $P_{Rm}$ are constant. Equation (35), with the substitution of $k_g$, may be combined with the material balance, equation (23), to give a relationship which can be integrated over the interface area across which diffusion is taking place. As in the case of the liquid film coefficient, the coefficient is evaluated on a volume basis by the introduction of the factor $a$, giving the surface per unit volume for a given type of packing.

$$\frac{GdP_A}{(\pi - P_A)^2} = \frac{LdC}{\int} = dN_A = k_g a (P_{A2} - P_{Al}) dV$$

Rearranging this equation, substituting $Sdh = dV$, expressing the gas and liquor rates as mass velocities,
and integrating over the tower height, the usual form of the equation defining \( k_a \) is obtained.

\[
k_{ga} = \frac{G \pi}{h} \int \frac{d \bar{P}}{(\bar{P} - \bar{P})^2(\Delta \bar{P})} \quad \ldots \ldots \ldots (38)
\]

where \( \Delta \bar{P} = \bar{P}_{A2} - \bar{P}_{A1} \)

\( \Delta \bar{P} \) is the partial pressure difference across the gas film.

\( \Delta \bar{P} = \bar{P}_g - \bar{P}_l \)

The partial pressure at the interface is determined from liquid film data, or in the case where the effect of the liquid film is subordinated directly from the liquor concentration and the solubility equilibrium data. In the work of this thesis on the gas film, the value of \( \bar{P}_l \) was assumed to be zero, since the data obtained with the use of strong caustic only was of interest. When the concentration of caustic at the liquid interface is sufficiently great, \( \bar{P}_l \) actually is zero.

Since the definition of \( k_{ga} \) includes the log mean inert pressure, it is better practice to calculate the value of \( k_{ga} (P_{Bm}) \) if \( P_{Bm} \) is likely to vary through the tower. This is done by adding \( P_{Bm} \) to both members of equation (38), and including \( P_{Bm} \) under the integral sign on the right.

\[
k_{ga} (P_{Bm}) = \frac{G \pi}{h} \int_{\bar{P}_1}^{\bar{P}_2} \frac{d \bar{P}}{(\bar{P}_1 - \bar{P})^2(\Delta \bar{P})} \quad \ldots \ldots \ldots (39)
\]
For the special case of the absorption of chlorine in strong caustic, equation (39) can be converted to give a more suitable form for calculation. As has been pointed out, \( P_i \) is zero for this case, and \( \Delta P = P \). Furthermore \( P_{\text{Em}} \) can be expanded and simplified similarly.

\[
P_{\text{Em}} = \frac{(\pi - 0) - (\pi - P)}{\ln \frac{\pi}{\pi - P}} = \frac{P}{\ln \frac{\pi}{\pi - P}} \quad \ldots \ldots \ldots (40)
\]

Substituting in equation (39), an expression which gives the values of the \( k_g a \) for all conditions is obtained.

\[
k_g a (P_{\text{Em}}) = \frac{G \pi}{h} \int_{P_1}^{P_2} \frac{dP}{(\ln \frac{\pi}{\pi - P})^2} \quad \ldots \ldots (41)
\]

Although this equation may be integrated analytically, it was found more convenient to use a graphical solution, since one solution could be used to obtain the value of the integral for all runs.

As it would be expected, \( k_g a \) is a function of the mass velocity of the gas through the tower. In cases where the rate of absorption is high it is necessary to use a feed gas relatively rich in solute gas if measurable driving force is to exist at the exhaust gas end of the tower. With the absorption of chlorine in caustic system, the rate of absorption is so rapid that it was necessary to use gas containing as much as 50 per cent chlorine at the entrance to the tower. When this high concentration is used, the gas rate through the
tower varies over a wide range, and hence, the $k_g a$ calculated by equation (41) is an average value. It is difficult, however, to determine what gas rate is associated with the average value, and the safest procedure is to refer to the range of gas rate rather than attempt to calculate an average.

To overcome this difficulty, an attempt was made to allow for the variation of gas rate in the calculation of the coefficient. The indications from the gas film data of other investigators and from heat transfer data are that $k_g a$ varies approximately as the 0.8 power of the mass velocity.

$$k_g a = d(G_1)^{0.8}$$

where $G_1$ is the total gas rate in lbs./ (hr.)(sq. ft.)

The molecular weight of the gas at any point in the tower when the partial pressure of chlorine is $P$ is given by

$$M_P = 71P + 29(\pi - P) = 42P + 29\pi$$

If the inert gas rate is $G$ mols/ (hr.) (sq. ft.), the total gas rate is $G\pi / \pi - P$, and the mass rate is

$$G_1 = \frac{G\pi}{\pi - P} (42P + 29\pi)$$

Let $k_g a (P_{BM})_1$ be the coefficient corresponding to the gas rate at the bottom of the tower where the partial pressure of chlorine is $P_1$. Then at some other point, $h$, in the tower, the value of the coefficient will be
\[ k_{a} \left( \frac{P_{m}}{P_{m}} \right)_{h} = k_{a} \left( \frac{P_{m}}{P_{m}} \right)_{1} \left( \frac{G_{1}h}{G_{1}} \right)^{0.8} \]

\[ = k_{a} \left( \frac{P_{m}}{P_{m}} \right)_{1} \left[ \frac{(42P_{1} + 29\Pi)(\Pi - P)}{(42P_{1} + 29\Pi)(\Pi - P)} \right]^{0.8} \cdots (45) \]

Substituting this equation in the differential equation (37), and integrating, the following equation is obtained.

\[ k_{a} \left( \frac{P_{m}}{P_{m}} \right)_{1} = \frac{G\Pi (42P_{1} + 29\Pi)}{\left( \Pi - P \right)^{0.8}} \exp \int_{P_{1}}^{P_{2}} \frac{P_{m}}{\left( 42P_{1} + 29\Pi \right)^{0.8}(P_{1} - P)} dP \cdots \cdots (46) \]

This equation defines the value of \( k_{a} \) at the mass rate when the partial pressure of chlorine is \( P_{1} \). For convenience, \( P_{1} \) has been taken as the inlet partial pressure of chlorine, and hence, all values of \( k_{a} \) have been based on the inlet gas rates. Theoretically, the power value of 0.8 should be modified after the first assumption to the value of the exponent actually found. In this work, the small difference found did not warrant recalculation of the data. The solution of the above equation was performed graphically, and is straightforward enough so as not to require further explanation.

**Relative Importance of Gas and Liquid Film**

As mentioned previously, the gas and liquid films adjacent to the interface can be regarded as series resistances to the process of diffusion from one phase to the other. Equations have been developed above for the calculation of coefficients on the basis of one film or
the other. The best that can be accomplished experimentally is the determination of an overall coefficient, since it is not possible to measure the concentration values at the actual interface. Furthermore, with changes in the operating variables, the relative effect of the two resistances would be expected to change, and hence, the value of the overall coefficient will change. Changes in value such as these would be extremely difficult to correlate in terms of the operating variables.

To overcome this difficulty, it is necessary to subordinate the effect of one film while studying the characteristics of the other. The most satisfactory method of accomplishing this is the judicious selection of the system. The factor having the greatest effect in determining the relative values of the two film resistances is the solubility of the gas in the liquid. In general, relatively insoluble gases constitute the systems where the liquid film is the controlling resistance. On the other hand, relatively soluble gases are cases where the gas film is the controlling resistance. Gases having intermediate solubility form the largest group of industrial gases, and in such cases, both films have an effect. The only logical method of studying this third group is in conjunction with absorption data from some system where either one or the other film is the controlling factor. In this way, the
overall coefficient can be broken into its individual film coefficients.

Since there can not be an accumulation in either film or at the interface, it is obvious that the rates through both films must be equal. Hence the following equality may be written.

\[ N = k_a \left( C_i - C_L \right) = \frac{k_a}{g} \left( P - P_i \right) \]  \hspace{1cm} (47)

and in terms of an overall coefficient

\[ N = \frac{K_a}{L} \left( C - C_L \right) = \frac{K_a}{g} \left( P - P_i \right) \]  \hspace{1cm} (48)

Using these equations and Henry's law to express the solubility relationship for the solute gas in the liquid, it can be shown that

\[ \frac{1}{K_a} = \frac{1}{Hg} + \frac{1}{k_f} \]  \hspace{1cm} (49)

and \[ \frac{1}{K_a} = \frac{1}{k_g} + \frac{H}{k_f} \]  \hspace{1cm} (50)

The term \( 1/K_a \) is simply the overall resistance of the films to diffusion, and hence these expressions may be used to evaluate the relative magnitudes of the individual film resistances.

These equations will be exact only when Henry's law applies to the system in question. However, they may be used as point equations, provided an effective value for Henry's law constant is calculated for the particular concentration in question. In the case of chlorine, where Henry's law does not apply even
approximately for the total chlorine in solution, values of the constant which is by definition c/P may be calculated at various values of the partial pressure, and the approximate effect of gas and liquid film determined. To carry out the calculation it is necessary to know the value of either \( k_{g,a} \) or \( k_{L,a} \) from data on some system where one or the other film was known to be controlling.

Using data for \( k_{g,a} \) obtained from the absorption of ammonia in acid by Doherty and Johnson (8), and the solubility data of this thesis for chlorine, it can be calculated that over the range of liquor rates from 1,000 to 20,000 lbs. per hr. - sq. ft. the relative effect of the gas film increased from less than 1 per cent to approximately 3 per cent. This percentage of the overall resistance is within the experimental error, and for practical purposes, it can be assumed that chlorine absorption in water should be a case of the liquid film controlling.

The absorption of chlorine in caustic is a case where the controlling resistance can vary from practically complete liquid film resistance at low caustic concentration to complete gas film resistance, if the caustic concentration is sufficiently high. The addition of caustic to the system introduces a non-reversible reaction, and gives rise to a multiple liquid film. Chlorine dissolves in the caustic solution, reacts with the caustic near the interface, and
lowers its concentration. To overcome this depletion, caustic must diffuse toward the interface, the rate being governed by the caustic concentration gradient in the film. The products of the reaction accumulate in the film until their concentration gradient is such that they diffuse out of the film toward the main body of the liquid at the rate at which they are formed. If the rate at which chlorine enters the liquid phase is greater than the rate at which caustic can diffuse across the film, a reaction boundary will be set up within the film. At low caustic concentration, this reaction boundary may be close to the main body of the liquid. As the caustic concentration is increased assuming a constant rate of chlorine absorption, the reaction zone or boundary moves toward the liquid face. The caustic concentration necessary to maintain this reaction boundary at the interface is known as the "critical caustic concentration". It is evident from this discussion that this critical concentration is a point function, dependent on the rate of absorption of chlorine, and hence, is a function of the many operating variables. At caustic concentrations greater than the critical, the reaction boundary remains at the interface.

Thus it is apparent that, at a constant rate of chlorine absorption, as the caustic concentration increases from zero the resistance of the liquid film to the diffusion of chlorine decreases from that for the
absorption of chlorine in water to zero when the critical concentration is reached. Since no changes have been made in the gas film its resistance remains constant, and its effect on the overall resistance varies with increasing caustic concentration from a negligible fraction at the low caustic concentrations to the total resistance to diffusion of chlorine at the critical concentration. At caustic concentrations above the critical, the absorption coefficient is representative of true gas film absorption and is independent of caustic concentration.

It should be pointed out that in the foregoing discussion, diffusion at a single point of the caustic liquor-gas interface was being considered. Since coefficients must be determined over a finite area of the interface, usually determined by a finite height of tower, it is evident that a part of the tower may be operating on a caustic liquor at a concentration greater than the critical, while in the remainder of the tower the liquid film resistance may be appreciable. The resulting coefficient will be an average, but lower than that for true gas film. To obtain true gas film coefficients, the liquor leaving the tower must have a caustic concentration greater than the "critical". For this reason, a plot of the coefficient for a finite height of tower vs caustic concentration will give a smooth curve
increasing from the value for the absorption of chlorine in water to that for true gas film absorption when the caustic concentration has not fallen to the critical value within the tower. This is in contradistinction to the forgoing discussion which applied to a single point in the tower, where a plot of \( k_g \) vs caustic concentration would give a break in the curve at the "critical" concentration. However, it is not experimentally feasible to obtain such data.

The main interest in the work of this thesis on the absorption of chlorine in caustic is to obtain true gas film data. The effect of caustic concentration is determined only to bear out the reasoning presented above, and to insure operation at caustic concentrations above the "critical" for the particular conditions of a run.

**Equilibrium Solubility of Chlorine in Water**

As a part of this research, it was necessary to determine experimentally the equilibrium solubility relationship for chlorine in water. Data published for this system by Adams and Edmonds\(^1\) had been calculated from the hydrolysis constants for the reaction determined by Yakovkin\(^41\). The experimental data of this thesis can be used to calculate the hydrolysis constants, and in turn calculate the Henry's law constant for the phase equilibrium between the partial pressure of chlorine in gas and the concentration of molecular chlorine in solution.
Chlorine would be expected to be irregular in its solubility relationship because of its reaction with water. The reaction may be written as follows.

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^- \] (51)

Since the solutions are relatively dilute, the hydrochloric acid formed may be assumed completely ionized. The equilibrium constant is given as follows.

\[ K = \frac{[\text{HOCl}][\text{H}^+][\text{Cl}^-]}{[\text{Cl}_2]} \] (52)

where the quantities in square brackets represent the activities of the products and reactant. The activities in this case can be assumed proportional to the concentrations without serious error, since only relatively dilute solutions are considered.

At equilibrium, there will be \( a \) mols of molecular chlorine in solution and \( b \) mols of hydrolysed chlorine. Hence, the total mols of chlorine in solution will be

\[ c = a + b \] (53)

For every mol of chlorine that hydrolyses when \( \text{Cl}_2 \) is dissolved in \( \text{Cl}_2 \)-free water, there will be \( a \) mol of \( \text{HOCl} \) and \( a \) \( \text{Cl}^- \) ion and \( \text{H}^+ \) ion.

Therefore, the equilibrium constant can be written as

\[ K = \frac{b^3}{a} \] (54)

and the concentration of hydrolysed chlorine will be

\[ b = \sqrt[3]{K_a} \] (55)

Assuming that the dissolved molecular chlorine is proportional to the partial pressure, \( P \), of chlorine in the gas phase, the relation between \( P \) and \( a \) can be
expressed as

\[ a = HP \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (56) \]

Combining equations (53), (55) and (56), an expression for the solubility of total chlorine in water can be written.

\[ c = HP + \sqrt[3]{KH} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (57) \]

It has been shown previously (Fig. 24) and published by Whitney and Vivian (38) that this equation expresses the experimental equilibrium data of this thesis within the experimental error. The values of H and K were determined by plotting the data in Fig. 24, and obtaining the slopes and intercepts of the isotherms. Equation (57) also gives a method of calculating the fraction of the total chlorine in solution that exists as molecular chlorine. Over the range of concentrations used in the absorption study of this thesis, the percentage of the total chlorine present as molecular chlorine varied from less than 5 to more than 25. The fact that equation (57) represents the experimental results as indicated in Fig. 24, is justification of the assumption that Henry's law does apply to the molecular chlorine in solution.

**Material Balances**

Material balances on the runs for the study of absorption of chlorine in water were made in several cases as a check on the experimental technique. There is a limit, however, as to the usefulness of the material
balance. In general, those conditions under which a material balance can be calculated with good precision are such that the resulting coefficient could contain appreciable error. This is particularly the case where the operating line tends to pinch the equilibrium line, as shown on an operating diagram. The driving force at the near equilibrium end of the operating line is so small that a normal error in the analytical procedure would not show up in the material balance, but would affect the calculated value of the coefficient considerably.

Just the reverse of this situation is the case where only a small amount of absorption occurs or at high liquor rate where the liquor concentrations are low. In these cases, the solute given up from the gas is calculated as the difference of two large values and a normal error in the analytical work would indicate considerable error in the material balance. In the determination of the driving force which is large in this case such error would have only a slight effect.

Material balances would not show any inherent errors in the analytical work on the gas side of the balance, since the same method of analysis is used for both the entering and exit gas analysis. The material balances serve as a check on the calibration of the gas and liquor meters and on the liquor analysis, since it
is only necessary to analyse the outlet liquor from the
tower. In general, satisfactory material balances could
be obtained for this system when the amount of chlorine
absorbed was appreciable. However, they indicate little
as to the precision to be expected in the resulting
coefficient.

The general method adopted in handling the data was
to perform an analysis on the exhaust gas from the tower,
and on the liquor outlet. From the gas and liquor
meters, the respective rates were obtained and from
these data a material balance was calculated. Since the
equilibrium data were determined by the use of the same
methods of analysis for gas and liquor, any constant
error existing in these techniques would not affect the
results of this thesis.

A few material balances were made on the runs for
the study of the absorption of chlorine in caustic.
These were difficult to perform, and due to the short-
age of time were not checked to any great extent. With
sufficient care and analytical work, material balances
could be obtained. The general procedure was to analyse
the gas entering and leaving the tower, measure the gas
and liquor rates, and check the residual caustic nor-
mality in the liquor leaving the tower.

No material balances were made on the runs for the
determination of the coefficients for oxygen in water.
Here also, the equilibrium data were checked by the same methods of analysis as used in the test runs, and inherent constant errors in the method of analysis would have no effect on the resulting coefficient.

**Operating Variables**

The range of variable was limited to that encountered in industrial absorption. Holloway\(^{(14)}\) demonstrated that it was economically unfeasible to operate a tower at liquor rates above the loading point. This imposed the upper limit for the liquor rate of this thesis. This rate is approximately 20,000 lbs./(hr.) (sq. ft.) for one inch rings. The lower limit was determined by three factors, - first, the lower limit found in industrial practice for cases of liquid film controlling; second, the limit at which the equipment could be operated without approaching equilibrium too closely; and third, the limit at which reliable data could be obtained because of non-uniform wetting of the packing. This lower limit was about 900 lbs./(hr.) (sq. ft.)

The range of gas rate covered was governed solely by the range necessary to establish the effect of gas rate on the coefficient. This range was about 60 to 600 lbs./(hr.) (sq. ft.)

The range of temperature was governed by that encountered in industrial practice, and necessary to determine the effect of temperature. During the winter,
36°F water was available, and by means of steam injection, a temperature of 90°F was used. Above this temperature, difficulty due to non-isothermal operation of the tower would become serious, as well as the fact that the solubility of chlorine decreases considerably with increase in temperature would render operation of commercial towers at temperatures much above 90°F impractical.

The concentration of chlorine in the gas stream entering the tower was chosen to give satisfactory operation of the experimental equipment. Except for the determination of the effect of gas concentration on the coefficient, this concentration had no bearing on the results.

The tower height selected was a compromise between a determination of the packed height with precision, the subordination of the bottom end effect, and the closeness to equilibrium conditions occurring at the bottom of the tower. The height of packing used in the preliminary work was eight feet, and this was reduced to four feet in the semi-commercial 14-inch tower. Two feet of packing were used in the 4-inch tower, and the end-effect determined experimentally, to give measurable driving forces over a greater range of liquor rates.

The cross-section of the towers was governed by the necessity of determining coefficients representative of commercial equipment. Since one-inch rings were available, it was desirable to use a tower of at least eight inches diameter, and a 14-inch tower was constructed.
The auxiliaries and the amount of gas available were not sufficient for the operation of this tower over the desired range of gas and liquor rates, and a four-inch tower was set up and checked for comparison with industrial size equipment by the absorption of oxygen in water for which data determined in semi-industrial size equipment were available.
B. DETAILED PROCEDURE

Materials of Construction

Because of the particularly corrosive nature of wet chlorine in contact with most materials, considerable care was necessary in the selection of materials of construction used for the experimental equipment.

Corrosion tests were conducted, and it was found that of the materials readily available, hard wood coated with a layer of plastic gum, was found to be the most satisfactory. Where possible, it was desirable to use glass, but due to the size of the equipment and the fact that it was to be set up in the Plant, the cost and the possibility of breakage precluded its use except for gas and liquor lines.

After the wood tower had been constructed, a method was developed for applying a satisfactory coating to iron pipe. This coating consisted of three individual layers of rubber paint known as Air-Vulc. Complete pickling of the surface of the metal was necessary prior to the application of the rubber, and due to the lack of facilities, this could not be accomplished on a large scale. This procedure was used to line a two and a half iron pipe line for the outlet liquor line and trap from the large tower.

A material known as transite made from cement, wood pulp and asbestos fibre bonded and formed under extreme pressure was found to give excellent operation in contact
with wet chlorine. This material was not available in sizes large enough for the semi-industrial tower, but the four-inch size was used to build the small experimental tower.

The commercial tower built by the plant was constructed of a concrete shell, lined with an acid-resisting brick, bonded in place by means of a chlorine resisting cement. Such construction was not practical for the experimental towers.

Various types of tile material were considered, but because of the difficulty of constructing the experimental equipment from standard shapes and the cost of having special shapes made, this material had to be discarded. Such tile as could have been used must have a glazed surface, otherwise the gas porosity of unglazed tile would have permitted considerable air leakage, with a corresponding error in the results. Unglazed tile can be cut and drilled fairly easily, but the glazed tile was found to be extremely brittle.

There are various materials on the market which are recommended as being satisfactory for chlorine water systems. One such material is known as Haveg, but because of its high cost, could not be considered in this work. Since this investigation was undertaken, it has been suggested that Carbate might be suitable material of construction. It is claimed\(^{(2)}\) that it can be machined, welded by means
of a suitable cement, and withstands the action of wet chlorine gas and liquid.

Since tile packing is readily available on the market, no difficulty was encountered in finding a suitable packing material.

**Details of Construction**

The majority of the data of this thesis was determined by the use of a four-inch tower, and this tower will be described in detail first.

The tower was constructed from two lengths of 4-inch transite pipe, one 30 inches long and the other 12 inches long. The arrangement for this tower has been shown in Figure 5. The two sections of pipe were fitted into a flange turned from a block of hard wood. A support for the packing material was formed by three one-quarter inch hard wood strips fastened across the opening of this flange. An opening for the gas inlet was drilled in the twelve-inch section of pipe immediately below this flange. The one-and-a-quarter-inch glass gas line was connected by means of a soft rubber sleeve set in plastic gum to insure against leakage. Near the upper end of the thirty-inch section, a similar connection was made to provide for the gas outlet.

The top of the thirty-inch section was fitted with a flange into which the liquor distributing system was built (see Figure 5). In this flange, short lengths of two- and four-inch copper tube were mounted concentrically, the inner tube acting as a circular weir. The liquor was fed to the center of this weir, and overflowed to the annular
space around it. This annular ring was drilled at four places equally spaced to which one-half-inch glass tubes were fastened by means of rubber sleeves. These glass tubes were of such length and shape that the liquor was conducted to the top of the packing without coming in contact with chlorine bearing gas. The discharge ends of these tubes were placed in a circle such that the area of the ring outside the circle was equal to the area of the circle enclosed. Since the tower was to be operated under a slight vacuum, a liquor seal was formed between the liquid in the weir and the outer ring. The liquor was fed through the center of the liquor seal.

The bottom of the tower was sealed with a blank wooden flange, and a liquor outlet provided by means of a glass tube connection similar to the gas line connections.

The whole tower was held together by three tie rods, and gas tight seals were insured by setting all joints in plastic gum. All wooden surfaces exposed to chlorine either in gas or liquor were coated with plastic gum.

Chlorine gas was taken from the plant cell gas line through a one-and-a-quarter-inch glass tube connected by rubber sleeves. Since it was desirable to be able to vary the gas composition, a tee was provided through which air could be mixed with the gas, and the ratio of chlorine cell gas to air controlled by rubber pinch valves.

The exhaust from the tower passed through a glass venturi-tube, constructed from one-and-a-quarter-inch pyrex tubing. The gas was drawn through the system by means
of a compressed air ejector, also constructed from pyrex glass. This ejector operated on approximately twenty pounds per square inch air pressure. To control the rate of gas flow, an air bleed was provided downstream from the air pressure. To remove disturbing influences due to variation of the air pressure, the compressed air line was controlled by a pressure reducing valve immediately before the ejector. The discharge from the ejector was connected to one of the Plant bleach towers. This system effectively disposed of the unabsorbed chlorine in the exhaust gas.

In the liquor system, water was taken from the plant main, and passed through an injection tee to which a steam line was connected. A thermometer in a well located immediately below the tee was used to indicate the rate of steam injection to maintain the desired temperature. The water then entered a constant head tank, located approximately ten feet above the top of the tower. The overflow from this tank was discharged to the sewer. From the head tank, the water passed through an orifice to the top of the tower.

The liquor from the bottom of the tower passed through a trap, to prevent gas leakage, made of one-and-one-quarter-inch glass tubing, and then discharged under the surface of a strong caustic solution in the Plant bleach tank. This procedure effectively disposed of the chlorine water solution, and in addition, prevented the waste of a consider-
able amount of chlorine.

Sampling points were provided in the gas lines immediately adjacent to the tower. A liquor sampling point was provided at the trap. In addition, three one-half inch cups to collect liquor at the base of the packing were installed; one was located at the center of the cross-section, one at the wall, and the other half way between these two. In this way, the liquor could be sampled without the effect of absorption in the bottom section of the tower.

Temperatures of the various streams were obtained from mercury thermometers in wells adjacent to the tower.

The liquor rates were determined by means of calibrated orifices. A set of three of these was constructed to cover the range of rates desired, and they could be placed in the liquor line interchangeably. These orifices were calibrated directly by weighing the amount of water collected during a measured interval of time. Provision was made in the installation of the liquor line so that the calibration of the orifices could be checked from time to time, and in this way the effect of corrosion on the reading of the orifices could be observed and corrected. The orifice calibrations are given in Figures 31 and 32, and were found to remain unchanged throughout the investigation. The differential across the orifice was measured directly in inches of water in inverted U-type manometer.
ORIFICE CALIBRATION
FOR
14-INCH TOWER

L - LBS./HR. - SQ. FT.

ΔH - INCHES OF WATER

NO. 1

NO. 3

NO. 4

9-23-40
The gas rate was determined by means of a glass venturi-tube. Two of these tubes were blown from pyrex glass, to cover the range of gas rates, and could be inserted in the gas line interchangeably. The pressure differential given by the venturi-tube was measured by a draft gauge. The static pressure at the upstream pressure tap was also measured. The venturi-tubes were calibrated by metering carbon dioxide gas into an air stream through the venturi, and then analysing the mixed gas for carbon dioxide. The calibration for these venturi-tubes is given in Figures 33 and 34.

For the runs on the absorption of chlorine in water, the tower was packed with 2 feet of one-inch tile Raschig rings. In the caustic runs, only one foot of packing was used. The system was essentially the same for the caustic runs, except that a tank was provided for preparing the desired caustic solution, and a pump to supply the liquor to the tower.

In the runs on the absorption of oxygen in water, oxygen from a cylinder was injected into the water line upstream from the steam injection tee. This allowed ample time for saturation of the water with oxygen, and the head tank provided a means for the escape of excess oxygen. In this case, no gas samples were taken since the concentration of oxygen in air would not be materially changed by the small amount of oxygen being desorbed from
VENTURI METER CALIBRATION
FOR
4-INCH TOWER

G - CUFT./HR.- SQFT.

ΔH - FT. OF FLUID FLOWING

FIG. 33
VENTURI METER CALIBRATION
FOR
14-INCH TOWER

G - CUFT./HR. = SQ.FT.

ΔH - FT. OF FLUID FLOWING

9-23-40
the liquor in the tower. Liquor samples were taken immediately before and after the tower.

The set up for the 14-inch tower was identical except that four feet of one-inch rings were used as packing, and larger orifices were used to determine the liquor rate. The large venturi described above was used to measure the gas rate.

Test Procedures

The actual operations required during the making of a run were comparatively few and straightforward once the equipment was ready for operation.

Usually the flow of gas through the tower was adjusted to the approximate value by turning on the ejector and adjusting the air bleed to the exhaust gas line. Then the analysis of the gas entering the tower was determined approximately by the use of an ordinary Orsat apparatus in which the chlorine was absorbed in caustic. On the basis of this analysis, the ratio of the rich chlorine gas rate to the air rate at the mixing tee was adjusted, and the analysis checked again with the Orsat.

When this gas composition had been adjusted, the liquor rate was set at the desired value, and the rate of steam injection controlled to maintain the desired liquor temperature within ±1°F. The tower was allowed to operate under these conditions for about ten to fifteen minutes at which time a sample of the liquor at the trap was taken and analysed. After another interval of ten or fifteen minutes, a second sample was taken and
analysed. If the analysis checked with the first, the tower was assumed to be in steady state operation. If a check was not obtained, samples were taken until it was evident that steady state existed. Readings of the manometers connected to the gas venturi-tube and the water orifice were recorded, as well as the temperature of the inlet water and inlet and exhaust gas. A sample of the exhaust gas was collected in a weighed evacuated gas bulb. A liquor sample was taken at the same time as the gas sample. The liquor sample was analysed immediately in the Plant. The gas bulbs were taken to the laboratory where they were weighed on the analytical balance, and the gas analysed.

The procedure in carrying out the runs where caustic liquor was used was similar except for the added operation of preparing and cooling the caustic solution. The normality of the solution was determined by titration with sulfuric acid in the presence of phenolphthalein. The gas rate and composition were then adjusted, and the liquor stream turned on to the desired rate. Due to the limited capacity of the feed tank, it was not possible at some of the high rates to operate a sufficient length of time to insure steady state operation. In every case examined when caustic liquor was used, steady state was established in less than ten minutes. Hence there are indications that steady state existed before data were recorded.
The test procedure in the oxygen runs was very simple. Air was drawn through the tower at a given rate, and the water rate adjusted to the desired value. Oxygen from a cylinder was injected into the water stream ahead of the head tank. The water temperature was controlled by the rate of steam injection. After the tower had been in operation for 10 - 15 minutes, samples of the entering and exit liquor were taken and analysed immediately. After another 10 minute interval, a second was taken, and the temperatures and manometer readings recorded. If the liquor analyses checked with the first set, the run was complete.

As a check on the analytical work in the study of oxygen absorption, the Henry's law constant was determined experimentally. Comparison of the experimental values with those of the literature\(^{(15)}\) was excellent, the agreement being better than 1%. The procedure consisted of bubbling air through distilled water at constant temperature and analysing for dissolved oxygen. The same procedure was applied to the water used in the plant and no change in the equilibrium solubility could be observed.

In the few tests run on the commercial tower, the usual procedure for runs on the absorption of chlorine in water was modified because of difficulty in the determination of the gas rate. Since there was no convenient method to measure this rate, the rate of caustic
production over a two to four hour period was determined, and the gas rate calculated from the caustic rate and gas analysis. For every mol of caustic produced in the Allen-Moore type brine cell, one half mol of chlorine is produced, and the cell reactions causing inefficiency consume both sodium and chlorine in this ratio.

The liquor rate was measured by a calibrated orifice in the plant water line, and the temperatures of the inlet and outlet liquor were recorded. Gas samples were taken in gas weighing bulbs and analysed.

**Analytical Procedures**

The analytical procedures used in the work on the absorption of chlorine in water were essentially standard procedures\(^{(26)}\), modified as to technique to satisfy the experimental conditions.

The analysis of the chlorine water was performed by collecting a sample in a 25 ml. pipette without allowing the sample to come in contact with the air, and introducing this sample below the surface of a solution of 10 ml. of 10 per cent potassium iodide solution in 25 ml. of water. The chlorine water solution liberated in equivalent amount of iodine, which was then titrated with 0.05N sodium thiosulfate solution. As long as the iodine remained in solution, a sufficient excess of KI had been used. The equations for the reactions are

\[
\begin{align*}
(1) \quad & \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCI} + \text{HCl} \\
(2) \quad & \text{Cl}_2 + 2\text{KI} \rightarrow 2\text{KCl} + \text{I}_2 \\
(3) \quad & \text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6
\end{align*}
\]
The chlorine concentration of the solution in mols per cu. ft. is given by

\[ C = \frac{623}{(2)(1000)} \left[ \frac{N_{\text{thio}}(\text{ml. thio used})}{25} \right] \]

In order to check the possibility of an irreversible chlorine reaction with impurities in the water used, and also to determine the presence of chloride in the water, an analysis for total chlorine was carried out in the early part of the work. The analysis described above gave the concentration of molecular chlorine in solution together with the hypochlorous acid and its equivalent of hydrochloric acid. Chloride in excess of this would not be evident. The presence of excess chloride would have the effect of changing the equilibrium solubility and would necessitate the calculation of a set of equilibrium data for a given initial chloride concentration in the entering liquid.

Chlorine not present as molecular chlorine or its equivalent as hydrolysed chlorine would be present as chlorites, chlorates and chlorides. It is the chlorides formed along with the chlorates which interfere with the equilibrium. The basis of the analytical method was the reduction of chlorates to chloride by the use of sodium nitrite(31).

A 2 ml. sample was pipetted into a 250 ml. flask containing 10 ml. of distilled water, 10 ml. of 10 per
cent sodium nitrite solution and 5 ml. of concentrated nitric acid. The solution was heated to boiling to reduce the chlorites and chlorates to chlorides. The equations for the reactions are

\[ \text{NaNO}_2 + \text{HNO}_3 \rightarrow \text{HNO}_2 + \text{NaNO}_3 \]
\[ \text{NaClO}_3 + 3\text{HNO}_2 \rightarrow \text{NaCl} + 3\text{HNO}_3 \]
\[ \text{HOCl} + \text{HNO}_2 \rightarrow \text{HCl} + \text{HNO}_3 \]

Vigorous boiling was avoided, since this might cause the loss of chlorine from the solution.

Heating was sufficient when the major part of the evolution of nitrogen oxides ceased. The solution was then cooled, and the excess reducing agent removed by the addition of solid urea.

\[ 2\text{HNO}_2 + \text{CO(NH}_2\text{)}_2 \rightarrow \text{CO}_2 + \text{N}_2 + 3\text{H}_2\text{O} \]

This is necessary to prevent the precipitation of silver nitrite in the subsequent titration. The end point of the addition of urea is indicated by the permanence of the pink color in contact with potassium permanganate on a spot test plate.

A known excess of silver nitrate was added, and the excess titrated with standard potassium thiocyanate, using 2 ml. of ferric ammonium sulfate solution in nitric acid as indicator.

The concentration of total chlorine in solution is given by:

\[ C = \frac{(62.3)}{(2)(1000)} \left[ \frac{(\text{ml. AgNO}_3) (\text{NaNO}_3) - (\text{ml. KSCN}) (\text{KSCN})}{2} \right] \]
The concentration of chlorine in the gas was determined by collecting a sample of the gas in a gas weighing bulb. This bulb was dried, evacuated to at least 23 inches Hg vacuum, and weighed on an analytical balance. The gross weight after sampling was determined, and then 10 per cent potassium iodide was introduced by cooling the bulb. As soon as some of the chlorine had reacted, no difficulty was encountered in introducing more iodide solution. When enough iodide solution had been added to dissolve the precipitated iodine, a sufficient excess of iodide was present, the stopper was removed, and the iodine titrated with 0.5 N thiosulfate solution. The equations for these reactions are the same as those discussed for the liquor analysis. The percentage of chlorine in the gas was calculated by subtracting the water vapor in the saturated volume of the bulb at the temperature of sampling from the net weight of the sample to give the weight of chlorine plus air. The weight of chlorine was calculated from the milli-equivalents of thiosulfate used, and the weight of air was obtained by difference. Dividing these weights by their respective molecular weights enabled the calculation of the mol per cent of chlorine in the gas.

In the experimental work to determine the equilibrium solubility of chlorine in water, the same sampling and analytical technique as was used in the absorption work was used to obtain the concentration of chlorine in the gas stream. The method of sampling the liquor, however,
was modified somewhat. Because of the relatively high room temperature, it was found impossible to prevent gas from separating from the liquid in the pipette. To overcome this, a 10 to 20 ml. sample was collected in a small evacuated gas weighing bulb, and the net weight of the sample obtained. Ten per cent potassium iodide solution was introduced in excess, and same procedure of titration and calculation as described above for the gas analysis was followed.

In the oxygen runs, the concentration of dissolved oxygen was determined by the Winkler method\(^{40}\) as modified by Holloway\(^{14}\), and by the work of this thesis. Four prepared reagents were required.

(1) Manganous sulfate \(4\text{N}\), - 45 gms. \(\text{MnSO}_4\cdot4\text{H}_2\text{O}\) dissolved in 100 ml. of water.

(2) Alkaline potassium iodide solution, - 36 gms. \(\text{NaOH}\) and 10 gms. \(\text{KI}\) dissolved in 100 ml. of water.

(3) Strong potassium iodide solution, - 1 gm. per ml.

(4) Concentrated sulfuric acid solution, - 100 ml. \(\text{H}_2\text{SO}_4\) in 100 ml. water.

The procedure was as follows. The sample was taken in a 250 ml. stoppered flask with as little contact with the air as possible. One ml. of manganous sulfate solution (No. 1) and one ml. of alkaline potassium iodide solution (No. 2) were added, both being introduced below the surface of the liquid. The flask was stoppered and shaken,
and the precipitate allowed to settle. After a second shaking and settling, three ml. of strong potassium iodide solution (No.3) and two ml. of conc. $\text{H}_2\text{SO}_4$ (No.4) added. The flask was again shaken. The resulting iodine solution was then used to titrate five ml. of 0.01 N thio-sulfate solution.

The equations for these reactions are:

$$\text{MnSO}_4 + 2\text{NaOH} \rightarrow \text{Mn(OH)}_2 + \text{Na}_2\text{SO}_4$$

$$\text{Mn(OH)}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{MnO}_3$$

$$\text{H}_2\text{MnO}_3 + 2\text{H}_2\text{SO}_4 + 2\text{KI} \rightarrow \text{MnSO}_4 + \text{K}_2\text{SO}_4 + 3\text{H}_2\text{O} + \text{I}_2$$

The concentration of dissolved oxygen in mols/cu.ft. is given by

$$C = \frac{62.3}{(4)(1000)} \left[ \frac{5.0 \text{ Nthio}}{\text{ml. I}_2\text{Soln.}} \right]$$
C. SUMMARIZED DATA

The data are summarized in the order of the number of the run. Runs 1 to 110 were made in the study of the absorption of chlorine in water.

Runs 1 to 22 and 39 to 50 were made to determine the effect of liquor rate, \( L \), on the value of \( K_{La} \). Runs 23 to 38 gave the effect of gas rate, \( G \), on \( K_{La} \). Runs 51 to 63 gave the effect of temperature, and Runs 64 to 70 were made to determine the effect of gas concentration on \( K_{La} \). Runs 1 to 70 were made on the 4-inch Tower, with two feet of one-inch Raschig rings (dumped) as packing.

Runs 71 to 83 were made on the 14-inch tower, with four feet of one-inch rings (dumped) as packing. Runs 84 to 106 were calculated from data obtained with the assistance of Practice School Group 2A40, using the 14-inch tower.

The data for the runs on the commercial tower are given as Runs 107 to 110, which were carried out with the assistance of Practice School Group 2A40.

The desorption of oxygen was studied in Runs 111 to 116 on the 4-inch tower, and Runs 117 to 120 on the 14-inch tower.

The data on the absorption of chlorine in caustic solutions are given in Runs 121 to 162. These data were obtained with the assistance of Practice School group 4A41.

The solubility data for chlorine in water are given in tabulated form.
### Absorption of Chlorine in Water

#### 4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)/(sq.ft.)</td>
<td>3,160</td>
<td>3,130</td>
<td>1,890</td>
<td>1,010</td>
<td>1,400</td>
<td>2,390</td>
<td>3,950</td>
<td>5,800</td>
<td>7,600</td>
</tr>
<tr>
<td>G, lbs./(hr.)/(sq.ft.)</td>
<td>129</td>
<td>129</td>
<td>127</td>
<td>127</td>
<td>130</td>
<td>127</td>
<td>126</td>
<td>125</td>
<td>124</td>
</tr>
<tr>
<td>Cl*, mols/(cu.ft.)(10^4)</td>
<td>13.4</td>
<td>10.7</td>
<td>11.2</td>
<td>12.5</td>
<td>15.7</td>
<td>11.3</td>
<td>9.3</td>
<td>8.6</td>
<td>7.9</td>
</tr>
<tr>
<td>Cl, mols/(cu.ft.)(10^4)</td>
<td>15.3</td>
<td>11.5</td>
<td>12.5</td>
<td>--</td>
<td>16.4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>P1, atmos.</td>
<td>0.197</td>
<td>0.196</td>
<td>0.171</td>
<td>0.163</td>
<td>0.232</td>
<td>0.171</td>
<td>0.161</td>
<td>0.161</td>
<td>0.156</td>
</tr>
<tr>
<td>P2, atmos.</td>
<td>0.183</td>
<td>0.184</td>
<td>0.164</td>
<td>0.159</td>
<td>0.226</td>
<td>0.161</td>
<td>0.147</td>
<td>0.143</td>
<td>0.134</td>
</tr>
<tr>
<td>T2, deg. F. (liquor)</td>
<td>69</td>
<td>69</td>
<td>70</td>
<td>70</td>
<td>71</td>
<td>71</td>
<td>70</td>
<td>70</td>
<td>71</td>
</tr>
<tr>
<td>t2, deg. F. (gas)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>71</td>
<td>71</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>KLa*, 1/hr.</td>
<td>32.6</td>
<td>22.0</td>
<td>16.2</td>
<td>11.2</td>
<td>16.2</td>
<td>21.2</td>
<td>27.0</td>
<td>35.8</td>
<td>50.6</td>
</tr>
<tr>
<td>KLa, 1/hr.</td>
<td>43.5</td>
<td>24.5</td>
<td>19.7</td>
<td>--</td>
<td>17.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>End Factor.</td>
<td>0.75</td>
<td>0.90</td>
<td>0.32</td>
<td>--</td>
<td>0.90</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>KLa**, 1/hr.</td>
<td>39</td>
<td>22</td>
<td>17</td>
<td>11</td>
<td>16</td>
<td>21</td>
<td>27</td>
<td>36</td>
<td>50</td>
</tr>
<tr>
<td>KLa*(Pseudo-coefficient)</td>
<td>73</td>
<td>39</td>
<td>34</td>
<td>21</td>
<td>27</td>
<td>39</td>
<td>53</td>
<td>70</td>
<td>87</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to KLa calculated from it.

** KLa calculated from the trap sample, and corrected by the average end factor. If no trap sample was taken, KLa** is the same as KLa*.

Subscript 1 refers to bottom of tower, and subscript to top of tower.
Absorption of Chlorine in Water

4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>2,420</td>
<td>10,100</td>
<td>13,600</td>
<td>19,000</td>
<td>25,200</td>
<td>21,300</td>
<td>18,000</td>
<td>15,400</td>
<td>12,300</td>
</tr>
<tr>
<td>G, lbs./(hr.)(sq.ft.)</td>
<td>122</td>
<td>127</td>
<td>128</td>
<td>126</td>
<td>122</td>
<td>124</td>
<td>126</td>
<td>125</td>
<td>126</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;, mols/(cu.ft.)(10&lt;sup&gt;4&lt;/sup&gt;)</td>
<td>9.4</td>
<td>7.8</td>
<td>8.6</td>
<td>6.9</td>
<td>4.3</td>
<td>6.2</td>
<td>7.8</td>
<td>7.5</td>
<td>8.1</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;, mols/(cu.ft.)(10&lt;sup&gt;4&lt;/sup&gt;)</td>
<td>--</td>
<td>8.1</td>
<td>8.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>P&lt;sub&gt;1&lt;/sub&gt;, atmos.</td>
<td>0.118</td>
<td>0.194</td>
<td>0.220</td>
<td>0.209</td>
<td>0.156</td>
<td>0.191</td>
<td>0.203</td>
<td>0.194</td>
<td>0.193</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;, atmos.</td>
<td>0.109</td>
<td>0.166</td>
<td>0.178</td>
<td>0.156</td>
<td>0.112</td>
<td>0.142</td>
<td>0.153</td>
<td>0.148</td>
<td>0.156</td>
</tr>
<tr>
<td>T&lt;sub&gt;2&lt;/sub&gt;, deg. F.(liquor)</td>
<td>70</td>
<td>72</td>
<td>72</td>
<td>71</td>
<td>69</td>
<td>70</td>
<td>69</td>
<td>70</td>
<td>69</td>
</tr>
<tr>
<td>t&lt;sub&gt;2&lt;/sub&gt;, deg. F.(gas)</td>
<td>70</td>
<td>70</td>
<td>72</td>
<td>71</td>
<td>72</td>
<td>71</td>
<td>70</td>
<td>71</td>
<td>70</td>
</tr>
<tr>
<td>K&lt;sub&gt;La&lt;/sub&gt;**, 1/hr.</td>
<td>23</td>
<td>44</td>
<td>67.5</td>
<td>73.5</td>
<td>76.8</td>
<td>77.2</td>
<td>80.0</td>
<td>69.5</td>
<td>59.3</td>
</tr>
<tr>
<td>K&lt;sub&gt;La&lt;/sub&gt;, 1/hr.</td>
<td>--</td>
<td>50.0</td>
<td>69.6</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>End Factor.</td>
<td>--</td>
<td>0.95</td>
<td>0.97</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>K&lt;sub&gt;La&lt;/sub&gt;**, 1/hr.</td>
<td>23</td>
<td>44</td>
<td>61</td>
<td>74</td>
<td>77</td>
<td>77</td>
<td>80</td>
<td>69</td>
<td>59</td>
</tr>
<tr>
<td>K&lt;sub&gt;La&lt;/sub&gt;(Pseudo-coefficient)</td>
<td>50</td>
<td>87</td>
<td>112</td>
<td>140</td>
<td>170</td>
<td>154</td>
<td>158</td>
<td>135</td>
<td>116</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to K<sub>La</sub> calculated from it.

** K<sub>La</sub> calculated from the trap sample, and corrected by the average end factor. If no trap sample was taken, K<sub>La</sub>** is the same as K<sub>La</sub>*</n>Subscript 1 refers to bottom of tower, and subscript 2 to top of tower.
Absorption of Chlorine in Water

4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>222</th>
<th>23</th>
<th>24</th>
<th>25</th>
<th>26</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>1,960</td>
<td>3,450</td>
<td>5,400</td>
<td>8,700</td>
<td>5,000</td>
<td>5,000</td>
<td>5,000</td>
<td>5,000</td>
<td></td>
</tr>
<tr>
<td>G, lbs./(hr.)(sq.ft.)</td>
<td>125</td>
<td>123</td>
<td>123</td>
<td>122</td>
<td>61.5</td>
<td>88.0</td>
<td>125</td>
<td>175</td>
<td>254</td>
</tr>
<tr>
<td>C_l*, mols/(cu.ft.)(10^4)</td>
<td>11.5</td>
<td>9.3</td>
<td>8.8</td>
<td>6.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>C_l, mols/(cu.ft.)(10^4)</td>
<td>12.1</td>
<td>11.3</td>
<td>9.9</td>
<td>7.5</td>
<td>11.2</td>
<td>10.7</td>
<td>10.6</td>
<td>9.4</td>
<td>11.2</td>
</tr>
<tr>
<td>P_1, atmos.</td>
<td>0.162</td>
<td>0.154</td>
<td>0.160</td>
<td>0.146</td>
<td>0.182</td>
<td>0.168</td>
<td>0.168</td>
<td>0.139</td>
<td>0.166</td>
</tr>
<tr>
<td>P_2, atmos.</td>
<td>0.155</td>
<td>0.142</td>
<td>0.142</td>
<td>0.124</td>
<td>0.141</td>
<td>0.140</td>
<td>0.148</td>
<td>0.126</td>
<td>0.154</td>
</tr>
<tr>
<td>T_2, deg. F.(liquor)</td>
<td>70</td>
<td>68</td>
<td>69</td>
<td>70</td>
<td>70</td>
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<td>70</td>
<td>70</td>
<td>69</td>
</tr>
<tr>
<td>t_2, deg. F.(gas)</td>
<td>74</td>
<td>73</td>
<td>71</td>
<td>72</td>
<td>70</td>
<td>68</td>
<td>68</td>
<td>69</td>
<td>70</td>
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<tr>
<td>K_{La*}, 1/hr.</td>
<td>19.1</td>
<td>23.8</td>
<td>33.3</td>
<td>43.0</td>
<td>--</td>
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</tr>
<tr>
<td>K_{La}, 1/hr.</td>
<td>20.5</td>
<td>32.9</td>
<td>40.4</td>
<td>48.6</td>
<td>43.4</td>
<td>42.4</td>
<td>40.9</td>
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</tr>
<tr>
<td>K_{La**}, 1/hr.</td>
<td>13</td>
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<td>36</td>
<td>43</td>
<td>38</td>
<td>37</td>
<td>36</td>
<td>36</td>
<td>39</td>
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<tr>
<td>K_{La}, (Pseudo-coefficient)</td>
<td>39</td>
<td>62</td>
<td>72</td>
<td>92</td>
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<td>--</td>
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</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to K_{La} calculated from it.

** K_{La} calculated from the trap sample, and corrected by the average end factor. If no trap sample was taken, K_{La}** is the same as K_{La*}.

Subscript 1 refers to bottom of tower, and subscript 2 to top of tower.
Absorption of Chlorine in Water

4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>28</th>
<th>29</th>
<th>30</th>
<th>31</th>
<th>32</th>
<th>33</th>
<th>34</th>
<th>35</th>
<th>36</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L, \text{lbf./hr.}(\text{sq.ft.}))</td>
<td>5,000</td>
<td>5,000</td>
<td>9,000</td>
<td>9,000</td>
<td>1,960</td>
<td>2,000</td>
<td>5,000</td>
<td>9,000</td>
<td>2,000</td>
</tr>
<tr>
<td>(G, \text{lbf./hr.}(\text{sq.ft.}))</td>
<td>550</td>
<td>653</td>
<td>539</td>
<td>286</td>
<td>286</td>
<td>562</td>
<td>387</td>
<td>178</td>
<td>182</td>
</tr>
<tr>
<td>(C_1{\text{*}}, \text{mols/(cu.ft.)(10^4)})</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(C_1, \text{mols/(cu.ft.)(10^4)})</td>
<td>11.7</td>
<td>11.2</td>
<td>8.8</td>
<td>9.5</td>
<td>13.3</td>
<td>13.4</td>
<td>11.9</td>
<td>10.0</td>
<td>13.6</td>
</tr>
<tr>
<td>(P_1, \text{atmos.})</td>
<td>0.166</td>
<td>0.160</td>
<td>0.150</td>
<td>0.177</td>
<td>0.165</td>
<td>0.160</td>
<td>0.203</td>
<td>0.199</td>
<td>0.178</td>
</tr>
<tr>
<td>(P_2, \text{atmos.})</td>
<td>0.167</td>
<td>0.156</td>
<td>0.144</td>
<td>0.163</td>
<td>0.161</td>
<td>0.158</td>
<td>0.197</td>
<td>0.177</td>
<td>0.170</td>
</tr>
<tr>
<td>(T_2, \text{deg. F. (liquor)})</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>71</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>(t_2, \text{deg. F. (gas)})</td>
<td>69</td>
<td>70</td>
<td>70</td>
<td>73</td>
<td>72</td>
<td>72</td>
<td>71</td>
<td>71</td>
<td>71</td>
</tr>
<tr>
<td>(K_{La*}, \text{1/hr.})</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(K_{La}, \text{1/hr.})</td>
<td>47.0</td>
<td>46.1</td>
<td>59.3</td>
<td>57.5</td>
<td>24.9</td>
<td>27.6</td>
<td>39.5</td>
<td>56.6</td>
<td>24.0</td>
</tr>
<tr>
<td>End Factor.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(K_{La**}, \text{1/hr.})</td>
<td>41</td>
<td>41</td>
<td>52</td>
<td>51</td>
<td>22</td>
<td>24</td>
<td>35</td>
<td>50</td>
<td>21</td>
</tr>
<tr>
<td>(K_{La}(\text{Pseudo-coefficient}))</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to \(K_{La}\) calculated from it.

** \(K_{La}\) calculated from the trap sample, and corrected by the average end factor. If no trap sample was taken, \(K_{La**}\) is the same as \(K_{La*}\).

Subscript 1 refers to bottom of tower, and subscript 2 to top of tower.
# Absorption of Chlorine in Water

## 4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>37</th>
<th>38</th>
<th>39</th>
<th>40</th>
<th>41</th>
<th>42</th>
<th>43</th>
<th>44</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$, lbs./(hr.)(sq.ft.)</td>
<td>2,000</td>
<td>9,000</td>
<td>2,700</td>
<td>3,700</td>
<td>6,700</td>
<td>1,450</td>
<td>1,300</td>
<td>910</td>
<td>12,200</td>
</tr>
<tr>
<td>$G$, lbs./(hr.)(sq.ft.)</td>
<td>63</td>
<td>62</td>
<td>127</td>
<td>128</td>
<td>129</td>
<td>128</td>
<td>127</td>
<td>128</td>
<td>128</td>
</tr>
<tr>
<td>$C_1$, mols/(cu.ft.)(10^4)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$C_1$, mols/(cu.ft.)(10^4)</td>
<td>16.7</td>
<td>9.9</td>
<td>13.7</td>
<td>12.7</td>
<td>11.7</td>
<td>15.4</td>
<td>15.5</td>
<td>15.8</td>
<td>9.3</td>
</tr>
<tr>
<td>$P_1$, atmos.</td>
<td>0.236</td>
<td>0.221</td>
<td>0.190</td>
<td>0.194</td>
<td>0.216</td>
<td>0.188</td>
<td>0.185</td>
<td>0.185</td>
<td>0.210</td>
</tr>
<tr>
<td>$P_2$, atmos.</td>
<td>0.211</td>
<td>0.158</td>
<td>0.177</td>
<td>0.177</td>
<td>0.188</td>
<td>0.180</td>
<td>0.176</td>
<td>0.180</td>
<td>0.170</td>
</tr>
<tr>
<td>$T_2$, deg. F.(liquor)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>$t_2$, deg. F.(gas)</td>
<td>72</td>
<td>72</td>
<td>73</td>
<td>73</td>
<td>72</td>
<td>71</td>
<td>72</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>$K_{L1}$*, l/hr.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$K_L$, l/hr.</td>
<td>26.6</td>
<td>54.5</td>
<td>30.3</td>
<td>35.5</td>
<td>49.5</td>
<td>21.8</td>
<td>20.7</td>
<td>15.0</td>
<td>68.5</td>
</tr>
<tr>
<td>End Factor.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$K_{L1}$**, l/hr.</td>
<td>23</td>
<td>48</td>
<td>26</td>
<td>31</td>
<td>44</td>
<td>19</td>
<td>18</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>$K_L$, (Pseudo-coefficient)</td>
<td>--</td>
<td>--</td>
<td>50</td>
<td>57</td>
<td>79</td>
<td>37</td>
<td>35</td>
<td>23</td>
<td>113</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to $K_{L1}$ calculated from it.

** $K_L$ calculated from the trap sample, and corrected by the average end factor. If no trap sample was taken, $K_{L1}$* is the same as $K_{L1}$.

Subscript 1 refers to bottom of tower, and subscript 2 top of tower.
Absorption of Chlorine in Water

4-inch Tower

<table>
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<tr>
<th>Run No.</th>
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<tbody>
<tr>
<td></td>
<td>46</td>
<td>47</td>
<td>48</td>
<td>49</td>
<td>50</td>
<td>51</td>
<td>52</td>
<td>53</td>
<td>54</td>
</tr>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>15,600</td>
<td>18,300</td>
<td>22,500</td>
<td>23,000</td>
<td>28,000</td>
<td>9,300</td>
<td>9,300</td>
<td>9,300</td>
<td>9,300</td>
</tr>
<tr>
<td>G, lbs./(hr.)(sq.ft.)</td>
<td>127</td>
<td>128</td>
<td>129</td>
<td>129</td>
<td>127</td>
<td>125</td>
<td>127</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>C₁*, mols/(cu.ft.)(10⁴)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C₁, mols/(cu.ft.)(10⁴)</td>
<td>3.2</td>
<td>8.4</td>
<td>7.4</td>
<td>6.7</td>
<td>6.9</td>
<td>9.0</td>
<td>9.0</td>
<td>9.4</td>
<td>9.4</td>
</tr>
<tr>
<td>P₁, atmos.</td>
<td>0.206</td>
<td>0.220</td>
<td>0.227</td>
<td>0.232</td>
<td>0.229</td>
<td>0.191</td>
<td>0.192</td>
<td>0.203</td>
<td>0.203</td>
</tr>
<tr>
<td>P₂, atmos.</td>
<td>0.161</td>
<td>0.166</td>
<td>0.171</td>
<td>0.169</td>
<td>0.163</td>
<td>0.161</td>
<td>0.162</td>
<td>0.172</td>
<td>0.172</td>
</tr>
<tr>
<td>T₂, deg. F.(liquor)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>69</td>
<td>90</td>
<td>80</td>
<td>51</td>
<td>50</td>
</tr>
<tr>
<td>t₂, deg. F.(gas)</td>
<td>72</td>
<td>69</td>
<td>70</td>
<td>70</td>
<td>72</td>
<td>85</td>
<td>80</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>K₉La,* 1/hr.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
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<td>K₉La, 1/hr.</td>
<td>74.2</td>
<td>67.0</td>
<td>87.1</td>
<td>94.5</td>
<td>100.0</td>
<td>66.0</td>
<td>60.0</td>
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<tr>
<td>End Factor.</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>K₉La**, 1/hr.</td>
<td>65</td>
<td>77</td>
<td>77</td>
<td>83</td>
<td>83</td>
<td>58</td>
<td>53</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>K₉La,(Pseudo-coefficient)</td>
<td>123</td>
<td>147</td>
<td>148</td>
<td>163</td>
<td>174</td>
<td>--</td>
<td>--</td>
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</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to K₉La calculated from it.

** K₉La calculated from the trap sample, and corrected by the average end factor. If no trap sample was taken, K₉La** is the same as K₉La*.

Subscript ₁ refers to bottom of tower, and subscript ₂ to top of tower.
Absorption of Chlorine in Water

<table>
<thead>
<tr>
<th>Run No.</th>
<th>4-inch Tower</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>9,300</td>
</tr>
<tr>
<td>G, lbs./(hr.)(sq.ft.)</td>
<td>130</td>
</tr>
<tr>
<td>C₁*, mols/(cu.ft.)(10⁴)</td>
<td>--</td>
</tr>
<tr>
<td>C₁, mols/(cu.ft.)(10⁴)</td>
<td>10.2</td>
</tr>
<tr>
<td>P₁, atmos.</td>
<td>0.198</td>
</tr>
<tr>
<td>P₂, atmos.</td>
<td>0.164</td>
</tr>
<tr>
<td>T₂, deg. F.(liquor)</td>
<td>37</td>
</tr>
<tr>
<td>t₂, deg. F.(gas)</td>
<td>45</td>
</tr>
<tr>
<td>Kₗa*, l/hr.</td>
<td>--</td>
</tr>
<tr>
<td>Kₗa, l/hr.</td>
<td>36.4</td>
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<tr>
<td>End Factor.</td>
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</tr>
<tr>
<td>Kₗa**, l/hr.</td>
<td>32</td>
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<tr>
<td>Kₗa,(Pseudo-coefficient)</td>
<td>--</td>
</tr>
</tbody>
</table>

* Refers to analysis of trap sample taken at the base plate, and to Kₗa calculated from it.  
** Kₗa calculated from the trap sample, and corrected by the average end factor. If no trap sample was taken, Kₗa** is the same as Kₗa*.  

Subscript ₁ refers to bottom of tower, and subscript ₂ to top of tower.
Absorption of Chlorine in Water

4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>64</th>
<th>65</th>
<th>66</th>
<th>67</th>
<th>68</th>
<th>69</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>9,300</td>
<td>9,300</td>
<td>9,300</td>
<td>9,300</td>
<td>9,300</td>
<td>9,300</td>
<td>9,300</td>
</tr>
<tr>
<td>G, lbs./(hr.)(sq.ft.)</td>
<td>120</td>
<td>128</td>
<td>138</td>
<td>130</td>
<td>131</td>
<td>125</td>
<td>120</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;*, mols/(cu.ft.)(10&lt;sup&gt;4&lt;/sup&gt;)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;, mols/(cu.ft.)(10&lt;sup&gt;4&lt;/sup&gt;)</td>
<td>6.3</td>
<td>10.3</td>
<td>14.5</td>
<td>10.1</td>
<td>13.4</td>
<td>8.5</td>
<td>5.9</td>
</tr>
<tr>
<td>P&lt;sub&gt;1&lt;/sub&gt;, atmos.</td>
<td>0.119</td>
<td>0.213</td>
<td>0.342</td>
<td>0.237</td>
<td>0.290</td>
<td>0.181</td>
<td>0.128</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;, atmos.</td>
<td>0.096</td>
<td>0.180</td>
<td>0.300</td>
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</tr>
<tr>
<td>T&lt;sub&gt;2&lt;/sub&gt;, deg. F.(liquor)</td>
<td>69</td>
<td>69</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>t&lt;sub&gt;2&lt;/sub&gt;, deg. F.(gas)</td>
<td>72</td>
<td>72</td>
<td>72</td>
<td>70</td>
<td>71</td>
<td>71</td>
<td>71</td>
</tr>
<tr>
<td>K&lt;sub&gt;La&lt;/sub&gt;*, 1/hr.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>K&lt;sub&gt;La&lt;/sub&gt;, 1/hr.</td>
<td>48.5</td>
<td>56.8</td>
<td>56.8</td>
<td>50.6</td>
<td>65.0</td>
<td>51.2</td>
<td>42.0</td>
</tr>
<tr>
<td>End Factor.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>K&lt;sub&gt;La**&lt;/sub&gt;, 1/hr.</td>
<td>43</td>
<td>50</td>
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<td>45</td>
<td>37</td>
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<tr>
<td>K&lt;sub&gt;La&lt;/sub&gt;, (Pseudo-coefficient)</td>
<td>102</td>
<td>95</td>
<td>84</td>
<td>81</td>
<td>95</td>
<td>89</td>
<td>84</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to K<sub>La</sub> calculated from it.

** K<sub>La</sub> calculated from the trap sample, and corrected by the average end factor. If no trap sample was taken, K<sub>La**</sub> is the same as K<sub>La*</sub>.

Subscript 1 refers to bottom of tower, and subscript 2 to top of tower.
## Absorption of Chlorine in Water

### 14-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>71</th>
<th>72</th>
<th>73</th>
<th>74</th>
<th>75</th>
<th>76</th>
<th>77</th>
<th>78</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>1,000</td>
<td>1,010</td>
<td>1,000</td>
<td>1,980</td>
<td>1,960</td>
<td>2,000</td>
<td>3,940</td>
<td>3,920</td>
</tr>
<tr>
<td>G_a, lbs. inert/(hr.)(sq.ft.)</td>
<td>77</td>
<td>77</td>
<td>77</td>
<td>77</td>
<td>77</td>
<td>77</td>
<td>77</td>
<td>76</td>
</tr>
<tr>
<td>C_1*, mols/(cu.ft.)(10^4)</td>
<td>16.3</td>
<td>16.1</td>
<td>16.2</td>
<td>15.2</td>
<td>14.8</td>
<td>15.0</td>
<td>13.3</td>
<td>13.2</td>
</tr>
<tr>
<td>C_1, mols/(cu.ft.)(10^4)</td>
<td>16.8</td>
<td>16.9</td>
<td>--</td>
<td>16.1</td>
<td>16.1</td>
<td>--</td>
<td>14.7</td>
<td>14.4</td>
</tr>
<tr>
<td>P_1, atmos.</td>
<td>0.169</td>
<td>0.160</td>
<td>0.166</td>
<td>0.174</td>
<td>0.155</td>
<td>0.159</td>
<td>0.175</td>
<td>0.164</td>
</tr>
<tr>
<td>P_2, atmos.</td>
<td>0.159</td>
<td>0.151</td>
<td>0.123</td>
<td>0.156</td>
<td>0.137</td>
<td>0.141</td>
<td>0.144</td>
<td>0.133</td>
</tr>
<tr>
<td>T_2, deg. F.(liquor)</td>
<td>66</td>
<td>65</td>
<td>65</td>
<td>68</td>
<td>65</td>
<td>66</td>
<td>66</td>
<td>65</td>
</tr>
<tr>
<td>t_2, deg. F.(gas)</td>
<td>69</td>
<td>68</td>
<td>66</td>
<td>68</td>
<td>66</td>
<td>66</td>
<td>69</td>
<td>68</td>
</tr>
<tr>
<td>K_{La*}, l/hr.</td>
<td>8.8</td>
<td>9.5</td>
<td>8.9</td>
<td>16.0</td>
<td>15.2</td>
<td>15.4</td>
<td>21.8</td>
<td>21.8</td>
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<tr>
<td>K_{La}, l/hr.</td>
<td>10.1</td>
<td>10.0</td>
<td>--</td>
<td>17.1</td>
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<td>--</td>
<td>25.6</td>
<td>--</td>
</tr>
<tr>
<td>K_{La**}, l/hr.</td>
<td>8.8</td>
<td>8.7</td>
<td>8.9</td>
<td>15</td>
<td>14</td>
<td>15</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), gas</td>
<td>--</td>
<td>0.024</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.121</td>
<td>--</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), liq.</td>
<td>0.027</td>
<td>0.027</td>
<td>--</td>
<td>0.051</td>
<td>0.049</td>
<td>--</td>
<td>0.093</td>
<td>0.146</td>
</tr>
<tr>
<td>% deviation from average</td>
<td>--</td>
<td>6</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>14</td>
<td>--</td>
</tr>
<tr>
<td>End Factor</td>
<td>0.97</td>
<td>0.95</td>
<td>--</td>
<td>0.94</td>
<td>0.92</td>
<td>--</td>
<td>0.85</td>
<td>--</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to K_{La} calculated from it.

** K_{La} calculated from the trap sample, and corrected by the average and factor.

Subscript 1 refers to bottom of tower, and subscript 2 to top of tower.
### Absorption of Chlorine in Water

#### 14-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>79</th>
<th>80</th>
<th>81</th>
<th>82</th>
<th>83</th>
<th>84</th>
<th>85</th>
<th>86</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>4,000</td>
<td>3,100</td>
<td>8,000</td>
<td>15,100</td>
<td>15,100</td>
<td>2,040</td>
<td>3,100</td>
<td>3,200</td>
</tr>
<tr>
<td>G_a, lbs. inert/(hr.)(sq.ft.)</td>
<td>76</td>
<td>75</td>
<td>76</td>
<td>74</td>
<td>74</td>
<td>42.5</td>
<td>45.2</td>
<td>49.7</td>
</tr>
<tr>
<td>C_1*, mols/(cu.ft.)(10^4)</td>
<td>12.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>15.7</td>
<td>15.1</td>
<td>10.2</td>
</tr>
<tr>
<td>C_1, mols/(cu.ft.)(10^4)</td>
<td>--</td>
<td>11.2</td>
<td>10.8</td>
<td>7.7</td>
<td>8.3</td>
<td>16.6</td>
<td>16.2</td>
<td>10.9</td>
</tr>
<tr>
<td>P_1, atmos.</td>
<td>0.165</td>
<td>0.167</td>
<td>0.187</td>
<td>0.185</td>
<td>0.187</td>
<td>0.183</td>
<td>0.168</td>
<td>0.112</td>
</tr>
<tr>
<td>P_2, atmos.</td>
<td>0.155</td>
<td>0.110</td>
<td>0.123</td>
<td>0.091</td>
<td>0.099</td>
<td>0.159</td>
<td>0.130</td>
<td>0.084</td>
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<tr>
<td>T_2, deg. F.(liquor)</td>
<td>64</td>
<td>66</td>
<td>66</td>
<td>66</td>
<td>67</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>t_2, deg. F.(gas)</td>
<td>66</td>
<td>68</td>
<td>69</td>
<td>68</td>
<td>69</td>
<td>69</td>
<td>69</td>
<td>69</td>
</tr>
<tr>
<td>K_La*, 1/hr.</td>
<td>21.2</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>17.9</td>
<td>31.3</td>
<td>22.4</td>
</tr>
<tr>
<td>K_La, 1/hr.</td>
<td>--</td>
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<td>29.2</td>
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<td>42.1</td>
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<td>33.6</td>
<td>23.3</td>
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<td>K_La**, 1/hr.</td>
<td>21</td>
<td>27</td>
<td>26</td>
<td>34</td>
<td>37</td>
<td>16</td>
<td>29</td>
<td>21</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), gas</td>
<td>--</td>
<td>0.168</td>
<td>0.182</td>
<td>0.211</td>
<td>0.253</td>
<td>0.055</td>
<td>0.076</td>
<td>0.062</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), liq.</td>
<td>--</td>
<td>0.146</td>
<td>0.139</td>
<td>0.187</td>
<td>0.201</td>
<td>0.054</td>
<td>0.080</td>
<td>0.056</td>
</tr>
<tr>
<td>% deviation from average</td>
<td>--</td>
<td>7</td>
<td>13</td>
<td>6</td>
<td>11</td>
<td>2</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>End Factor.</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.95</td>
<td>0.93</td>
<td>0.94</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to K_La calculated from it.
** K_La calculated from the trap sample, and corrected by the average end factor.
Subscript 1 refers to bottom of tower, and subscript 2 to top of tower.
## Absorption of Chlorine in Water

### 14-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>87</th>
<th>88</th>
<th>89</th>
<th>90</th>
<th>91</th>
<th>92</th>
<th>93</th>
<th>94</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L ), lbs./(hr.)(sq.ft.)</td>
<td>3,200</td>
<td>3,940</td>
<td>4,250</td>
<td>4,510</td>
<td>4,950</td>
<td>5,820</td>
<td>5,900</td>
<td>6,050</td>
</tr>
<tr>
<td>( G_a ), lbs. inert/(hr.)(sq.ft.)</td>
<td>49.9</td>
<td>45.2</td>
<td>46.0</td>
<td>50.8</td>
<td>46.5</td>
<td>39.5</td>
<td>48.8</td>
<td>47.2</td>
</tr>
<tr>
<td>( C_1^* ), mols/(cu.ft.)(10^4)</td>
<td>10.0</td>
<td>13.9</td>
<td>14.0</td>
<td>9.1</td>
<td>12.5</td>
<td>16.5</td>
<td>9.0</td>
<td>11.9</td>
</tr>
<tr>
<td>( C_1 ), mols/(cu.ft.)(10^4)</td>
<td>11.2</td>
<td>15.5</td>
<td>16.7</td>
<td>10.6</td>
<td>14.6</td>
<td>19.4</td>
<td>11.0</td>
<td>13.3</td>
</tr>
<tr>
<td>( P_1 ), atmos.</td>
<td>0.111</td>
<td>0.173</td>
<td>0.168</td>
<td>0.118</td>
<td>0.163</td>
<td>0.275</td>
<td>0.134</td>
<td>0.162</td>
</tr>
<tr>
<td>( P_2 ), atmos.</td>
<td>0.082</td>
<td>0.134</td>
<td>0.121</td>
<td>0.078</td>
<td>0.114</td>
<td>0.204</td>
<td>0.087</td>
<td>0.104</td>
</tr>
<tr>
<td>( T_2 ), deg. F.(liquor)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>( t_2 ), deg. F.(gas)</td>
<td>69</td>
<td>69</td>
<td>69</td>
<td>70</td>
<td>69</td>
<td>70</td>
<td>69</td>
<td>69</td>
</tr>
<tr>
<td>( K_{La}^* ), 1/hr.</td>
<td>22.2</td>
<td>28.7</td>
<td>34.4</td>
<td>25.3</td>
<td>31.8</td>
<td>33.4</td>
<td>27.1</td>
<td>37.4</td>
</tr>
<tr>
<td>( K_{La} ), 1/hr.</td>
<td>25.0</td>
<td>31.9</td>
<td>33.5</td>
<td>29.4</td>
<td>37.0</td>
<td>39.3</td>
<td>33.1</td>
<td>41.5</td>
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<tr>
<td>( K_{La}^{**} ), 1/hr.</td>
<td>22</td>
<td>28</td>
<td>34</td>
<td>26</td>
<td>32</td>
<td>34</td>
<td>29</td>
<td>36</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), gas</td>
<td>0.062</td>
<td>0.086</td>
<td>0.110</td>
<td>0.090</td>
<td>0.110</td>
<td>0.175</td>
<td>0.104</td>
<td>0.127</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), liq.</td>
<td>0.058</td>
<td>0.098</td>
<td>0.107</td>
<td>0.077</td>
<td>0.116</td>
<td>0.182</td>
<td>0.102</td>
<td>0.129</td>
</tr>
<tr>
<td>% deviation from average</td>
<td>4</td>
<td>6</td>
<td>2</td>
<td>8</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
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<td>0.90</td>
<td>0.99</td>
<td>0.96</td>
<td>0.96</td>
<td>0.95</td>
<td>0.82</td>
<td>0.90</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to \( K_{La} \) calculated from it.
** \( K_{La} \) calculated from the trap sample, and corrected by the average end factor.

Subscript 1 refers to bottom of tower, and subscript 2 to top of tower.
### Absorption of Chlorine in Water

**14-inch Tower**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>95</th>
<th>96</th>
<th>97</th>
<th>98</th>
<th>99</th>
<th>100</th>
<th>101</th>
<th>102</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>5,960</td>
<td>8,300</td>
<td>8,100</td>
<td>8,300</td>
<td>8,300</td>
<td>8,700</td>
<td>9,800</td>
<td>11,800</td>
</tr>
<tr>
<td>G_a, lbs. inert/(hr.)(sq.ft.)</td>
<td>40.5</td>
<td>46.2</td>
<td>49.9</td>
<td>46.6</td>
<td>45.7</td>
<td>49.2</td>
<td>47.3</td>
<td>42.2</td>
</tr>
<tr>
<td>C_1*, mols/cu.ft. ((10^4))</td>
<td>13.1</td>
<td>11.3</td>
<td>7.4</td>
<td>10.9</td>
<td>10.9</td>
<td>9.6</td>
<td>9.4</td>
<td>13.2</td>
</tr>
<tr>
<td>C_1, mols/(cu.ft.) ((10^4))</td>
<td>15.3</td>
<td>13.7</td>
<td>9.3</td>
<td>13.6</td>
<td>13.7</td>
<td>11.4</td>
<td>11.5</td>
<td>15.2</td>
</tr>
<tr>
<td>P_1, atmos.</td>
<td>0.215</td>
<td>0.204</td>
<td>0.134</td>
<td>0.200</td>
<td>0.204</td>
<td>0.164</td>
<td>0.181</td>
<td>0.280</td>
</tr>
<tr>
<td>P_2, atmos.</td>
<td>0.150</td>
<td>0.122</td>
<td>0.080</td>
<td>0.118</td>
<td>0.125</td>
<td>0.084</td>
<td>0.104</td>
<td>0.165</td>
</tr>
<tr>
<td>T_2, deg. F. (liquor)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>t_2, deg. F. (gas)</td>
<td>70</td>
<td>69</td>
<td>69</td>
<td>69</td>
<td>69</td>
<td>69</td>
<td>69</td>
<td>70</td>
</tr>
<tr>
<td>K_La*, 1/hr.</td>
<td>30.6</td>
<td>37.5</td>
<td>28.2</td>
<td>36.7</td>
<td>34.9</td>
<td>41.2</td>
<td>37.5</td>
<td>48.5</td>
</tr>
<tr>
<td>K_La, 1/hr.</td>
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<td>45.8</td>
<td>35.3</td>
<td>45.9</td>
<td>43.6</td>
<td>49.0</td>
<td>45.8</td>
<td>55.7</td>
</tr>
<tr>
<td>K_La**, 1/hr.</td>
<td>31</td>
<td>40</td>
<td>31</td>
<td>40</td>
<td>33</td>
<td>43</td>
<td>40</td>
<td>48</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), gas</td>
<td>0.145</td>
<td>0.191</td>
<td>0.118</td>
<td>0.186</td>
<td>0.182</td>
<td>0.178</td>
<td>0.178</td>
<td>0.289</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), liq.</td>
<td>0.146</td>
<td>0.182</td>
<td>0.121</td>
<td>0.182</td>
<td>0.182</td>
<td>0.182</td>
<td>0.159</td>
<td>0.181</td>
</tr>
<tr>
<td>% deviation from average</td>
<td>0</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>7</td>
<td>1</td>
<td>0</td>
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<tr>
<td>End Factor.</td>
<td>0.86</td>
<td>0.32</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.34</td>
<td>0.82</td>
<td>0.98</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to K_La calculated from it.
** K_La calculated from the trap sample, and corrected by the average end factor.

Subscript 1 refers to bottom of tower, and subscript 2 to top of tower.
### Absorption of Chlorine in Water

<table>
<thead>
<tr>
<th>Run No.</th>
<th>14-inch Tower</th>
<th>Commercial Tower</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>103 104 105 106</td>
<td>107 108 109 110</td>
</tr>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>12,100 12,300 14,100 14,500</td>
<td>4,450 3,450 6,000 4,000</td>
</tr>
<tr>
<td>G_a, lbs. inert/(hr.)(sq.ft.)</td>
<td>49.1 49.0 49.9 49.9</td>
<td>7.2 7.7 4.9 4.9</td>
</tr>
<tr>
<td>C_1*, mols/(cu.ft.)(10^4)</td>
<td>7.3 7.5 7.1 6.9</td>
<td>-- -- -- --</td>
</tr>
<tr>
<td>C_1, mols/(cu.ft.)(10^4)</td>
<td>9.6 9.4 8.9 8.6</td>
<td>44.5 44.7 46.2 45.1</td>
</tr>
<tr>
<td>P_1, atmos.</td>
<td>0.173 0.169 0.167 0.164</td>
<td>0.720 0.696 0.764 0.745</td>
</tr>
<tr>
<td>P_2, atmos.</td>
<td>0.030 0.077 0.070 0.066</td>
<td>0.583 0.531 0.516 0.506</td>
</tr>
<tr>
<td>T_2, deg. F. (liquor)</td>
<td>70 70 70 70</td>
<td>71 71 70 71</td>
</tr>
<tr>
<td>t_1, deg. F. (gas)</td>
<td>69 69 69 69</td>
<td>87 88 92 92</td>
</tr>
<tr>
<td>t_2, deg. F. (gas)</td>
<td>69 69 69 69</td>
<td>72 71 73 72</td>
</tr>
<tr>
<td>K_{La*}, 1/hr.</td>
<td>41.5 40.7 45.2 45.0</td>
<td>-- -- -- --</td>
</tr>
<tr>
<td>K_{La}, 1/hr.</td>
<td>51.3 49.2 56.5 56.3</td>
<td>21.0 20.4 27.0 17.3</td>
</tr>
<tr>
<td>K_{La**}, 1/hr.</td>
<td>45 43 49 49</td>
<td>-- -- -- --</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), gas</td>
<td>0.211 0.212 0.219 0.222</td>
<td>0.310 0.336 0.452 0.304</td>
</tr>
<tr>
<td>Mols abs./(hr.)(sq.ft.), liq.</td>
<td>0.185 0.186 0.202 0.200</td>
<td>0.319 0.247 0.445 0.290</td>
</tr>
<tr>
<td>% deviation from average.</td>
<td>7 7 4 5</td>
<td>1 15 1 2</td>
</tr>
<tr>
<td>End Factor.</td>
<td>0.31 0.35 0.30 0.30</td>
<td>-- -- -- --</td>
</tr>
</tbody>
</table>

* Refers to analysis of sample taken at the base plate, and to K_{La} calculated from it.

** K_{La} calculated from the trap sample, and corrected by the average end factor.

Subscript 1 refers to bottom of tower, and subscript 2 refers to top of tower.
### Desorption of Oxygen from Water

#### 4-inch and 14-inch Towers

<table>
<thead>
<tr>
<th>Run No.</th>
<th>111</th>
<th>112</th>
<th>113</th>
<th>114</th>
<th>115</th>
<th>116</th>
<th>117</th>
<th>118</th>
<th>119</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>8,000</td>
<td>16,000</td>
<td>7,900</td>
<td>3,950</td>
<td>2,240</td>
<td>970</td>
<td>2,000</td>
<td>4,000</td>
<td>8,000</td>
<td>15,000</td>
</tr>
<tr>
<td>G, lbs./(hr.)(sq.ft.)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>C₁, mols/(cu.ft.)(10^5)</td>
<td>1.97</td>
<td>2.21</td>
<td>2.13</td>
<td>2.01</td>
<td>2.12</td>
<td>1.91</td>
<td>1.86</td>
<td>2.00</td>
<td>2.03</td>
<td>2.05</td>
</tr>
<tr>
<td>C₂, mols/(cu.ft.)(10^5)</td>
<td>2.30</td>
<td>3.17</td>
<td>3.17</td>
<td>2.78</td>
<td>3.89</td>
<td>2.24</td>
<td>4.73</td>
<td>6.53</td>
<td>5.72</td>
<td>5.11</td>
</tr>
<tr>
<td>Cₑ, mols/(cu.ft.)(10^5)</td>
<td>1.91</td>
<td>1.89</td>
<td>1.89</td>
<td>1.89</td>
<td>1.89</td>
<td>1.89</td>
<td>1.83</td>
<td>1.83</td>
<td>1.83</td>
<td>1.81</td>
</tr>
<tr>
<td>T₂, deg. F. (liquor)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>66</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>66</td>
</tr>
<tr>
<td>t₂, deg. F. (gas)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>66</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>66</td>
</tr>
<tr>
<td>K₁, l/hr.</td>
<td>97</td>
<td>170</td>
<td>97</td>
<td>60</td>
<td>37</td>
<td>21</td>
<td>33</td>
<td>54</td>
<td>95</td>
<td>156</td>
</tr>
</tbody>
</table>

Subscript ₁ refers to bottom of tower, and subscript ₂ refers to top of tower.
Absorption of Chlorine in Caustic

4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>121</th>
<th>122</th>
<th>123</th>
<th>124</th>
<th>125</th>
<th>126</th>
<th>127</th>
<th>128</th>
<th>129</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
</tr>
<tr>
<td>$G_a$, mols inert/(hr.)(sq.ft.)</td>
<td>3.75</td>
<td>4.99</td>
<td>3.68</td>
<td>5.05</td>
<td>3.83</td>
<td>3.38</td>
<td>5.64</td>
<td>7.82</td>
<td>6.80</td>
</tr>
<tr>
<td>$N_1$</td>
<td>2.32</td>
<td>1.74</td>
<td>3.08</td>
<td>2.46</td>
<td>2.51</td>
<td>2.24</td>
<td>2.49</td>
<td>2.27</td>
<td>2.23</td>
</tr>
<tr>
<td>$N_2$</td>
<td>3.68</td>
<td>2.12</td>
<td>4.48</td>
<td>3.20</td>
<td>3.20</td>
<td>2.90</td>
<td>3.51</td>
<td>3.51</td>
<td>3.29</td>
</tr>
<tr>
<td>$P_1$, atmos.</td>
<td>0.503</td>
<td>0.314</td>
<td>0.60e</td>
<td>0.381</td>
<td>0.429</td>
<td>0.475</td>
<td>0.437</td>
<td>0.376</td>
<td>0.426</td>
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<tr>
<td>$P_2$, atmos.</td>
<td>0.0403</td>
<td>0.010</td>
<td>0.031</td>
<td>0.013</td>
<td>0.012</td>
<td>0.013</td>
<td>0.020</td>
<td>0.023</td>
<td>0.066</td>
</tr>
<tr>
<td>$T_1$, deg. F.(liquor)</td>
<td>97</td>
<td>43</td>
<td>101</td>
<td>90</td>
<td>90</td>
<td>91</td>
<td>94</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>$T_2$, &quot; &quot;</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>$t_1$, &quot; &quot; (gas)</td>
<td>74</td>
<td>70</td>
<td>71</td>
<td>73</td>
<td>75</td>
<td>76</td>
<td>70</td>
<td>70</td>
<td>69</td>
</tr>
<tr>
<td>$t_2$, &quot; &quot;</td>
<td>77</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>79</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>$G_1$, lbs./(hr.)(sq.ft.)</td>
<td>396</td>
<td>309</td>
<td>516</td>
<td>372</td>
<td>329</td>
<td>332</td>
<td>433</td>
<td>545</td>
<td>558</td>
</tr>
<tr>
<td>$K_{ga}(P_{Bm})$</td>
<td>26.6</td>
<td>28.4</td>
<td>39.3</td>
<td>32.7</td>
<td>32.6</td>
<td>29.3</td>
<td>42.5</td>
<td>44.3</td>
<td>28.6</td>
</tr>
</tbody>
</table>

Subscript 1 refers to bottom of tower, and subscript 2 refers to top of tower.
### Absorption of Chlorine in Caustic

#### 4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>130</th>
<th>131</th>
<th>132</th>
<th>133</th>
<th>134</th>
<th>135</th>
<th>136</th>
<th>137</th>
<th>138</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
</tr>
<tr>
<td>G&lt;sub&gt;a&lt;/sub&gt;, mols inert/(hr.)(sq.ft.)</td>
<td>0.26</td>
<td>0.60</td>
<td>0.34</td>
<td>10.10</td>
<td>7.05</td>
<td>2.58</td>
<td>3.12</td>
<td>3.42</td>
<td>6.21</td>
</tr>
<tr>
<td>N&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2.58</td>
<td>2.29</td>
<td>2.31</td>
<td>2.11</td>
<td>2.88</td>
<td>2.34</td>
<td>2.40</td>
<td>2.20</td>
<td>1.67</td>
</tr>
<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4.01</td>
<td>3.55</td>
<td>4.01</td>
<td>3.55</td>
<td>4.48</td>
<td>3.36</td>
<td>2.90</td>
<td>2.96</td>
<td>2.61</td>
</tr>
<tr>
<td>P&lt;sub&gt;1&lt;/sub&gt;, atmos.</td>
<td>0.404</td>
<td>0.421</td>
<td>0.519</td>
<td>0.429</td>
<td>0.469</td>
<td>0.397</td>
<td>0.416</td>
<td>0.462</td>
<td>0.392</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;, atmos.</td>
<td>0.074</td>
<td>0.060</td>
<td>0.177</td>
<td>0.117</td>
<td>0.100</td>
<td>0.006</td>
<td>0.003</td>
<td>0.013</td>
<td>0.097</td>
</tr>
<tr>
<td>T&lt;sub&gt;1&lt;/sub&gt;, deg. F. (liquor)</td>
<td>102</td>
<td>101</td>
<td>109</td>
<td>105</td>
<td>104</td>
<td>84</td>
<td>89</td>
<td>90</td>
<td>93</td>
</tr>
<tr>
<td>T&lt;sub&gt;2&lt;/sub&gt;, &quot; &quot;</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>t&lt;sub&gt;1&lt;/sub&gt;, &quot; &quot; (gas)</td>
<td>72</td>
<td>70</td>
<td>72</td>
<td>71</td>
<td>70</td>
<td>73</td>
<td>77</td>
<td>71</td>
<td>70</td>
</tr>
<tr>
<td>t&lt;sub&gt;2&lt;/sub&gt;, &quot; &quot;</td>
<td>79</td>
<td>79</td>
<td>87</td>
<td>84</td>
<td>79</td>
<td>74</td>
<td>79</td>
<td>74</td>
<td>77</td>
</tr>
<tr>
<td>G&lt;sub&gt;1&lt;/sub&gt;, lbs./(hr.)(sq.ft.)</td>
<td>643</td>
<td>686</td>
<td>868</td>
<td>834</td>
<td>653</td>
<td>201</td>
<td>247</td>
<td>328</td>
<td>444</td>
</tr>
<tr>
<td>K&lt;sub&gt;ga&lt;/sub&gt;(P&lt;sub&gt;Bl&lt;/sub&gt;)</td>
<td>30.4</td>
<td>37.2</td>
<td>25.0</td>
<td>29.4</td>
<td>26.6</td>
<td>22.3</td>
<td>26.6</td>
<td>29.3</td>
<td>17.6</td>
</tr>
</tbody>
</table>

Subscript 1 refers to bottom of tower, and subscript 2 refers to top of tower.
Absorption of Chlorine in Caustic

4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>139</th>
<th>140</th>
<th>141</th>
<th>142</th>
<th>143</th>
<th>144</th>
<th>145</th>
<th>146</th>
<th>147</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./(hr.)(sq.ft.)</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
</tr>
<tr>
<td>G_a, mols inert/(hr.)(sq.ft.)</td>
<td>5.84</td>
<td>10.10</td>
<td>9.15</td>
<td>7.46</td>
<td>5.30</td>
<td>3.81</td>
<td>4.31</td>
<td>4.77</td>
<td>2.96</td>
</tr>
<tr>
<td>N_1</td>
<td>2.27</td>
<td>1.03</td>
<td>1.24</td>
<td>1.49</td>
<td>1.49</td>
<td>1.77</td>
<td>0.09</td>
<td>0.33</td>
<td>1.44</td>
</tr>
<tr>
<td>N_2</td>
<td>3.29</td>
<td>2.41</td>
<td>2.77</td>
<td>2.61</td>
<td>2.48</td>
<td>2.48</td>
<td>0.30</td>
<td>1.33</td>
<td>2.10</td>
</tr>
<tr>
<td>P_1, atm.</td>
<td>0.426</td>
<td>0.426</td>
<td>0.375</td>
<td>0.373</td>
<td>0.469</td>
<td>0.438</td>
<td>0.381</td>
<td>0.365</td>
<td>0.540</td>
</tr>
<tr>
<td>P_2, atm.</td>
<td>0.050</td>
<td>0.174</td>
<td>0.095</td>
<td>0.094</td>
<td>0.100</td>
<td>0.029</td>
<td>0.210</td>
<td>0.028</td>
<td>0.022</td>
</tr>
<tr>
<td>T_1, deg. F.(liquor)</td>
<td>93</td>
<td>100</td>
<td>98</td>
<td>97</td>
<td>94</td>
<td>97</td>
<td>76</td>
<td>84</td>
<td>89</td>
</tr>
<tr>
<td>T_2, °C</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>t_1, °C (gas)</td>
<td>68</td>
<td>71</td>
<td>72</td>
<td>71</td>
<td>70</td>
<td>71</td>
<td>71</td>
<td>71</td>
<td>75</td>
</tr>
<tr>
<td>t_2, °C</td>
<td>75</td>
<td>83</td>
<td>81</td>
<td>78</td>
<td>75</td>
<td>72</td>
<td>74</td>
<td>77</td>
<td>75</td>
</tr>
<tr>
<td>G_1, lbs./(hr.)(sq.ft.)</td>
<td>452</td>
<td>835</td>
<td>658</td>
<td>537</td>
<td>463</td>
<td>331</td>
<td>316</td>
<td>312</td>
<td>334</td>
</tr>
<tr>
<td>K_{ga}(P_{Bm})</td>
<td>28.9</td>
<td>20.7</td>
<td>25.3</td>
<td>20.9</td>
<td>19.1</td>
<td>25.3</td>
<td>5.3</td>
<td>23.2</td>
<td>28.4</td>
</tr>
</tbody>
</table>

Subscript 1 refers to bottom of tower, and Subscript 2 refers to top of tower.
Absorption of Chlorine in Caustic

4-inch Tower

<table>
<thead>
<tr>
<th>Run No.</th>
<th>148</th>
<th>149</th>
<th>150</th>
<th>151</th>
<th>152</th>
<th>153</th>
<th>154</th>
<th>155</th>
<th>156</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./hr. (sq. ft.)</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>12,300</td>
<td>6,460</td>
</tr>
<tr>
<td>Gₐ, mols inert/ hr. (sq. ft.)</td>
<td>3.23</td>
<td>4.50</td>
<td>4.50</td>
<td>4.97</td>
<td>5.30</td>
<td>7.20</td>
<td>8.35</td>
<td>5.70</td>
<td>4.40</td>
</tr>
<tr>
<td>N₁</td>
<td>1.47</td>
<td>0.28</td>
<td>1.22</td>
<td>2.33</td>
<td>0.44</td>
<td>0.45</td>
<td>1.62</td>
<td>0</td>
<td>0.39</td>
</tr>
<tr>
<td>N₂</td>
<td>2.10</td>
<td>0.66</td>
<td>1.69</td>
<td>2.33</td>
<td>0.95</td>
<td>0.94</td>
<td>2.29</td>
<td>0</td>
<td>3.54</td>
</tr>
<tr>
<td>P₁, atmos.</td>
<td>0.494</td>
<td>0.308</td>
<td>0.340</td>
<td>0.305</td>
<td>0.293</td>
<td>0.263</td>
<td>0.261</td>
<td>0.276</td>
<td>0.353</td>
</tr>
<tr>
<td>P₂, atmos.</td>
<td>0.024</td>
<td>0.055</td>
<td>0.012</td>
<td>0.005</td>
<td>0.029</td>
<td>0.094</td>
<td>0.021</td>
<td>0.236</td>
<td>0.065</td>
</tr>
<tr>
<td>T₁, deg. F. (liquor)</td>
<td>86</td>
<td>80</td>
<td>82</td>
<td>83</td>
<td>84</td>
<td>84</td>
<td>70</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>T₂, °</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>t₁, ° (gas)</td>
<td>74</td>
<td>73</td>
<td>77</td>
<td>72</td>
<td>70</td>
<td>63</td>
<td>70</td>
<td>70</td>
<td>72</td>
</tr>
<tr>
<td>t₂, °</td>
<td>75</td>
<td>76</td>
<td>75</td>
<td>75</td>
<td>74</td>
<td>70</td>
<td>70</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>G₁, lbs./hr. (sq. ft.)</td>
<td>332</td>
<td>303</td>
<td>310</td>
<td>306</td>
<td>304</td>
<td>404</td>
<td>448</td>
<td>310</td>
<td>293</td>
</tr>
<tr>
<td>Kₐₑ(Pₑm)</td>
<td>27.2</td>
<td>15.6</td>
<td>30.4</td>
<td>33.3</td>
<td>21.0</td>
<td>12.5</td>
<td>35.0</td>
<td>1.53</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Subscript 1 refers to bottom of tower, and subscript 2 refers to top of tower.
Absorption of Chlorine in Caustic

<table>
<thead>
<tr>
<th>Run No.</th>
<th>157</th>
<th>158</th>
<th>159</th>
<th>160</th>
<th>161</th>
<th>162</th>
</tr>
</thead>
<tbody>
<tr>
<td>L, lbs./hr.(sq.ft.)</td>
<td>6,510</td>
<td>6,570</td>
<td>11,010</td>
<td>5,360</td>
<td>6,590</td>
<td>6,950</td>
</tr>
<tr>
<td>(G_a), mols inert/(hr.)(sq.ft.)</td>
<td>3.41</td>
<td>3.42</td>
<td>3.24</td>
<td>3.97</td>
<td>3.77</td>
<td>5.01</td>
</tr>
<tr>
<td>(N_1)</td>
<td>1.03</td>
<td>1.15</td>
<td>1.24</td>
<td>1.09</td>
<td>1.23</td>
<td>1.23</td>
</tr>
<tr>
<td>(N_2)</td>
<td>3.92</td>
<td>3.92</td>
<td>3.92</td>
<td>4.67</td>
<td>4.67</td>
<td>4.67</td>
</tr>
<tr>
<td>(P_1), atmos.</td>
<td>0.455</td>
<td>0.454</td>
<td>0.479</td>
<td>0.391</td>
<td>0.408</td>
<td>0.274</td>
</tr>
<tr>
<td>(P_2), atmos.</td>
<td>0.039</td>
<td>0.037</td>
<td>0.023</td>
<td>0.049</td>
<td>0.039</td>
<td>0.007</td>
</tr>
<tr>
<td>(T_1), deg. F.(liquor)</td>
<td>109</td>
<td>102</td>
<td>98</td>
<td>124</td>
<td>117</td>
<td>97</td>
</tr>
<tr>
<td>(T_2), &quot; &quot; &quot;</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>(t_1), &quot; &quot; (gas)</td>
<td>72</td>
<td>72</td>
<td>72</td>
<td>74</td>
<td>74</td>
<td>74</td>
</tr>
<tr>
<td>(t_2), &quot; &quot; &quot;</td>
<td>82</td>
<td>81</td>
<td>79</td>
<td>88</td>
<td>84</td>
<td>81</td>
</tr>
<tr>
<td>(G_1), lbs./hr.(sq.ft.)</td>
<td>305</td>
<td>305</td>
<td>309</td>
<td>295</td>
<td>297</td>
<td>281</td>
</tr>
<tr>
<td>(K_a(P_{Bm}))</td>
<td>22.2</td>
<td>22.7</td>
<td>25.9</td>
<td>17.6</td>
<td>21.3</td>
<td>27.0</td>
</tr>
</tbody>
</table>

Subscript 1 refers to bottom of tower, and subscript 2 refers to top of tower.
### Solubility of Chlorine in Water

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Partial Pressure (Atmospheres)</th>
<th>Solubility (Gms per 100 gms H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0581</td>
<td>0.111</td>
</tr>
<tr>
<td></td>
<td>0.0611</td>
<td>0.115</td>
</tr>
<tr>
<td></td>
<td>0.140</td>
<td>0.195</td>
</tr>
<tr>
<td></td>
<td>0.145</td>
<td>0.201</td>
</tr>
<tr>
<td></td>
<td>0.291</td>
<td>0.330</td>
</tr>
<tr>
<td></td>
<td>0.297</td>
<td>0.330</td>
</tr>
<tr>
<td></td>
<td>0.488</td>
<td>0.477</td>
</tr>
<tr>
<td></td>
<td>0.490</td>
<td>0.480</td>
</tr>
<tr>
<td></td>
<td>0.951</td>
<td>0.825</td>
</tr>
<tr>
<td></td>
<td>0.951</td>
<td>0.825</td>
</tr>
<tr>
<td>20</td>
<td>0.0665</td>
<td>0.112</td>
</tr>
<tr>
<td></td>
<td>0.1195</td>
<td>0.160</td>
</tr>
<tr>
<td></td>
<td>0.260</td>
<td>0.262</td>
</tr>
<tr>
<td></td>
<td>0.260</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>0.487</td>
<td>0.415</td>
</tr>
<tr>
<td></td>
<td>0.490</td>
<td>0.422</td>
</tr>
<tr>
<td></td>
<td>0.985</td>
<td>0.725</td>
</tr>
<tr>
<td>25</td>
<td>0.0621</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td>0.0655</td>
<td>0.106</td>
</tr>
<tr>
<td></td>
<td>0.104</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>0.109</td>
<td>0.143</td>
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<tr>
<td></td>
<td>0.174</td>
<td>0.189</td>
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<td></td>
<td>0.270</td>
<td>0.246</td>
</tr>
<tr>
<td></td>
<td>0.551</td>
<td>0.391</td>
</tr>
<tr>
<td></td>
<td>0.589</td>
<td>0.418</td>
</tr>
<tr>
<td></td>
<td>0.961</td>
<td>0.628</td>
</tr>
</tbody>
</table>
D. SUPPLEMENTARY DISCUSSION

As mentioned in the Supplementary Introduction and briefly discussed in the Discussion of Results, equation (25), derived to define the liquid film coefficient, is applicable only where the rate of change of solute concentration across the film is constant at any one point in the tower, that is, where dc/dx is independent of x. This is the case for pure physical absorption, where the solute and solvent are inert to one another. This is not the case, however, with chlorine and water, where a large part of the chlorine in solution hydrolyses to form hypochlorous and hydrochloric acids according to the following equation.

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{H}^+ + \text{Cl}^- \]

In the dilute solutions encountered up to one atmosphere chlorine pressure, the products of this reaction may be assumed not to exert vapor pressures. Hence, the vapor pressure of chlorine over a solution is in equilibrium with the dissolved Cl₂ in molecular form. From the results of the equilibrium determinations in this thesis, it has been shown that the concentration – chlorine pressure relationship for the molecular chlorine in solution follows Henry's law.

The molecular chlorine concentration at the interface will therefore be in equilibrium with the partial pressure of chlorine in the gas. If this system
were a case of pure physical absorption, this molecular
chlorine in solution at the interface would diffuse
across the liquid film, and since the diffusivity, \( D \),
is assumed to be independent of concentration, the
decrease in molecular chlorine concentration would be a
linear function of \( x \), the distance diffused across the
film. In this system, however, in addition to this
diffusion, there is further depletion of the molecular
chlorine due to the hydrolysis reaction.

If an elemental thickness of the film, \( dx \), is
considered, the rate of diffusion into this layer will
be \( -\frac{dC}{dx} \), and the rate of diffusion from this section
will be \( -(\frac{dC}{dx} + D \frac{d^2C}{dx^2} \ ) dx \). The difference between
these two rates will be the rate of depletion due to
the hydrolysis reaction. The rate of the reaction may
be written as follows.

\[
-\frac{d(Cl_2)}{d\theta} = m(Cl_2) - n(HOCl)(H^+)(Cl^-) \tag{58}
\]

The equilibrium constant for this reaction is defined as,-

\[
K_e = \frac{(HOCl)(H^+)(Cl^-)}{(Cl_2)} \tag{59}
\]

At equilibrium \( \frac{dC}{d\theta} = 0 \), hence,

\[
m(Cl_2) = n(HOCl)(H^+)(Cl^-) \tag{60}
\]

and \( K = \frac{m}{n} \) \tag{61}

If A moles of chlorine dissolve in unit volume of water,
assume that \( c \) moles remain unhydrolysed, and \( b \) moles are
hydrolysed. There will also be \( b \) moles of HOCl, \( b \) H\(^+\)ions
and b Cl⁻ ions. Substituting in equation (58), and combining with equation (61), the following expression for the rate of hydrolysis may be obtained.

\[ \frac{dc}{dt} = m(c) - \frac{m}{K}(b^3) \] ................................. (62)

Now \( \frac{dc}{dx} \) is the difference in the rates of diffusion, dN, of molecular chlorine into and out of the thickness of film, dx. Therefore,

\[ dN = -\frac{dc}{dx} + \left[ \frac{Ddc}{dx} + \frac{Dd^2c}{dx^2} \right] = \left[ m\frac{c}{m} - \frac{mb^3}{K} \right] dx \] ................................. (63)

Hence, \( \frac{d^2c}{dx^2} = mc - \frac{mb^3}{K} \) ................................. (64)

A further restriction is imposed on this equation in that at every point in the film, the following equation must hold.

\[ A = c + b \] ................................. (65)

Unfortunately, a suitable solution for these equations has not been developed. If, however, certain assumptions are made, a solution can be obtained which is indicative of the operation of the system. When it is assumed that the factor \( mb^3/K \) in the differential equation is small, it is possible to obtain a solution after the manner of Sherwood(27). The solution is

\[ c = A_1e^{hx} + A_2e^{-hx} \] ................................. (66)

where \( h = \sqrt{\frac{m}{D}} \) ................................. (67)

After substitution of limit \( C_i \) at the interface \( (x=0) \), and \( C_L \) in the main body of the liquid \( (x=x_L) \), the particular solution is as follows.
\[ c = \frac{C_L \sinh hx + C_i \sinh h(x_L - x)}{\sinh hx_L} \] ............... (68)

The rate of absorption of chlorine at the interface can be calculated by obtaining the slope of the concentration curve at \( x = 0 \), and multiplying by \((-D)\).

\[ N = -\frac{dce}{dx} = \frac{hD[C_i \cosh h(x_L - x) - C_L \cosh hx]}{\sinh hx_L} \] .......(69)

When \( x = 0 \), \( N_0 = \frac{hD[C_i \cosh hx_L - C_L]}{\sinh hx_L} \) ............... (70)

Equation (70) may be used to compare the rate of absorption of chlorine with ordinary liquid film absorption under the same conditions of film thickness and overall driving force.

At a liquor rate of 13,000 lbs./(hr.)(sq.ft.), the value of \( K_La \) for the absorption of oxygen in water is 150 (with units of reciprocal hours). In terms of diffusivity and film thickness, \( K_La = Da/x \) where 'a' is the area per unit volume of packing. Assuming that 30 per cent of the dry area is effective for absorption, the value of 'a' for one-inch rings wetted is approximately 20 feet\(^{-1}\). The diffusivity of oxygen is about \( 1.8 \times 10^{-5} \) cm.\(^2\)/sec., which gives \( x_L \) a value of 0.00028 cm.

Shilov(30) has published some data on the rate of hydrolysis of chlorine, and reported a value of 11.7 sec\(^{-1}\) for the specific reaction rate constant at 18\(^o\)C. The diffusivity of chlorine is given(16) as \( 1.4 \times 10^{-5} \) cm.\(^2\)/sec. at 16\(^o\)C. These values give \( h = 915 \) cm.\(^{-1}\) from equation (67), which is a constant for this system at
a given temperature. Assuming the concentration of molecular chlorine in the main body of the liquid to be zero, and $C_1$ at the interface, $N_0$ for chlorine is 0.0510 $C_1$. Thus, if $C_1$ is 0.001 mols/cu. ft. or $1.6 \times 10^{-5}$ gm. mols/cm$^3$, the rate of chlorine diffusion is $8.2 \times 10^{-7}$ gm. mols/sec. -cm$^2$. From the specific reaction rate constant ($11.7$ sec.$^{-1}$), the mols of chlorine hydrolysed in a sq. cm. of the film at this liquor rate, L-15,000 lbs./(hr.)(sq. ft.), is somewhat less than $2.3 \times 10^{-8}$ mols/sec. -cm$^2$ that is, less than 3 per cent of the chlorine entering the film hydrolyses in the film under these conditions.

For the absorption of oxygen under similar conditions of concentration gradient and film thickness, $N_0$ has a value of 0.0645 $C_1$. Thus it is seen that from the point of view of pure physical absorption the actual rate of chlorine absorption is about 80 per cent that for $O_2$ at that particular film thickness. As the film thickness increases, the ratio of the rate of chlorine absorption to oxygen absorption increases. For example, increasing the film thickness ten times increases this rate from 0.2 to 1.4. This is in agreement with the data of this thesis when calculated from point of view of pure physical absorption. It was found that the values of $K_La$ calculated on the basis of a driving force determined from the molecular chlorine concen-
trations were on the average about the same as the values for oxygen at corresponding liquor rates. Furthermore, these values varied as the 0.6 power of the liquor rate instead of the 0.75 power as for oxygen absorption, the values at low liquor rates being higher than the O\textsubscript{2} coefficients. Hence, although these calculations are not considered quantitative, there is qualitative agreement between the data of this thesis and that predicted by the ratio of reaction rate constant to diffusivity.

Using equation (68), the shape of the molecular chlorine concentration curve has been calculated, and is shown in Fig. 35 and 36 as curve C for two extreme conditions. For purposes of simplicity, the concentration in the main body of the liquid was assumed to be zero. The abscissa are plotted in terms of the fraction of the film thickness from the interface, x/x\textsubscript{L}, and the ordinates are plotted as values of c/c\textsubscript{1} in order that the calculations may be applied generally.

For the case of a thick film, L=150 lbs./(hr.) (sq. ft.), it is seen from Fig. 35 that the concentration of molecular chlorine decreases very rapidly due to the relatively high reaction rate in comparison with the diffusion rate, and on the assumption of negligible reverse reaction, practically all chlorine
FIG 35

CL₂ CONCENTRATION GRADIENTS IN LIQUID FILM

CONDITIONS

\( X_L = 0.0086 \text{ CMS.} \)
\( L = 150 \text{ LBS/HR-SQ FT} \)
\( K_{LA} = 4.9 \text{ HR}^{-1} \)
\( C_L = 0 \)
FIG 36

CL₂ CONCENTRATION GRADIENTS IN LIQUID FILM

<table>
<thead>
<tr>
<th>CONDITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xₐ = 0.00028 CMS.</td>
</tr>
<tr>
<td>L = 13,000 LBS/HR-FT²</td>
</tr>
<tr>
<td>KₐA = 150 HR⁻¹</td>
</tr>
<tr>
<td>Cₐ = 0</td>
</tr>
</tbody>
</table>

CURVE A
CURVE B
CURVE C

\( \frac{C}{C_0} \) vs. \( \frac{x}{x_L} \)
molecules are hydrolysed before diffusing out of the film. Since there is a reverse reaction, and a corresponding equilibrium concentration for the molecular chlorine, the indications from these calculations are that reaction equilibrium would be established essentially before the diffusing molecules reached the main body of the liquid. The curve shows further that about half the diffusing molecules have reacted in one tenth of the film thickness.

As mentioned above, the rate at which chlorine enters the liquid phase can be calculated from the slope of the curve C, (Fig. 35) at \( x = 0 \). This follows from the fact that chlorine can enter the liquid phase only as molecular chlorine. Since there can be no accumulation of chlorine, either molecular or hydrolysed, within the film, the initial rate of chlorine absorption must represent the rate of total chlorine diffusion across the interface, and must be constant and equal to the sum of the rates of diffusion for molecular and hydrolysed chlorine.

Assuming for the moment that there are no restrictions on the concentration of hydrolysed chlorine in solution due to equilibrium solubility relationships, the rate of total chlorine diffusion can be calculated, and the concentration curve determined. This calculation is based on the assumption that the diffusivities of molecular chlorine and
hydrolysed chlorine are the same as that of the total chlorine. Since liquid diffusivities in general are of the same order of magnitude, further refinement for this calculation is not justified.

The total concentration curve is shown as curve A, (Fig. 35) and for the assumptions on which the calculation is based, the slope has the value equal to $c_1 \sqrt{\frac{m}{D}}$. The curve showing the variation in concentration of hydrolysed chlorine is given as curve B. It can be seen that, as a result of the hydrolysis reaction, the total chlorine concentration in the film is built up to a value about nine times the molecular chlorine concentration at the interface.

These calculations show that, without restrictions as to the limit of solubility of hydrolysed chlorine, the concentration of total chlorine at the interface is limited by the rate reaction, although it is relatively high. If the equilibrium solubility imposes the limitation of a concentration lower than that given by the ratio $c_1 \sqrt{\frac{m}{D}}$ (curve D, Fig. 35) the initial rate of absorption would be limited by the solubility and not the rate of reaction, and the curve C (Fig. 35) would decrease less rapidly.

Equilibrium conditions would be expected to exist at the interface for all practical purposes, that is, equilibrium for the hydrolysis reaction as well as for the gas-liquid solubility equilibrium for
molecular chlorine. Under these conditions, the determination of the interface concentration from the equilibrium solubility data would lead to an actual value of the driving force causing the total chlorine diffusion.

However, if the equilibrium solubility for total chlorine is greater than that allowed by the rate of reaction (Fig. 35, curve E), equilibrium concentration for the total chlorine would not be established at the interface, since the ratio of the rate of reaction to the diffusivity would be the controlling factor for the interface concentration. Under these conditions, the determination of the driving force from the equilibrium solubility data would be in error, the driving force so obtained being greater than actually existed. The values of the coefficients calculated from this driving force would be correspondingly low. For the conditions of Fig. 36, over 95 per cent of the diffusing Cl₂ gets through the film without reacting. In this case, the pseudo-coefficient, based on molecular chlorine concentration, would be expected to agree, and does agree, with the coefficients for the case of pure physical absorption.

At 70°F, the ratio of total chlorine to molecular chlorine in equilibrium varies from 2 at high concentrations to about 20 at low concentration.
Hence, with due allowance for the conservative assumptions on which the calculations are based, it is evident that when the concentrations of chlorine in the gas and liquor are low, the ratio of rate of reaction to diffusivity will be the controlling factor in the rate of absorption. Furthermore, the relative effect of this factor will vary with the film thickness; in general the thinner the film the greater will be the controlling effect of the reaction and the greater the error in using the driving force calculated from the total chlorine equilibrium solubility data. This is in agreement with the data, and accounts for the lower power correlation found for the variation of $K_{La}$ with liquor rate than was expected. It should be pointed out that, since the determination of $K_{La}$ based on total $Cl_2$ involves an integration over a finite height of tower, and the controlling effect of the rate of reaction only occurs over a fraction of the tower, a sharp break in the function correlating $K_{La}$ (total chlorine) and film thickness will not be observed. The expected result would be a curved relation which becomes asymptotic to the relation representing true liquid film absorption at low liquor rates, and the deviation between the two functions becoming greater as the liquor rate increased.

Thus it may be concluded that, over part of the range of absorption, there are qualitative indica-
tions that the rate of reaction is controlling the rate of absorption of chlorine in water, and that some error is introduced by the use of driving forces calculated from the total chlorine equilibrium solubility data. The relative effect of this reaction rate is in agreement with the data, and affords an explanation for the low value of the 0.6 power found in correlating the effect of liquor rate on $K_La$. Until a satisfactory solution is developed for the differential equations expressing the rate of absorption of chlorine without the necessity for the broad assumptions used in this discussion, the results of the calculations as to the effect of the rate of reaction must be considered as qualitative only.

It should be remembered that the error incurred by the use of driving forces based on total chlorine solubility data is serious only when the absorption data for chlorine is to be correlated with other liquid film data. It has been shown that the empirical use of the data of this thesis with the total chlorine solubility data is satisfactory for design purposes. The suggestion is made that the factor of solute-solvent interaction be kept in mind when estimates of $K_La$ are being made from the general liquid film correlation.
E. SAMPLE CALCULATIONS

Calculation of $K_L a$ for Chlorine in Water

The data for Run No. 5 have been selected as an illustration of this calculation.

(a) Calibration of Orifice No. 5

Manometer reading, 27.55 - 17.30 = 9.75 in. H$_2$O

Water collected, 6.5 lbs.

Time interval, 172 secs.

Temperature of water, 70°F.

Diameter of tower, 4 in.

Cross-sectional area of tower, $\frac{(4)^2\pi}{12^2} = 0.0372$ sq. ft.

Mass rate, $\frac{(6.5)(3600)}{(172)(0.0372)} = 1,560$ lbs./hr. (sq. ft.)

Fig. 31 and 32 were constructed from these and similar data.

(b) Calculation of water rate for Run No. 5

Manometer reading, 7.6 in. H$_2$O

From Fig. 31, $L = 1,400$ lbs./hr. (sq. ft.)

(c) Concentration of chlorine in outlet liquor.

Volume of sample, 25 ml.

Normality of Na$_2$S$_2$O$_3$, 0.120

Temperature, 70°F.

Milli-equivalent weight for chlorine, 0.0355

Density of solution at 70°F., 62.3 lbs./cu.ft.

Concentration, $\frac{(ml. thio.)}{(0.120)(0.0355)(62.3)}$ (25) (71)

= (0.000150) (ml. thio.)

Thio used at trap, 10.95 ml.
Thio used at base plate, 10.50 ml.

Concentration, at trap, 0.001642 mols/cu.ft.
  at base plate, 0.001575 mols/cu.ft.
(d) Mols chlorine absorbed in liquor, $L_{Ch}$
  = 0.0369 (at trap)
  = 0.0353 (at base plate)

(e) Calibration of gas venturi-meter No. 2.
Venturi was calibrated by the dilution method, using
air to which CO$_2$ gas was added at a known rate. The
CO$_2$ rate was measured by a calibrated wet-test meter.
CO$_2$ concentrations were determined by weighing 530 ml.
of gas in weighing bulbs, and, after absorbing the CO$_2$
in 25 ml. of 0.5N NaOH, using 0.5N HCl to bring the
solution to a phenolphthalein end-point, and then
titrating with 0.05N HCl to a methyl-orange end-point.
The CO$_2$ was vaporized from a cylinder of liquid CO$_2$,
analysis of which showed this gas to be more than 99% CO$_2$.

Barometer, 29.31 in.Hg.
Temperature at wet gas meter, 71.0°F., 53.1°R.
Pressure at wet gas meter, 0.06 in.Hg. gage.
Partial pressure of water at 71.0°F., 0.765 in.Hg.
Partial pressure of CO$_2$, (29.81 + 0.06) - 0.765 = 29.10 in.Hg.
Molal volume of wet CO$_2$, \[
\frac{(359)(531)(29.92)}{(492)(29.10)} = 398 \text{ cu.ft/mol}
\]
CO$_2$ feed rate, expressed as time per 0.100 cu.ft. in secs.,
  = 18.0 secs.

Volume of CO, \[
\frac{(0.100)(3600)}{(13.0)} = 20.0 \text{ cu.ft./hr.}
\]
Mols \( \text{CO}_2 \), \( 20.0/398 = 0.0495 \text{ lb. mols/hr.} \)

Humidity of entering air, \( 0.007 \text{ lb. } \text{H}_2\text{O/lb. air} \)

Mols \( \text{H}_2\text{O/mol air} \), \( (0.007)(29)/(18) \) or 0.0113

Volume of gas weighing bulb, 530 ml.

Mols gas in bulb at 71°F and 29.81 in.\( \text{Hg} \),
\[
\frac{(530)(492)}{(22400)(531)(29.92)} \text{ or } 0.0218 \text{ gm.mols.}
\]

When bulb is filled with air, gms. \( \text{H}_2\text{O} \) in bulb are
\[
(0.0218)(0.0113)/(1.0113) \text{ or } 0.0044 \text{ gms.}
\]

Water from \( \text{CO}_2 \) gas (saturated), \( 0.765/(29.81 - 0.765) \)

or 0.026 mols \( \text{H}_2\text{O/mol CO}_2 \)

If gas analysed contained as much as 10% \( \text{CO}_2 \), water entering with \( \text{CO}_2 \)-air mixture from \( \text{CO}_2 \) gas in excess of that in the air displaced is \( (0.0218)(0.10)(0.026 - 0.0113) \)

or 0.00003 gms. This small increase may well be neglected in the calculations.

Weight of \( \text{CO}_2 \) in bulb, \( (0.05)(\text{ml. HCl used - ml. HCl blank)/(44}(2) \)

or 0.0568 gms.

Weight of sample, 0.6020 gms.

Weight fraction of \( \text{CO}_2 \), 0.0568/0.6020 or 0.0945

Weight fraction of \( \text{H}_2\text{O} \), 0.0044/0.6020 or 0.0073

Weight fraction of air,
\[
\frac{0.3982}{1.0000}
\]

Mols air per mol \( \text{CO}_2 \), \( (0.3982)(44)/(28.8)(0.0945) \) or 14.5

Mols air per hr., \( (0.0495)(14.5) \) or 0.720

Total mols per hr., \( - \text{mols air + mols } \text{H}_2\text{O + mols } \text{CO}_2 \)

or \( (0.720)(1 + 0.0113) + (0.0495)(1 + 0.026) \)

or 0.730
Cu.ft. per hr. = (0.780)(393) or 309
Cu.ft. per hr. - sq.ft., 309/0.0872 or 3540

Density of gas mixture:
Mol. wt., 0.0073/18 + 0.0945/44 + 0.8982/23.8 or 29.6

Density, 29.6/393 or 0.0748 lbs./cu.ft.

Feet of fluid flowing, \( \frac{(h)(62.3)}{12} \cdot \frac{(0.33)(62.3)}{12} \cdot \frac{(0.0748)}{0.0748} \) or 20.8 ft.

where \( h \) = manometer reading in in.\( \text{H}_2\text{O} \).

The results of these and similar calculations are shown on the calibration plots in Fig. 33 and 34.

(f) Analysis of chlorine-air mixtures.

The data used are for the exhaust gas in Run No. 5

Volume of bulb, 530 ml.
Temperature at time of sampling, 72\(^{0}\)F., 295\(^{0}\)K.
Vapor pressure of \( \text{H}_2\text{O} \) at 72\(^{0}\)F., 0.767 in.\( \text{Hg} \).
Gms. \( \text{H}_2\text{O} \) in sample, \( \frac{(0.767)(530)(18)}{(295)(82.1)(29.9)} \) or 0.0101 gms.

Weight of sample, 0.7717 gms.

Normality of thio., 0.120
Gms. \( \text{Cl}_2 \), \( \frac{(N \text{thio.})(\text{ml. thio.})(0.0355)}{0.325} \) or 0.325
Gms. air, 0.7717 - 0.325 = 0.0101 or 0.4366
Mols \( \text{Cl}_2 \), \( 0.325/71 \) or 0.00458
Mols \( \text{H}_2\text{O} \), 0.0101/18 or 0.00056
Mols air, 0.4366/28.3 or 0.0152
Total mols in bulb, 0.0203
Mol fraction \( \text{Cl}_2 \), \( \frac{0.00458}{0.0203} \) or 0.226
Mol fraction \( \text{H}_2\text{O} \), 0.00056/0.0203 or 0.027
Mol fraction air, 0.0152/0.0203 or 0.747
(g) Calculation of exhaust gas rate.
Mol. wt. of gas, wt. of sample/mols in sample
or 0.7717/0.0203 = 38.0
Density of gas, \( \frac{38.0}{(359)(532)} \langle 29.90 - 0.35/13.6 \rangle \)
or 0.0981 lbs./cu.ft.
Venturi No. 2.
Manometer reading, 0.6 in.\( \text{H}_2\text{O} \)
Feet of fluid flowing, \( \text{fff} \), \( \frac{(0.6)(62.3)}{(12)(0.0981)} \)
= 31.7 ft.
From Fig. 33, total gas rate is 1,320 cu.ft./hr. (sq.ft.)
Mols gas/(hr.)(sq.ft.), 1320/398 or 3.42
Mols air/(hr.)(sq.ft.), 3.42/0.747 or 2.56
Total gas rate, (3.42)(38.0) or 130 lbs./(hr.)(sq.ft.)
(h) Calculation of feed gas composition.
Mols \( \text{Cl}_2 \)/mol air (in exhaust gas), 0.226/0.747 or 0.300
Mols \( \text{Cl}_2 \) absorbed per mol air, 0.0353/2.56 or 0.014
Mols \( \text{Cl}_2 \)/mol air (in feed gas), 0.300 + 0.014 or 0.314
Mol fraction \( \text{Cl}_2 \) + mol fraction air = 1.0 - mol fraction \( \text{H}_2\text{O} \)
that is, 1.0 - 0.027 or 0.973
Mol fraction \( \text{Cl}_2 \) (in feed gas), \( \frac{(0.314)(0.973)}{(1.314)} \)
or 0.232
Partial pressure of \( \text{Cl}_2 \) (in feed gas), \( \frac{(0.232)(29.90)}{(29.92)} \)
or 0.232 atmos.
(i) **Calculation of driving-force.**

Since the operating and equilibrium lines are straight over the region involved, the log-mean driving-force may be used. At the top of the tower, \( c \) is zero, and from the equilibrium data, \( c_e \) is 0.00203 at a partial pressure of 0.226 atmos. and 71°F. (Fig. 37)

At the bottom of the tower, \( c \) is 0.00157, and from the equilibrium data, \( c_e \) is 0.00207 at a partial pressure of 0.232 atmos. and 71°F. (Fig. 37)

Therefore \( \Delta c_1 \) is 0.00207 - 0.00157 or 0.00050

\[ \Delta c_2 \text{ is 0.00203} \]

Log-mean driving-force, \( \Delta c_{Bm} \) is \((0.00203 - 0.00050)/\ln 203/50 \)

or 0.00109

(j) **Calculation of coefficient, \( K_L a \), (based on base plate sample)**

Height of tower, 2 ft.

\[ K_L a = \frac{L(C - 0)}{\gamma h \Delta c_{Bm}} = \frac{(1400)(0.00157)}{(62.3)(2.0)(0.00109)} = 16.2 \text{ hr.}^{-1} \]

(k) **Coefficient, \( K_L a \), (based on trap sample) is 17.9 hr.\(^{-1}\)**

(l) **Calculation of end factor**

End factor, \( K_L a(\text{base})/K_L a(\text{trap}) = 16.2/17.9 = 0.90 \)

**Calculation of pseudo-coefficient, \( K_L a \).**

The calculations for the determination of this value are the same as for the regular \( K_L a \) given above in sections (a) to (h) inclusive. In determining the driving-force for the pseudo-coefficient, it is assumed that only molecular chlorine concentrations
FIG. 37

SOLUBILITY OF CHLORINE
IN WATER

PRESSURE - ATMOSPHERES

TEMPERATURE - °F

0 0.0005 0.0010 0.0015 0.0020

9-16-40
contribute to the diffusion phenomenon. Reference is made to Fig. 28 on which two equilibrium lines are shown, one for the total chlorine concentration and the other for the molecular chlorine concentration at corresponding partial pressures of chlorine in the gas phase. It has been shown elsewhere in this work that the equation for the total chlorine concentration curve at a fixed temperature is:

\[ c = H^P + \sqrt{K} \]

Where \( c \) is total chlorine concentration,

\( P \) is partial pressure of chlorine in the gas phase,

\( H \) is Henry's Law constant, and

\( K \) is equilibrium constant for the hydrolysis reaction.

At any given value of \( P \), the total concentration is \( c \), the molecular concentration is \( H^P \), and the hydrolysed concentration is \( \sqrt{K} \). Thus, knowing the total concentration from the experimentally determined equilibrium data, it is a simple matter to calculate the molecular chlorine equilibrium concentration. The value of \( H \) as a function of temperature is given in Table II and shown in Fig. 38.

To calculate the pseudo-coefficient, the operating line representing the material balance for the run is placed on the equilibrium plot, line AE, Fig. 28. Now the concentration of total chlorine at A (and B) has in equilibrium with it a molecular chlorine concentra-
FIG. 38

HENRY'S LAW CONSTANT
MOLECULAR CHLORINE IN WATER

$H \times 10^3 - \text{lb} \text{mols/} \text{C} \text{ft} = \text{ATMOS}$
tion represented by point C. This, then, is the
molecular chlorine at the same point in the tower where
the total chlorine concentration is A, and hence, is
a point on the pseudo-operating line. This can be
done for every point on the pseudo-operating line,
and the line DE is obtained. Driving-forces are com-
puted by reading the differences between values
represented by line DE and the molecular chlorine con-
centration curve at various values of P. When line
DE does not curve too greatly, the log-mean difference
may be calculated. Data for Run No. 5, (trap sample)
are used, and the end factor is included in the
height, h = 2.2 ft.

\[ \Delta c_1 = 0.00107 - 0.00075 = 0.00032 \]

\[ \Delta c_2 = 0.00104 \]

\[ \Delta c = \frac{0.00104 - 0.00032}{\ln \frac{104}{32}} = 0.00061 \]

\[ K_a = \frac{(1400)(0.00164)}{(62.3)(2.2)(0.00061)} = 27 \text{ hr}^{-1} \]
Calculation of $K_a$ for Oxygen in Water

(a) Equilibrium data are given by Winkler\(^{(40)}\) in terms of Henry's Law constant, $H$, and temperature, Fig. 39, $c_e = HP$

where $c_e$ is equilibrium concentration of $O_2$ in water; $P$ is corresponding partial pressure of $O_2$ in gas phase. These data were checked for the water used by bubbling saturated air through a sample of the mill water until equilibrium was reached.

Temperature, $25.9^\circ$C, $78.6^\circ$F.

Concentration of $O_2$ in liquid, $1.55 \times 10^{-5}$ mols/cu.ft.

Calculating concentration from equilibrium data,

$$P_{O_2} = (1 - x)(\text{Baro. Pressure})\left(\frac{29.92}{29.30}\right)$$

where $x$ = vapor pressure of water at $78.6^\circ$F.

$P_{O_2} = (1 - 25/760)(29.92)/(29.30) = 0.202$ atmos.

$c_e = (0.202)(7.88)(10^{-5}) = 1.59 \times 10^{-5}$ mols/cu.ft.

In view of this agreement and similar checks at other temperatures, the data of Winkler were used in the calculations.

(b) Liquor analyses

For the system of analysis used, a variable amount of sample was used together with a fixed amount of $Na_2S_2O_3$ (4.95 ml.). The normality of the thio. was $0.0105$.

$$\text{Mols } O_2/\text{cu.ft.} = \frac{(4.95)(0.0105)(0.003)(62.3)}{(\text{ml. of sample})(32)} = 31.0 \times 10^{-5}$$
HENRY'S LAW CONSTANT
OXYGEN IN WATER

$H \times 10^5$ - HENRY'S CONSTANT - LB MOL / CUFT - ATOMS

TEMPERATURE - °C
(c) **Partial pressure of O₂ in gas.**

The amount of O₂ given up by the liquor is so small that the analysis of the gas does not differ significantly from that of air, and hence is constant throughout the tower. The concentration of O₂ is therefore

\[
(0.210)(1 - P_{H₂O})(\pi)/(29.92)
\]

(d) **Calculation of gas and liquor rates.**

The same meters were used in both the chlorine and the oxygen work. Sample calculations connected with these meters are given above.

(e) **Calculation of Kₜa.**

Equation defining \( K_{t/a} \) is

\[
\frac{(L/\rho)}{(c_{\text{top}} - c_{\text{bottom}})} = K_{t/a} \left( h \right) \left( c - c_e \right)_{\text{ave}} = K_{t/a} \left( h \right) \left( \frac{c_{\text{top}} - c_e}{c_{\text{bottom}} - c_e} \right) \ln \left( \frac{c_{\text{top}} - c_e}{c_{\text{bottom}} - c_e} \right)
\]

since \( P_{O₂} \) does not change through the tower

\[
(c_e)_{\text{bottom}} = (c_e)_{\text{top}}
\]

Thus \( K_{t/a} = \frac{L}{\rho h} \ln \left( \frac{c_{\text{top}} - c_e}{c_{\text{bottom}} - c_e} \right) \)

For Run No. 117.

Temperature, 66°F.

Tower pressure, 29.7 in. Hg.

Equilibrium concentration, \( c_e = (0.206)(3.37)(10^{-5})\frac{(29.7)}{(29.92)} \)

or \( 1.31 \times 10^{-5} \) mols/cu.ft.
Concentration in liquor, \( c_t = 4.73 \times 10^{-5} \text{ mols/cu.ft.} \)

\( c_b = 1.86 \times 10^{-5} \text{ mols/cu.ft.} \)

Liquor rate, 2,000 lbs./(hr.)(sq.ft.)

\[
K_{La} = \frac{(2000)(2.3)}{(62.3)(4)} \log \frac{4.73 - 1.81}{1.86 - 1.81}
\]

\( = 33 \text{ hr.}^{-1} \)
Calculation of $K_{e,a}$ for Cl$_2$ in Caustic.

(a) Gas and liquor rates were determined in the same type of meters used in the work described previously for which calculations have already been given.

For Run No. 125, $L = 12,300$ lbs./hr. (sq. ft.)

Entering gas rate, $G_1 = 7.00$ mols/hr. (sq. ft.)

Inert gas rate, $G = 4.00$ mols/hr. (sq. ft.)

(b) Gas analyses.

Gas analyses were performed in the same manner as described under Cl$_2$ absorption in water.

Entering gas partial pressure, $P_1 = 0.429$ atmos.

Exhaust gas partial pressure, $P_2 = 0.0121$ atmos.

(c) Normality of Caustic.

Entering caustic titrated with 0.1N HCl to methyl-orange end-point, $N = 3.20$

Exit caustic titrated to methyl-orange end-point after destroying NaOCl by boiling with concentrated ammonium hydroxide, $N = 2.51$

(d) Calculation of $K_{e,a}(P_{BM})$.

Equation defining $K_{e,a}(P_{BM})$ is

$$K_{e,a}(P_{BM}) = \frac{G\pi(42P_1 + 29\pi)^{0.8}}{h(\pi - P_1)0.8} \int \frac{P_1}{(42P + 29\pi)^{0.3}(\pi - P)L^2\ln \frac{\pi}{\pi - P}} dP$$

This equation was integrated by plotting

$$\frac{1}{(42P + 29\pi)^{0.3}(\pi - P)^{1.2}\ln \frac{\pi}{\pi - P}}$$

vs $P$
and determining the area under the curve between $P_1 = 0.429$ and $P_2 = 0.0121$; the value of the integral so obtained is 0.240.

Also \((42P_1 + 29\pi)^{0.8} = 21.7\)
and \((\pi - P_1)^{0.8} = 0.639\)

Therefore \(K_a \frac{P_{Bm}}{\delta} = \frac{4.00(21.7)(0.240)}{1(0.639)} = 32.6\)

at entering gas rate, \(G_1\), in \(\text{mols/}(\text{hr.})(\text{cu.ft.})(\text{atmos.})\)

Molecular weight of entering gas, 47.0 lbs.

Entering gas rate, \(G_1 = (7.00)(47.0) = 329 \text{ lbs./}(\text{hr.})(\text{sq.ft.})\)
F. TABLE of NOMENCLATURE

C  Solute concentration in liquid phase, mols/cu.ft.
D  Diameter, ft.
D  Diffusivity, cm./sec.²
G  Gas rate, mols/(hr.)(sq.ft.)
H  Henry's law constant, mols/(cu.ft.)(atmos.)
H_T U  Height of transfer unit, ft.
K_g  Overall coefficient, lb.mols/(hr.)(cu.ft.)(atmos.)
K_L  Overall coefficient, lb.mols/(hr.)(cu.ft.)(lb.mols per cu.ft.)
K  Equilibrium constant, mols²/cu.ft.²
L  Liquor rate, lbs./(hr.)(sq.ft.)
M  Molecular weight, lbs.
N  Mols transferred/(hr.)(sq.ft.)
P  Partial pressure of solute gas, atmos.
R  Gas constant, (atmos)(cu.ft.)/(mols)(deg.Rankine.)
S  Cross sectional area, sq.ft.
T  Temperature, deg.F. or deg.C.
V  Volume, cu.ft.
a  Surface area per unit volume, ft. -¹
a  Total chlorine equilibrium concentration, mols/cu.ft.
b  Hydrolysed chlorine concentration, mols/cu.ft.
c  Molecular chlorine concentration, mols/cu.ft.
h  Tower height, ft.
k  Film coefficient, mols/(hr.)(sq.ft.)(unit driving force.)
m  Specific reaction rate constant, sec. -¹
n  Specific reaction rate constant, mols² sec. -¹
n  Power function of a variable.
\( x \) Film thickness, ft. or cm.
\( a \) Proportionality constant
\( \Delta \) Difference (driving force)
\( \pi \) Total pressure, atmos.
\( \rho \) Density, lbs./cu.ft.
\( \mu \) Viscosity, lbs./hr.-ft.

**Subscripts.**

A Solute component of the system.
B Solvent component of the system.
\( \bar{m} \) Log mean solvent concentration, mols/cu.ft. or log mean inert pressure, atmcs.
e Equilibrium condition.
G Gas phase.
i Interface, gas or liquid.
L Liquid phase.
1 Refers to conditions at bottom of tower.
2 Refers to conditions at top of tower.
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