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ABSORPTION OF CARBON DIOXIDE
BY SODIUM CARBONATE SOLUTIONS
IN A
GAS-BUBBLE COLUMN

BY

JOSEPH D. SINGALEWITCH

A THESIS
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1957

APPROVAL OF THESIS

FOR

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NEWARK, NEW JERSEY

JUNE, 1957

ABSTRACT

A study was conducted on the absorption of pure carbon dioxide by sodium carbonate-sodium bicarbonate systems in a gas-bubble column (in which bubbles, formed by passing a gas through a porous plate at the base of the column, rise up through a descending continuous liquid phase). This equipment was found to be extremely efficient under the conditions of the experiments, which covered high liquid rates (9,000 to 15,000 pounds per hour per square foot) with gas rates of 30 to 60 pounds per hour per square foot. The absorption section of the column was two inches in diameter and one foot in height. Sodium carbonate normalities were varied from 0 to 1.2 normal with bicarbonate fractions ranging from 0 to 0.65. The effects of temperature, column height, and column diameter were not investigated.

A correlation equation was obtained for Kga at 25° Centigrade and one foot column height which gave agreement with the main body of data to within ±8%.

$$K_g a = 1.00 \times 10^{-4} L^{0.834} G^{0.308} (0.800 - 0.110N) \ \text{lb-mols}/\text{hr-ft}^3\text{-atm.}$$

The values of Kga obtained were as much as five times greater than those given in the literature for packed towers.

A qualitative analysis of the data indicated that the process was probably primarily one controlled by diffusion of the carbon

dioxide through the liquid film, the sodium carbonate serving mainly to prevent a buildup of carbon dioxide back pressure.

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INTRODUCTION

The absorption of carbon dioxide by sodium carbonate-sodium bicarbonate solutions has been investigated by a number of authors. Harte and Baker[1] obtained data using a one inch diameter wetted-wall column, recirculating the absorbing liquid which was progressively converted from sodium hydroxide to sodium carbonate to sodium carbonate-bicarbonate mixtures. Williamson and Mathews[2] have reported results obtained on similar apparatus which contained a series of conical baffles in the column to promote turbulence.

Comstock and Dodge[3] have given absorption correlations for a three inch diameter tower packed with glass Raschig rings. Furnas and Bellinger[4] published an attempt to correlate some of the above work together with absorption data collected by them for a twelve inch diameter tower packed variously with Raschig rings and Berl saddles.

Recently, Shulman and Molstad[5] published data on the perfor-

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[1] Harte, C.R., and E.M. Baker; Ind. Eng. Chem., 25, 1128 (1933).

[2] Williamson, R.V., and J.H. Mathews; Ind. Eng. Chem., 16, 1157 (1924).

[3] Comstock and Dodge; Ind. Eng. Chem., 29, 520 (1937).

[4] Furnas and Bellinger; Trans. A.I.Ch.E., 34, 251 (1938).

[5] Shulman, H.L. and M.L. Molstad; Ind. Eng. Chem., 42, 1058 (1950).

mance of gas-bubble columns for absorption of carbon dioxide in water and desorption of carbon dioxide and hydrogen from water. The data given showed a high absorption efficiency for slightly soluble gases and an ability to operate at high liquid rates and liquid-gas ratios much higher than those obtainable with wetted-wall or packed absorption columns. From this information, it was felt that an investigation of absorption mechanism and efficiency could be profitably carried out on the system carbon dioxide-sodium carbonate-sodium bicarbonate.

A two inch diameter column was set up together with a stainless steel porous plate as the bubble former and a series of runs were made using pure carbon dioxide as the solute gas. The liquid rates were varied from 9,000 to 15,000 pounds per hour per square foot, the gas rates from 30 to 60 pounds per hour per square foot, and total sodium normalities from 0 to 1.2 normal with sodium bicarbonate fractions from 0 to 0.65. The column height and operating temperature were maintained relatively constant at one foot and 25° Centigrade, respectively.

The data obtained were correlated graphically to give a generalized expression for Kga in terms of the variables studied, and analyzed qualitatively for information both on the behavior of the column and mechanism of the absorption process.

DESCRIPTION OF EQUIPMENT

The test equipment, a photograph of which appears as Figure 1, was adapted in large part from that described by Shulman[5]. A schematic drawing of the system is shown in Figure 2. The liquid reservoir (A) is an open-top 55 gallon steel drum with a 3/8 inch copper tubing exit line located 3 inches from the bottom of the tank. Liquid flows by gravity from the tank to the one gallon per minute capacity gear pump (B). The pump discharge is divided into a return line to the reservoir and a stream leading to the liquid rotameter (C). From the rotameter the liquid passes into the top of the column and is released in the column at the desired height as horizontal jets at the liquid surface. The absorbing column (D) is a 3 foot section of flared 2 inch pyrex pipe bolted to the base of the column.

To obtain reproducibility and consistency with the data published by Shulman[5], a conical end design for the lower end of the column was adopted as recommended by Blanding and Elgin[6] in their work on liquid-liquid spray columns. The cone (E), of 0.006 inch thickness brass, is 1 and 5/8 inches in height and diminishes from 2 and 3/4 inches in diameter at its base to 2 inches in diameter at

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[5] Shulman, H.L. and A.L. Molstad; op. cit.

[6] Blanding, F. and J. Elgin; Trans A.I.Ch.E., 38, 305 (1942).

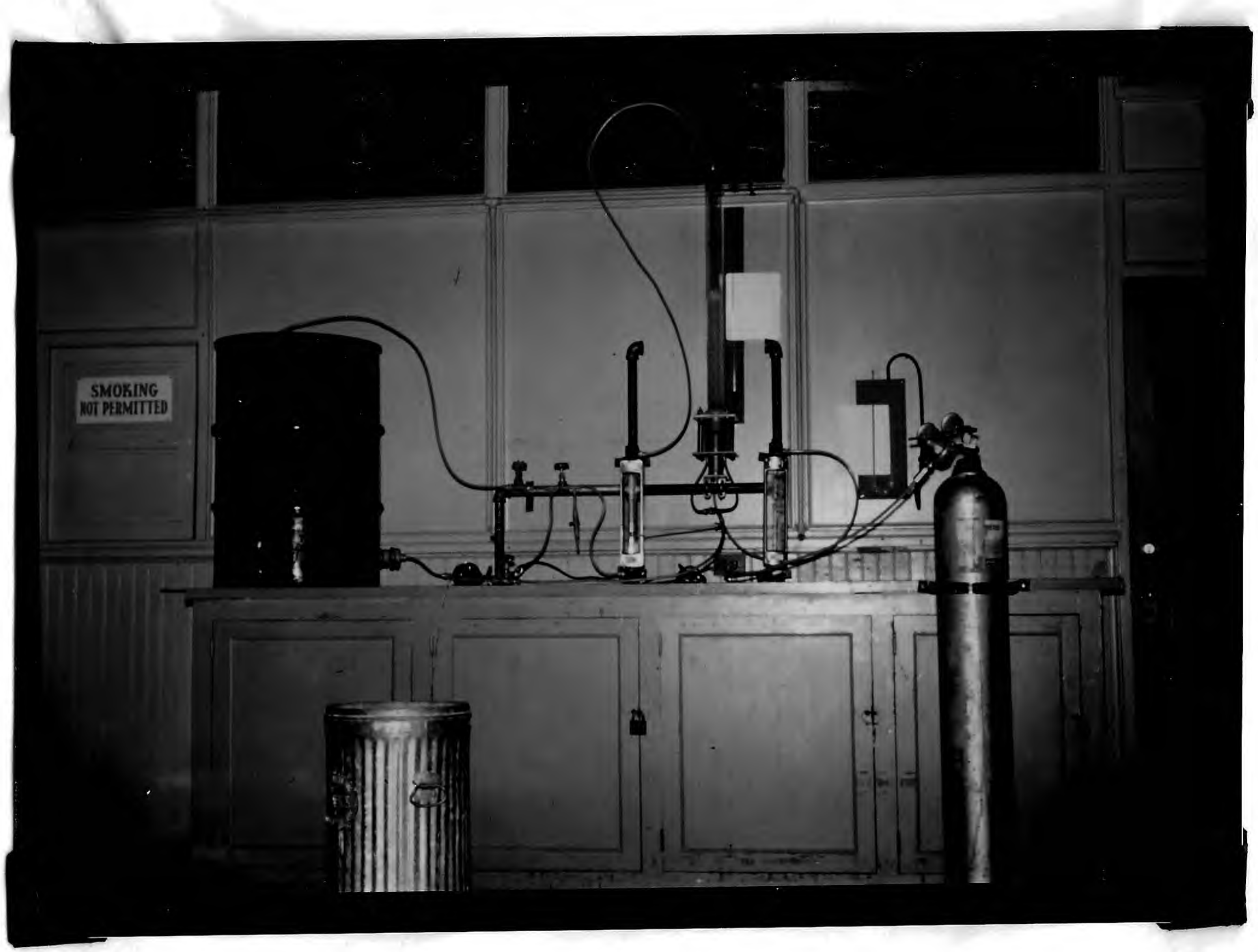

Figure 1

Absorption Equipment

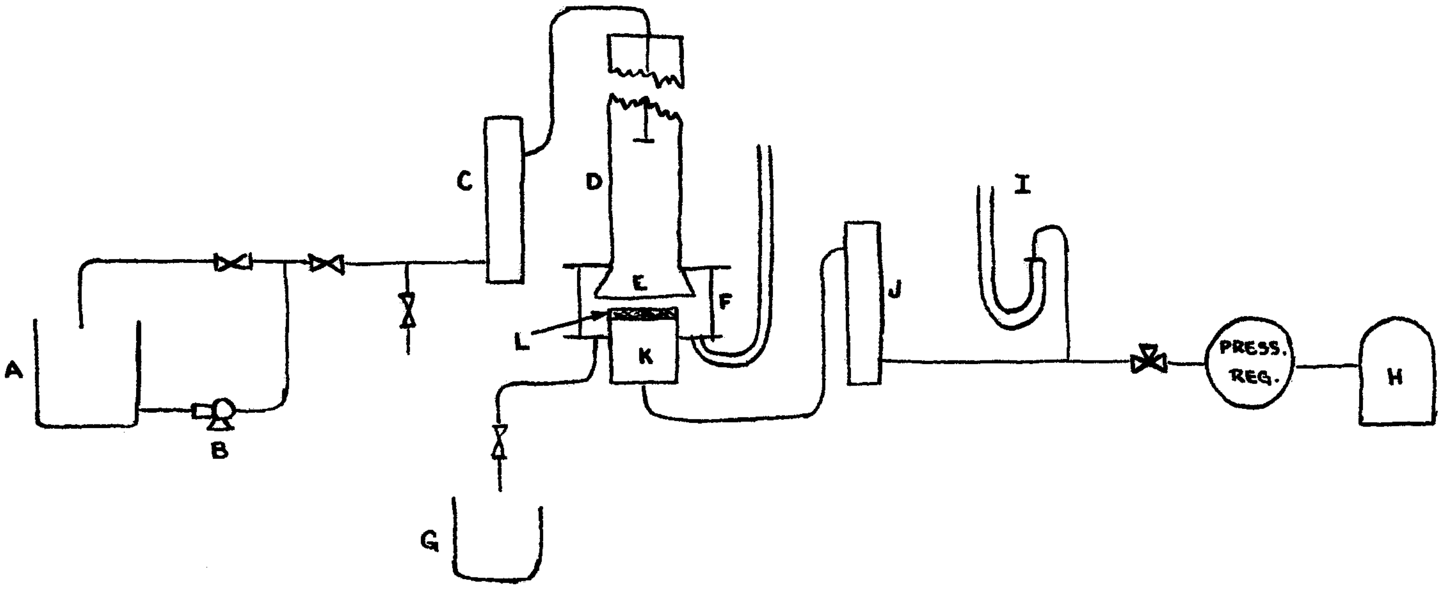

Figure 2

Schematic Sketch

of

Absorption Equipment

Figure 3

Column in Operation

(Run 21)

its entrance into the column.

The base of the column consists of two 6 inch square bolted brass plates with a 3 inch inside diameter, 5 and 1/16 inch high lucite cylinder (F) supported between them. The liquid leaves the column through two diametrically opposed 1/4 inch holes in the lower brass plate and passes through a 1/4 inch bronze globe valve to a galvanized 55 gallon receiver (G). A third hole in the lower brass plate is connected by copper tubing to a water manometer to obtain the liquid pressure at the level of the porous plate.

The carbon dioxide used in these experiments is supplied from a commercial cylinder of bone-dry carbon dioxide (H). A pressure regulator and needle valve serve to control the flow of gas to the column. A manometer (I), using tetrabromoethane as the fluid is inserted in the line following the needle valve for pressure data necessary to calculate the gas flow through the rotameter. From the pressure-reducing system the gas passes through the gas rotameter (J) and thence to the "gas chamber" (K) at the base of the column. This chamber is a 6 inch length of 2 inch diameter type M copper water tubing soldered to the lower 6 inch brass plate. The tubing extends 2 and 3/4 inches up into the lower section of the column and 3 inches down below the brass plate. A 3 inch square brass plate is soldered to the lower end and the stainless steel porous plate (L) cemented with a Laminac resin in a shoulder turned in the upper end of the copper tubing. The upper face of the porous plate is 1/2 inch below the base of the brass cone. The 5 inch square brass plate is centrally tapped to receive a 3/8 inch brass compression fitting. The gas enters the chamber through this fitting and leaves by passing through the porous plate into the column. Care was exercised to assure alignment and concentricity between the column and the porous plate. A length of 2 and 1/2 inch diameter reinforced rubber hose (not shown in the photograph) taped over the top end of the column and extended out a convenient window leads the unabsorbed carbon dioxide to the atmosphere away from the actual scene of operations.

The porous plate used in these experiments was a 2 inch diameter 0.125 inch thick section of Grade D stainless steel purchased from the Micro Metallic Corporation, Brooklyn, New York. The plate contained some fused areas on both faces resulting from cutting operations after purchase, but visual inspection of the plate during test runs, showing only a fraction of the openings being utilized at any condition, led to the conclusion that no important or deleterious effects were introduced.

All glass to brass and lucite to brass contact surfaces were gasketed with 1/16 inch Teflon sheet.

Three-eighths inch flexible copper tubing and brass compression fittings were used fro all flow lines in both the liquid and gas systems.

OPERATING PROCEDURE

The following procedure was used for the test runs:

The absorbing solution was brought to the desired sodium ion and bicarbonate ion concentration by addition of solutions of technical grade sodium carbonate and sodium hydroxide. The solution in the reservoir was then recirculated through the pump at about one gallon per minute for 15 minutes. In addition, the solution was stirred with a wooden paddle at intervals.

The gas flow was started into the column at a rate somewhat higher than that to be used for the run. By an adjustment of the valves on the pump discharge, the recirculation to the liquid reservoir was cut down and the liquid feed to the column brought up to the operating point. The globe valve on the column discharge was kept almost closed until the liquid level in the column approached the desired point for the run and was then adjusted to maintain this level. During these processes it was necessary to maintain close watch on the gas rotameter since variations in the liquid level in the column, varying the pressure on the face of the plate, caused the gas rate to fluctuate.

While it would have been simpler to set the liquid conditions before allowing the carbon dioxide to enter the column, early runs showed that such a procedure allowed seepage of the liquid into the porous plate, gas chamber, and gas lines, causing pulsations in the gas feed to the column. In addition, under such conditions, the gas passing through the rotameter and into the column would have been partially or completely saturated with water vapor, adding another variable to those already under investigation.

When the column had operated for 5 minutes a portion of the inlet liquid was taken in a clean beaker from the petcock between the pump and the rotameter. One portion of the sample was analyzed for total sodium ion and one for bicarbonate content.

When the column had operated for a minimum of 15 minutes with only minor fluctuations an outlet sample of liquid was taken by filling a clean beaker at the outlet above the receiver and pipetting the requisite sample into and Erlenmeyer flask. This sample was titrated for bicarhonate concentration only.

The column was kept in controlled operation during the titration of the first outlet sample. When the first sample had been completed, a second outlet sample was taken in the same manner as the first and again analyzed for bicarbonate. Again the column was kept in operation during the titration. The amounts of sodium hydroxide equivalent to the bicarbonate present were approximately calculated for both samples. If the results agreed, the run was considered ended. If the results varied by more than 2-3% a third sample was taken to resolve the discrepancy.

The inlet temperature of the liquid was obtained by stirring the solution in the reservoir with a mercury thermometer. The outlet temperature was read on a mercury thermometer shortly past the junction of the two liquid discharge lines from the column.

The data collected for the carbon dioxide-sodium carbonate-sodium bicarbonate runs is given in Table I in the Appendix.

The titration for total sodium ion concentration was carried out in the following manner; To a 50 milliliter sample were added 2-3 drops of phenolphthalein indicator solution. Hydrochloric acid of approximately the normality of the sample solution was added until the solution became colorless. At this point, 2-3 drops of bromphenol blue solution was added and the titration continued to a green endpoint. The sample was then boiled for 1-2 minutes, the dissolved carbon dioxide being expelled and the solution changing from green to blue to indigo in color. The sample was then cooled to room temperature by immersion in a running cold water bath and the titration then carried to a green endpoint. The final increment of hydrochloric acid added was of the order of 1, 2% of the total acid used.

In the determination off bicarbonate concentration the sample was first treated with an excess of sodium hydroxide to convert all bicarbonate to carbonate. Saturated barium chloride solution (4-6 times the stoichiometric quantity) was then added to precipitate all carbonate as barium carbonate. The excess sodium hydroxide was then backtitrated, using phenolphthalein as an indicator.

The hydrochloric acid used in these runs was standardized against mercuric oxide as outlined by Kolthoff and Sandell.[7]

The sodium hydroxide solutions used were prepared fresh for each day's work from chemically pure pellets. The hydroxide was standardized against the hydrochloric acid, a portion of saturated barium chloride solution being added prior to titration. The amount of barium chloride solution added was equal to that intended for use in that day's bicarbonate titrations.

Preceding the absorption work with sodium carbonate solutions a total of 15 runs were made absorbing carbon dioxide in water. These served to give experience in operation of the column and, more importantly, as a check of the efficiency of this experimental column. Table II in the Appendix compares some figures obtained in these check runs with Shulman's data.[5]

For these carbon dioxide-water runs, inlet and outlet samples were obtained as previously described for sodium bicarbonate solutions.

[7] Kolthoff, I. and E. Sandell: Textbook of Quantitative Inorganic Analysis, The Macmillan Co., New York, 1952.

[5] Shulman, H.L. and M.C. Molstad: op. cit.

An excess of sodium hydroxide was added to the sample to convert the carbonic acid to sodium carbonate plus excess sodium hydroxide Saturated barium chloride solution (4-6 times stoichiometric quantity) was added to precipitate barium carbonate and the remaining sodium hydroxide titrated with standard hydrochloric acid to a phenolphthalein endpoint.

All titrations were carried out in a room removed from the absorption equipment to reduce the possibility of error from any carbon dioxide leakage from the equipment.

CALCULATION OF RESULTS

Gas Rates

A rotameter calibrated for air flow measurements was used for determination of carbon dioxide feed to the absorption column. The correction factor applied to the rotameter readings was given by the following equation

$$G_{CO_2} = G_{AIR}\left(\frac{44 \times \left[1 + \frac{3.42\,\Delta p}{408}\right]}{29}\right)^{\frac{1}{2}}$$

where G is the mass flow rate in pounds per hour per square foot of empty column, and Δp is the gage pressure of the carbon dioxide, measured shortly upstream of the rotameter, in inches of tetrabromonethane.

Liquid Rates

A rotameter calibrated for water was used for liquid flow measurements.

Flow rates for sodium carbonate-sodium bicarbonate solutions were calculated on the basis of three assumptions. First, densities of sodium bicarbonate solutions were assumed equal to densities of sodium carbonate solutions of the same weight composition. Second, Concentrations of sodium carbonate and sodium bicarbonate were assumed additive for purposes of determining solution densities. Third, coefficients of discharge were assumed invariant throughout all the runs.

Based on these assumptions, the following equation was derived for calculation of liquid feed rates

$$L_{SOLN} = L_{H_2O}\left(\frac{7.8-\rho_s}{7.8-\rho_w} \times \frac{\rho_w}{\rho_s}\right)^{\frac{1}{2}}$$

where L is the mass flow rate in pounds per hour per square foot, and ρ_w and ρ_s are the densities, respectively, of water and the experimental solution at the run temperature.

Since the results of the experimental runs showed no tendency to give deviations all in one direction proportional to flow rate, density, concentration, or viscosity, it can be stated that refinements in in the calculation of liquid feed rates would not have given a more self-consistent body of data.

Calculation of f

A variable whose influence was first discussed by McCoy,[8] f, the fraction of total sodium ions which are present as sodium bicarbonate, is simply given by the ratio

$$f = \frac{N_{NaHCO_3}}{N_{NaHCO_3} + N_{Na_2CO_3}}$$

The normalities specified in the above equation were calculated

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[8] McCoy, H. N., Amer. Chem. Jour., 29, 437 (1903).

from the titrations previously described in the section of this report on Operating Procedure.

Table III in the Appendix shows data on the compositions of the absorbing solutions expressed both as normality and in terms of the McCoy coefficient, f.

Height of an Overall (Liquid) Transfer Unit (HTU_{OL})

The data obtained in the carbon dioxide-water runs were used to calculate HTU_{OL}, the height of an overall transfer unit, based on the composition of the liquid phase. The following equations, adapted from Shulman,[5] served to determine this quantity.

$$P_{CO_2} = 760 \left(1 + \frac{Z H_L}{2 \times 408}\right)$$

$$x^* = P_{CO_2} / H$$

$$HTU_{OL} = Z \Big/ \frac{x_1 - x_2}{(x^* - x)_{LM}}$$

Henry's Law Constant, H, was found for each run from the data given by Bohr.[9] The carbon dioxide pressure used in evaluation of equilibrium concentrations was taken as atmospheric pressure plus

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[5] Shulman, H.L. and M.C. Molstad: op. cit.

[9] Bohr, N.: Ann. Physik, 68, 500 (1894).

one-half the liquid head on the porous plate. Thus the equilibrium concentrations were considered equal at both top and bottom of the column. Liquid concentrations, X, were expressed in pounds of carbon dioxide per pound of water. The height of the column, Z, was measured in feet. Shulman's correlations for the effect of temperature and column height were applied to allow direct comparison with his data.[5]

Overall Coefficient of Absorption (Kga)

In order to derive an equation correlating the absorption characteristics of the test column with such variables as flow rates and liquid compositions, and to provide a basis for comparison with other work in the field, all data were reduced to the overall coefficient of absorption, Kga, expressed as pound-mols of carbon dioxide transferred per hour per cubic foot of column per atmosphere pressure difference of carbon dioxide.

The expression for the observed value of Kga is

$$K_g a = \frac{\Delta N_{HCO_3^-}}{2 \times 10^3 \times \rho_s} \times L \times \frac{1}{Z} \quad \text{lb-mols/hr-ft}^3\text{-atm}$$

The term $\Delta N_{HCO_3^-}$ represents the difference in normality of sodium bicarbonate between the outlet and inlet liquid.

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[5] Shulman, H.L. and M.C. Molstad: op. cit.

CONCLUSIONS

Column Operation

The gas-bubble column was found extremely simple to operate. Visual inspection of the liquid and gas rotameters and of the liquid level of the column were sufficient to show at a glance whether the column was operating at the desired steady-state conditions, fluctuating about a point, or moving gradually away from the preset conditions.

Corrective actions to return the column to steady-state operations most frequently consisted of adjusting the carbon dioxide needle valve or the liquid discharge valve, more rarely the liquid feed valves.

It was found during column operation that liquid rates could be held to within ±2% without difficulty. Gas rates, however, tended to vary by as much as ±5% with a consequent variation of similar magnitude in the liquid level of the column.

The liquid level, per se, could have been held more closely to a given setting by use of a vented takeoff line which rose to the desired liquid level height before dropping back into the receiver. Such an arrangement would probably have reduced the liquid level variation to about ±1% as opposed to the figure of ±4% observed in the experimental runs.

The greatest obstacle to smooth operation of the column under test was discovered to be the maintenance of a steady gas flow rate. As the equipment was set up, the problem resolved itself into reducing the gage pressure of the carbon dioxide from approximately one thousand pounds per square inch in the commercial cylinder to slightly less than one pound per square inch feed to the porous plate.

Though this variation did not have a great effect on the Kga in the runs made, it would become a matter of increased importance in the use of this system for absorption of carbon dioxide-air mixtures, particularly lean gas compositions. For such experimentation, a modification of the gas feed arrangement would be required.

In the runs described in this report, the carbon dioxide driving force was assumed constant at 760 millimeters of mercury. This assumption causes a maximum of 1% error in the observed Kga. However, in runs where the partial pressure of the carbon dioxide in the feed mixture approached the carbon dioxide vapor pressure of the absorbing liquid, fluctuations in the carbon dioxide feed rate (and thus its pressure) could cause large errors in the determination of Kga.

Foam formation, which Shulman described as having occurred only in one inch diameter columns, was observed quite frequently in the two-inch column used in this work. The phenomenon was aggravated both by increase in solution concentrations and increase in gas rates. High gas rates obtainable for the runs on absorption in water were impossible of achievement for the sodium carbonate runs, a limiting value of about 60 pounds per hour per square foot being found for the test solutions.

This foam may be caused by either chemical or physical properties of the operation. Chemical factors might include functions of the viscosity and surface tension of the solutions entering the column. A physical explanation of the foam would require study of the effects of various types of apparatus for introducing the liquid into the column, and the properties and behavior of the liquid jets produced.

Correlation of Data

A preliminary attempt to correlate the data obtained in this work was made based upon the exact driving force expressed as pressure difference of carbon dioxide in millimeters of mercury. The equilibrium values of carbon dioxide vapor pressure over solutions of sodium carbonate and sodium bicarbonate were obtained from the equations of Mai and Babb.[10]

For the conditions encountered in the experimental runs, the calculated carbon dioxide equilibrium pressures ranged from 0 to 15 millimeters of mercury. This is well within the range of normal

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[10] Mai and Babb, Ind. Eng. Chem., 47, 1749 (1955).

atmospheric variation. The carbon dioxide pressure in the gas phase was in all cases approximately 10 millimeters greater than atmospheric, on an overall column average. Since actual barometric pressures had not been recorded in conjunction with the experimental runs, it was decided to assume the average overall driving force throughout the column as exactly 760 millimeters of mercury.

Using this driving force, the data obtained was correlated to fit the general equation

$$K_{ga} = k\, L^{m}\, G^{n}\, \mathcal{F}(N, f)$$

where N is the normality of the sodium carbonate (a parameter chosen on the basis of preliminary correlations and later shown to have a possible theoretical foundation), and the other symbols have meanings as previously discussed.

Graphical analysis of the data, presented in Table IV and Figures 4 through 7 of the Appendix, gave the following equation, which should be assumed valid only at or about 20° to 25° Centigrade.

$$K_{ga} = 1.00 \times 10^{-4}\, L^{0.834}\, G^{0.308}\, (0.800 - 0.110N) \quad \text{lb-mols}/\text{hr-ft}^{3}\text{-atm.}$$

Table V of the Appendix gives a comparison between observed values of Kga (calculated from increase in bicarbonate concentration) and those calculated from the above correlating equation. It shows that, except for a few runs which are discussed on page 26, agreement is found to within ±8%.

The method of correlation is outlined immediately below.

As a first approximation, Kga was assumed proportional to $L^{1.000}$ and independent of N. This can be expressed as the equation $Kga/L = k_1 G^n$, which, plotted on log-log paper should give a straight line with a slope equal to n.

This graph, shown as Figure 4 of the Appendix, gave an exponent of 0.308 for G.

The next step was to check the assumed exponent of L. To accomplish this, the equation $Kga/G^{0.308} = k_2 L^m$ was plotted on log-log paper to give a straight line whose slope was m, the exponent of L.

This graph, shown as Figure 5 of the Appendix, gave an exponent of 0.834 for L, indicating that the original choice of 1.000 had introduced very little error in the correlation.

A study of the data and the correlation thus far obtained led to the belief that the most acceptable method of introducing a term indicative of solution composition was by means of a multiplying factor of the type (a-bN). Plotting $Kga/L^{0.834}G^{0.308}$ against N on equal-division graph paper led to the equation $Kga = 1.00 \times 10^{-4} L^{0.834} G^{0.308} (0.800 - 0.110 N)$. This graph appears as Figure 6 of the Appendix.

As a final check, a log-log plot was drawn of $Kga/L^{0.834}(0.800-0.110 N)$ against G (Figure 7 of the Appendix), which showed the exponent of G indistinguishable from 0.308.

The exponent of L, 0.334, indicates that the liquid film offers the major resistance to mass transfer in this process. This would imply that the absorption system under consideration is mainly influenced by the physical diffusion of the carbon dioxide through the liquid film. Had the reaction between carbon dioxide and sodium carbonate been the controlling factor, the exponent of L could still have been large but Kga would have shown a rise with increase in carbonate concentration. A reasonable belief is that the primary function of the sodium carbonate is to prevent the absorbed carbon dioxide from exerting any great back pressure, which would slow the absorption.

Previous investigators, using varied types of equipment, have given exponents for L ranging from 0.44 to 1.00. This difference is probably due to both the means used for liquid-gas contacting and to the interrelation of the other factors of the correlating equations.

In absorption using pure carbon dioxide as the gas phase, a superficial deduction would be that the gas rate would have no effect on the value of Kga since there exists no concentration gradient across the gas bubble, and consequently no gas film resistance exists. However, in the type of gas-bubble column operated in this work, the gas rate does affect the absorption rate in at least two ways. First, higher gas rates necessarily require an inter- increase in the size or number of bubbles or both. Thus the facial area available for mass transfer, a, will be some function of the gas rate. Second, the prescence of either larger bubbles or a greater number of bubbles affects the path of the downcoming liquid, making that path longer and more varied directionally, somewhat increasing the turbulence of the liquid phase.

These phenomena are thus included in the correlation equation which shows Kga being proportional to the 0.308 power of G, the gas rate.

A correlation of Kga with f, the ratio of sodium ions present as sodium bicarbonate to the total sodium ions present, could not be made from the runs detailed in this report. Harte and Baker[1] have published data which would indicate that Kga varies greatly with f, their work being carried out in a wetted-wall column.

When the experimental values of $Kga/L^{0.834}G^{0.308}$ were plotted against N, the sodium carbonate normality of the entering liquid, a good correlation was obtained, seemingly independent of the value of f except as it is used to calculate the sodium carbonate normality.

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[1] Harte, C.R. and E.M. Baker; op. cit.

The proportionality of Kga to the factor (0.800 - 0.110 N) can be hypothesized as due mainly to changes in the physical proporities of the absorbing liquid, an increase in viscosity with increase in concentration being one possible explanation. As mentioned previously, the negative coefficient of N lends credence to the belief that the absorption process, as carried out in this work, is primarily one controlled by diffusion of the carbon dioxide through the liquid film, rather than one of chemical reaction.

In this connection it is important to note that the correlation equation would indicate Kga to be a maximum at a solution normality of zero, or pure water. Some offhand calculations, however, showed Kga from the carbon dioxide-water runs to be about one-half those found for sodium carbonate solutions. Thus the prescence of sodium carbonate does exert some influence on Kga, but the exact mechanism at these low normalities (0 to 0.1N) is not clear.

Correlation with the Literature

It was not found possible to make a rigorous comparison of values of Kga obtained in this work with those given in the literature for three reasons.

First, the vast majority of data published was obtained from absorption of relatively lean carbon dioxide-air mixtures and from a practical viewpoint, extrapolation of these empirical correlations to the absorption of pure carbon dioxide could be a misleading procedure.

Second, the correlations in the literature run a gamut of physical and chemical variables to describe the behavior of Kga. Examples of these factors include pH, the logarithm of the viscosity, and various powers of a, the interfacial area.

Finally, the gas and liquid rates and ratios used in this work are quite far removed from those in the literature due to the nature of the absorbing equipment used. The wetted-wall column, using a thin film of liquid and a large volume of gas is diametrically opposed to the gas-bubble column wherin a large liquid volume contacts a relatively small amount of gas. The packed tower falls between these two types of equipment in relation to gas and liquid rates.

The liquid rates used in this work are two to ten times greater than those in the literature, while the gas rates are one-tenth to one-half those published for other types of absorption apparatus.

Some calculations were made to give a qualitative comparison with the correlation of Furnas and Bellinger.[4] These authors had used their own work plus the results of previous investigators to derive an equation showing Kga independent of the gas rate and approximately proportional to the one-half power of L, the liquid mass rate. For a liquid rate of 10,000 pounds per hour per square foot

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[4] Furnas, C.C. and Bellinger: Trans. A.I.Ch.E., 34, 251 (1938).

in a packed tower containing one-inch Berl saddles, a K_ga of about 0.13 is found. For the same liquid rate in the gas-bubble column K_ga is of the order of 0.60 to o.75, depending on the other conditions of the run. This variance is in the expected direction since the gas-bubble column is, from a theoretical point of view, best suited of all three types of contacting equipment for use in processes in which practically all resistance to absorption is in the liquid film.

Pressure Drop

Though no detailed analysis was made of the factors affecting the pressure drop through the column, some comments may be made based on observations over the course of the experimental runs.

The pressure drop across the dry porous plate was approximately four inches of water at the gas rates used in these experiments.

The pressure drop across the (wet) porous plate during actual column operation was about ten inches of water. The variation in pressure drop across the plate with gas rate was considered quite small.

A slow tendency was found for pressure drop across the plate to increase from run to run. This can probably be attributed to fouling of the pores of the plate by a combination of iron rust from the liquid reservoir and caking out of sodium salts during the intervals between runs.

The pressure drop through the liquid portion of the column was dependent on both the liquid and gas rates (and to a smaller degree on solution concentration), usually being of the order of 75 to 90% of the column liquid height.

Agreement of Data

It was found during calculation and graphing that two runs, 21 and 24, consistently gave points above the correlating line, while three runs, 28, 29, and 34, as regularly fell below the line.

No simple single explanation was deducible for this behavior. A longer series of runs would probably tend to smooth out such discrepancies as column and operation fell into a more uniform pattern.

APPENDIX

TABLE I

EXPERIMENTAL DATA

Run	L	G	Z	ZH_L	p	T_2	Length of run
14	9690	32.9	12.6	11.8	6.6	11.9	70
19	9920	56.1	13.4	11.0	6.5	20.2	30
20	14000	51.0	12.6	10.9	6.5	20.4	30
21	9700	36.4	13.6	11.0	6.6	23.5	50
22	14300	53.5	12.2	10.6	6.5	24.2	40
23	9700	33.8	13.8	12.7	6.9	23.8	55
24	9740	54.6	13.4	11.3	6.6	24.5	55
25	13660	54.6	13.6	11.7	6.8	24.4	55
26	9700	34.8	13.1	12.2	6.8	25.0	30
27	9540	52.5	13.2	11.1	6.8	25.7	45
28	13660	51.9	13.9	11.2	8.3	18.3	45
29	10100	34.4	13.8	12.6	7.6	19.3	50
30	9950	51.1	13.8	11.9	8.6	23.8	65
31	11880	51.4	13.6	11.1	10.6	24.2	70
32	10060	35.9	13.0	11.6	8.4	21.1	60
33	11340	52.7	13.4	10.7	11.3	21.8	50
34	9660	56.5	13.4	10.7	14.0	23.6	55

Units; L and G = pounds/ hour-foot^2
Z and ZH_L = inches
p = inches of tetrabromoethane
T_2 = °Centigrade
Length of run in minutes

TABLE II

CARBON DIOXIDE-WATER CHECK RUNS

Run	G	L	HTU_{OL} from Shulman[5]	HTU_{OL} from Experimental Run
10	34.4	4000	1.10	1.37
11	61.2	8190	0.70	0.92
12	39.8	12740	1.52	1.62
13	70.4	5950	0.59	0.75

Note: Values of HTU_{OL} from Shulman are corrected to column height and temperature of experimental run.

Units: G and L = pounds / hour-foot^2
HTU_{OL} = feet

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[5] Shulman, H.L. and M.C. Molstad: op. cit.

TABLE III

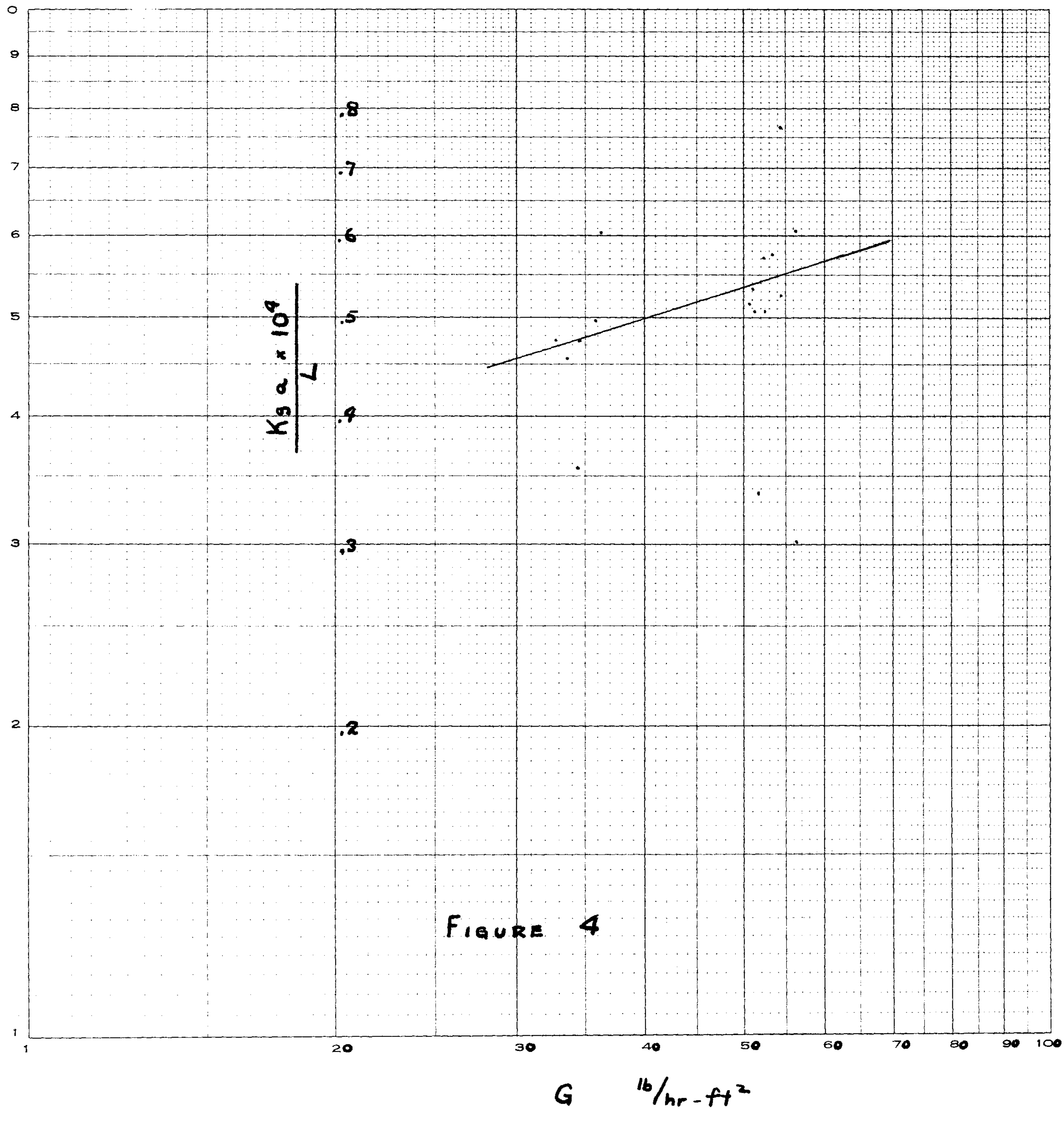
COMPOSITION OF ABSORBING SOLUTIONS

Run	N_{TOTAL}	$N_{Na_2CO_3}$	$\Delta N_{HCO_3^-}$	f_{in}	f_{out}	$f_{avg.}$
14	0.1427	0.1370	0.0998	0.0401	0.7230	0.3815
19	0.1915	0.1698	0.1381	0.1136	0.8405	0.4770
20	0.1915	0.1698	0.1103	0.1136	0.6901	0.4018
21	0.3166	0.2985	0.1402	0.0572	0.5000	0.2786
22	0.3166	0.2053	0.1201	0.3200	0.6998	0.5099
23	0.5323	0.5230	0.1103	0.0017	0.2135	0.1076
24	0.5323	0.5230	0.1302	0.0017	0.3570	0.1793
25	0.5323	0.4203	0.1249	0.2106	0.4452	0.3279
26	0.7338	0.5757	0.1120	0.2154	0.3680	0.2917
27	0.7338	0.4969	0.1314	0.3229	0.5020	0.4125
28	0.6522	0.3168	0.0764	0.5143	0.6315	0.5729
29	0.6522	0.2676	0.0852	0.5897	0.7204	0.6550
30	0.9422	0.8280	0.1325	0.1212	0.2647	0.1930
31	0.9422	0.7362	0.1148	0.2187	0.3405	0.2796
32	0.9495	0.6524	0.1163	0.3103	0.4332	0.3718
33	0.9495	0.5825	0.1236	0.3842	0.5156	0.4499
34	1.2418	1.0734	0.0740	0.1356	0.1952	0.1654

TABLE IV

VALUES FOR GRAPHICAL CORRELATION

Run	$K_g a$	$\frac{K_g a \times 10^4}{L}$	$\frac{K_g a}{G^{0.308}}$	$\frac{K_g a \times 10^4}{L^{0.834} G^{0.308}}$	$\frac{K_g a \times 10^4}{L^{0.834} (0.800 - 0.110 N)}$
14	0.455	0.475	0.155	0.734	1.37
19	0.604	0.609	0.174	0.810	1.76
20	0.724	0.517	0.216	0.755	1.62
21	0.591	0.605	0.196	0.927	1.33
22	0.824	0.576	0.242	0.833	1.32
23	0.445	0.459	0.151	0.715	1.47
24	0.750	0.770	0.218	1.027	2.37
25	0.719	0.526	0.209	0.742	1.74
26	0.467	0.477	0.156	0.740	1.50
27	0.536	0.562	0.158	0.757	1.72
28	0.462	0.338	0.135	0.481	1.08
29	0.359	0.356	0.121	0.552	1.06
30	0.533	0.535	0.158	0.734	1.74
31	0.601	0.507	0.179	0.713	1.62
32	0.501	0.498	0.166	0.764	1.58
33	0.578	0.509	0.170	0.705	1.63
34	0.290	0.301	0.083	0.397	1.01



.8
.7
.6
.5
.4
.3
.2
$\frac{K_g a \times 10^4}{L}$
20
30
40
50
60
70
80
90
100
G lb/hr-ft²

FIGURE 4

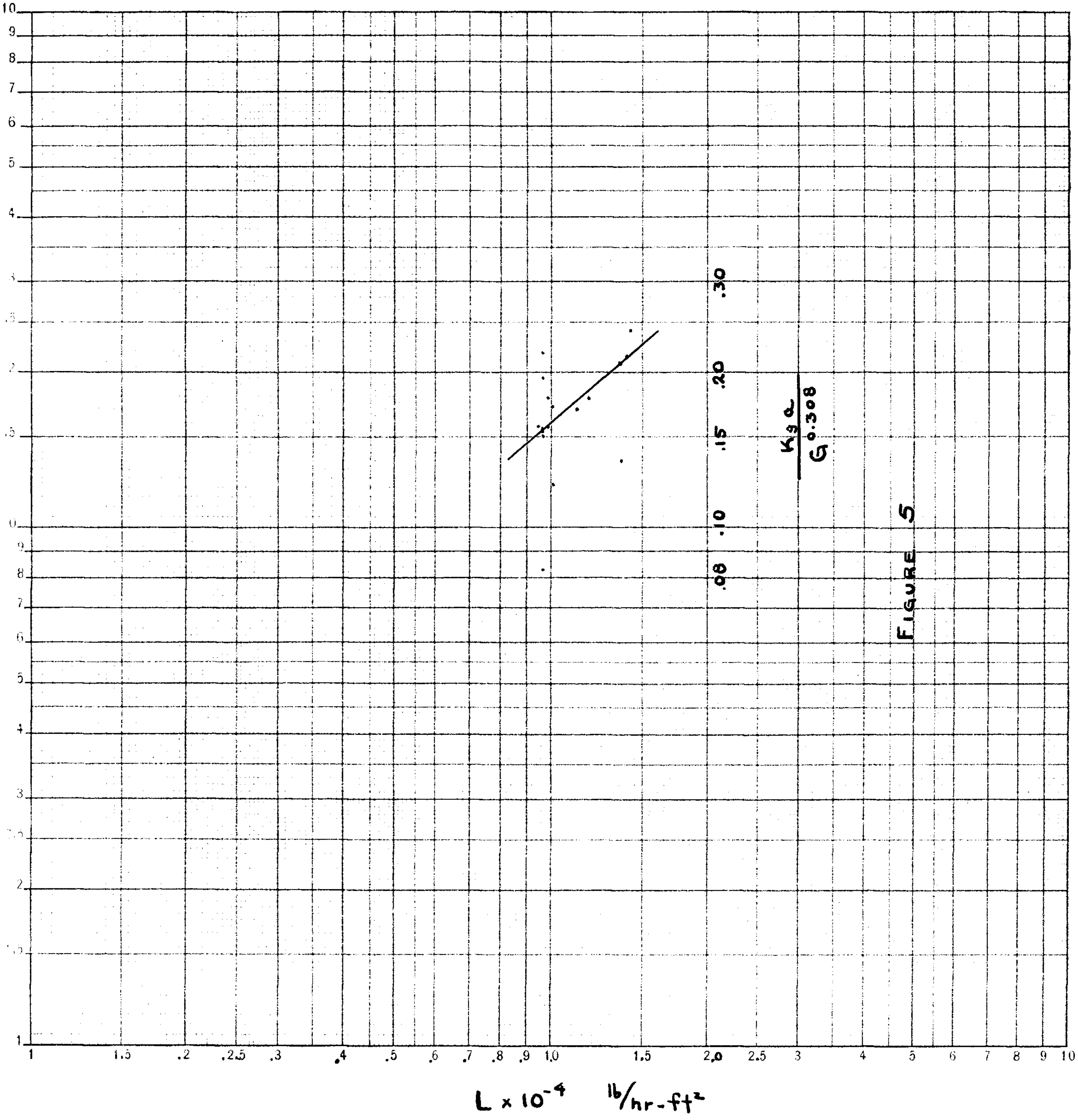

$\frac{K_g a}{G^{0.308}}$
.08
.10
.15
.20
.30
1
1.5
2
2.5
3
4
5
6
7
8
9
10
1
1.5
.2
.2.5
.3
.4
.5
.6
.7
.8
.9
1.0
1.5
2.0
2.5
3
4
5
6
7
8
9
10
L × 10^{-4} lb/hr-ft^2

FIGURE 5

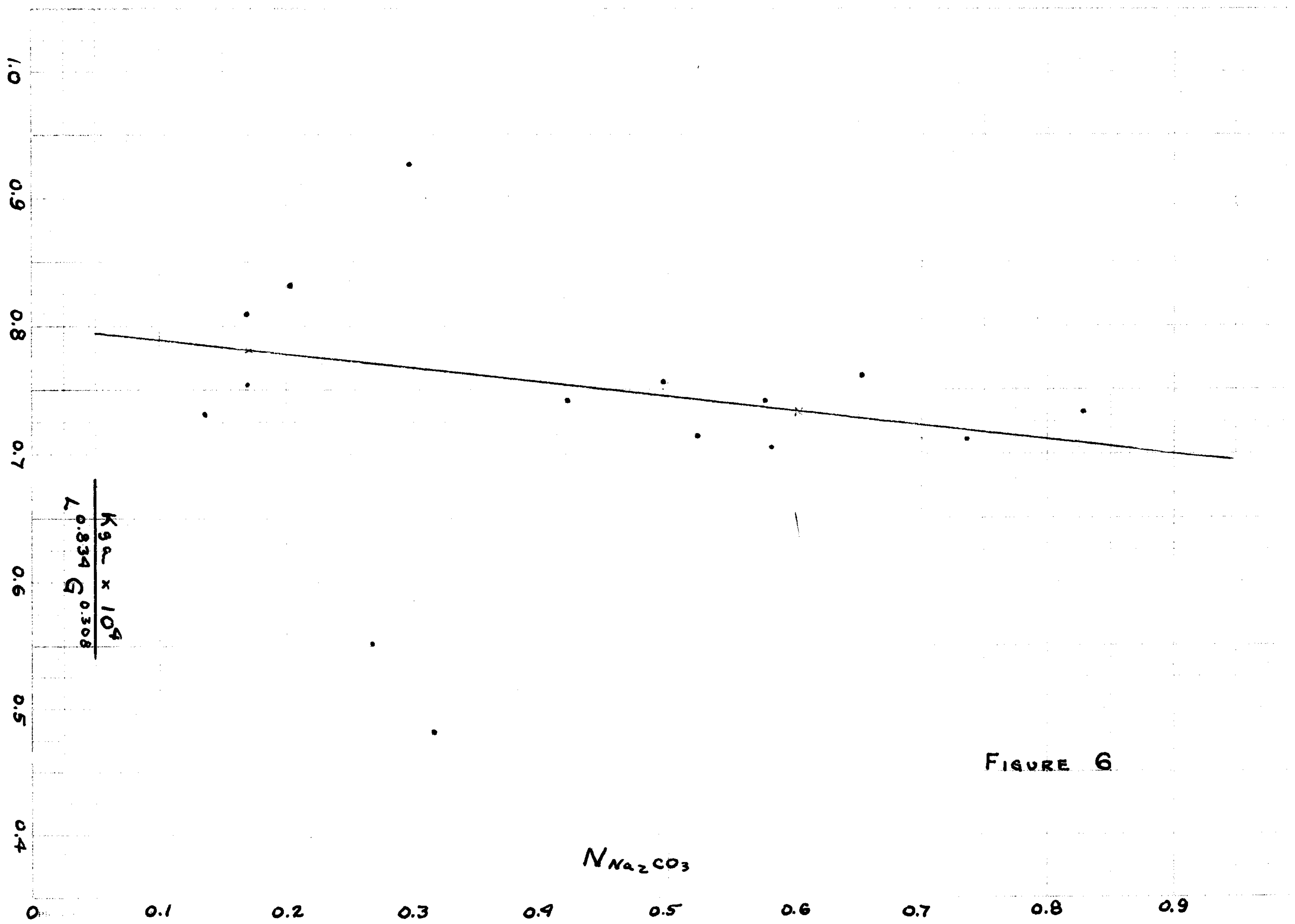
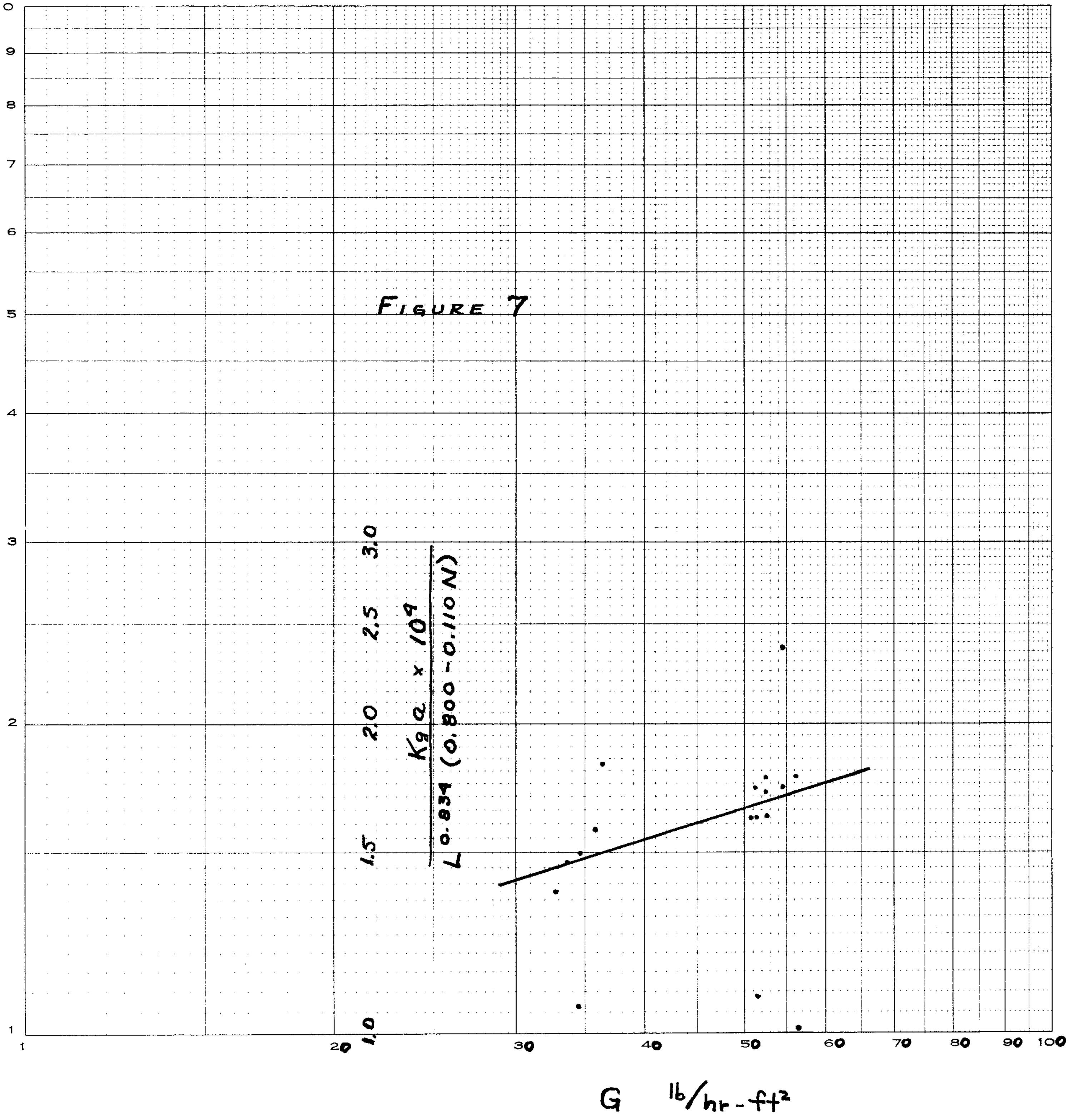

1.0
0.9
0.8
0.7
0.6
0.5
0.4
$\frac{K_g a \times 10^4}{L^{0.834} G^{0.308}}$
$N_{Na_2CO_3}$
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

FIGURE 6

FIGURE 7



$\frac{K_g a \times 10^9}{L^{0.834}(0.800 - 0.110N)}$
1.0
1.5
2.0
2.5
3.0
1
2
3
4
5
6
7
8
9
0
1
20
30
40
50
60
70
80
90
100
G lb/hr-ft²

TABLE V

COMPARISON OF Kga VALUES

Run	Kga from Correlation Equation	Kga from Run Titrations	% Deviation
14	0.492	0.455	- 7.5
19	0.589	0.604	+ 3.9
20	0.760	0.724	- 4.8
21	0.495	0.591	+19.4
22	0.777	0.824	+ 6.0
23	0.469	0.445	- 5.0
24	0.550	0.750	+36.4
25	0.763	0.719	- 5.9
26	0.470	0.467	- 0.5
27	0.534	0.536	+ 0.3
28	0.745	0.462	-38.0
29	0.508	0.359	-29.3
30	0.520	0.533	+ 2.4
31	0.614	0.601	- 2.1
32	0.483	0.501	+ 3.7
33	0.610	0.578	- 5.3
34	0.503	0.290	-42.5

TABLE OF NOMENCLATURE

G	Gas mass rate in lb./ hr.- sq. ft.
HTU_{OL}	Height of an overall transfer unit (liquid) in feet
Kg	Absorption coefficient in lb.-mols/ hr.- sq. ft.- atmos.
L	Liquid mass rate in lb./ hr.- sq. ft.
N_{TOTAL}	Total sodium normality
N	Sodium carbonate normality
$\Delta N_{HCO_3^-}$	Change in sodium bicarbonate normality
P_{CO_2}	Average pressure of gas in millimeters of mercury
ΔP	Carbon dioxide driving force in atmospheres
T	Temperature in degrees Centigrade
Z	Column height in feet
ZH_L	Liquid head in column in feet
a	Interfacial area for mass transfer in sq. ft. per cu. ft.
f	Fraction of sodium ions present as sodium bicarbonate
k	A constant
Δp	Carbon dioxide gage pressure at rotameter (inches of CBr_4)
x	Carbon dioxide concentration in lbs. CO_2 / lb. water
x*	Equilibrium concentration in lbs. CO_2 / lb. water
ρ_s	Density of the solution in grams/ cu. cm.
$\mathcal{F}$	A function

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