THE FERRIC SULPHATE-SULPHURIC ACID PROCESS

COMPiled BY
OLIVER C. RALSTON

WITH A CHAPTER ON

PRODUCING SMALL BUBBLES OF GAS IN LIQUIDS BY SUBMERGED ORIFICES

BY
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THE FERRIC SULPHATE-SULPHURIC ACID PROCESS

By Oliver C. Ralston

INTRODUCTION

In the course of its efforts to increase efficiency in the mineral industries, the Bureau of Mines has investigated hydrometallurgical methods of treating partly oxidized copper ores, such as are found in the intermountain region and in the Southwest.

The process described in this paper is one for preparing solutions of ferric sulphate or sulphuric acid by passing a mixture of air and sulphur dioxide, preferably in the form of very small bubbles, through solutions containing varying amounts of iron as sulphate. If dilute solutions of sulphuric acid are desired for such purposes as the leaching of ores, the amount of iron in the solution need be only 0.25 to 0.5 per cent. On the other hand, if solutions of ferric sulphate are desired, solutions of ferrous sulphate of any concentration up to saturation can be converted into the ferric form without the formation of more than small amounts of sulphuric acid; but as soon as all the iron is oxidized the sulphur dioxide in the gases used is converted to sulphuric acid, which continues to build up. A brief description of the process has already been published.¹

The work reported here comprises merely a study of the chemistry of the process and the mechanical conditions that would have to be observed in practice. The chapter by C. G. Maier, “Producing small bubbles of gas in liquids by submerged orifices,” gives data obtained in a study of methods of making bubbles in liquids. That study was undertaken in order to make possible the design of the mechanical parts of a practicable commercial plant using the process.

A report on the design and operation of a semicommercial type of apparatus will appear later.

ACKNOWLEDGMENTS

This report is the result of work by a series of investigators at the Pacific experiment station and the Southwest experiment station of the Bureau of Mines. Their separate reports on various phases of the process constitute such a volume of material that much condensation has been necessary, and this paper presents only illustrative sets of figures and in many places only the conclusions drawn from

¹ Leaver, E. S., and Thurston, R. V., Ferric Sulphate and Sulphuric Acid from Sulphur Dioxide and Air: Reports of Investigations, Serial 2556, Bureau of Mines, December, 1923.
the results. These men, who should be regarded as coauthors, are named here in the chronological order in which they contributed to the advancement of the work: L. R. Eckman, E. S. Leaver, L. E. Roberts, W. D. Bonner, C. G. Maier, R. V. Thurston, L. L. McDaniel (of the Phelps Dodge Corporation, which investigated the process during its development), and F. S. Wartman. Because of this coauthorship, the terms "we" and "our" are used in discussions of experiments and results.

**IMPORTANCE OF THE PROBLEM**

 Doubtless all recent investigators of the hydrometallurgy of copper, silver, gold, lead, or zinc have been struck by the fact that solutions of ferric salts frequently can be used not only for dissolving the oxidized ores of these metals but also for attacking some or all of the sulphides. High extractions of desirable metals have often been obtained in the laboratory by the use of solutions of ferric salts and have lured men to attempt commercial development. In every instance, however, the problem of how to reoxidize the ferrous solutions resulting from ferric leaching and precipitation has proved too difficult. Long ago it was recognized as highly desirable that air should be used as an oxidizing agent for this purpose, in order to avoid the expense incident to the use of more powerful oxidizers, like chlorine gas, or of anodic oxidation in an electrolytic cell. Until the Bureau of Mines undertook the problem all use of other oxidizers had resulted in commercial failure; the use of air as an oxidizer was likewise a technical failure because of the slow rate of oxidation. The solution of the problem, as presented in this bulletin, promises to enable ferric leaching solutions to be prepared much more cheaply than by any other process; moreover the equipment required is simple and inexpensive, and the ability to prepare sulphuric acid, in addition to solutions of ferric sulphate, will widen the field in which the ferric solutions can be used.

**DISCOVERY OF THE PROCESS**

 As mentioned in the preliminary report, the discovery of the process came during the application of the sulphur dioxide leaching process for the treatment of mixed oxidized sulphide ores. An unexpectedly large amount of sulphuric acid was found in one of the leaching solutions that had been treated with sulphur dioxide and air mixtures. Search for the cause revealed that the presence of iron in solution was necessary for rapid oxidation of the sulphur dioxide. Further investigation of this discovery showed that the iron was itself oxidized during the process.

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THE PROCESS

In general, it may be said that when a mixture of sulphur dioxide and air, containing not too much sulphur dioxide, is passed through a solution of ferrous sulphate the ferrous iron and the sulphur dioxide are simultaneously oxidized in approximately equivalent proportions and ferric sulphate is formed as represented by the following equation, which expresses only the beginning and end products:

\[ 2 \text{FeSO}_4 + \text{SO}_2 + \text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 \]  

(1)

If the gas mixture is supplied in sufficiently small bubbles and not too rapidly, the above reaction takes place exclusively; otherwise there is a simultaneous formation of sulphuric acid. As soon as oxidation of the iron reaches a limit (a "steady state" to be described later), the sulphur dioxide entering the apparatus is oxidized to sulphuric acid, as represented by equation (2):

\[ \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{SO}_4 \]  

(2)

Sulphuric acid is also formed by a side reaction, No. (3):

\[ \text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \]  

(3)

This third reaction is not of great importance under conditions that favor (1) and (2), but a certain amount of the ferric sulphate always is likely to be reduced back to the ferrous state. Reaction (1) can be made to take place to the exclusion of (2) and (3) until 98 or 99 per cent of the iron has been oxidized, if proper conditions, described later, are maintained.

This report discusses the conditions under which reactions (1) and (2) can be made to take place and gives illustrative data from a study of each variable investigated.

The reader should note that the use of air alone for oxidation of ferrous salts is too slow to be of commercial importance and that the use of sulphur dioxide alone reduces iron according to equation (3). The success of the process depends upon proper mixtures of air and sulphur dioxide and proper application of the mixture to the solution. If water alone is used, the sulphur dioxide is oxidized very slowly. The presence of iron is absolutely necessary for rapid action. In fact, the ferrous iron and the sulphur dioxide mutually induce each other to be oxidized. As will be seen later in the report, we have found in the literature other similar examples of "induced" oxidations.

PREVIOUS WORK

WORK OF AUSTIN

Use of air to oxidize slightly acid ferrous sulphate solutions was tried by the Cananea Consolidated Copper Co., at Cananea, Sonora, Mexico, and was described by W. L. Austin, who based his paper on

\footnote{Austin, W. L., Leaching applied to copper ore: Mines and Methods (Salt Lake City), vol. 2, September, 1910, p. 5.}
original notes supplied by David Cole, assistant general manager. Compressed air heated to 200 to 400° F. served to oxidize and agitate the solution. Basic ferric sulphate slowly formed and was neutralized by the addition of sulphuric acid, but the oxidizer was never rapid enough, and most of the air went through without reacting, in spite of all attempts to modify the oxidizer for more efficient oxidation. In one test 1,200 times the theoretical supply of air was used, as based on the yield of ferric iron.

In some of our work, by feeding the sulphur dioxide to the reaction vessel as a solution as much as 60 per cent of the oxygen in the air supplied and all of the sulphur dioxide could be utilized, although the apparatus used was not of much better form than the one used at Cananea. The difference in results is to be attributed to the additional use of the sulphur dioxide.

WORK OF BANERJEE, MAQUENNE AND DEMOUSSEY, AND ENNOS

Air oxidation of ferrous solutions has long been known, and studies too numerous to review have been made of it. In virtually all cases the oxidation is very slow, but yet fast enough to be a nuisance to chemists who desire to store solutions of ferrous salts. A few catalysts, such as platinum, have been discovered and studied, but they proved of no practical value.

Banerjee⁴ found that the rate of oxidation of ferrous sulphate does not follow exactly the unimolecular reaction formula, but the oxidation approximates it. The average oxidation per hour of 0.1N FeSO₄ solution at approximately 32° C. is 0.063 per cent, calculated from an experiment that lasted 1,488 hours. Sodium sulphate, magnesium sulphate, zinc sulphate, manganous sulphate, and ammonium sulphate retarded the oxidation slightly, and sulphuric acid and copper sulphate retarded it greatly. Potassium sulphate was a slight accelerator.

Maquenne and Demoussy,⁵ who investigated the catalytic action of copper salts on the oxidation of ferrous compounds by air, found that oxidation took place more rapidly in the presence of copper salts. Iron salts of weak acids oxidized more readily than those of strong acids, showing the inhibiting effect of the hydrogen ion, an effect that we found very important in the work to be described.

Ennos⁶ found that in passing air or oxygen at the rate of 1 liter per three hours through a 0.1N solution of ferrous salt, in the absence of free acid, oxidation proceeded at the rate of 0.03 per cent per hour; the rate was doubled with a rise in temperature of 10° C. At 60°

the oxidation of the chloride was about one-tenth and of the acetate ten times that of the sulphate. The reaction seemed to be of the second order with respect to the ferrous salt, and to be proportional to the partial pressure of the oxygen. The oxidation was attributed to the nonionized portion of the ferrous salt, as indicated by the influence of temperature, dilution, and the nature of the acid radical.

**HYPOTHESES OF OXIDATION**

The literature on the general theory of oxidation by atmospheric oxygen is extensive, and a bewildering array of hypotheses has been proposed in explanation of the mechanism of the reactions. Such men as Van’t Hoff, Traube, Clausius, Brodie, Bodlander, Engler, Manchot, Bach, and Just have studied these reactions. Schönbein is credited with the first statement of a hypothesis that when a substance is oxidized by air a part of the oxygen is transformed into ozone, hydrogen peroxide, or is taken up in the oxidation of some other substance, a principle that seems to apply to the oxidation of solutions containing ferrous sulphate and sulphur dioxide. This “autoxidation” has been reviewed by Manchot, who believes that one of the substances unites directly with an oxygen molecule to form a peroxide, and that this peroxide then gives up one of its oxygen atoms to a second substance called an acceptor.

Another instance of such simultaneous oxidation is that of sulphur dioxide and arsenious oxide, where the arsenious oxide was regarded as the inducer and sulphur dioxide as the acceptor. These numerous instances of rapid induced oxidations have justified us in not spending too much time in studying the mechanism of the reaction of simultaneous oxidation of ferrous sulphate and sulphur dioxide; after doing enough work to convince us that the mechanism of the reaction is complicated, in order to collect data of industrial value we have studied the variables that are important with respect to practice.

The work that came nearest to anticipating that described in this bulletin was done by an Australian metallurgist, J. B. Du Faur, who obtained a patent in Australia for oxidizing ferrous sulphate solutions by air and sulphur dioxide, but he repeatedly mentions the need of the presence of a carbonate, like calcium carbonate, to use

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up excess acid and thereby permit rapid oxidation. Our work has shown that although acidity depresses the rate of oxidation, we are able not only to prepare ferric sulphate solutions but also to prepare rather strong acid solutions. Du Faur's work deserves recognition, although it was unknown to us when we began work late in 1919.

Our own work has been covered by a United States patent granted to E. S. Leaver.

**APPARATUS USED DURING RESEARCH**

As the work developed the form of the apparatus proved important, for a large surface of contact of gas with liquid and a long period of treatment were absolutely necessary. Several forms of rotating drums, spray and scrubbing towers, column aerators, subaeration flotation machines, and static apparatus were tried, but only the more successful are described here. In general, it was found that the gas must pass through the liquid in the form of small bubbles.

![Diagram of apparatus](image)

**Figure 1.**—Drum for leaching with SO₂

**EARLY APPARATUS**

Figure 1 shows the form of apparatus in which the reaction was first discovered. This is the so-called SO₂ drum used in the SO₂ leaching process. A stream of the ore pulp to be leached enters at one trunnion and leaves at the other, while a stream of hot roaster gases carrying sulphur dioxide and excess air passes countercurrent to the stream of pulp. When more than a certain minute amount of iron is present in solution in the water of the pulp, dissolution of the copper minerals, especially the sulphide minerals, is much more rapid, and the amounts of sulphuric acid and ferric sulphate in the solutions issuing from the drum are larger. By leaving out the ore pulp and passing only water or ferrous sulphate solutions through the drum, the reactions were discovered and studied. However, as compared to the later forms of apparatus, the drum does not break up the solution into small enough droplets, and therefore its action is too slow for most purposes. Although the drum does not offer conditions for the manufacture of maximum amounts of sulphuric acid or ferric sulphate, its simplicity of operation makes it a practical apparatus for handling certain low-grade copper ores and tailings.

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Figure 2 shows the second form of apparatus used. A glass graduate of 1-liter capacity contained the solution of ferrous sulphate; into its bottom a mixture of air and sulphur dioxide under pressure was led through a piece of 3-mm. glass tubing with no constriction at the bottom. The gas passed through the solution in relatively large bubbles.

**LATER APPARATUS**

Figure 3 shows a later form of apparatus. It had about the same dimensions as the one shown in Figure 2, but the top was arranged so that samples of the exit gas could be caught and analyzed. Air was supplied by a compressor and sulphur dioxide from a tank of the liquefied gas; the flow was regulated and measured by flow meters of glass which consisted of a restricted glass-tube orifice and a U tube to measure the drop in pressure during passage through the orifice. The apparatus conveniently held about 500 c.c. of the solution. The gas bubbles were of the same size as those in the apparatus shown by Figure 2, for no effort was made to produce small bubbles. Later it was discovered that absorption of sulphur dioxide and oxygen in this apparatus was inefficient, but the apparatus was convenient for comparing the rates of reactions.

Figure 4 shows a more convenient form of glass apparatus, designed by Thurston and called by us the "column aerator." It consisted of a piece of glass tube about 5 cm. in diameter and nearly 2 meters high stoppered at the bottom with a four-hole rubber stopper through which passed small glass tubes to supply air. Over the end of each glass tube was placed a small section of rubber tubing, closed at the end but punctured with numerous needle holes on the sides in order to produce fine bubbles. With this apparatus bubbles 0.75 to 1.00 mm. in diameter were produced, which rose slowly through the solution and gradually coalesced to form large bubbles that rose more rapidly. An inner smaller tube, about 15 mm. in diameter, filled with solution, was placed in such a position that no gas bubbles could rise in it. The solution flowed down this tube and up the outer tube. In some
of the experiments the sulphur dioxide was mixed with the air and in others it was introduced separately. This apparatus proved thoroughly satisfactory.

Later, a tall circular wooden tank holding 75 gallons was made after the design of Figure 4, except that the air was introduced through a perforated inner tube of an automobile tire in the bottom of the tank. The bubbles were somewhat larger, but otherwise the tank functioned satisfactorily. A commercial plant for using the ferric sulphate and sulphuric acid process could doubtless be constructed in units equivalent to this.

For investigating the reactions under pressures higher than those due to the atmosphere plus the depth of the column of solution, the apparatus shown in Figure 5 was made of heavy-walled pyrex tubing;
it was about 15 mm. in diameter and 2 meters high. To provide connection, heavy-walled, wire-wrapped rubber tubing was slipped over the ends, which had been drawn down; a pinchcock in the exit line regulated the pressure in the tube. The pressure gauge was in the inlet line; it recorded the pressure within the reaction tube plus the total pressure necessary to blow the gas mixture through the inlet.

Mixtures of SO₂ and air were made up in an ordinary oxygen cylinder, used as a mixer, by running in first, from a separate cylinder, the SO₂ gas under the pressure natural to its liquid, and then running in, from the ordinary commercial cylinders, oxygen and nitrogen in the proportions to form air, until the desired pressure was obtained. This cylinder was used as the reservoir from which to blow gas through the reaction tube. A rubber tube full of needle holes, as in Figure 4, was slipped over the glass inlet tube at the bottom. A convenient glass tube at the side allowed samples of solution to be removed as desired; it was closed with a stopcock. In this apparatus pressures up to about 100 pounds per square inch were maintained easily.

A number of experiments were also made in a closed system under static pressure in an apparatus constructed of pyrex tubing, as pictured in Figures 5 and 6. The glass tube was about half filled with a solution of ferrous sulphate in which the desired amount of sulphur dioxide was dissolved; then air under the desired pressure was run into the gas space and the rubber-tube inlet closed by the pinchcock (screw clamp). When the tube was inverted solution ran into the constricted outlet over which the rubber tube was slipped, and when the tube was turned back to its original position capillary attraction held a certain amount of solution in the constricted part. This solution effectively sealed the tube against gas leaks at both ends. By tilting the tube every eight hours the pressure could be maintained in the apparatus without difficulty. Usually the apparatus was left in a horizontal position, so that the solution would lie in the tube in a layer not over 8 mm. deep (generally less) and the gas would have easy access to it. These static experiments were of value in helping to interpret the mechanism by which the reaction took place.

Another type of apparatus tested, suggested by W. E. Greenawalt, consists of a small glass subaeration flotation apparatus with a hollow shaft and impeller. Rotation of the impeller draws the gas mixture through the shaft and expels it into the solution through the hollow impeller, which beats it into fine bubbles. Although we found the apparatus effective, it was not adapted to closely controlled experiments and the collection of exit samples of gas, so it was not thoroughly tested.

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ANALYTICAL METHODS

Most of the work was done with solutions containing only the ferrous and ferric salts, consequently the only chemical determinations necessary were for ferrous iron, ferric iron, sulphates, sulphites, and acidity. For the gas phase the three constituents were oxygen, inerts (nitrogen, argon, etc.), and sulphur dioxide—an easy analytical problem, as sulphur dioxide could be absorbed in iodine solution and the oxygen by any of the ordinary reagents. The problem of analyzing the solutions was not easy. The methods given below were finally adopted as the most practicable compromise, with full recognition of the complexities and the chances for error that existed.

FERROUS IRON

The solution was acidified with sulphuric acid to prevent oxidation of sulphur dioxide by ferric sulphate, boiled in vacuo to expel sulphur dioxide, and titrated with permanganate in the usual manner. If any sulphur dioxide was not removed it reacted with the permanganate titrating solution. Also there was doubtless some reaction between ferric salts and sulphur dioxide or sulphites in solution. To reduce this reaction to a minimum the samples were acidified and titrated immediately after collection.

FERRIC IRON

Direct titration of ferric iron with titanous sulphate solution proved fairly reliable except for solutions high in sulphur dioxide or sulphites; then the sulphur dioxide was reduced partly to hydrogen sulphide by the titanous sulphate solution. Our usual method was to determine total iron and ferrous iron and to call the difference the content of ferric iron.

SULPHUR DIOXIDE

A fresh sample, acidified as in the ferrous iron determination, was immediately titrated with permanganate without boiling off the sulphur dioxide as in the ferrous iron determination. The difference between the permanganate titrations with and without boiling off sulphur dioxide was taken as a measure of the sulphur dioxide (or sulphites) in the solution. A check study of probable oxidation of sulphur dioxide before titration was made by removing the sulphur dioxide from the solution in partial vacuum during aeration with an inert gas, such as CO₂. This method of removing sulphur dioxide checked that of boiling in vacuo, so we felt justified in assuming that there was very little oxidation of the sulphur dioxide between the sampling and the titration.

SULPHATES

A fresh sample acidified with hydrochloric acid and boiled in vacuo, as in the ferrous iron and sulphur dioxide determinations, left a solution in which sulphates could be determined by precipitation with barium chloride.
ACIDITY

A sample was treated by the regular method to expel sulphur dioxide, cooled to 80° C., and a few drops of potassium iodide solution added; the latter reacts with the ferric salts to liberate iodine without any change in acid concentration. The solution was allowed to stand long enough for complete reaction, was decolorized with sodium thiosulphate solution (no change in amount of acid present), and then was titrated with normal sodium carbonate, methyl orange being the indicator. The iron salts cause difficulty in seeing the end point, but the method proved accurate enough for the work at hand.

Bonner developed another method. He titrated a solution containing the ferric sulphate, ferrous sulphate, and sulphuric acid (after expulsion of SO₂) with barium hydrate solution, using air agitation and an air electrode as indicator. The air electrode was a short spiral of bright platinum wire placed in the aerated solution; the salt bridge from a calomel electrode was also placed in the solution for reference. A Poggendorff potentiometric set-up was used and the actual e. m. f. of the air electrode was not determined, but instead the bridge readings were noted frequently during the titration and were plotted; the end point taken was the point where the curve had a maximum slope. A sample series of burette and bridge readings is as follows:

<table>
<thead>
<tr>
<th>Burette reading</th>
<th>Bridge reading</th>
<th>Burette reading</th>
<th>Bridge reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0--------------</td>
<td>-415</td>
<td>17.0</td>
<td>-220</td>
</tr>
<tr>
<td>5.0--------------</td>
<td>415</td>
<td>18.0</td>
<td>+5</td>
</tr>
<tr>
<td>10.0-------------</td>
<td>415</td>
<td>19.0</td>
<td>5</td>
</tr>
<tr>
<td>15.0-------------</td>
<td>380</td>
<td>20.0</td>
<td>5</td>
</tr>
<tr>
<td>16.0-------------</td>
<td>330</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

End point by plotting, 17.5 c. c.

The end point represented the total sulphate titration of the solution, which included ferric sulphate, ferrous sulphate, and sulphuric acid. Subtracting the equivalents of ferrous and ferric iron left a remainder due to sulphuric acid. This method was checked against synthetic solutions. Barium hydrate was necessary in order to get consistent results, and with sodium carbonate or sodium hydroxide as the titrating agent inconsistent and contradictory results were obtained, probably due to basic sulphate precipitates of the iron.

RESULTS OF EXPERIMENTS

NATURE OF THE ACID FORMED

Although the solutions in the early work on this process were known to be acid, as Leaver and Eckman had observed, it was thought best to see if the acidity in the solutions was due to sulphuric acid or, at least in part, to some other acid. Roberts made two careful runs in the
apparatus shown in Figure 3. The first run lasted 10 hours; samples
were taken every hour and analyzed for acidity, ferrous and ferric
iron, and sulphates. The results indicated that the equivalents of
SO$_4$ formed were exactly equal to the sum of the equivalents of hydro-
gen ion and ferric iron, which proved that the sulphur was all or nearly
all oxidized to the form of sulphate and the acid was sulphuric acid.
This run was made under conditions that permitted ferric salts and
acid to form simultaneously.

A second run under similar conditions was made with a solution
containing 0.5 per cent of ferrous iron as sulphate, of which 500 c. c.
were aerated with 10 liters per minute of air containing 0.36 per cent
of SO$_2$. The run was made in a thermostat at 30° C. with precautions
to prevent the solution losing water by evaporation. Samples of the
solution were taken every 10 minutes during the first hour and there-
after every 15 minutes until two and one-half hours in all had elapsed.
Results of the analyses are plotted in Figure 7, where the acidity is
expressed as equivalents of hydrogen ion and the amount of ferrous
iron oxidized to ferric is also expressed in equivalents. The sum of
these two is also plotted and compared with the equivalents of sul-
phur present in the solution as sulphates. The agreement is fairly
satisfactory. At first only ferric sulphate was formed, but after the
first 10-minute interval some acid began to form; this formation of
acid is noticeable in the more efficient types of apparatus.

**INITIAL STEP OF IRON OXIDATION**

The experiment of Roberts, as reported in Figure 7, shows that
apparently at least one-half the formula weight of sulphur dioxide is
oxidized per formula weight of iron oxidized, but sulphuric acid can
also form through the independent oxidation of sulphur dioxide or
the reduction of ferric sulphate by sulphur dioxide. In the more
efficient form of apparatus (fig. 4) it was noticed that when the
solution of ferrous sulphate was neutral at the start a “neutral”
solution of ferric iron was obtained and no excess acidity appeared
until nearly all the ferrous iron was oxidized. Figure 21 shows this,
and the same tendency can be seen in the curves of Figures 15, 16, 17,
18, 19, and 20. In the less efficient forms of reaction apparatus,
where the depth of the column of solution was less and the amount of
gas used per unit of solution was frequently high, more or less acid
tended to form while ferrous sulphate was being oxidized to ferric.

Our work on the effect of the size of bubbles also indicates that
when bigger bubbles of gas are used (inefficient apparatus) there is
less and less oxidation of iron and a greater tendency to form sulphuric
acid in proportion to the amount of iron oxidized. This explains why
very little oxidizing of iron solutions has ever been accomplished in a
tower with less surface of contact between solution and gas. Those
RESULTS OF EXPERIMENTS

persons, however, who attempt to reduce ferric sulphate solutions completely to ferrous in towers fed with roaster gases will also be disappointed, for there is always some oxidation of ferrous to ferric as long as the gases used contain any oxygen. The fact that sulphur dioxide is more soluble than oxygen means that with inefficient absorbers the effective sulphur dioxide in solution will be proportionately greater than the effective oxygen, and the reducing effect of sulphur dioxide will come to a steady state, balanced against the oxidizing effect of oxygen, at a ratio of ferrous to ferric that is too low for practical use.

![Graph](image)

**Figure 7.**—Simultaneous oxidation of sulphur dioxide and ferrous sulphate: Curve marked Fe⁺⁺ gives gram equivalents Fe⁺⁺ oxidised; curve marked H⁺ gives gram equivalents H⁺ calculated from acidity; curve marked S gives gram equivalents S oxidized to sulphate; Fe⁺⁺⁺H⁺ gives gram equivalents Fe⁺⁺ calculated

**EFFECT OF ACIDITY**

Early in the work we noticed that the acidity of the ferrous sulphate solution greatly depressed the rate at which the iron could be oxidized and hindered to some extent the rate of formation of acid. Some results of the work by Eckman in the apparatus pictured in Figure 2 appear in Figure 8. Ferrous sulphate solutions containing 5.2 grams of iron per liter (0.9 gram atom per liter) were aerated with big bubbles of air containing 0.5 per cent of SO₂ at room temperature, at a space velocity of 20 (20 liters of gas passed through 1 liter of solution per minute). Each test consumed three hours. The curves of Figure 8 show the equivalents of iron oxidized and of sulphuric acid that were formed in three-hour periods with differing initial acidities.

In this particular apparatus the velocity of oxidation of both iron and sulphur became negligible at about 2 per cent of sulphuric acid
solutions. In the better forms of apparatus (fig. 4) this effect is not so important, but instead oxidation of iron or sulphur dioxide, or both, is inhibited for a certain short period of time; the length of this period of induction increases with the acidity of the original ferrous sulphate solution. This effect is well shown in Figure 9, which gives the acid and ferrous iron content of solutions aerated with 800 c. c. of air and 80 c. c. of sulphur dioxide per minute in the apparatus of Figure 4 during four different tests (by Thurston and Wartman) in which the only variable was the amount of sulphuric acid initially present in the ferrous sulphate solution before aeration. No induction period is visible in the neutral solution (curve 1), only a slight lag is noticeable in curve 2, where 5 grams of acid per liter were present, but with 6.2 grams of acid per liter at the beginning the period of induction was nearly one-half hour, and with 11 grams of acid in the original solution (curve 4), the period of induction was more than one hour.

As the solutions at first contained only ferrous sulphate and sulphuric acid, evidently some compound or complex must form before rapid oxidation can take place. Either the solution must wait until enough sulphur dioxide can dissolve in the solution to counteract the effect of the sulphuric acid, or the solution is inert until enough ferric iron forms slowly to form some intermediate complex or to act as a catalyst. At least, these two effects—the accumulation of sulphur dioxide after the beginning of the run and the
formation of a small amount of ferric iron—are the only things that can be easily imagined as happening during the period of induction. Investigations of these possibilities are discussed later in this bulletin.

One of the most important observations made during the study of acidity was that to get the reactions started in the presence of acid was hard, but after the period of induction was over more acid could be formed and more ferrous sulphate oxidized in spite of the accumulation of acid. Evidently a certain acidity at the beginning of a run was different from a certain acidity later in the run. Something not yet identified is present, in small amounts at least, in the solutions. Although we never found that something, the following report presents certain data that allow a number of interesting hypotheses to be formed.

In order to see how long the solution would continue to form acid, a 60-hour run was made in the column aerator apparatus shown in Figure 4. Results are shown in Figure 10. This was our most efficient type of apparatus, because the bubbles of gas formed in it were small.

During the run the sulphur dioxide inlet gradually was plugged with an accumulation of salts, and finally the run had to be stopped momentarily to permit removal of the obstruction. The solution contained nearly 11 grams of iron per liter, most of which oxidized in the first hour. Thereafter the main action in the apparatus was the formation of acid, a process which went on rapidly for 12 hours, then began to decrease in rate, and was accelerated again after the removal of the accumulation of incrusted salts from the sulphur dioxide inlet. At the end of the run the solution contained nearly 180 grams of sulphuric acid per liter, and acid for-
mation was still proceeding. The commercially important rate of acid formation was during the first 12 hours, and the concentration of acid at the end of that time was about 110 grams per liter, a good indication of the technical limitations of the process as an acid producer.

SEARCH FOR OTHER CATALYSTS

Soon after we discovered the increased rate of oxidation of ferrous sulphate solutions by air containing sulphur dioxide, we thought that possibly other elements were acting as catalysts; and Roberts and others made a short search for other catalysts, using pure

![Graph showing SO2 efficiency and iron content over time](image)

**Figure 10.—Run 224, March 18, 1924—2½-inch tube, 2-liter solution; air, 700 c.c. per minute.**

- Curve 1, percentage SO2 efficiency;
- Curve 2, acid formed;
- Curve 3, percentage SO2 in solution;
- Curve 4, percentage ferrous iron in solution

solutions of ferrous sulphate. They used an apparatus of the type shown in Figure 3.

With a ferrous sulphate solution alone and with pure air the rate of oxidation of a solution containing 2.127 grams of ferrous iron per liter was only 0.07 per cent per hour, and the efficiency of the utilization of oxygen from the air was only 0.004 per cent. This illustrates how very slow is the oxidation of a neutral solution of ferrous sulphate. An acidified ferrous sulphate solution oxidizes even more slowly.

A similar solution that contained finely ground manganese dioxide was aerated at a space velocity of 20 (20 liters air per minute per
liter of solution) for five hours, when 29.14 per cent of the ferrous iron had oxidized, of which 27.79 per cent was precipitated as basic ferric sulphate. Manganese dioxide thus appears to have an accelerating effect on the oxidation of the neutral solution, but the iron oxidized is lost by hydrolysis.

When this experiment was repeated with an acidified solution, the ferrous iron was oxidized in a short time, but the oxidation was done almost entirely by the manganese dioxide which went into solution and was found there later as manganous sulphate.

Copper sulphate and chromic sulphate in concentration up to 0.001 molar had no effect. Potassium fluoride in the same concentration had no measurable effect, although at higher concentrations it forms a complex ferrifluoride ion which permits ferrous solutions to be oxidized by rather weak oxidizing agents.

Sodium nitrate in 0.01 molar concentration considerably increased the rate of oxidation of ferrous sulphate solutions, but through the sweeping away of the nitrous gases from the solution the action gradually ceased. Part of the oxidation could of course be attributed to the nitrate itself, but this experiment was inspired by a number of statements by other investigators to the effect that nitrous gases, dissolved in solutions whose oxidation was being studied, had seemingly acted as carriers of the oxygen.

None of these catalysts were as good as the reaction we have already described for the simultaneous oxidation of ferrous iron and sulphur dioxide, and finally the search narrowed down to the effects of the various products of the reaction. The effect of acid has already been mentioned; it seems to act as a "negative" catalyst or at least to make the oxidation more difficult. Ferric iron has the opposite effect, so that the reaction could in that sense be regarded as autocatalytic.

EFFICIENCIES OF OXYGEN AND SULPHUR DIOXIDE

In the diagrams dealing with the data collected, which are to be discussed from now on, we have plotted the efficiencies of oxygen and sulphur dioxide; that is, the percentage of the total oxygen or of the total sulphur dioxide which is utilized in the chemical reactions. From the amount of either constituent put in and the analyses of the solutions at intervals it was possible to calculate what percentage of the stream of oxygen or of sulphur dioxide was being utilized; this was checked by occasional analyses of the exit gases.

As in the operation of the process there is always an excess of air over sulphur dioxide the oxygen efficiency can be calculated in another way. Equation (1) shows that 1 molecule of oxygen is required to oxidize 1 molecule of sulphur dioxide and 2 molecules of ferrous sulphate. This ratio of 1 oxygen to 1 sulphur dioxide means that all oxygen in excess of the sulphur dioxide (by volume) has no opportunity to react and
should not be used in calculating the oxygen efficiency. Therefore, during the period in which ferric sulphate is the main product of the reaction, all oxygen in excess of the volume of sulphur dioxide is unnecessary and merely lowers the apparent oxygen efficiency.

In equation (2), which applies to the period during which sulphuric acid is the main product of the reaction, only half as much oxygen is necessary to oxidize 1 molecule of sulphur dioxide; with the same stream of mixed gas this would mean an even lower theoretical efficiency of oxygen. As reaction (2) does not exclusively follow reaction (1), but goes on more or less simultaneously with it, this method of
calculating oxygen efficiency is rendered difficult by the varying proportions in which oxygen takes part in reactions (1) and (2), and the over-all efficiency is much easier to calculate. In virtually every one of our diagrams, therefore, we mean by oxygen efficiency the total amount of oxygen consumed divided by the total amount of oxygen blown into the solution.

**EFFECT OF CONCENTRATION OF FERRIC IRON**

Much difference of opinion existed among the investigators at the two experiment stations as to the effect of ferric iron concentration on the reactions. Correlation of their results, however, showed that the real differences were in the size of gas bubbles passed through the solutions and in the acidity of the solutions used.

Roberts, in the laboratory of the Pacific experiment station at Berkeley, Calif., working with the apparatus shown in Figure 3, which gives very large bubbles of gases, obtained the results shown graphically in Figures 11 and 12. Solutions containing 0.10 gram atom of ferrous iron per liter (5.6 grams per liter) were acidified with 0.05 mole of sulphuric acid per liter (5 grams per liter) to prevent any hydrolysis that might tend to take place. Then the solutions were aerated at a space velocity of 20 bubbles at least 1 cm. in diameter and with gas containing 99.5 per cent of air and 0.5 per cent of sulphur dioxide. The solutions were sampled and analyzed periodically.

Figure 11 compares the amounts of ferric iron and sulphuric acid formed, in different time intervals, as a function of the initial ferric iron concentration. The ferric iron was added to the solutions in differing amounts, and the most noticeable effect of the first small addition of ferric iron is a very large increase in the velocity of oxidation of ferrous iron and in the rate of formation of acid. With increasing concentration of ferric iron the rate of oxidation of the ferrous iron is not greatly affected, although it goes through a slight maximum and then falls off somewhat. We noted the same effect on the rate of formation of sulphuric acid.

Figure 12 gives the results of a similar study with solutions containing at the start twice as much sulphuric acid as was used in the tests of Figure 11; otherwise conditions were the same. Again, the decidedly beneficial effect of ferric iron on the oxidation of the ferrous iron is noticeable, although more ferric iron is necessary to get the same effect. In this second set of tests the rate of formation of sulphuric acid likewise increased with increasing concentration of ferric iron.

Bonner at Berkeley made a test in which all the iron at the beginning of the test was present in the ferric state and the formation of acid alone was studied. The data are plotted in Figure 13, which
shows the percentages of total iron oxidized at any moment (the first effect was a partial reduction of the ferric iron), the amount of acid formed, and the percentages of sulphur dioxide in the ingoing and outgoing gases. The apparatus used was the same as that used by Roberts, the big-bubble apparatus, Figure 3 (p. 7).

The most marked effect was the partial reduction of ferric iron during the first part of the test. Later this iron reoxidized and reached a "steady state" with 99.3 per cent of the iron in the ferric condition. The formation of sulphuric acid went on steadily at an almost constant rate. This initial reduction is to be compared with the period of induction observed earlier. Repetition of the experiment with the more efficient small-bubble apparatus of Figure 4, by Thurston and Wartman, did not show this initial reduction of the iron either in neutral or acid solutions.

Figure 14 shows a series of results that Bonner obtained in studying the rate of formation of sulphuric acid in the presence of varying percentages of ferric iron. A very small amount of ferrous iron, corresponding to the "steady state" already mentioned, was present in each test. The most rapid rate of formation of acid in this apparatus (fig. 3) with 0.5 per cent of $\text{SO}_4$ gas was when 0.362 mole of ferric iron per liter (20.3 grams per liter) was present. With higher percentages of ferric iron the rate of formation of the acid was somewhat slower, but the rate of formation of acid in water containing no iron, as compared with the rate in water containing even very small amounts of iron, was exceedingly low. Curve 2 was made with only 0.01 of the amount of iron used in obtaining curve 4, the most favorable test, and yet the rate of formation of acid was rather large—20 to 35 per cent of the rate in the most favorable test. This result means that sulphuric acid solutions can be made at satisfactory rates of speed from water containing only 0.5 to 1 gram of ferrous iron per liter. This small amount of iron would be acceptable in dilute acid solutions for many industrial purposes other than leaching ore.
FIGURE 13.—Run 47—Initial reduction of ferrie iron followed by reoxidation to a "steady state." Solution contained: 17.68 grams Fe\textsuperscript{+++} per liter; 0.655 gram Fe\textsuperscript{+} per liter; 0.045 mole H\textsubscript{2}SO\textsubscript{4}. Temperature, 30° C. 20 liters gas passed per minute per liter solution. Curve 1, percentage oxidation Fe; curve 2, percentage SO\textsubscript{2} in entering gas; curve 3, percentage SO\textsubscript{2} in exit gas; curve 4, mole H\textsubscript{2}SO\textsubscript{4} per liter

FIGURE 14.—Rate of formation of sulphuric acid. Curve 1, no iron; curve 2, 0.003 mole Fe\textsuperscript{+} per liter and 0.0032 mole Fe\textsuperscript{+++} per liter; curve 3, 0.008 mole Fe\textsuperscript{+} per liter and 1.216 moles Fe\textsuperscript{+++} per liter; curve 4, 0.0025 mole Fe\textsuperscript{+} per liter and 0.392 mole Fe\textsuperscript{+++} per liter
In the Copper Queen laboratory at Douglas, Ariz., McDaniel collected the data shown in Figure 15. He used apparatus of the type shown in Figure 4 and made two tests of the oxidation of neutral ferrous sulphate solutions containing different amounts of ferric iron. When the ferric iron was low at the start, the formation of acid was delayed until most of the iron was oxidized; when most of the iron was present in the ferric condition the generation of sulphuric acid began almost immediately and at about the same rate as the prevailing rate of the first test. However, toward the end of the second test (high ferric iron) the rate of formation of sulphuric acid fell off faster than in the first test. The efficiency of utilization of the sulphur dioxide was parallel to this effect.

Figure 15 also gives data on the temperature of the solution and of the room, which were not included in previous tests. The reaction of formation of the ferric iron and sulphuric acid was rapid enough to maintain the aerated solution at a temperature about 10° C. higher than the temperature of the room. The reader will note also, that the oxidation of the ferric iron never quite reached 100 per cent, but instead a "steady state" prevailed when 97 to 99 per cent of the iron was in the ferric state.
Wartman and Thurston, in the Southwest experiment station at Tucson, using the same type of apparatus as McDaniel, tested the effect of initial ferric iron on the period of induction due to acid. Two solutions, each containing 10 grams of sulphuric acid per liter and 5 grams of ferrous iron, were tested. To one of them 5 grams of ferric iron were added. The solution with no ferric iron underwent a period of induction of more than 60 minutes before anything took place; then, although the rate of formation of the sulphuric acid was high, the rate of oxidation of ferrous iron was low. In the solution containing original ferric iron virtually no period of induction was observed, and the rates of oxidation of ferrous iron and of formation of sulphuric acid were rapid.

The conclusion to be drawn, therefore, is that with the lower concentrations of ferrous iron the presence of ferric iron decidedly favors the operation of the reactions considered here, and also counteracts the ill effects of acidity; with the higher concentrations of neutral solutions of ferrous sulphate the effect of ferric iron on the rate of oxidation of the iron is practically negligible.

EFFECT OF CONCENTRATION OF FERROUS IRON

Early in the work Roberts determined that virtually any concentration of ferrous sulphate solution, from zero to saturation, could be oxidized rapidly to the ferric state by the method described. This observation was checked by every experimenter that followed him.

Using the inefficient apparatus of Figure 3, Bonner found that for every concentration of SO₂ in the aerating gas there was an apparent optimum concentration of ferrous sulphate, but when the better forms of apparatus were used later, his finding was disproved; it may have resulted from inability to get all reactants together in the inefficient apparatus with sufficient rapidity.

With the efficient column aerator shown in Figure 4, Thurston, at Tucson, collected the data presented in Figure 16, which shows the rate of oxidation of five different concentrations of ferrous sulphate solution with gas consisting of 90.9 per cent of air and 9.1 per cent of SO₂, at a space velocity of 0.5, with bubbles about \(\frac{3}{4}\) mm. in diameter, and at a temperature of 30° C. The curves showing the ferrous iron content of the solution at any moment have about the same slope in the solutions containing enough ferrous iron for efficient reaction; this indicates that the rate of oxidation was the same regardless of the concentration of ferrous iron. Evidently the rate and the effectiveness of aeration are more important. The curves showing sulphuric acid concentration at any moment likewise show the same slope after the ferrous iron has been oxidized and the main function of the apparatus has become the formation of sulphuric acid. This constancy of
slope is only approximate; the actual oxygen efficiency varied somewhat, as shown by the oxygen-efficiency curves.

As might be expected, the greatest oxygen efficiency could be obtained in solutions containing the highest concentration of ferrous iron. A similar relation was noticed in the efficiencies of sulphur dioxide. By slowing the rate of aeration, the efficiencies of oxygen and of sulphur dioxide could have been made to approach constant values for all concentrations of solutions, but we were interested, of course, in obtaining the highest possible rates of aeration consistent with reasonable efficiency of sulphur dioxide and of oxygen.
The apparatus, therefore, usually was forced somewhat beyond the limit where maximum efficiency in the utilization of the gases could be obtained.

McDaniel, at Douglas, working with the same type of apparatus, used a gas containing only 7.3 per cent of SO₂ but a space velocity of 1.5, and found that with less than 5 grams of ferrous iron per liter the sulphur dioxide efficiency was too far below 100 per cent to be acceptable. With 1.25 grams of Fe per liter the iron was oxidized rapidly; for a time sulphuric acid formed rapidly, but its formation ceased when about 3.5 per cent of it had formed. With a solution containing 2.5 grams of Fe per liter the formation of acid ceased at about 9 per cent; with higher concentrations of ferric iron the formation of acid proceeded satisfactorily at 12 per cent, although sulphur dioxide efficiency was beginning to fall off at that point. Evidently the higher rate of aeration supplied more oxygen and sulphur dioxide than could find the necessary ferrous iron in solution and in reactive condition.

The conclusion to be drawn is that the concentration of ferrous iron is immaterial as long as the solution contains enough available ferrous iron to react with oxygen and sulphur dioxide as fast as they are effectively supplied. At the space velocities and with the bubble sizes we investigated, a solution containing more than 3 grams of ferrous iron per liter is satisfactory for preparing acid solutions suitable for leaching ores.

**EFFECT OF RATIO OF SULPHUR DIOXIDE TO OXYGEN**

During the early part of our work Eckman, working with the apparatus of Figure 2, investigated the effect of varying the ratio of sulphur dioxide to air. This “big-bubble” apparatus was quite sensitive to changes of SO₂ concentration in the gas used. In general, Eckman found that ferrous iron could be oxidized to ferric iron, in part, by use of air and SO₂ mixtures containing as much as 3 per cent SO₂, but for each concentration there seemed to be a definite ratio of ferrous to ferric beyond which no further oxidation of iron took place and all the sulphur dioxide that reacted after this “steady state” was reached went to form sulphuric acid. With SO₂ concentrations of 0.1 to 0.3 per cent by volume, the iron could be almost completely oxidized and during its oxidation very little free sulphuric acid formed. With gas containing 0.5 to 2.5 per cent of SO₂ (1 volume of SO₂ to 40 of oxygen), the proportion of the ferrous iron that could be oxidized was still high (about 98 per cent), but more acid formed during the oxidation of the iron. With still higher concentrations of sulphur dioxide the portion of the iron that was oxidizable fell off, and at the same time the acid formed more rapidly. All of this work was done at room temperature and with no attempt at temperature control; numerous minor variations were therefore unexplained.
A better idea of the effect of sulphur dioxide concentration was obtained in the "small-bubble" apparatus of Figure 4. Figure 17 shows part of the data obtained at Douglas by McDaniel. He used four different concentrations of gas, 1, 3, 7, and 13 per cent of SO₂ (1 volume of SO₂ to 20, 6.7, 2.75, and 1.38 volumes of oxygen, respectively), and the numbers of the curves in the figure correspond to these concentrations. He also used a constant volume of air, 1.5 liters per liter of solution per minute, and mixed the sulphur dioxide with it before blowing it into the bottom of the apparatus. This procedure increased the space velocity of the total volume of gas, for the concentration of sulphur dioxide was increased. The solution used in these experiments contained about 5 grams of iron per liter.
By reference to Figure 17 the following conclusions on McDaniel's work can be drawn: The most rapid oxidation of the iron took place when the gas stream contained 7 per cent of sulphur dioxide \((\text{SO}_2 : \text{O}_2 = 1 : 2.75)\); a gas with 13 per cent of sulphur dioxide \((\text{SO}_2 : \text{O}_2 = 1 : 1.38)\) was definitely slow in oxidizing the iron, promising to reach a steady state with only about two-thirds of the iron oxidized. Formation of acid was likewise fastest with the 7 per cent gas but was nowhere near as depressed by the use of 13 per cent gas as was...
the oxidation of iron, although the \( \text{SO}_2 \) efficiency of 13 per cent gas was uniformly less than 80 per cent and fell off with increasing acidity. The effect of the concentration of \( \text{SO}_2 \) on the efficiency of utilization of \( \text{SO}_2 \) is quite plain. Evidently, for solutions containing

![Graph showing the effect of varying air-\( \text{SO}_2 \) ratio (\( \text{SO}_2 \) introduced separately). Air, 330 c. c. per minute per liter solution; bubbles, \( \frac{1}{4} \) mm. in diameter. Temperature, 30 to 35°C. \( \text{SO}_2 \) variable, introduced into solution passing down circulation pipe. Solution, 5 grams Fe\( ^{++} \) per liter (approx.) at beginning of experiment. Curve 1, percentage \( \text{SO}_2 \) efficiency, 20 and 41 c. c. \( \text{SO}_2 \) per minute; curve 2, percentage \( \text{SO}_2 \) efficiency, 60 c. c. \( \text{SO}_2 \) per minute; curve 3, percentage \( \text{SO}_2 \) efficiency, 80 c. c. \( \text{SO}_2 \) per minute; curve 4, percentage oxygen efficiency, 60 c. c. \( \text{SO}_2 \) per minute; curve 5, \( \text{H}_2\text{SO}_4 \) formed, 60 c. c. \( \text{SO}_2 \) per minute; curve 6, \( \text{H}_2\text{SO}_4 \) formed, 80 c. c. \( \text{SO}_2 \) per minute; curve 7, \( \text{H}_2\text{SO}_4 \) formed, 41 c. c. \( \text{SO}_2 \) per minute; curve 8, \( \text{H}_2\text{SO}_4 \) formed, 20 c. c. \( \text{SO}_2 \) per minute; curve 9, \( \text{Fe}^{++} \) in solution, 20 c. c. \( \text{SO}_2 \) per minute; curve 10, \( \text{Fe}^{++} \) in solution, 41 c. c. \( \text{SO}_2 \) per minute; curve 11, \( \text{Fe}^{++} \) in solution, 60 c. c. \( \text{SO}_2 \) per minute; curve 12, \( \text{Fe}^{++} \) in solution, 41 c. c. \( \text{SO}_2 \) per minute.]

only 5 grams of iron per liter, the use of gas containing more than 7 per cent \( \text{SO}_2 \) is inadvisable.

Thurston, at Tucson, working with the same type of apparatus, collected the data given in Figures 18 to 20. He used three different
space velocities of air, namely, 0.25, 0.35, and 0.5 liter of air per liter of solution per minute. Whereas McDaniel mixed the air and SO₂ before they were blown into the apparatus, Thurston passed the SO₂ separately into the circulation tube shown in Figure 4, at rates of 20, 40, 60, and 80 c. c. per minute. In the experiments with 250 c. c. of air per minute (fig. 18) these rates corresponded to gas with a concentration of 7.4, 14.1, 19.35, and 24.2 per cent of SO₂, respectively (SO₂: O₂ = 1: 2.7, 1.71, 1.32, and 1.13). Other experiments with 350 c. c. of air per minute (fig. 19) likewise had commensurate equivalents of gas with 5.4, 10.5, 14.6, and 18.6 per cent of SO₂, respectively.

*Figure 20.* Effect of varying air–SO₂ ratio (SO₂ introduced separately). Air, 500 c. c. per minute, introduced into 1 liter solution; bubbles, \( \frac{1}{4} \) mm. in diameter. Solution, 5 grams Fe per liter. SO₂ dissolved in solution while passing down circulation pipe. Temperature, 30 to 35° C. Curve 1, percentage SO₂ efficiency, 17 c. c. SO₂ per minute; curve 2, percentage SO₂ efficiency, 41 c. c. SO₂ per minute; curve 3, percentage SO₂ efficiency, 60 c. c. SO₂ per minute; curve 4, percentage SO₂ efficiency, 89 c. c. SO₂ per minute; curve 5, H₂SO₄ formed, 80 c. c. SO₂ per minute; curve 6, H₂SO₄ formed, 60 c. c. SO₂ per minute; curve 7, H₂SO₄ formed, 41 c. c. SO₂ per minute; curve 8, H₂SO₄ formed, 17 c. c. SO₂ per minute; curve 9, Fe⁺ in solution, 80 c. c. SO₂ per minute; curve 10, Fe⁺⁺ in solution, 60 c. c. SO₂ per minute; curve 11, Fe⁺⁺ in solution, 17 c. c. SO₂ per minute; curve 12, Fe⁺⁺ in solution, 41 c. c. SO₂ per minute.
(SO₂ : O₂ = 1:4.05, 1.77, 1.70, and 1.37), and experiments with 500 c. c. of air per minute (fig. 20) had correspondingly the equivalents of 3.29, 7.41, 10.87, and 13.80 per cent of SO₂ (SO₂ : O₂ = 1:6.55, 2.71, 2.13, and 1.74). At the lower equivalent concentrations the difference between the experiments in which the SO₂ was mixed with the air and those in which it was introduced separately, as a solution, was not noticeable. By this separate introduction of SO₂, however, it was possible to operate with relative efficiency with a much higher ratio of SO₂ to air.

In Figure 18, the experiments with 20 c. c. of SO₂ per minute are shown by curves marked 1, 6, 9, and 14; the ones with 41 c. c. of SO₂ per minute by curves marked 2 and 10; those with 60 c. c. of SO₂ per minute by curves 3, 8, and 12; those with 80 c. c. of SO₂ per minute by curves 4, 5, 7, and 11; and that with 91 c. c. of SO₂ per minute by curve 13. Iron oxidation was rapid only with 20 and 41 c. c. of SO₂ per minute, which respectively correspond to 7.4 and 14.1 per cent of SO₂. At higher ratios the rate of iron oxidation fell off greatly and tended slowly to approach a steady state with rather large amounts of ferrous iron unoxidized. The oxygen efficiency, high at the beginning in every test, approached a steady value of 16 per cent with 20 c. c. of SO₂ per minute and of 36 per cent with 80 c. c. of SO₂ per minute. The rate of acid formation increased until 40 c. c. of SO₂ per minute were being introduced; after that the rate was virtually the same in all the experiments. This change was reflected in the SO₂ efficiencies, which fell off after a rate of 41 c. c. of SO₂ per minute (14.1 per cent) was exceeded.

In Figure 19, curves 1, 8, and 10 represent experiments with 20 c. c. of SO₂ per minute; curves 1, 7, and 12, 41 c. c. of SO₂ per minute; curves 2, 4, 5, and 11, 60 c. c. of SO₂ per minute; and curves 3, 6, and 9, 80 c. c. of SO₂ per minute. The larger relative volume of air used altered conditions somewhat, and good oxidation of the iron could be obtained up to a rate of 60 c. c. of SO₂ per minute (14.6 per cent by volume). Formation of acid likewise was most rapid at this point and fell off with higher rates of use of sulphur dioxide. As the curves for oxygen efficiency fell close together, only the one for 60 c. c. of SO₂ per minute is given. The curves for sulphur dioxide efficiency indicated complete utilization of the SO₂ up to 41 c. c. per minute; the first half of the curve with 60 c. c. per minute likewise showed a high SO₂ efficiency, but after that the efficiency fell off as sulphuric acid accumulated in the solution.

Finally, in all those experiments of Figure 20 wherein twice as much air was used as in the experiments of Figure 18 a satisfactorily rapid rate of oxidation of iron was obtained, although the rate was fastest with 40 c. c. of SO₂ per minute (7.41 per cent by volume). The rate of formation of acid increased regularly with the amount of SO₂ used but seemed to be approaching a maximum at a point
RESULTS OF EXPERIMENTS

higher than 80 c. c. of SO₂ per minute (13.80 per cent by volume). The sulphur dioxide efficiency fell off too rapidly with acidity in the experiment with 80 c. c. of SO₂ per minute but was satisfactory up to 60 c. c. of SO₂ per minute (10.87 per cent of SO₂).

Evidently, by introducing the sulphur dioxide and air separately, satisfactory velocities of oxidation of iron and of formation of sulphuric acid can be obtained up to the point where the SO₂ is about 14 per cent of the total volume of gas introduced, although for satisfactory utilization of the sulphur dioxide the ratio of SO₂ to air should be kept down to less than about 10 per cent (SO₂:O₂ = 1:2.2).

The ratio of sulphur dioxide to oxygen required by equation (1) (p. 3) is only half that required by equation (2); this relationship permits the inference that during the oxidation of ferrous to ferric iron only half as much sulphur dioxide was needed as during the formation of sulphuric acid by equation (2).

Thurston, therefore, tried increasing the rate of introduction of SO₂ at the time that most of the iron was oxidized. His results are shown in Figure 21. The runs were all made with solutions containing 5 grams of iron per liter, which virtually could be oxidized completely in 35 minutes, as shown by the curve for run 37, provided that air was introduced at the rate of 800 c. c. per minute and SO₂ at 80 c. c. per minute (volume of solution, 1,800 c. c.). In run 49, at the end of 35 minutes the rate of addition of SO₂ was raised to 100 c. c. per minute; there was a resulting increase in the rate of formation of sulphuric acid and virtually no sacrifice of SO₂ efficiency.
In later experiments further increases in the rate of addition of SO\textsubscript{2}—until 200 c. c. of SO\textsubscript{2} per minute (SO\textsubscript{2}:O\textsubscript{2}=1:0.83) or 20 per cent by volume were introduced during the second half of the experiment—still showed satisfactory gains in the rate of formation of sulphuric acid and only small losses in sulphur dioxide efficiency. The oxygen efficiency was highest in this last run, averaging nearly 45 per cent.

We may therefore infer that the permissible ratio of sulphur dioxide to oxygen is higher (probably by a factor of 2) for the reaction involving the formation of acid than for the reaction involving mainly the oxidation of iron.

Working with the apparatus of Figure 5, designed for experiments at higher pressures, Maier, at Berkeley, collected numerous figures given in the curves of Figures 31 and 32 and summarized in Figure 33, where the rate of oxidation of the iron per minute is plotted against the percentage of SO\textsubscript{2} used in a mixed gas. Figure 33 gives a curve for the rate of oxidation at the end of 30 minutes and another for the rate at the end of 60 minutes. These curves show a regular increase in the rate of oxidation of the iron up to the point where mixtures of air and sulphur dioxide that contained almost exactly 6 per cent of SO\textsubscript{2} by volume (SO\textsubscript{2}:O\textsubscript{2}=1:3.25) are used; beyond that point the rate of oxidation of the iron fell off. Under a pressure of 5.6 atmospheres the maximum rate of oxidation of iron was when the gas contained between 6 and 7 per cent of SO\textsubscript{2}. As Maier and McDaniel both used apparatus giving bubbles of about the same size their results are in striking agreement, although the space velocity used by Maier was only about 0.666 and that of McDaniel was more than 1.5. These results are discussed on a later page.

The general conclusion that can be drawn from the data presented is that for an apparatus which makes gas bubbles about 1 cm. in diameter the maximum permissible ratio of sulphur dioxide to oxygen by volume is about 1:40 (0.5 per cent of SO\textsubscript{2}); with higher ratios the iron in solution is oxidized too slowly. Although the rate of formation of sulphuric acid is not affected so quickly, it is impaired by too high concentration of gas. With gas bubbles 1 mm. in diameter the maximum percentage of sulphur dioxide permissible in a mixture is about 7 per cent by volume (SO\textsubscript{2}:O\textsubscript{2}=1:2.75). If the sulphur dioxide at this concentration is introduced as a solution and only the air is introduced as 1-mm. bubbles, over 10 per cent of SO\textsubscript{2} based on volume of air (SO\textsubscript{2}:O\textsubscript{2}=1:1.86) can be safely used during the oxidation of the iron. After the iron is oxidized the ratio of sulphur dioxide to air can be safely doubled in order to increase the rate of formation of sulphuric acid.
RATE OF SUPPLY OF GAS TO SOLUTION

No doubt exists that in the early work, when the apparatus shown in Figures 2 and 3 were used, the rate at which gases were supplied to the liquid was too high. In most of that work the space velocity was 20 liters of gas per liter of solution per minute, and the bubbles were of large size. In consequence, the absorption of oxygen from the gas mixture was inefficient, and even the more soluble sulphur dioxide was not absorbed completely.

By interpolation of the smoothed curves of Figures 18, 19, 20, and 23 (Thurston's work) the curves of Figure 22 were derived; these show the effect of varying the volume of gases passed through 1 liter of solution. The points chosen for comparison were those for seven hours of aeration with gas containing 7.4 per cent of SO₂ and bubbles approximating 1 mm. in diameter.

The amount of sulphuric acid formed in seven hours' aeration with gas containing 7.4 per cent of SO₂ increased steadily with the rate at which the gas was introduced. With gas containing 13 per cent of SO₂, however, the amount of acid that could be formed in seven hours approached a maximum when the gas rate was about 800 c. c. per minute per liter of solution. At higher space velocities (only one observation) less acid could be formed with this strong gas, possibly because of the large supply of sulphur dioxide; the
latter is quite soluble and probably accumulated in sufficient quantity to reduce much of the ferric iron, without which the formation of more acid in already acidified solutions becomes difficult. The oxygen efficiency was at a maximum at 400 to 500 c. c. of gas per minute; it fell off slowly as the rate increased and rapidly as the rate decreased, consequently extrapolation to lower velocities than those actually used indicated that no reaction would take place with a space velocity

![Figure 23](image)

**Figure 23.—Effect of rate of supply of gas on rate of reaction. SO₂, 7.5 per cent solution, 1,000 c. c. (approx.); 5 grams Fe³⁺. SO₂ efficiency given in curves 1, 3, 5, and 13; oxygen efficiency given in curves 6, 7, and 8; Fe²⁺ given in curves 3, 10, 11, and 18; H₂SO₄ formed given in curves 15, 14, 16, and 18. Air, 250 c. c. per minute in curves 2, 6, 9, and 13; air, 500 c. c. per minute in curves 1, 8, 10, and 14; air, 1,000 c. c. per minute in curves 3, 7, 11, and 15; air, 1,500 c. c. per minute in curves 4, 8, 12, and 16.**

only slightly over 100 c. c. per minute per liter of solution. Extrapolating to lower space velocities the two curves showing formation of sulphuric acid likewise indicated zero formation of acid when the space velocity fell to slightly less than 100 c. c. per minute. At first it was thought that possibly the explanation was to be found in the tendency of the iron to oxidize first without formation of “free” acid, a thing that had been especially noticeable before in tests at
lower space velocities, but this hypothesis was discarded when results obtained at Douglas checked the Tucson work and also indicated that at lower space velocities no iron was oxidized. The Douglas results are described in the paragraph that follows.

McDaniel, at Douglas, made a similar series of tests with his apparatus. The results are given in detail in Figure 23, and from these smoothed curves the curves in Figure 24 are derived for comparison with Thurston's data. In all these tests the oxygen efficiency was entirely consistent. With a space velocity of only 250 c. c. per minute (curve 1, fig. 23), virtually a steady state was reached in seven hours; no further acid was being formed nor iron oxidized, and the oxygen efficiency fell nearly to zero, although the sulphur dioxide efficiency had not yet come down. The iron behaved erratically in this run. Oxidation was rapid at first, then it halted after about
one-third of the iron was oxidized; later the iron was rapidly reduced again until by the time the steady state was reached about two-thirds of the total iron was oxidized. Seemingly this test was at such a low space velocity that the effect predicted by extrapolation, mentioned in the last paragraph, was nearly realized. The other tests acted normally. Extrapolation of the curves in Figure 24 again shows a space velocity below which no iron could be oxidized in 15 minutes after the start, and no sulphuric acid formed even in seven hours. The point of zero reaction with the Douglas apparatus was about 180 c. c. of gas per minute.

This entirely unexpected result—zero reaction with a finite space velocity—was not discovered until the final report was in preparation; hence no actual test at the low indicated space velocity has been made to see if zero reaction would be obtained. As the industrially important end of the curve is at the high space velocities, further investigation has not been deemed worth while. Probably the curves do not actually reach a zero reaction velocity at the particular space velocity, but instead bend sharply over to the origin, as indicated by the dotted line in Figure 24.

The explanation of this anomaly is probably related to some effects that Maier observed when watching a single small orifice through which gas was introduced at various velocities. There was a certain optimum velocity at which the smallest bubbles formed. With lower velocities the bubbles increased rapidly in size to a certain maximum at the point where the gas was introduced at virtually zero velocity. The diameter of the bubbles at these low velocities was rather large, and therefore the rate at which oxygen could be absorbed from the bubbles during their rapid rise through the liquid was low. The steepest part of the curves in Figure 24 doubtless corresponds to the minimum size of bubbles observed by Maier, and the less steep parts correspond to the larger bubbles formed when the velocities of gas supply were either higher or lower than the optimum velocity.

In Figure 24 a curve was also drawn to indicate the maximum rate of formation of sulphuric acid noted in each test, as a function of the space velocity of aeration of the solution. This rate increased with increasing space velocity, but not proportionately, indicating that with space velocities higher than those investigated the further increase in the rate of acid formation would not be as large. The curve for oxygen efficiency in this figure was taken for the four-hour interval because the results at other points were somewhat erratic. The SO₂ efficiency at the end of the seventh hour gradually fell off with increasing space velocity.

In general, the curves indicate that a certain minimum space velocity is needed in aerating solutions with the gas, and that above
that minimum the oxidation of iron and the formation of sulphuric acid proceed with increasing speed, as higher space velocities of aeration are employed, but with the efficiency of the oxygen and sulphur dioxide constantly (though slowly) dropping, as long as a gas mixture suited to the apparatus is used. In one test, with gas high in sulphur dioxide, an optimum space velocity was indicated, but the efficiencies of oxygen and sulphur dioxide were too low to be satisfactory, and this one exception to the general statement need not be heeded.

With the apparatus shown in Figure 5, Maier, at Berkeley, made two runs in a manner somewhat different from that used in either of the foregoing series of experiments. He started with a low space velocity, ran long enough to get a measurable oxidation of the iron, then raised the space velocity to a new value and ran long enough to get the increased rate of oxidation of the iron, and so on until he reached his highest space velocity. Results of his two runs, which checked each other, are plotted in Figure 25, where the abscissas are the gas rates (in c.c. per minute passed through 150 c.c. of solution), and the ordinates are the percentages of the total iron oxidized per minute. The runs lasted in all more than two hours, and the iron was about 80 per cent oxidized at the end.

The results Maier obtained (fig. 25) show that in his apparatus, which was the most efficient of any of those tested, there was no minimum allowable space velocity like that observed in the apparatus used at Tucson and Douglas; at least, if there was, the minimum allowable space velocity was very small. His curve, however, bends so that it is concave upward, indicating an increasing velocity of oxidation of the iron with increasing space velocity, probably because smaller bubbles tend to form at the higher space velocities. Visual investigation of a very small orifice, such as those in the apparatus Maier used, revealed that the minimum size of bubble did not come until the relative space velocity was much higher than with the larger orifices. Maier's results are therefore not inconsistent with those of Thurston and of McDaniel. If the upper part of his curve is extrapolated back it cuts the axis of zero
rate at a finite space velocity, in agreement with extrapolations of previous curves. The value of this part of Maier's work lies in its showing the variation in results that is to be expected when very small orifices are used.

EFFECT OF BUBBLE DIAMETER

During the early part of the work discussed in this report, the size of the bubbles used was not investigated, as it was not anticipated that their size would have an effect as great as later work proved. Disagreements between investigators in the three different laboratories soon forced a comparison of results, however, and enough indirect data had been collected by the men at Tucson to force an investigation of the effect of bubble diameter.

Maier, at Berkeley, finally prepared a series of glass tips differing in diameter and introduced the gas into the solution in the apparatus shown by Figure 5, displacing the rubber aerator by the glass tips. In Figure 26 the rates of oxidation of iron with gas containing 7.6 per cent of SO$_2$ and 85 per cent of oxygen are plotted as a function of the diameter of the orifice used. One series of observations was made with a gas rate of 200 c. c. per minute (150 c. c. of solution) and the other with a rate of 50 c. c. per minute (these two rates expressed in space velocity are 1.67 and 0.33, respectively). The plot shows that the rate of oxidation of the iron increased as the size of the bubbles decreased. In order to find a possible relation between the diameter of the orifice and the rate of oxidation of the iron the results of the smoothed curves of Figure 26 were plotted logarithmically in Figure 27, where they give reasonably straight lines. Evidently then $\log R = n \log D + \log k$, where $n$ and $k$ are constants and $R$ is the rate of oxidation of the iron and $D$ the diameter of the orifice. The value of $n$ in the upper curve of Figure 27 is $-0.58$ and in the lower one, $-0.51$. If $n$ were exactly equal to $-0.50$, we could say that the rate of oxidation is inversely proportional to the square root of the diameter of the orifice used and presumably, therefore, inversely proportional to a function of the
square root of the bubble diameter. Since \( n \) is not exactly equal to \(-0.50\), the relationship is only approximate. The values of \( k \) are obtained by finding the intercept of the curve at the point where \( D = 1 \) or \( \log D = 0 \), and are, respectively, 0.441 and 0.131. These values of \( k \) are true only for a gas consisting of 7.6 per cent of \( \text{SO}_2 \) and 85 per cent of \( \text{O}_2 \) and for diameters of orifice in millimeters.

The orifices had been rather carefully prepared and ground flat across on a lap. Although we were unable at the time these experiments were made to measure the diameters of the bubbles, we assumed that they were in proportion to the diameters of the orifices. Later work showed the relationship is more complex. Our value of \( n \) for

![Figure 27](image)

**Figure 27.** Logarithmic plot to show relation of oxidation rate to orifice diameter. Curve 1, gas rate, 200 c. c. per minute, \( n = -0.58 \); curve 2, gas rate, 50 c. c. per minute, \( n = -0.51 \)

the lower rates of gas flow justifies us in concluding that the inverse square root law holds with respect to orifice diameter, but the value of \( n \) for the higher rates means that the same effect is obtained as would be given by a somewhat smaller orifice. This result is in accordance with the deviation of the curve in Figure 25 and also with visual observation. When the velocity of the gas was low, the bubbles were larger than when the velocity was high, and at a certain rate of flow the gas issued from the jet in an unbroken cone which "exploded" into very small bubbles at a certain distance from the tip of the jet; some of these bubbles were considerably smaller than those formed when the velocity of the gas was low. In view of these disturbing influences, it is surprising that the lines in Figure 27 are as straight as they are.
The general conclusion is therefore justified that the velocity of oxidation of iron and of sulphur dioxide by aeration is inversely proportional to the square root of the orifice diameter, and consequently of a function of the bubble diameter, provided the space velocities used are always of comparable magnitude.

**EFFECT OF DEPTH OF COLUMN OF SOLUTION**

As the reactions in this research are between a gas and a solution and are probably limited by the amount of surface of the gas that can be exposed and by the time of contact of the gas with the solution, one might naturally expect that a deeper column of solution would favor longer time of contact of the gas with the solution and therefore increase the efficiency of the reaction and its rate. Thurston, at Tucson, built three different pieces of apparatus that were of identical construction and volume, but differed in depth and, of course, in cross section to compensate for changes in depth. In runs made with them he used a constant amount of air but varied the percentage of SO$_2$ introduced, and he noted the maximum amount of sulphur dioxide that could be introduced into the circulation pipe without any odor being perceptible at the gas exit. This corresponded to the maximum amount of sulphur dioxide which could be introduced with 100 per cent efficiency.

Figure 28 summarizes the results. The curves of this figure plainly show that with increasing depth (compared to the cross section) of solution the efficiency of the reaction increased, but the advantage gained with each increase in depth was progressively less. This was probably due to the fact that the bubbles were coalescing during their travel up the column of solution, so that the bubbles near the top were rather large and less available for reaction than the smaller ones nearer the bottom. In fact, the curve for oxidation of iron showed that little advantage would be gained by having the solution deeper than 300 cm. (10 feet). The efficiency in the formation of sulphuric acid fell off a little less quickly, and the slope of the curve indicated that some further advantage might be expected, although it would not be great. The amount of sulphur dioxide that could be successfully absorbed per minute increased greatly with relative depth of the reacting column.

The general conclusion is that an aerator which can produce gas bubbles 1 mm. in diameter should have a column at least 300 cm. deep in order to absorb as much of the oxygen from the air as possible and to permit the introduction of a large amount of sulphur dioxide. For depths much greater than 300 cm. the useful effect rapidly diminishes, because the small bubbles coalesce into big ones.
RESULTS OF EXPERIMENTS

EFFECT OF TEMPERATURE

One of the most important factors in many chemical reactions is temperature. Bonner, at Berkeley, therefore, made a series of runs with the apparatus shown in Figure 3. He used a silica tube carrying an electric heating element to keep the bath at a constant temperature.

Bonner tried two different concentrations of ferrous sulphate solution and two different concentrations of SO₂ gas in air. The results are plotted in Figure 29, which shows the time necessary to reach 90 per cent oxidation of the iron as a function of temperature. In all the tests made the reaction velocity of the big-bubble apparatus from a temperature of 15°C upward was greatly increased by raising the temperature, but to heat the solution much higher than 40°C is not advantageous, as the temperature effect beyond that point is not great and may even be deleterious. This temperature effect is doubtless connected with too many physical properties to be easily analyzed. The failure of temperatures higher than 40°C. to speed up the reaction further is possibly connected with the decreased
solubility of the gases in the solution at these temperatures. A solution aerated with 1-mm. bubbles at room temperature naturally heats itself to 35° or 40° C., so evidently we have already investigated the most favorable conditions.

EFFECT OF CONCENTRATION OF OXYGEN

As oxygen is one of the reactants, its partial pressure in the gas used should be important. Bonner, therefore, made a few experiments at Berkeley with the Figure 3 apparatus, substituting various amounts of oxygen from a cylinder of compressed gas for part of the air used in the normal experiments. Two different solutions were aerated, one with 5.6 grams of iron per liter (curves 1, 2, and 3, of fig. 30, drawn with circles to represent each datum) and one with 56 grams of iron per liter and stronger SO₂ gas (curves 4 and 5, drawn through points represented by crosses).

At once it is evident qualitatively that increase in the concentration of oxygen cuts down the time necessary to oxidize the iron and that the effect is roughly in proportion to the partial pressure of the oxygen. Because of their differing shapes it is hard to compare the curves quantitatively, but by reference to curves 1, 2, and 3 at the points where only 3 grams of ferrous iron remain unoxidized the following data become evident:

<table>
<thead>
<tr>
<th>Gas, per cent SO₂</th>
<th>Oxygen ratio</th>
<th>Time</th>
<th>Time ratio</th>
<th>Reciprocal of time ratio</th>
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</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>17</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td>40</td>
<td>2</td>
<td>10</td>
<td>0.612</td>
<td>1.7</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>6</td>
<td>0.354</td>
<td>2.83</td>
</tr>
</tbody>
</table>
Comparison of column 2 with column 5 shows that the rate of oxidation is approximately, but not exactly, proportional to the partial pressure of the oxygen in the gas used.

Similar figures for the strong solutions showed that, by changing the oxygen pressure from 20 to 50 per cent of the gas used, the time of oxidation of the iron was divided by a factor of about 2.8, somewhat more than was expected. Because of experimental error and the difficulty in choosing appropriate points on the curves for comparison, one can merely conclude that the reaction velocity is roughly proportional to the partial pressure of oxygen in the gas used, but this conclusion applies only to the conditions used by Bonner.

![Graph showing the effect of oxygen concentration on the rate of oxidation]

**Figure 30.—Effect of oxygen concentration. Points designated *, weak solution; points designated x, strong solution. Curve 1, 5.6 grams Fe per liter, 0.5 per cent SO₂, 20 per cent O₂; curve 2, 5.6 grams Fe per liter, 0.5 per cent SO₂, 40 per cent O₂; curve 3, 5.6 grams Fe per liter, 0.5 per cent SO₂, 60 per cent O₂; curve 4, 5.6 grams Fe per liter, 1.5 per cent SO₂, 20 per cent O₂; curve 5, 5.6 grams Fe per liter, 1.5 per cent SO₂, 50 per cent O₂.**

**EFFECT OF PRESSURE**

The foregoing results encouraged us to carry out some tests with gas pressures higher than atmospheric. Roberts, at Berkeley, made a few tests in which sulphur dioxide was introduced into the receiver of an air compressor and the receiver was pumped full of air to the desired pressure. This air was then passed through a small bubbling column under a pressure somewhat below that of the receiver. As a big-bubble apparatus was used and as the results indicated a disadvantage in place of an advantage, the work was abandoned temporarily.
After the discovery of the importance of the size of the gas bubbles in the aerator a new apparatus was devised and tried at Berkeley by Maier. He used apparatus illustrated in Figures 5 and 6 (p. 8) and by throttling the gas exit line could maintain any desired pressure in the solution. Maier made two series of runs—one at atmospheric pressure and the other under a pressure of 5.6 atmospheres. Half molar solutions of ferrous sulphate (28 grams of iron per liter) were used in amounts approximating 150 c. c. at the beginning of each run but decreasing in volume through occasional sampling for analysis. The gas mixtures of sulphur dioxide, oxygen, and nitrogen were synthesized in an oxygen cylinder and then passed through the apparatus at a rate of 100 c. c. per minute, corresponding to a space velocity of 0.67 at the beginning and therefore increasing as the volume of solution decreased. Only data on mixtures of sulphur
dioxide and air are reported in Figures 31 and 32, which give the instantaneous rates of oxidation of the iron at various time intervals with a series of gas mixtures containing from 2 per cent SO₂ to 14.56 per cent SO₂ (SO₂:O₂ = 1:10.1 to 1:1.21). The curves show that with high concentrations of SO₂ the rates of oxidation decrease with time, and with low concentrations they increase somewhat, but with about 7.45 per cent SO₂ they are virtually constant.

\[\text{Figure 32.—Effect of pressure and SO}_2\text{ concentration. Solution, 150 c. c., 28 grams Fe}^{++}\text{ per liter, 100 c. c. gas per minute. Full lines, 5.6 atmospheres pressure. Dotted lines, 1 atmosphere pressure. 7.45 per cent SO}_2\text{ used in curves 1 and 2; 9.55 per cent SO}_2\text{ used in curves 3 and 4; 11.09 per cent SO}_2\text{ used in curves 5 and 6; 14.56 per cent SO}_2\text{ used in curves 7 and 8.}\\]

In order to compare the data better, points have been chosen from the smoothed curves for plotting the curves of Figures 33 and 34. The data for 30 minutes of oxidation and for 60 minutes of oxidation were chosen. In Figure 33 the rate of oxidation for each of these time intervals and for each of the two pressures under which the work was done is plotted against the percentage of sulphur dioxide in the gas used. The fastest rate of oxidation in all cases is at 6 to 7 per cent.
of SO₂. By dividing the rate at 5.6 atmospheres by the rate at 1 atmosphere a ratio which is the measure of the effectiveness of pressure was obtained; this is plotted in the upper part of Figure 33. It is seen that the greatest increase in rate of oxidation produced by an increase in pressure amounting to 5.6 times is only 1.74 times, and the effectiveness of the use of pressure is different with different concentrations of SO₂. More than 9 per cent of SO₂ in the 60-minute curve and more than 10 per cent of SO₂ in the 30-minute curve is positively deleterious, and the rate of oxidation is slower with the gas under higher pressure.

A study of the oxygen efficiency, made in the same way, is plotted in Figure 34. Two different oxygen efficiencies were calculated. One
was the total or over-all oxygen efficiency—that is, the total oxygen absorbed divided by the total oxygen fed to the apparatus—the other was the ratio of the total oxygen used to the theoretical possible content usable on the assumption that only 1 volume of oxygen can be used per volume of SO₂ in the gas, as deduced from the amounts of reactants predicted by equation (1) (p. 3). Of course, as mentioned earlier in this paper, equation (2) calls for a different ratio of oxygen to sulphur dioxide, and if any acid forms during the oxidation of the iron the oxygen efficiency calculated on the basis of equation (1) will be in error.

Figure 34 shows that the maximum total oxygen efficiency is attainable when using gas containing 7.5 per cent of SO₂ (SO₂/O₂ = 1:2.55). However, the maximum efficiency of oxygen in oxidizing iron was attained with gas containing 5.3 per cent of SO₂ (SO₂/O₂ = 1:3.7).
In both these cases the maxima were observed for pressures of 1.0 and 5.6 atmospheres. Plotting the effectiveness of pressure in altering oxygen efficiency (see curve at the top of Figure 34) reveals that the use of pressure is most effective when gas containing 3 to 4 percent of SO\textsubscript{2} is used (SO\textsubscript{2}:O\textsubscript{2}=1:5.7). With a gas containing 10 percent of SO\textsubscript{2} no difference could be detected between the results at the two different pressures.

A rough measure of the effectiveness was made, assuming that \( m \) was the order of effectiveness, and then the ratio of the rates of oxidation at the two pressures should obey the following equation:

\[
\frac{\text{Rate at 5.6 atm.}}{\text{Rate at 1 atm.}} = \left( \frac{5.6 \times \text{percentage original O}_2}{100} \right)^m
\]

By logarithmic plotting of the two members of the equation the value of \( m \) could be determined or

\[
m = \frac{\log \left( \frac{\text{Rate at 5.6 atm.}}{\text{Rate at 1 atm.}} \right)}{\log \left( \frac{5.6 \times \text{percentage O}_2}{100} \right)}
\]

This value of \( m \) is used as the effectiveness with respect to oxygen because under the conditions of our experiments the sulphur dioxide was always completely absorbed. The rates of oxidation were taken from the curves of Figure 33, and the resulting calculated values of \( m \) varied with the percentage of SO\textsubscript{2}, but the maximum value was 0.33. This means that the maximum effectiveness of increase of pressure of the reacting gases varies approximately as the cube root of the pressure, and for most conditions the effectiveness is even less.

**EFFECT OF IMPURITIES IN THE SOLUTION**

As this method of making ferric sulphate or sulphuric acid solutions is probably of most value in the treatment of copper ores, it was thought best to investigate the effects in the solution of the various impurities likely to be encountered in the treatment of the ores.

Bonner investigated the effects of aluminum sulphate and zinc sulphate in the solutions and reported he found no effect when he used the amounts likely to be found in the leaching solutions. Thurston and Wartman tried stronger solutions and found that when over 30 grams of zinc per liter is present the oxidation of iron is hindered. McDaniels, at Douglas, made similar observations but found that the foamy nature of the solutions of these metals assisted in disseminating the gas bubbles and was to that extent an advantage. Sodium and calcium sulphates in the solution seemed to be harmless, and arsenic in small quantities had no noticeable effect. Copper, Bonner found, was deleterious when present in the amounts likely to
be met in practice. Thurston and Wartman found that with up to 1 per cent of copper in the solution (see fig. 35) the oxidation of the iron was not affected seriously; 2 per cent of copper did not greatly retard the acid-forming reaction but retarded the oxidation of the iron; with 3 per cent of copper the oxidation of iron was seriously retarded; and with 4 per cent of copper virtually no iron was oxidized. Wartman found that addition of ferric iron to a ferrous sulphate solution containing copper in sufficient amounts to affect seriously

![Graph](image)

**Figure 35**—Effect of presence of copper sulphate. SO$_2$, 80 c. c. per minute. Air, 800 c. c. per minute. Run 85, 5.1 grams Cu per liter; run 86, 10.3 grams Cu per liter; run 87, 20 grams Cu per liter; run 88, 28.6 grams Cu per liter; run 89, 40.9 grams Cu per liter. Curves: Steeply inclined group gives acid formed; top group gives percentage SO$_2$ efficiency; middle group gives oxygen efficiency; bottom group gives ferrous iron content

the rate of oxidation counteracted the effect to some extent, but not to the same extent that ferric iron counteracted the effect of acid. When 4 per cent of copper was present in the solution, ferric iron could not seem to overcome the effects, and no ferrous iron could be oxidized.

Evidently, if the solutions made by this process are to be used for the leaching of copper ores, the copper will have to be precipitated
from them before they can be reoxidized. McDaniel carried out 
some work at Douglas on tailing from a flotation plant at Morenci, 
Ariz. Most of the copper in the tailing was in the oxidized form 
and all this copper could be easily extracted, together with part of 
the remaining sulphide copper, after treatment for one-half hour 
with ferric sulphate-sulphuric acid solution. Precipitation of the 
copper with iron and reuse of the leaching solution showed that the 
solution tended to reoxidize more slowly but not slowly enough to 
interfere with the formation of the solution desired. A solution con-
taining 1.35 per cent of \( \text{SO}_2 \) and 0.10 per cent of \( \text{Fe} \) was satisfactory 
for the Morenci ore, and acid solutions containing 2 to 3 per cent 
could be made in less than two hours’ aeration. The iron oxidized 
more slowly in the leach solutions, by a factor of 2 to 3, but the rate of 
formation of acid was not altered, and the \( \text{SO}_2 \) efficiencies were 
about the same.

Several runs were made to determine the effect of adding success-
itive amounts of chlorides to the solutions. Sodium chloride up to 
2 or 3 per cent did not affect the rates of the reactions, but when 
the oxidation of small amounts of iron in a saturated brine was 
attempted by this method virtually no oxidation was possible—only 
11 per cent in two hours.

**EFFECT OF LIGHT**

As nearly as could be determined, the reactions went on as well 
in the dark as in sunlight.

**ENGINEERING ASPECTS**

This paper has dealt thus far almost wholly with the fundamental 
characteristics of the chemical reactions involved. The bearing of 
these facts on the conditions that must be met in practice and the 
probable cost of power remains to be considered.

**MATERIALS OF CONSTRUCTION**

The materials so far shown to be suitable for use with dilute sulphuric 
acid solutions containing large amounts of the sulphates of iron are 
glass, lead, vitrified clay shapes, wood (only the types of wood nor-
mally used in chemical engineering), hard rubber (soft rubber hardens 
under the action of \( \text{SO}_2 \)), Monel metal (not thoroughly tested), and 
Duro cloth (an impregnated wool fabric). Bakelite, Vitreosil, sul-
phur concrete, mastic, and similar materials commonly used in 
chemical engineering work should also be suitable.

**ATMOSPHERIC PRESSURE AT LABORATORIES**

The elevations above sea level of the three laboratories that have 
contributed to this work are given herewith, so that the data obtained 
can be easily reduced. The “factor” is the constant by which the
volume of gas at standard conditions should be multiplied in order to get the volumes at 21° C. at the various laboratories.

**Correction factors for barometric pressure at laboratories**

<table>
<thead>
<tr>
<th>Place</th>
<th>Altitude</th>
<th>Barometer</th>
<th>Factor</th>
<th>Weight of air at 25° C.</th>
<th>Weight of SO₂ at 25° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feet</td>
<td>Millimeters</td>
<td></td>
<td>1 cubic foot</td>
<td>1 liter</td>
</tr>
<tr>
<td>Berkeley, Calif</td>
<td>300</td>
<td>756</td>
<td>1.080</td>
<td>0.0751</td>
<td>1.220</td>
</tr>
<tr>
<td>Tucson, Ariz.</td>
<td>2,386</td>
<td>692</td>
<td>1.180</td>
<td>0.0697</td>
<td>1.117</td>
</tr>
<tr>
<td>Douglas, Ariz.</td>
<td>4,500</td>
<td>640</td>
<td>1.275</td>
<td>0.0644</td>
<td>1.032</td>
</tr>
</tbody>
</table>

**RELATIVE WEIGHTS AND VOLUMES**

From the chemical reactions as written in equation form the theoretical weights and volumes can be deduced. Some observed figures on volumes are appended.

For the equation expressing the oxidation of iron these relationships are:

Reaction: 2 FeSO₄ + SO₂ + O₂ = Fe₂(SO₄)₃.
Volumes: 1 SO₂ to 1 O₂ (1 volume O₂ in 4.83 volumes air).
Weights: 1 Fe + 0.571 SO₂ + 0.286 O₂.

Therefore, 1 gram Fe requires 195 c. c. SO₂ + 195 c. c. O₂ (943 c. c. air) at standard conditions; 1 pound Fe requires 3.58 cubic feet SO₂ + 1.79 cubic feet O₂ (8.64 cubic feet air).

The figures for the sulphuric acid reaction are:

Reaction: SO₂ + 1/2 O₂ + H₂O = H₂SO₄.
Volumes: 2 SO₂ to 1 O₂ (4.83 volumes air).
Weights: 0.653 SO₂ + 0.163 O₂ + 0.184 H₂O = 1 H₂SO₄.

Therefore, 1 gram H₂SO₄ requires 226 c. c. SO₂ + 111 c. c. O₂ (536 c. c. air); 1 pound H₂SO₄ requires 3.58 cubic feet SO₂ + 1.79 cubic feet O₂ (8.64 cubic feet air).

These figures are for theoretically perfect absorption of oxygen from the gas stream. It is of interest to calculate the air requirements for conditions that are actually attainable. Much of the work reported on preceding pages showed an oxygen efficiency of 25 per cent when the 5-foot column aerator was used, although with a 10-foot column oxygen efficiencies as high as 65 per cent were attained, and an average efficiency of 50 per cent might be reasonably expected. Therefore, in the following table (Table 2) of the volumes of gas required, on the assumption that SO₂ is to be absorbed in the solution separately and the solution is then to be aerated with air, calculations have been made for the theoretical amount of air (100 per cent oxygen efficiency) and for 50 and 25 per cent oxygen efficiency.
TABLE 2.—Volumes of gases (introduced separately)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Efficiency</th>
<th>Standard conditions</th>
<th>Berkeley</th>
<th>Tucson</th>
<th>Douglas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Per cent</td>
<td>Cubic feet</td>
<td>Cubic feet</td>
<td>Cubic feet</td>
<td>Cubic feet</td>
</tr>
<tr>
<td>SO₂</td>
<td>100</td>
<td>3.15</td>
<td>3.88</td>
<td>3.70</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>100</td>
<td>15.15</td>
<td>16.35</td>
<td>17.90</td>
</tr>
<tr>
<td></td>
<td>...do</td>
<td>50</td>
<td>30.30</td>
<td>32.70</td>
<td>35.30</td>
</tr>
<tr>
<td></td>
<td>...do</td>
<td>25</td>
<td>60.60</td>
<td>65.40</td>
<td>71.60</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>100</td>
<td>8.64</td>
<td>9.32</td>
<td>10.20</td>
<td>11.00</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>100</td>
<td>17.25</td>
<td>18.68</td>
<td>20.40</td>
</tr>
<tr>
<td></td>
<td>...do</td>
<td>25</td>
<td>54.69</td>
<td>57.93</td>
<td>60.75</td>
</tr>
</tbody>
</table>

In this table the gas volumes at 25 per cent efficiency and also the amounts of sulphur dioxide are printed in italic type as being figures that can be used without any assumptions or reservations, whereas the figures for 50 per cent air efficiency represent reasonably fair expectations.

RATIO OF SULPHUR DIOXIDE TO OXYGEN

If the solution is to be aerated with a mixed gas, preferably a gas from a roaster or sulphur burner, the important point to be noted is the ratio of sulphur dioxide to oxygen. The air from the roaster has been partly depleted of its oxygen, and only the excess oxygen is left to mix with the nitrogen and the sulphur dioxide. Therefore, we must use the most satisfactory SO₂: O₂ ratios found in the experimental work. When bubbles of gas 1 mm. in diameter were used, the optimum ratio was 1 SO₂: 2.75O₂ during the period while iron was being oxidized, but during the period of acid formation this ratio changed to 1 SO₂: 1.50 O₂. During the earlier work, when 10-mm. bubbles were used, the ratio was 1 SO₂: 40 O₂.

It will now be necessary to calculate the SO₂ content of roaster gases or of sulphur-burner gases that will give this desired ratio. The calculation for sulphur-burner gas is, briefly, as follows: The chemical equation outlined is S + O₂ = SO₂; it signifies that 1 volume of oxygen produces 1 volume of sulphur dioxide. The original air contained 20.7 per cent of O₂, and so the final air should contain SO₂ + O₂ = 20.7. We know that the final gas must show the ratio SO₂: O₂ = 1: 2.75. These are two simultaneous equations with the concentrations of SO₂ and of O₂ in the final gas as the unknowns. Solving them we find SO₂ = 5.52 per cent.

For roasting pyrite the calculation is slightly more involved. The equation is 2 FeS₂ + 11/2 O₂ = Fe₂O₃ + 4 SO₂; it signifies that 11/2 volumes of O₂ produce 4 volumes SO₂ or, simplified, that 1.375 volumes of O₂ produce 1 volume of SO₂. Therefore, 1.375 SO₂ + O₂ = 20.7, and we desire that SO₂: O₂ = 1: 2.75. Solving the two simulta-
neous equations we find \( \text{SO}_2 = 5.02 \) per cent in the roaster gas. These calculations are only approximately correct because formation of \( \text{SO}_2 \) has been neglected.

From the foregoing method of calculation the tabulation for the percentages of \( \text{SO}_2 \) in both sulphur-burner gas and in roaster gas to meet these desirable \( \text{SO}_2 : \text{O}_2 \) ratios is as follows:

**Table 3.—SO\(_2\) content necessary to give desirable ratios of SO\(_2\) to O\(_2\)**

| Reaction and bubble size | Ratio \( \frac{\text{SO}_2}{\text{O}_2} \) | \( \text{SO}_2 \) in— |  
|-------------------------|--------------------------------|-----------------|-----------------|
|                         |                                | Burner gas | Roaster gas |  
| Fe oxidation, using 1-mm. bubbles | 1:2.75 | 5.52 | 5.02 |  
| Acid formation, using 1-mm. bubbles | 1:1.50 | 8.28 | 7.21 |  
| Fe oxidation, using 10-mm. bubbles | 1:40 | .5 | .5 |  

The figures for 10-mm. bubbles are inserted in the table to show the inefficiency of such bubbles and to show that for satisfactory commercial work the 1-mm. bubbles, or smaller, are to be preferred. The dilution of the roaster gas necessary to satisfy the conditions needed for 10-mm. bubbles is extreme and probably impractical. On the other hand, the concentrations of \( \text{SO}_2 \) in either roaster gas or burner gas to meet the optimum conditions for 1-mm. bubbles are easily attainable. The use of mixed gas from roasters or sulphur burners is therefore practical.

**Bubble Size**

As has been mentioned repeatedly, the desirable maximum diameter of gas bubbles is 1 mm. The other conditions used for calculations, on both the preceding and following pages, are based on this assumed diameter. Larger bubbles are simply to be avoided; smaller bubbles would be welcome if they could be produced without too great an expenditure of power, for they would permit shallower aeration columns, more rapid work, smaller area of aeration tanks, and more concentrated gas, and would be of great advantage in every way.

**Depth of Column**

Figure 28 shows that for iron the oxidation conditions improve rapidly as the depth of the aerating column is increased to 5 feet, and that they are somewhat further improved with increase of depth to at least 10 feet. The other factors of the rate of formation of acid, sulphur dioxide efficiency, and oxygen efficiency are likewise affected, and in general it seems justifiable to state that a 10-foot aeration column is preferable when 1-mm. bubbles of gas are used, although a 5-foot column is acceptable if the use of a 10-foot column presents engineer-
ing difficulties. The question of pressures and of pumps for supplying gas at these pressures is discussed below.

**SPACE VELOCITY**

The space velocities revealed as possible by previous work on this subject are from 0.5 volume of gas per unit volume of solution aerated per minute to 1.5 volumes of gas per unit volume of solution per minute. In cubic feet this means 0.5 to 1.5 cubic feet of gas per minute per cubic foot of solution.

**PRESSURE OF GASES**

In order to force gases through small openings in the bottom of an aerating column, the pressure on the gases must be enough to overcome three main resistances, as follows: (1) Hydrostatic head of solution above orifice, (2) capillary head, and (3) friction head.

By capillary head is meant the tendency of a liquid to enter a small capillary. For instance, the orifice can be regarded as being the end of a small tube; by capillarity a liquid can rise to a certain height in the tube, and to force air down the capillary enough pressure must be used to overcome this head.

**HYDROSTATIC PRESSURE**

The hydrostatic pressure of the liquid above the gas orifice is easily calculated, for it is the weight over a unit area of the column of liquid above it. If the liquid is pure water at ordinary temperatures, every foot of depth causes a pressure of 0.433 pound per square inch. For a solution of greater density this figure should be multiplied by the density. If of water, the 10-foot aeration column would therefore exert a pressure of 4.33 pounds, and the sulphuric acid solutions or ferric sulphate solutions will never be of greater density than enough to cause about 0.5 pound of pressure per foot of depth.

**PRESSURE DUE TO CAPILLARY FORCES**

The height to which a liquid will rise in a small capillary tube is given by the familiar equation,

\[ h = \frac{2T \cos \theta}{r \cdot d \cdot g} \]

where

- \( T \) = surface tension of liquid,
- \( r \) = radius of tube,
- \( d \) = density of liquid,
- \( g \) = gravitational acceleration,
- \( \theta \) = angle of contact of liquid with tube (zero for complete wetting).

From this equation it is evident that the capillary rise is inversely proportional to the radius of the tube. The capillary rise of water in a 1-mm. tube at various temperatures is usually available in tables.
of physical constants, and the rise in a tube of different radius is calculated by this relationship. The figures given in Landolt-Börnstein’s Physikalisch-Chemische Tabellen for water at several temperatures that are of interest in this work are tabulated in Table 4, together with the calculated rise in tubes of smaller radius.

**Table 4.—Capillary rise of water**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Capillary rise of 1 mm. radius</th>
<th>Calculated ( h ) for tubes of radius—</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Mm. )</td>
<td>0.05 mm.</td>
</tr>
<tr>
<td>0</td>
<td>15.4084</td>
<td>308.1</td>
</tr>
<tr>
<td>10</td>
<td>15.1922</td>
<td>302.5</td>
</tr>
<tr>
<td>15</td>
<td>14.9528</td>
<td>299.6</td>
</tr>
<tr>
<td>20</td>
<td>14.8420</td>
<td>296.8</td>
</tr>
<tr>
<td>21.8</td>
<td>14.7911</td>
<td>295.8</td>
</tr>
<tr>
<td>25</td>
<td>14.7004</td>
<td>294</td>
</tr>
</tbody>
</table>

From these figures those in Table 5 have been calculated. In Table 5, the values of \( h \) in millimeters (Table 4) have been converted into equivalent pressures in pounds per square inch. As the pressure due to a 1-foot head of water at ordinary temperatures is 0.433 pound per square inch, the pressure due to a head of 1 mm. of water is 0.00142 pound per square inch. At the same time the readings have been converted from the radius of the orifice to the diameter of the orifice. The calculations are for 25° and for 21.8° C, the temperature at which some of our own measurements were made.

**Table 5.—Capillary pressures**

<table>
<thead>
<tr>
<th>Orifice diameter, mm.</th>
<th>Capillary pressure, pounds per square inch</th>
<th>Capillary pressure, pounds per square inch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25° C.</td>
<td>21.8° C.</td>
</tr>
<tr>
<td>0.05</td>
<td>0.850</td>
<td>0.918</td>
</tr>
<tr>
<td>.1</td>
<td>.4175</td>
<td>.459</td>
</tr>
<tr>
<td>.1182</td>
<td>.380</td>
<td>.420</td>
</tr>
</tbody>
</table>

These calculations show how extremely desirable it is to use the largest orifices that will give small bubbles. If an orifice 1 mm. in diameter could be used to form bubbles only 1 mm. in diameter, the pressure necessary to overcome the capillary force would be very small. However, the empirical tests by Maier, which are discussed in another part of this bulletin, showed that the bubbles near 1 mm. in size actually formed from small glass tips were at least 10 times as big as the internal diameter of the tip. Consequently, a pressure of about 0.5 pound per square inch, at least, must be exerted to overcome the resistance due to capillarity.

All the foregoing calculations are for water, but the equation for capillary rise (p. 54) shows that this rise is directly proportional to
the surface tension of the liquid used. Therefore, in solutions containing ferric sulphate and sulphuric acid, which in general have a surface tension slightly higher than that of water and possibly 10 per cent higher as a maximum, the capillary pressure exerted will be somewhat higher; the increased pressure is not large enough to cause material change in the assumptions made, and the friction factors to be taken into account later are so large that this small difference caused by increased surface tension is not important. The reader should note that for our work the instantaneous surface tension—not the tension of an aged surface—is of interest, and this instantaneous tension is much nearer that of water than that of an old surface.

PRESSURE NECESSARY TO OVERCOME FRICTION IN ORIFICE

The friction head in the gas stream varies with the velocity of the gas through the orifice; in general it is low for small velocities and high for high velocities. It is therefore desirable to have many orifices through which the gas enters slowly instead of only a few through which it is driven rapidly. Although there are many formulas given for calculating the flow of air through orifices of various diameters, these formulas have been developed for air discharging into a free space, whereas here the problem involves discharge of air or a gas into water—a heavy viscous medium as compared to that for which most of the formulas have been developed.

Maier's studies of the discharge of air through orifices into water appear later in this bulletin, but data on two of the glass tips studied by him are incorporated in Table 6. The pressures given in the table are those necessary to drive the gas through against the capillary pressure and also against the frictional resistance encountered in and near the orifice.

Table 6.—Discharge of air into water through glass tips

| TIP 16 | Inside diameter of tip, 0.1182 mm.; outside diameter of tip, 0.941 mm.; length, 16.3 mm; submergence, 4.6 cm.; temperature of water, 21.8° C. |
|---|---|---|---|---|---|
| Pressure | Lbs. per square inch | Volume, c. c. per second | Diameter of bubbles, mm. | Remarks |
| Cm. Hg | | | | |
| 2.10 | 2.6 | 3.1 | 4.2 | 6.9 | 8.7 | 12.6 | 16.2 | 27.7 | 39.3 | 47.6 | 56.1 | 0.407 | .693 | .600 | .81 | 1.33 | 1.69 | 2.42 | 3.14 | 7.30 | 7.60 | 9.22 | 10.55 | .00 | .0903 | .0699 | .0875 | .119 | .188 | .281 | .366 | .865 | .922 | 1.06 | 1.20 | 1.65 | 1.55 | 1.04 | 1.16 | 1.36 | 1.91 | 2.17 | 2.46 | 2.78 | 2.80 | 2.85-1.23 | 3.62-1.50 | Static bubbles. Dynamic (air flowing). Turbulent flow. |
Table 6.—Discharge of air into water through glass tips—Continued

TIP 17

[Inside diameter of tip, 0.0355 mm.; outside diameter of tip, 0.564 mm.; length, 15.30 mm.; submergence, 4.1 cm.; temperature of water, 21.0° C.]

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Volume, c.c. per second</th>
<th>Diameter of bubbles, mm.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cm. Hg</td>
<td>Lbs. per square inch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.6</td>
<td>1.28</td>
<td>0.00186</td>
<td>1.35</td>
</tr>
<tr>
<td>25.5</td>
<td>4.94</td>
<td>.00916</td>
<td>1.10</td>
</tr>
<tr>
<td>26.2</td>
<td>5.07</td>
<td>.00896</td>
<td>1.06</td>
</tr>
<tr>
<td>35.9</td>
<td>6.93</td>
<td>.0141</td>
<td>1.06</td>
</tr>
<tr>
<td>53</td>
<td>6.97</td>
<td>.0133</td>
<td>1.05</td>
</tr>
<tr>
<td>59.9</td>
<td>10.25</td>
<td>.0193</td>
<td>1.10</td>
</tr>
<tr>
<td>60.3</td>
<td>11.67</td>
<td>.0221</td>
<td>1.11</td>
</tr>
<tr>
<td>60.7</td>
<td>11.75</td>
<td>.0199</td>
<td>1.13</td>
</tr>
<tr>
<td>71.5</td>
<td>13.53</td>
<td>.0264</td>
<td>1.18-0.93</td>
</tr>
<tr>
<td>85.5</td>
<td>16.15</td>
<td>.0330</td>
<td>1.24-1.90</td>
</tr>
</tbody>
</table>

From the preceding figures for total pressure, which have been corrected to eliminate the hydraulic or static head, one can deduce the capillary pressure. For tip No. 16 the capillary pressure is 0.420 pound per square inch, and for tip 17 it is 1.177 pounds per square inch, provided the temperature and diameter of orifice are correctly given. These two figures check reasonably near the pressure necessary to blow a static bubble on the end of each tip, as shown in the table. The diameters were measured with a micrometer eyepiece in a microscope and are the mean of the measurements taken. Neither orifice was perfectly circular.

The figures illustrate one point observed by Maier, that the use of a tip much less than 0.1 mm. in diameter is hardly justified by the size of bubbles obtained, and the friction head mounts rapidly with decreasing size of orifice. Also, the size of bubble varies with the velocity through the orifice and consequently with the pressure necessary to drive the gas through. A minimum size of bubble was obtained for the 0.1182-mm. orifice with a pressure of 0.6 pound per square inch; for all other pressures the average size of bubble was larger. The reason for this effect was not clear at first, but the following explanation is probably very nearly true. To make the largest bubble, the gas must be blown in slowly in order to avoid shaking off the bubble before it has enough buoyancy to overcome the surface tension of the liquid and break away from the tip. Consequently, as the velocity of the gas through the orifice increases, the size of the bubbles released diminishes. This relation does not continue indefinitely, because at higher velocities a point is reached where the inertia of the water (viscosity) is such that a bubble will be blown rapidly to a definite size before the water gets completely out of the way, and in consequence the bubble space is filled with
partly compressed gas. As the bubble moves upward in the liquid, this pressure is released during the first few intervals of time, and the bubble expands considerably. Maier learned this by photographing bubbles being blown from tips. He photographed tip 16 and tip 17 (Table 6) when bubbles were escaping under a series of pressures.

Calculated on the basis of the gas rate of 0.0629 c. c. per second, which corresponds to the optimum pressure 0.6 pound per square inch observed by Maier for tip 16, the rate of discharge of the orifice is 3.78 c. c. of air per minute. If a perforated diaphragm is to be used for aerating the solution and the orifices are to have the same size as those in tip 16, the closeness of spacing of the holes in the diaphragm over the bottom of the tank being aerated becomes of interest. As has already been pointed out, a 10-foot (300-cm.) column of liquid is needed, and if this column contains one liter and is to be aerated with 500 to 1,500 c. c. of gas per minute, the column will have a cross section of 3.33 sq. cm. and must contain at least \( \frac{5}{3.78} = 132 \) orifices, or 11.5 orifices per linear distance of 1.83 cm., or the spacing is 1.6 mm. apart. As each orifice is only 0.1182 mm. in diameter, this spacing is not physically impossible. If the maximum gas rate of 1,500 c. c. per minute is to be maintained, the spacing of the holes must be 0.92 mm. With fabrics like canvas or perforated rubber sheet, this requirement is not at all difficult.

**TOTAL PRESSURE**

For the conditions chosen—namely, 10-foot head of liquid and 0.1182-mm. holes to form bubbles about 1 mm. in diameter at 21.8° C.—when 500 c. c. of gas passes through each liter of solution in one minute (3.78 c. c. of gas per orifice), the total pressure is involved as follows:

<table>
<thead>
<tr>
<th>Kind of pressure:</th>
<th>Pounds per square inch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrostatic</td>
<td>4.33</td>
</tr>
<tr>
<td>Capillary</td>
<td>0.42</td>
</tr>
<tr>
<td>Kinetic</td>
<td>0.18</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4.93</strong></td>
</tr>
</tbody>
</table>

If the diaphragm is not chosen carefully and air is not passed through each orifice at the best relative velocity to form small bubbles, the kinetic pressure can easily be 10 pounds instead of 0.18 pound per square inch. The design of the diaphragm is therefore of paramount importance in getting a low pressure. Whereas a cheap cycloidal blower will give, with fair efficiency, the 4.93 pounds of pressure above determined for pressure greater than about 6 pounds per square inch, only a more costly blowing engine will function satisfactorily.
DESIGN OF DIAPHRAGM

A great many porous acid-proof materials have been tested for diaphragms. One of the best materials yet tried is perforated sheet rubber; it can be pierced with needles and seems to give smaller bubbles for a definite pressure than the rigid diaphragms, but on long contact with solutions containing sulphur dioxide it hardens and weakens. When air alone is blown through it and the sulphur dioxide is absorbed separately, sheet rubber has a reasonable life.

Canvas of the type commonly used for the bottoms of flotation cells gives bubbles somewhat larger than the desired size. The openings between the threads seem small enough, and there are enough openings to give the desired space velocity, but by looking at a canvas diaphragm operating within a glass tank one can see that individual bubbles do not form over each opening in the canvas; frequently many bubbles coalesce during formation and two or more openings blow into a single larger bubble. Some way of spacing the openings of canvas or other cloth farther apart without making the openings larger is therefore desirable.

Thin sheet lead can be penetrated by needles, but the holes are somewhat too large. Work needs to be done in preparing sheet lead with closely spaced holes and then rolling it thinner in order to decrease the diameter of the holes to the desirable proportion without increasing the spacing of the holes too much.

Screens of acid-resistant wire cloth might also be rolled out in order to decrease their orifice diameters and increase the spacing between the orifices.

In studying the spacing of the orifices necessary to prevent coalescence Maier used a glass-sided cell, in which glass capillaries were placed side by side and spaced differently. He found that the spacing should be about ten times the orifice diameter, a finding that coincides with his observation that the bubble diameters are about ten times the size of the opening. Evidently serious coalescence does not happen at this spacing because not all the bubbles form at the same moment from the contiguous openings—a large bubble is being released at an opening while a small bubble is just beginning to form at one adjacent.

The problem of finding a satisfactory diaphragm is therefore only in course of solution, although results of commercial value have been collected with diaphragms at present known and tested.

POWER EXPENDED IN COMPRESSING GAS

From data collected from numerous sources, such as the blowing engines in smelting plants and the blowers for flotation cells, the curves in Figure 36 have been drawn in order that an estimate could be
gained of the necessary amount of power as a function of the pressure to which the gas would need to be compressed. The conclusion is that the gas should be used at as low pressure as possible, and the use of a blower, as suggested earlier, with a total pressure not to exceed 5 pounds per square inch is greatly to be preferred.

In most of the mining districts of the Southwest power can be generated by the use of Diesel engines for about 1 cent per kilowatt-hour, and very few mining districts can get power for less than 2 cents per kilowatt-hour. If the sulphur dioxide is to be absorbed separately and the solution aerated with air alone, we can gain an idea of the power cost per pound of iron oxidized or per pound of sulphuric acid formed. By referring to Table 2 and the gas volumes

![Figure 36.—Power requirements for air supply](image)

given for an average locality like Douglas, Ariz., one sees that each pound of iron requires about 75 cubic feet, and each pound of sulphuric acid requires about 45 cubic feet of free air. As power at Douglas costs close to 1 cent per kilowatt-hour, the power charge for air will be about 0.034 kilowatt-hour per pound of iron oxidized or 0.02 kilowatt-hour per pound of sulphuric acid, which is also the rate in cents per pound of iron or of sulphuric acid. This rate is far from being unfavorable.

To gain an idea of the power requirements for a copper-leaching plant that is to use leaching solution made by this method, assume that the ore contains 2 per cent Cu and acid-consuming constituents equivalent to about half the acid consumption of the copper alone.
This means that about 2 pounds of sulphuric acid would be needed per pound of copper if the latter were present as carbonate. If the copper were present as chalcocite, a sulphide, sulphuric acid would not be an efficient leaching agent and ferric sulphate would be needed in amounts of 2.5 to 3 pounds per pound of copper. As ferric sulphate requires more power than sulphuric acid, we will assume that all the copper will require ferric sulphate to render it soluble. At a plant treating 1,000 tons of 2 per cent copper ore daily, 40,000 pounds of copper must be rendered soluble, requiring at least 100,000 pounds of ferric iron in the solutions, and this corresponds to the expenditure of 3,400 kilowatt-hours, or a continuous 24-hour requirement of 142 kilowatts. Compared to the power necessary to crush and convey the ore, this amount is very small. It can be reduced to the general unit of about 3.5 kilowatts of motor drive for the air blower for every 1,000 pounds of copper leached in 24 hours. For ores with virtually no impurities that consume acid or ferric sulphate the unit figure would be nearer 3 kilowatts, and for relatively impure ores the consumption of power would mount proportionately.

The total power consumption at a plant of this type cannot be estimated until the design of the plant has been prepared, but the estimate given should cover the major part of the power consumed in making either sulphuric acid or ferric sulphate.

**FORM OF COMMERCIAL APPARATUS**

No attempt will be made here to describe commercial apparatus for carrying out the process as outlined in this paper. We have shown the fundamental requirements of the chemical reactions involved and have discussed the general type of mechanical apparatus needed. Maier, in the chapter that follows, discusses the means of forming small bubbles with a minimum power expenditure, and his conclusions should be considered coincidently with those given in this bulletin when the design of commercial apparatus is undertaken.

A future report will consider the whole question of apparatus for use on a commercial scale.
PRODUCING SMALL BUBBLES OF GAS IN LIQUIDS BY
SUBMERGED ORIFICES

By Charles G. Maier

INTRODUCTION

NEED FOR INVESTIGATION

The physical and mechanical factors that determine the size of the
gas bubbles produced in liquids by submerged orifices are not immedi-
ately or obviously predictable in any quantitative sense. One phase
of the fundamental work that the Bureau of Mines did at the South-
west experiment station, Tucson, Ariz., and the Pacific experiment
station, Berkeley, Calif., to determine the best conditions under
which the mutually catalytic autoxidation of solutions containing
ferrous sulphate and sulphur dioxide might be carried out, showed the
need of data on bubbles. The tests made demonstrated that rapid
oxidation and a relatively high efficiency of oxygen absorption were
more easily obtained by bubbling air and sulphur dioxide through
suitable iron solutions than by spraying solutions through the gases.

BUBBLES VERSUS MIST

Although experiments seemed to show that almost any size of gas
bubble blown through a solution gave more efficient oxidation than
even a very fine spray of the solution in a similar gas, ease of oxida-
tion and maximum utilization of the gas were obtained only when
the bubbles were rather small. In general, the desirable range of
bubble size for autoxidation is smaller than that ordinarily pro-
duced by technically well-developed froth-flotation devices, whether
of the porous bottom or agitator type.

Whether the most practical type of aerator for chemical purposes
will eventually turn out to be an improved flotation unit somewhat
like machines now in use for concentrating ores, or whether a funda-
mentally different type of aerator based on the principles discussed
in this report will eventually prove better, is still uncertain. Tests
on a largerscale than those the author could undertake will be required.
Such work is being done at the Southwest (Tucson) experiment
station of the bureau. The experiments described in this report
show clearly, however, that certain fundamental principles must be
followed if bubbles of minimum size are to be produced with least expenditure of power.

SCOPE OF THE WORK

In order that the results of the experimental work might not be entirely empirical, and possibly un reproducible in practice, it seemed necessary to consider in detail the theoretical analysis of the problem of bubble formation from submerged orifices. The considerations embodied under the heading "Theoretical analysis" are an abridged and simplified version of the original analysis, which was made before experimental work began.

Before the size of the bubbles produced under varying conditions could be measured it was necessary to find suitable measuring devices and methods. Five methods, of varying degrees of usefulness, were tried; they are described in some detail in the section on "Methods of determining the size of bubbles."

The subsequent experiments on the determination of actual bubble sizes are only in part to be regarded as checks on the accuracy of the theories developed. Although the first part of the experiments was done largely with the intent of checking the theories, the last part was almost wholly an attempt to produce smaller bubbles through larger orifices. As far as the laboratory work is concerned this attempt was successful.

THEORETICAL ANALYSIS OF THE PROBLEM

TATE'S LAWS—WORK OF LATER INVESTIGATORS

The first way to attack the theoretical prediction of bubble size might seem to be by recalculating Tate's laws for liquids dropping from capillary tips, in order to include the buoyant effect of gas bubbles rising in a liquid medium. Tate's laws seem to have been questioned by subsequent investigators; for example, Guye and Perrot say, in effect, that the laws of Tate are not general laws and even for static (slowly forming) droplets represent only first approximations.

Much of the subsequent work on Tate's laws had as its primary purpose the determination of surface tension by the drop-weight method, and an inaccuracy of 5 per cent, for example, though perhaps a heinous fault for scientific work, would be entirely adequate here. Consequently, the work of Morgan and coworkers, Harkins and coworkers, and Löhnhstein can be considered here as adequately pertinent to our needs.

1 Tate, T., On the magnitude of a drop of liquid formed under different circumstances: Phil. Mag., 4th ser., vol. 27, 1894, p. 176.
Despite the apparent discrepancies noted by previous workers, Morgan and Stevenson\(^3\) concluded from a somewhat extensive series of experiments that the laws of Tate are true if the proper form of tip is used. They point out that the usual form in which Tate's laws are generalized is

\[
W = 2\pi r \gamma
\]

where \(W\) is the weight\(^3\) of the drop, \(r\) the radius of the tip on which it forms, and \(\gamma\) the surface tension of the liquid; but this form does not in reality express Tate's results, which imply only that

\[W = K_1 \gamma D\]

where \(K_1\) is, in general, some empirical constant that is not necessarily equivalent to the circumference of contact.

Morgan's experimental work enabled a fairly accurate estimate to be made of the three portions of actual drops, namely, the pendant or total drop before rupture, the falling or free drop, and the clinging or remaining drop. Table 1 (Morgan's)\(^4\) shows the value of \(\frac{W}{\gamma} = K\) for nine liquids, where the surface tension ranged from 16.8 to 70.6 dynes per centimeter, as follows:

\[
\begin{align*}
K_{P.D.} \text{ (average nine liquids)} &= 1.94 \pm 0.10 \\
K_{F.D.} &= 1.248 \pm 0.012 \\
K_{C.D.} &= 0.68 \pm 0.071
\end{align*}
\]

For subsequent work Morgan used only the falling drop because of its superior constancy.

If one calculates the theoretical value of \(K\), from the expression (using the given tip diameter, 0.622 cm.)

\[
\frac{W_{\text{mer.}}}{\gamma_{\text{dynes}}} \times \frac{981}{1,000} = \left(\frac{W}{\gamma}\right)_{\text{C.G.S. units}} = K_{\text{(Morgan)}} \times \frac{981}{1,000} = \pi D
\]

\[
K_{\text{Morgan}} = \pi D \times \frac{1,000}{981}
\]

\[
= 3.142 \times 0.622 \times \frac{1,000}{981}
\]

\[= 1.99\]

From this it seems that Morgan's pendant drop, though not as constant as the falling drop he used in his subsequent work, does, in fact, agree fairly well with the theoretical value of contact surface tension.

On this basis

\[
\begin{align*}
K_{F.D.} &= \frac{1.94}{1.99} = 97.5 \text{ per cent of theoretical} \\
K_{F.D.} &= \frac{1.25}{1.99} = 62.7 \text{ per cent of theoretical} \\
K_{C.D.} &= \frac{0.68}{1.99} = 34.1 \text{ per cent of theoretical}
\end{align*}
\]


The slight discrepancy noted, in that
\[ K_{F,D} + K_{C,D} \pm K_{F,D}, \]
may perhaps be ascribed to experimental error.

Morgan's work, though furnishing excellent experimental values, was ultimately faulty because he considered all drops to have the same shape and to break up with constant ratios. A previous theoretical analysis of Löhnstein,\(^6\) which is too highly mathematical to be intelligible to the ordinary reader, indicated that the weight of a drop is given by the expression
\[ W = Mg = 2\pi r\gamma f\left(\frac{r}{a}\right) \]
where \(a\) is the square root of the capillary constant, \(a^2\). The value of the function \(f\left(\frac{r}{a}\right)\), which corresponds perhaps to 0.627 in Morgan's work, is not in general constant as Morgan supposed, but may vary from about 0.5 to nearly unity. Values may be deduced from the theoretical differential equations of the shape of a drop, equations that are integrable only by mechanical methods or by approximation.

Harkins and Brown\(^6\) have shown that Löhnstein's fundamental equation is indeed usable, but that the value of \(f\left(\frac{r}{a}\right)\) is best determined experimentally by tests with materials of known properties, as the theoretical values calculated by approximate integration are somewhat in error. Without the cumbersome mathematics of Löhnstein it is also possible to define the weight as
\[ W = Mg = 2\pi r\gamma \psi\left(\frac{r}{\sqrt[3]{v}}\right) (v \text{ is the volume of the drop}) \]
where \(\psi\left(\frac{r}{\sqrt[3]{v}}\right)\) is equivalent and equal to \(f\left(\frac{r}{a}\right)\).

Inasmuch as \(v\) leads to implicit relationships in our work, whereas \(a\) is determinable from external data, the latter form only is of interest here. Harkins and Brown show tables and curves for the variation of the value of \(f\left(\frac{r}{a}\right)\) versus \(\frac{r}{a}\), from a number of tips, which are reproduced in Figures 37, 38, 39, and 40.

The reader should note that this work all implies perfect wetting of the tip by the liquid; that is, a zero contact angle.


\(^6\) Harkins, W. D., and Brown, F. E., The determination of surface tension (free surface energy) and the weight of falling drops; the surface tension of water and benzene by the capillary height method: Jour. Am. Chem. Soc., vol. 41, 1919, p. 499.
Figure 37.—Surface-tension correction curves, reproduced from Figure 3a of Harkins and Brown's paper: a, $\phi \left( \frac{L}{V_1} \right)$; b, Löhnein; c, $f \left( \frac{L}{a} \right)$; d, Morgan's correction.

Figure 38.—Drop-weight correction curve, reproduced from Figure 3b of Harkins and Brown's paper: Curve is a composite of points on water from glass, benzene from glass, and water from brass.
Figure 39.—Drop-weight correction curve of Harkins and Brown, with Raleigh's data to illustrate the disadvantages in the use of open thin-walled tubes. Crosses are Raleigh's data on water from open tubes. Circles are Raleigh's data on water from metal tips. The curve is reproduced from Figure 4 of Harkins and Brown's paper.

Figure 40.—Drop-weight corrections, reproduced from Harkins and Brown's paper. The curve is a composite from data on water from glass, benzene from glass, and water from brass.
### Classification of Bubbles

On the basis of this classical work it seems fairly safe to develop a probable theoretical relationship for ascending bubbles. An analysis might be preceded by the following classification of methods of forming bubbles at orifices:

**Methods of forming bubbles**

<table>
<thead>
<tr>
<th>Class I.—Bubbles ruptured by buoyant effects only</th>
<th>Class II.—Bubbles ruptured by forces having resultants in the direction of gas flow</th>
<th>Class III.—Bubbles ruptured by forces having resultants at an angle to the gas flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Static bubbles at low gas velocity.</td>
<td>A. Bubbles with nonturbulent gas flow. (1) Modification of static bubbles by impact effects, (2) modification of static bubbles by viscosity effects, (3) modification of static bubbles by friction effects, (4) modification of static bubbles by liquid momentum effects. B. Bubbles with turbulent gas flow.</td>
<td>A. Disruptive gas jets. B. Bubbles ruptured by shearing forces.</td>
</tr>
</tbody>
</table>

In the table of classification of bubbles, classes I A and II A (1), (2) are capable of relatively simple mathematical analysis. Class II A (3) can be discussed only in a qualitative way because of the lack of data on the frictional forces and the slippage at the gas-liquid surfaces. Classes II B and III A are incapable of simple mathematical analysis but are discussed on the basis of photographic results. Class III B has been investigated in an entirely empirical manner.

**Class I A: Pure static bubbles.**—As the first step in analysis the bubble may be considered to form so slowly that the buoyant effect can be equated against the surface tension forces tending to hold the bubble to the tip.

In this equation let

\[ R = \text{radius of free bubble (assumed spherical at instant of rupture) in centimeters}; \]
\[ r = \text{radius of tip (assumed to be circular in cross section) in centimeters}; \]
\[ \gamma = \text{surface tension of liquid, dynes per square centimeter}; \]
\[ \delta = \text{difference in density of liquid and gas (for our purpose the density of the liquid represents the difference accurately enough)}; \]
\[ g = \text{acceleration of gravity}; \]
\[ a = \sqrt{\text{capillary constant}, \left( a^2 = \frac{2\gamma}{\delta g} \right)}; \]
\[ \theta = \text{contact angle of gas, liquid, jet; for perfect wetting} = 0^\circ. \]

Obviously the buoyant effect in grams is

\[ \text{Buoyant effect} = \frac{4}{3} \pi R^3 \delta \]

---

7 This assumption is justified in some cases, as discussed later.

8 We shall not specify here whether this is actually the internal or external diameter of the tip. With falling drops of liquid in air it is obviously the external, but there is no a priori method of predicting which of these must be used under our conditions. One purpose of our experimental work was incidentally to elucidate this question.
The restraining force of surface tension at the time of rupture should be

\[
\text{Restraining force} = 2 \pi r \gamma (\cos \theta) f \left( \frac{r}{a} \right), \quad \text{in dynes}
\]

\[
= \frac{2 \pi r \gamma}{g} (\cos \theta) f \left( \frac{r}{a} \right), \quad \text{in grams}
\]

Equating we have for the static bubble

\[
\frac{4}{3} \pi R^3 \delta = \frac{2 \pi r \gamma}{g} (\cos \theta) f \left( \frac{r}{a} \right)
\]

(1)

For an ideal bubble, with perfect wetting \( \theta \) is zero degrees, and perfect spherical shape implies a shape factor of unity, so we may simplify with

\[
R = \sqrt[3]{\frac{3 \pi r \gamma}{2 \delta g}}
\]

\[
= 0.115 \sqrt[3]{\frac{r \gamma}{\delta}}
\]

(2)

If the liquid be water at 20°, this is further

\[
R = 0.115 \sqrt[3]{r}
\]

\[
R = 0.48 \sqrt[3]{r}
\]

(Note.—\( R \) and \( r \) must be expressed in centimeters.)

(2a)

or \( r = 9.05R^3 \) (b)

(2b)

Furthermore, a form in which we shall use equation (1) will be to calculate the "shape factor" of a bubble, equivalent to Morgan's 62.7 per cent theoretical.

\[
\frac{\text{Volume free bubble}}{\text{Volume ideal bubble}} = f \left( \frac{r}{a} \right) = \frac{2 R^3 \delta g}{3r \gamma}
\]

(3)

\( \theta \) is assumed to be zero degrees.

In view of the attempt made below to apply these formulas to actual measurements, it may be well to restate the assumptions involved, which are not explicitly stated above. These assumptions are as follows:

1. That the volume of the bubble can be adequately expressed by the assumption of spherical shape.

2. That no forces other than pure buoyant effect cause rupture.

3. That the surface tension of an expanding bubble surface is correctly given by formal surface-tension values.

\textit{Class II A: Bubbles with finite gas velocities.}—When the conditions for static or slowly forming bubbles do not hold, the problem of analysis of the various factors influencing bubble size can be solved

---

Example: Suppose 1-mm. bubbles=0.1 cm. are desired.

\( r=9.05 \times 0.1^3 \)

\( = .009 \) cm, approximately, or about \( \frac{1}{10} \) of the bubble size. Compare actual values given under "Experimental results."
only in a qualitative way. At the beginning of this work a number of mathematical formulas were derived, on the basis of simple mechanics, by which it was hoped that the various effects such as impact, viscosity, friction, and liquid momentum could be estimated, at least semiquantitatively. These formulas, although simple in themselves, lead to complex and finally unwieldy formulas for bubble size. Accordingly, this semimathematical speculation is omitted here.

All of these derivations, which are possible in simple mechanical terms, depend on the assumption of a uniform gas velocity in the orifice, and it requires only cursory examination of an actual orifice producing bubbles to realize that the gas velocity is by no means unvarying with time.

In a general way, the tendency for gas impact, friction at the liquid-gas-tip junction, and the effect due to liquid momentum are all of such a nature as to decrease the size of bubble at rupture; they all influence the maximum size to which a bubble may grow before it is released from the material of the orifice. In contrast to these effects, the viscosity of the liquid, and perhaps to a less degree the external friction of the bubble as a whole in its motion through the liquid, cause the pressure of gas inside the bubble at the moment of rupture to be greater than that corresponding to the total hydrostatic head and the pressure due to surface tension only. The net result of these effects is an increase in the size of free bubbles, which takes place within a few hundredths of a second after rupture is effected.

If the mathematical series of formulas, not reproduced here, did not furnish an adequate basis for accurate estimate of bubble size when finite gas velocities were used, they nevertheless enable one to reject certain of the supposed effects as negligible compared to others. For example, the gas impact can be shown to be not greater than twice the value:

\[
\text{Force of impact} = \frac{\pi \varphi^2 D v^2}{g} \left(1 - \frac{v^2}{R^2}\right)
\]  

(4)

where \(D\) is the absolute density of the gas and \(v\) the linear velocity in the orifice, and where the other symbols have the same significance as above. To anticipate somewhat, if a series of actual values be substituted in this formula the possible force of gas impact is found to be only a very small fraction (less than one one-thousandth) of the buoyant effect of a bubble, and therefore negligible.

Without going into further details, consideration of the entire list of hypothetically possible modifying factors that influence the size of bubble, as noted in the classification table, leads to the rejection of all but two as of secondary importance. The two that are of similar magnitude with the forces of buoyancy are (1) the effect of liquid circulation (called liquid-momentum effect) produced by the rapidly ascending stream of bubbles when the gas velocity is appreciable and
(2) the excess pressure or viscosity effect. Without specifying the constants or the exact nature of the functions included, the final equation of bubble size might be expressed as

\[
R_{\text{free}} = \sqrt{3 \left[ \frac{2 \gamma (\cos \theta)}{g \delta} \left( \frac{r}{a} \right) F(\delta, v, R^{-2}) \right] \left[ 1 + F'(\eta, v, R^{-3}) \right]}
\]

(5)

where \( \eta \) is the viscosity of the liquid and the other symbols are as before. The exponent of \( v \) may not be unity.

Such a formula requires that \( R \) go through either a maximum or minimum value. If \( F(\delta, v, R^{-2}) \), which may be called the added disruptive effect due to liquid velocities, increases with \( v \) more rapidly than \( F'(\eta, v, R^{-3}) \) a maximum may occur; conversely, a minimum results.

METHODS OF DETERMINING THE SIZE OF BUBBLES

During the course of these experiments five methods of determining bubble size were tried; they can be designated as (1) method of counting, (2) the bubble burette, (3) photographic determination, (4) conductivity methods, and (5) method based on Stokes's law.

No one of these methods, with the possible exception of the photographic, is usable under all circumstances. Method 5 has very limited utility, the others are seemingly good under certain conditions.

METHOD 1. COUNT

The counting method is adaptable to the determination of average bubble sizes when the gas flows slowly and the aeration is by a single orifice.

Procedure.—The method is the obvious one of catching a counted number of bubbles in some suitable measuring device, and calculating their average diameter from the total volume of gas and the number of the bubbles, which are assumed to be spherical.

Apparatus.—An ordinary burette graduated to 0.05 c. c. provided with a funnel inlet at the open end, as shown in Figure 41, A, was inserted in the liquid and filled by suction through the stopcock. The funnel opening was shifted over the ascending stream of bubbles and the count taken. After a period the total volume of gas was read, and the time was determined with a stop watch. Suitable corrections for the change in pressure due to head of water in the instrument were noted.

Limitations of method.—Trials showed that not more than three bubbles per second could be counted by eye with any degree of accuracy. Moreover, when the tips are large, at low rates of gas flow the bubbles tend to come in doublets, triplets, or quadruplets in such a manner that the total final number of bubbles can only be
guessed. The method is workable, however, for single tips less than 0.1 mm. in internal diameter delivering less than three bubbles per second. Results of the method will be found in the section on "Comparison of theory and experiment."

**METHOD 2. BUBBLE BURETTE**

The bubble-burette method is adaptable to low or moderate rates of bubbling.

*Procedure.*—An apparatus for catching single bubbles seemed capable of furnishing some data when the bubbles produced were of uniform size; it also seemed capable of indicating the extent of actual variation of size under given conditions, when the deviation from an average size was marked.

*Apparatus.*—The bubble burette used consisted of a conical taper tube of glass, about \( \frac{1}{2} \) mm. in inside diameter at the top and 12 to 14 mm. at the bottom and some 20 cm. long (fig. 41, B). Arbitrary millimeter graduations were provided lengthwise of the taper.

The inside was calibrated by inserting round cylindrical steel plugs with squared ends, whose diameters were true and were determined with micrometer calipers, then recording the penetration (millimeters on the scale) in the tube and the diameter of the plug. Results were plotted on a large scale, circular menisci were graphically constructed at suitable intervals, and the top meniscus reading for a bubble of given size was determined from the scaled chart. From these constructions a calibration curve was plotted.

A stopcock attached to the small end of the taper facilitated rapid refilling with liquid after a reading was made. The reading consisted in momentarily shifting the inverted burette over the bubble stream and catching preferably a single bubble. The bubbles rose until just in contact with the glass; then the top of the meniscus was read and the corresponding diameter determined from the calibration curve.

The drawing of accurate glass tapers is discussed in the appendix to this bulletin.
Limitations of method.—Trials demonstrated that with patience and a little practice single bubbles could be caught even when the rate of flow was moderately high. As the bubbles may vary considerably in size, a number of determinations must be made. With low rates of gas flow, reproducible and consistent readings were easily obtained.

The assumption of spherical menisci introduces a certain error, as the bubbles are slightly deformed on touching the glass. The effect is decidedly marked for large bubbles, but the shape of the very small bubbles does not differ markedly from spherical. Instead of the primary calibration, as made above, a secondary calibration, introducing bubbles of known size, determined by some other method, would eliminate this error, but for the purpose in hand the arbitrary calibration was thought sufficient.

To assure minimum deformation of bubbles, the glass must be perfectly clean and free from oil or grease, so that the angle of contact with the liquid is zero. Results of the experiments are given on later pages under "Comparison of theory and experiment."

METHOD 3. PHOTOGRAPHY

With the best photographic equipment the photographic method is adaptable to nearly all conditions of aeration, but even with simple photographic equipment it is widely useful.

Procedure.—For photographing under a magnification of a few diameters an ordinary camera lens and shutter can be used by increasing the focal length and bringing the subject to be photographed within a few inches of the lens. By photographing a standard scale under the same focal conditions the actual bubble size is easily determinable.

Apparatus.—A small bubble cell, with plane parallel windows, was constructed, as shown in Figure 42. An ordinary anastigmat lens, F 6.3, was removed from the original camera and attached to a homemade camera having a fixed focal length of 24 inches, as shown in Figure 43. The shutter attached to the lens had a maximum speed of one three-hundredths second. A focal plane shutter would have been better.
but was not necessary. Reference to the photographs shows that although the bubbles moved while being photographed the image distortion due to motion in one three-hundredth second did not seriously interfere with the determination of diameter. Accessory apparatus for illumination consisted of a small electric arc light with condenser lens, as shown in Figure 43. Photographs and desired bubble diameters for various tips are shown in the section headed "Comparison of theory and experiment."

**METHOD 4. ELECTRICAL CONDUCTIVITY**

The conductivity method is usable for bubbles of a certain size with respect to the apparatus but is not recommended as a method for use when bubbles of uniform size are not produced.

*Theory and procedure.*—Bubbles ascending a long narrow cylinder increase the electrical resistance of a conductive liquid contained therein. The increase of resistance is, in general, affected by these factors: (1) The total volume of gas contained, (2) the distribution of bubbles, and (3) the average size of bubbles.

If the distribution be at all times uniform, factor (2) becomes constant, and the final resistance of the column is a function of but two variables—the total volume of contained gas and the average size of the bubbles. The volume of contained gas is determinable by the rise of the liquid in the cylinder, and a measurement of the resistance should determine the size of the bubbles. Calibration is, of course, necessary.

Methods of calibration of a conductivity bubble meter may be either empirical or theoretical. Data on empirical calibration are given in the appendix; only the principles by which calibration curves may be constructed from the spatial dimensions of an apparatus are given here.

*Mathematical derivation of calibration curves.*—For a cylindrical tube of uniform cross section, through which spherical nonconduct-
ing shapes are passing or are at rest, the notation adopted is as follows:

\[ R_e = \text{radius of cylindrical cross section} \]
\[ r_{nc} = \text{radius of spherical nonconductors} \]
\[ L = \text{distance between electrodes} \]
\[ \xi = \text{specific resistance of liquid in cylinder} \]
\[ \Delta \nu = \text{volume of spheres between electrodes} \]
\[ B_o = \text{electrical resistance between electrodes without spheres} \]
\[ B_1 = \text{electrical resistance between electrodes containing a volume, } \Delta \nu, \text{ of spheres} \]
\[ N = \text{number of spheres between electrodes} \]
\[ x = \text{as per diagram (fig. 44).} \]

![Diagram of differential quantities used in conductivity method: a, Cylinder, conducting; b, Sphere, nonconducting](image)

**Figure 44.**—Diagram of differential quantities used in conductivity method: a, Cylinder, conducting; b, Sphere, nonconducting 

The conducting area of the differential shell between the cylinder and sphere is

\[ \text{Conducting area} = \pi R_e^2 - \pi (r_{nc}^2 - x^2) \]

The electrical resistance of the differential conductor is

\[
\text{Differential resistance} = \frac{\xi dx}{\pi (\sqrt{R_e^2 - r_{nc}^2} + x)^2}
\]

Let \( A^2 = R_e^2 - r_{nc}^2 \)

The resistance of a section of cylinder of length \( 2r \), containing the sphere, is, by symmetry

\[
\text{Resistance of section} = \frac{2\xi}{\pi} \int_0^{r_{nc}} \frac{dx}{A^2 + x^2} = \frac{2\xi}{\pi} \left[ \tan^{-1} \frac{x}{A} \right]_0^{r_{nc}}
\]

\[
= \frac{2\xi}{\pi} \sqrt{R_e^2 - r_{nc}^2} \tan^{-1} \frac{r_{nc}}{\sqrt{R_e^2 - r_{nc}^2}}
\]

Now

\[
\frac{4}{3} \pi r_{nc}^2 N = \Delta \nu, \text{ and } N = \frac{3\Delta \nu}{4\pi r_{nc}^3}
\]

Adding obstructed and unobstructed sections of the tube

\[
B_1 = \frac{\xi (L - 2N r_{nc})}{\pi R_e^2} + \frac{2\xi N}{\pi \sqrt{R_e^2 - r_{nc}^2}} \tan^{-1} \frac{r_{nc}}{\sqrt{R_e^2 - r_{nc}^2}}
\]

Eliminating \( N \), by substitution of (3) in (4)

\[
B = \frac{\xi (L - \frac{6\Delta \nu}{4\pi r_{nc}^3})}{\pi R_e^2} + \frac{6\xi \Delta \nu}{4\pi r_{nc}^3} \tan^{-1} \frac{r_{nc}}{\sqrt{R_e^2 - r_{nc}^2}}
\]

23912°—27—6
From our condition without spheres

\[ B_o = \frac{\xi L}{\pi R^2_e} \quad \text{and} \quad \xi = \frac{\pi R^2_e B_o}{L} \]  

(6)

Substituting (6) in (5) to eliminate \( \xi \)

\[ \frac{\pi R^2_e B_o}{L} \left( \frac{L - 3\Delta v}{2\pi r^2_{nc}L} \right) + \frac{3\pi R^2_e B_o \Delta v}{2L\pi r^3_{nc}} \tan^{-1} \frac{r_{nc}}{\sqrt{R^2_e - r^2_{nc}}} = B_1 \]

Simplifying

\[ B_o \left( 1 - \frac{3\Delta v}{2\pi r^2_{nc}L} \right) + \frac{3\pi R^2_e B_o \Delta v}{2L\pi r^3_{nc} \sqrt{R^2_e - r^2_{nc}}} \tan^{-1} \frac{r_{nc}}{\sqrt{R^2_e - r^2_{nc}}} = B_1 \]

But \( B_1 - B_o = \Delta B = \text{change in resistance due to spheres, making this substitution, and solving for} \ \frac{\Delta B}{B_o} \) (the fractional change of resistance, due to spheres).

\[ \frac{\Delta B}{B_o} = \frac{3\Delta v}{2\pi r^2_{nc}L} \left( \frac{R^2_e}{r_{nc} \sqrt{R^2_e - r^2_{nc}}} \tan^{-1} \frac{r_{nc}}{\sqrt{R^2_e - r^2_{nc}}} - 1 \right) \]  

(7)

Now the values of \( \frac{\Delta B}{B_o} \) and \( \Delta v \) are experimentally determinable quantities, \( R_e \) and \( L \) are fixed by the size of apparatus used, and \( r_{nc} \) is what we wish to determine. The analytic solution of equation (7) for \( r_{nc} \) is too intricate for practical purposes, so that graphic methods must be used. Note that

\[ \frac{\partial}{\partial \Delta v} \left( \frac{\Delta B}{B_o} \right) = \frac{3}{2\pi r^2_{nc}L} \left( \frac{R^2_e}{r_{nc} \sqrt{R^2_e - r^2_{nc}}} \tan^{-1} \frac{r_{nc}}{\sqrt{R^2_e - r^2_{nc}}} - 1 \right) \]  

(8)

where \( \frac{\partial}{\partial \Delta v} \left( \frac{\Delta B}{B_o} \right) \) is the slope of the curve obtained by plotting \( \frac{\Delta B}{B_o} \) against \( \Delta v \). Since \( \Delta B \) is zero when \( \Delta v \) is zero, the curve starts from the origin of coordinates. For a given value of \( R_e \) and \( L \) and a definite size sphere \( r_{nc} \), the plot must be a straight line. A number of these isoradic lines may be constructed, each for a given assumed value of \( r_{nc} \), as in Figure 45.

From Figure 45 we may interpolate for values of \( \frac{\Delta B}{B_o} \) for a number of assumed values of \( \Delta v \), that is, \( \Delta v_1, \Delta v_2 \), and make a new series of curves (fig. 46) from these data, plotting isovolume curves \( \frac{\Delta B}{B_o} \) against \( r_{nc} \).
These latter curves are the calibration curves proper for any piece of apparatus.

Apparatus.—Glass cylinders of suitable size (see appendix) were provided with fixed platinum-ring electrodes near the top and bottom and filled with suitably conductive solutions of dilute electrolyte (sulphuric acid). Resistance was determined by passing a small alternating current from a lighting main, using an external series rheostat for regulation, reading the current with an a. c. milliammeter and the voltage across the electrodes with a high-resistance volt-

\[
\left[ \frac{\partial (L B)}{\partial (\Delta v)} \right]_v = \frac{3}{2\pi r_1 L} \left[ \frac{r_3}{r_1 \sqrt{R^2 - r_1^2}} \tan^{-1} \frac{r_4}{\sqrt{R^2 - r_4^2}} - 1 \right]
\]

Figure 45.—Isoradial lines for preparation of calibration curves. The specific value of

Figure 46.—Isovolume curves from final calibration curves of Figure 45

meter of suitable scale, and then calculating the resistance, unit power factor being assumed.

Limitations of method.—The appendix shows typical results of measurements with the conductivity meter. Here it need only be noted that the change in resistance is a function of the bubble size only when that is large in proportion to the size of the cylinder
used. For very fine bubbles the change of resistance becomes almost exactly an explicit volume function. Moreover, the method inherently requires use only for a uniform formation of bubbles.

**METHOD 5. STOKES’S LAW**

The method that makes use of Stokes’s law is theoretically adaptable to determining average bubble sizes at high rates of aeration, especially when the bubbles are of fairly uniform size.

*Theory.*—Consider a cylindrical tube rather long compared to the cross section, and suppose a constant uniform stream of bubbles to be introduced at the bottom of the tube.

Let $L=$ length of tube  
$a=$ cross sectional area of tube  
$Q=$ rate of flow of gas  
$u=$ mean velocity of bubbles rising in the tube.

The time for a bubble to rise is $\frac{L}{u}$, and the amount of gas in the tube at any time is $\frac{QL}{u}$, but this is also the increase in volume of the liquid-bubble phase, $\Delta v$, which is determinable by noting the rise of liquid if the tube be calibrated. $L$ is, however, a variable equal to $L_o + \frac{\Delta v}{a}$, where $L_o$ is the original length of liquid column before aeration.

In the equation

$$\frac{\left( L_o + \frac{\Delta v}{a} \right)}{u} Q = \Delta v$$

we may solve for $u$

$$u = \frac{\left( L_o + \frac{\Delta v}{a} \right) Q}{\Delta v} \quad (8)$$

Now from Stokes’s law, $u$ should be given at least approximately by the expression

$$u = \frac{\frac{\Delta v}{2}}{g R^2 \delta} \quad (9)$$

where $g$ is the acceleration of gravity, $R$ the radius of the bubble, $\delta$ the difference in density between liquid and bubble, and $K'$ the coefficient of viscosity.

Equating (8) and (9) gives

$$\frac{\left( L_o + \frac{\Delta v}{a} \right) Q}{\Delta v} = \frac{\frac{\Delta v}{2} g R^2 \delta}{K'}$$
in which all factors except $R$ are directly measurable or known quantities.

Solving

$$R = \sqrt{\frac{9K'(L_o + \Delta v)}{2\Delta v} Q}$$  \hspace{1cm} (10)

For experimental purposes we may write this equation

$$R = K_1 \sqrt{\frac{(L_o + \Delta v)}{\Delta v} Q}$$  \hspace{1cm} (11)

**Apparatus.**—Although the foregoing equation seemingly gives $R$ directly from a measurement of $Q$ and $\Delta v$, for any given apparatus, it was thought necessary to check such values against actual values of $R$; that is, to obtain an empirical calibration curve. Stokes’s law in the simple form given is not exactly accurate for all conditions, especially when distortable spheres of gas rise in a rather restricted volume of liquid.

The apparatus used to test equation (11) is shown in Figure 47, where the cell shown in Figure 43 is replaced by a cylinder 15 mm. in diameter by 100 cm. long. The cylinder had a graduated scale at the top and two plane parallel glass windows at the bottom for photographing the bubbles as they left a tip. $Q$ was determined by measuring the overflow from a gas container connected to the top of the cylinder, and small values of $\Delta v$ were determined with a cathetometer.

Experimental results appear in the appendix.

**Limitations of method.**—Reference to the data in the appendix (p. 120) will show that Stokes’s law does not hold for the size or distribution of bubbles that were of interest in this work, instead, the time of rising of bubbles in a liquid column depends largely on the “randomness” of the upward motion. The method is conceivably usable for very minute bubbles in a perfectly quiescent liquid, when not much aeration is involved, but these conditions are not suitable for the purpose in hand.

**COMPARISON OF THEORY AND EXPERIMENT**

**DATA ON BUBBLES PRODUCED BY VARIOUS SUBMERGED ORIFICES**

The experimental data reproduced here are selected from a considerable accumulation and are included in two groups.

The first group deals with tests with a few single glass tips of uniform bore and cylindrical shape, with square ends. Tables 7 to 12 give measurements of pressures, gas velocities, and bubble diameters by the method of count or by the bubble burette.
The second group deals with photographs of bubbles from glass, metal, and rubber tips of miscellaneous shapes and sizes. The complete data, of which the photographs show significant factors,

![Figure 47](image)

*Figure 47.*—Stokes's-law bubble meter: a, Camera and lens; b, microslide cover-glass windows; c, light axis; d, to leveling bottle; e, gas inlet to capillary tip; f, atmospheric outfit; g, water refill inlet; h, air release; o-o, original water level; \( \Delta p \), \( L_0 \), and \( Q \), as in the derivation of formulas

included determination of bubble sizes, pressures, conditions of turbulent flow, and varying factors, such as the effect of the concentration of ferric and ferrous salts and also of sulphuric acid
dissolved in the liquid medium, as well as the effect of temperature on bubble size.

*Early measurements.*—The experiments represented in Tables 9 and 11 were made before the idea of the bubble burette had been developed and so contain only the values obtained by the method of count. With the large tips used counting was very difficult, as has been noted under the discussion of bubble measuring methods. In the experiments represented by Tables 7, 8, and 9 the bubble burette was used, and Tables 7 and 8 permit some comparison, which is discussed more fully on succeeding pages in connection with the comparison with theoretical calculations.

**Table 7.—Bubble characteristics of tip 17**

[Dimensions of tip: Inside diameter, 0.0355 mm.; outside diameter, 0.564 mm.; length of capillary, 15.30 mm.; submergence, 4.1 cm. Water at 21° C.]

**A. STATIC BUBBLES**

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure, cm. Hg</th>
<th>Number of bubbles</th>
<th>Volume of bubbles, c.c.</th>
<th>Time, seconds</th>
<th>Gas rate, c.c. per second</th>
<th>Diameter of bubbles by count, mm.</th>
<th>Diameter of bubbles by bubble burette, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.6</td>
<td>173</td>
<td>0.41</td>
<td>220.7</td>
<td>1.86 x 10^-1</td>
<td>1.65</td>
<td>1.55</td>
</tr>
<tr>
<td>2</td>
<td>10.5</td>
<td>300</td>
<td>0.70</td>
<td>243.6</td>
<td>2.18 x 10^-1</td>
<td>1.84</td>
<td>1.82</td>
</tr>
<tr>
<td>3</td>
<td>10.6</td>
<td>200</td>
<td>0.50</td>
<td>156.7</td>
<td>3.25 x 10^-3</td>
<td>1.89</td>
<td>1.98</td>
</tr>
<tr>
<td>4</td>
<td>15.4</td>
<td>200</td>
<td>0.40</td>
<td>67.8</td>
<td>5.90 x 10^-3</td>
<td>1.59</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>16.1</td>
<td>200</td>
<td>0.40</td>
<td>68.8</td>
<td>5.82 x 10^-3</td>
<td>1.59</td>
<td>1.10</td>
</tr>
</tbody>
</table>

**B. PRESSURE CHARACTERISTIC**

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure, cm. Hg</th>
<th>Volume of bubbles passed, c.c.</th>
<th>Time, seconds</th>
<th>Gas rate, c.c. per second</th>
<th>Diameter of bubbles by bubble burette, mm.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.5</td>
<td>0.50</td>
<td>54.5</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>26.2</td>
<td>0.50</td>
<td>55.9</td>
<td>8.96 x 10^-4</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>26.9</td>
<td>0.50</td>
<td>35.5</td>
<td>1.41 x 10^-3</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>36</td>
<td>0.70</td>
<td>36.2</td>
<td>1.33 x 10^-3</td>
<td>1.08</td>
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</tr>
<tr>
<td>5</td>
<td>53</td>
<td>1.50</td>
<td>68.8</td>
<td>1.98 x 10^-2</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>59.9</td>
<td>1.90</td>
<td>36.2</td>
<td>2.21 x 10^-2</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>60.3</td>
<td>1.80</td>
<td>36.2</td>
<td>1.99 x 10^-2</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>60.7</td>
<td>1.25</td>
<td>63</td>
<td>2.64 x 10^-2</td>
<td>1.14</td>
<td></td>
</tr>
</tbody>
</table>

Maximum  Minimum

| 9   | 71.5             | .80                           | 30.3          | 2.64 x 10^-2             | 1.18                                      | Turbulent flow. |
| 10  | 83.5             | .80                           | 24.2          | 3.30 x 10^-2             | 1.24                                      | Do.            |
### Table 8.—Bubble characteristics of tip 16

[Dimensions of tip: Inside diameter, 0.1182 mm.; outside diameter, 0.941 mm.; length of capillary, 16.30 mm.; submergence, 4.6 cm. Water at 21.8° C.]

#### A. STATIC BUBBLES

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure, cm. Hg</th>
<th>Number of bubbles</th>
<th>Volume of bubbles, c.c.</th>
<th>Time, seconds</th>
<th>Gas rate, c. c. per second</th>
<th>Diameter of bubbles by count, mm.</th>
<th>Diameter of bubbles by bubble burette, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.10</td>
<td>300</td>
<td>1.02</td>
<td>118.7</td>
<td>8.60×10⁻²</td>
<td>1.80</td>
<td>1.65</td>
</tr>
<tr>
<td>2</td>
<td>2.15</td>
<td>300</td>
<td>1.21</td>
<td>104.2</td>
<td>1.16×10⁻²</td>
<td>1.97</td>
<td>1.60</td>
</tr>
<tr>
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<td>2.10</td>
<td>300</td>
<td>1.02</td>
<td>290</td>
<td>3.98×10⁻²</td>
<td>1.86</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>2.10</td>
<td>300</td>
<td>1.39</td>
<td>79.8</td>
<td>1.74×10⁻²</td>
<td>2.05</td>
<td>1.65</td>
</tr>
</tbody>
</table>

#### B. PRESSURE CHARACTERISTIC

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure, cm. Hg</th>
<th>Volume of bubbles passed, c. c.</th>
<th>Time, seconds</th>
<th>Gas rate, c. c. per second</th>
<th>Diameter of bubbles by bubble burette, mm.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.6</td>
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<td>46.6</td>
<td>4.93×10⁻²</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.1</td>
<td>2.30</td>
<td>36.6</td>
<td>6.29×10⁻²</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
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<td>4.2</td>
<td>2.30</td>
<td>26.3</td>
<td>8.73×10⁻²</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
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<td>6.9</td>
<td>5.30</td>
<td>69.7</td>
<td>1.19×10⁻¹</td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8.7</td>
<td>5.30</td>
<td>28.2</td>
<td>1.88×10⁻¹</td>
<td>1.91</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>12.6</td>
<td>8.30</td>
<td>29.5</td>
<td>2.81×10⁻¹</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>16.2</td>
<td>8.30</td>
<td>22.7</td>
<td>3.66×10⁻¹</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>37.7</td>
<td>8.30</td>
<td>9.3</td>
<td>8.93×10⁻¹</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>32.3</td>
<td>8.30</td>
<td>9</td>
<td>2.22×10⁻¹</td>
<td>2.80</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>47.6</td>
<td>8.30</td>
<td>7.5</td>
<td>1.06</td>
<td>2.83</td>
<td>Maximum Minimum</td>
</tr>
<tr>
<td>11</td>
<td>54.1</td>
<td>8.30</td>
<td>6.6</td>
<td>1.26</td>
<td>3.02</td>
<td>Minimum 1.36</td>
</tr>
</tbody>
</table>

### Table 9.—Bubble characteristics of tip 14

[Dimensions of tip: Inside diameter, 0.150 mm.; outside diameter, 1.053 mm.; length of capillary, 16.60 mm.; submergence, 4.3 cm. Water at 20.8° C.]

#### PRESSURE CHARACTERISTIC

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure, cm. Hg</th>
<th>Volume of bubbles passed, c. c.</th>
<th>Time, seconds</th>
<th>Gas rate, c. c. per second</th>
<th>Diameter of bubbles by bubble burette, mm.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7</td>
<td>4.30</td>
<td>61.6</td>
<td>7.05×10⁻²</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.9</td>
<td>8.30</td>
<td>24.2</td>
<td>3.43×10⁻¹</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>11.9</td>
<td>10.30</td>
<td>16.8</td>
<td>6.14×10⁻¹</td>
<td>2.79</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>21.5</td>
<td>10.30</td>
<td>9.5</td>
<td>1.087</td>
<td>3.18</td>
<td>Maximum Minimum</td>
</tr>
<tr>
<td>5</td>
<td>30.5</td>
<td>10.30</td>
<td>6.9</td>
<td>1.492</td>
<td>3.40</td>
<td>1.09</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>10.30</td>
<td>5.5</td>
<td>1.87</td>
<td>1.87</td>
<td></td>
</tr>
</tbody>
</table>

1 The diameters of 13 bubbles, measured in succession at this pressure, were:

<table>
<thead>
<tr>
<th>No.</th>
<th>Diameter, mm.</th>
<th>Volume of bubble, c. c. X 10⁻³</th>
<th>No.</th>
<th>Diameter, mm.</th>
<th>Volume of bubble, c. c. X 10⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.63</td>
<td>2.28</td>
<td>8</td>
<td>2.30</td>
<td>6.40</td>
</tr>
<tr>
<td>2</td>
<td>3.26</td>
<td>18.17</td>
<td>9</td>
<td>3.40</td>
<td>20.65</td>
</tr>
<tr>
<td>3</td>
<td>1.44</td>
<td>1.57</td>
<td>10</td>
<td>1.30</td>
<td>1.16</td>
</tr>
<tr>
<td>4</td>
<td>2.70</td>
<td>10.33</td>
<td>11</td>
<td>3.15</td>
<td>16.43</td>
</tr>
<tr>
<td>5</td>
<td>2.75</td>
<td>10.92</td>
<td>12</td>
<td>2.96</td>
<td>4.7</td>
</tr>
<tr>
<td>6</td>
<td>3.39</td>
<td>18.90</td>
<td>13</td>
<td>1.97</td>
<td>4.01</td>
</tr>
<tr>
<td>7</td>
<td>2.63</td>
<td>9.53</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total volume of 13 bubbles, 120.82 c. c.; equivalent volume per bubble, 9.29 c. c.; equivalent diameter per bubble, 2.61 mm.
### Table 10.—Bubble characteristics of tip 8

[Dimensions of tip: Inside diameter, 0.225 mm.; outside diameter, 2.36 mm.; length of capillary, 16.21 mm.; submergence, 3.9 cm. Water at 20.8° C.]

**PRESSURE CHARACTERISTIC**

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure, cm. Hg</th>
<th>Volume of bubbles, c.c.</th>
<th>Time, seconds</th>
<th>Gas rate, c.c. per second</th>
<th>Diameter of bubbles by bubble burette, mm.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.15</td>
<td>8.30</td>
<td>121.8</td>
<td>6.83 x 10^{-3}</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.30</td>
<td>8.30</td>
<td>52</td>
<td>1.60 x 10^{-3}</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.80</td>
<td>8.30</td>
<td>36.5</td>
<td>2.26 x 10^{-3}</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.20</td>
<td>8.30</td>
<td>23.7</td>
<td>2.89 x 10^{-3}</td>
<td>2.64</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.75</td>
<td>8.30</td>
<td>20.8</td>
<td>3.96 x 10^{-3}</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.55</td>
<td>8.30</td>
<td>15.7</td>
<td>6.28 x 10^{-3}</td>
<td>3.18</td>
<td></td>
</tr>
</tbody>
</table>

Maximum  Minimum

| 3.58 | 0.90 | Turbulent flow. Do. |
| 3.66 | .91  |                        |
| 3.74 | .63  |                        |

### Table 11.—Bubble characteristics of tip 15

[Dimensions of tip: Inside diameter, 0.429 mm.; length of capillary, 16.57 mm.; submergence, 3.5 cm. Water at 22.2° C.]

**STATIC BUBBLES**

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure, cm. Hg</th>
<th>Estimated number of bubbles</th>
<th>Volume of bubbles, c.c.</th>
<th>Time, seconds</th>
<th>Gas rate, c.c. per second</th>
<th>Diameter of bubbles, mm. (estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.60</td>
<td>300</td>
<td>12.8</td>
<td>180</td>
<td>0.077</td>
<td>4.4</td>
</tr>
<tr>
<td>2</td>
<td>.50</td>
<td>500</td>
<td>19.5</td>
<td>244</td>
<td>.080</td>
<td>4.2</td>
</tr>
<tr>
<td>3</td>
<td>.70</td>
<td>600</td>
<td>22.4</td>
<td>105</td>
<td>.214</td>
<td>4.1</td>
</tr>
<tr>
<td>4</td>
<td>1.05</td>
<td>600</td>
<td>21</td>
<td>79</td>
<td>.265</td>
<td>4</td>
</tr>
</tbody>
</table>

*Exact count impossible owing to formation of doublets and triplets. May be 50 to 100 bubbles in error.*

### Table 12.—Bubble characteristics of tip 2

[Dimensions of tip: Inside diameter, 0.695 mm.; length of capillary, 16 mm.]

**STATIC BUBBLES**

<table>
<thead>
<tr>
<th>No.</th>
<th>Pressure, cm. Hg</th>
<th>Estimated number of bubbles</th>
<th>Volume of bubbles, c.c.</th>
<th>Time, seconds</th>
<th>Gas rate, c.c. per second</th>
<th>Diameter of bubbles, mm. (estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>300</td>
<td>18.5</td>
<td>240</td>
<td>0.077</td>
<td>4.9</td>
</tr>
<tr>
<td>2</td>
<td>.50</td>
<td>300</td>
<td>26.2</td>
<td>200</td>
<td>.131</td>
<td>5.5</td>
</tr>
<tr>
<td>3</td>
<td>.50</td>
<td>500</td>
<td>26.8</td>
<td>105</td>
<td>.350</td>
<td>5.2</td>
</tr>
<tr>
<td>4</td>
<td>.50</td>
<td>600</td>
<td>41.2</td>
<td>85</td>
<td>.185</td>
<td>5.1</td>
</tr>
</tbody>
</table>

*Exact count impossible owing to formation of doublets and triplets. May be 50 to 100 bubbles in error.*

Aside from the specific implications of the numerical data to be discussed below, certain general conclusions may be drawn from the data. Especially should the reader note that bubble size is greatly
influenced by gas pressure or the velocity of the gas in the tip. Except under very narrow conditions there is no such thing as a definite bubble size for a given tip, although the effect of varying the conditions is most marked with the larger tips.

The data show that small bubbles produced by simple tip devices require extremely small orifices and, in consequence, higher gas pressures than are economically obtainable by desirable types of blowing engines. Much of the later work was consequently done with the intent of finding, if possible, some clue to methods of producing small bubbles at low gas pressures.

Photographs.—Results of measurements from all the photographs taken are summarized in Tables 13 to 17.

No extended discussion of each photograph will be undertaken, inasmuch as the copies reproduced here are only illustrative. The pictures themselves are intrinsically interesting and certain pertinent general conclusions were drawn from the several hundred that were taken.

Perhaps the most obvious general conclusion to be drawn is that when a perfectly wet material such as glass is used for the tip and the velocity of the gas is low, the bubbles are almost exactly spherical. The stem of the bubble, making contact with the sharp edge of the orifice, is very small indeed.

### Table 13.—Bubble sizes from photographs—square-end glass tips

[Water at about 22° C.]

<table>
<thead>
<tr>
<th>Tip No.</th>
<th>18</th>
<th>17a</th>
<th>16</th>
<th>8</th>
<th>Double</th>
<th>10</th>
<th>Elliptic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inside diameter, mm</td>
<td>0.014</td>
<td>0.032</td>
<td>0.118</td>
<td>0.247</td>
<td>0.279</td>
<td>0.349</td>
<td></td>
</tr>
<tr>
<td>Outside diameter, mm</td>
<td>.25</td>
<td>.58</td>
<td>.94</td>
<td>3.01</td>
<td>.389</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>Length of capillary, mm</td>
<td>12.70</td>
<td>17.27</td>
<td>16.30</td>
<td>16.3</td>
<td>22</td>
<td>16.23</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Photograph series</th>
<th>VII</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>XIV–XV</th>
<th>VI</th>
<th>VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement</td>
<td>Pressure, cm. Hg</td>
<td>Bubble diameter, mm</td>
<td>Pressure, cm. Hg</td>
<td>Diameter, mm</td>
<td>Pressure, cm. Hg</td>
<td>Diameter, mm</td>
<td>Pressure, cm. Hg</td>
</tr>
<tr>
<td>Photograph 1</td>
<td>20.9</td>
<td>13.1</td>
<td>1.07</td>
<td>1.60</td>
<td>0.98</td>
<td>3.10</td>
<td>2</td>
</tr>
<tr>
<td>Photograph 2</td>
<td>22.9</td>
<td>14</td>
<td>1.10</td>
<td>2.5</td>
<td>1.75</td>
<td>1.5</td>
<td>3.05</td>
</tr>
<tr>
<td>Photograph 3</td>
<td>29.7</td>
<td>80</td>
<td>1.12</td>
<td>3.9</td>
<td>1.80</td>
<td>2.1</td>
<td>3.55</td>
</tr>
<tr>
<td>Photograph 4</td>
<td>56.6</td>
<td>93.3</td>
<td>1.15</td>
<td>5.7</td>
<td>1.82</td>
<td>4.4</td>
<td>4.6</td>
</tr>
<tr>
<td>Photograph 5</td>
<td>100.4</td>
<td>129.8</td>
<td>1.05</td>
<td>12.3</td>
<td>2.25</td>
<td>7.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Photograph 6</td>
<td>120.7</td>
<td>92</td>
<td>35.1</td>
<td>(1)</td>
<td>30.1</td>
<td>3.30</td>
<td>1.60</td>
</tr>
<tr>
<td>Estimated static bubble</td>
<td>15.7</td>
<td>90</td>
<td>6.8</td>
<td>1.05</td>
<td>1.8</td>
<td>1.62</td>
<td>.92</td>
</tr>
</tbody>
</table>

4 Attached bubbles only, not full size.

5 Turbulent flow.
### Table 14.—Bubble size from photographs—miscellaneous materials and shapes

<table>
<thead>
<tr>
<th>Tip material</th>
<th>Lead Plate orifice</th>
<th>Lead Monel Plate orifice</th>
<th>Paraffin Plate orifice</th>
<th>Rubber Plate orifice</th>
<th>Glass Diagonal tip</th>
<th>Glass Pointed tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter of capillary, mm</td>
<td>0.244</td>
<td>0.407</td>
<td>0.473</td>
<td>0.125</td>
<td>0.432</td>
<td>0.217</td>
</tr>
<tr>
<td>Length of capillary, mm</td>
<td>1.3</td>
<td>1.3</td>
<td>.270</td>
<td>6 (approx.)</td>
<td>1.70</td>
<td>12 (approx.)</td>
</tr>
</tbody>
</table>

#### Photograph series

<table>
<thead>
<tr>
<th>Measurement</th>
<th>V</th>
<th>IX</th>
<th>X</th>
<th>XI</th>
<th>XIX</th>
<th>XII</th>
<th>XIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, cm. Hg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter, mm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photograph 1</td>
<td>3</td>
<td>4.8</td>
<td>0.7</td>
<td>0.6</td>
<td>3.9</td>
<td>0.55</td>
<td>4.0</td>
</tr>
<tr>
<td>Photograph 2</td>
<td>4.7</td>
<td>5.1</td>
<td>.85</td>
<td>3.75</td>
<td>.7</td>
<td>4.5</td>
<td>.55</td>
</tr>
<tr>
<td>Photograph 3</td>
<td>6</td>
<td>5.8</td>
<td>1.5</td>
<td>3.9</td>
<td>1.4</td>
<td>5.57</td>
<td>3.6</td>
</tr>
<tr>
<td>Photograph 4</td>
<td>7.7</td>
<td>(5)</td>
<td>3.1</td>
<td>4.8</td>
<td>2.6</td>
<td>(6)</td>
<td>8.7</td>
</tr>
<tr>
<td>Photograph 5</td>
<td>9.9</td>
<td>(5)</td>
<td>4.7</td>
<td>4.51</td>
<td>5.8</td>
<td>(3)</td>
<td>15.8</td>
</tr>
<tr>
<td>Photograph 6</td>
<td>11.8</td>
<td>(6)</td>
<td>10</td>
<td>(7)</td>
<td>6.4</td>
<td>4.8</td>
<td>23.9</td>
</tr>
<tr>
<td>Estimated static bubble</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Hole made by needle. Actual hole, without distension, much smaller.
2 Bubble attached.
3 Turbulent flow.
4 Disruptive gas jet.

### Table 15.—Bubble sizes from photographs

**EFFECT OF FeSO₄ CONCENTRATION AT 22° C.**

<table>
<thead>
<tr>
<th>Photograph</th>
<th>Concentration of FeSO₄, molality</th>
<th>Bubble diameter, mm.</th>
<th>Photograph</th>
<th>Concentration of FeSO₄, molality</th>
<th>Bubble diameter, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>2.00</td>
<td>4</td>
<td>1.16</td>
<td>2.05</td>
</tr>
<tr>
<td>2</td>
<td>.50</td>
<td>1.4</td>
<td>5</td>
<td>1.37</td>
<td>1.90</td>
</tr>
<tr>
<td>3</td>
<td>.88</td>
<td>2.10</td>
<td>6</td>
<td>1.53</td>
<td>1.97</td>
</tr>
</tbody>
</table>

1 Bubble attached.

### Table 16.—Bubble sizes from photographs

**EFFECT OF H₂SO₄ AND Fe₂(SO₄)₃**

<table>
<thead>
<tr>
<th>Photograph</th>
<th>Concentration of FeSO₄</th>
<th>H₂SO₄</th>
<th>Fe₂(SO₄)₃</th>
<th>Bubble diameter, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>XVI-1</td>
<td>(5)</td>
<td>(5)</td>
<td>(5)</td>
<td>2.00</td>
</tr>
<tr>
<td>XVII-1</td>
<td>1.53</td>
<td>17.4</td>
<td>.00</td>
<td>1.97</td>
</tr>
<tr>
<td>2</td>
<td>1.43</td>
<td>17.4</td>
<td>.00</td>
<td>1.97</td>
</tr>
<tr>
<td>3</td>
<td>1.29</td>
<td>33.1</td>
<td>.00</td>
<td>1.97</td>
</tr>
<tr>
<td>4</td>
<td>.97</td>
<td>24.8</td>
<td>.04</td>
<td>2.02</td>
</tr>
<tr>
<td>5</td>
<td>.73</td>
<td>18.6</td>
<td>.07</td>
<td>1.85</td>
</tr>
<tr>
<td>6</td>
<td>.55</td>
<td>13.9</td>
<td>.10</td>
<td>1.95</td>
</tr>
</tbody>
</table>

1 Molality.
2 Per centage H₂SO₄.
3 Pure water, same tip.
PRODUCING SMALL BUBBLES OF GAS IN LIQUIDS

TABLE 17.—Bubble sizes from photographs

EFFECT OF TEMPERATURE IN DISTILLED WATER

[Photographs of series XVIII]

<table>
<thead>
<tr>
<th>Photograph</th>
<th>Temperature, °C.</th>
<th>Bubble diameter, mm.</th>
<th>Photograph</th>
<th>Temperature, °C.</th>
<th>Bubble diameter, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5.8</td>
<td>1.92</td>
<td>5</td>
<td>36.2</td>
<td>1.90</td>
</tr>
<tr>
<td>3</td>
<td>15.6</td>
<td>2.00</td>
<td>6</td>
<td>47</td>
<td>1.85</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>1.98</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Evidence of convection currents producing some smaller bubbles. Figures given are for maximum diameter.
2 Attached bubble.

It does not require, however, any very great velocity of gas (yet one that corresponds to a fairly high pressure with small tips) to alter materially the shape of the bubbles as they form. With increasing pressure the stem of the bubbles gradually elongates, until it may be some millimeters or, in extreme cases, even centimeters long, and bears at the end the bubble proper. See, for example, series IV, Nos. 5 and 6. Such a condition is the beginning of what we have called turbulent flow. This term implies no reference to turbulence within the capillary, but rather to the phenomena in the stem of the bubble and in the bubble itself. Whether turbulence in the capillary is related to turbulence in the bubble is not directly answerable, largely because adequate data for such small tubes is lacking.

If, however, we assume the same formula holds for small glass capillaries as for rather large steel or brass pipes, we may calculate the approximate velocity at the critical point for the tube to be in the neighborhood of 15,000 cm. per second for the tip 0.118 mm. in diameter shown in the photographs of series IV (fig. 48), whereas the turbulence of bubble formation is noted at velocities in the neighborhood of 10,000 cm. per second (from Table 2).

\[
\pi r^2 v = 0.9 \text{ c. c. per second}
\]

\[
v_{\text{turb.}} = \frac{0.9}{\pi (0.0059)^2} = 10^4 \text{ (approx.)}
\]

Consequently it seems probable that turbulent flow in the capillary is, as far as the data indicate, closely connected with this phenomenon.

When the stem of the bubble becomes of appreciable length, it clearly shows whorls and vortices, and these result occasionally in small bubbles visible in the field of vision of the picture. The bubble at the end of the stem, moreover, is no longer spherical but oscillates in various heartlike or truncated-cone shapes. In general, we may say that turbulent flow is undesirable because of the formation of many large bubbles.

Figure 48.—Bubbles of series IV from a glass tip 0.118 mm. in internal diameter, showing effect of varying gas pressures. The pressures in ascending order are as follows: b (No. IV-1), 2.0 cm. Hg; f (No. IV-2), 2.3 cm. Hg; e (No. IV-3), 3.9 cm. Hg; c (No. IV-4), 5.7 cm. Hg; a (No. IV-5), 12.3 cm. Hg; d (No. IV-6), 30.1 cm. Hg. b shows the small stem and spherical shape of the static bubbles; f and d show detached bubbles; e, a, and d show the beginning of turbulence and elongation of stem. Note especially in e, a, and d the progressive increase in size of the detached bubbles as they move away from the tip; this increase is due to expansion after rupture from the stem.
Figure 49.—Bubbles issuing from tips of different materials, showing change of contact angle and other effects: a and b (photographs XIX-1 and XIX-6), rubber sheet, pierced by 0.452-mm. needles, c at 14.3 cm. Hg pressure and d at 94.3 cm. Hg pressure, showing great increase of bubble size (from distension of orifice); e (photograph IX-1), lead plate, 0.407-mm. hole, 0.7 cm. Hg pressure; f (photograph X-2), Monel metal plate, 0.558-mm. hole, 0.7 cm. Hg pressure; g (photograph XI-1), paraffin tip 0.125-mm. hole, 0.55 cm. Hg pressure; h (photograph XI-6), paraffin tip at high pressure (29.9 cm. Hg) showing disruptive gas jet producing small bubbles by swirls in liquid. Note especially changing contact angle in IX-1, X-2, and XI-1 as compared with glass of Series IV, shown by spreading of stem of bubble at its base.
The pictures in series IX to XI (see fig. 49), which show, respectively, lead, Monel metal, and paraffin tips, indicate that a new factor is entering into the phenomena of bubble formation; that is, the contact angle between gas, liquid, and the material of the tip. The effect is most marked with paraffin, which is much more wet by air than water, is intermediate with Monel, and is least for lead. For example, in X–2 (Monel) the stem diameter is about half the attached bubble diameter, and in XI–1 (paraffin) the effect is much exaggerated, the bubble being nearly cylindrical at the bottom. At high velocities (XI–6) a new condition of turbulent flow is produced, for instead of the bubble stem bearing a single distorted bubble at the top there are a great number of eddies and swirls, which produce a multiplicity of bubbles of much smaller size than that corresponding to the static bubble. This condition is the disruptive jet mentioned in the previous classification.

From these photographs it is obvious that in order to produce bubbles of minimum size some material that is perfectly wet by the liquid must be used for the tip or aerator.

With a diagonal tip (not reproduced) the bubble issuing at low velocities from a capillary at an angle with the liquid-tip surface tends to come off at right angles to the surface, rather than coaxially with the aperture. This tendency may be utilized in the design of tips.

Photographs of a conical or pointed tip (not reproduced) showed that with a tip material perfectly wet by the liquid the radius of tip material external to the orifice has no marked effect on bubble size; in other words, the same results should be expected with a plate orifice as with a tube orifice.

Photographs (not reproduced) of multiple tips show that too close spacing causes coalescence of bubbles to a marked degree, even at fairly low gas velocities. The separation of orifices by amounts equivalent to the bubble diameter or slightly less is therefore indicated if coalescence is to be avoided.

Photographs of a rubber tip with an orifice produced by a 0.017-inch needle indicate that the actual aperture produced by the puncture is much smaller. Although very small bubbles are produced the size of the orifice is now largely a function of the pressure of the gas, and through distension there is a decided increase of bubble size (about fivefold) in the range of pressures covered. With more than one aperture the effect would be even more noticeable, and in consequence the distension would be more marked because of the consequent weakening of the tip structure.

Numerical values of bubble sizes, determined by comparison with the photograph scale, appear in Tables 13 to 17. An attempt has been made to estimate the size of a static bubble by a comparison of values for various pressures, although these estimates may be considerably in error because of a somewhat rapid change of bubble size
with pressure in certain tests. The estimated static pressures are those due to capillary forces in perfectly wet circular orifices, as calculated from a surface-tension value of 73 dynes per centimeter for water.

Table 15 indicates that the presence of ferrous sulphate up to 1.53 molal causes no very noticeable change in bubble size, and Table 10 indicates that concentration of acid up to 33 per cent and of ferric iron up to 0.1 molal are also nearly without measurable effect, despite the fact that the density of these solutions is decidedly increased. Perhaps an increase of surface tension nearly balances the effect of increased buoyancy. It should be noted that pure air was used in all these experiments; the surface tension against air containing SO₂ gas might well be noticeably different, and the size of bubbles appreciably changed.

The effect of temperature, at least up to 50°C, on bubble size, as indicated by Table 11, is also negligible, as far as the implications of the results of present work are concerned, for the design of a practical apparatus.

**Calculation of Bubble Size**

In a consideration of whether or not the mathematical development given on pages 63 to 67 is empirically justified, the comparison of the calculated and the experimental values will naturally have two aspects, (1) with respect to static bubbles and (2) with respect to the effect of increasing gas velocities.

To facilitate comparison with respect to bubble size Table 18 was prepared. It shows the measured and calculated values of bubble size and the values of \( f\left(\frac{r}{a}\right) \) as used by Harkins and Löhneinstein.

**Table 18.—Comparison of measured with theoretical bubbles, static conditions**

<table>
<thead>
<tr>
<th>Tip number</th>
<th>Table</th>
<th>Internal radius of tip, mm.</th>
<th>Measured diameter by count, mm.</th>
<th>Measured diameter by burette, mm.</th>
<th>Measured diameter by photograph, mm.</th>
<th>Theoretical static bubble diameter, mm.</th>
<th>( f\left(\frac{r}{a}\right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17, glass 1</td>
<td>1</td>
<td>0.018</td>
<td>1.65</td>
<td>1.35</td>
<td>1.21</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>16, glass</td>
<td>2.7</td>
<td>0.099</td>
<td>1.86</td>
<td>1.05</td>
<td>1.36</td>
<td>1.73</td>
<td>0.83</td>
</tr>
<tr>
<td>14, glass</td>
<td>3</td>
<td>0.158</td>
<td>2.17</td>
<td>3.10(?)</td>
<td>2.14</td>
<td>1.92</td>
<td>1.92</td>
</tr>
<tr>
<td>8, glass</td>
<td>5</td>
<td>0.215</td>
<td>4.4</td>
<td>2.66</td>
<td>2.66</td>
<td>3.12</td>
<td>3.12</td>
</tr>
<tr>
<td>15, glass</td>
<td>6</td>
<td>0.348</td>
<td>4.9</td>
<td>3.12</td>
<td>3.66</td>
<td>3.66</td>
<td>3.66</td>
</tr>
<tr>
<td>18, glass</td>
<td>7</td>
<td>0.657</td>
<td>9.0</td>
<td>1.26</td>
<td>1.26</td>
<td>1.26</td>
<td>1.26</td>
</tr>
<tr>
<td>178, glass</td>
<td>7</td>
<td>0.016</td>
<td>1.05</td>
<td>1.16</td>
<td>1.16</td>
<td>1.16</td>
<td>1.16</td>
</tr>
<tr>
<td>Double glass</td>
<td>7</td>
<td>0.139</td>
<td>3.00</td>
<td>2.30</td>
<td>2.30</td>
<td>2.30</td>
<td>2.30</td>
</tr>
<tr>
<td>10, glass</td>
<td>7</td>
<td>0.175</td>
<td>3.5</td>
<td>0.85</td>
<td>0.85</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>Lead plate</td>
<td>8</td>
<td>0.203</td>
<td>3.8</td>
<td>2.61</td>
<td>2.61</td>
<td>2.61</td>
<td>2.61</td>
</tr>
<tr>
<td>Monel metal</td>
<td>8</td>
<td>0.239</td>
<td>4.6</td>
<td>2.74</td>
<td>2.74</td>
<td>2.74</td>
<td>2.74</td>
</tr>
<tr>
<td>Paraffin</td>
<td>8</td>
<td>0.062</td>
<td>4.5</td>
<td>1.76</td>
<td>1.76</td>
<td>1.76</td>
<td>1.76</td>
</tr>
<tr>
<td>Glass, diagonal</td>
<td>8</td>
<td>0.108</td>
<td>2.5</td>
<td>1.92</td>
<td>1.92</td>
<td>1.92</td>
<td>1.92</td>
</tr>
<tr>
<td>Glass, pointed</td>
<td>8</td>
<td>0.124</td>
<td>2.6</td>
<td>2.22</td>
<td>2.22</td>
<td>2.22</td>
<td>2.22</td>
</tr>
<tr>
<td>Glass, elliptic 1</td>
<td>7</td>
<td>0.0745</td>
<td>1.5</td>
<td>1.66</td>
<td>1.66</td>
<td>1.66</td>
<td>1.66</td>
</tr>
<tr>
<td>(0.00185)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.90</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.01±0.17</td>
</tr>
</tbody>
</table>

1 Square end. 
2 Contaminated. 
3 Major diameter. 
4 Minor diameter. 
5 Allowing for elliptic shape of orifice.
The calculated theoretical values of bubble size were determined from formula (2), page 69, \( R = 0.115 \frac{3}{\delta} \sqrt{\frac{r\gamma}{\delta}} \) (see also fig. 50). This obviously assumes both \( \cos \theta \) and \( f\left(\frac{r}{a}\right) \) to be equal to unity. The value of \( f\left(\frac{r}{a}\right) \) in the last column was calculated from formula (3)

\[
f\left(\frac{r}{a}\right) = \frac{2R^2g}{3\gamma},
\]

using for \( R \) the best value of observed bubble size. The table shows that where the value of \( f\left(\frac{r}{a}\right) \) is given the agreement with a perfectly spherical bubble with a negligible stem, requiring a value of unity for \( f\left(\frac{r}{a}\right) \), is fair, and on the average, \( f\left(\frac{r}{a}\right) \) is \( 1.01 \pm 0.17 \). This deviation seems rather large, but the equation expressing \( R \) is a cube root; consequently, the effect of 17 per cent deviation in \( f\left(\frac{r}{a}\right) \) is less than 6 per cent in \( R \), and the experimental errors involved in the actual determination of \( R \) are certainly of the same order of magnitude.

The conclusion is that for small glass tips or perfectly wet tips one is justified in assuming both \( \cos \theta \) and \( f\left(\frac{r}{a}\right) \) equal to unity, and that formula (2) may safely be used for calculating the size of the static bubble under these conditions and for engineering purposes.
For tip materials that are not perfectly wet by liquid, such as Monel and paraffin, neither \( f\left(\frac{r}{a}\right) \) nor \( \cos \theta \) is unity, and no values of \( f\left(\frac{r}{a}\right) \) are given. As a matter of fact, it is doubtful whether formula (1) (see p. 69) would be adequate for these conditions even though \( \cos \theta \) and \( f\left(\frac{r}{a}\right) \) were determined, for the radius of adherence is no longer the sharp edge of the tip aperture, as is quite evident from the photographs. For practical purposes it is necessary to note only that the use of a nonwet material may increase the bubble size several times.

In a consideration of the possibility of calculating bubble size when the gas velocity in a submerged tip is appreciable formula (5), page 71, is of interest. As previously intimated, a theoretical analysis adequate for the prediction of the complex effects involved could only be obtained in a qualitative way.

Plotting the results of Tables 7, 8, and 10, showing the effects of gas pressure on bubble size (fig. 51), demonstrates that the bubble

---

**Figure 51.** Variation of measured bubble size with gas pressure: a, Turbulence; b, 0.225-mm. tip; c, minimum capillary pressure; d, 0.1182-mm. tip; e, 0.0535-mm. tip
size goes through a very sharp minimum value, at least for two of the three tips plotted, as the pressure of gas increases. This agrees with the theoretical prediction that a minimum might occur. For purposes of comparison with the terms of the formula it is better to plot the values of bubble size against the gas velocity, as is done in Figure 52.

**Figure 52.** Variation of measured bubble size with gas rate: \(a\), 0.225-mm. tip; \(b\), turbulence; \(c\), 0.1182-mm. tip; \(d\), 0.0355-mm. tip

**Figure 53.** Variation of rate of gas giving minimum bubble size with dimensions of orifice

To furnish an approximate empirical rule, the values of velocity showing minimum bubble size in Figure 52 are collected below:

<table>
<thead>
<tr>
<th>Diameter of tip, mm.</th>
<th>(Q_{\text{min}}) c. c. per second</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0355</td>
<td>1.5 (10^{-2})</td>
</tr>
<tr>
<td>.118</td>
<td>5.0 (10^{-2})</td>
</tr>
<tr>
<td>.225</td>
<td>10.0 (10^{-2})</td>
</tr>
</tbody>
</table>

Plotting these values on a new chart (fig. 53), it is evident that \(Q_{\text{min}}\) is related to the tip size, and this relationship is fairly well

\(v\) is the linear velocity in the tip and is related to the gas quantity \(Q\) by the relationship \(\pi r^2 v = Q\).
represented by a straight line passing through the origin, corresponding to
\[ Q_{\text{min}} = 4.31 \text{ times diameter of tip} \]
\[ = 8.62r \]
but since
\[ \pi r^2 v = Q \]
\[ v_{\text{min}} = \frac{8.62r}{\pi r^2} \]
\[ = \frac{2.74}{r} \quad (6) \]

Actually, then, empirical results seem to indicate that the minimum value of bubble size occurs when the corresponding linear velocity of gas in the tip is inversely proportional to the radius of the aperture.

The general conclusion to be drawn from a comparison of observed and theoretical values of bubble size is that, although one may calculate the static bubble satisfactorily from purely theoretical formulas and estimate the special velocity giving a minimum bubble from an empirical equation (6), final determination of actual bubble size for a given gas velocity can best be made experimentally.

**PRACTICAL ASPECTS OF EXPERIMENTS MADE**

**OPTIMUM CONDITIONS OF AERATION AS SHOWN BY WORK ON SUBMERGED TIPS**

At the risk of some repetition, the conditions to be observed to obtain bubbles of minimum size, as indicated by the experiments so far discussed, are generalized below.

*Material of orifice.*—The prime consideration, except corrosiveness of the liquors to be used, is one of contact angle. The material of which an aerator is made should be wet by the liquor as perfectly as possible. Glass is ideal, but probably unsuitable for large-scale or technical use. No tests were made of bakelite or hard rubber, but these materials are known to verge on the nonwet side with respect to water and will consequently give bubbles larger than will a wetted material. Among the metals lead is probably best, perhaps because it rapidly becomes coated with an easily wetted oxidized film. Lead, moreover, is the easiest metal to puncture with small apertures.

If nonrigid materials, such as woven fabrics, are to be used, it would seem desirable to coat the filaments of those materials that might be oily or waxy, such as woolen fabrics, with some hydrophilic varnish; conceivably a preparation of sodium silicate might be used.

*Shape and size of orifice or tip.*—The internal circumferential length of the orifice is of importance solely with perfectly wetted materials. In order to produce small bubbles by buoyant effect only, it is necessary to have the orifice radius, if circular, approximately equal to \( r = 9.05 R^3 \), for a given size bubble, \( R \), in solutions where the surface tension approximates that of pure water. The reader should note that the dimensions of the formula must be in centimeters.
Surface-tension control of bubble size.—The radius of the static bubble is a function of the cube root of the surface tension. Obviously a certain amount of control of bubble size through the medium of addition agents, capable of changing the surface tension of the liquid with respect to the gas, is possible. Since the variation is as the cube root, however, the probable effectiveness of such control is much lessened. Moreover, the addition of any material, such as oils, that might change the contact angle at the same time as the surface tension might even increase the bubble size. One of the measurements of Table 18, in which the tip was accidentally contaminated by grease, shows the bubble produced to be noticeably larger than it should be.

Distribution of bubbles and their recoalescence.—If there are in the liquid medium no convection currents tending to bring the bubbles into contact, the spacing of orifices in a practical aerator should be not much less than the bubble size for which it is designed. In water, or solutions of analogous surface tension, the ratio between static bubble radius and orifice radius is approximately 10:1 for about 1-mm. bubbles, and for that range of bubble sizes the distance between orifices should not be less than about ten times the diameter of aperture used. This rule seems to eliminate screens, porous diaphragms, and cloth as suitable materials for aerators if bubbles of minimum size are desired. One must remember, however, that in these materials there is considerable variation in the sizes of individual openings, and at low gas rates only the largest apertures produce bubbles. Many of the apertures will also become clogged, so that, as a matter of fact, such materials are still usable. Certain types of fabric materials have practical advantages that may more than counterbalance these considerations—a subject that is discussed more in detail on later pages.

Pressures necessary to produce bubbles.—The data plotted in Figure 50 show the diminishing effect of gas velocity on bubble size as the orifice becomes smaller. For bubbles produced by buoyant effect only, the smaller orifices, capable of furnishing bubbles of the order of 1 mm. in diameter, may be assumed, at least as a first approximation, to give the static bubble of uniform size. Under these circumstances the formula for bubble size in water, at 20° C., for a perfectly wet orifice, \( r = 9.05 \, R^3 \), may be combined with the usual formula for capillary rise, \( \gamma = \frac{1}{2} \, g \cdot \rho h \), where \( h \) is the rise in centimeters, to give a relationship between bubble size and capillary pressure.

Thus, eliminating \( r \) and correcting for units, if \( h = p \) in centimeters of mercury,

\[
P_{cm.Hg} = \frac{1.21 \times 10^{-3}}{R^3} \quad (R \text{ in centimeters})
\]

or in pounds per square inch,

\[
P_{lbs. \text{ per sq. in.}} = \frac{2.33 \times 10^{-4}}{R^3} \quad (R \text{ in centimeters})
\]
Some calculated values from the above formulas are given in Table 19, and the results for pressures in pounds per square inch are plotted in Figure 54.

**Figure 54.**—Theoretical capillary pressures in water at 20° C.

**Table 19.**—Calculated values for bubble size and capillary pressure

<table>
<thead>
<tr>
<th>Diameter of bubble, mm.</th>
<th>Capillary pressure, cm. Hg</th>
<th>Capillary pressure, pounds per square inch</th>
<th>Diameter of bubble, mm.</th>
<th>Capillary pressure, cm. Hg</th>
<th>Capillary pressure, pounds per square inch</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1,210</td>
<td>234</td>
<td>0.7</td>
<td>25.3</td>
<td>5.44</td>
</tr>
<tr>
<td>0.25</td>
<td>621</td>
<td>120</td>
<td>1</td>
<td>9.7</td>
<td>1.89</td>
</tr>
<tr>
<td>0.50</td>
<td>77.6</td>
<td>15.1</td>
<td>2</td>
<td>1.21</td>
<td>0.23</td>
</tr>
<tr>
<td>0.50</td>
<td></td>
<td></td>
<td>3</td>
<td>.36</td>
<td>.07</td>
</tr>
</tbody>
</table>
Table 19 and Figure 55 show that for bubbles of size greater than 0.7 or 1.0 mm. in diameter the gas pressure required to overcome the force of surface tension in a submerged orifice is not a serious problem because of engineering difficulties. If, however, bubbles of smaller size are requisite or desirable, the pressure of capillary forces, which must of course be added to the hydrostatic head of liquid above the aerator to give working pressures, becomes excessive. This is especially true because, with the corrosive gases under consideration, the usual type of rotary blower, which is quite inefficient at higher pressures, seems the only practical type.

In the face of this difficulty two methods of working are open. The first of these will involve some sacrifice of speed and efficiency of chemical reaction by the use of bubbles more than 0.7 mm. in diameter. The second course will entail methods other than the use of buoyant effect for severing bubbles. It is essentially necessary under this second condition to produce smaller bubbles from larger orifices than are given under the conditions previously worked out. Descriptions of experiments that indicate how this may be done follow.

**PRODUCTION OF SMALL BUBBLES AT LOW GAS PRESSURES
AGITATORS AND IMPPELLERS**

A number of "agitator" aerators have been designed for use in concentrating minerals by flotation. In these machines bubbles that originally are of considerable size are "beaten up" into smaller units by violent agitation. In some types air is drawn into a vortex produced by the shallow submergence of a rotary "impeller" in the liquid; or occasionally the "impeller" is mounted on a hollow shaft, and the air is introduced through vanes or ports in the impeller.
Devices of this type have at least three evident disadvantages for the production of small bubbles for processes involving chemical absorption.

In the absorption of a slightly soluble gas, such as oxygen, under the conditions discussed here, a fairly long time of contact of bubble and solution is essential. Data that show the minimum depth of solution that may be used efficiently, varying perhaps from 5 to 10 feet, have been given in preceding pages (pp. 53 and 54). It is true that smaller bubbles will probably enable this limit to be decreased, but if good efficiency of gas absorption is desired the required depth will probably be too great to permit the use of the "vortex impeller." Moreover, the hollow-shaft type of machine would be difficult to construct in suitable, practical dimensions. The great length, if the shaft were submerged from the top, would necessitate very heavy construction and careful balancing, and submergence through the bottom would require troublesome packing glands.

Another serious disadvantage of the "impeller" type of machine is the lack of operating control of either bubble size or gas admitted. In view of the large masses of gas that must be handled to make the autoxidation of sulphur dioxide-ferrous sulphate solution technically effective, this lack of flexibility is serious.

Finally, machines of the usual "impeller" type, which rely on violent agitation, beyond doubt are only crudely effective in the useful application of the desired forces. Violent agitation produces shearing forces in the liquid, but such forces may be produced without agitation, and consequently with much less consumption of random energy.

Seemingly the use of shearing forces to furnish smaller bubbles from larger orifices would be made more readily in a plane perpendicular to the axis of a submerged orifice than in a direction coaxial with it. A small laboratory machine, designed to test the effectiveness of this shear principle, was built. As the machine proved useful in validating the foregoing reasoning, a brief description of it follows.

ORIGINAL "SHEAR" TYPE OF BUBBLER

The shear machine shown in Figure 56 consisted essentially of a hollow drum mounted on the end of a hollow shaft and bearing orifices on the peripheral surface. The diameter of these orifices was 0.4 mm. (The normal static buoyant-effect bubble produced by this size orifice would be approximately 2.5 mm. in diameter, and at moderate gas velocities the diameter would be 4 or 5 mm.)

The shaft proper was mounted inside a hollow cylinder or gas-inlet box, the ends of which served as bearings for the shaft. The top
bearing was fixed in the bottom of an aerating column; the lower was a bushing and spring, as shown. Conical bearing surfaces, ground in place and polished with very fine abrasive, were used.

The shaft, turned as true as possible with respect to the bearings and well balanced, was rotated at fairly high speed. Most of the experiments were at a speed of 1,500 to 1,700 revolutions per minute. A system of vanes about the drum (in the liquid) prevented the liquid rotating with the drum and increased the shear at its peripheral surface. The clearance was as small as practicable. The vanes were an essential part of the apparatus, both to prevent the formation of a vortex and to produce the maximum shear.

Because the surface of the drum was smooth and its rotation was symmetrical, the drag on the drum from the slippage of liquid past it was small—in fact, was negligible compared to the friction of the bearings. No difference of input could be detected, as measured on a small electric motor drive, between runs in air and in water, although the available measuring instruments were not as sensitive as desired.

Before rotation, this machine produced bubbles 3.5 to 4.0 mm. in diameter at a moderate gas velocity, but when it was rotated 1,700 revolutions per minute the size of the bubbles decreased immediately to about 0.4 mm. in diameter—approximately the size of the orifice. The gas pressure did not change appreciably between the stationary and rotating condition and was about 2 cm. of Hg. To produce an equivalent aeration with glass
tips by buoyant effect alone would require a gas pressure of about 200 cm. (30 to 40 pounds gauge) and apertures less than 0.01 mm. in diameter.

The successful demonstration of the shear principle effectively applied, as with this machine, encouraged further experiments. It seemed especially necessary to use the same effect in a more simple apparatus. It was obvious that the shear force used could equally well be obtained by rapid motion of the liquid past a stationary drum, for the relative motion only is of importance. The aim of further experimental work was to show that the motion of the liquid past the drum could be produced without excessive loss of energy through liquid friction. In the first plan tried (fig. 57), apertures of moderate size were made in a stationary drum mounted coaxially in a short length of constricted cylindrical extension at the bottom of an aerating column. Liquid was pumped through the constricted area to give the shear.

MODIFIED “SHEAR” TYPES OF BUBBLER

Two types of liquid-motion shear bubblers were used. They are described in the order of experimentation, which also happens to be the order of increasing usefulness.

Parallel-wall type.—The first type of apparatus used corresponds to a single element (single orifice) of the kind of aerator shown in Figure 57. The apparatus actually used is shown in Figure 58. It consisted of two glass plates 1 by 3 inches by 1 mm. (microscope slides) held parallel by 1-mm. spacers at the corners and by a 1-inch rubber tube slipped over the whole under slight tension. The rubber tubing was somewhat longer than the plates; its ends served as connection with the water inlet at the bottom and an aerating column at the top. At the centers of the parallel plates (flat side) the rubber was cut away on one side to permit the insertion of an orifice and on the other side to permit the action to be seen. The orifice tube was ground flat at the end. It was cemented into a hole drilled in the center of one of the plates and was perpendicular to the plane of the plates. The inner end of the orifice tube was in
the same plane as the inner surface of the plate to which it was cemented.

With this apparatus measurements of liquid velocity, gas velocity, gas pressure, and bubble size were made. The liquid velocity was calculated from measurements of overflow in a given time; the gas velocity by collecting the bubbles on effluence in a graduated cylinder with a funnel bottom. At high velocities of liquid the gas velocities could not be obtained because of the great scattering of the bubbles. The size of the bubbles was measured with the bubble burette previously described, and, inasmuch as the size of individual bubbles varied a little, a number of readings were taken and only the estimated average recorded. The accuracy of measurement is probably no better than several tenths of a millimeter. Results of this test are recorded in Table 20 and are plotted in Figure 59.

The curve showing the variation of bubble diameter indicates, as expected, that increasing the liquid velocities past the tip causes at first a very rapid decrease of bubble size, but after a linear velocity of 100 cm. per second is reached further increase of velocity causes a more or less steady decrease, of less magnitude. The dotted line at the left of the curve meets the ordinate axis at the normal bubble size calculated for a static bubble. Actually, as the normal bubble from the size of aperture used is greater than the plate spacing, the bubble is flattened against the sides of the walls, and thus at low or zero liquid velocity it is so hindered from leaving the slot that it is blown to nearly twice its normal size.

This run was made at a fixed setting of the regulating valve supplying the gas line, and the results show that the actual velocity of the gas decreases appreciably with the velocity of the liquid, whereas the pressure of the gas increases rather rapidly. The gas pressure
recorded is the sum of the static liquid pressure, capillary pressure, orifice-velocity head, and one-half the friction head of the liquid through the plates. As the actual gas velocity decreased, the orifice-velocity head must have decreased. The static and capillary pressures are constant, and it is evident that the friction head of the liquid flowing between the plates is by no means a negligible quantity, even for a plate length of 3 inches.

The conclusions to be drawn from this first experiment may be summarized as follows:

With a linear velocity of liquid of 310 cm. per second at right angles to an orifice greater than 0.5 mm. in diameter, the desired bubble size of 1-mm. diameter or less could be produced. The gas pressure

![Figure 20. Characteristics of shear bubbler, parallel-wall type; dimensions of slot, 1 mm., plate width, 2.54 cm., plate length, 7.62 cm., orifice, 0.554 mm. in internal diameter; a, Gas pressure; b, bubble diameter; c, gas velocity.]

**Table 20. Measurements with shear bubbler, parallel-wall type**

[Dimensions of bubbler: Plates, 2.54 cm. wide, 7.62 cm. long, 1-mm. spacing, 0.554-mm. orifice, at right angles, at center]

<table>
<thead>
<tr>
<th>No.</th>
<th>Liquid rate, Q, c.c. per second</th>
<th>Liquid velocity, V, cm. per second</th>
<th>Gas rate, c.c. per second</th>
<th>Bubble diameter, mm.</th>
<th>Gas pressure, cm. Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.43</td>
<td>29</td>
<td>2.02</td>
<td>6.3</td>
<td>2.50</td>
</tr>
<tr>
<td>2</td>
<td>21.6</td>
<td>66.4</td>
<td>2.00</td>
<td>3.5</td>
<td>2.82</td>
</tr>
<tr>
<td>3</td>
<td>42.7</td>
<td>131.3</td>
<td>1.77</td>
<td>2.50</td>
<td>3.31</td>
</tr>
<tr>
<td>4</td>
<td>78.1</td>
<td>240.5</td>
<td>1.16</td>
<td>1.82</td>
<td>4.51</td>
</tr>
<tr>
<td>5</td>
<td>96.2</td>
<td>321</td>
<td>1.10</td>
<td>1.50</td>
<td>6.95</td>
</tr>
<tr>
<td>6</td>
<td>104.1</td>
<td></td>
<td>0.90</td>
<td>9.52</td>
<td></td>
</tr>
</tbody>
</table>

required for an aeration of 2 c. c. per second rises rather rapidly with increasing velocity of gas. The principle of shear is just as
effective as in the rotating-drum machine and does not require the use of excessive liquid velocities, but the elimination, if possible, of the friction due to liquid velocity in the slot is desirable. A desirable type of apparatus should have a gas-pressure characteristic that is nearly flat with respect to liquid velocity.

Grid type.—Because of the above conclusions no further work was done with the parallel-plate type of shear bubbler; the solution of the problem of eliminating the friction head in the slot was immediately evident—to cut down the length of slot to a minimum. An easy and practical method of obtaining this result is to make a grid to parallel pipes spaced closely, with orifices near the plane of minimum slot size; that is, the plane of the axes of the pipes, as in Figure 60. Moreover, in this sort of aerator, by placing the orifices slightly above the plane of the axes of the pipes it seemed

![Figure 60](Image)

*FIGURE 60.—Diagram of grid-type shear bubbler: a, Plane of axes; b, gas from orifice; c, liquid motion*

![Figure 61](Image)

*FIGURE 61.—Experimental shear bubbler, grid type: a, ½-inch brass pipe, soldered to wall; b, clearance slot, 1 mm.; c, solder joint; d, adjustable back, held in place by gasket compression; e, water inlet; f, to water-pressure manometer; g, sheet-rubber gasket; h, orifice, ½ mm. above plane of axes; i, gas line and gas-pressure manometer*

possible to put the gas under a slight suction or perhaps to flatten the curve of pressure characteristic.

The apparatus consisted of a single element (orifice) of the grid bubbler shown in Figure 60. (See fig. 61 for details.) An accessory outlet was provided to permit measurement of the pressure of liquid
required to produce a given velocity in the slots. Liquid velocity, gas velocity, and bubble size were determined as for the parallel-wall type of aerator. The pressure drop in the gas due to the flow of liquid through the slot was determined by the difference in pressure between no liquid velocity and that at any desired setting.

The experimental results comprise a series of seven runs, each at a definite liquid velocity (including no velocity). Only the gas rate was varied in each set, and the gas pressure, gas velocity, and bubble size were measured. For each of the seven settings the liquid velocity (a constant) was determined and also the pressure due to liquid velocity through the slot.

An accessory run was made in which the gas was shut off and the pressure and velocity of the liquid only were determined.

Table 21 shows the results obtained in these seven experiments. In Figure 62 the values for bubble size have been plotted against the gas velocity, giving seven curves of similar shape, each for a definite liquid velocity, including no velocity. Since, however, the size of bubble as a function of the liquid velocity, but at a definite gas rate, is of greater present interest, Table 22 has been prepared.
Table 21.—Shear-bubbler measurements, grid type

[Dimensions: %4-inch brass pipe; 1-mm. slot spacing; orifice, 0.335-mm. drill, %2 mm. above plane of pipe axes]

H₂O velocity = 0

<table>
<thead>
<tr>
<th>Pressure of gas, cm. Hg</th>
<th>Gas rate, c. c. per second</th>
<th>Bubble diameter, mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.531</td>
<td>3.9</td>
</tr>
<tr>
<td>1.30</td>
<td>2.96</td>
<td>4.4</td>
</tr>
<tr>
<td>1.79</td>
<td>7.69</td>
<td>5.5</td>
</tr>
<tr>
<td>2.58</td>
<td>10.2</td>
<td>6.15</td>
</tr>
<tr>
<td>3.52</td>
<td>12.8</td>
<td>6.5</td>
</tr>
</tbody>
</table>

H₂O velocity = 13.5 c. c. per second = 40.4 cm. per second in slot; liquid pressure head = 0.14 cm. Hg

| 0.91 | 2.09 | 3.05 |
| 0.88 | 2.52 | 3.35 |
| 1.29 | 4.95 | 3.65 |
| 1.60 | 6.59 | 4.55 |
| 2.90 | 11.1 | 5.5  |

H₂O velocity = 30.8 c. c. per second = 92.1 cm. per second in slot; liquid pressure head = 0.58 cm. Hg

| 0.98 | 1.82 | 2.3  |
| 1.13 | 2.89 | 2.8  |
| 1.39 | 4.90 | 3.35 |
| 2.08 | 7.25 | 4.0  |
| 2.91 | 9.08 | 4.8  |

H₂O velocity = 53.8 c. c. per second = 161 cm. per second in slot; liquid pressure head = 1.36 cm. Hg

| 0.73 | 1.00 | 1.5  |
| 1.02 | 2.89 | 1.9  |
| 1.35 | 4.66 | 2.45 |
| 1.81 | 6.67 | 3.0  |
| 2.68 | 9.80 | 4.0  |

H₂O velocity = 73.5 c. c. per second = 219 cm. per second in slot; liquid pressure head = 2.58 cm. Hg

| 0.65 | 1.73 | 1.1  |
| 0.99 | 3.87 | 1.5  |
| 1.47 | 5.15 | 2.5  |
| 2.01 | 8.2  | 3.0  |
| 2.61 | 10.4 | 3.5  |

H₂O velocity = 107 c. c. per second = 320 cm. per second in slot; liquid pressure head = 5.25 cm. Hg

| 0.91 | 1.85 | 0.90 |
| 1.41 | 4.35 | 1.25 |
| 1.77 | 5.88 | 1.90 |
| 2.58 | 8.35 | 2.80 |

H₂O velocity = 125 c. c. per second = 374 cm. per second in slot; liquid pressure head = 6.43 cm. Hg

| 0.70 | 1.47 | 0.6  |
| 1.10 | 2.63 | 1.0  |
| 1.52 | 3.70 | 1.15 |
| 2.40 | 5.62 | 1.5  |
| 3.25 | 8.33 | 2.0  |
Table 22.—Summary of experiments on bubble size with shear bubbler of grid type

<table>
<thead>
<tr>
<th>H2O velocity, cm. per second</th>
<th>Gas rate, 1 c. c. per second</th>
<th>Gas rate, 2 c. c. per second</th>
<th>Gas rate, 4 c. c. per second</th>
<th>Gas rate, 7 c. c. per second</th>
<th>Gas rate, 10 c. c. per second</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.85</td>
<td>2.95</td>
<td>4.38</td>
<td>5.21</td>
<td>6.06</td>
</tr>
<tr>
<td>40.4</td>
<td>2.92</td>
<td>3.02</td>
<td>3.50</td>
<td>4.52</td>
<td>5.33</td>
</tr>
<tr>
<td>92</td>
<td>2.15</td>
<td>2.35</td>
<td>2.93</td>
<td>4.01</td>
<td>5.08</td>
</tr>
<tr>
<td>161</td>
<td>1.52</td>
<td>1.64</td>
<td>2.11</td>
<td>3.10</td>
<td>4.09</td>
</tr>
<tr>
<td>210</td>
<td>1.04</td>
<td>1.10</td>
<td>1.56</td>
<td>2.53</td>
<td>3.52</td>
</tr>
<tr>
<td>320</td>
<td>.84</td>
<td>.85</td>
<td>1.31</td>
<td>2.26</td>
<td>3.26</td>
</tr>
<tr>
<td>374</td>
<td>.56</td>
<td>.65</td>
<td>1.09</td>
<td>1.95</td>
<td>2.95</td>
</tr>
</tbody>
</table>

In this table interpolated values for definite gas rates have been taken from the curves of Figure 62 and recorded against the liquid velocity in each case. These results plotted in Figure 63, which shows the variation of bubble diameter with liquid velocity, give five curves for gas rates of 1 to 10 c. c. per second. These curves, of similar shape, are comparable to the curve for the parallel-wall apparatus, but are corrected here for constant rates of gas flow.

The curves show a rather sharp but more uniform decrease of bubble size with increasing velocity of liquid and, as before, it is evident that a linear velocity of 300 cm. per second of liquid in the smallest slot opening again can produce bubbles 1 mm. or less in diameter, even up to gas rates of approximately 3 c. c. per second per orifice.
The pressure required to produce a given liquid velocity is of importance in design and in the determination of power costs. Table 23, A, gives the observed pressures (velocity drop) collected for the conditions of aeration, whereas Table 23, B, shows the values obtained in the accessory experiment where the gas was shut off.

Table 23.—Data on liquid pressures through slot

<table>
<thead>
<tr>
<th>Table No.</th>
<th>H$_2$O velocity, cm. per second</th>
<th>$\Delta p$, cm. Hg</th>
<th>$\Delta H$, cm. fluid</th>
<th>$\sqrt{\Delta p(\Delta H)}$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. WITH AERATION</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>40.4</td>
<td>0.14</td>
<td>1.89</td>
<td>61</td>
<td>0.66</td>
</tr>
<tr>
<td>10</td>
<td>92.1</td>
<td>1.58</td>
<td>7.86</td>
<td>124</td>
<td>0.74</td>
</tr>
<tr>
<td>11</td>
<td>161</td>
<td>2.38</td>
<td>18.4</td>
<td>190</td>
<td>0.85</td>
</tr>
<tr>
<td>12</td>
<td>219</td>
<td>5.25</td>
<td>34.9</td>
<td>262</td>
<td>0.84</td>
</tr>
<tr>
<td>13</td>
<td>320</td>
<td>6.63</td>
<td>70.9</td>
<td>414</td>
<td>0.90</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.81±0.07</td>
</tr>
<tr>
<td><strong>B. WITHOUT AERATION</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Determination No.:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>38.5</td>
<td>0.68</td>
<td>1.68</td>
<td>46</td>
<td>0.84</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>1.53</td>
<td>7.19</td>
<td>118.8</td>
<td>0.83</td>
</tr>
<tr>
<td>3</td>
<td>131.3</td>
<td>1.95</td>
<td>12.9</td>
<td>159</td>
<td>0.83</td>
</tr>
<tr>
<td>4</td>
<td>162</td>
<td>1.53</td>
<td>20.7</td>
<td>202</td>
<td>0.89</td>
</tr>
<tr>
<td>5</td>
<td>192.5</td>
<td>1.93</td>
<td>26.3</td>
<td>227</td>
<td>0.85</td>
</tr>
<tr>
<td>6</td>
<td>252</td>
<td>3.23</td>
<td>43.8</td>
<td>303</td>
<td>0.86</td>
</tr>
<tr>
<td>7</td>
<td>290</td>
<td>4.43</td>
<td>60</td>
<td>342</td>
<td>0.85</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.84±0.014</td>
</tr>
</tbody>
</table>

To one attempting to calculate the value of pressure drop for this type of slot, the usual formula for the standard orifice, or Venturi meter, seems adequate.

$$V = \sqrt{2g \ (\Delta H)}$$

or

$$\sqrt{V_2^2 - V_1^2} = C \sqrt{2g \ (\Delta H)}$$

where $V$ is the linear velocity in the constriction, $g$ the acceleration of gravity, $\Delta H$ the pressure drop measured in units of fluid, and $C$ a constant dependent on the design of the orifice. For sharp-edge orifices the value of $C$ is 0.61, for a good Venturi 0.98. For pipes of moderate size, $\frac{3}{4}$ to 1 inch, it seems probable that the value of $C$ is intermediate between 0.61 and 0.98.

Table 23 contains values for $\Delta H$ ($\Delta p$ in cm. Hg times the density of Hg, 13.54), and calculated values of $\sqrt{2g \ (\Delta H)}$. The actual value of $C$, in the last column, is then the ratio

$$\frac{v \ (observed)}{\sqrt{2g \ (\Delta H)}}$$

Where no aeration is done (Table 23, B) the value of $C$ is virtually constant over the range of velocities covered and is equal to 0.84 ± 0.014. When, however, aeration also goes on, the values of $C$ from
Table 23, A, are less constant but average 0.81 ± 0.07. At high velocities of liquid the effect of aeration is less, and on the whole one may say the average disturbance is probably not greater than 5 per cent.

**Figure 64.**—Pressure characteristics of grid-type shear bubbler: a, H2O = 374 cm. per second; b, H2O = 320 cm. per second; c, H2O = 92 cm. per second; d, H2O = 161 cm. per second; e, normal pressure at 0 cm. per second; f, H2O = 40.4 cm. per second; g, H2O = 219 cm. per second; h, capillary pressure for 0.335-mm. orifice

These results on liquid pressures seemed definite enough to render unnecessary experiments with various slot spacings and pipe sizes, although for very large pipes the friction factor would doubtless be of importance.
The last question of practical interest with respect to the grid type of aerator is the effect of liquid velocity on gas pressure. The data on this relationship, taken from Table 21, have been plotted as Figure 64, showing gas pressure versus gas velocity for each liquid velocity used. As in the treatment of data on bubble size, interpolated values of pressure for a definite gas velocity have been read from this plot; they appear in Table 24.

Table 24.—Gas-pressure characteristics of shear bubbler of grid type

<table>
<thead>
<tr>
<th>Table No.</th>
<th>H₂O velocity, cm. per second</th>
<th>Gas rate, 1 c. c. per second</th>
<th>Gas rate, 2 c. c. per second</th>
<th>Gas rate, 4 c. c. per second</th>
<th>Gas rate, 7 c. c. per second</th>
<th>Gas rate, 10 c. c. per second</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0</td>
<td>0.74</td>
<td>0.82</td>
<td>1.03</td>
<td>1.59</td>
<td>2.52</td>
</tr>
<tr>
<td>9</td>
<td>40.4</td>
<td>.78</td>
<td>.87</td>
<td>1.15</td>
<td>1.71</td>
<td>2.54</td>
</tr>
<tr>
<td>10</td>
<td>92.1</td>
<td>.80</td>
<td>.95</td>
<td>1.28</td>
<td>1.99</td>
<td>3.04</td>
</tr>
<tr>
<td>11</td>
<td>161</td>
<td>.73</td>
<td>.87</td>
<td>1.12</td>
<td>1.72</td>
<td>2.58</td>
</tr>
<tr>
<td>12</td>
<td>219</td>
<td>.60</td>
<td>.89</td>
<td>1.01</td>
<td>1.59</td>
<td>2.52</td>
</tr>
<tr>
<td>13</td>
<td>320</td>
<td>.78</td>
<td>.94</td>
<td>1.32</td>
<td>2.80</td>
<td>3.88</td>
</tr>
<tr>
<td>14</td>
<td>374</td>
<td>.62</td>
<td>.91</td>
<td>1.60</td>
<td>2.76</td>
<td>4.15</td>
</tr>
</tbody>
</table>

1 Gas pressures in cm. Hg.

The results of Table 24, as plotted in Figure 65, are of considerable interest. There are produced a number of slightly undulating curves of somewhat similar shape but showing a definite minimum in the range of velocities from 100 to 280 cm. per second of liquid. This minimum point is doubtless due to the "suction" effect produced by having the orifice slightly above the plane of the axes of the pipes, as mentioned above. For practical purposes one may say that for gas velocities less than 4 c. c. per second per orifice for this particular orifice size a virtually flat pressure characteristic is obtained and the liquid velocity has no effect. For higher gas velocities there is some

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increase of gas pressure due to liquid velocity, but this effect becomes marked only for liquid velocities greater than 280 to 300 cm. per second. This value also is consistent with the velocity desired to produce small bubbles.

TENTATIVE DESIGN OF GRID-TYPE AERATOR

In order to show that the characteristics of a shear bubbler of the grid type do not involve difficult engineering factors, calculations for a tentative design of aerator of this type have been made. These calculations are not intended to represent a final recommendation on the design of this type, for certain preliminary assumptions can probably be improved as a result of the smaller bubbles furnished by the shear machine.

The assumptions made as a basis for this design, which involves the preparation of ferric salts only, are as follows:

Assumptions used in calculations for bubbles

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value required</th>
<th>Basis of assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Gas rate</td>
<td>3 c. c. per second per orifice</td>
<td>Data of this report, selected value.</td>
</tr>
<tr>
<td>2. Liquid velocity</td>
<td>300 cm. per second</td>
<td>Do.</td>
</tr>
<tr>
<td>3. Bubble size</td>
<td>Less than 1 mm. in diameter</td>
<td>Work at Tucson, Ralston’s calculations, etc.</td>
</tr>
<tr>
<td>4. Orifice diameter</td>
<td>0.4 mm.</td>
<td>Data of this report.</td>
</tr>
<tr>
<td>5. Orifice spacing</td>
<td>4 mm.</td>
<td>Do.</td>
</tr>
<tr>
<td>6. Ratio</td>
<td>1</td>
<td>Ralston’s estimates.</td>
</tr>
<tr>
<td>7. Height column</td>
<td>10 feet</td>
<td>Do.</td>
</tr>
<tr>
<td>8. Oxygen efficiency</td>
<td>50 per cent.</td>
<td>Work at Tucson, etc.</td>
</tr>
<tr>
<td>9. Concentration, Fe</td>
<td>28 grams per liter</td>
<td>Arbitrary assumption.</td>
</tr>
<tr>
<td>10. Capacity</td>
<td>1 ton Fe a day</td>
<td>Do.</td>
</tr>
<tr>
<td>11. Minimum time of aeration</td>
<td>1½ hours</td>
<td>Best average results at Tucson and Berkeley.</td>
</tr>
<tr>
<td>12. Pumping efficiency</td>
<td>50 per cent.</td>
<td>Best centrifugal pumps 80 per cent, 30 per cent allowance for pipe friction and motor losses.</td>
</tr>
</tbody>
</table>

Calculation of slot spacing.—From (1) and (6), gas rate = liquid rate = 3 c. c. per second per orifice; therefore, if \( w = \) width of slot, from (2), (5), (1)

\[
300 \times 0.4 \times w = 3
\]

\[
w = \frac{3}{120} \text{ cm.}
\]

\[
= .25 \text{ mm.}
\]

\[Q_{\text{Liquid}} = 0.025 \times 300 = 7.5 \text{ c. c. per second per linear cm. of slot.}\]

Total volume of air required per unit volume of solution.—

- \(2 \text{ FeSO}_4 + \text{SO}_2 + \text{O}_2 = \text{Fe}_2 (\text{SO}_4)_3\)
- \(56 \times 2 \text{ grams Fe require 32 grams O}_2\)

(9) \(28 \text{ grams Fe require 8 grams O}_2\), and with the density of \(\text{O}_2\)

at 1.42 grams per liter, 1 liter of solution requires

\[
\frac{8}{1.42} = 5.6 \text{ liters O}_2
\]

(8) at 50 per cent efficiency, 1 liter of solution requires

\[
57.2 \text{ liters air}
\]
From this it is obvious that, under the assumption of 1 volume of liquid per unit of time to 1 volume of gas per unit of time, each liter of solution must be treated 57 times to obtain the requisite conditions for satisfactory oxidation.

**Time of treatment.**—A circulation of 57 times in $1\frac{1}{2}$ hours requires that each circulation take \( \frac{90}{57} = 1.58 \) minutes = 95 seconds.

**Velocity of liquid above grid.**—Let \( V \) = linear velocity of liquid above grid. If the height of treater is 10 feet (305 cm.) the liquid must be replaced in 95 seconds as shown.

\[
V \times 95 = 305 \\
V = 3.21 \text{ cm. per second.}
\]

**Calculation of pipe size in grid.**—\( y \) = diameter of pipe = thickness of liquid column above grid; 3 c. c. per second of liquid must pass in a length of slot of 0.4 cm., therefore

\[
y \times 0.4 \times 3.21 = 3 \\
y = 2.34 \text{ cm.} = 0.92 \text{ inch, or, say, 1-inch pipe.}
\]

**Total volume of solution to be treated.**—At 1 ton of Fe a day,

\[
2,000 \times 454 = 9.08 \times 10^5 \text{ grams Fe a day} \\
\text{At 28 grams per liter} = \frac{9.08 \times 10^5}{28} = 32,500 \text{ liters a day} \\
\text{= 60} \times 60 \times 24 \\
\text{= 377 c. c. of solution per second}
\]

**Calculation of grid area.**—The 377 c. c. per second of solution must be treated 57 times. With respect to capacity, it seems obvious that there is no difference between circulating 377 c. c. per second of solution through 57 units in series (a continuous process), in an indicated time of $1\frac{1}{2}$ hours, or circulating $57 \times 377 = 21.5$ liters per second of solution through 57 times the unit grid area for a period of $1\frac{1}{2}$ hours in a single aerator. The calculations compare as follows:

Continuous: \( \frac{377}{7.5} = 50.4 \text{ cm., average slot length per unit} \)

\( = 1.65 \text{ feet} \)

Batch: \( 1.65 \times 57 = 94 \text{ feet slot length} \)

\( = 7.8 \text{ square feet of grid, approximately.} \)

**Calculation of liquid pressure.**—

\[
V = 0.84\sqrt{2g(\Delta H)} \quad \text{(per unit)} \\
300 = 0.84\sqrt{2g(\Delta H)} \\
\Delta H = \frac{358^2}{1961} = 65 \text{ cm. H}_2\text{O} = 2.13 \text{ feet by batch system}
\]

For 57 applications, series system, \( 2.13 \times 57 = 121.5 \text{ feet} \) (about 60 lbs. per square inch).
Calculation of power for pumping liquid.—

Continuous:

\[
\text{Water hp.} = \frac{\text{Pounds H}_2\text{O per minute} \times \text{total head in feet}}{33,000}
\]

\[
= \frac{60 \times 377}{454} \times 121.5
\]

\[
= \frac{33,000}{0.184}
\]

\[
= 0.184 \text{ hp.}
\]

At 50 per cent eff. = \(\frac{0.184}{0.5} = 0.37\) hp. energy consumed.

Batch: As the head is now \(\frac{1}{57}\) but the capacity 57 times, the power is the same.

For accurate calculations the density of the iron solutions should be considered, but the effect will, in general, be less than 10 per cent of total power consumed.

Ralston’s figure for power necessary to blow gas was 0.034 kw. h. per pound of iron, or 68 kw. h. or 90 hp. h. per ton of Fe oxidized. This is the minimum power consumption obtainable on the assumption of ability to develop a satisfactory diaphragm. The total power calculated in capillary aeration is for air pumping, although Ralston’s suggested design that involves Christensen absorbers would also call for a small additional amount of power.

For pumping the liquid the shear bubbler calls for \(0.37 \times 24 = 8.9\) hp. h. per ton of iron oxidized. For pumping gas, about \(\frac{4.4}{4.8} \times 90 = 82.5\) hp. h. (see Ralston’s estimate) are needed. Therefore, the total power is \(8.9 + 82.5 = 91.4\) hp. h. per ton of iron oxidized. The reader should note that this is for a practical design in which there is no uncertainty about the diaphragm for aerating and that the bubbles are slightly smaller than those on which Ralston based his calculations.

Calculation of rise of liquid in aerator.—If the rate of aeration is excessive, the aerating column will “blow” out of the apparatus. In previous work on the Stokes’s law bubble meter the average velocity found for “random” packed bubbles was about 20 cm. per second and was nearly independent of the size of bubble.

In a cross-sectional area 0.4 by 2.34 cm. there are supplied 3 c. c. per second of gas at a bubble velocity of 20 cm. per second. As a first approximation one may take 10 feet (305 cm.) as the actual height of liquid.

\[
\text{Time} = \frac{305}{20} = 15 \text{ seconds}
\]

\[
= 45 \text{ c. c. of gas.}
\]

The rise of liquid will be

\[
\frac{45}{0.4 \times 2.34} = 48 \text{ cm.}
\]

\[
= 1.6 \text{ feet, or 16 per cent.}
\]
The pressure will not be changed, as the apparent density of the column is decreased in the same proportion as the length is increased. Higher percentage increments of volume have been used in small tubes in laboratory work without "blowing" the liquid. The upward flow of liquid, 3.21 cm. per second, is small enough compared to the normal bubble velocity of 20 cm. per second to warrant the assumption that the upward streaming of bubbles will not be much influenced by the liquid velocity above the grid.

FACTORS INFLUENCING CHOICE OF AERATING DEVICES

Although the final selection of a particular type of aerating device will necessarily depend upon actual technical performance, as yet indefinite, certain general comparisons may be made at this time.

ADVANTAGES AND DISADVANTAGES OF GRID TYPE

The advantages of the grid-type aerator may be summarized as follows:
1. It produces bubbles somewhat smaller, and of more nearly uniform size, than those produced by other devices, such as fabric materials, when comparison is made on the basis of similar gas pressures.
2. It may be constructed of noncorrodible materials and is of mechanically permanent form.
3. The power cost, including the cost of pumping gas and liquid, is not greater than for the similar aeration rates of other devices.
4. No mechanical appliances not already in commercial use are needed.

The disadvantages of the grid-type machine may be these:
1. The orifices or slots may possibly become plugged, either with solid particles in the gas or liquid stream or by the gradual incrustation of salts through chemical action.
2. The first cost of a grid aerator, because of special construction, possibly, some lead burning, may be somewhat greater than that of an equivalent fabric aerator.

Screens of finer mesh than the apertures, if inserted in the gas line, would entirely prevent the clogging of the orifices with solid materials. If the cross section of the screens were large enough, the pressure drop of gas through them would be negligible.

Actual continuous operating tests of the grid aerator for a period long enough to prove or disprove the potential plugging by incrustation are lacking, and no definite prediction may be made as to the extent of this fancied disadvantage.
As intimated by the terms of the above comparison, the only other aerating device which is considered to compare in efficiency with the grid type is an aerator having a fabric membrane of noncorrodible fibers. Some types of woolen filter-cloth fabric seem to have the desired characteristics. The advantages of the fabric type of aerator are:

1. Moderately small bubbles may be produced at gas pressures obtainable by standard rotary blowers.
2. Tests to date indicate that materials are available which are noncorrodible. Whether these fabrics have economical length of life in actual operation still remains to be proved.
3. The cost of power for pumping gas is about equivalent to that for the grid type.
4. The pumping of corrosive liquors may be eliminated or minimized.
5. Solid materials in the gas stream, which may eventually cause plugging, are easily removed by vibration of the fabric or reversal of the flow.

Disadvantages of the fabric type of aerator are as follows:

1. The bubbles produced by fabrics are not as uniform in size as those produced by the grid aerator, nor in general are they as small, and since the apertures usually are as close as, or closer than, the average bubble diameter the danger of coalescence of bubbles is much enhanced.
2. Accidental enlargement of one or a few of the apertures will largely cause the remainder of the medium to become ineffective.
3. Vibration of the fabric surface causes mechanical strains and possibly zones of weakness, magnifying the tendency of localized bubbling. In view of this, fabric diaphragms will require reinforcing slats.
4. In the use of roaster gases, which if not screened contain solid particles, the pressure required to aerate varies with the time, and a relatively short campaign must be followed by the cleansing operations, during which the aerator must be shut down. Material actually embedded in the fabric will not be easily removable and may be expected ultimately to increase the pressure resistance excessively after long periods of operation.
5. Replacements or repairs will probably be more common than for the grid type of machine.

Uniformity of bubble size is a somewhat more serious matter than appears at first sight, because the volume of a bubble increases very rapidly (in a cubic ratio) with the radius of the bubble. Some figures and calculations in this respect are of interest.
A given aerator of fabric material gave normal bubbles 1 to 1.5 mm. in diameter, but a small percentage of large bubbles, estimated as about 5 mm. in diameter, was formed. The number of large bubbles was estimated as 1 or 2 per cent of the total. Assuming more or less arbitrarily that 1 per cent of 5-mm. bubbles is formed with 99 per cent of 1-mm. bubbles, the relative volumes of gas in large and small bubbles are easily estimated.

In 100 bubbles,

\[ 99 \times \frac{4}{3} \times (0.5)^2 = 52 \text{ cu. mm.} \]

\[ 1 \times \frac{4}{3} \times (2.5)^2 = 65.6 \text{ cu. mm.} \]

Total volume of gas = 118 cu. mm.

Then \( \frac{52}{118} = 44 \) per cent of the gas only is in the effective form, and 56 per cent is in the less effective form. As it is certain that the efficiency and rate of absorption increase rapidly as the bubbles become smaller, the disadvantage of the formation of even such a small percentage of large bubbles is evident. The surface per unit volume of gas is decreased nearly one-half, and the absorption rate of gases is a direct function of the contact surface.

Although the grid type of aerator seems superior in view of the foregoing comparison, the fabric type has commended itself to those engaged in commercializing the oxidization process. It is perhaps economically justifiable first to prove or disprove those methods that bear closest resemblance to present practice in other fields. If the inherent disadvantages of the fabric type of diaphragm ultimately prove too serious for its technical use, a new type of aerator that will probably do better work in every respect is available.

**APPENDIX**

**ACCURATE TAPER TUBES OF GLASS**

In order to produce a glass taper tube drawn accurately enough to serve as the bubble burette described on page 72, the following procedure was adopted:

A piece of Acheson graphite rod was turned down in a lathe to form a true taper mandrel of the size desired. Care was taken not to break the point, but to make it fine and true. The rod was carefully smoothed with the finest French emery paper. The base of the rod was attached to a steel rod, of slightly less diameter, by ordinary screw threads, as shown in Figure 66.

A tube of pyrex glass with fairly heavy walls, slightly larger in internal diameter than the base of the mandrel, was blown into a
test tube. The closed end of the glass was thickened somewhat, but uniformly.

After the glass tube had been inserted over the mandrel, resting with the closed end over the point, the whole was slowly moved upward into an electric tube furnace heated to about 900° C. With a little care the tube could be moved upward in such a way that the glass collapsed down onto the mandrel, starting at the point. As soon as the taper was formed the whole was at once removed from the furnace, and the glass was loosened by gentle tapping. The glass should be annealed in a smoky gas flame and finally cooled in cotton wool.

To eliminate the formation of gas pockets between glass and graphite, several very fine scratches should be made lengthwise of the graphite taper. If care is taken not to overheat, the glass will not penetrate into the scratches.

**EMPIRICAL CALIBRATION OF CONDUCTIVITY BUBBLE METER**

**TESTS WITH PARAFFIN SHOT**

A series of graded sizes of paraffin shot, comparable in diameter to the bubble sizes desired, were made as follows:

A glass cylinder, some 3 feet long and 4 inches in diameter, was provided with a tangential water inlet at the middle and a screened overflow at the top. (Fig. 67.) At the bottom of the tube was a pipette with a capillary, its outlet turned upward the top tube being bent downward and extending through a large rubber cork closing the bottom of the large tube. The pipette had about it an electric heating coil of suitable size.

To operate the apparatus, fill the pipette with paraffin containing a little beeswax—say 20 per cent—to make it less brittle, put enough water into the large tube to just cover the pipette and tip, and turn the current on until the paraffin is wholly melted. Gently turn on cold water at the center tangential inlet and apply a slight air pres-
sure to the top tube of the pipette, forcing out a stream of liquid paraffin. The droplets of paraffin that are formed rise in the tube, and as they meet the cold water at the inlet are chilled solid. Adjust the current in the heating coil so that the cold water in the top half of the tube does not circulate downward fast enough to chill the pipette. Remove the shot at the top and screen them to size.

In order to use the paraffin shot to calibrate a bubble meter, the following expedient was adopted.

An electrolyte of dilute sulfuric acid was so made up as to give an electrical resistance equal to carbon granules of the same size as the shot to be used. The final adjustment of the acid was made by trial and error until, when the space between the electrodes was filled with acid and granular carbon, the resistance did not differ appreciably from that of acid alone. By vacuum treatment the carbon granules had been impregnated with acid of the same resistance.

To make the actual measurements, the apparatus shown in Figure 68 was used. Increasing masses (volumes) of shot were mixed with impregnated granular carbon; the volume of the latter was decreased accordingly, so that equal volumes of solids were always present between electrodes. The paraffin shot were carefully disseminated throughout the mass.

Typical results of the measurements are given in Table 25 and Figure 69. Two sets of curves appear in this plate; the first (series α) indicate the increase of resistance caused by increasing masses or volumes) of a definite size of shot, and the second (series B) the true calibration curves for a particular apparatus, showing the variation of resistance change with shot size for a given volume of the latter.
**Figure 68.**—Calibration set-up of conductivity bubble meter: a, To vacuum pump; b, platinum wire, 16 B. & S. gauge; c, acid level; d, ring electrode, 1.5 cm. in diameter; e, intimate mixture of granular carbon and paraffin shot; f, to stopcock and leveling bottle with iso-ohmic $H_2SO_4$; g, high-resistance regulating rheostat; v. m., high-resistance volt meter; a. m., millimeter

**Figure 69.**—Calibration curves of conductivity bubble meter: A—a, 10 to 14 mesh; b, 8 to 10 mesh; c, 4 to 6 mesh. B—a, 20 grams; b, 15 grams; c, 10 grams.
### Table 25.—Resistance in conductivity tube

**RESULTS WITH 8 TO 10 MESH SHOT**

<table>
<thead>
<tr>
<th>Current, amperes</th>
<th>Ohmic drop, volts</th>
<th>Resistance, ohms</th>
<th>Grams of shot used</th>
<th>$\Delta R$, ohms</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.463</td>
<td>20.05</td>
<td>43.3</td>
<td>0</td>
<td>0</td>
<td>Acid only.</td>
</tr>
<tr>
<td>0.460</td>
<td>19.9</td>
<td>43.25</td>
<td>0</td>
<td>0</td>
<td>Acid and granular carbon.</td>
</tr>
<tr>
<td>0.452</td>
<td>21.3</td>
<td>47.1</td>
<td>4.5</td>
<td>3.8</td>
<td>Acid, carbon, and shot.</td>
</tr>
<tr>
<td>0.440</td>
<td>22.8</td>
<td>51</td>
<td>9.4</td>
<td>7.7</td>
<td>Do.</td>
</tr>
<tr>
<td>0.430</td>
<td>24.4</td>
<td>55.5</td>
<td>14.2</td>
<td>12.2</td>
<td>Do.</td>
</tr>
<tr>
<td>0.426</td>
<td>25.4</td>
<td>58.9</td>
<td>19</td>
<td>15.6</td>
<td>Do.</td>
</tr>
<tr>
<td></td>
<td>26.8</td>
<td>62.9</td>
<td>23.9</td>
<td>19.6</td>
<td>Do.</td>
</tr>
<tr>
<td></td>
<td>27.7</td>
<td>65</td>
<td>28.9</td>
<td>21.7</td>
<td>Do.</td>
</tr>
</tbody>
</table>

**RESULTS WITH 4 TO 6 MESH AND 10 TO 14 MESH SHOT**

<table>
<thead>
<tr>
<th>Shot, 4 to 6 mesh</th>
<th>Grams of shot</th>
<th>$\Delta R$</th>
<th>Shot, 10 to 14 mesh</th>
<th>Grams of shot</th>
<th>$\Delta R$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.3</td>
<td>2.6</td>
<td></td>
<td>6.8</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>11.2</td>
<td>6.7</td>
<td></td>
<td>15</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>17.8</td>
<td>11.6</td>
<td></td>
<td>21.2</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>24.3</td>
<td>14.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**METHOD OF CHECKING MATHEMATICAL FORMULA FOR METER**

In order to make certain that the mathematical formula developed for the change in resistance of a cylindrical conductor carrying spherical nonconductors is correct, apparatus was set up as shown in Figure 70.

A glass tube, radius 0.3622 cm. (calibrated by water contents) and length about 50 cm., was provided with two ring electrodes of platinum wire spaced 44.28 cm. apart. Sulphuric acid of such concentration that about 1,800 ohms resistance was produced between the electrodes was used as a conductor, enabling the tube to be thrown directly across the laboratory mains, using the most sensitive a. c. ammeter available. Twenty glass beads about 0.5 cm. in diameter
and as uniform as possible in size and shape were cemented together with short pieces (1.5 cm.) of No. 100 cotton thread having a minute amount of do Khotinsky cement at each end. The string of beads produced was just about long enough to extend from electrode to electrode.

By noting the rise of liquid in the tubes when the beads were immersed the total volume of 20 beads was found to be 1.462 c. c. = 0.0731 c. c. per bead.

\[ \frac{4}{3} \pi r^3_{nc} = 0.0731 \text{ c. c.} \]

\[ r_{nc} = 0.259 \text{ cm.} \]

Two readings of line voltage and current were then made, one without and one with beads, as follows:

<table>
<thead>
<tr>
<th>Readings of voltage and current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amperes</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Without beads</td>
</tr>
<tr>
<td>With beads</td>
</tr>
</tbody>
</table>

The resistance was calculated, as shown below, by assuming Ohm's law and a unit power factor and neglecting the resistance of the leads and the electrodes.

By measurement

\[ \left( \frac{\Delta B}{B_o} \right) = \frac{2.177 - 1.905}{1.905} = 0.143 \]

By formula (7)

\[ \left( \frac{\Delta B}{B_o} \right) = 3 \times 1.462 \times 4.428 \times \left( \frac{0.3622}{0.259 \sqrt{0.3622^2 - 0.259^2}} \right) \tan^{-1} \left( \frac{0.259^{-1}}{0.253} \right) = 0.141. \]

As the calculations involve differences that cause any inaccuracy of resistance to be magnified about 10 times in \( \Delta B \), and as the beads were not absolutely spherical, the agreement of observed with calculated values is regarded excellent, and the formula is concluded to be correct.

**APPARATUS FOR MEASURING BUBBLE SIZE**

Formulas (7) and (8) also enable the choice of suitable size of apparatus for measuring a given range of bubble sizes to be determined. It is obvious that if \( r_{nc} \) is very small compared to \( R_c \), that \( \frac{\Delta B}{B_o} \) for a given value of \( \Delta \nu \) becomes smaller than is capable of easy measurement. For a given sensitivity of measurement of electrical resistance a limiting size of tube must be used.

Let us assume that the order of magnitude of bubble size to be measured is 2 mm. in diameter, that is, \( r_{nc} = 0.1 \). We can calculate the value of \( \frac{\Delta B}{B_o} \) for unit \( \Delta \nu \), assuming, say 0.2, 0.3, 0.5, 1.0 for \( R \) and any convenient value of \( L \), say, 100. Large values of \( \frac{\Delta B}{B_o} \) are.
of course, desirable for experimental accuracy, and it would seem at first sight from formula (7) that a small value of $L$ should be used. This is not, however, practical for other reasons, chiefly because $L$ should be rather large in order to insure a fairly uniform average distribution of bubbles.

With these assumed values, the value of $\left(\frac{\Delta B}{B_0}\right)_0$ for unit $\Delta v$ has been calculated, and is recorded in the second column of Table 26

![Graph](image)

**Figure 71.** Variation of $\left(\frac{\Delta B}{B_0}\right)_0$ for unit $\Delta v$ and 2 mm. diameter bubbles with change of tube size: a, To infinity asymptotic to 0.1 (see also fig. 71). If we consider a 15 per cent increase in volume of solution due to aeration (a figure obtained in previous experiments), we may calculate the value of $\left(\frac{\Delta B}{B_0}\right)_1$ which would be actually obtained,

$$\left(\frac{\Delta B}{B_0}\right)_1 = 0.15 \cdot 100 \cdot \frac{R}{2} \cdot \left(\frac{\Delta B}{B_0}\right)_0$$

and these figures are shown in the last column. For tubes with a radius less than 0.75 cm., there is virtually no change in the sensitivity
of the apparatus, but above that figure the sensitivity falls sharply. The variation of the calculated figures from a smooth curve is due to slide-rule error and also to calculation by difference, which involves a magnification of errors. For the tube of 0.75-cm. radius the change in resistance is 15 per cent. If we desire to obtain an accuracy of 5 per cent in \( \frac{\Delta B}{B_0} \), it will be necessary to determine the resistance to \( 5 \times 0.15 = 0.75 \) per cent; this does not require the use of exceptionally delicate electrical apparatus.

**Table 26.—For 2-mm. bubbles, 100-cm. tube, 15 per cent aeration**

<table>
<thead>
<tr>
<th>Radius of tube, ( R )</th>
<th>( \left( \frac{\Delta B}{B_0} \right)_0 )</th>
<th>Volume between electrodes, ( 100 \times R^2 ) c.c.</th>
<th>( \Delta \rho ), c.c.</th>
<th>( \frac{\Delta B}{B_0} ), per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.100</td>
<td>12.6</td>
<td>1.88</td>
<td>19</td>
</tr>
<tr>
<td>0.3</td>
<td>0.038</td>
<td>28.3</td>
<td>4.25</td>
<td>18.5</td>
</tr>
<tr>
<td>0.5</td>
<td>0.015</td>
<td>78.6</td>
<td>11.8</td>
<td>18</td>
</tr>
<tr>
<td>0.75</td>
<td>0.006</td>
<td>176.7</td>
<td>25.5</td>
<td>15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.0006</td>
<td>314.2</td>
<td>47.3</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^1\) For unit \( \Delta \rho \).

**TESTS WITH A STOKES'S-LAW BUBBLE METER**

A considerable number of measurements with the Stokes's-law bubble meter were made, but since, as previously stated, the time of rise proved to be nearly independent of bubble size in constricted tubes, only a single illustrative set of measurements (Table 27) is presented here. The actual times given in Table 27 are the mean of some 36 determinations. The determinations showed relatively large deviations of individual readings from the mean.

Evidently, although the theoretical times of rise, as calculated from Stokes's law, show large changes of time with bubble size, the actually observed times are nearly constant whether the bubbles are 1 or 2 mm. in diameter. What small difference exists is too minute for workable determinations, and one must conclude that for high degrees of aeration and bubbles of this order of magnitude, Stokes's law is not even approximated by rising bubbles. The time is determined almost entirely by the "randomness" of the upward motion of a bubble.

**Table 27.—Theoretical bubble rates, Stokes's-law meter**

<table>
<thead>
<tr>
<th>Diameter of bubble, cm.</th>
<th>Theoretical velocity, cm. per second</th>
<th>Theoretical time for apparatus, seconds</th>
<th>Actual time, estimated average, seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>19.6</td>
<td>2.91</td>
<td>3.2</td>
</tr>
<tr>
<td>0.05</td>
<td>54.5</td>
<td>1.05</td>
<td>2.9</td>
</tr>
<tr>
<td>0.10</td>
<td>218</td>
<td>0.20</td>
<td>2.7</td>
</tr>
<tr>
<td>0.15</td>
<td>491</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>872</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>
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