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The preparation of pure silicic acid gels by the oxidation of silane

William G. Gapcynski
Union College - Schenectady, NY

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The Preparation of Pure Silicic
Acid Gels by the Oxidation of Silane

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A thesis, presented to the Department
of Chemistry of Union College, in partial ful-
fillment of the requirements for the Degree of
Bachelor of Science in Chemistry, by

William E. Gapszynski

Approved by Charles B. Hurd.

Dated June 1937

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Introduction

The oxidation of silane, SiH_4 , with ozone to give a hydrosol of silica of a very high degree of purity has been accomplished by Baibajew and Kargin.^I Such a sol is practically free from any electrolytes or other impurities. The purpose of this research work was to prepare by this method pure silica sols of a concentration great enough to eventually form a gel free from any electrolytes. It was desired to study some of the properties of such gels, especially the time of set and the changes if any in the pH of the gel during the time it is setting, with the underlying idea that any differences in these properties between those of pure sols and those of the ordinary gel made from sodium silicate and any of various acids might yield new information about the actual formation of silicic acid gels.

Due to various difficulties, however, only very dilute hydrosols of silica could be prepared by this method, and all experimental work was done in an attempt to obtain sols of a concentration sufficient to form gels.

Historical

Although silicic acid sols have been studied by countless investigators for many years, almost all experimental work has been done on gels formed by mixing sodium silicate and any one of various acids. It was not until recently that silica sols in which there were practically no electrolytes present, became the object of any extensive investigation.

The present ideas concerning the electrochemical

1) - See Bibliography

properties of SiO_2 sols and concerning the relation of these properties to the stability of the sols rests upon the work of Pauli and other investigators. Pauli made use of electrodialysis for the purification of the SiO_2 sols and found that the sols prepared and purified thru electrodialysis contain a definite amount of H^+ ions. Sols which Pauli obtained thru the saponification of silicic acid ethyl esters likewise show acid properties. Robinowitsch and Laskin also purified silica sols by means of electrodialysis and found that the pH reached 3.23 with a SiO_2 content of .25%

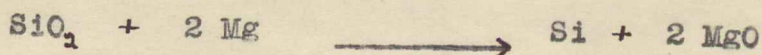
Baibajew and Kargin continued the work of preparing and of studying the properties of pure sols which they purified by electrolysis and also by various other methods. In one experiment they used sols which were prepared from SiCl_4 . These sols were prepared by leading a current of dry air saturated with SiCl_4 vapors, into ice cold water where the vapors were hydrolyzed to silica. After aging for several days the sols were purified by dialysis in collodion membranes in distilled water and further purified by electrodialysis. These sols also could not be entirely freed from H^+ ions.

Besides preparing sols which had to be purified, Kargin and Baibajew also used a method of production which excluded all electrolytes and other impurities. This method of obtaining a pure sol by means of the oxidation of silane was used in this research work in an endeavor to prepare sols of pure silica of sufficient concentration to form a gel. These experimenters came to the conclusion that a pure SiO_2 sol forms a completely inactive electrochemical system that possesses no acid properties.

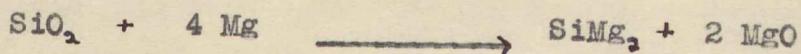
From the results of their work on the electrochemical properties of SiO_2 sols Baibajew and Margin came to the conclusion that the usual procedure of purification by electrodialysis is not satisfactory for the complete purification of the SiO_2 sols, but that very pure sols which are neutral are obtained by the oxidation of silane by ozone.

The Preparation of Magnesium Silicide

For the preparation of the silane, Magnesium silicide was used and reacted with 10% hydrochloric acid. The method used to prepare the silicide was that originally used by Stock.^{2,3} It is prepared by reacting commercial powdered magnesium with powdered silica. If equal amounts of magnesium and silica are used, however, there is no silicide formed as all the magnesium is used to reduce the silica to free silicon as shown by the following equation.³



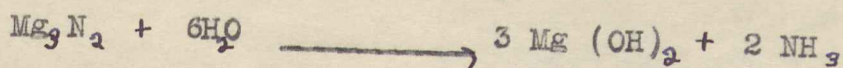
If, however, twice as much magnesium stoichiometrically as silica is used, there is enough magnesium present to form the magnesium silicide instead of free silicon.



Therefore, for each gram of silica two grams of magnesium were used. These substances were mixed together very thoroughly in a mortar and then placed in an iron crucible. The crucible was placed in a container of cold water as the amount of silicide formed increases as the temperature decreases. A short fuse of magnesium ribbon was used to ignite the mixture and start the reaction. When the fuse burns down to the mixture a violent reaction takes place and an intensive light appears which penetrates the whole mixture. The reaction is so violent that

a part of the reaction mixture is thrown out of the crucible with a blinding sheet of flame. To partially prevent this loss a piece of clay plate was placed over the top of the crucible leaving a large enough opening to permit the fuse to burn down to the mixture. After the most violent part of the reaction was over a stream of hydrogen was passed over the reaction mixture which was allowed to cool for a half hour under an atmosphere of hydrogen. As good a yield is obtained, however, if instead of using hydrogen the clay plate is removed and the crucible cover put on to exclude any excess oxygen and so prevent the oxidation of the mixture.

The product obtained is a half melted mass which is for the most part colored steel blue but which also has streaks of bright green and white in it. The magnesium silicide can be seen in the mixture in the form of a large number of small hard bluish gray crystals. After it has been cooled the product was crushed into a fine powder. During the crushing process there appears a very strong odor which is very much like that of NH_3 . The ammonia is probably due to the hydrolysis of the small amount of magnesium nitride formed during the preparation of Mg_2Si .

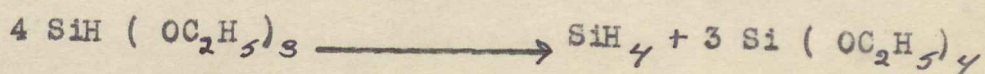


Two different batches of magnesium powder were used to prepare the silicide. The first type used was a very fine blue powder which was several years older than the second type. When this magnesium was used in the preparation of the magnesium silicide very few crystals of the silicide were formed and the product was in the form of a fine powder. When reacted with

the hydrochloric acid this product gave only small amounts of silane. The magnesium powder II was more nearly gray in color and was not as finely powdered. The product of the reaction with SiO_2 was a half melted mass which contained many crystals of magnesium silicide. Large amounts of silane were formed when it was added to hydrochloric acid.

Silane and Its Preparation ^{4, 8, 9}

Although mono silane, SiH_4 , was prepared by Wohler and Buff ⁵ as early as 1857 and by many other workers. Our knowledge of its chemical and physical properties is due almost entirely to Stock and co-workers who began an extensive investigation in 1916. Stock prepared silane by reacting magnesium silicide with dilute hydrochloric acid. The gas obtained in this way is very impure as it contains hydrogen and a mixture of the higher silane compounds as well as silane. Of the silane mixture 40% is SiH_4 , 30% Si_2H_6 , 15% Si_3H_8 , 10% Si_4H_{10} and 5% of the higher hydrogen compounds. According to Stock the total yield of silicon containing compounds was such that only 23% ⁴ of the silicon in the magnesium silicide was converted into the various silanes. Gatterman ³ found that the gas mixture formed from the silicide which had been prepared from quartz sand contained only 5% of the mono-silane, SiH_4 . The preparation of silane in the pure condition was accomplished successfully by Friedel and Ladenburg by the cautious heating of silicoformic acid ethyl ester in the presence of sodium. The reaction runs according to the equation:



The role played by the sodium has not yet been explained. The evolved gas is collected over mercury.

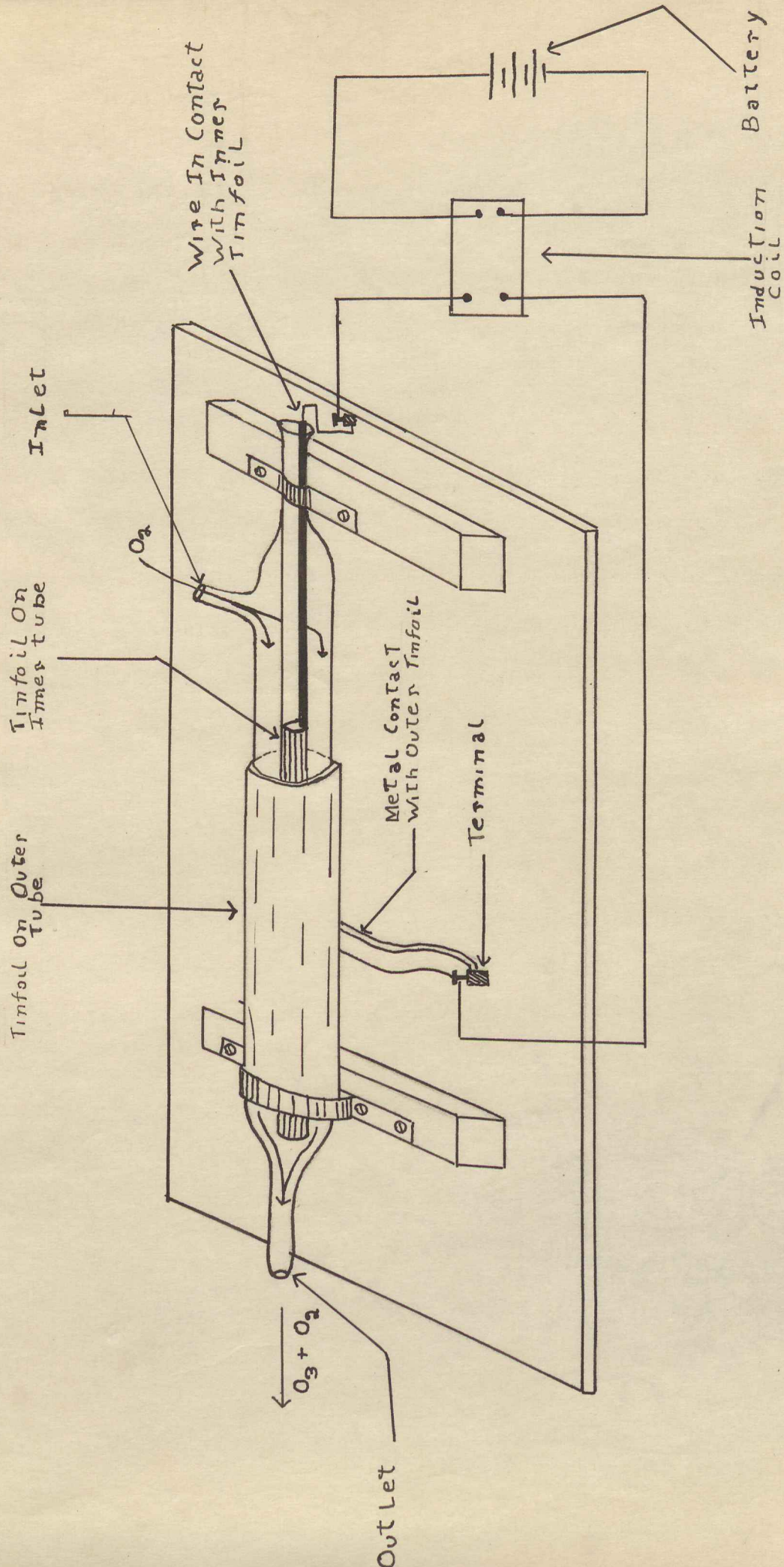
Silane can be isolated from the mixture by cooling the gasses to about - 180 degrees C by means of liquid air. As the hydrogen does not liquify at this temperature it can be separated out. When the apparatus is slowly brought back to ordinary temperatures the higher silanes remain behind as liquids and solids while the SiH_4 is evolved as a gas.

At ordinary temperatures silane is a colorless gas and is not inflamable in the pure state, but is when mixed with hydrogen. By warming and decreasing the pressure, however, SiH_4 will easily explode. It unites violently with oxygen to form SiO_2 and water. Acid solutions do not decompose the silicon hydrides, but water slowly deposes it. On the introduction of SiH_4 in an NaOH solution, there is a rapid evolution of hydrogen and a simultaneous formation of the alkali silicate.

For the preparation of silane, hydrochloric acid is used because it introduces the least disturbing side reactions. The amount of silane formed depends upon the temperature of the acid. At low temperatures a greater amount is formed but the reaction is very slow and therefore a temperature of about 50 degrees is the most efficient. There is also a greater amount of silane formed when the silicide is added slowly to the acid instead of the acid being added to the silicide.

The Preparation of Ozone

A saturated aqueous solution of ozone was used to accomplish the oxidation of the silane because it can be prepared with very few impurities. The ozone was prepared in a form of the Siemens tube and is shown in diagram I. The apparatus consists of two concentric tubes both of which are



coated on their outside surfaces with a layer of tinfoil which is connected to a terminal. The two terminals are connected to an induction coil and a battery. A slow stream of cold dry oxygen is passed through the space between the two concentric tubes and is there subjected to the action of a silent discharge which is operated by the induction coil and the battery. The gas leaving the ozonator contains from 3 to 8%⁶ ozone.

In an attempt to produce ozone for this work the inner surface of the inside tube was first covered with the tinfoil as it is in the Siemens tube but all efforts to obtain ozone with this apparatus were unsuccessful until the tinfoil was transferred to the outer surface of the tube.

The yield of ozone is dependent on the temperature of the oxygen and at high temperatures almost no ozone is formed and that which is formed is very quickly decomposed. This method of producing ozone by the action of a silent discharge seems to be the most efficient method as subjecting oxygen to the action of an electric spark will not produce appreciable amounts of the gas and as soon as it is formed it is decomposed by the high temperatures on the spark.

Ozone is much more soluble in water than is oxygen, but it is decomposed rapidly in aqueous solutions. The solubility of the gas depends greatly on the temperature of the water. At 0° C about 40 mg. of ozone are dissolved per liter of water while at 60° C no ozone can be dissolved.⁶

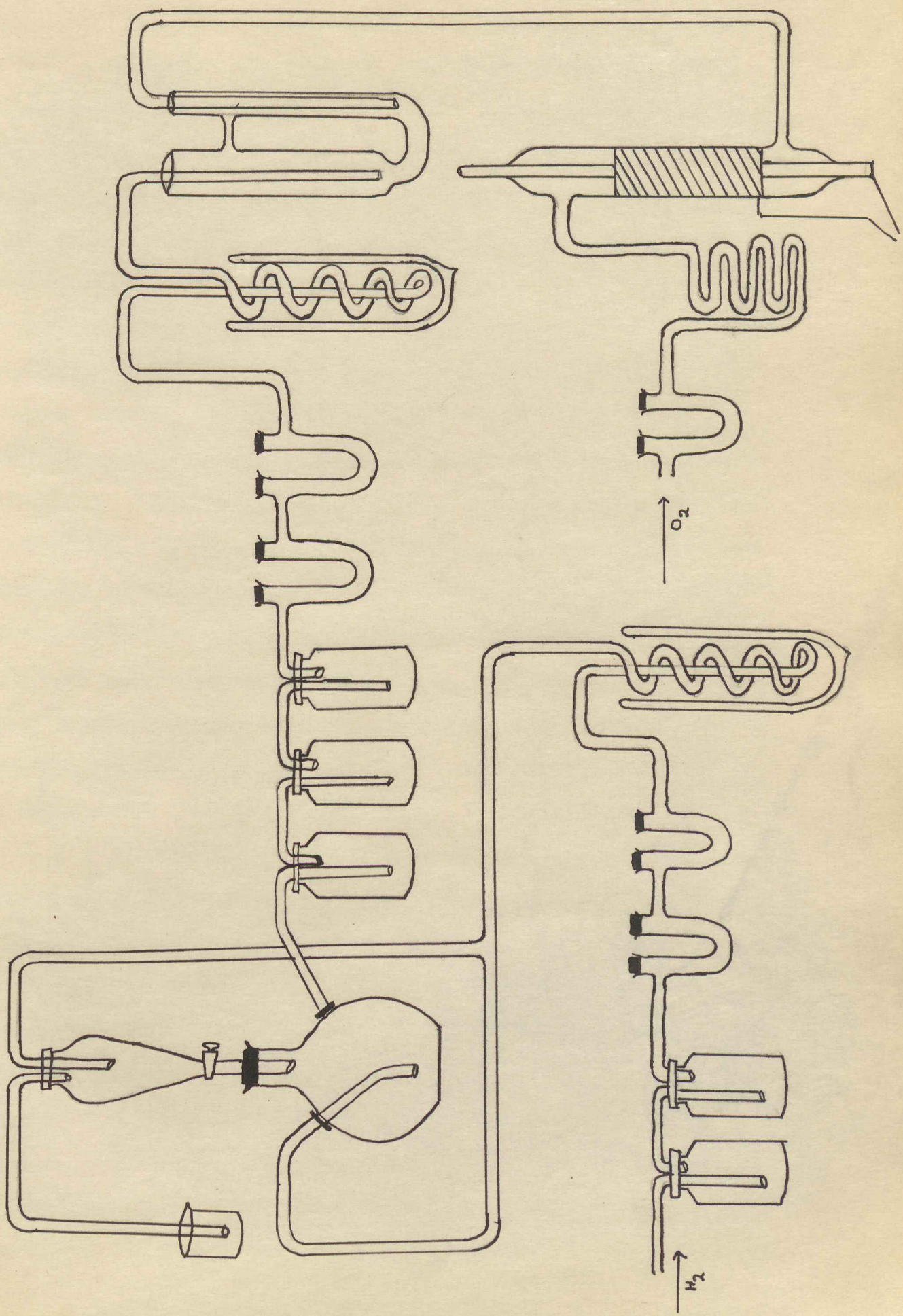
Apparatus

Because silane reacts so violently with oxygen, all the air in the system must be removed and replaced by hydrogen.

Electrolytically prepared hydrogen is the most desirable as it is usually very pure and will not introduce impurities into the ozone solution.

Hydrogen was first prepared for this research by means of an electrolytic cell containing a dilute solution of NaOH and equipped with nickel electrodes. The evolution of the hydrogen was so slow, however, that it was decided to use hydrogen prepared in some other manner in preference to that prepared electrically. The gas was next prepared in a Kipp generator by the action of hydrochloric acid on zinc. As the hydrogen could not be used directly because of a pressure large enough to force the gas thru the system could not be formed and therefore the pressure in the generator forced the acid away from the zinc, the gas was stored in a gasometer. However, even with the gasometer it was difficult to produce the necessary pressure and it was difficult to obtain a steady stream of hydrogen through the system. Therefore, this method was abandoned and commercial hydrogen in a tank was used with satisfactory results.

After leaving the tank the hydrogen passed through an empty widemouth bottle and then through a sulphuric acid washer and two calcium chloride tubes for drying. The empty bottle at the beginning of the system was used to prevent the overflow of the sulphuric acid in case the pressure was suddenly released at that end of the system. After drying, the hydrogen was led through a spiral cooling coil which was placed in a wide mouth thermos bottle. This coil was placed in the system because it was originally intended to cool the hydrogen with liquid air to remove any impurities remaining in the gas.



The liquid air, however, was not used in this work as the stage of the experiment where it was necessary to have a high degree of purity was not reached. After being cooled, the hydrogen stream was split and part of the gas went in the Mg_2Si storage chamber and part into the generating flask. The storage chamber had a separate outlet for the hydrogen. The gas was led out through a tube and bubbled thru a beaker of water to prevent air entering the system after the hydrogen flow had been cut off. In the other branch of the system the hydrogen was bubbled through the acid in the generating flask and after leaving, it was led through a series of three wash bottles to remove any hydrochloric acid which might be present in the gases. The hydrogen was then dried once more and passed thru a second cooling coil in a vacuum bottle in which it was originally intended to be cooled by a mixture of solid carbonic acid and acetone. Liquid air could not be used as the silanes would have been condensed in the coil. The gases then passed thru a filter into the oxidizing chamber. The gases remaining after the oxidation escaped into the air and were removed by the ventilator.

On the ozone side of the system the oxygen was first dried by $CaCl_2$ and then cooled with ice to increase the yield of ozone. The oxygen passed between the two concentric tubes in the ozonator and was then led into the oxidizing chamber where some of the gas dissolved, the rest was removed by the ventilator.

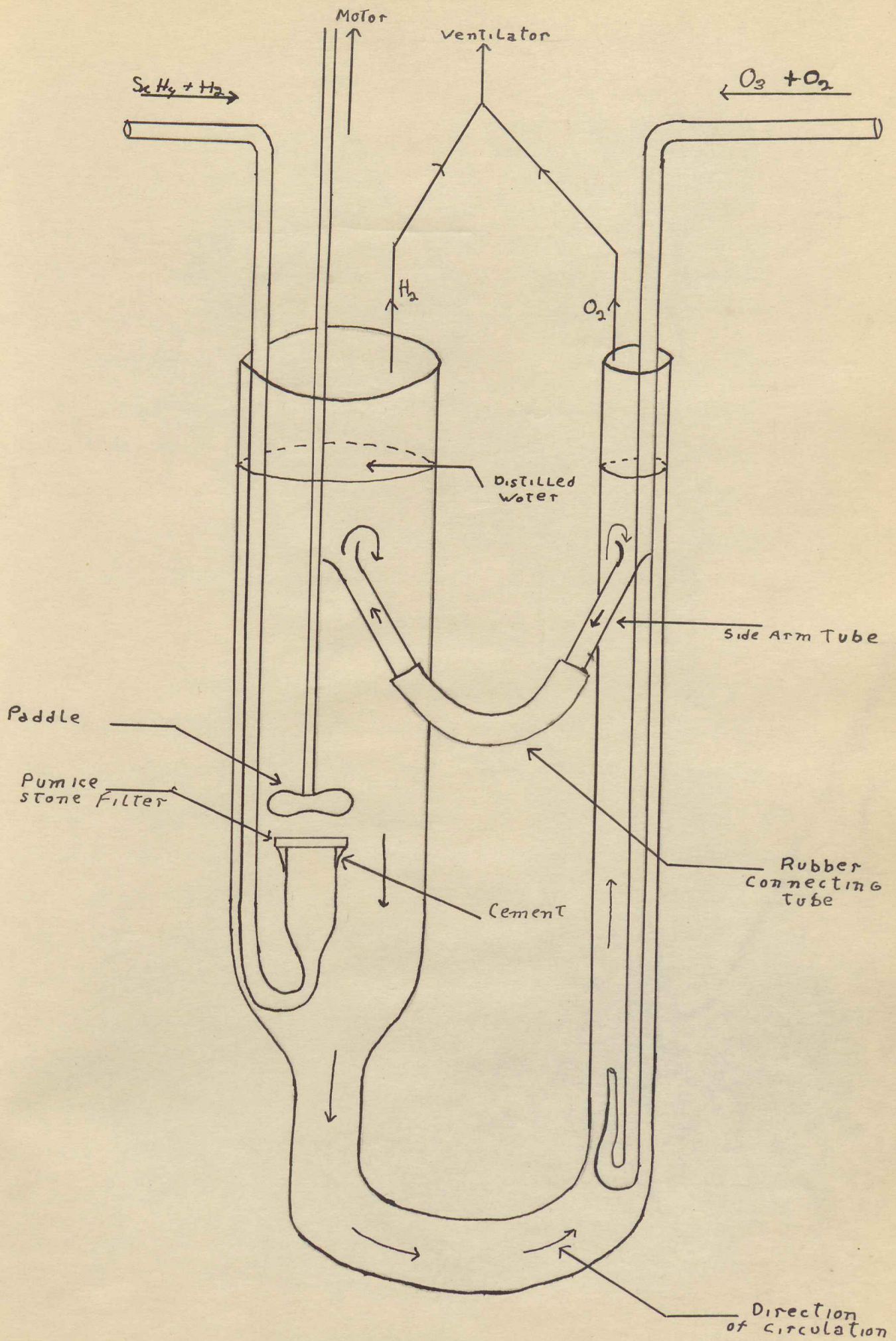
The Silane Generator

As it was necessary to add the magnesium silicide to the acid slowly in order to increase the yield, the Mg_2Si was stored in a 500 cc separatory funnel above the flask containing

the acid. The hammer of an electric bell was placed so that it tapped continually at the lower part of the funnel and kept the silicide moving down the tube into the acid. A two and a half liter flask was used for the reaction chamber. The flask was placed in a ten quart pail which was partially filled with water at about 50°C to keep the acid at its most efficient temperature. The heat of the reaction helps to keep the temperature from falling too far and by adding small amounts of hot water from time to time the acid may be kept at a fairly constant temperature. The pail also serves as a measure of safety in case all the air has ^{not} been removed from the flask and an explosion occurs.

The Oxidation Chamber

The oxidation chamber shown in the diagram consisted of two tubes of about 18 inches high and which are connected at the bottom and near the top. The wider of the tubes had a diameter of about two inches and the other a diameter of about three-quarters of an inch. The bottom connecting tube was a continuation of the narrower tube and the top connecting tube had a diameter of about $1/8$ in. The wide tube contained the silane outlet, the end of which was bent upwards and fitted with a filter to make the bubbles of the silane as fine as possible to increase the percentage of gas oxidized by the saturated solution of ozone. The narrow tube contained the ozone outlet. This outlet was also bent upwards and the end drawn into a fine opening. When the gases are led through each side of the oxidizing chamber there results a circulation of the water around the U- shaped tubes as shown in the diagram. In this way the ozone saturated water is distributed about the chamber and the ozone comes into contact with the silane.



The oxidation chamber was constructed of pyrex glass and had a volume of about 800 cc.

A wooden hood was placed above to prevent the gases from escaping and forming an explosive mixture of hydrogen and oxygen. As the ozone is more soluble in cold water than in water at ordinary temperatures, the oxidation chamber was placed in a mixture of brine and ice so that the lower part only was cooled. In order to increase the rate of circulation of the water through the tubes, and therefore increase the amount of ozone in contact with the silane bubbles as well as to increase the time required for the bubbles to reach the surface, a small glass propellor was lowered into the water and driven by a small motor placed on top of the ventilator hood.

Experimental Part

In order to be certain that all the air in the system had been replaced by hydrogen, the gas was allowed to flow thru the apparatus for about half an hour before any magnesium silicide was added to the acid. For the first few minutes the hydrogen was allowed to flow only thru the empty storage chamber, and then about 45 gr. of the silicide was poured into the funnel and the gas passed thru for a few minutes longer. This part of the system was then closed off by means of a Hoffman clamp and the hydrogen bubbled thru the acid and thru the rest of the system. As the end of the hydrogen outlet for the storage chamber was under water no air entered after the flow of hydrogen was stopped. The branch of the system into the separatory funnel must be kept closed during the remainder of the run, because there is a great enough difference in the pressures of

of the two branches to cause the acid in the generator to be forced back and into the Mg_2Si where it will start generating silane. Next the oxygen cooling coil and the oxidation chamber were cooled by a mixture of salt and ice and the acid was warmed by hot water placed in the pail containing the generating flask. It is necessary to add hot water at first to maintain a temperature of about 50° but after the beginning of the generation of silane the heat of reaction serves to keep the temperature from falling very far. During the half hour in which the hydrogen is passing thru the apparatus, the mixture of oxygen and ozone must also be flowing into the oxidation chamber in order to make sure that all of the water on both sides of the U- shaped chamber is saturated with ozone.

After the air has been removed the stream of hydrogen is slowed down so that the added pressure of the silane formed will not force a leak in the system. The hammer of the electric bell is set going so that it strikes the separatory funnel at a point just above the stopcock which is opened and adjusted so that only a small amount of silicide is added to the acid at a time. At first, although a reaction takes place, there is no sign of any silane being generated and then cloudy white fumes are formed which probably are the higher silanes which are carried along with the gases and deposited in the three wash bottles and along the connecting tubes. The higher silanes are solid or liquids at ordinary temperatures. By the time the gas reaches the oxidizing chamber all the white particles have been deposited along the way and the gas is colorless.

If too much silicide is added at once most of the silane formed escapes oxidation by the ozone but is oxidized in

the air and forms small white puffs. The silicide reacts rapidly with the acid and forms a foamy, light tan precipitate which floats on top of the acid and as it accumulates rapidly it tends to prevent the silicide from reaching the acid. The flask, therefore, must be shaken gently from time to time to allow the silicide to reach the acid. Forty-five grams of the silicide is about the most that can be used at a single run as so much of the precipitate forms that it is difficult for the substances to react. After the reaction has been going for some time the water in the oxidation chamber becomes opalescent and fairly large amounts of silica particles are precipitated out as a suspension.

The actual addition of the forty-five grams of silicide requires from one and one half to two hours. The hydrogen, however, must continue to flow thru the system for about an hour after the final addition of the silicide as the generation of silane continues for about a half hour and the flask must be shaken to be sure that all the silicide is in contact with the acid. After the completion of the reaction the system must be cleared of all silane before it is opened.

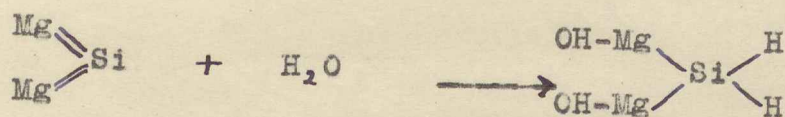
In order to find the composition of the precipitate, it was filtered from the acid and washed. Approximately sixteen gr. of the precipitate was formed when forty-five grams of the silicide was used. It did not react with sulphuric, hydrochloric or nitric acids or with aqua regia. With NaOH however, even fairly dilute solutions react rapidly with the precipitate to evolve hydrogen. Most of the precipitate was dissolved but even with hot concentrated NaOH there were small amounts which remained unchanged. When this residue

was filtered off and the filtrate was made slightly acid it became opalescent and after several days a gel was formed. The precipitate also reacted with NH_4OH but there was a greater amount of unreacted residue left behind.

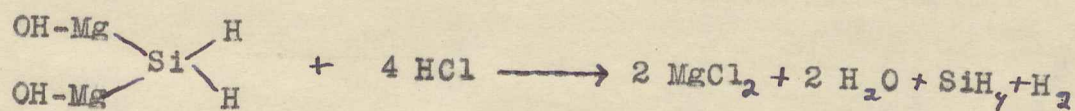
According to Schwarz and Hoefer⁷ the apparent reaction of the Mg_2Si and HCl takes place in several stages and the resulting precipitate consists of three components.

- 1) A solid silicon hydride
- 2) Prosiloxene SiH_2O
- 3) Silicon Dioxide SiO_2

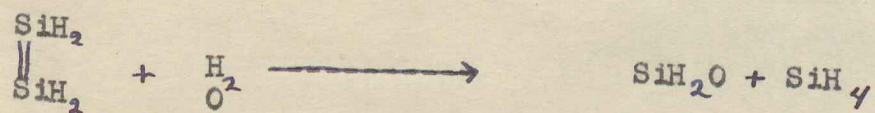
At ordinary temperatures the atmospheric oxygen oxidizes the hydride to SiO_2 . The first stage of the reaction is one of the hydrolysis of the Mg_2Si



This substance is very unstable and is quickly decomposed. The HCl removes the magnesium as the chloride and the silicon appears in the form of an unstable unsaturated compound.



The SiH_4 molecule is not stable and immediately combines with one or more other SiH_4 molecules. The polymerized compound formed is sensitive to water and reacts to form prosiloxene.



This reaction scheme is therefore able to account for the occurrence of the higher silanes and it also accounts for the presence of SiO_2 in the precipitate, as the prosiloxene is hydrolyzed to form silica and hydrogen as shown by the following equations:



In the first experiment there was no filter used on the end of the silane outlet in the oxidation chamber and therefore the small amount of silane formed rose to the surface in large bubbles and almost all of it escaped. In this run the magnesium silicide used was that prepared from the first type of magnesium. In order to find the amount of silica per liter present in colloidal form in the sol, about 200 cc of the sol were filtered and evaporated to dryness in a pyrex beaker. Practically no silica had been formed as only a slight trace of silica was left in the beaker. In the following runs the solutions were evaporated in porcelain evaporating dishes.

In order to increase the amount of silane oxidized it was necessary to decrease the size of the silane bubbles and therefore increase the amount of silane in contact with the ozone dissolved in the distilled water. To accomplish this the end of the silane outlet was bent upwards and fitted with a glass bulb which had been pierced with many small holes. This filter decreased the size of the silane bubbles somewhat, but not enough to make any great difference and practically the same results as in the first run were

obtained. So little silica was formed that the water was not opalescent and no visible particles of silica were formed. A small round porcelain disk with many holes was also tried but the bubbles obtained with this were about as large as previously.

An osmosis extraction tube produced a cloud of very fine bubbles which were about as fine as could be hoped to obtain, but after a half hour of the run had passed, the water made the tube pulpy and the bubbles gradually became larger until they were no longer efficient and the run was discontinued.

It was at this point in the research work that the new type of magnesium was used to prepare the magnesium silicide. Much more silane was produced by this silicide as could be seen by the fairly large amounts oxidizing in the air above the oxidizing chamber. As the bubbles were still large almost all of the silane escaped oxidation by the ozone. To still further decrease the size of the bubbles a thin sheet of brass was filled with a large number of holes made with a pin and the openings were hammered as nearly shut as possible. This plate worked fairly well and nearly doubled the previous amount of silica formed, but the amount formed was still far below the amount required for a 1% silica sol necessary to form a gel.

Very fine bubbles were finally produced by sealing a thin slice of pumice stone over the opening of a pipette which had been cut in half and fastened on to the silane outlet. This filter works very well for about two runs, after which it must be replaced, as the gases gradually enlarge the fine holes in the pumice and the bubbles gradually became larger.

In order to increase the length of time it took the silane bubbles to reach the surface and so increase the time in which the silane was in contact with the ozone saturated water, a small glass propellor was made at the end of a long glass rod which extended up thru the ventilator hood and was driven by a small motor on top of the hood. Besides increasing the time it took the bubbles to rise to the surface, the propellor also helped to increase the rate of circulation of the water in the oxidation chamber. This circulation was made visible by adding a small amount of starch and potassium iodide solution to one side of the chamber. When the ozone liberated the iodine, the purple color could be seen circulating rapidly thru the system.

To increase the amount of ozone dissolved, this outlet was also fitted with a pumice stone filter but this was not successful as that side of the oxidation chamber was so narrow that the end of the outlet tube could not be bent upward with the pumice on it. When the pumice faced downward the fine bubbles which were formed, collected underneath and formed even larger bubbles than those formed without the filter. Therefore, no filter was used on the ozone outlet tube. Instead, the end of the tube was bent upwards and drawn out into a fine nozzle.

Attempts to increase the silica content by bringing the silane and oxygen outlets close together were unsuccessful because the bubbles of each combined with each other and although more silica was formed almost all of it went into the form of large particles instead of colloidal form. The distance between the two outlets was varied in another container but no noticeable improvement was found.

Results and Discussion

All attempts to produce a sol of silica of a concentration great enough to form a gel were unsuccessful, but very pure dilute silica sols were easily obtained. From the information obtained by this research and from other experimentors the production of a gel by this method does not seem possible.

According to Johnson⁴ only 23% of the silicon present in the magnesium silicide is transformed into the form of a mixture of silanes. The mixture consists of 40% SiH_4 ; 30% Si_2H_6 ; 15% Si_3H_8 ; 10% Si_4H_{10} and 7% of the higher silanes. Therefore only about 9% of the silicon is in the form of silane and reaches the oxidation chamber. Since there are only about seven grams of silicon in forty-five grams of the silicide, the highest possible yield of colloidal silica is about 1.3 grams /liter, and this is far short of the amount necessary to form a gel. Furthermore, over 50% of the silica which is formed by the oxidation is in the form of coarse flakes which settle out as soon as the circulation of the water has stopped. The greatest amount of silica was formed in the final run. Of the 1.13 grams of silica formed only .558 grams were in the form of a sol, all the rest precipitated out of solution.

According to this information it would require at least 450 grams of the silicide to form a gel assuming that the silicide is pure, and that all the silica is in the form of a sol. As less than 50% is in this form, however, it would require about 1000 grams of silicide to form the 1% solution necessary to make a gel.

This is practically impossible, however, as only 45 gr. of magnesium silicide can be used in one run and each run requires from four to five hours. Even if runs were made continuously it would be difficult to obtain the necessary concentration, as, long before the last of the silicide had been used the silica formed in the first run would have coagulated and settled out. The greater part of the silica is precipitated out within twelve hours of its preparation.

Therefore, it is not possible to prepare pure silica gels, which contain no electrolytes, by this method, but very pure dilute silica sols may easily be prepared by the oxidation of silane by ozone.

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