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THE CONSTITUTION OF SILICA GEL

by

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of Doctor of Philosophy

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TABLE OF CONTENTS

Page

HISTORY AND INTRODUCTION..................... 1

EXPERIMENTAL

   Apparatus........................................ 23

   Procedure........................................ 25

   Preparation of Samples....................... 27

   X-ray Analysis.................................. 38

DISCUSSION......................................... 39

SUMMARY........................................... 45

BIBLIOGRAPHY....................................... 46
THE CONSTITUTION OF SILICA GEL

INTRODUCTION

A search of the literature reveals that as early as 1864 a paper containing many observations in regard to the composition and nature of silica gel had been published by Thomas Graham (1). The question of the constitution of silica gel has been the subject of much speculation even up to the present. The widespread interest in this problem is evidenced by the number of reports that have appeared in the literature dealing with this subject. In spite of the large amount of data that have been thus compiled, there are still a great many phases that remain as far from solution today as they were fifty years ago. Such a fundamental question, for instance, as the proof of whether silica forms hydrous hydrates or not is still probably the object of as varied and extensive investigations as any other problem connected with silica.

Graham's report is largely qualitative in nature, containing no quantitative information regarding the constitution of silica gel. It is interesting to note however, that although no hypothesis was made in regard to the state of the adsorbed water Graham did make extensive studies to show that the water in a silica gel could be replaced by many other liquids such as alcohol, ether, benzene, and carbon disulfide without alteration in the various physical properties of the gel such as its elasticity, transparency, etc.
The first quantitative work is contained in the classical series of papers published some thirty years later by van Bemmelen (2) in connection with his isothermal dehydration and rehydration studies upon silica gel. This extensive series of studies embraces nearly all phases of this interesting subject and forms the basis for most of the work that has since been carried out. van Bemmelen carried out his isothermal studies by placing a weighed amount of silica gel inside a desiccator which held varying concentrations of sulfuric acid at constant temperature. Since the vapor pressure of sulfuric acid solutions depend upon the concentration, van Bemmelen was able to maintain whatever vapor pressure he desired within the desiccator by using the proper concentration of acid. The samples were kept in contact with the various sulfuric acid solutions until equilibrium had been reached as indicated by the attainment of constant weight. Thus van Bemmelen obtained values for the compositions and the corresponding vapor pressures. It is remarkable that essentially the same results were obtained as have since been reported by means of modern precision types of apparatus where equilibrium is attained in a few minutes in contrast to the many weeks required by van Bemmelen. The major portion of this work was in connection with the phenomena of the hysteresis loop, with establishment of the fact that silica does not form hydrates, and with the effect of the aging of the gels on the shape of
the isothermal curves.

The so-called hysteresis loop results from the failure of the isothermal dehydration and rehydration curves to coincide throughout the central part of the diagram. Many experiments were carried out by van Bemmelen in an effort to show the nature and cause of this hysteresis region. It is a matter of common knowledge that the initially clear silica gels become markedly opaque during a rather definite intermediate period of dehydration and then become permanently transparent throughout the remainder of the dehydration. van Bemmelen found that the sharp transition from the transparent to the opaque gel corresponded to the beginning of the hysteresis loop on isothermal dehydration and that the return to the transparent appearance of the gel occurred at the end of the hysteresis region. It had already been suggested by Zsigmondy (3), and since been corroborated by Bachmann and co-workers (4, 5, 6, 7, 8, 9), that samples of silica gel consisted of a very large number of minute pores or capillaries. The existence of these fine pores whose walls were essentially submicroscopic or amicroscopic in nature was indicated by the ultramicroscopic studies of Zsigmondy originally and was later confirmed and extended by Bachmann with an improved ultramicroscope. This capillary picture of the gel structure was further borne out by the numerous experiments of Zsigmondy which showed that the gel could be used as an excellent ultrafiltration membrane. van Bemmelen concluded that the dehydration occurred in stages. The initial
stages of the dehydration were reversible and he concluded that this portion of the curve represented the removal of the free surface water. The middle stage where the hysteresis and cloudy appearance occur was assumed to consist in the removal of the water in the pores or cells. The cloudy appearance, according to van Bemmelen, was due to the presence of air which replaced the water in the pores. As soon as all of the pores were full of air the end of the hysteresis region was reached and the gel became clear again.

The final stage of the dehydration is assumed to consist in the removal of the final traces of adsorbed water. This portion of the curve was also found to be reversible. No explanation was given to account for the hysteresis region. However the inflection point is attributed to a change in the diffusion rate of the water out of the inner surface to the outer surface of the sample as the water content of the gel changed.

All of the isothermal curves exhibited inflection points which might be interpreted as evidence for the existence of definite hydrates. However, as van Bemmelen took great pains to emphasize, such an interpretation is entirely unwarranted since the position of the inflection points was found to depend solely upon the conditions of formation of the gels, being different for silica gels from water glass and from various silicates and even from dilute and concentrated samples of the same water glass, instead of obeying
the necessary criterion for compound formation, namely the occurrence of the inflection point at a fixed composition.

The studies upon gels which had been aged for periods varying from several weeks to several years revealed that the magnitude of the hysteresis area was a function of the age of the gel becoming decidedly smaller as the gel became older. The ultimate conclusion to the aging process was believed by van Bemmelen to be represented by hydrophan, a natural product of geologic aging, which exhibits an isothermal curve devoid of any indication of an inflection point or hysteresis area. For any given gel the hysteresis was found to occur at essentially the same vapor pressure regardless of the age of the gel. The ability of the gel to adsorb water was also found to decrease with increasing age of the gel. Consequently, it was assumed that the aging process resulted somehow in a decrease of some of the minute capillaries originally present in the gel.

After van Bemmelen's classical investigations were reported, Lowenstein (10) made a more extended study of the gels prepared from a number of different silicates. The same type of dehydration curves were obtained as van Bemmelen's and it was also concluded that no hydrates of silica were formed.

Zsigmondy (5) repeated much of the preceding work using an improved form of apparatus and obtained excellent agreement with the experimental results reported by van
Bemmelen. In addition, further experiments were made on the aging of the gels by means of artificial methods, such as heat treatment, in contrast to the process of natural aging previously employed. The procedure followed was to heat the gel after its initial formation to various elevated temperatures prior to carrying out the isothermal studies upon it. As in the case of the normally aged gels studied by van Bemmelen, it was found that the size of the hysteresis region was a function of the amount of aging, being smaller at the higher aging temperatures. As before, the hysteresis was found to occur at approximately the same vapor pressure for all samples of the same gel regardless of the heat treatment received.

Zeigmondy offered the first suggestion to account for the existence of the hysteresis loop. According to his theory, the difference between the curves for dehydration and rehydration is caused by the entrance of air into the pores, thus preventing the water from completely wetting the pores during the rehydration. It is a well known fact that the vapor pressure of a liquid in a small capillary space is greater than that observed under normal conditions. In connection with the experiments upon the samples aged by heat treatment, Zeigmondy points out that the reason the hysteresis areas commence at the same vapor pressure before and after heat treatment is because the heat treatment has not affected the pore size of the capillaries as shown by
the ultramicroscopic examination, and consequently since the vapor pressure is a function of the pore size, it would also remain unchanged; however, the heat treatment destroys some of the pores or closes them off and consequently decreases the hysteresis areas.

From the volume required to fill the pores at the saturation pressure of water, Zsigmondy was able to calculate the average pore size by means of a theoretical equation relating the size of a capillary and the consequent lowering in the vapor pressure of a liquid contained in it. That the calculated value agreed remarkably well with the average size obtained from the ultramicroscopic measurements must be considered strong evidence for the existence of pores in the silica samples.

Among the other investigators who have repeated and confirmed the earlier results of van Bemmelen and Zsigmondy are Berl and Urban (11). Their work is of interest because it shows the remarkable stability of the gel structure and also because in place of the usual static method, a dynamic method was used in obtaining the isothermal dehydration and rehydration curves. This method consisted essentially in passing air containing definite amounts of water over the samples until equilibrium had been reached. The stability of the pore structure of a silica gel was revealed by the fact that a marked hysteresis was still observed in the curves for a sample which had been heated to 1000°C for
ten minutes.

As previously mentioned, qualitative experiments indicated that the water content of silica gel could be replaced by many other liquids without apparently affecting the physical character of the gel. In 1914 Anderson (12) published the first quantitative studies upon this property. The results of his isothermal studies indicate that irrespective of the liquid used the same volume of each is adsorbed at the saturation pressure. This is further evidence pointing to the conclusion that silica does not form a hydrate because it is difficult to conceive of compounds of silica with inert organic liquids. The results also confirm the capillary concept of the gel structure since from this theory the same volume of any liquid would be expected to fill the pores. In this connection it must be noted, however, that the results of several more recent investigators are not in entire accord with Anderson's observations. For instance, Rao (13) has recently reported that isothermal studies upon the adsorption of carbon tetrachloride by silica shows a marked hysteresis loop but that the volume of liquid adsorbed is somewhat less than that corresponding to water. The results reported by Lambert and co-workers (14,15) are contradictory in themselves since it was first reported that no hysteresis was found for the adsorption of benzene and alcohol upon silica and in a later report hysteresis was described for the adsorption of the alcohol.
The whole question of the existence and cause of the hysteresis was recently revived by Patrick and his co-workers (16,17,18). These investigators took drastic precautions to insure the complete removal of air from their samples and also from the apparatus. Since no hysteresis was observed under such conditions, it was reported that the hysteresis was caused by the existence of air in the system which prevented the attainment of equilibrium. However, examination of Patrick's data reveals that his experiments were carried out over a pressure range below that in which the hysteresis is to be expected. Numerous investigators have since taken precautions to remove the last traces of gases from their samples and apparatus and all have obtained the characteristic hysteresis loop when working in the correct range. The recent results of Rao (loc. cit.) upon the question of hysteresis which will be discussed later in some detail, establish beyond a doubt the reality and permanence of this phenomenon even in the absence of air.

Numerous types of evidence other than that given above have been offered to support the belief that silica does not form hydrates. Lenher (19) made an interesting series of experiments in which he subjected a silica gel which initially contained 80-90% water to various pressures from 340 to 272,000 kg./in. by means of a hydraulic press. Analyses were made of the water content of the samples after subjection to each pressure. From the resulting data
Lenher showed that a continuous loss of water resulted from increasing pressure and concluded that the so-called silicic acid and its gels should be regarded as having the general formula \( x\text{SiO}_2 \cdot y\text{H}_2\text{O} \) in which the quantities of water and silica can vary from a true solution of \( \text{SiO}_2 \) in water successively through the highly hydrated gels which pressure alone will convert from a water content of nearly 98% to only a few percent.

Since water must always exert a vapor pressure irrespective of its condition in a gel, it is difficult to draw definite conclusions as to the condition of the water from measurements based directly or indirectly upon the vapor pressure exerted by the gel because such conclusions must be based upon the changes in the direction of the vapor pressure curve rather than upon direct measurements of the amounts of the water in each of the possible conditions in which it may exist within the gel. Consequently many observers have carried out experiments designed to determine directly the condition of the water in the gel. Most of these studies have been based directly or indirectly upon freezing point studies. Such studies involve the assumption that hydrate water cannot be frozen. The initial work of this sort upon silica gels was done by Lottermoser (20). Bruni (21) froze silica gels and then analyzed the residues. He found that the composition of the residues was variable and concluded therefore that no hydrates were present. The
results of Bruni were extended by Vanzetti (32). The latter prepared samples by the addition of hydrochloric acid to dilute and concentrated water glass solutions obtaining gels from the former and granular precipitates from the latter. These samples were frozen at various temperatures and the residues analyzed. Vanzetti concluded that no hydrates were formed and that the final composition depended entirely upon the initial composition and the age of the gel. His experiments upon the freezing of aged gels confirms the earlier results of van Bemmelen's since the freezing of the older gels produced more advanced dehydration. An obvious objection to the preceding technique involving freezing the gels is the difficulty of separating the water from the residue after melting; consequently, constant results should not have been expected.

In the attempt to overcome this objection a different procedure was adopted by Foote and Saxton (33), which consisted in freezing a gel of known water content in a dilatometer and measuring the expansion produced during the freezing. Foote and Saxton point out that upon consideration of the isothermal curves of preceding investigators and upon the basis of the other information available, such as the ultramicroscopic studies, it seems probable (a) that the initial stages of dehydration where the vapor pressure is the same as that for pure water consists in the removal of free water, i.e., water which has merely condensed upon the sur-
face; (b) but that the water which comes off immediately after and at a vapor pressure below that for pure water is capillary water; while (c) the last water which comes off at very low pressures is "combined" water or water in solid solution. According to Foote and Saxton there is a regular initial decrease in the dilatometer readings due to the contraction of the bulb and its contents. At a temperature several degrees below zero this initial decrease is followed by a sudden expansion which is interpreted as being due to the freezing both of the free water and that part of the capillary water whose freezing point has been reached.

Further lowering of the temperature is accompanied by a small regular expansion attributed to the freezing of the water in progressively smaller capillaries and finally by a slow steady contraction. The unfrozen water or "combined" water is gotten by difference from the original water content of the gel and the amount of water frozen as indicated by the dilatometer readings. Further evidence for the existence of extremely fine pores in the gel structure is indicated by the fact that even at temperatures as low as \( -33^\circ C \), an increase in the dilatometer readings shows that water in the capillaries is still being solidified. On the basis of such measurements, Foote and Saxton reported the amounts of "combined" water in two samples as being 28.1 and 29.7%, corresponding to the empirical formulas \( SiO_2 \cdot 1.21\text{H}_2\text{O} \) and \( SiO_2 \cdot 1.35\text{H}_2\text{O} \). It is admitted that accurate results are difficult to obtain.
due to the occurrence of supercooling not only of the water but also of the dilatometer itself and it was also suggested that the amounts of "combined" water reported were probably high because of capillary water that had not been frozen. In the correlation of their experimental results and the isothermal curves of previous observers, Foote and Saxton believe that after the removal of the free water further dehydration involves one of two possibilities: (a) the capillary water will be entirely removed followed by the "combined" water or (b) the capillary water will be partly removed followed by the "combined" water. It was first assumed that the vapor pressure of all the capillary water exceeded that of the "combined" water and that consequently the amounts of the "combined" and capillary water could be determined from the dilatometer experiments. However, there seems to be no reason why all the capillary water should have a higher vapor pressure than the "combined" water; it seems much more likely that the "combined" water may begin to be removed before all the capillary water is gone. In this case the dilatometer data will not indicate the composition on the vapor pressure curve at which the "combined" water begins to be removed. In either case, if the "combined" water were hydrate water a horizontal portion should exist on the vapor pressure isotherm. Since such a horizontal portion had not been reported by the previous investigators, it was concluded that the "combined" water was in the nature of a solid sol-
ution rather than in the form of a hydrate.

Additional evidence as to the nature of the "combined" water has been made available by the experiments of Bartell and Almy (24) upon the heat of wetting of silica samples. In these experiments it was assumed that the heat of wetting could be taken as a measure of the activity of the gel. It was found that the most active gel was one which had been heated at about 300°. Since heating to temperatures as high as this decreases the water content of the gel, it is not obvious why the gel with the lower water content should have the lower heat of adsorption. In order to explain this, Bartell was forced to conclude that the water present in the gel before activation was not all held in the same manner. A part was apparently held in large capillary spaces and was easily removed by moderate heat treatment, thereby accounting for the increased activity as measured by the heat of wetting. The remainder is "bound" apparently much more firmly in such minute pores or capillaries in the gel that the binding forces are those of adhesion rather than those of cohesion (Fells and Firth (25) and Jones and Gortner (26)). Removal of water from these pores results in a partial collapse of the structure, thereby decreasing the effective surface and also the activity.

It is generally assumed that the power of gelatinization of a sol is closely related to the solvation of the disperse phase. Gaunt and Usher (27) have made measurements upon the change in the concentration of an indifferent solute caused by gelatinized silica on the assumption that if hydration of the micelle occurs the proportion of the ref-
ference substance in the intermicellar liquid will be increased to an extent depending upon the hydration. This method was previously used for a similar purpose by McBain and Jenkins (28) in the case of some soap solutions. An essential condition for the successful application of the method is that the reference substance be chemically indifferent to the disperse phase and that it be not appreciably adsorbed by it. Sulfuric and nitric acid were found to be best suited for this purpose. The procedure followed was to pour a solution of water glass into an excess of acid solution containing the reference substance, the quantities and compositions of the liquids being such that gelatinization would not occur during the time necessary for a sample to be taken, weighed, and diluted. Then after the remaining solution had gelled and been allowed to undergo syneresis, a sample of the syneretic liquid was taken and analyzed. From a comparison with the original analysis the amount of water associated with the silica was deduced. The mean value of the mole ratio of water to silica for sixteen samples was found to be $1.04 \pm 0.03$. On the basis of these results and assuming that a gel is composed of long fibrils intermeshing the intermicellar liquid, gelatinization may be regarded as a chemical process in which the fibrils are actually merely long chains of metasilicic acid. However, on the basis of other considerations in connection with jelly formation, these authors conclude that the close approach
of the $\text{SiO}_2/\text{H}_2\text{O}$ ratio to a value of one is accidental and
of no chemical significance in regard to hydrate formation.
This conclusion is further strengthened by the results of
additional work by the same procedure reported by Ferguson
and Applebey (29), who studied the effect of increased $\text{pH}$
upon the bound water in silica gels. The results showed
that the amount of bound water increased continuously rather
than stepwise with the $\text{pH}$ of the sol from a value of 0.87
at a $\text{pH}$ of about 4.4 to a value of almost two moles of sil-
ica to one of water at a $\text{pH}$ of about 10.

Pascal (30) analyzed three different types of
hydrous silica samples by magnetic means and found no evi-
dence of hydrate formation since all of these samples be-
haved like mixtures of the anhydrous oxide and water.

Perhaps the most far-reaching evidence against the
formation of hydrates of silica is to be found in the results
of an x-ray study made upon silica gels by Krejci and Ott (31).
The presence of crystal nuclei is reported by these observers
to have been found in a series of gels, none of which had
been heated to temperatures approaching $1000^\circ\text{C}$. and in par-
ticular in one sample which had not been heated above $100^\circ\text{C}$.
The pattern obtained was not that of a silicic acid but was
identical with the cristobalite pattern of silica itself.
It would appear from Krejci and Ott's work that crystalline
nuclei of colloidal dimensions are present initially in at
least some gels of hydrous silica; but unfortunately no one
has been able to confirm their observations.

Although the evidence against the formation of hydrates appears fairly conclusive, many attempts have been made to isolate the various hypothetical hydrates. Among the early workers who claimed to have obtained evidence for the existence of such hydrates, the most prominent authorities were probably Tamman (32) and Tschermak (33). Tamman argued that the inflection points obtained in the first curves reported by van Bemmelen indicated the existence of definite hydrates. However as more extensive studies were published by van Bemmelen it became quite apparent that the inflection points were influenced by the temperature at which the samples were dried, by the nature of the drying agent, and by the age and history of the sample; consequently, such inflections did not represent the existence of a definite hydrate. Tschermak did not use a vapor pressure method in his studies but measured instead the velocity of the change in loss of water and plotted the change in weight per unit time vs the time. The resulting curves contained inflection points which were assumed to represent hydrates. Based upon the water content corresponding to these inflections, Tschermak assigned definite formulas to the hydrates. Mugge (34) and also van Bemmelen showed that the inflections thus obtained not only were not sharp so that almost any number of formulas could be assumed from an examination of the curves but also that the inflections changed considerably with the temperature.

Still more recently Thiessen and Koerner (35) have
claimed the existence of acids with $\text{SiO}_2/\text{H}_2\text{O}$ ratios of 2:5, 1:2, and 2:3 from vapor pressure isotherms for silica gels prepared by the slow hydrolysis of ethyl silicate. The work of these investigators has recently been very carefully checked by Weiser, Milligan, and Coppoc (36), who found no support for the existence of these hydrates. It was suggested that the results of Thiessen were due to faulty technique or to failure to attain equilibrium.

Many investigators claim to get stepwise curves for samples of silica that have been prepared with non-aqueous solvents. The chemically combined water in a hydrous system according to Willstatter, Kraut, and their co-workers (37) may be detected and estimated either by procedures which distinguish between the two kinds of water or by procedures which depend upon the separation of the two types. Willstatter believes that the results of investigators such as Foote and Saxton, who used procedures based on the first of these two methods, are unsatisfactory since the adsorbed water is held by very strong forces approximating those of chemical union and the method cannot be of value unless it is known that all such adsorbed water has been frozen.

Willstatter and Kraut have, therefore, attempted to realize the second possibility by keeping the moist gels over sulfuric acid or phosphorus pentoxide in a high vacuum until constant weight was attained by the samples. During the time necessary to reach equilibrium, however, chemical
changes were noticed which made the subsequent analytical measurements of doubtful value. In order to overcome this defect, a much more rapid drying procedure was adopted which consisted in treating the gel repeatedly with dry acetone, then with ether, and finally removing the ether in a high vacuum. Under these conditions the water content of the gel is considered to represent solely the amount of the "combined" water. At room temperature the amount of "combined" water was found by this procedure to correspond to that of a so-called "mono-silicic" acid. In a series of further experiments based upon passing silicon tetrachloride into water solutions in which the pH was carefully controlled by the addition of Ag₂O or by the addition of suitable mixtures of organic salts and acids, Willstatter and his co-workers have claimed the formation of a large number of silicic acids. The chief evidence for the existence and identity of these acids is found from the measurements of freezing point depressions, potentiometric data, analyses of the resulting solutions, and from the differences in ability to dialyse and to produce a precipitate with egg albumin. The mono and di-hydrates are said to be fairly unstable, indeed to exist at all only in a very narrow pH range, and are supposed to polymerize with loss of water, thus forming the higher acids. Willstatter is thus of the belief that well defined hydrates are present in the original gel but that in the presence of water such hydrates are unusually labile and rapidly under-
go inter- and intra-molecular dehydration.

Because of the failure to isolate the various hypothetical silicic acids in the presence of water, many observers have attempted to prepare the acids in the absence of excess water by various types of decomposition reactions. Schwarz and Menner (38) claim to have prepared sodium meta-, di-, and tri-silicates by a fusion method consisting in heating the calculated amounts of powdered quartz and sodium carbonate at elevated temperatures. Upon the addition of 90% sulfuric acid to such samples at 10°C, the corresponding silicic acids are claimed to result. The excess water can be removed, it is said, by washing the samples in alcohol and ether and the analysis of the resulting products indicate the correct composition for these acids. In addition it is stated that breaks in the desiccation curves at room temperature occur at the theoretical compositions for the hydrates $\text{H}_2\text{SiO}_3$ and $\text{H}_3\text{SiO}_4$. In a later report made by Schwarz and Richter (39) upon these two acids, it is claimed that the monohydrate has an amorphous pattern whereas the dihydrate has a distinctly crystalline diffraction pattern. Since no information is given as to how the pattern was obtained, it appears likely that it resulted either from an impurity in the gel or from cristobalite.

Biltz and Rahlfs (40) prepared silicic acids by the method of Schwarz. They claim to have obtained a distinct x-ray pattern from an acetone-dried sample of di-silicic acid
prepared from synthetic Na$_2$SiO$_3$. Indications of a crystalline x-ray diffraction pattern was obtained also from a similarly treated sample of the monosilicic acid prepared from a synthetic sample of Na$_2$SiO$_3$.

Simon and Rath (41) have obtained indications of the existence of ortho, pyro, and meta silicic acids in their studies with a modified form of the Huttig (42) tensimeter.

Although some of the above evidence when considered by itself appears to be fairly conclusive evidence for the existence of hydrates yet when surveyed as a whole it is evident that there is very little agreement among the results reported by the various investigators. It seems probable that many of the breaks and inflection points obtained by the above workers and attributed by them to the presence of hydrates are largely due to the failure to attain equilibrium.

Two years ago it was reported from this laboratory (36) that dehydration isotherms for hydrous silica gels prepared from silicon tetraethylate contained a point of inflection analogous to those obtained by van Bemmelen for gels prepared from water glass, but, in contrast, smooth curves were found for gels prepared from sodium metasilicate. The purpose of the present investigation has been twofold, being in the first place to extend the previous studies in the hope of explaining the apparently anomalous results obtained for gels from sodium metasilicate, and in the second place to study more fully the effect of different temperatures of
formation upon the nature of silica gel.
EXPERIMENTAL

Apparatus:

Among the methods which have been found most convenient in determining the presence or absence of hydrate formation are isothermal phase rule studies and x-ray diffraction procedures. In the present investigation both of these time honored methods were used.

Many varieties of apparatus have been devised for carrying out isothermal dehydration and rehydration studies. The essential parts of any apparatus for such work are devices for measuring the vapor pressure of the sample and the corresponding composition of the solid. The apparatus varies from the comparitively crude types used by van Bemmelen and the other early workers to the much more complicated types such as the one described by Shidei (47). From the standpoint of accuracy, simplicity, and compactness, it was decided to use a modified form of the apparatus previously described by Weiser, Milligan, and Coppoc (loc. cit.). It consisted essentially of an all glass system containing an oil manometer and a McBain-Bakr silica spring balance (48). The apparatus was improved by the addition to the system of a small tube containing barium chloride hydrate whereby isothermal rehydrations could be effected without the dehydrated sample coming into contact with the atmosphere. Thus by means of a small flame water could be driven out of the
barium chloride and introduced into the system in any desired amount by means of a connecting stopcock.

Vacuum pump oil having a density of 0.9204 gr./cc. at 25°C was used in the manometer. An Eberbach cathetometer capable of being read to ± 0.1 mm. was used to measure the difference in the oil levels in the manometer. In order to maintain the manometer at a constant temperature, water from a thermostat maintained at 25°C. was circulated through a glass tank surrounding the manometer.

A small glass fiber suspended beside the silica spring served as a standard for measuring changes in the length of the spring. The fiber was of such length that the end of the spring and the end of the fiber were close together when the empty sample container was suspended from the spring. A precision measuring microscope was used to measure the changes in the length of the spring. Readings could be duplicated to 0.005 mm. (approximately equivalent to 0.02 mg.). The range of adjustment of the microscope was such that a 100 mg. sample could be conveniently measured. The spring was calibrated by means of a set of analytical weights calibrated against a standard weight from the National Bureau of Standards. The samples were placed in aluminum buckets suspended well below the water level in the thermostat by means of a long quartz fiber attached to the spring. Because of the tendency to "bump" it was found necessary partially to close the open end of the
bucket to prevent loss of the sample during the dehydration.

The temperature in the thermostat was maintained at a temperature of 13.0°C. quite easily by means of a mercury-toluene regulator which, in conjunction with a system of sensitive electrical relays, was capable of maintaining a constant temperature of 0.05°C.

Procedure:

The general procedure for carrying out a complete isothermal dehydration and rehydration was as follows. After introduction of the sample, the apparatus was evacuated for about ten minutes in order to insure complete removal of the air in the system. For this purpose a Cenco Hyvac pump was employed. During this stage, the part of the apparatus in which the sample was suspended was surrounded by an ice-salt bath in order to prevent excessive removal of water from the sample. The system was then closed to the pump and allowed to reach equilibrium at 13.0°C. as indicated when a change of not more than 0.1 mm. could be detected in successive readings at half-hour intervals in the oil level of the manometer. In most cases it was found that equilibrium was established within two or three hours. After equilibrium was attained a reading was made of the difference in length of the silica spring and recorded with the corresponding vapor pressure as indicated by the manometer. The remainder of the dehydration consisted in pumping off successive portions of the water and making measurements of the
vapor pressure and the corresponding changes in the length of the spring after equilibrium had been reached. The same procedure was then repeated for the rehydration except that water vapor was now added to the system by means of the barium chloride tube.

In order to convert the readings for the changes in composition to moles of $H_2O/\text{SiO}_2$ it is necessary to determine the $\text{SiO}_2$ content of the sample. This was done by transferring the entire sample upon completion of the run to a weighed crucible and igniting it to constant weight. This procedure was made possible due to the fact that the silica did not stick to the aluminum buckets and consequently could easily be removed in its entirety.

**Preparation of the Samples:**

**(A) Hydrous Silicon Dioxide from Water Glass**—Samples 1, 2, 3, and 4 were prepared by the rapid addition accompanied by rapid stirring of 40 cc. of Philadelphia Quartz Company "D" Brand water glass to 50 cc. of a solution containing 15 cc. of glacial acetic acid at temperatures of 0, 25, 60, and 100 °C., respectively. The solutions of both acid and water glass were brought to the desired temperature before mixing and after mixing were maintained at this temperature until gelling or precipitation was complete. The hydrous silica thus obtained was washed repeatedly with distilled water and centrifuged until the supernatent liquid was no longer acid to litmus. All samples except 1 and 3 were dried
at room temperature by a current of air. Samples 1 and 3 for reasons given later were only partially dried before being placed in the apparatus.

(B) **Hydrous Silicon Dioxide from Sodium Metasilicate**

The sodium metasilicate solution was prepared by dissolving Philadelphia Quartz Brand powder in enough water so that each cubic centimeter of solution contained 0.130 g. of \( \text{SiO}_2 \) in order to correspond to the experimentally determined silica content of the water glass solutions used above. In analogous manner to the procedure followed above, samples 5, 6, and 7 were prepared by the addition of 40 cc. of sodium metasilicate solution to 50 cc. of a solution containing 15 cc. of glacial acetic acid at the respective temperatures of 0, 25, and 100° C. Sample 3 was prepared by initially boiling the metasilicate solution for several hours under reflux before adding it to the acetic acid. The samples were subsequently washed free of acid and dried in air as described above, with the exception of sample 5, which was only partially dried before use. Typical data for one of the isothermal runs is given in the accompanying table. The dehydration and rehydration isotherms obtained for these samples are given in figures 1 to 9.
Table of Sample Data
(Silica Gel Prepared from Water Glass - Sample 2)

Wt. of empty bucket determined directly on spring--0.08592 g.
Wt. of SiO₂ in sample determined by ignition-------0.04495 g.

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<th>Composition* Moles H₂O/SiO₂</th>
<th>Vapor Pressure of Oil cm.</th>
<th>Vapor Pressure of Hg mm.</th>
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* Calculated on the basis that a load of 1 mg. was found to produce an extension of 0.3268 mm. in the spring.
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<th>Spring Extension in cm.</th>
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FIGURE 2, SAMPLE 2
FIGURE 3, SAMPLE 3
FIGURE 4, SAMPLE 4
FIGURE 5, SAMPLE 5
FIGURE 6, SAMPLE 6
Figure 7, Sample 7
FIGURE 8, SAMPLE 9
**X-ray Analysis:**

The x-radiograms were made with a Phillips Metalix crystal analysis unit using filtered Cu Kα radiation. Samples of the dehydrated gel as well as samples of the moist gel were used. The dehydrated sample was prepared by filling an x-ray sample tube with the gel followed by evacuation of the tube at room temperature for a period of twelve hours by means of a Cenco Hyvac pump. The tube was then sealed off under vacuum. The moist sample was prepared by saturating a sample of the gel kept at 13.0°C with water vapor before placing it in the sample tube. The most satisfactory exposure time for the samples was found to be about ninety minutes when using Eastman "No-Screen" x-ray film in the cameras. The resulting x-radiograms are of the amorphous type and are identical, except that the pattern for the wet gel shows the bands from the water pattern superimposed on the bands from the silica. There is no indication of the formation of a definite hydrate.
DISCUSSION

In the present investigation several different procedures have been followed in the isothermal dehydrations and hydrations. Since the amount of water retained by most of the samples after drying in air at room temperature is rather low, the general procedure has been to dehydrate initially the samples in the apparatus before beginning the actual runs. Thus the points shown on the curves (2, 4, 6, 7, and 8) represent the values obtained for subsequent hydrations and dehydrations. This procedure has the obvious defect of making it impossible to detect the presence of any higher hydrates which might be irreversibly decomposed during the drying process. In order to eliminate this possibility, several dehydrations were carried out on gel samples that had been only partially dried before being placed in the apparatus. These curves (1, 3, and 5) are essentially the same as the others and show only a single point of inflection. The only significant difference is that the first dehydration isotherm for the moist gels is displaced in its initial portion from the subsequent hydration and dehydration curves. The position of this curve as shown in the figures indicates that a larger amount of water is retained by the gel for a given vapor pressure during the first dehydration than during any of the subsequent hydrations. Evidently some irreversible change takes place in the phys-
ical characteristics of the gel structure during this initial dehydration such as possibly the destruction of some of the larger capillary spaces that one would expect to be present initially in the fresh gel. As shown in the figures, the curves for the subsequent hydration and dehydration do not coincide except in the upper and lower portions, namely the regions of higher and lower vapor pressures, respectively, thus giving rise to the familiar hysteresis loop. This hysteresis loop might at first thought be attributed to failure to attain equilibrium along this portion of the curve. However, this possibility has been carefully tested experimentally by allowing periods of from 8-10 hours to elapse between readings. Even over such long intervals no detectable change could be observed on the manometer. The hysteresis loop shows a remarkable reproducibility and permanence. As is shown in figure 5, the points taken on a third hydration and dehydration fall on the same curves as resulted from the initial hydration and dehydration. In a recent report, Rao (loc. cit.) has shown that even after as many as 18 or 19 dehydrations of a heat-treated gel the same path was followed on the 19th dehydration and hydration as was followed in the initial run.

In figure 9 is shown the results on "scanning" the hysteresis loop of a typical gel, namely the gel whose complete isothermal curve is shown in figure 6. The present
results are in good agreement with the results recently published by Rao. The essential facts, as can be seen from the figure, are twofold. In the first place, if dehydration is begun from any part of the sorption branch of the hysteresis loop, the resulting desorption curve follows a horizontal course with a downward sweep finally coinciding with the desorption branch of the loop. In the second place, if sorption is begun from any point on the desorption branch of the loop, the resulting curve follows an upward course sloping toward the sorption branch. However, it never coincides with the sorption curve except at the extreme uppermost part of the curve.

Curves 1 to 4 show the results of isothermal studies made upon silica gels prepared at 0, 25, 60, and 100°C. by the addition of acetic acid to water glass solutions. An inspection of these curves reveals that a point of inflection exists in all cases, occurring at a vapor pressure of approximately 4-5 mm. of Hg. Such a point of inflection for a system such as this might indicate the existence of a definite hydrate, provided such an inflection occurred in all cases for various samples at the same composition. From figures 1 to 4, it will be observed that the inflection points do not occur at a constant composition but vary with the temperature of formation for the different samples. For instance, the inflection point in figure 1 for the sample prepared at 0°C. occurs at a composition of about 1.5 moles of water per
mole of silica as compared to the value of 0.65 for the sample prepared at 100°C, as shown in figure 4.

The results for the isothermal studies upon silica gels prepared by the addition of acetic acid to sodium metasilicate solutions rather than to water glass under analogous conditions of temperature, are shown in figures 5 to 8. As can be seen, sharp inflections occurring at different compositions are obtained for the various samples just as was found true for the gels formed from water glass. These results and the analogous ones obtained for water glass confirm the historical investigations of van Bemmelen and the more recent work of other investigators (Anderson, Zeigmondy, Bachmann, etc.), who concluded that silica did not form any definite hydrates.

The curves obtained for the gels prepared from the metasilicate solutions are in disagreement with the results of a previous report made from this laboratory (36) in which it was claimed that smooth curves were obtained for gels prepared from sodium metasilicate. In the present study all solutions were freshly prepared at the same temperatures to be later used in the actual preparation of the gels. In the earlier investigations all the metasilicate samples were previously warmed in order to hasten solution of the solid sodium metasilicate. In order to test the effect of such warming, an isotherm was run upon a sample prepared at 100°C from a solution of sodium metasilicate that had been pre-
viously heated for several hours under reflux. As can be seen from figure 8, a smooth curve is now obtained in contrast with the curve for a gel prepared under the same conditions from a fresh sample of sodium metasilicate that had not been previously heat treated. Thus the explanation for the smooth curves previously reported is apparently due to the effect of the heat treatment.

The essential difference between the gels prepared from sodium metasilicate and those prepared from water glass under similar conditions appears to be the increased aging of the samples prepared from water glass. Examination of curves 1 to 8 reveals that not only the hysteresis areas but also the inflections are more marked for the gels prepared from metasilicate than for those prepared from water glass under similar conditions.

Water glass is generally considered to consist of a colloidal solution of silica particles. On the other hand a sodium metasilicate solution probably consists to a large extent of silicate ions and to a smaller extent of colloidal silica particles produced through hydrolysis. In other words, a metasilicate solution differs from water glass solution mainly in that such solutions are not so completely hydrolyzed as the water glass solutions under analogous conditions. One should therefore expect that upon heating a metasilicate solution, it would be more completely hydrolyzed and consequently such a sample should be more closely analogous to the corresponding water glass sample. The final
product of such heat treatment and aging should be a sample such as natural opal which gives a smooth isothermal dehydration and rehydration curve with no indication of hysteresis or inflection points. This condition has been closely approached in the case of the silica gel prepared from water glass at 100°C., since this isotherm exhibits only a very small hysteresis loop and the inflection is much less definite than in the other isotherms. With continued heat treatment a sample should result that would represent the final extent of aging, being analogous to the naturally occurring opals. This supposition was not tested experimentally in the case of a gel prepared from water glass. However, such a sample actually resulted in the case of a gel prepared at 100°C. from a sodium metasilicate solution that had previously been aged by refluxing for several hours at 100°C. Thus, the marked aging resulting from heat treatment of sodium metasilicate solutions probably accounts for the smooth curves previously reported for the gels prepared from such solutions.

van Bemmelen as well as more recent investigators have shown very clearly the effect of aging upon the characteristics of the isothermal curves by making studies upon samples of a gel taken at various intervals after its initial formation. These studies have indicated that the sharpness of the inflection point as well as the extent of the hysteresis loop itself become less and less pronounced as
the age of the sample increases from a few hours to many months until finally in the case of a natural opal, which was considered to represent the maximum extent of aging; all hysteresis and traces of an inflection point have disappeared and the resulting curve is smooth and shows no sign of discontinuity. van Bemmelen also found that the amount of water held by the gel decreased steadily with its age. In order to account for this fact, he assumed that the aging of silica samples consisted of a process which caused a decrease of capillary spaces in the gel.

In the present study the phenomenon of aging is shown perhaps more strikingly than ever before. Curves 2 and 3 indicate that quite a noticeable increase in aging has been caused by merely raising the temperature of gel formation from 25 to 60°C. A still more marked increase in the aging is produced by raising the temperature to 100°C. as can be seen from comparison of figures 3 and 4.

The effect of increasing temperature cannot be the sole explanation for the aging process for silica since samples which have been activated in dry air at temperatures as high as 450°C for 4 hours still exhibit a marked inflec-
tion. It is a well known fact that the aging of crystalline materials is much more rapid in the wet state than in the dry state due to the process of dissolution and reprecipitation from the saturated solution (45). Silica is fairly soluble in water and therefore it seems plausible to assume
that the process of aging of silica is hastened by some sort of dissolution process.

The question of the hysteresis loop and inflection point have aroused much interest and speculation and numerous suggestions have been offered to explain their existence. These phenomena were first observed by van Bemmelen (2) and have since been observed by many investigators. Both van Bemmelen and Anderson (12) explain the hysteresis loop from the fact that liquid in a capillary tube has a greater vapor pressure when being filled than when being emptied as in the former case there is a diminution of the curvature of the liquid meniscus due to incomplete wetting. van Bemmelen and Anderson attribute the inflection point to two different kinds of adsorption, a capillary and a surface adsorption. Zsigmondy (5) offered the suggestion that the hysteresis could be attributed to the presence of adsorbed air which prevented the wetting of the capillary surface by water in the hydration process. Such an explanation is apparently untenable in view of the fact that Anderson worked in the absence of air. However, this issue has once again been brought into prominence by Patrick and co-workers (16,17,18) who attempted to show that hysteresis did not occur in the absence of air. Their experiments were performed on silica samples that had previously been activated by intense heating to $350^\circ C$. Numerous objections have been raised in regard to Patrick's results. The rehydration curves were run by
introducing a large amount of water vapor into the system and allowing it to come to equilibrium with the samples. Pidgeon (4b) points out that under these conditions the sample is forced to approach equilibrium with water vapor under constantly decreasing vapor pressure. According to Pidgeon, the outer portion of the gel would reach equilibrium quickly at a vapor pressure considerably above the final equilibrium pressure and would then lose water to the rest of the gel until the water vapor in all parts of the gel exerted the same vapor pressure. Thus Patrick's experimental curves are a mean of the true adsorption and desorption curves since both processes were occurring spontaneously in different parts of the gel, Pidgeon, as well as Lambert, Foster, and co-workers (14,15), repeated Patrick's experiments on highly evacuated silica samples but took precautions to insure a constant vapor pressure over the sample while equilibrium was being attained. Under these conditions hysteresis was found actually to exist for the system silica-water but was not found to be a general phenomenon for the system silica-adsorbate. The strongest argument against Patrick's conclusions is the fact that his experiments were all conducted over a composition range where no one has ever reported that hysteresis was observed. In the present investigation it seems unlikely that any appreciable amounts of air could be present in the system so that the hysteresis apparently cannot be attributed to residual air in the system.
Recently Rao (13) has published the results of a very extensive and exhaustive study of the hysteresis phenomena for the SiO₂-H₂O system as well as for many other similar systems. Since Rao's procedure was closely analogous to Patrick's with the exception that Rao worked over a higher composition range and since Rao obtained marked hysteresis loops in spite of elaborate precautions to insure the absence of air, it must be considered that Patrick's conclusions are fallacious.

Many recent observers, such as Rao, ascribe to the constricted capillary concept originally suggested by McBain (47) in order to explain the hysteresis phenomenon. According to McBain there are numerous types of capillaries present in a normal silica gel such as v-shaped capillaries, capillaries of uniform cross-section, and capillaries with restricted openings. If the pores are v-shaped, they will empty or fill gradually and continuously with decreasing or increasing pressure. If the capillaries are of uniform cross-section, they will empty or fill at a definite pressure. However, if the pores are irregular with various constrictions so that the larger cavities in the pores are accessible only through smaller channels, the picture of the hydration and dehydration is quite different. As the relative pressure is increased condensation of liquid will begin at the narrowest cross-section and will extend to wider cross-sections only as the pressure is increased until the vapor pressure reaches the saturation point when the pore will be completely filled. Upon subsequent diminution of pressure
no dehydration will occur in general until the relative humidity has fallen to the value corresponding to the largest orifice or passage leading to the larger enclosed cavity. Thus the curve for the dehydration will lie above that for hydration.

On the basis of the constricted capillary concept, Rao was able to present a very plausible explanation for the experimental results obtained by him in "scanning" the hysteresis loop. Rao stresses the fact that according to the cavity concept only capillaries with constricted ends are responsible for the hysteresis effect whereas with a system of purely v-shaped pores, the sorption and desorption curves should coincide. At any point along the main sorption curve, there are always some cavities completely filled with water, some partially filled, and some still unfilled. If at this stage desorption is begun, the partially filled cavities are progressively emptied in the same way as the v-shaped pores. Completely filled cavities, however, entrap water and retain it until a minimum pressure is reached at which the water condensed at the necks of the cavities will be just in equilibrium with the water vapor. Below this minimum pressure the cavities are completely emptied. Owing to this entrapping of water, the hysteresis loop is crossed and the main desorption curve is finally reached. At any intermediate point along the main desorption curve enclosing the hysteresis loop, some cavities are completely filled and some complete-
ly emptied, there being no possibility of a cavity being only partially emptied. If at any such intermediate point sorption is begun, a separate curve results extending upward and sloping away from the composition axis until it finally intersects the normal sorption branch of the hysteresis loop at the uppermost portion of the loop.

McBain suggests as a possible alternative to his theory a mechanism suggested at about the same time by Engelhard (48) to explain the hysteresis loop encountered in connection with his studies upon the adsorption of phoeogene by various activated charcoals. The explanation offered by Engelhard is that the weak forces between the water and charcoal surface are such that the vapor will diffuse very slowly to the inner charcoal surfaces and it will therefore remain concentrated only at the entrance to the pores. In the case of dehydration the water conversely vaporizes from the outer surface while the inner surface remains filled. The outermost adsorbed water will have a higher vapor pressure than the innermost adsorbed water, thus accounting for the hysteresis.

Another explanation of the hysteresis phenomenon has been suggested by Cohan (49). In this theory it is assumed that gels exhibiting the hysteresis loop contain cylindrical capillaries which fill by condensation on the concave cylindrical surface constituting the wall of the capillary. During dehydration the completely filled cylin-
drical capillaries empty from the concave spherical surface constituting the meniscus at the end of the capillary. Cohan deduced the following expressions for the pressure relationships involved:

Hydration (Condensation): \[ P_c = P_o - \frac{\sigma V}{\gamma RT} \]

Dehydration (Evaporation): \[ P = P_o - 2 \frac{\sigma V}{\gamma'R} \]

where \( P_c \) = pressure of condensation, \( P_o \) = pressure of evaporation, \( \sigma \) = surface tension, \( V \) = volume, \( R \) = gas constant, \( T \) = absolute temperature, \( r \) = radius of cylindrical film of liquid, and \( r' \) = radius of curvature of the spherical meniscus.

Although Rao is of the belief that no other explanation than one based on the constricted cavity concept furnishes a satisfactory explanation of the remarkable permanence and reproducibility of the hysteresis loop, there appear to be several possible defects in this concept that should be considered carefully before deciding upon its final acceptance. In the first place, the whole theory depends upon the unknown assumption that there are numerous capillaries with constricted openings present in the gel, which as yet is not subject to definite proof. In the light of the present knowledge of clays, it is difficult to visualize the presence of constricted cavities in such materials and
yet these materials also exhibit characteristic hysteresis loops in their isothermal hydration and dehydration curves. If the resolution of the electron microscope can be further improved, perhaps the presence or absence of capillaries of this type can be definitely proven. Another method of proving or disproving this theory would be to discover some process of dissolution whereby pores of uniform cross-section might be produced in the surface to be studied. On the basis of the cavity concept, it must be supposed that there is a wide variation in the cross-section of the constricted capillaries. If this is true, it seems reasonable to expect that when a given surface has been saturated with different materials, the volumes of the adsorbed materials should be dependent upon the relative sizes of the molecules. In other words, a greater volume of a material such as water should be adsorbed than of a material such as benzene which consists of larger molecules since in the latter case the molecules would be unable to enter many of the capillaries with necks of very small cross-section. Numerous adsorption studies to test this point have been carried out in which various liquids have been substituted for water. However, the results obtained are by no means in agreement. The earliest studies, made by Anderson (12), indicated that equal volumes of various liquids such as alcohol and water were required to fill the pores of the gel. Such results are of course contrary to what would be expected on the basis of
the cavity theory. More recently Lambert and Foster (14,15) have reported, in direct contrast to Anderson's results that hysteresis did not exist in the system silica-benzene and silica-alcohol. Still more recently, Rao (13) has reported hysteresis for the system silica-carbon tetrachloride and attributes the smaller volume of carbon tetrachloride needed for saturation in comparison with water as being due to inaccessible cavities.

Since there is no experimental evidence available that will distinguish between the various types of capillaries postulated in the theories discussed above, the present author prefers the following explanation in which no assumptions are made as to the type of capillary structure in the gels.

During the initial stage of the dehydration most of the water in the pores of the gel structure is released gradually and uniformly as the vapor pressure is reduced, the equilibrium curve following a smooth path. This is followed by a second stage of dehydration in which the surface layer of adsorbed water is released gradually and uniformly, the equilibrium curve again following a smooth course but with a slope different from that observed in the first stage of the dehydration. The difference in slope of the dehydration curves for the two processes accounts for the point of inflection in the dehydration curve as a whole. During hydration the water is taken up uniformly in amounts de-
pending upon the vapor pressure and no point of inflection is observed. This means that adsorption on the surface and capillary condensation are occurring simultaneously throughout a wider range on hydration than on dehydration with the result that the hydration curve appears smooth throughout its entire course. Since the pore structure is not destroyed by the initial dehydration and hydration, a subsequent dehydration again gives an inflection point.

Further evidence against the formation of hydrates by silica is found on the basis of x-ray studies made in the present investigations. If silica actually did form a hydrate, the hydrated sample of the gel would be expected to exhibit a different pattern from the anhydrous sample. No detectable differences, however, were observed between the x-ray patterns of the anhydrous and wet gels. Actually the pictures for both samples are almost identical with the pattern obtained for vitreous silica except that the latter shows a larger amount of small angle scattering.
SUMMARY

1. An earlier investigation indicated that silica gels prepared from sodium metasilicate apparently gave smooth dehydration isotherms in contrast to the gels prepared under analogous conditions by the hydrolysis of silicon tetra-ethylate and by the addition of acetic acid to water glass solutions.

2. Hydrous gels were prepared from both sodium metasilicate and water glass by the addition of acetic acid at 0, 25, and 100°C. and further samples were prepared by the addition of acetic acid to a water glass solution at 60°C. and by the addition of acetic acid at 100°C. to a solution of metasilicate that had previously been refluxed for several hours at 100°C.

3. Isothermal dehydrations and hydrations upon these samples were carried out at 13.0°C. in an apparatus especially designed to effect isothermal hydrations without permitting the dehydrated sample to come into contact with the atmosphere. The resulting curves, except for the case of the gel formed from the boiled sample of metasilicate, all show points of inflection and definite hysteresis loops. However, since the inflection points occur at varying compositions, their presence does not indicate the existence of definite hydrates.

4. The isothermal dehydration and hydration of the
silica gel prepared from a previously boiled solution of sodium metasilicate gave a smooth curve which was reversible in all portions. It is evident that the preliminary aging of the metasilicate solution gives a silica possessing a surface relatively free of capillaries or other type of surface structure from which the hysteresis results. This behavior explains the apparent anomaly in the behavior of the gels prepared from the metasilicate previously reported since in the earlier investigation the solutions were heated in order to hasten solution of the solid sodium metasilicate.

5. Further evidence against the formation of definite hydrates by silica is indicated by the absence of detectable differences in the x-ray diffraction patterns obtained from the hydrated and anhydrous samples.

6. A brief review has been given of the constricted capillary concept and its validity as an explanation of the observed hysteresis and inflection phenomena has been questioned. It is suggested that there are two distinct types of adsorption, a surface adsorption and a capillary adsorption. Each of these types of adsorption gives rise to a smooth dehydration curve but since the slopes of these curves are different, there is an inflection point in the dehydration curve as a whole. The hysteresis is due to the fact that the surface adsorption and capillary condensation take place uniformly and simultaneously over a wider range on hydration than on dehydration.
BIBLIOGRAPHY


2. van Bemmelen: Z. anorg. Chem. 13, 234 (1896); 18, 14, 98 (1898); 32, 265 (1902); 59, 225 (1908); 62, 1 (1909); Die Absorption, 196-357, 453-472, and 518-540.


4. Bachmann: Z. anorg. Chem. 73, 125 (1911).


20. Lottermoser: Ber. 41, 3976 (1908).
30. Pascal: Compt. rend. 175, 814 (1922).
34. Mugge: Centrbl. fur Mineralogie usw. 5, 129 (1908); 5, 325 (1908).
37. Willstatter, Kraut, and Lobinger: Ber. 58B, 2462 (1925); also a previous paper, 57B, 1082 (1924).
38. Schwarz and Menner: Ber. 57B, 1477 (1924); 58B, 73 (1925), also a subsequent paper by Schwarz: Z. Elektrochem. 32, 415 (1926).


44. McBain and Bakr: J. Am. Chem. Soc. 48, 690 (1926)


49. Cohan: J. Am. Chem. Soc. 60, 433 (1938)