THEORIES FOR THE MECHANISM OF THE SETTING OF SILICIC ACID GELS

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Received October 1, 1937

I. INTRODUCTION

Any theory which will successfully explain the mechanism involved in the setting of gels of hydrated silica, or silicic acid gels, as they are commonly called, should explain not only the properties of the gel when set but also any of the phenomena observed during the setting process. The present paper presents not only a discussion of the various theories which have been proposed, but also such observations of various investigators in the field of silicic acid gels as may appear important in the discussion.

In order that this paper may be kept within reasonable limits, no attempt is made to present a complete bibliography, nor can more than one vital reference be cited, ordinarily, for each point. More extensive bibliographies are available in the literature (79, 6).

The matter of terminology should be clarified at the start. By the term "colloidal silicic acid," or "sol of hydrated silica," will be understood the fluid mixture containing hydrated silica. The term "silicic acid gel," or "gel of hydrated silica," will indicate the semisolid elastic mass which results when the gel has, as we say, set. The term "silica gel" will be used to designate the harder, partially dehydrated product.

The presentation of the theories for the setting of the gel will be made easier if we first consider the various methods of preparation of sol and gel, the significant phenomena during the sol-to-gel transformation known as setting and, lastly, any properties of the sol and gel which substantiate or refute the various theories.

II. PREPARATION OF SOLS OF HYDRATED SILICA

Colloidal silicic acid has been known for about two hundred years. Berzelius (4) mentioned that he prepared "soluble" silicic acid by the action of ammonium hydroxide upon hydrofluorosilicic acid. What he had prepared was a sol of hydrated silica. A reference to earlier work is given by Walden (76).

Probably the most common method consists of the action of a solution of sodium silicate and an acid, as performed by Graham (24) and many others. Some investigators have used a solution of an ammonium salt instead of the acid (5).

By electrolysis of solutions of sodium silicate, Treadwell and Wieland (74) and Kröger (48) have removed nearly all of the sodium by deposition in a special mercury cathode. A reference will be made later to the fact that they reduced the hydroxyl-ion concentration as well as the sodium-ion concentration. They prepared relatively stable sols. Their process consisted practically of the hydrolysis of the sodium silicate solution and the nearly complete removal of the sodium hydroxide.

The hydrolysis of various silicon compounds has been used to prepare sols of hydrated silica, among them the chloride (51), the fluoride (14), the sulfide (19), and a number of esters of orthosilicic acid (13), such as methyl silicate (25).

Mention of these methods may introduce an objection—namely, that with the silicic acid other substances are formed in the solution. Many investigators have removed the greater portion of these soluble impurities by dialysis, but at least the colloidal silicic acid was first formed in their presence. Also, dialysis apparently never removes the last traces of electrolytes.

Two methods have apparently avoided the presence of these impurities in the original sol. The first of these was the preparation of colloidal silica by Lenher (54), who ground Ottawa sand to a fine powder and then heated it to 300–400°C. with water in a bomb. He was able to hydrate the silica. The other is the method of Kargin and Rabinovich (42), who oxidized silane (SiH_4) by means of ozonized oxygen in the presence of water.

Sols have been prepared by peptizing freshly prepared silicic acid gel by means of ammonium hydroxide (69) or potassium hydroxide (45). The peptizing agent was then removed.

III. PREPARATION OF SILICIC ACID GEL

Silicic acid gels result from practically any sol of hydrated silica, merely with the lapse of time. It is essential, of course, that the sol contain a large enough concentration of silica to give sufficient strength or rigidity for the gel to set. A sol which contains less than 0.5 per cent SiO_2 will give a very weak gel, or no gel at all. Sols which are strongly alkaline may not set at all.

Certain conditions, such as concentration of silica, temperature, hydrogen-ion concentration, and concentration of other substances, will be found to govern the time required for gelation or "time of set", as it is called, but it is safe to say that any sol containing over 2 per cent SiO_2 will set eventually to a gel, unless it is strongly alkaline.

Methods, therefore, for the preparation of silicic acid gel are essentially those for the preparation of the hydrosol of silica. Some time may be required for the gel to set.

IV. THE SOL-GEL TRANSFORMATION OR SETTING OF THE GEL

The sol of hydrated silica, when first prepared, is transparent. The viscosity is practically that of water. As the material stands, a faint opalescence becomes apparent which increases, ordinarily, until after the gel has set. The viscosity shows no noticeable change until the opalescence becomes quite marked. Then the viscosity increases rapidly, and soon the material develops elasticity, showing not only the resistance to flow characteristic of the increasing viscosity, but also a rapidly increasing tendency for the material to resist a stress and to return toward its original form after deformation. Any of the various tests will soon show that the gel has set. The setting process continues, of course, for some time after the test pronounces the gel set. Probably this fact is most clearly shown by the optical method of Prasad, Mehta, and Desai (66).

V. SIGNIFICANT PROPERTIES OF THE SOL OF HYDRATED SILICA

When first formed, the silicic acid appears to be in the form of simple molecules of low molecular weight. This has been shown by many investigators. Gruner and Elöd (27) found an apparent molecular weight of 60 in a freshly prepared sol, as did Willstätter, Kraut, and Lobinger (80). Treadwell (72) reported the first value to be 149. The apparent molecular weight has been found to increase rapidly with time, however, showing in the work of H. and W. Brintzinger (8) a value of 8260 after 45 days. Since, in all of these molecular weight determinations, an allowance has been made for electrolytes present in the solution, one can not feel too certain of the absolute value of the molecular weight of the silicic acid. The first low values are, however, undoubtedly reliable, and the trend toward the higher values is certainly indicated.

When first formed, considerable silicic acid passes easily with the electrolytes through the membranes used for dialysis. With the lapse of time, all of the silicic acid becomes unable to pass through the membrane. This fact, as well as the change in molecular weight, points unmistakably to the belief that silicic acid, when first formed, consists of small molecules, but that with the lapse of time these condense, polymerize, or coalesce to form large groups.

Mylius and Groschuff (59) have used albumin to test the silicic acid formed. At first they found that it would not coagulate albumin, a characteristic which they ascribe to simple molecules. They call this form α-silicic acid. Upon standing, α-silicic acid goes over into the β-form, the molecules of which, being larger, do coagulate albumin.

Although Karsten (43) claimed that hydrochloric acid forms a partial or temporary compound with silicic acid, this point of view appears completely disproven. Although it does appear impossible to remove the last traces of impurities, especially electrolytes, by dialysis, it has also been shown that silver nitrate will react with the chloride ion in the sols containing this minimum of chloride ion. In this respect these silicic acid sols would, therefore, show a marked difference from alumina sols containing a little chloride, as explained by Thomas (71).

Probably this difficulty of removing residual traces of electrolytes from these sols of hydrated silica serves to explain the divergence in pH values measured. A pH as low as 3.2 was reported by Rabinovich and Laskin (67), while Brintzinger and Troemer (9) found a value of 4.6. Upon washing gelatinous silicic acid by means of a supercentrifuge, Bradfield (7) found that the pH approached 6.5, whether he started with alkaline or acid mixtures. The sol prepared by Kargin and Rabinovich (42) by the oxidation of silane gave a pH very nearly 7.0.

An unfortunate feature of these measurements is that they give the pH for a sol, not just as it is formed, but after it has stood for some time, during which time the process of condensation has undoubtedly progressed for some distance. They fail, therefore, to inform us concerning the silicic acid when first formed.

The electrical charge on the particles of the sol has been shown by Losenbeck (55) to be negative in alkaline, neutral, or weakly acid solution. In more strongly acid solution the particles become positively charged. The idea has been held that this charge is entirely due to preferential adsorption, but it will be shown in this paper that it is probably due to the ionization of the silicic acid, which, owing to the amphoteric character of the molecule, occurs in two ways, leaving the silicon in either a negative or positive ion.

One of the most striking properties of the particles in a sol of hydrated silica is their great insensitivity toward ions which ordinarily cause coagulation of colloids. This has been shown by Laskin (52) and others. The data available, while confusing, in general, demonstrate conclusively this insensitivity of the colloidal silicic acid toward electrolytes.

The sols at first show no Tyndall cone, but this develops as they stand (47). They probably show no optical rotation (12), although the data are not absolutely conclusive. Microscopic studies have failed to detect any visible structures in the sol, or even in the gel, for that matter. The ultramicroscopic data are not at all conclusive.

The statement has been made that the silicic acid present in a sol containing hydrochloric acid has a small effect in decreasing the conductivity of the hydrochloric acid (55). The conductivity of sols of hydrated silica has been found to change very little, if at all, even when the mixture sets to form a gel (59, 23).

VI. FACTORS GOVERNING THE TIME OF SET

Among the factors which affect the time of set of silicic acid gels are the concentration of silica, the temperature, the acid used, the hydrogen-ion concentration, and the concentrations of other materials present.

It is a well-known fact that the higher the silica concentration the more rapidly will the gel set. Some study has been made of this factor, but a thorough investigation is needed.

The fact that a rise of temperature hastened the setting of silicic acid was noted by Maschke (56) and many others. Although the earlier work (15) failed to find any definite relation between temperature and time of set, recent work by Hurd and Miller (38) has demonstrated that the effect of temperature upon the time of set of gels produced by mixing solutions of sodium silicate and acetic acid is the same, regardless of the soda–silica ratio of the sodium silicate used. By considering the process as a chemical reaction, they obtained a value for the energy of activation for the process of 16,640 calories. As a result of further studies, Hurd (32) has shown that the energy of activation is practically the same using either acetic, citric, succinic, or tartaric acid, all, of course, being weak acids.

The use of strong acids adds the complication of a change in pH of the mixture during setting. By making allowances for this (34) it is possible to show that the energy of activation is approximately the same when strong acids are used.

The earlier investigators observed that, in acid gel mixtures, an increase in the concentration of acid also increased the time of set greatly (56). The curve for time of set against concentration of hydrochloric acid was plotted by Holmes (29), and was found to give a peculiar hump. This showed a minimum time of set in faintly alkaline solutions, as was also observed earlier by Fleming (18), and later by Hurd and Letteron (37) and by Prasad and Hattiangadi (65). Holmes also showed that at high concentrations of acid the time of set diminishes. The optimum limits of pH consistent with setting have been reported by Ray and Ganguly (68).

In a quantitative study of the relation between hydrogen-ion concentration and time of set, Hurd, Raymond, and Miller (39) have shown that for acid gels prepared from sodium silicate and acetic or hydrochloric acid between pH = 4.0 and 6.0, the time of set shows a linear relation to the hydrogen-ion concentration. In the same study, it was shown that if a constant hydrogen-ion concentration were maintained in mixtures containing increasing concentrations of acetic acid by addition of the correct amount of sodium acetate, the time of set was very slightly affected by the concentration of acetic acid. This would indicate that the hydrogen-ion concentration, rather than the concentration of acid, is the important factor in governing the rate of the setting process.

Work in alkaline gel mixtures presents much greater difficulties, due chiefly to the variation of the hydrogen-ion concentration. We may state, however, from completed but unpublished work in this laboratory, that in alkaline gel mixtures an approximately linear relation exists between time of set and hydroxyl-ion concentration.

The data available upon the effect of various electrolytes and non-electrolytes upon the time of set of silicic acid gel mixtures show considerable lack of agreement. As Hurd and Carver (33) have pointed out, this has arisen in many instances because of neglect of the simultaneous change of the hydrogen-ion concentration. This was particularly true in the case of ammonia, the amines, and pyridine.

It is apparently true that some non-electrolytes show a specific effect upon the time of set of these silicic acid gel mixtures. The effect is usually greater in alkaline gel mixtures than in acidic mixtures, as shown by Munro and Alves (58). They showed, as did Hurd and Carver, that glycerol caused an increase in the time of set, a fact which is very surprising when one considers the dehydrating power of glycerol. The main point to be noted here appears to be that non-electrolytes have little effect unless added in reasonably large amounts (traces show no effect at all), and that they affect alkaline gel mixtures more than acid mixtures.

The effect of salts upon the time of set is also not particularly marked. For example (39), it was shown that a concentration of sodium chloride of 1 *M* in a gel mixture produced from sodium silicate and acetic acid decreased the time of set by half. A similar concentration of sodium sulfate decreased the time of set by about 20 per cent.

The effect of radiant energy upon the time of set has not been fully studied. Although Ray and Ganguly have noted that ultraviolet light accelerated the setting, the effect of all forms of radiant energy must be small, if the thermal effects are excluded. One can easily show this by determining the very small difference between the times of set for two portions of the same mixture, one in the light and the other in the dark.

VII. PROPERTIES OF SILICIC ACID GELS

Certain specific properties of silicic acid gels interest us here because of their bearing upon the several theories for the mechanism of the setting process. These properties are the elasticity of the gel, syneresis, thixotropy, the apparently very high molecular weight, the failure to retain chloride, the results of magnetic analysis, the x-ray analysis, and the electrical conductivity.

Attempts have been made for many years to obtain conclusive evidence of the presence of definite silicic acids or definite hydrates of silica in the sol of hydrated silica or, more particularly, in coagulated silicic acid or in the gel. To cite merely two references, the work of Tschermak (75) and others has been interpreted to show the existence of several definite silicic acids, among them ortho-, meta-, or pyro-silicic acid. Schwarz (70) has claimed that two different kinds of water are in the gel,—free water and bound water. The latter may be considered as chemically combined.

The opposite point of view—namely, that the gel does not contain definite hydrates—was stated by van Bemmelen (3), whose extended studies on the hydration and dehydration of silicic acid gel failed to show the existence of any definite hydrates. Pascal's (64) magnetic analysis showed no evidence of the existence of ortho-, meta-, or pyro-silicic acids, but did show that the material consisted of silica and water. The x-ray determinations by Krejci and Ott (46) showed the cristobalite pattern.

The sol of hydrated silica, as it is setting, suddenly shows the development of elasticity. No comprehensive data on this development are available, but, as Langmuir (50) has observed, the material shows a stretch up to a certain limit, somewhat like rubber bands. As the gel sets, the limits of this stretch become smaller. According to Holmes (30) this elasticity is due, in part, to the tension developed in the gel.

Syneresis appears to be due to a contraction of the gel after it has set, resulting in the expression of a certain amount of fluid. It has been studied especially by Gaunt and Usher (22). The condensation and shrinkage, apparently, occur for some time after the gel has set, the extent of syneresis depending upon various factors (30), among them the concentration of silica, the hydrogen-ion concentration, and the temperature.

The phenomenon of thixotropy is shown by the gel mixture in the early stages of setting, that is, the gel will knit itself together after being stirred or separated. This power is lost after the gel has set. The behavior of silicic acid gel in this respect differs somewhat from the ordinary gels which show thixotropy.

Silicic acid gel is affected very little if treated with strong acid. On the other hand, a solution of sodium hydroxide will dissolve the gel quickly and easily.

The fact that little, if any, change occurs in the electrical conductivity during the sol–gel transformation is of great importance.

There is practically no thermal effect when the gel sets (74). This has occasioned some comment in the literature, but it will be shown that the result is exactly as would be expected.

VIII. THEORIES OF GEL STRUCTURE

Theories of gel structure, although they show many different characteristics, fall naturally into three general classes. The large number of individual modifications of the basic theories has resulted from the fact that many workers in the field have discovered and investigated an almost unlimited number of gels. The reader interested in the general subject of gels and gel structure is referred to the papers by Ostwald (61) and von Weimarn (78). The many gels investigated show differences in properties, not only differences of degree, but often of type.

The words "jelly" and "gel" have been used in a different sense by many writers, the usual custom being to use "jelly" for the more dilute, elastic type, such as a gelatin jelly, and to use the word "gel" for the partially dehydrated product known technically as silica gel. The writer will use the word "gel", particularly "silicic acid gel," throughout this paper.

The three general theories for gel structure are: (A) the emulsion theory; (B) the cellular theory; and (C) the fibrillar or micellar theory.

Specialists in colloid chemistry will note the omission of what is frequently called the solid solution theory (44). This really is not a theory of gel structure, but refers to a mechanism by which solvent is imbibed in the process known as swelling. While it postulates, for example, that water enters gelatin in the form of a solution in the solid, it does not explain the resulting structure.

An attempt will now be made to consider each of the three theories, in order to present a satisfactory theory for the structure of silicic acid gel. We shall consider those properties of the sol and gel of silicic acid which aid in confirming or disproving the theory.

A. The emulsion theory

This theory was explained by Ostwald (62, 61). The theory assumes that the gel consists of a liquid–liquid system with an emulsoid structure, although Ostwald pointed out that he considered both liquids to be abnormal and one somewhat more concentrated than the other. The theory did not receive Ostwald's complete support in the case of silicic acid gel, but he did consider it as a possibility, perhaps explaining a temporary structure formed during the setting of silicic acid gel.

The theory fails, in the case of silicic acid gels, when one considers viscosity and elasticity. An emulsion is characterized by a high viscosity, but it does possess the ability to flow. Dilute silicic acid gels show considerable flow when subjected to a deforming force. As the concentration of silica increases, the gels show greater elasticity and less tendency to flow. Gels containing over 3 per cent silica flow very little when subject to a force. This problem has not been thoroughly studied.

The calculations of Hatschek (28) of a series of stress–strain curves, assuming an emulsoid structure for gels, and the failure of these curves to agree in any particular with measured stress–strain curves for gelatin and rubber are often quoted as a general refutation of the emulsoid structure for gels. While the proper work has, apparently, not been done on the elasticity of freshly formed silicic acid gel, it does appear that the gel follows Hooke's law. It has a low elastic limit.

At present the weight of opinion is very decidedly against the emulsion theory for any gel.

B. The cellular theory

This theory, which is credited to Bütschli (11), postulates that the liquid part of the gel is held in the form of small droplets in a cellular structure made up of the solid phase. The theory is sometimes called the honeycomb theory, because of the assumed structure of the framework.

While a cellular framework has actually been observed microscopically in the case of some gels, such as von Weimarn's (77) barium sulfate gels, there is the best of evidence to show that Bütschli's observations showed something much coarser than the original structure. His estimates gave a wall thickness in silicic acid gel of 0.3μ, while the pockets appeared to be from 1.0 to 1.5μ in diameter. The work of Zsigmondy (81) gave an estimate of 5 mμ for the pore diameter for silicic acid gel, while Anderson's (1) estimate showed even smaller pores. Such a structure could not possibly be observed by the microscope, being several hundred times as small as the structures seen by Bütschli.

The gels in which von Weimarn observed the cellular structure were very different from silicic acid gels, and were called by him coarse-cellular gels. They were made by mixing two concentrated solutions of inorganic substances into a coarse mixture like an emulsion. The reaction precipitated material along the boundary surfaces.

The cellular structure best explains the retention of water in a gel such as silicic acid gel. While gels such as the barium malonate gel (17) have been discovered, from which some water may be withdrawn even by touching the gel with filter paper, the same thing is not true of silicic acid gel, which holds the water much more firmly. Yet, while the cellular structure explains well the ability of silicic acid gel to hold water, it does not provide any satisfactory explanation for syneresis, nor for the phenomena observed when water evaporates from a silicic acid gel.

Soon after a silicic acid gel has set, liquid appears upon its surface. This squeezing out of some of the fluid is called syneresis. It has been studied by Gaunt and Usher (22), by Kuhn (49), and especially in silicic acid gels by Ferguson and Applebey (16). Syneresis appears to occur to a much smaller degree as the gel becomes older. The fluid is a solution of the salts or acids present. It is difficult to see how this fluid could be squeezed out by the gel without destroying its cellular structure.

When a cylinder of silicic acid gel is allowed to stand in the air it will shrink, retaining approximately its original proportions. If the structure were cellular, it seems reasonable to suppose that water would come most easily from the outer cells, and that distortion or cracking would result.

A serious point against the cellular theory for silicic acid gels is that practically no increase in the electrical resistance occurs when the gel mixture sets (40). This fact has been mentioned previously and is true in the case of gels other than silicic acid gels. It is difficult to conceive of the formation of solid or semisolid walls, cutting up the gel into small cells containing fluid, without a noticeable increase in electrical resistance.

A cellular structure would explain very satisfactorily the elasticity of silicic acid gels. This, and the explanation of a structure to hold the fluid portion of the gel, are the chief points in favor of the cellular theory.

C. The fibrillar theory

The fibrillar or micellar theory is sometimes called the sponge theory (79). It is usually credited to Nägeli (60). It postulates a solid and a liquid phase, each continuous, with the solid forming a fibrous structure and containing the liquid in the pores. It is the theory favored by most workers in the field. The differences in their points of view relate to the method of forming this fibrillar structure. They may be considered under three general headings.

(1) Structure formed by coagulation of the colloid. Many workers have believed that a silicic acid gel is formed simply by the coagulation of the silicic acid or hydrated silica in the sol. The structure of the gel would result from the mechanical agglomeration of the colloid, which would leave spaces filled with water. This was suggested by Pappada and Sadowsky (63).

This would be a very simple mechanism, if it were verified. Practically, however, the weight of evidence is against it. It is readily apparent that sols of hydrated silica are very insensitive to coagulation by electrolytes (52). The setting of a silicic acid gel resembles in no way the coagulation of a sol, such as arsenious sulfide sol. There the addition of low concentrations of the ion of correct charge, particularly a polyvalent ion, will cause a cloudy appearance within a few seconds, followed very shortly by a coagulation of the precipitate. Nothing resembling this behavior occurs with silicic acid. The sol is not coagulated by either positive or negative ions in low concentrations, even by polyvalent ions. Nevertheless there are many contributions in the literature by those, such as Prasad and Hattiangadi (65), who believe that silicic acid gel results from coagulation of the sol by ions. Some writers even go so far as to discuss the effect of non-electrolytes upon the power of various ions for coagulating the sol of hydrated silica.

Without entering into a long discussion, the writer must rest the case with the following example, taken from the paper by Hurd, Raymond, and Miller (39). A sol of hydrated silica containing the following concentrations in gram-moles per liter—SiO_2, 0.645; Na^+, 0.385; CH_3COO^- and excess CH_3COOH, 0.502—and having a pH of 5.09 set in 53 minutes. The addition of 0.500 gram-mole of sodium sulfate per liter to the original mixture decreased the time of set to 44 minutes. The same concentration of sodium chloride in another mixture decreased the time of set to 28 minutes.

It has been shown that silicic acid or hydrated silica in a sol as acid as this is positively charged (55). Sodium sulfate should, therefore, be more effective than the chloride, because of the divalent negative ion. It is actually less effective and both are extremely ineffective if they are really acting to coagulate the hydrated silica.

We must conclude, therefore, either that here we have a very unusual type of coagulation of a sol, or that the setting of a silicic acid gel is not a coagulation at all, but occurs by some totally different process.

(*2*) *Structure formed by a mat of fine crystals.* Gels such as the myricyl alcohol of Buchner (10) are known, which undoubtedly consist of a mat of fine crystals. They are interlaced or tangled mechanically, and retain their water by capillarity.

It has been suggested many times that the silica in silicic acid gels is in the form of silica crystals. LeChatelier (53) reported that he polished metal by rubbing with silicic acid gel, concluding from this that the gel consisted of anhydrous silica and water, but Bancroft (2) has observed that the pressure used in polishing, or the heat generated, might have caused a dehydration of some of the hydrated silica. The data of Krejci and Ott (46), who found, by x-ray analysis, a cristobalite pattern in freshly prepared silicic acid gels, should be considered seriously. Pascal's (64) magnetic analysis, also, must be considered. His data indicated a complete absence of ortho-, meta-, or pyro-silicic acid molecules in the gel, but did indicate silica and water.

Many observers have claimed to show the presence of definite silicic acids, or definite hydrates of silica, in the gel. This has already been discussed, the references for definite hydrates being represented by Tschermak's paper. The evidence against the existence of definite silicic acids, represented in this paper by van Bemmelen, Pascal, and Krejci and Ott, has been cited. A careful perusal of the literature will convince the reader of the strong position held by the opposition. It appears quite safe to believe that, whatever the structure may be, silicic acid gels do not consist of mats of crystals of simple silicic acids.

One property possessed by these crystal mat gels is that of thixotropy (20), namely, the ability of the gel to be liquefied by some disturbance, usually by shaking, and then to reset, apparently forming the same structure that it possessed before the disturbance. While a silicic acid gel passes through a period where it may be broken apart, after which it will knit together again, this is not true thixotropy, since the final gel does not knit itself again if it is broken into lumps after it has set. The lumps will remain separate, either under water, which has been added, or in the presence of the liquid due to syneresis. In addition, it proved impossible to liquefy silicic acid gel by the use of ultrasonic waves (21), although gels showing thixotropy were easily liquefied.

It is worth noting one piece of contrary evidence. In washing silicic acid gel very thoroughly, Hurd and Griffeth (36) broke the gel into a very fine suspension by means of a high-speed beater in an excess of distilled water. When the suspended material had settled, it was found to knit together into a firm but fairly weak structure. This can not be considered as ordinary thixotropy.

(*3*) *Polysilicic acid fibrillar theory.* This theory suggests that a silicic acid gel consists of an interlaced fibrillar or brush heap structure consisting of very large polysilicic acid molecules, the spaces being filled by liquid. The structure is produced by condensation (41), water being split out between two simpler silicic acid molecules to form a more complex structure (35). The polysilicic acid structure is probably very heavily hydrated.

There appears to be little doubt of the formation of simple silicic acid molecules by the reaction of sodium silicate with an acid or by the hydrolysis of silicon tetrahalides or of an alkyl ester of orthosilicic acid. The low molecular weight of the silicic acid in the freshly formed sol has been discussed in this paper under the properties of the sol of hydrated silica (27, 72), the significant point being that, although an apparent molecular weight of about 100 was found in the fresh sol, this value increased to something over 8000, after which experimental error made calculations useless. The ease with which the silicic acid first formed passes through a dialyzer membrane has been mentioned, also the fact that this ability is soon lost. The albumin test of Mylius and Groschuff (59), showing low molecular weight in freshly formed sols of silicic acid, has been cited. They found that the sol, upon standing, changed from the simple α-silicic acid to the very complex β-silicic acid. All of this evidence supports the theory that a simple monosilicic acid is first formed.

Mylius and Groschuff suggested that their β-silicic acid consisted of very large molecules, formed by condensation of the simple silicic acids first formed. This condensation is analogous to the organic reaction in which water is split out from the two hydroxyl groups of neighboring molecules, resulting in a larger molecule held together by the common oxygen atom. As this procedure continues (31), we picture the formation of more and more complicated structures, causing, ultimately, the complete immobilization of the fluid, which Ostwald says is the most important characteristic of a gel. The gel has now set.

This interconnected branched polysilicic acid structure is almost certainly heavily hydrated. It also holds the fluid in its structure by capillarity. This structure explains, better than any other, the properties of silicic acid gels (32).

This theory is in agreement with the evidence that the silicic acid, when first formed, is in the form of simple molecules, and that the molecular weight increases to very large values. The molecules first formed are undoubtedly quite soluble, but as they condense the resultant product becomes quite insoluble.

The insensitivity to electrolytes is explained. Such a condensation process should be affected very little by the presence of the ions of ordinary salts. The sensitivity to hydrogen and hydroxyl ions is of a different type, and will be explained later.

The heavily hydrated polysilicic acid threads do not become large enough, nor are they of sufficient density, to be visible in the microscope.

The absence of any increase in electrical resistance is understandable, in the light of this theory. While, with the cellular theory, there should be an increase in resistance because of the membranes through which the ions must pass, here the structure remains reasonably open, the passages being continuous.

The measurements of the diameter of the "pores" in the gel by Zsigmondy (81) and by Anderson (1), already quoted, of 5mμ and less, are of about the correct order of magnitude to accord with this theory.

As the gel forms the condensation process continues, undoubtedly, beyond the empirical time, which we term the time of set. The structure already having reached sufficient solidity to set, that is, to pass from the liquid stage to a semisolid stage, any further contraction should squeeze out fluid through the capillaries. This process is what we call syneresis. The tension set up has been commented on by Holmes (30) and others.

The fact that the gel is not thixotropic adds a considerable support to this theory. A gel formed of loose contacts between crystals should be liquefied, if shaken. The silicic acid gel, because of its firm bonds, which are due to its condensed structure, is not easily broken, even by ultrasonic waves. If it is broken up after it has set, it will not knit together. If it is still in the process of vigorous condensation and it is torn apart, it will easily knit together. Probably, in the very thorough disruption of the structure by Hurd and Griffeth (36), enough of the bonds were broken so that the gel did go through some degree of condensation after settling to the bottom.

This theory offers an explanation of the fact that such a gel retains its proportions if allowed to evaporate fluid in the open. The fluid can come out through the pores to the outside, causing a general shrinkage throughout. When the gel has become well dried, however, the water in the capillaries becomes replaced by air, although the capillaries have shrunk from their original size. This occurs when the water content is from 1.5 to 3.0 moles per mole of silica.

When a well-dried gel is moistened with water it will crack apart, often violently, snapping into pieces. The gel has apparently swelled on the outside before water could penetrate the interior. The strain bursts the lump into pieces.

A structure of this fibrous brush heap character should possess elasticity, as does the silicic acid gel. A distortion should cause a change in shape of the filaments, with an increasing resistance. It is apparently not a lengthening of each filament, but rather a straightening out of irregular chains. When these are straightened out, the structure breaks. It is known that silicic acid gel has a low elastic limit, which is reached, apparently, when most of the filaments have straightened out.

While it is true that the cellular theory presents a somewhat better structure for holding the fluid in the gel, and while some evidence favors the crystal mat theory, we can see that the greater weight of evidence favors the polysilicic acid fibrillar theory. It will be worthwhile, therefore, to present evidence for a reasonable mechanism by which this polysilicic acid structure can be built up.

IX. THE MECHANISM OF CONDENSATION

From the evidence available and from some new data as yet unpublished, we can present a clear and reasonable picture of the mechanism involved in the condensation of silicic acid to form a polysilicic acid structure, resulting in the formation of a silicic acid gel. To do this, we assume: (*1*) That a monosilicic acid is formed in the first step of the process, or perhaps more correctly, silicon hydroxide. (*2*) That this acid, or hydroxide, is amphoteric, giving either hydrogen or hydroxyl ions. (*3*) That condensation occurs when the positive and negative ions containing the silicon come into contact. (*4*) That water remains combined, or adsorbed, in the structure.

We may now discuss these four assumptions:

(*1*) We shall assume that the first premise is admitted. The low molecular weight and ability to pass through the dialysis membrane have been cited.

(*2*) The amphoteric character of the silicic acid has been mentioned by Willstätter, Kraut, and Lobinger (80), although it has been tacitly assumed by anyone who has spoken of the condensation mechanism. A clear statement was given by Treadwell and König (73). It is probably impossible to prove this assumption, as it has been found very difficult to measure the ionization constants of any of the well-recognized amphoteric hydroxides.[1]

It will probably be impossible to measure accurately either the acid or basic ionization constants of silicon hydroxide, which, when formed, apparently immediately begins condensation. Treadwell has given what he believes is a reliable value for the acid ionization constant,—namely, $K_1 = 2 \times 10^{-10}$. The great amount of data on the pH of sols of hydrated silica is very confusing, complicated as it is by the presence of impurities, by the age of the sol, and by the method of measurement. What is needed is the pH of a pure sol of the monosilicic acid, measured at the instant of formation. Such data are not available. The only thing of which we may feel certain is that the purest sol, prepared by Kargin and Rabinovich (42) by the oxidation of silane by ozonized oxygen, gave a pH of 7.0, but this material had had ample time for condensation. The data of other observers (67, 9) showed the reaction of a weak acid such as would be expected from Treadwell's constants. The acid ionization is apparently somewhat stronger than the basic ionization.

It is apparently well established that the particles in a sol of hydrated silica are positive in strongly acid solution, but that they become negative in weakly acid, neutral, and basic solution. It has also been observed that the so-called isoelectric point changes with the age of the sol (26). While some difficulty was experienced in explaining this on the basis of the adsorption of ions from the solution, it is very easily explained on the assumption that we have an amphoteric compound. In strongly acid solution the acid ionization of the silicon hydroxide is very strongly repressed, and few silicic acid anions are present. This would be equally true of the condensed acid. The basic ionization would be much increased and most of the silicon would be in the form of the cations. As the acidity of the solution is decreased, leaving lower and lower concentration of hydrogen ions, the acidic type of ionization would be increased and, because the acidic type probably occurs more easily than the basic type, would

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[1] Although the Landolt-Bornstein Tables give ionization constants for amphoteric organic electrolytes, none are given for the inorganic amphoteric hydroxides.

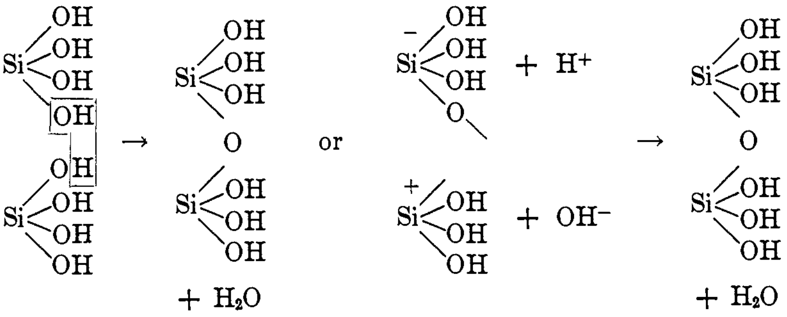
equal the basic type even in slightly acid solutions. The particles which were measured were probably condensed, since the charge on the particles was determined by cataphoresis. The particles were thus electrically neutral in slightly acid solution where the two types of ionization, occurring in different parts of the same large particle, left it neutral. In basic solution the acidic type of ionization would be much increased and most of the particles would be negative. The process is shown for the simplest silicon hydroxide.

$$\begin{gathered}OH^- + Si(\overset{+}{O}H)_3 \leftarrow Si(OH)_4 \rightarrow SiO(\overset{-}{O}H)_3 + H^+ \\ \text{in acid solution} \leftarrow \text{favored} \rightarrow \text{in basic solution}\end{gathered}$$

The condensed acid is certainly ionized to a much smaller degree than the monosilicic acid, which some observers (57) claim is a reasonably strong acid. The final product of condensation of the purest silicic acid prepared (42) gave a pH about 7.0, and is probably ionized to a very slight degree. It must be at least very slightly ionized in order that sodium hydroxide may dissolve the gel as it does.

Grundmann's (26) observation that the isoelectric point shifted in a given sol of hydrated silica is interesting. He found that the particles tended toward a more negative charge as the sol became older. Apparently, with the larger polysilicic acid molecules, the acidic ionization is decreased less than the basic ionization. It is well known that silicic acid gel is soluble in or, perhaps better, is peptized by alkali, indicating that the acidic type of ionization is still present in the gel.

(*3*) Condensation of this type occurs by the splitting out of water from two molecules containing OH groups. This is equivalent to the following:



Theoretically such a process should occur more readily if the number of positive and negative ions [$Si(\overset{+}{O}H)_3$ and $SiO(\overset{-}{O}H)_3$] containing silicon were of the same order of magnitude, and if collisions occurred more frequently.

The second idea agrees with the fact, already noted, that the same gel mixture will set more rapidly the higher the temperature. The writer and his coworkers (37, 38) have determined the energy of activation to be about 17,000 calories.

The quantitative relation between time of set and the hydrogen-ion concentration was found by Hurd, Raymond, and Miller (39) for acid gel mixtures. The time of set is a linear function of the hydrogen-ion concentration down to a minimum at about pH = 8.0. This substantiates the idea that the condensation occurs more readily when the two kinds of ions containing the silicon are present in concentrations of about the same order of magnitude.

Measurements of the relation between time of set and the hydrogen-ion concentration in alkaline gel mixtures have proved very difficult, owing to the fact that the hydrogen-ion concentration changes as the gel mixture proceeds toward setting. The shift in the hydrogen-ion concentration in the poorly buffered solutions produced by mixing a solution of sodium silicate with insufficient hydrochloric acid to neutralize it is always toward lower hydrogen-ion concentrations (34). In other words, at first the monosilicic acid formed is enough of an acid to contribute a measurable concentration of hydrogen ions, but as condensation proceeds the polysilicic acids are less and less ionized, resulting in a shift toward lower hydrogen-ion concentration. This net action as an acid is the result of two factors,—(*1*) that the acidic ionization of silicon hydroxide is greater than the basic ionization and (*2*) that the basic solution encourages the acidic type of ionization.

Recent measurements obtained in this laboratory, but as yet unpublished, have shown that the time of set in these basic mixtures is nearly proportional to the hydroxyl-ion concentration. Special precautions were used to prevent the shift of hydrogen-ion concentration.

The influence of non-electrolytes upon the time of set doubtless lies in the fact that they have some effect, though not a large one, upon the ionization of the silicon hydroxide.

The fact that very little thermal change occurs as the gel sets has been mentioned (74) and also that this result was unexpected. The fact, however, is entirely in agreement with the theory that is being discussed. The condensation has been occurring steadily since the monosilicic acid was formed in the first reaction. The thermal effect, if measurable, would have been spread out over the whole time and no sudden evolution of heat could be expected as the last of the process was occurring, namely, as the gel set. The process of condensation also includes the ionization of the silicic acids, which would almost nullify the heat produced by the condensation.

Our theory, then, shows reasonable agreement with the facts observed. It presents ideas which may subsequently be tested further by experiment.

(*4*) While it is perhaps not possible to prove that water remains either chemically combined or strongly adsorbed by the filamentous structure, the facts point strongly toward such a condition. van Bemmelen's observation that from 0.5 to 1.0 mole of water per mole of silica remained very strongly attached to the silica and could be removed only by vigorous heating, is significant. The idea of free and bound water has already been mentioned.

Undoubtedly, when a silicic acid gel is subjected to a drying process, the free water in the capillaries is the first to escape. This causes a shrinkage of the capillary diameters and compresses the fibrous structure. When the fibrous structure can contract no more, a condition which occurs, apparently, when less than 3 moles of water are present per mole of silica, the water still in the capillaries evaporates, leaving air in the capillaries with about 1 mole of water per mole of silica in the structure.

X. SUMMARY

A review has been given of some of the significant properties of hydrosols of silica and of silicic acid gels. Methods of preparation have been discussed.

The process of the setting of the sol to form a gel has been examined, particularly in regard to conditions affecting the time of set.

The several theories of gel structure have been examined critically, in regard to their application to the formation of silicic acid gels.

The evidence favors the fibrillar theory for gel structure.

A mechanism for the formation of this fibrillar structure is described. A monosilicic acid is first formed in the sol. This condenses, owing to the amphoteric nature of the hydroxide of silicon. The influence of various factors upon this process is discussed, chiefly the hydrogen-ion and hydoxyl-ion concentration and the temperature. Long chains of condensed polysilicic acids are formed.

These gels are called silicic acid gels, not because we believe that any simple silicic acid is present in the final gel, but because it appears certain that the starting material is a monosilicic acid.

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