[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNION COLLEGE]

Studies on Silicic Acid Gels. XII. The Time of Set of Acidic and Basic Mixtures Containing Phosphoric Acid

BY CHARLES B. HURD AND ANGELO J. MAROTTA[1]

Introduction

The time of set of silicic acid gels is known to be affected by a number of factors, among them the temperature and hydrogen ion concentration of the gel mixture.[2] With acidic mixtures of solutions of sodium silicate and acetic acid[3] it was found that the *p*H remained constant throughout the runs. For the effect of temperature on the time of set, a constant energy of activation was found, namely, about 17,000 calories.[4] The same conditions were found to hold with mixtures containing citric, succinic or tartaric acids.[5] It should be noted that all four are weak acids and that acidic mixtures of these acids with sodium silicate contain excess acid with the sodium salt and, hence, are well buffered.

When mixtures of sodium silicate with a strong mineral acid with *p*H less than 7 were studied in our laboratory,[6] the *p*H of the mixtures was found to increase steadily before and during gelation. The energy of activation was also found to vary.

Since variation was largest with the dibasic acid, sulfuric, we have also investigated mixtures containing the tribasic acid, phosphoric. This was a fortunate choice, since it has given us alkaline gel mixtures whose *p*H has remained constant during the run, giving us, for the first time in five years' work, results which we consider reliable in the alkaline range, upon which the energy of activation has been calculated.

The general relation between time of set and acidity of the solution has been reported by Holmes,[7] by Hurd and Letteron,[8] and, recently, by Batchelor.[9]

Changes in *p*H of the gel mixtures have been reported by Hanks and Weintraub[10] and by Batchelor.[9] Measurements of time of set of alkaline gel mixtures have been reported by Munro and Alves[11] and by Munro and Pearce.[12]

In the present paper we report results of the study of the setting of silicic acid gels containing phosphoric acid. The data on energy of activation of the alkaline mixtures are available for the first time. The data on the increase of *p*H of the gel mixtures before and during setting and the failure of the di- and trivalent ions to accelerate the setting process are important in their relation to the theory of the mechanism of setting.

Experimental

Gel mixtures were prepared by the same methods used in former studies in this Laboratory.[3,4] The silicate solution, prepared by dilution of "E" brand silicate, Philadelphia Quartz Company, titrated 1.25 normal sodium hydroxide equivalent. A 2.0 N phosphoric acid solution was prepared, titrated using methyl orange for the first hydrogen, or for the nitric acid equivalent of the three hydrogens by adding a slight excess of lead nitrate before titration with sodium hydroxide.

Time of set was determined by the tilted rod method.[3] All gel mixtures were carefully thermostated in electrically controlled water thermostats.

In acidic mixtures, the *p*H was determined by a quinhydrone potentiometer with a bright platinum wire electrode as formerly reported.[13] For alkaline mixtures, a Beckmann glass electrode potentiometer was used. We found the life of a glass electrode to be short. The electrode was checked each time with a buffer and replaced when necessary. In spite of careful cleaning, from ten to fifteen runs, only, could be obtained from one electrode.

While others[11,14] have reported successful determinations of *p*H in alkaline silicic acid gel mixtures with indicators, we have been unable to obtain sufficiently accurate or consistent results with them to permit calculation of energy of activation, during five years of work.

In some acidic mixtures, we have made both quinhydrone and glass electrode measurements of *p*H. These gave good checks. All *p*H measurements were made at 25°.

Since most of the gel mixtures were not strictly reproducible in *p*H from volume measurements of solutions mixed, we have prepared double quantity (160 cc.) of each mixture. Half was used for *p*H measurement and half for time of set.

In mixtures of *p*H range 3.3 to 4.7, a small amount of white precipitate formed. This apparently did not affect the gel formation.

---

[1] Present address: Consolidated Car Heating Company, Albany, N. Y.

[2] Hurd, *Chem. Rev.*, **22**, 403 (1938).

[3] Hurd, Raymond and Miller, *J. Phys. Chem.*, **38**, 663 (1934).

[4] Hurd and Miller, *ibid.*, **36**, 2194 (1932).

[5] Hurd, *ibid.*, **40**, 21 (1936).

[6] Hurd, Frederick and Haynes, *ibid.*, **42**, 85 (1938).

[7] Holmes, *ibid.*, **22**, 510 (1918).

[8] Hurd and Letteron, *ibid.*, **36**, 604 (1932).

[9] Batchelor, *ibid.*, **42**, 575 (1938).

[10] Hanks and Weintraub, *ibid.*, **41**, 583 (1937).

[11] Munro and Alves, *Can. J. Research*, **B15**, 353 (1937).

[12] Munro and Pearce, *ibid.*, **B16**, 390 (1938).

[13] Hurd and Griffeth, *J. Phys. Chem.*, **29**, 1155 (1935).

[14] Prasad and Hattiangadi, *J. Indian Chem. Soc.*, **6**, 893 (1929).

All gel mixtures contained 0.64 gram mole of silica per liter.

Experimental Results

To conserve space, data are presented chiefly in graphs. In Fig. 1 are shown curves for logarithm of time of set against *p*H for several temperatures. The linear shape of the curves each side of the rather flat minimum is evident. When one remembers that it requires a certain amount of time to mix the two solutions, the rather flat minimum is understood.

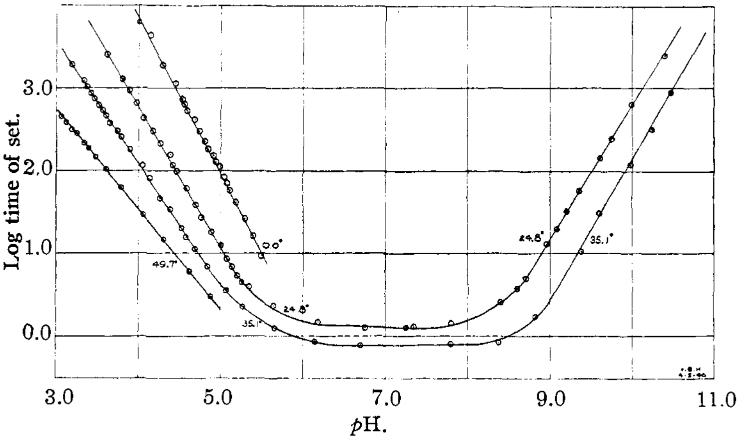

Fig. 1.—Time of set of silicic acid gels containing phosphoric acid as a function of *p*H and temperature.

From the curves of Fig. 1, data were obtained for logarithm of time of set, at different temperatures, by erecting perpendiculars at fixed *p*H values. These data for logarithm of time of set are plotted against reciprocal absolute temperature in Fig. 2 for acidic mixtures and in Fig. 3 for basic mixtures. These resemble curves previously reported for acidic mixtures of sodium silicate and acetic acid[3] and those containing hydrochloric, nitric or sulfuric acids.[6]

By multiplying the slopes of the curves of Fig. 2 by 2.30*R*, as in previous papers of this series,[4] values for the energy of activation were obtained. They are given in Table I.

One large advantage in the use of phosphoric acid and sodium silicate for preparation of silicic acid gels lies in the fact that basic gel mixtures are well buffered. This holds the *p*H constant before and during setting. In the acidic mixtures, the *p*H varied with phosphoric acid just as with mixtures containing hydrochloric, nitric or sulfuric acid, already reported.[6] Because of the significance of this variation, a special study was made of it here. The data are shown in Fig. 4. The characteristic shape of the curves is apparent.

TABLE I

THE ENERGY OF ACTIVATION OF SILICIC ACID GELS CONTAINING PHOSPHORIC ACID

*p*H	*Q*, cal.	*p*H	*Q*, cal.
3.0	30,500	9.0	23,860
3.5	27,020	9.5	24,590
4.0	24,720	10.0	24,780
4.5	21,340	10.5	24,870
5.0	18,320		

Discussion

One purpose of this study of silicic acid gel mixtures containing phosphoric acid was to investigate the fact, already noted in poorly buffered gel mixtures containing one of the mineral acids,[6] that a rise in *p*H occurred from time of mixing until even after the gel had set. The curves of Fig. 4 show this for mixtures containing phosphoric acid. This *p*H shift is significant. It was pointed out by Hurd, Frederick and Haynes[6] that condensation of monosilicic acid, giving weaker and weaker acids of the polysilicic acid type, would cause a measurable decrease in hydrogen ion concentration, or an increase in *p*H until condensation was practically completed. This would agree with the shape of the curves of

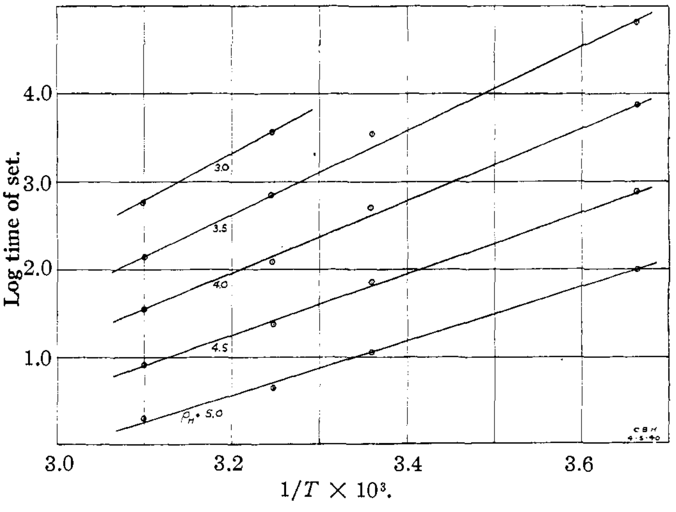

Fig. 2.—Time of set of acidic gels containing phosphoric acid as a function of temperature.

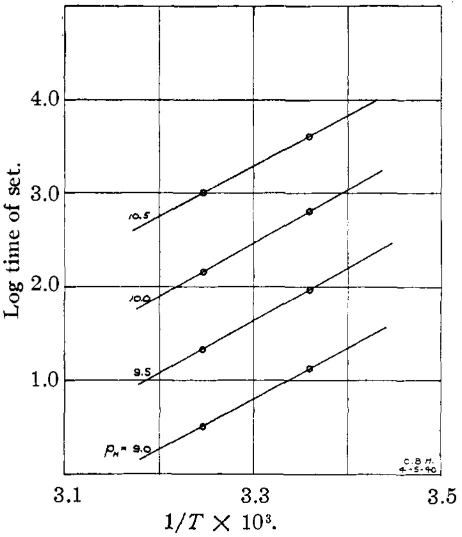

Fig. 3.—Time of set of basic gels containing phosphoric acid as a function of temperature.

Fig. 4. It would also be expected that less change in *p*H should occur for the more acidic gels, *p*H 2, than for the less acidic. The curves appear to show this, also.

It should be noted here that the curves of Fig. 4 agree with those of Hanks and Weintraub[10] in direction, but are contrary to Batchelor's[9] results on acidic mixtures.

The greater change in *p*H during setting for mixtures of *p*H 4 than for those of *p*H 2 appears reasonable. If one accepts Kargin and Rabinovitch's[15] value of 7.0 for the *p*H of a sol of hydrated silica, prepared by oxidation of silane and, hence, free from other acids, it is apparent that the final material in a sol of hydrated silica is practically un-ionized. This would correspond to a very highly condensed polysilicic acid. Treadwell and Wieland[16] gave the ionization constant for monosilicic acid, $K_1 = 2 \times 10^{-10}$, while Hägg[17] gave $K_1 = 1 \times 10^{-9}$. An acid of this strength, changing by condensation to an essentially neutral final result, should give a change in *p*H similar to that shown by Fig. 4, but of smaller amount. We are reminded here of the statement by Mukherjee[18] that monosilicic acid is a much stronger acid than is commonly believed.

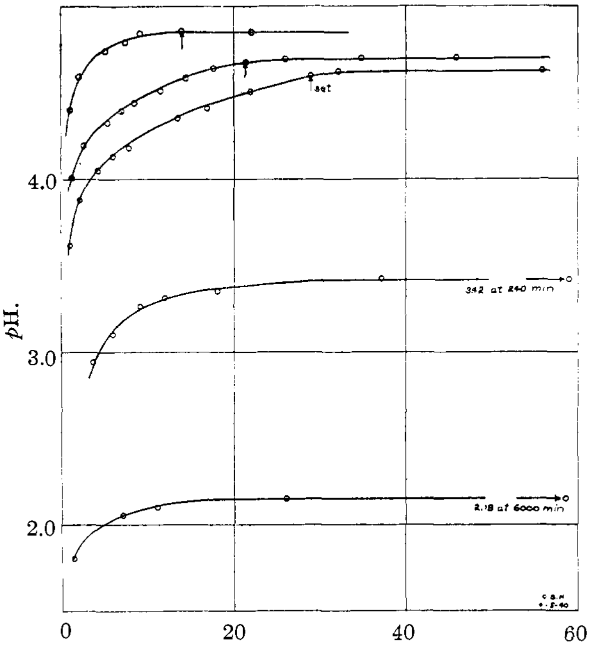

Fig. 4.—Variation of *p*H of silicic acid gel mixtures with time.

The view has often been stated that the setting of a silicic acid gel results from the coagulation of colloidal hydrated silica,[19,20] although Freundlich later[21] has inclined toward the condensation theory. To refute the view that the setting of a silicic acid gel is simply a coagulation of colloidal, hydrated silica, we present here data from the paper on gel mixtures containing nitric, hydrochloric or sulfuric acid,[6] together with the present data on gel mixtures containing phosphoric acid. This combination is given in Table II.

TABLE II

LOGARITHM OF TIME OF SET FOR SILICIC ACID GELS CONTAINING STRONG ACIDS AT 24.9°

*p*H	HCl	HNO_3	H_2SO_4	H_3PO_4
3.0	3.48	3.44	3.32	4.50
3.5	2.90	2.90	2.82	3.64
4.0	2.34	2.36	2.30	2.80
4.5	1.76	1.82	1.79	1.93
5.0	1.18	1.28	1.28	1.06

A similar relation for three of these acids is shown by the graph of Davis and Hay.[22]

To interpret the data of Table II in its relation to the theory of setting of silicic acid, we recall that Losenbeck[23] reported that the charge on colloidal particles of hydrated silica in solutions of moderate to high acidity is positive. Table II

---

[15] Kargin and Rabinovitch, *Trans. Faraday Soc.*, **31**, 284 (1935).

[16] Treadwell and Wieland, *Helv. Chim. Acta*, **13**, 842 (1930).

[17] Hägg, *Z. anorg. Chem.*, **155**, 21 (1926).

[18] Mukherjee, *Kolloid Z.*, **67**, 178 (1934).

[19] Pappada and Sadowsky, *ibid.*, **6**, 292 (1910).

[20] Freundlich and Cohn, *ibid.*, **39**, 28 (1926).

[21] Freundlich, *J. Phys. Chem.*, **41**, 901 (1937).

[22] Davis and Hay, THIS JOURNAL, **61**, 1020 (1939).

[23] Losenbeck, *Kolloidchem. Beihefte*, **16**, 27 (1922).

shows, however, for silicic acid gels containing the same silica concentration at same temperature and same pH (3.0) that gel mixtures containing divalent sulfate ion set no more rapidly than those which contain monovalent chloride or nitrate ions. Those containing polyvalent phosphate ions set much more slowly. Anyone, who has coagulated colloid sols with di- or trivalent ions of opposite charge is aware of the great sensitivity of the sols to such ions. Only at pH of 5.0 do the gel mixtures containing phosphate ions set a little more rapidly.

The case against the theory of silicic acid gel formation by simple coagulation appears very strong, in view of the great insensitivity of the gel mixture toward electrolytes, as shown here.

The curves of Fig. 1 show the linear relation of logarithm of time of set and pH on each side of the neutral point. In acidic mixtures, time of set decreases with increase of pH, while in basic mixtures, time of set increases with increase of pH. This linear relation between logarithm of time of set and the pH has been shown in the case of acidic mixtures containing the weak acids[3] and in those containing strong acids.[6] A discussion of a possible role for the hydrogen ion was given in these papers and also in a later paper[2] devoted to a theoretical discussion.

The fact that the hydrogen ion concentration decreased before and during setting of the gel mixture in the acidic mixtures caused a variation in velocity of the setting process. This undoubtedly caused an error in calculation of the energy of activation and probably accounts for the variation of this quantity in Table I from pH 3.0 to 5.0. The accuracy should be sufficient to show that the energy of activation in gel mixtures containing phosphoric acid is greater than the steady value of 17,000 calories for gels containing weak acids.

The energy of activation should be reliable in the basic gel mixtures containing phosphoric acid owing to their constant pH. The mean value is about 24,700 calories. This is the first value reported for energy of activation in basic mixtures and shows the energy of activation to be nearly 50% higher here than the reliable value of 17,000 calories for well-buffered acidic mixtures containing acetic or other weak acids. Definitely, the effect of temperature on time of set in basic gel mixtures differs in degree from that in acidic gels.

Summary

The effects of temperature and pH on the time of set of silicic acid gel mixtures, prepared by mixing solutions of sodium silicate and phosphoric acid, have been described.

In acidic mixtures, the pH was found to increase until the gel had set. This agreed with the data already reported for mixtures containing hydrochloric, nitric or sulfuric acid.

Curves for the logarithm of time of set against pH show linear portions rising from a flat minimum near the neutral point.

The first data available for calculation of the energy of activation in the basic range (pH 9.0 to 10.5) give a value about 24,700 calories.

The data support the Polysilicic Acid Fibrillar or the Condensation Theory for formation of silicic acid gels and offer evidence against the acceptance of the Coagulation Theory.

The data suggest that monosilicic acid is a much stronger acid than commonly believed.

SCHENECTADY, N. Y. RECEIVED APRIL 8, 1940