[Contribution from the Butterfield Chemical Laboratory, Union College]

Studies on Silicic Acid Gels. XV. The Effect of Temperature upon the Time of Set of Alkaline Gel Mixtures

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Introduction

The effect of temperature on the time of set of silicic acid gels is definite for gel mixtures with *p*H below 7. With these acidic mixtures, a rise in temperature causes a decrease in the time of set[4] in mixtures containing weak acids,[5] or strong acids.[6,7] The energies of activation for these acidic mixtures have been reported.[5,6,7]

The behavior of alkaline gel mixtures, with *p*H values above 8.0, shows some surprising results when the effect of temperature on time of set is studied. Increased temperature with alkaline gel mixtures of solutions of sodium silicate and phosphoric acid has been shown to decrease the time of set.[8] A calculation of the energy of activation gave about 24,000 calories. For these mixtures, due to the buffering power of the phosphates formed, the *p*H remained constant from the first reading after the solutions were mixed until the gel had set.

With alkaline gel mixtures made from solutions of sodium silicate and acetic acid having *p*H values above 8.5, the results of Munro and Pearce,[9] and results in this laboratory, have shown a curvature in the relation between logarithm of time of set and the reciprocal temperature. This made calculation of the energy of activation impossible. In addition, the *p*H of the sol has been shown to increase noticeably from the time of mixing until the gel has set. Our own earlier experiments showed that, in the highest *p*H range where it is possible for a gel to set, raising the temperature increased the time of set. This phenomenon deserved further investigation. The results are given herewith.

Experimental

The gel mixtures were prepared by mixing solutions of sodium silicate, E brand Philadelphia Quartz Company, diluted to 1.25 *N* in NaOH equivalent, and dilute acetic acid in the manner previously described.[4,5] Time of set was found by the "tilted rod" method.[4]

Measurement of the *p*H presented difficulty. The Quinhydrone method, which has been shown satisfactory for acidic mixtures[10] in the presence of silicic acid, fails above *p*H 8. Earlier work on alkaline gel mixtures,[11] and the more recent work of Munro and his co-workers,[12,13,9] have utilized indicators and standardized buffers to measure the *p*H. Munro and Pearce[9] found the *p*H measured by the glass electrode, in the range *p*H 9.5-11.0, to be 0.2 to 0.4 unit lower than that given by indicators. In our work on alkaline mixtures containing phosphoric acid,[8] we have found that the life of a Beckmann glass electrode was very short, the alkali and silica destroying the surface and also the reproducibility of the readings of the electrode after four or five determinations.

In the work reported here, we have used both the indicator method and the glass electrode. The indicators were phenol red for *p*H 7.8-8.4; thymol blue, *p*H 8.0-9.8, and LaMotte purple, 9.6-11.0. The buffer solutions were made up from directions from Clark[14] of boric acid, potassium chloride and sodium hydroxide, or of sodium carbonate and borax. The *p*H of the buffers was determined by the Beckmann Glass Electrode Apparatus, but the particular glass electrode was not allowed to come into contact with any silicates. The indicator method procedure was standard, using a white porcelain spot plate.

In addition, some determinations were made by the Leeds and Northrup Glass Electrode Apparatus, using home-made glass electrodes. These were blown from Corning #015 special electrode glass, and were checked in a buffer after each immersion in silicate mixtures. They were discarded when they failed to check.

Time of set was determined at three temperatures for a series of mixtures, using a fixed volume of sodium silicate solution and varying quantities of acetic acid. Mixtures were reproducible, that is, two mixtures made up with the same volumes of acetic acid gave the same *p*H and time of set.

In Fig. 1 are shown the logarithm of time of set against reciprocal absolute temperature for a series of silicic acid gel mixtures produced by mixing solutions of sodium silicate and acetic acid. Temperatures were 0°, 25.1°, and 38.5°. All mixtures were alkaline. The *p*H was determined with indicators. Between the first reading and the time of set, the *p*H rose 0.2 to 0.5 of a *p*H unit, especially in the higher range. The concentrations of Na^+, 0.391 gram ion per liter, and SiO_2, 0.642 gram mole per liter, were the same for all. The concentration of Ac^- in gram ions per liter, and the *p*H, are given by Table I. The *p*H given was recorded immediately after mixing.

Table I

Concentration of Acetate Ion and *p*H of the Gel Mixtures Shown in Fig. 1

Ac^-	0.379	0.366	0.353	0.341	0.328	0.315
*p*H	6.8	7.4	8.0	8.3	8.6	8.9
Ac^-	0.302	0.289	0.277	0.265	0.252	0.246
*p*H	9.3	9.8	10.1	10.3	10.43	10.45
Ac^-	0.239	0.227	0.214	0.201	0.189	0.176
*p*H	10.50	10.55	10.63	10.70	10.73	10.75

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[4] Hurd and Miller, *J. Phys. Chem.*, **36**, 2194 (1932).

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

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

[7] Hurd and Barclay, *ibid.*, **44**, 847 (1940).

[8] Hurd and Marotta, This Journal, **62**, 2767 (1940).

[9] Munro and Pearce, *J. Phys. Chem.*, **44**, 1024 (1940).

[10] Hurd and Griffeth, *ibid.*, **39**, 1155 (1935).

[11] Prasad and Hattiangadi, *J. Indian Chem. Soc.*, **6**, 653 (1929); **6**, 893 (1929); **6**, 991 (1929).

[12] Munro and Alves, *Can. J. Res.*, **B15**, 353 (1937).

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

[14] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Company, Baltimore, Md., 3rd ed., 1928, pp. 195, 201.

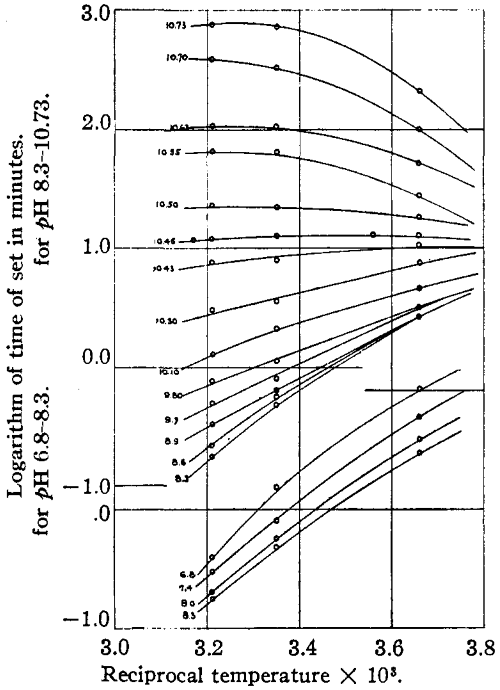

Fig. 1.—Logarithm of time of set of silicic acid gel mixtures of different *p*H as a function of the reciprocal absolute temperature.

The curvature shown by Munro and Pearce[9] is apparent here. Their Figs. 1, 2, 3, 4, and 5 for their control gels are duplicated among the 18 curves of our Fig. 1, although we have not found the decrease of logarithm of time of set at our highest temperature as pronounced as theirs. It is apparent that at least in our mixtures above *p*H 10.5, a rise of temperature from 0 to 38° increased the time of set. For *p*H 10.45, there was very little change in the time of set as the temperature was increased. This was checked at several more temperatures, and is shown in Fig. 1 by extra points for the mixture in Table I containing 0.246 gram ion of Ac^- per liter. This value is italicized in Table I.

Unfortunately, for simplicity of treatment, the *p*H in these mixtures was found to change somewhat with time and with temperature. Also, the concentration of silica changed, to a small degree, the slope of the curves, which are shown in Fig. 1. We have not yet studied this second effect carefully.

The change in *p*H with time was studied, using the Leeds and Northrup apparatus and Corning #015 home-made glass electrodes. Two curves are shown in Fig. 2, the *p*H being corrected for Na^+ ion effect. The concentrations are for Curve 1, $Na^+ = 0.394$, $SiO_2 = 0.652$, $Ac^- = 0.253$, and for Curve 2, $Na^+ = 0.394$, $SiO_2 = 0.652$, and $Ac^- = 0.238$. The *p*H is seen to rise and become constant after the gel has set. These mixtures contain a strong base and less than an equivalent amount of a weak acid.

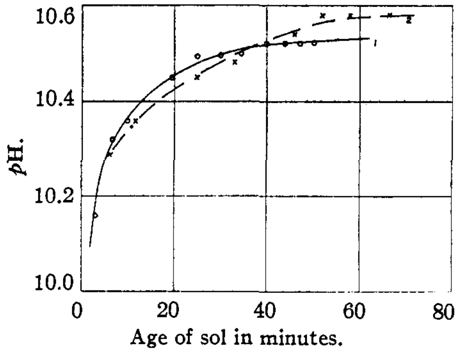

Fig. 2.—Effect of age of sol upon *p*H.

We have tried to liquefy these alkaline gels with *p*H over 10.5 by allowing them to set at 25° and then rapidly raising the temperature to 50° or dropping it to 0°. In no case have we been able to liquefy the gel. Apparently, once the gel is set, it remains set, even though the rate of setting at the higher temperature would not have allowed it to set in the time elapsed in setting at the lower temperature and the short time required for heating.

Discussion

There is general agreement that silicic acid gels produced by the setting of gel mixtures with *p*H above 8.0 differ in many ways from the acid gels. Several workers have noted that gel mixtures of *p*H above 11.0 apparently do not set to form gels.[15] Our results substantiate this. It is also well known that gels already set may be dissolved in dilute sodium hydroxide solution, *i. e.*, by raising the *p*H well above 11.0.

There must, therefore, be two processes possible so far as the hydrous silica is concerned. One may be described as the formation of a monosilicic acid, or at least a simple silicic acid, from the silicate ions. These simple silicic acids condense to form polysilicic acids and eventually form a gel.[16] This may be shown as follows:

$$\text{Silicate ion} \rightleftarrows \text{Simple silicic acid} \rightleftarrows \text{Polysilicic acid} \rightleftarrows \text{Gel}$$
$$\text{Setting of gel} \longrightarrow \qquad \longleftarrow \text{Solution of gel}$$

The action of strong alkali reverses the process which occurs during gelation. This occurs easily in solutions of *p*H 13 or higher.

In gel mixtures with *p*H between 11 and 13, the tendency to form a gel must be opposed by the reverse effect. This makes the gels set more and more slowly as the *p*H is raised, until somewhere between *p*H 11 and 13, the mixtures will never set. It is hardly likely that a rise in temperature will affect these two opposed tendencies equally. Such a situation is true in simple chemical equilibria, the temperature affecting the rates of the opposing reactions unequally, thus causing a change in the equilibrium constant.

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(15) Ray and Ganguly, *J. Phys. Chem.*, **34**, 352 (1930); **35**, 596 (1931).

(16) Hurd, *Chem. Rev.*, **22**, 403 (1938).

We find with silicic acid gels ample verification of this theory. With acidic mixtures containing weak acids, where the *p*H remains constant,[5] the logarithm of time of set is a linear function of the reciprocal absolute temperature. This gives a constant for the energy of activation. However, in these mixtures of low *p*H, the tendency to dissolve the gel is negligible, and a linear relation naturally results.

As the *p*H of the mixtures is increased, the difference in the effect of temperature on the gel-forming and gel-dissolving processes causes curvature in the formerly straight line relation between logarithm of time of set and reciprocal absolute temperature. This curvature is seen in the control curves of Munro and Pearce[9] and our curves of Fig. 1. It is unfortunate that only two temperatures were used for the alkaline gel mixtures containing phosphoric acid,[8] otherwise curvature might have been found there, also.

It would appear possible to find silicic acid gels in a very narrow *p*H range, above 11, which would be thermally reversible, since it is apparent that rise of temperature accelerates the dissolving process more than the setting process. We have been unable to find reports of such gels in the literature. We have made careful experiments to try to find such thermal reversibility, but have been unable to liquefy any of our alkaline gels by raising the temperature. Possibly this was because the gels could not be liquefied in the time available. We are attempting to find such gels, but the experiments will take a very long time, probably over six months or a year. They must be very slow setting gels and, if found, will be in a fairly narrow *p*H range between 11 and 13.

A second effect which changes the rate of the setting process is a change in the *p*H of the mixture between the time of mixing and time of set. This does not occur to a measurable degree in acidic mixtures which contain weak acids,[5,17] nor in the alkaline mixtures containing phosphoric acid,[8] since all of these mixtures are well buffered. It does occur, however, in acidic mixtures containing strong acids,[6,7] and in alkaline mixtures containing acetic acid, reported by Munro and Pearce,[9] and also in all of our work here. Figure 2 shows this.

In unbuffered mixtures, the *p*H rises between the time the mixture is produced and the time it sets to form a gel. This rise of *p*H is almost certainly due to the decrease in ionizability of the silicic acids during the condensation. This effect has already been described for acidic gel mixtures.[6] Now the same thing is occurring in the alkaline range, the relatively stronger monosilicic acids being replaced by more and more complex polysilicic acids which are capable of producing fewer H ions. Since these alkaline gels set more slowly as the *p*H is increased, this concurrent increase in *p*H will cause a change in the rate as the process is occurring. This also will tend to cause curvature in the curves for logarithm of time of set against reciprocal temperature.

A third point to discuss is the structure of the gels themselves. Acidic silicic acid gels are relatively firm, elastic, and only slightly opalescent. Alkaline gels are much softer and strongly opalescent. In acidic gels, the reverse tendency. which causes solution of the gel, is certainly negligible. Condensation therefore gives very large molecules, probably with many cross linkages. The gels are firm and elastic. In the alkaline range, condensation does not proceed so completely and cross linkages are probably absent. This is more true the higher the *p*H, since eventually a *p*H can be reached where the final stage of gel formation cannot take place. Probably, also, the degree of hydration is different at higher *p*H values, giving greater opacity.

Summary

A study has been made of the setting of alkaline silicic acid gels containing sodium silicate and acetic acid, especially as to the anomalous effect of temperature. In the higher *p*H range, above 10.5, rise of temperature produces increase in time of set. This differs from the effect with gel mixtures of *p*H below 10, where rise of temperature causes decrease in time of set.

No energy of activation can be calculated for these gel mixtures with *p*H above about 10.

The effect is probably due to the fact that rise of temperature accelerates the process of dissolving of the gel to a greater extent than it accelerates gel formation.

In mixtures with *p*H much above 11, the solution process is predominant and gels do not form.

During the process of setting, the *p*H of these poorly buffered alkaline mixtures increases considerably. This affects the rate of the process. It is probably due to the fact that the more complex the polysilicic acid is, the less is its tendency toward ionization.

No thermally reversible silicic acids were found.

Alkaline gels are softer and less elastic than acid gels, since condensation and cross linkage formation probably do not proceed so far in the alkaline gels.

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