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# Time of set and pH in silicic acid gels

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A Thesis, presented to the Department of Chemistry  
of Union College in partial fulfillment of the require-  
ments for the Degree of Bachelor of Science in Chemistry.

BY E. August Laurence

Approved By Charles B. Sturd

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## INTRODUCTION

The purpose of this investigation was to determine the time of set and the hydrogen ion concentration of a silicic acid gel, basic in nature. A gel prepared from a mixture of 1.2511 normal sodium silicate solution and 1.0158 normal ammonium chloride was used for this purpose. The possibility of measuring the hydrogen ion concentration by the indicator method was used with considerable success by Prasad and Halliangadi (1). Previous work on this problem at Union by Marotta (2) pointed out the uncertainty of the glass electrode method due to the effect of the silicate on the electrode. The possibility of measuring the hydrogen ion concentration with the quinhydrone electrode was studied in this laboratory.

## HISTORICAL

The relationship between the time of set and the hydrogen ion concentration in silicic acid gels is well established by numerous investigators. The important factor that the hydrogen ion concentration exercises on the time of set has been recognized for a long time. Holmes (3) pointed out that the time of set is at a minimum in the very slightly alkaline mixture and that gels very acidic in nature also have a minimum time of set. This minimum in the very acid region comes at a pH of about one.



The presence of certain salts has been found to have an effect upon the time of set. As the concentration of these salts increase their effect upon the gel likewise increases. Rothemich (4) found that while sodium acetate shortened the time of set somewhat sodium chloride had no effect. Prasad and Halliangadi (1) found that the addition of Ammonium acetate decreased the time of set. They also found that alcohols hastened the time of set in basic gels but retarded the time of set in gels in the acid region. Using the indicator method of determining the hydrogen ion concentration, they found that in a basic gel there was an increase in the hydrogen ion concentration during gelation, but that in an acidic gel there is no appreciable increase.

At Union College, Dr. Hurd (5) studied the effect of temperature on the time of set. He found that by plotting the logarithm of the time of set against the reciprocal of the absolute temperature and by making certain assumptions, it is possible to obtain the energy of activation. These assumptions are as follows:

1. That we are dealing with a process which follows the laws of ordinary chemical reaction as far as its velocity is concerned.
2. That the Arrhenius equation may be applied to our results.



3. That for a given run the time of set measures the time when a certain fixed proportion of the silica, in whatever form, in solution, has reacted.

The mathematical expression used to determine this energy of activation is--

$$Q = \frac{RT \ln t'}{d \frac{1}{T}}$$

He found that for gels prepared from a solution of sodium silicate equivalent to 1.25 normal sodium hydroxide and from 2.00 normal acetic acid solution to be approximately 16,600 calories. This value of the energy of activation falls between the limits of the energy of activation of ordinary chemical reactions.

Hurd (6) investigated the heats of activation of a number of gels made from weak acids. These acids included acetic, citric, succinic, and tartaric. The average values of the heat of activation for these acids were found to be 17,140, 16,940, 17,190 and 17,530 calories respectively. The differences in the values in the first three acids are within the limits of experimental error, but the value of the heat of activation of the tartaric acid was too large to be due to experimental error. Since the tartaric acid is the strongest of the four by a rather large margin, it was thought that this was the reason for the discrepancy in this value. A wider range of pH was covered in the case of the stronger acids and the differences in the energy of activation was found to vary considerably with the pH.

This difference is thought to be due to the fact that in mixtures of strong acids and sodium silicate there is very little buffering power, while the mixture of the sodium salt of the weak acid and the excess weak acid gives excellent buffering power.

In the determination of the energy of activation all variables except the temperature are kept constant. The time of set for a group of gel mixtures varying in the acid content is found at three different temperatures. These temperatures are usually taken at 0 C, 25 C, and 40-50 C.



## APPARATUS

Since any change in the temperature has a marked effect on the time of set in a silicic acid gel, a self regulating thermostat was used. The thermostat used by this investigator kept a constant temperature to within  $\pm .1^{\circ}\text{C}$ . for a period of twenty-four hours. A vacuum tube regulator was used to control the heater in the water bath. A stirrer driven by an electric motor kept a constant temperature throughout the bath. At the temperature of  $50^{\circ}\text{C}$  a large pail heated at intervals with a bunsen burner kept the temperature constant to within  $\pm .2^{\circ}\text{C}$ .

The sodium silicate solution used was the Brand "E" sodium silicate manufactured by the Philadelphia Quartz Company. This silicate solution has the weight ratio of  $\text{Na O}:\text{SiO}_2$  3.25. This solution was diluted with recently boiled distilled water until a solution equivalent to 1.25 normal sodium hydroxide was obtained. The ammonium chloride solution used was 1.0158 normal. The chloride in the ammonium chloride was titrated with standard ammonium thiocyanate using ferric ammonium alum solution as an indicator. The ammonium thiocyanate solution was standardized using pure silver nitrate dissolved in 3 normal nitric acid using ferric ammonium alum as an indicator.

One hundred cc K beakers were used in the preparation of the gel. In one beaker was placed 25 ml. of sodium

silicate solution while to the other the ammonium chloride solution and distilled water were added. The ammonium chloride was the variable factor. Gels containing 15, 16, 17, 18, 19, and 20 cc of Ammonium chloride and diluted to 55 cc with distilled water thus keeping the total volume of the components constant at 80 cc. The volumes were measured by means of pipettes. These two beakers were placed in the thermostat and allowed to stand for twenty minutes so that they could come up to the temperature of the bath. The ammonium chloride solution was then poured into the sodium silicate solution and poured back and forth from one beaker to the other, three or four times in order to insure complete mixing.

There is no universal method for determining the time of set. Holmes (3) considered his gels set when the gels no longer ran out of an inverted test tube. The obvious imperfection in this method is that the gel structure is disturbed every time the test tube is inverted. Flemming (7) determined his time of set by running his gels through a capillary tube. The method used in this laboratory consisted of inserting a ten cm. long three mm. thick glass stirring rod at an angle of twenty degrees to the vertical. The gel was considered set when this rod did not fall over when placed in the mixture at this angle. Care has to be taken to start this test when the gel is very near set so as not to disturb the gel with many punctures.



Since only a very little previous work had been done on gels made from ammonium chloride and sodium sillicate the pH of the gels was not known. The first attempt to measure this pH by this investigator was with a quinhydrone electrode. This method did not prove satisfactory as the hydrogen ion concentration was of a lower value than the lowest limit reached by this device. The indicator method was the next one attempted. Phenol Red or phenolsulfonphthalein with a pH range of 7 - 8.6 was first indicator used. The method used was to prepare a set of buffer solutions, measure their pH's with a glass electrode, then place a fixed amount of indicator in a definite volume of these buffers (8) a like amount of indicator in the same definite volume of gel mixture. The color of the gel mixture is matched with one of a set of gels of a known pH. The buffer used was one which consisted of .2 M Boric acid, .2 M molar KCl, and .2 molar NaOH. (No. 8 .) The range of this set of buffer solution is from a pH of 7.8 to 10. It was found that the gel mixture had a pH above that of the range of the phenol red. The next indicator attempted was thymol blue, with a pH range of 8 - 9.6. This, too, was found to be unsatisfactory because its range was too low.

Next the Hellige pH meter was attempted. The Hellige pH meter is a device for measuring pH values by colormetric discs. Each indicator has a disc corresponding to its

color values for pH measurements. The disc consists of concentric circles. The inner circle is a glass disc which is the color of the neutral indicator in solution. The outer part of this disc has a circular arrangement of small colored glass discs showing color changes for the pH range of the indicator at pH intervals of .2. The colormetric disc is set into a frame which allows it to be turned for comparison with the solution used. To allow this we find two glass tubes set behind the disc. The tubes are especially prepared to allow light to enter from the back, which is open and permits the investigator to see through the front, the tubes being behind the disc. The sides of the tubes are of opaque glass so that no color is lost or reflected from one to the other. These glass tubes are so placed that one is directly behind the center circle and the other at its side so that it is behind the small colored discs on the outer circle. To find the pH of a solution, we fill the tube behind the colored discs with pure solution and the tube behind the clear disc with 10 cc. of same solution to which has been added .5 cc. of the proper indicator. We can see the color of the second solution through the clear disc. The disc is then turned until the pure solution as seen through one of the small colored discs corresponds to the color of the solution of the indicator as seen through the clear glass. The apparatus is so arranged that the color areas are side by side thus



facilitating the comparison and allowing for estimating pH values to the nearest tenth. The disc used by this investigator was the one corresponding to the indicator cresol pthalein with a pH range from 8 - 10. This range was found to be too low when working with ammonium chloride and sodium silicate gels.

Alizarine yellow was the next indicator used in the attempt to determine the pH of these basic gels. This indicator has a pH range from 10 - 12. Since the previous buffer solution was of a too low pH range a new set of buffer solutions had to be prepared. Examination of literature failed to disclose a suitable buffer and it was at the suggestion of Dr. Langmuir that a buffer made from potassium chloride and sodium hydroxide was used. This buffer was of the desired range.

## RESULTS

Using 1.0058 normal ammonium chloride solution and 1.25 normal sodium silicate solution the gels that contained more than twenty one cc. of this ammonium chloride solution set immediately. The average time of set of a group of gels, their ammonium chloride concentration varying is as follows:

cc. of Ammonium Chloride	Times of Set		
	26°C	31°C	50°C
20 cc.	31.12 min.	26.06 min.	11.90 min.
19 cc.	69.53 min.	59.06 min.	27.83 min.
18 cc.	153.58 min.	126.0 min.	66.33 min.
17 cc.	306.8 min.		
16 cc.	639.5 min.		
15 cc.	970.0 min.		

As it was already pointed out it was impossible to obtain the pH of the gel mixtures with the quinhydrone electrode, the indicators phenol red and thymol blue, and the Hellige pH meter. Alizarine yellow was in the correct range of hydrogen ion concentration and it was possible to distinguish the differences in the color of the gel mixture and the indicator at the different concentrations used. The buffer solution of KCl and NaOH, also, proved satisfactory for this range. Due to the break down of



the glass electrode it was impossible to measure the pH of the set of buffers so that they could be compared to the gel mixtures.

Excess ammonium chloride as well as ammonium silicate were present in the gels made up from ammonium chloride and sodium silicate. These substances are fairly good buffers and tend to keep the pH of the mixtures constant. The variation in the energy of activation proved this was not entirely true. This leads us to the conclusion that in the case of strong acids the energy of activation is approximately a linear function of the pH.



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