

6-1939

The Regulation of Silicic Acid Gels

Louis W. Thompson Jr
Union College - Schenectady, NY

Follow this and additional works at: <https://digitalworks.union.edu/theses>

 Part of the [Chemistry Commons](#)

Recommended Citation

Thompson, Louis W. Jr, "The Regulation of Silicic Acid Gels" (1939). *Honors Theses*. 2152.
<https://digitalworks.union.edu/theses/2152>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact digitalworks@union.edu.

THE REGELATION OF SILICIC ACID GELS

UNION COLLEGE
LIBRARY

A thesis, presented to the Department of
Chemistry of Union College, in partial fulfillment
of the requirements for the Degree of Bachelor of
Science in Chemistry

Presented by Louis W. Thompson Jr.

Approved by Charles B Hurd

May, 1939

UN⁹92

T 47

C. 2

INTRODUCTION

Colloidal silicic acid and silicic acid gels have been studied for more than 100 years. A paper by Berzelius on this subject was printed in 1820. What he prepared was a sol of hydrated silica. Even earlier work was reported by others.

A silicic acid gel will result in time from almost any sol of hydrated silica. Sufficient silica must be present, however, to give the necessary strength to really form a gel from the sol. A gel can be formed with as little as .5% SiO_2 under other certain conditions. Unless too strongly alkaline, any sol containing over 2% SiO_2 will eventually form a gel. The most common method of preparation is the action of a solution of sodium silicate and an acid.

The time of set is governed by such factors and conditions as the concentration of silica, temperature, pH and concentration of other substances.

Hurd, Fiedler and Raymond¹³ made a study to determine the effect of the soda silica ratio on the time of set. They found no apparent effect when other factors were kept constant. Hurd and Carver¹² found an effect on the time of set when other solutions are added. The materials added were for the most part organic substances. Hurd and Rothenich¹⁶ studied the effect of sodium acetate - sodium chloride on the time of set. Sodium chloride gave no apparent effect, but sodium acetate hastened the time for gelation. This is due to a common ion effect. The method of gel formation used was the action of acetic acid and sodium silicate which gives sodium acetate. The result was then quite logical. The common ion effect then repressed hydrogen and silicate ions and thus hastened gelation. Kerns¹⁹ in his studies found that the pH's increased with increased silica concentrations, though not linearly. The pH's

of the minimum point were higher with increased silica concentration. All pH's at the minimum point were on the alkaline side.

There are three general theories for gel structure. They are the emulsion theory, the cellular theory, and the fibrillar theory. Ostwald²¹ explained the emulsion theory. It assumed a liquid - liquid system of emulsion structure, though both are considered somewhat abnormal, and one more concentrated than the other. Ostwald did not believe that this theory explained silicic acid gels. Batschli⁵ is credited with the cellular theory, which assumes that the liquid is held in droplet form in a cellular structure made up of the solid phase. Because of the assumed type of framework, this is also called the honeycomb theory. Silicic acid gels are not easily explained by this theory, since the electrical conductivity does not change as the gel sets. The fact that syneresis takes place is also difficult to explain by this theory. The fibrillar theory is usually credited to Nageli²⁰. It assumes a solid and a liquid phase, both of which are continuous; the solid material forming a fibrous structure containing the liquid in the pores. The fibrillar theory is the one favored by most workers in this field of chemistry. The differences are due to the different ideas on how the fibrous, long chains result. More recent theories have been proposed by Holmes¹⁰ and Prakash²². A theory has been proposed by Hurd¹¹ to explain the condensation of silicic acid to form a poly-silicic acid structure. It is a theory for the explanation of the mechanism for the formation of the fibrillar structure. It assumes that first a monosilicic acid is formed. This condenses, due to the amphoteric nature of the hydroxide of silicon. Long chains of condensed polysilicic acid are thus formed.

When first mixed, much of the silicic acid can be dialyzed out of solution with the electrolytes. In time, however, no silicic acid can pass through the membrane. This fact, as well as the increase in molecular weight, supports the belief that silicic acid first consists of small molecules, but that in time they condense to form large groups.

It was shown by Losenbeck that the gel was negatively charged in alkaline, neutral and weakly acidic gels, while in strongly acid gels it was positively charged. It was postulated by Hurd¹¹ that due to the amphoteric nature of the acid upon ionization of the acid, the silicon will be found in either the negative or positive ion.

The sol as it sets suddenly shows elastic properties after a time, which increases as the gel sets. It has been noticed that gels have a certain amount of stretch, though this limit gets smaller as time goes on. The phenomenon of thixotropy is shown early in setting, i.e., it will knit together again after stirring or separating. After setting, however, the gel does not show this property. For instance, if a gel is allowed to set in a test tube and it is then shaken, it will not break up and liquefy and then regel. It will not break up to any appreciable extent, and will certainly not liquefy.

Thixotropy is a property known to many sols which gel. Considerable work has been done and is still being done. A thixotropic gel is one that can be shaken after it has set, and after liquefying and standing, will regel.

After a study of thixotropy of Fe_2O_3 gels, Barry¹ advanced the theory that the gel was composed of a network of micelles, polymerized in chains, which were easily broken by mechanical agitation and would re-knit upon standing.

It was shown by others that dialysed alkaline and acid earths did not show thixotropy as well as the undialyzed earths, though the addition of electrolytes brought the property back.

Probably the next most important discovery in the field of thixotropy was that of rheopexy. It was reported by H. Freundlich and F. Juliusberger⁷. They found that if a gel of anisometric particles, namely V_2O_5 , set spontaneously in one hour, it would set in a few seconds if the particles were oriented by a gentle rolling motion of the container. This property was called rheopexy. In a report of their work, E. A. Hauser and C. A. Reed⁹ showed that bentonite gels had rheoplectic properties, and they also decided in the same study that particle size is the paramount effect in thixotropy.

B. S. Kandiclay¹⁸ in his study of Fe_2O_3 gels found that a sol containing as little as 6.3 grams per liter of Fe_2O_3 showed thixotropy. He set forth the idea that the gel had a net structure, composed of cells in which the water is mechanically enclosed. He found that the particles were rod shaped after shaking. He also decided that a charge on the particles was necessary as did G. Broughton and R. S. Hand², who thought that the presence of certain metallic ions might be necessary for thixotropy.

F. Juliusberger and A. Pirquet¹⁷ showed that V_2O_5 gels were composed of needle shaped particles after shaking, and did show the property of rheopexy. H. Freundlich and A. D. Jones⁶ found that a paste of markedly anisometric particles, especially plate like particles (Mosaic gold, mica, graphite, etc.) gave thixotropic pastes with rheoplectic properties.

Though thixotropy is said generally not to be a property of silicic acid gels except in the early stages of setting, it was observed by Hurd and Griffith¹⁴ that after a gel was broken up and washed, it would regel. This property is related to thixotropy somewhat, though it is not true thixotropy.

Thixotropy of silicic acid gels was studied by Freundlich, Bogowski and Soellner⁸. This property was studied with ultrasonic vibrations as the medium of agitation. They found, however, that silicic acid gels did not exhibit the property of thixotropy. More recent work has shown this to be not quite true. A study by H. Freundlich and D. W. Gillings⁵ has shown that gels of pH of 8.5 to 9.5, especially dialysed, could be liquefied by ultrasonic vibrations. They returned to the gel form on standing. Other ranges showed no thixotropic properties as studied by ultrasonic waves. This range, pH 8.5 to 9.5, is the range at which Freundlich and Cohn⁴ showed that silica sols could be coagulated by electrolytes.

The discovery of Hard and Griffith, that a silicic acid gel will regel after breaking up and washing, is not true thixotropy, but it would be of interest to study this. This paper is concerned with just this matter, the regelation of silicic acid gels.

METHOD AND MATERIALS

In the experimental work, "E" Brand sodium silicate of the Philadelphia Quartz Company was used. 5 liters of this material was diluted to 17 liters, to make up a solution that was 1.194 normal with respect to hydrochloric acid, titrated with phenolphthalein as the indicator. The acetic acid used was made up to .9832 normal.

The pH of the original acid gels was measured with a quinhydrone apparatus using a Leeds and Northrup potentiometer. The pH of the basic gels was measured colorimetrically. The pH of the wash water of the gels was measured by means of a La Motte colorimetric pH outfit. The quinhydrone apparatus, using a calomel electrode, is accurate only in the acid range. The glass electrode cannot be used on gels because the gels attack the glass electrode and render it useless for further measurements. While the pH measured colorimetrically is not too accurate, it gave sufficiently close results for this work since the pH was not of prime importance.

In order to break up the gel into very small particles, a very high speed motor was used with a small steel agitator. The motor ran at a speed of 3600 r.p.m. with the agitator fastened directly to the shaft. The agitator was of the type seen in every drug store for the purpose of beating up fountain drinks. The gels attacked chrome plating and nickel plating, making it necessary to use an agitator of high grade stainless steel.

To settle the solid particles out of the resulting suspension, a centrifuge was used. The centrifuge was hand driven, and was of the type to accommodate babcock test bottle. It was built to run at about 1000 r.p.m.

In all the experimental work, the gel was made up to 80 c.c., 25 c.c. of which was silicate solution, varying amounts of acetic acid and water to

make up the remainder. Three gels of each concentration were made up. One was used to determine the pH of the gel and the other two were used to study the regelation and as a check on each other.

Since some time elapsed between the time the gel was made up until it would no longer regel (up to one month), it was necessary to keep the gel from drying out. Watch glass coverings were certainly not good enough for the requirements. It was found that a desiccator with water in the bottom to keep the space saturated was just the right thing. It could easily hold the one 100 c.c. K beaker and the three 30 c.c. beakers necessary. Some small amount of water would condense and collect on top of the gel, but it caused no serious difficulty, because of the small amount.

The gel was first made up in a 100 c.c. K beaker and allowed to set. 40 c.c. were removed and the remaining 40 c.c. broken up with a stirring rod, and then 40 c.c. of water added. This was then put under the agitator, and the whole thing mixed up. The amount of agitation was kept as nearly constant as possible for each gel. The mixture was agitated for five minutes, after which time the resulting mixture was somewhat like a thick, mudlike suspension. The amount of settling under the influence of gravity was very small. Due to the size of the centrifuge receptacles it was necessary to pour the 80 c.c. of resulting suspension into three 30 c.c. beakers. The beakers were placed in the centrifuge and centrifuged for fifteen minutes. After this the wash water was poured off and kept for a pH determination with the La Motte apparatus. The solid particles have then collected in the bottom of the beaker and appear very much like a mush or a thick mud. The 30 c.c. beakers with the solid material are then placed in the desiccator and left for a considerable time, so that they have time to regel.

If this material did regel, it was transferred back to the original 100 c.c. K beaker. Water was added to make up 80 c.c., and the whole process repeated.

The method used for determining whether or not a gel had set, or more correctly, reset, was that of the tilted rod method developed by Hurd and Miller¹⁵. This method is to insert a pointed glass rod 9 cm. long and 3 m.m. in diameter, into the gel at an angle of about 15° to the vertical. If the rod will stand up the gel is considered set. This method in itself was not enough to establish the fact of whether or not the gel had reset. After centrifuging the suspension of the gel particles in water and pouring off the water, the mushy material in the beaker would support a 9 cm. glass rod with only three-fourths of an inch of gel material which was definitely not set. Due to the variability in the angle, the length of the rod could not be varied to such a length that the mush would not support it and the regelled material would. Even in a 24-hour period a rod did not fall over in a mushy material that was not set. Thus it is easily seen that in the absence of other better methods of determination this method would have to be used, with slight variations for allowances to be made. It so developed that it was a matter of testing to a certain extent the elasticity of the material and whether or not the rod would fall over if the beaker and its contents were jarred and shaken. This was at best a method which left the final decision up to the experimenter and into which the human element is bound to enter. Since the gels did regel less and less rigidly after several regelations, it was quite a problem to decide whether or not the gel had reset.

DATA

The following tabulations are the amounts of solution to
make the gel and pH of gel:

<u>No.</u>	<u>Silicate</u>	<u>Acetic Acid</u>	<u>Water</u>	<u>pH</u>
1(a) and 1(b)	25 c.c.	50 c.c.	5 c.c.	5.15
1(c) and 1(d)	25	47.5	7.5	
2(a) and 2(b)	25	45	10	5.23
2(c) and 2(d)	25	42.5	12.5	
3(a) and 3(b)	25	40	15	5.35
3(c) and 3(d)	25	37.5	17.5	
4(a) and 4(b)	25	35	20	5.69
4(c) and 4(d)	25	32.5	22.5	
5(a) and 5(b)	25	30	25	7.03
5(c) and 5(d)	25	27.5	27.5	
6(a) and 6(b)	25	25	30	9.35
6(c) and 6(d)	25	22.5	32.5	
7(a) and 7(b)	25	20	35	10.8
7(c) and 7(d)	25	17.5	37.5	
8(a) and 8(b)	25	15	40	11.1
8(c) and 8(d)	25	12.5	42.5	
9(a) and 9(b)	25	10	45	11.3

Number of times of regulation and pH of wash water:

<u>Gel.No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
1(a)	4.9	4.9	5.1	5.2	5.2	5.3	5.3	5.5	<u>5.5</u>	
1(b)	4.9	5.0	5.1	5.2	5.2	5.3	5.4	5.4	<u>5.1</u>	
1(c)	5.0	5.1	5.1	5.2	5.2	5.3	5.4	5.4	<u>5.5</u>	
1(d)	5.0	5.1	5.1	5.2	5.2	5.3	5.4	5.4	<u>5.5</u>	
2(a)	5.1	5.2	5.2	5.2	5.3	5.3	5.4	5.4	<u>5.4</u>	
2(b)	5.1	5.2	5.2	5.3	5.3	5.3	5.4	<u>5.4</u>		
2(c)	5.2	5.3	5.3	5.4	5.4	5.5	5.6	<u>5.8</u>		
2(d)	5.2	5.3	5.4	5.4	5.5	5.5	5.6	<u>5.6</u>		
3(a)	5.3	5.5	5.6	5.6	5.7	5.7	<u>5.7</u>			
3(b)	5.4	5.5	5.6	5.6	5.7	5.7	<u>5.7</u>			
3(c)	5.4	5.5	5.6	5.6	<u>5.6</u>					
3(d)	5.4	5.5	5.6	5.6	5.6	<u>5.6</u>				
4(a)	5.5	5.7	5.7	<u>5.8</u>						
4(b)	5.5	5.6	5.7	<u>5.8</u>						
4(c)	6.5	6.7	<u>6.8</u>							
4(d)	6.2	6.4	<u>6.5</u>							
5(a)	6.9	9.0	<u>9.0</u>							
5(b)	6.6	9.4	<u>9.3</u>							
5(c)	9.7	<u>9.6</u>								
5(d)	9.6	9.6	<u>9.5</u>							
6(a)	10.6	<u>10.5</u>								
6(b)	10.5	<u>10.5</u>								
6(c)	<u>10.9</u>									
6(d)	<u>10.8</u>									
7(a)	<u>11.0</u>									
7(b)	<u>11.1</u>									
7(c)	<u>11.2</u>									
7(d)	<u>11.1</u>									
8(a)	<u>11.3</u>									
8(b)	<u>11.3</u>									
8(c)	<u>11.4</u>									
8(d)	<u>11.4</u>									
9(a)	<u>11.5</u>									
9(b)	<u>11.4</u>									

The underlined pH indicates that the gel did not reset.

During the course of the process outlined on previous pages, a few other things were noticed. After beating and centrifuging gels numbered 1 through 3 the first time, it was noticed that the solid material settled out occupied about $5/8$ to $3/4$ of the total volume of the suspension. The amount of solid material left after successive washing approached more nearly $1/2$ the total volume. In gels 4 and 5 the volume of the solids was very nearly $1/2$ after the first washing, and became slightly less than $1/2$ after successive washings. In the gels numbered 6 through 9, the volume of the solid material settled was less than $1/2$ after the first washing, and the settled material was also very much more mushy or soupy; even though they were more mushy, no more water could be centrifuged out.

Syneresis, or the shrinking of a gel after setting, was noticed in only six of the gels used, and the syneresis took place only after the first regelation. The gels that syneresis took place in were those of number 4(a) through 5(c), with the exception of 5(a). This particular range received no different treatment from the rest of the gels so far as it could be ascertained. All of the gels were left at least 24 hours between centrifuging, though were necessarily kept as long as four days before they were worked with again. When viewed with a microscope, the gels in which syneresis had taken place looked the same as the others.

The microscope study did show one interesting thing, however. A gel that had regeled was stirred and a portion of it put on a microscope slide. One could easily see the larger particles of the gel and the state of subdivision. The interesting thing to note was not this subdivision, but the subdivision within these aggregates. Throughout the fairly large particles could be seen smaller pieces of gel which were apparently the small particles that the high speed beater produced. The largest of these smaller particles

was about two one-thousandths of a centimeter. There were many other particles going down in size to where they could not be seen with the microscope. In between the particles that were visible was just a gray opalescent haze in which nothing could be distinguished. However, it was interesting to note the size of the particles which the beater produced.

RESULTS

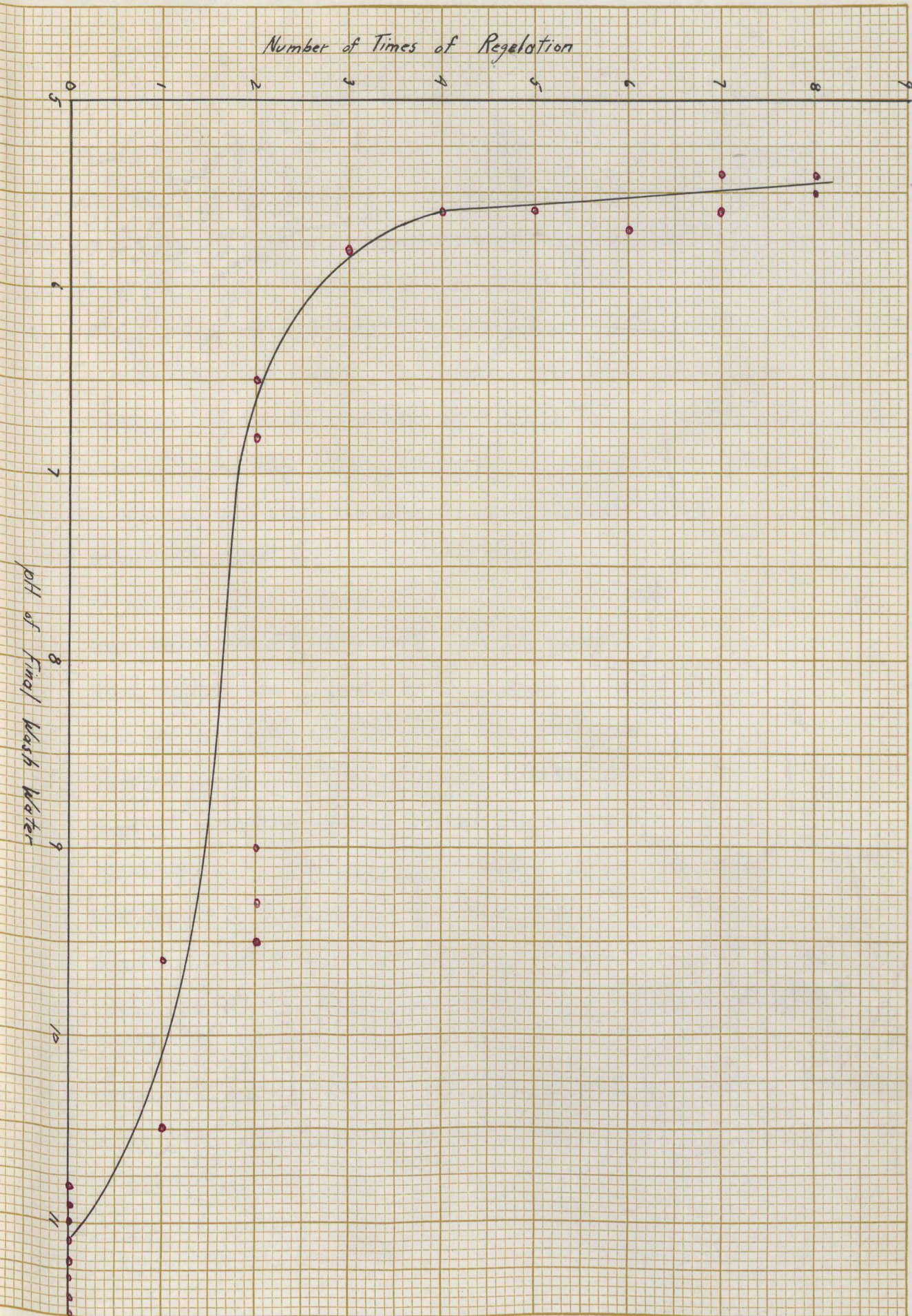
A plot of the number of times the gel reset against the pH of the solution was made to see if any relation between the two existed. It is apparent that the acid gels were the ones that regelled the greatest number of times, while those in the stronger alkaline range would not regel. The data, however, is apparently not sufficient to draw any well founded conclusions.

There is too large a gap through the neutral and weakly alkaline range particularly, and data concerning the more acid gels would be helpful to find out whether or not the number of times of regelation hits a maximum or whether the curve will continue on up.

On the alkaline side the curve drops off to the axis (the gels would not regel). This may be due to the fact that insufficient time was allowed for the gel to regel. The alkaline gels require more time to regel than the other gels, and very alkaline gels may not gel at all. Thus it might be expected that the regelation time of the alkaline gels may be even longer than a week, which was the time allowed. If this is the case this curve would not be too much unlike a curve of time of set against pH. In such a curve there is a minimum time of set on the slightly alkaline side, and rising again as the more alkaline gels are used.

The most difficult part of obtaining this data is determining whether or not the gel has set. This becomes increasingly difficult as the gel is beaten up a number of times. Perhaps a different method of determination would be helpful, though this method has proved most reliable in past instances.

If any conclusion at all is to be drawn from this data, it would be that the number of times that a gel will regel is some function of the hydrogen ion concentration alone, and not a function of both hydrogen and hydroxyl ion concentration as might be expected from the work on time of set of gels.



BIBLIOGRAPHY

1. Barry, P. - Compt. Rend. 193, 183-4 (1933)
2. Broughton, G. and Hand, R.S. - Nature 142, 255 (1938)
3. Butschli, O. - Untersuchungen über Strukturen Leipzig (1898)
4. Freundlich, H. and Cohn - Kolloid Z. 39, 28 (1928)
5. Freundlich, H. and Gilling, D - J. Chem. Soc. (1938) p. 548
6. Freundlich, H. and Jones, A. - J. Phys. Chem. 40, 1217-36 (1936)
7. Freundlich, H. and Juliusberger, F. - Trans. Faraday Soc. 31, 920-1 (1935)
8. Freundlich, H., Rogowski and Soellner - Kolloid Beih. 37, 215 (1935)
9. Hauser, E.A. and Reed, C.A. - J. A. C. S. 56, 1822 (1934)
10. Holmes - J. Phys. Chem. - 22, 510 (1918)
11. Hurd, C.B. - Chem. Review, Vol. 22, No. 3, June 1938
12. Hurd and Carver - J. Phys. Chem. 37, 321 (1932)
13. Hurd, Fiedler and Raymond - J. Phys. Chem. 41, 553 (1937)
14. Hurd and Griffith - J. Phys. Chem. 39, 1155 (1935)
15. Hurd and Miller - J. Phys. Chem. 36, 2194 (1932)
16. Hurd and Mothemich - Theses, Union College (1930)
17. Juliusberger, F. and Pirquet, A. - Trans. Faraday Soc. 32, 445-52 (1936)
18. Kandelay, B.S. - Kolloid Z. 74, 200-5 (1938)
19. Kerns - Thesis, Union College (1935)
20. Nageli, K. von - Pflanzen Physiologischen Untersuchungen Zurich (1858)
21. Ostwald, W. - Kolloid Z. 46, 248 (1928)
Ostwald, W. and Fischer, W. - An Introduction of Phys. Chem. p. 102 (1917)
22. Prakash - J. Ind. Chem. Soc. 50, 387 (1931)