

6-1939

The formation of silicic acid gels in very strongly acid solutions

Raymond William Barclay
Union College - Schenectady, NY

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

 Part of the [Chemistry Commons](#)

Recommended Citation

Barclay, Raymond William, "The formation of silicic acid gels in very strongly acid solutions" (1939). *Honors Theses*. 1743.
<https://digitalworks.union.edu/theses/1743>

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 FORMATION OF SILICIC ACID GELS

IN VERY STRONGLY ACID SOLUTIONS

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

By Raymond W. Barclay

Approved by Charles B. Hurst

May 1939

8
UN92
B24
c.2

INTRODUCTION

In the past few years much work has been done at Union College in attempting to determine the mechanism of the setting of silicic acid gels. All of this work, however, has been done in alkaline, weakly acid, or moderately acid solutions, and practically no investigation of silicic acid gels in very strongly acid solutions has been made. The purpose of this research was to undertake such an investigation.

The effect of temperature and pH upon the time of set was studied. Three different temperatures were used, and the pH of all gels studied was below 1. Concentrated hydrochloric and concentrated sulfuric acids were used to obtain this low pH. The heat of activation was calculated from the data obtained.

HISTORICAL

Silicic acid gels have been known for about two hundred years.

Berzelius prepared such gels in 1820, and Walden refers to the earlier work of Potts done before 1800. Since that time many theories have been presented to account for the mechanism involved in the setting of gels. At present, three general theories for gel structure exist; namely, the emulsion theory, the cellular theory and the fibrillar theory. The emulsion theory was formulated by Ostwald¹. This theory does not explain viscosity and elasticity of silicic acid gels, and is not generally accepted. The cellular theory proposed by Butschli postulates that water in the gel is held by a cellular framework resembling that of a honeycomb. This theory explains the elasticity of a gel and the fact that silicic acid gels do hold water in their structure. However, it does not account for syneresis, nor does it explain the observation that practically no increase in the electrical resistance occurs when the gel sets as found by Hurd and Seanker². The theory now most generally accepted was proposed by Proctor and Robertson in 1914³. This theory, called the fibrillar theory, pictures the gel as being composed of long thread-like chains which lengthen and branch out as the molecules of silicic acid interconnect with one another. The final fibrous structure may be compared to a sponge, since the gel is thought to hold its liquid similarly as a sponge holds water. This theory explains the structure of silicic acid gel fairly well, and is described in detail by Hurd⁴.

However, the true mechanism involved in the setting of silicic acid gels has not been definitely solved. With this in mind, much work has been done at Union College during the past few years in accumulating data which will give a further insight into the true theory of gel structure. The majority of

this work, however, has been confined to gels prepared from acetic acid and sodium silicate, the resulting mixture being alkaline or weakly acid.

For these acetic acid - sodium silicate gels Hurd and Letteron⁵ have shown the log of the time of set to be a linear function of the reciprocal of the absolute temperature. They also calculated the Arrhenius heat of activation Q , which was found to be 18,940 cal./gs. mole. Hurd and Haynes⁶ continued this work using other weak acids (tartaric, succinic and citric), and found the linear relationship to hold.

Silicic acid gels in moderately acid solutions have been prepared by the action of strong acids and concentrated solutions of acetic acid upon a solution of sodium silicate. Fleming⁷ used hydrochloric and sulfuric acids. His conclusion was that the type of gel produced did not depend upon the kind of acid used. Holmes⁸ employed nitric, hydrochloric and sulfuric acids, and varied the normality of the acids using the same amount of sodium silicate. In all of his work he used an excess of the acid above that required to neutralize the sodium hydroxide of the silicate present in the solution. The conditions, then, were similar to those under which this research was carried out. From the data he obtained Holmes plotted normality of the acid against time of set. He also studied the effect of temperature on the time of set and plotted curves showing the relation between degrees Centigrade and the time of set for the various acids. He concluded that hydrogen ions affect the process catalytically, and that the dehydrating influence of non-ionized molecules of the acid is an important factor. He also found that for each acid mixed with the silicate there is a concentration of hydrogen ions which delays the set to an infinite time. At still higher concentrations of the acid, the time of set again becomes measurable, rapidly decreasing to an almost immediate set.

Ray and Ganguly⁹ later determined accurately the optimum conditions for the formation of gels by the action of hydrochloric and sulfuric acids upon alkali silicates. They found in each case, for a definite concentration of silicate, a point beyond which no gelation occurred. Hurd and Letteron⁵ used a fixed concentration of sodium silicate and increased the concentration of acetic acid from .1750 up to a maximum of 15.00 N. They obtained a peculiarly humped shaped curve, discovered by Holmes, and concluded that the excess hydrogen ions affect the process catalytically.

Fels and Firth¹⁰ worked with different concentrations of hydrochloric acid and sodium silicate of density 1.15 at temperatures ranging from 0° to 45° C. and found the time of set did not vary with the temperature. They mixed equal volumes of silicate and acid and found a gel set in 10-15 minutes. As the strength of the acid solution was gradually diminished, the time of setting increased. Thus, when the concentration of the acid was 2 N, a firm gel was not obtained until a period of from two to three weeks had elapsed after mixing. When they reduced the concentration to 1.5 N, a gel formed immediately upon mixing. As the strength of the acid was further diminished, they found the time of set again increased. They concluded that the molecules of the acid exert a catalytic influence upon the silicic acid produced; the influence being in the nature of a dehydrating action.

Hurd, Raymond and Miller¹¹ worked with mixtures of sodium silicate and hydrochloric acid. They found the time of set to be a linear function of the hydrogen ion concentration over a range of pH from 4.20 to 5.50. Hanks and Weintraub¹² found that the pH of gels prepared from silicates and hydrochloric acid rises during and following the setting of the gel. A constant pH value is reached. They concluded that the time for the gels to attain pH equilibrium depends upon the temperature.

Hurd, Frederick and Haynes¹³ studied gels prepared from sodium silicate and strong acids (hydrochloric, nitric and sulfuric) over pH range from 3 to 6. They obtained time of set and pH data, and from this calculated the heat of activation for each of the three acids used. They also found the pH to increase with time, most of the change taking place before the setting of the gel. Batchelor¹⁴ prepared silica gels and found that the rate of the reaction is limited by at least two factors - concentration and temperature. He also found the pH shift in strongly acid solutions is toward less acid reactions, and that the shifts are less marked in strongly acid solutions than in moderately acid reactions.

EXPERIMENTAL

The sodium silicate used in this research was the "E" brand furnished by the Philadelphia Quartz Company. The $\text{Na}_2\text{O}:\text{SiO}_2$ ratio by weight was 1:3.25. Approximately 8 liters of this silicate was diluted to about 21 liters with distilled water. This large volume, having a normality of 1.28 with respect to sodium hydroxide, proved adequate for all needs of this research. The silicate solution was titrated with standard hydrochloric acid, using methyl orange as the indicator. Both the hydrochloric and sulfuric acids used were the concentrated solutions furnished by the Graselli Company. All water used in making up the original silicate solution and in preparation of the gels was distilled water which had been previously boiled to expel carbon dioxide.

The total volume of the gel mixture on which time of set measurements were taken was 80 c.c., with the exception of the runs made at 0° C. The gels worked with at the two higher temperatures were allowed to set in 100 c.c. K beakers covered with tightly fitting watch glasses. In each 80 c.c. mixture there was present 25 c.c. of the 1.28 N silicate and sufficient water and acid to make the total volume equal to 80 c.c. However, it was found to be more suitable to make up a double mixture in each case, and take half of the mixture for time of set measurements and the other half for pH measurements. Thus, 50 c.c. of the silicate solution was measured by a pipette into a 100 c.c. K beaker, and 110 c.c. of acid and water was measured using burettes into a 250 c.c. beaker. These beakers, covered with watch glasses and held down by lead weights, were placed in a thermostated water bath 1.5° C. below the temperature of the bath in which the gels were to set. This difference in temperature has been found to correct for the heat given out in the reaction which takes place when the solutions were mixed. Upon mixing the solution was poured back and forth three times in the two beakers. 80 c.c. of the mixture was

poured into a 100 c.c. K beaker and placed in the bath at the desired temperature. The other half of the mixture was poured into the 100 c.c. beaker previously used for the silicate and placed in the thermostated bath where pH readings were taken.

The time of set was determined by the tilted rod method as described by Hurd and Letteron⁵. The gel was considered set when a rod 3 mm. in diameter and 10 cm. long was supported at an angle of about 20° to the vertical.

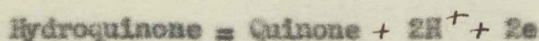
The gels run at 0° C. were allowed to set in small 2 oz. bottles stoppered with paraffined corks. These bottles were found to be more convenient than Erlenmeyer flasks. It was found that about 60 c.c. of the gel mixture in one of these bottles when tested with the same size rod gave results which agreed with those obtained for the 80 c.c. mixture in a 100 c.c. beaker.

The gels in this research were run at three different temperatures, namely, 0° C., 25.0° C., and 38.2° C. The 0° C. thermostats consisted of insulated tubs filled with a mixture of snow and water. Fresh snow was added from time to time and the excess water removed. Before mixing it was found necessary to cool the acid in a separate 0° bath, in order that any escaping fumes would not lower the temperature of the regular bath. The 2 oz. bottles in which the gel was allowed to set were packed firmly in the snow.

For the two other temperatures, water thermostats were used. The temperatures of the baths were controlled by means of a mercury thermoregulator; and in one bath telephone relays were used and in the other a thyatron tube circuit was used. Electrical heaters were placed in the regulator circuit. The water was circulated by means of a stirrer run by a small motor. An effort was made to keep the temperature of the baths as constant as possible, since a change of temperature would affect the time of set. All of the temperatures were measured with a calibrated Bureau of Standards thermometer.

The quinhydrone electrode method was used for determining the hydrogen ion concentration. Platinum wire was used as an electrode, since this is not affected by colloidal silicic acid as shown by Hurd and Griffith¹⁵. The reference electrode was a saturated calomel cell, which was made up as described in Daniels, Matthews and Williams¹⁶. The ordinary Leeds and Northrup quinhydrone potentiometer could not be used for measurement of the pH since the pH's to be measured in this research were so low that the potential readings were off scale. To overcome this difficulty it was necessary to set up an apparatus using Leeds and Northrup potentiometer No. 79550 arranged with the standard cell outside the box. This apparatus is shown in Figure I.

The calculation of the potential depends on an excess of the solid quinhydrone. Therefore, in adding quinhydrone it is essential to add an excess so that some of the solid remains on the bottom of the beaker. The addition of this quinhydrone has no effect upon the time of set as found by Malone¹⁷. Quinhydrone is an equimolar mixture of quinone and hydroquinone. The reaction taking place is:



The equilibrium constant is:

$$K = \frac{(\text{Quinone})(\text{H}^+)^2}{\text{Hydroquinone}}$$

The potential is:

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{\text{hydroquinone}}}{(a_{\text{H}^+})^2 (a_{\text{quinone}})}$$

However, quinone and hydroquinone form the equimolecular compound called quinhydrone, which gives constant and equal concentrations of quinone and hydroquinone so the relation is:

$$E = E_0 + .0591 \log a_{H^+}.$$

This reduces to:

$$pH = \frac{.4552 - E}{.0591} \quad (A)$$

when the readings are made at 25° C. using a saturated KCl solution in the calomel cell.

Care must be taken to keep the platinum electrode clean. This was done by immersing it in hot caustic, then in distilled water, and finally flashing in a flame. All pH's were taken at 25.0° C. After the quinhydrone was added, the solution was stirred well and allowed to come to the temperature of the bath. The calomel and platinum electrodes were lowered into the solution and measurements of the potential were made. These can be most conveniently converted into pH units by reading the values from a curve. Therefore, a graph was constructed with the help of formula (A), plotting pH against potentiometer reading (Graph VII).

Frederick¹⁹, working with strong acids and sodium silicate in the pH range from 3 to 6, found a definite drift of pH toward higher values. The same phenomenon was observed in this research. However, the pH drift does not appear to be as marked as in the less acid region in which Frederick worked, and disappears completely in very acid solutions (about pH = 0). This observation may be explained by assuming that there is some reaction tending to deplete the H^+ ions present. This would account for the drift toward higher pH, that is, lower H^+ ion concentration. However, in the case of very acid solutions, the concentration of H^+ ions is so great that any decrease in it will not be observed and hence no pH drift will occur.

The solution always drifted toward higher pH's, that is, toward lower hydrogen ion concentration, and finally slowed up to a practically constant value.

It was this value that was recorded as the pH. These pH's were of the correct magnitude and plotted against the log of time of set gave a straight line, over the range studied, and hence were assumed to be correct values.

As the strength of the acid was increased in the gel mixture, the pH naturally decreased to lower values. However, beyond a certain point, the pH readings began to increase again, and to vary up and down, as the H^+ ion concentration was increased. Since the pH cannot possibly increase with greater addition of H^+ ions, it was assumed that the limit of the apparatus had been reached. This limit for hydrochloric acid gels was a pH reading of about -1.5 , and for sulfuric acid gels of about -1.3 . Beyond these values no reliable measurements of pH could be made with the quinhydrone electrode. Therefore, another method was sought to measure the pH of very concentrated acid solutions. A search through the literature proved futile. Apparently very little or no work has been done in attempting pH measurements in such a high concentration of H^+ ions.

The time of set of the more acid gels, however, was taken. In the case of the gels made with hydrochloric acid, the color was yellow and the depth of color became more marked as the concentration of the acid was increased. This yellow color is believed to be due to the high concentration of Cl^- ions.

In the more concentrated hydrochloric acid gels run at $0^\circ C.$, a precipitate of sodium chloride separated out. Even though the solubility product of sodium chloride is high, the very large concentration of Na^+ and Cl^- ions was apparently great enough to exceed the solubility product. Although the solubility of sodium chloride remains practically constant for temperature changes, no precipitate appeared in similar gels run at the two higher temperatures.

According to Hurd, Raymond and Miller¹¹, sodium chloride added to the gel mixture decreases the time of set without causing any considerable change in pH. Thus, this separation of sodium chloride may affect the gel in some manner. The gels that showed this property were those whose H^+ concentration was so high that it could not be measured for reasons stated above.

The sulfuric acid gels were white and opaque, and this opacity increased as the concentration of the acid was increased.

RESULTS AND DISCUSSION

The data obtained, consisting of time of set and pH measurements for concentrated hydrochloric and sulfuric acid gels at three different temperatures, are given in the following tables. The time of set of the hydrochloric acid gels ranged from 1 minute to over 18,000 minutes, and for the sulfuric acid gels from almost immediate set to gels which did not set in about 20 days and were considered to be infinite time of set. The pH ranged from .5 to -.5 for the hydrochloric acid gels, and from .96 to -.35 for the sulfuric acid gels. A very slight decrease of the hydrogen ion concentration will bring the pH from less than 1 up to about 7, and cause the gel to set immediately. The gels which took a long time to set were those of less acid concentration, and were not as rigid as those which set in a shorter time.

For each set of gels the logs of times of set are plotted against the pH's. These results are shown in Graphs I and II. Since these curves for the range of pH studied were found to be straight lines, then the reaction for this range of pH is apparently unimolecular.

The heat of activation was obtained from data given in Table III. The log time was plotted against the reciprocal of the absolute temperature for each of the acids and at the pH's shown in the table (Graphs III and IV). By making the same assumptions as used by Hurd and Letteron⁵, the heat of activation may be calculated by multiplying the slopes of the curves by 2.305 R where R is the gas constant expressed in calories per gram mole per degree. The heat of activation obtained was about 11,000 calories for the hydrochloric acid gels and about 9,000 calories for the sulfuric acid gels. These values are much lower than the results obtained by other investigators

who have worked in the less acid range and who have obtained about 17,000 calories for the heat of activation. This lower heat of activation in the more acid range may perhaps be due to the dehydrating effect of the concentrated acids. The increased hydrogen ion concentration seems to act as a catalyst since the gels tend to set more quickly when the acid concentration is increased.

In Graphs V and VI the time of set is plotted against the corresponding pH. It is seen that the time of set approaches zero asymptotically as the pH is decreased.

The pH drift may be caused by the splitting out of water from ortho silicic acid to form more complex acids. This condensation should be increased by the dehydrating effect of concentrated acids and this was found to be the case. This data then would tend to uphold the fibrillar theory, the exact method of interconnecting of the silicic acid molecules being unknown.

In conclusion, the author would suggest an investigation into methods of measuring pH in very acid solutions, since this was one of the principal obstacles encountered in this research. It may also be interesting to use acids other than those used in this research to study the formation of the gels in very acid solutions.

TABLE IHYDROCHLORIC ACID GELS

50 c.c. of 1.28 N sodium silicate present in all mixtures

Temperature 25.0° C.

<u>Conc. HCl</u>	<u>H₂O</u>	<u>pH</u>	<u>Time (min.)</u>	<u>log time</u>
7 c.c.	103 c.c.	.51	18560	4.218
8	102	.36	13920	4.144
9	101	.26	8200	3.914
10	100	.22	5690	3.819
15	95	.10	2520	3.401
20	90	.02	1150	3.061
25	85	-.05	840	2.924
30	80	-.16	423	2.628
35	75	-.25	220	2.343
40	70	-.31	132	2.121
45	65	-.38	85	1.930
50	60	-.43	57	1.756
55	55	-.47	47	1.672
60	50	-.51	34	1.532
65	45	-.53	24.5	1.389
70	40	-	17.5	1.243
75	35	-	13.5	1.130
80	30	-	12.5	1.097
85	25	-	9.3	.969
90	20	-	7.1	.851
95	15	-	5.6	.748
100	10	-	4.5	.653
105	5	-	3.2	.505
110	0	-	2.8	.447

TABLE I (cont.)

HYDROCHLORIC ACID GELS

Temperature 0° C.

<u>Conc. HCl</u>	<u>H₂O</u>	<u>pH</u>	<u>Time (min.)</u>	<u>log time</u>
10 c.c.	100 c.c.	.22	never set	-
15	95	.10	10,000	4.000
20	90	.02	6015	3.779
25	85	-.05	3210	3.507
30	80	-.16	1708	3.232
35	75	-.25	1075	3.032
40	70	-.31	564	2.751
45	65	-.38	330	2.519
50	60	-.43	268	2.428
55	55	-.47	175	2.243
60	50	-.51	150	2.176
65	45	-.53	126	2.101
70	40		55	1.740
75	35		40	1.602
80	30		32	1.505
85	25		19.8	1.297
90	20		15.1	1.179
95	15		10.9	1.037
100	10		9.2	.964
105	5		8.5	.929
110	0		6.5	.799

TABLE I (cont.)HYDROCHLORIC ACID GELS

Temperature 38.2° C.

<u>Conc. HCl</u>	<u>H₂O</u>	<u>pH</u>	<u>Time (min.)</u>	<u>log time</u>
7 c.c.	103 c.c.	.51	6760	3.830
8	102	.56	4170	3.620
9	101	.26	3840	3.584
10	100	.22	2880	3.460
15	95	.10	965	2.985
20	90	.02	555	2.744
25	85	-.05	310	2.491
30	80	-.16	178	2.250
35	75	-.25	93	1.969
40	70	-.31	55	1.740
45	65	-.38	35	1.544
50	60	-.43	29	1.462
55	55	-.47	22.5	1.352
60	50	-.51	14	1.146
65	45	-.53	12	1.079
70	40		10	1.000
75	35		7.4	.869
80	30		4.5	.653
85	25		3.7	.568
90	20		2.5	.392
95	15		2.0	.301
100	10		1.6	.204
105	5		1.3	.114
110	0		1.0	0.0

HYDROCHLORIC ACID GELS

5.0

4.0

3.0

2.0

1.0

log time of set

pH

0%

25°C

38.2°C

-1.5

0

+5

R.W.B.

TABLE II

SULFURIC ACID GELS

50 c.c. of 1.28 N sodium silicate present in all mixtures

Temperature 25.0° C.

<u>Conc. H_2SO_4</u>	<u>H_2O</u>	<u>pH</u>	<u>Time (min.)</u>	<u>log time</u>
4	108	.98	10,170	4.007
6	104	.80	4407	3.644
8	102	.34	2460	3.391
10	100	.05	1078	3.038
15	95	-.81	378	2.577
20	90	-.83	129	2.110
25	85		54	1.732
30	80		24.5	1.389
35	75		11.5	1.061
40	70		4.25	.628
45	65		2.5	.398
50	60		1.2	.079
55	55		.7	-.155
60	50		.2	-.699

TABLE II
(cont.)

SULFURIC ACID GELS

Temperature 0° C.

<u>Conc. H₂SO₄</u>	<u>H₂O</u>	<u>pH</u>	<u>Time (min.)</u>	<u>log time</u>
4	108	.96	never set	-
6	104	.80	16,000	4.204
8	102	.34	10,200	4.008
10	100	.05	3990	3.601
15	95	-.31	1510	3.179
20	90	-.33	490	2.690
25	85		185	2.267
30	80		72	1.857
35	75		30	1.477
40	70		15.0	1.178
45	65		5.8	.763
50	60		2.4	.380
55	55		1.1	.041
60	50		.8	-.097
65	45		.3	-.523
70	40		about .1	-1.0

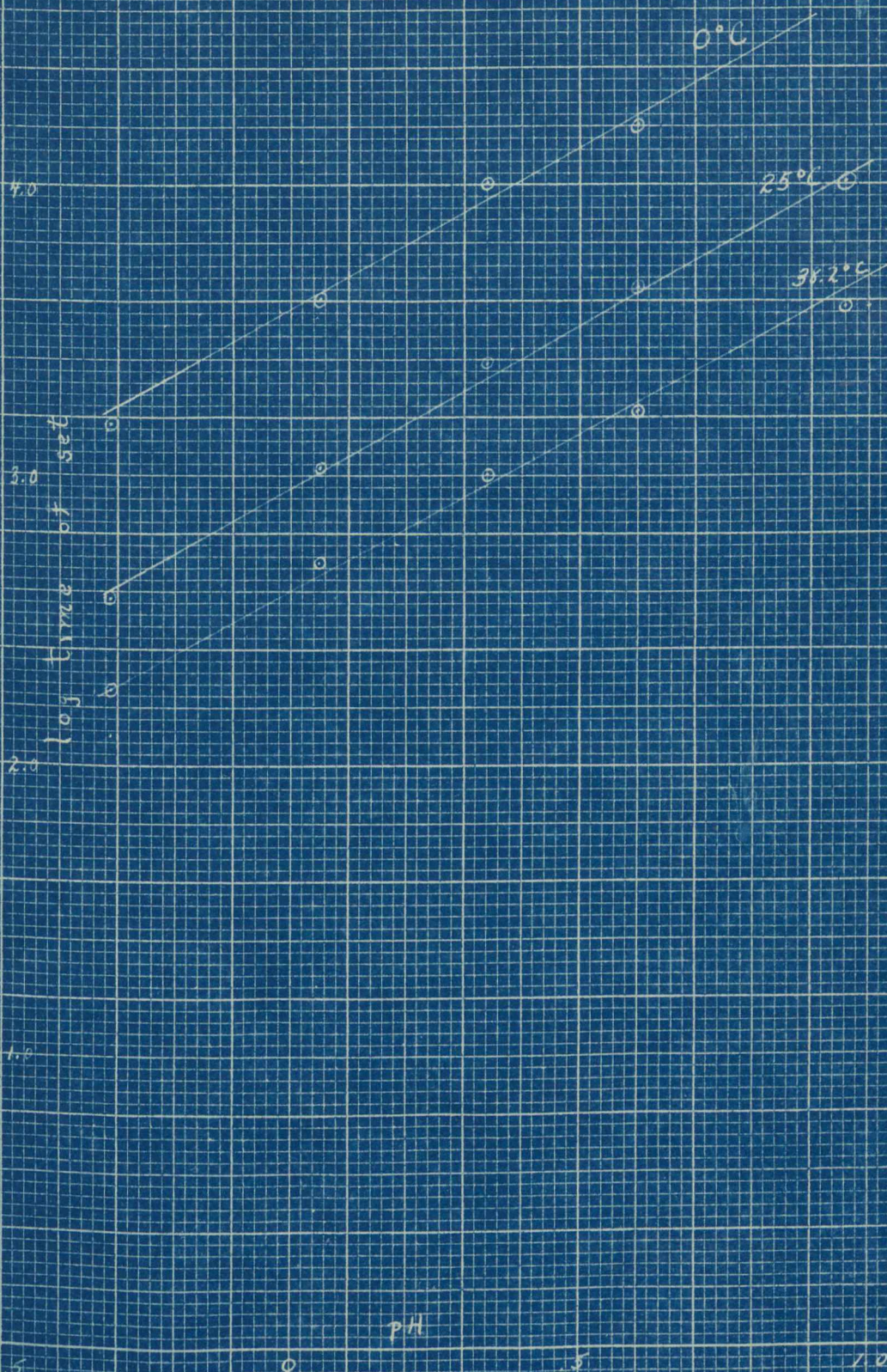
TABLE II (cont.)

SULFURIC ACID GELS

Temperature 38.2° C.

<u>Conc. H₂SO₄</u>	<u>H₂O</u>	<u>pH</u>	<u>Time (min.)</u>	<u>log time</u>
4	105	.98	5849	3.568
6	104	.60	1860	3.220
8	102	.34	1000	3.000
10	100	.05	505	2.703
15	95	-.31	185	2.263
20	90	-.35	68	1.833
25	85		27	1.431
30	80		13	1.114
35	75		5.9	.771
40	70		3.0	.477
45	65		1.5	.176
50	60		.7	-.155
55	55		.3	-.523
60	50		about .1	-1.0

SULPHURIC ACID GELS



R. W. B.

TABLE IIIData for Calculation of Heat of Activation

<u>Deg. C.</u>	<u>1/T</u>
0	.00368
25.0	.00335
38.2	.00321

Hydrochloric Acid Gels

<u>pH</u>	<u>log time</u>		
	<u>0° C.</u>	<u>25.0° C.</u>	<u>38.2° C.</u>
.02	3.779	3.061	2.744
-.16	3.232	2.626	2.250
-.31	2.751	2.121	1.740
-.43	2.428	1.756	1.482
-.51	2.176	1.532	1.146

Heat of Activation = 2.303 R slope

Heat of Activation for hydrochloric acid gels = 11,000 cal.

Sulfuric Acid Gels

<u>pH</u>	<u>log time</u>		
	<u>0° C.</u>	<u>25.0° C.</u>	<u>38.2° C.</u>
.96	-	4.007	3.586
.60	4.204	3.644	3.220
.34	4.008	3.391	3.000
.05	3.801	3.033	2.705
-.31	3.179	2.578	2.263

Heat of Activation of sulfuric acid gels = 9,000 cal.

HYDROCHLORIC ACID GELS

H.5

4.0

3.5

3.0

2.5

2.0

1.5

1.0

.5

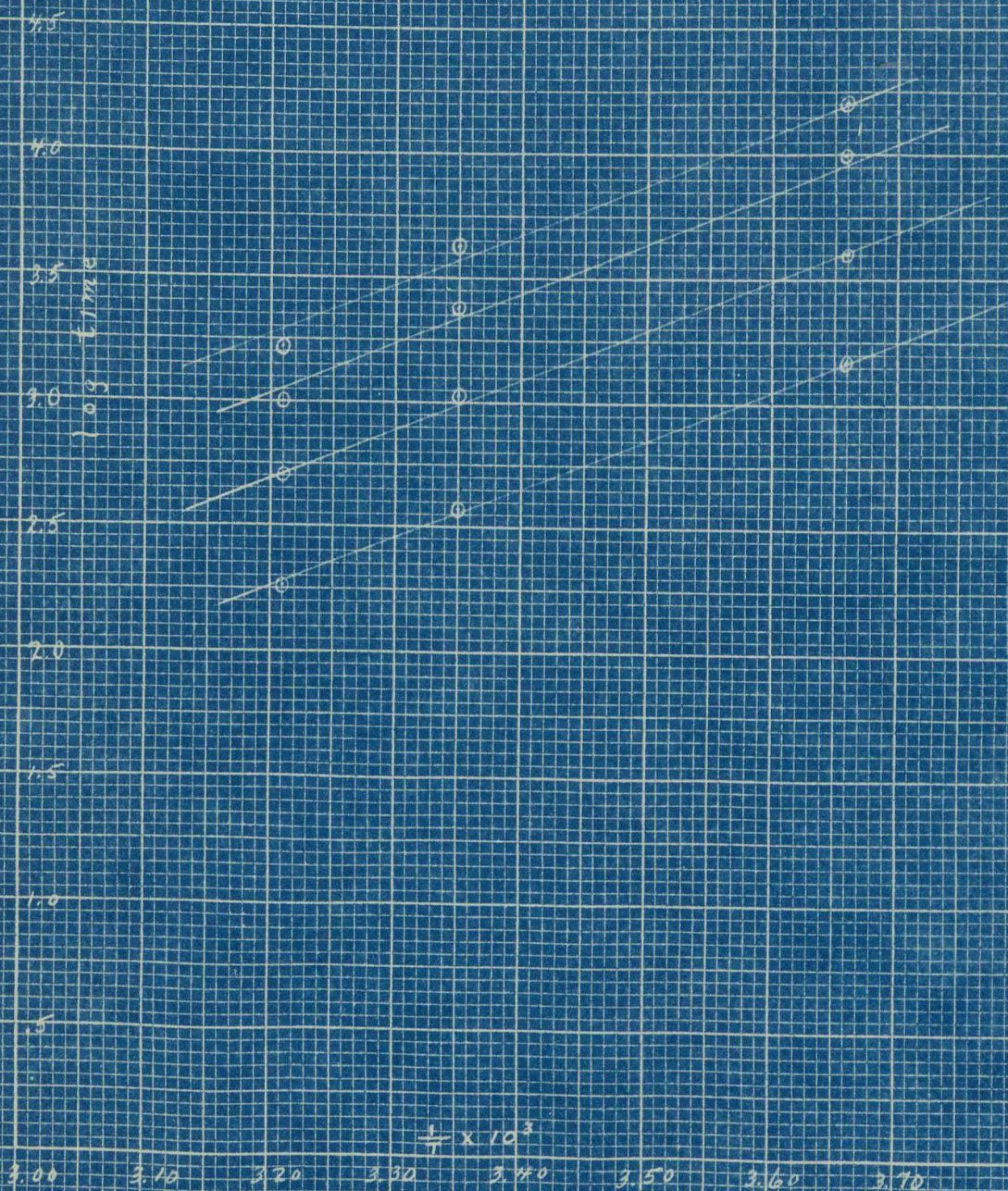
log time

$\frac{1}{t} \times 10^3$

3.00 3.10 3.20 3.30 3.40 3.50 3.60 3.70

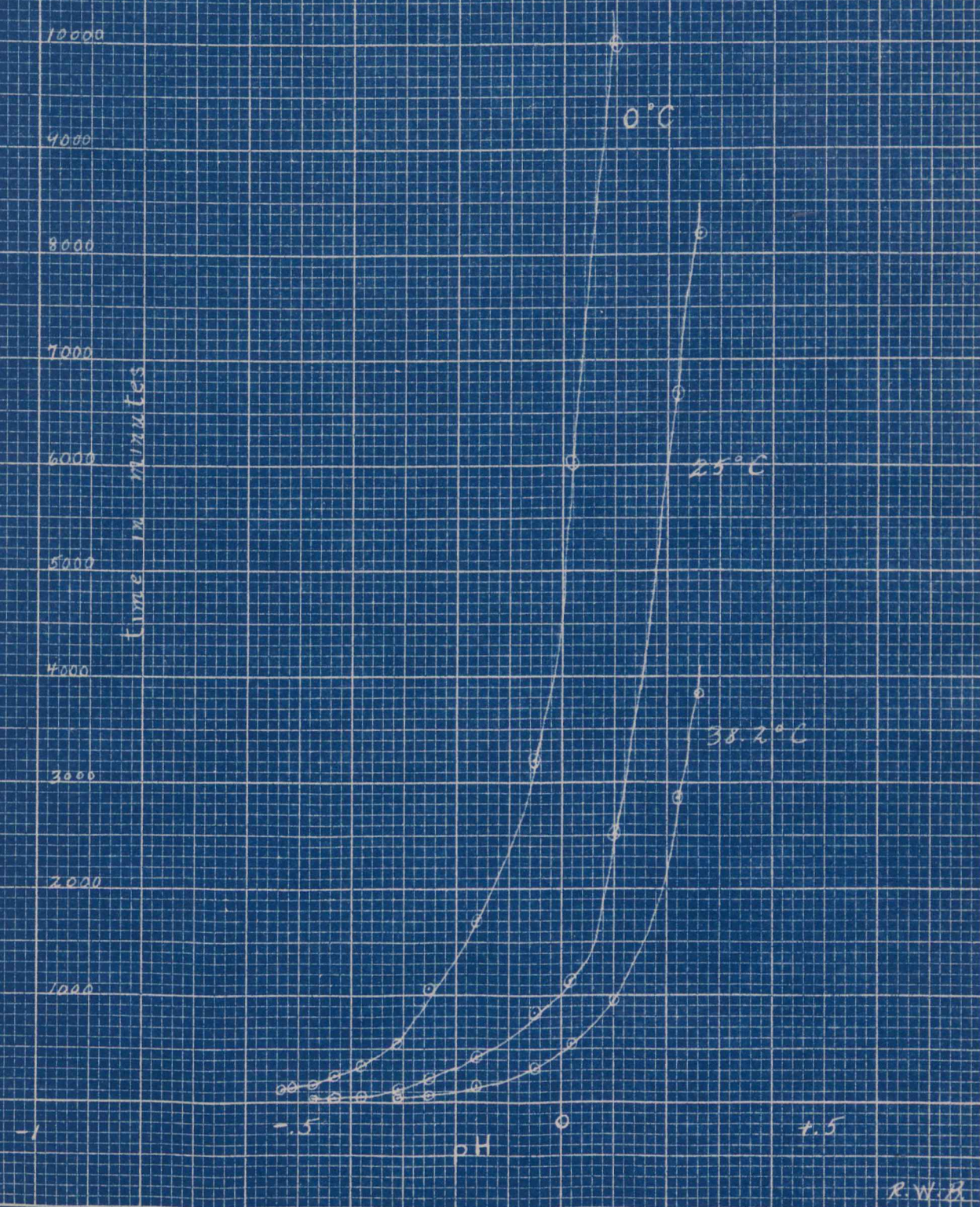
R. W. S.

SULPHURIC ACID GELS



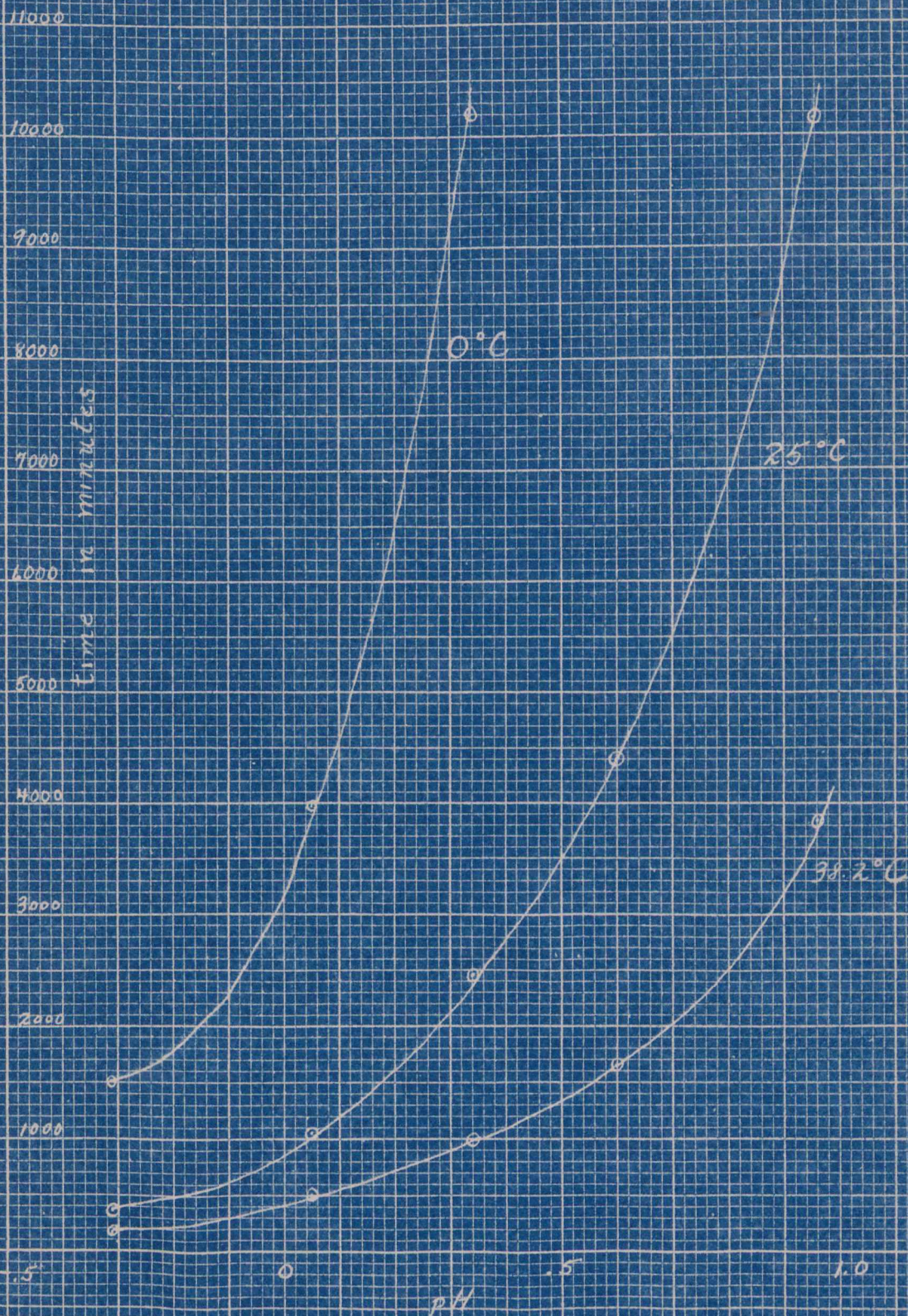
R. W. B.

HYDROCHLORIC ACID GELS



R. W. B.

SULPHURIC ACID GELS



R. W. B.

GRAPH USED TO CONVERT
POTENTIOMETER
READING
TO PH

2

1

pH

0

-1

1.30

1.33

1.40

1.42

1.48

1.50

1.51

Potentiometer Reading in Volts

R. W. B.

SUMMARY

The formation of silicic acid gels in very strongly acid solutions has been studied. The gels were made by mixing sodium silicate of 1.28 N and concentrated solutions of strong acids, namely hydrochloric and sulfuric. The gels were allowed to set at three different temperatures: 0° C., 25° C., and 38.2° C. The log time of set was found to vary linearly with the pH over the range studied which was from a pH of 1 to that of -.5. The lower range of pH was limited by the apparatus. The quinhydrone electrode gives apparently unreliable results for a pH lower than -.5. The heat of activation of these gels was calculated and found to be 11,000 cal./g.mol for hydrochloric acid gels, and 9,000 cal.g.mol for sulfuric acid gels. A pH drift was noted, which became more apparent as the solution became less acid.

BIBLIOGRAPHY

1. Ostwald, W. and Fischer, M.H. - An Introduction of Theoretical and Applied Colloid Chemistry, p. 102
2. Hurd and Swanker - J. Am. Chem. Soc. 55, 2607 (1933)
3. Proctor and Robertson - Chem. Soc. Trans. 105, 813 (1914)
4. Hurd, C. B. - Chem. Reviews 22, 403 (1938)
5. Hurd and Letteron - J. Phys. Chem. 36, 604 (1932)
6. Hurd, C. B. - J. Phys. Chem. 40, 21 (1936)
7. Flemming - Zeit. Physik Chemie 41, 427 (1902)
8. Holmes - J. Phys. Chem. 22, 510 (1918)
9. Ray and Ganguly - J. Phys. Chem. 34, 352 (1930)
10. Fels and Firth - J. Phys. Chem. 29, 241 (1925)
11. Hurd, Raymond and Miller - J. Phys. Chem. 38, 663 (1934)
12. Hanks and Weinstraub - J. Phys. Chem. 41, 583 (1937)
13. Hurd, Frederick and Raynes - J. Phys. Chem. 42, 85 (1938)
14. Batchelor - J. Phys. Chem. 42, 575 (1938)
15. Hurd and Griffeth - J. Phys. Chem. 39, 1155 (1935)
16. Daniels, Matthews and Williams - Experimental Physical Chemistry
17. Malone - Thesis, Union College (1933)
18. Frederick, Thesis, Union College (1933)