

DETERMINATION OF HEAT OF REACTION
IN THE
SETTING PROCESS FOR SILICIC ACID GELS

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SETTING PROCESS FOR SILICIC ACID GELS

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

The underlying purpose of this work was to gain a further insight into the mechanism of the setting of silicic acid gels. The primary purpose was to determine the heat of reaction during the setting process for the gels.

Previous investigators have sought to determine the structure of gels by investigating the effect of certain factors as: temperature, concentration of both acid and silica, pH, and addition of soluble organic and inorganic materials on the time of set. Certain properties of the silicic acid gels have a bearing on the theories for the mechanism of the setting process. These properties are the elasticity of the gel, the molecular weight, thixotropy, syneresis, the x-ray analysis, and the electrical conductivity. It is the author's opinion that any information concerning thermal changes during the setting of the gel would be of aid in favoring one theory over the others, and would perhaps offer experimental proof of this theory.

HISTORICAL

Early workers in the field of colloidal phenomena were led to the study of various compounds which were prepared in the form of a suspension of particles of colloidal dimensions, and gradually were set to a rigid elastic solid, which was called a gel. Although early workers were aware of these properties, there was little of an investigative nature known about silicic acid gels until the middle of the nineteenth century.

Berzelius⁽¹⁾ however, discussed silicic acid gels in 1820. Since that time much work has been done covering the various factors of these gels until at present this work is one of the important phases of colloidal chemistry.

A great deal of work has been done to determine the nature of the mechanism of the setting process, and many different theories with varied modifications have been proposed. They may all be classified into three general theories. They are: (1) the emulsion theory; (2) the cellular theory; and (3) the fibrillar or micellar theory.

The emulsion theory is credited to Ostwald⁽²⁾ This theory assumes that the gel consists of a liquid-liquid system of an emulsoid structure. The weight of opinion is decidedly against this theory due to its inability to conform in the consideration of viscosity and elasticity.

An emulsion has a high viscosity, but it does possess the ability to flow, while the silicic acid gels show very little tendency to flow if the silica content is great enough.

The cellular theory is credited to Butschli,⁽³⁾ who in 1898 proposed a theory of gel formation in which a type of honey-comb mesh was built up of microscopic cells formed by the liquid being held in droplet form in a cellular structure by the solid phase. This cellular structure does not offer a satisfactory explanation for syneresis effects in silicic acid gels. According to this theory, it seems reasonable to expect an increase in electrical resistance yet with silicic acid gels, there is no noticeable change in electrical conductivity.

The third theory is called the fibrillar or micellar theory. This theory is credited to Nageli.⁽⁴⁾ It assumes a solid-liquid phase, both of which are continuous. The solid material forms a fibrous structure, which contains the liquid in its pores. This is the most favored theory among colloidal chemists at the present time. Hurd⁽⁵⁾ proposed a theory to explain the condensation of silicic acid to form a poly-silicic acid structure of long thread-like chains. These chains spread out on polymerization to form a structure similar to that of a cobweb. Hurd based this theory on four assumptions: (1) that a monosilicic acid is formed in the first step of the process;

(2) that the acid or hydroxide is amphoteric, giving either hydrogen or hydroxyl ions; (3) that condensation occurs when the positive or negative ions containing the silicon come into contact; (4) that the water remains combined in the structure.

Experimental fact seems to confirm all of these assumptions. Work by Treadwell and Konig⁽⁶⁾ has shown the amphoteric nature of silicic acid.

The condensation takes place by the splitting out of water from two molecules of silicic acid.

Any thermal effect if measurable, would have been spread out over the whole time of set, and no sudden evolution of heat should be expected as the gel set, for the condensation has been occurring steadily since the monosilicic acid was formed in the first reaction.

Substantiation of this has been given by Lipatow⁽⁷⁾ who claims that a gelatin gel evolves heat upon setting. Treadwell and Wieland⁽⁸⁾ state that very little thermal change occurs as the gel sets.

The ionization of the silicic acids during the condensation could probably nullify the heat produced by the condensation process.

Thiessen and Koerner⁽⁹⁾ speak of heat evolved during gelation as a heat of hydration of the silicic acid.

EXPERIMENTAL PROCEDURE AND DATA

In order to measure any thermal changes which might occur as the gel set, the silicic acid sols were allowed to set in a vacuum jacketed calorimeter and the temperature of the gel mixture was measured by means of a Beckmann thermometer. The Beckmann gave temperature readings to a thousandth of a degree with an accuracy of $\pm .001^{\circ}\text{C}$. The arrangement consisted of a Dewar flask closed by means of a rubber stopper through which the Beckmann thermometer was placed. The whole unit was placed in a thermostated water bath so as to keep the heat loss through conduction down to a constant factor. The thermostat was electrically heated and stirred by an electric motor stirrer. The temperature was controlled by means of a mercury thyatron unit.

In the preparation of the silicic acid gel mixtures, solutions of 1.25 normal sodium silicate and of 2 normal acetic acid were used. The "E" brand sodium silicate of the Philadelphia Quartz Company was diluted 1:3.2 with freshly distilled water. The sodium silicate solution was standardized by titrating with standard sulfuric acid using methyl orange as the indicator. The acetic acid was titrated with sodium hydroxide using phenolphthalein as the indicator. The acetic acid was 2.011 N; the sodium silicate was 1.240 N in sodium hydroxide equivalent.

The thermostat was set at 25.0° and the solutions were thermostated for at least twenty minutes in all cases. Acetic acid and water were placed in one beaker and twenty-five milliliters of sodium silicate in another. The relative amount of acetic acid and water was changed to secure gels with various times of set but the total volume was fifty-five milliliters giving a total of eighty milliliters of silicic acid. Immediately after mixing the solution was placed in the Dewar flask and it was sealed with the stopper containing the Beckmann thermometer. The Beckmann had previously been placed in the thermostat so that it was at the same temperature of the solutions upon mixing.

An immediate effect was a sharp rise in temperature due to the heat of reaction of the acetic acid and the hydroxide equivalent of the sodium silicate. This was followed by a normal cooling curve for the solution. Theoretically if the Dewar flask were a perfect insulator there would be no thermal loss. This is a practical impossibility for several factors come into account which allow for heat loss. The most important of these is heat loss through the stopper. Consequently we must try to control the temperature gradient between the gel temperature and the room temperature.

An immediate observation was that if there were any thermal effects as the gel set it was spread out over the

whole time for there was no sudden evolution of heat at any time during setting process. These first observations were for gels with the time of set varying from two minutes to three hours.

Cooling curves were obtained for a gel setting in twenty minutes and for one setting in one hundred and ninety minutes. Since the thermal effect was assumed to be spread out over the whole period of gelation, there should be a difference in the two curves of temperature versus time during the first twenty minutes, that is while the one gel set, for if there were a heat of reaction during the setting process, it would manifest itself during the twenty minutes. In the other gel the heat would be distributed over one hundred and ninety minutes and therefore would produce a smaller deviation from a normal cooling curve.

Great difficulty was encountered in trying to reproduce the same temperature in different runs for if the initial or final temperatures were not the same in the case of both gels, there would be cooling curves of different slopes and consequently little could be inferred from these results.

The initial temperature was entirely dependent upon the temperature of the thermostated solutions and upon the heat of neutralization of the acetic acid and the hydroxide equivalent of the sodium silicate. Since this

heat of neutralization differed in the case of the twenty minute gel and the one hundred and ninety minute gel due to the different concentrations of acid, it was practically an impossibility to reproduce the initial temperature better than to within .05 of a degree. The temperature rise due to neutralization was from 1.5 to 1.7 degrees.

In the cooling of the gel mixture, it is quite probable that the heat was lost through the rubber stopper connection. Variations in room temperature during runs produced a change in the cooling curves and it was imperative to control the room temperature as much as possible.

One must realize what difficulties there are in attempting to reproduce similar conditions in two runs, for a difference of .1° in room temperature would cause a decided change in successive cooling curves where the temperature is being measured in thousandths of a degree.

Although many runs were made throughout the year, very few were controlled well enough to gain reliable data concerning the thermal changes during setting.

Table 1 shows the results of one of several runs similar in nature.

TABLE I

Gel A

25 milliliters sodium silicate
17 milliliters acetic acid
38 milliliters water

t = 20 minutes at 20.8° C

Run A

Bath temperature = 1.811°
Room temperature = 3.217°

Gel B

25 milliliters sodium silicate
30 milliliters acetic acid
25 milliliters water

t = 120 minutes at 20.8° C

Run B

Bath temperature = 1.842°
Room temperature = 3.411°

<u>Time (Min.)</u>	<u>Temp.</u>
0	1.811
1	.800
2	.721
3	.717
4	.719
5	.122
6	.729
7	.737
8	.750
9	.763
10	.777
11	.791
12	.811
13	.828
14	.842
15	.857
16	.857
17	.888
18	.904
19	.917
20	.928
21	.939
22	.949
23	.958
24	.967
25	.975
27	.986
29	.997
31	1.008
33	1.019
35	1.027

<u>Time (Min.)</u>	<u>Temp.</u>
0	1.842
1	.813
2	.730
3	.724
4	.722
5	.732
6	.739
7	.749
8	.757
9	.769
10	.784
11	.802
12	.819
13	.838
14	.852
15	.865
16	.883
17	.896
18	.912
19	.925
20	.937
21	.949
22	.959
23	.970
24	.978
25	.984
26	.994
28	1.004
30	1.014
32	1.022
34	1.032

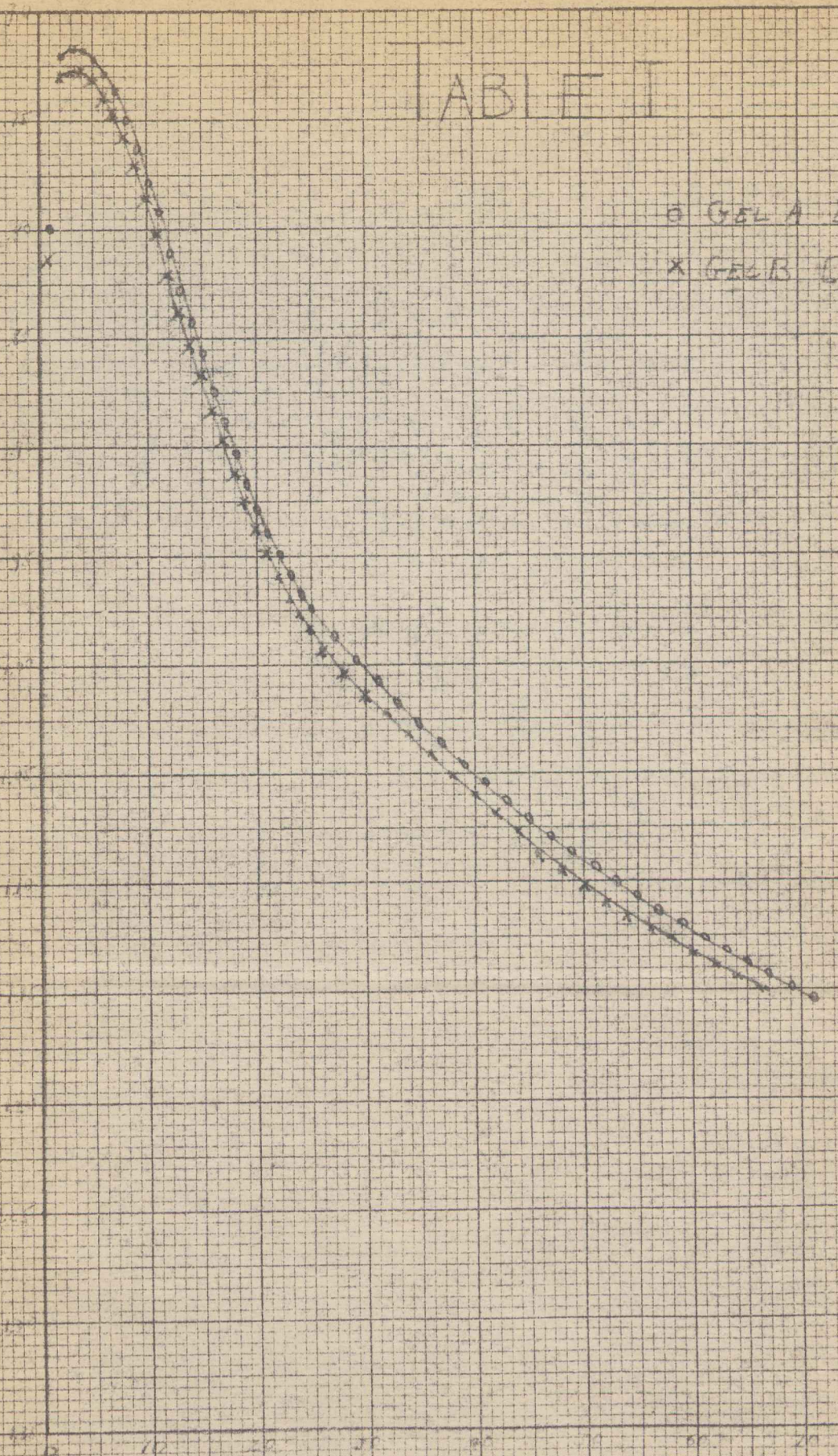
TABLE I Continued

<u>Run A</u>		<u>Run B</u>	
<u>Time (Min.)</u>	<u>Temp.</u>	<u>Time (Min.)</u>	<u>Temp.</u>
37	1.035	36	1.041
39	1.045	38	1.051
41	1.054	40	1.060
43	1.063	42	1.067
45	1.072	44	1.076
47	1.080	46	1.086
49	1.086	48	1.095
51	1.093	50	1.102
53	1.110	52	1.110
55	1.116	54	1.117
57	1.122	56	1.121
59	1.126	58	1.126
61	1.129	60	1.132
63	1.132	62	1.139
65	1.137	64	1.144
67	1.143	66	1.149
69	1.149		
71	1.154		

TABLE I

TEMP. (BECKMAN READINGS)

o GEL A (20 MIN)
x GEL B (190 MIN)



TIME (MIN)

A different approach was also attempted in determining the heat of reaction. The acetic acid and the sodium silicate and water solution were cooled to almost zero degrees, and after mixing were placed in a small tube immersed in a water bath at constant temperature. For all runs this was kept at 30.0°C . A thermometer giving temperature readings accurately to one-tenth of a degree was inserted through a stopper. Immediately after mixing and placing the gel mixture in the 30° bath, the temperature of the solution rose sharply and gradually tapered off, asymptotically approaching a temperature slightly less than thirty degrees. Temperature readings were taken versus time for a period even after the gel set. For this set of runs, a gel was used which set in three and one-half minutes at 20.3°C .

The solidified gel was then cooled to lower temperature slightly above zero degrees, and it was placed in the 30° bath where values of temperature versus time were observed. If there were any thermal effects during the setting process, there would be a difference in the two curves.

Due to the inability to start both the liquid gel solution and the recooled solidified gel at the same temperature, it was realized that any thermal effects could be determined by a variation in the difference of displacement of the two curves at various intervals of time.

TABLE II

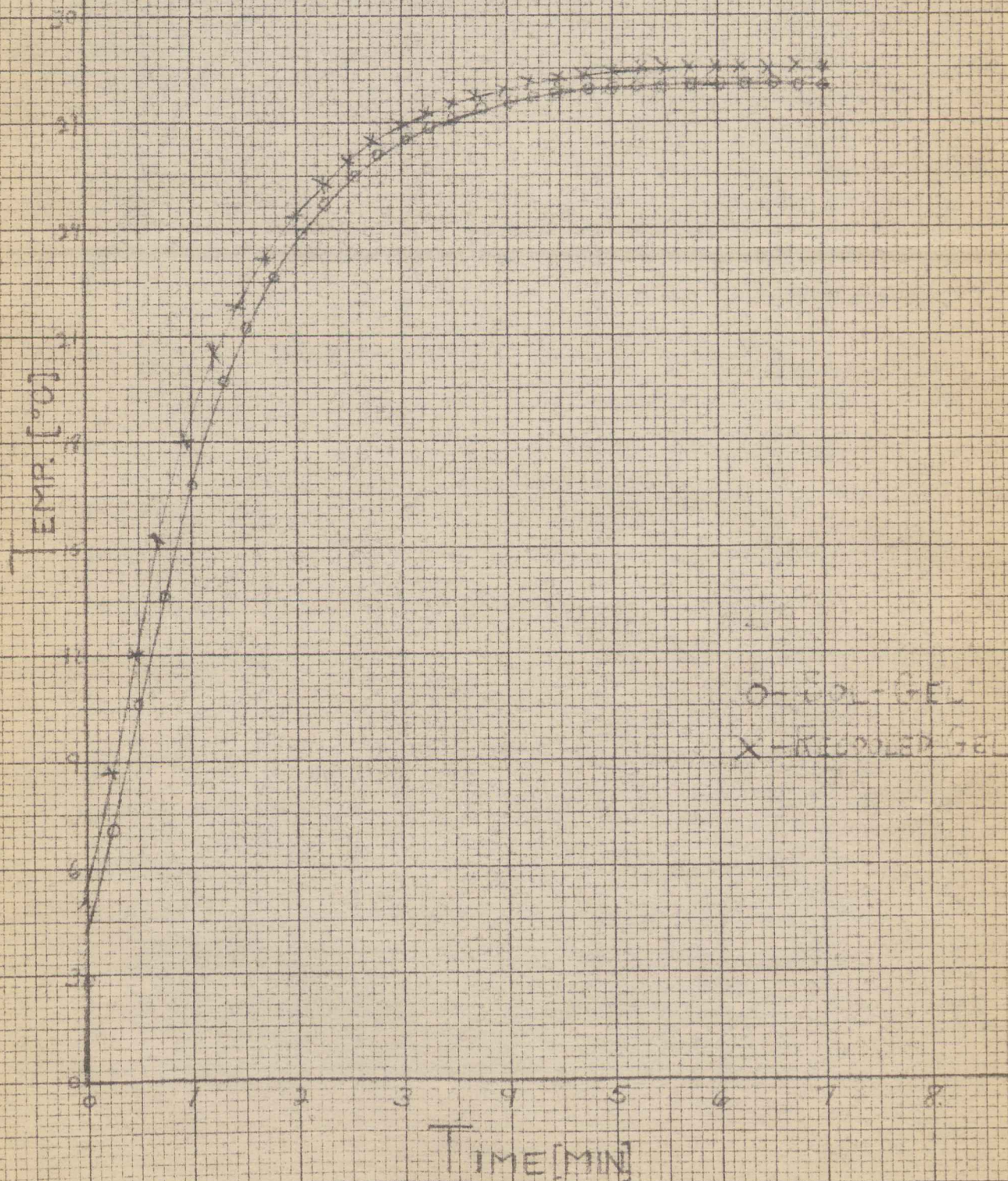
25 milliliters sodium silicate
15 milliliters acetic acid
40 milliliters water

Time of set = 3 minutes 35 seconds at 20.3° C.

<u>Time (Sec.)</u>	<u>Temperature (°C)</u>	
	<u>A</u>	<u>B</u>
0	2.7	4.9
15	7.0	8.6
30	11.5	11.9
45	13.6	15.2
60	10.8	17.9
75	19.7	20.3
90	21.1	21.7
105	22.5	23.1
120	23.8	24.2
135	24.7	25.3
150	25.5	25.8
165	26.1	26.4
180	26.5	26.8
195	26.9	27.1
210	27.2	27.5
225	27.4	27.7
240	27.6	27.9
255	27.7	28.0
270	27.8	28.1
285	27.9	28.2
300	28.0	28.3
315	28.1	28.4
330	28.1	28.4
345	28.1	28.4
360	28.2	28.5
375	28.2	28.5
390	28.2	28.5
405	28.2	28.5
420	28.2	28.5

A - sol-gel mixture
B - recooled gel

TABLE II



DISCUSSION OF RESULTS

It seems quite evident from the results obtained that if there is any thermal effect during the setting of a silicic acid gel, it is not discernible by the means or apparatus used.

Referring to Table I, one can roughly calculate the quantity of heat necessary to produce a deviation in the shape of one of the two curves. Since each small unit on the vertical scale is equivalent to $.005^{\circ}$, a temperature change of about this magnitude would be necessary to produce the necessary deviation. Since the Beckmann thermometer gives readings of temperature to one-one thousandth of a degree with a fair degree of accuracy, our inability to obtain a value of thermal change is due therefore to the inability to analyze the graphic results rather than to obtaining temperature values.

In order to obtain enough heat to show a perceptible variation in the cooling curves at a point, there must be about four calories of heat per gel mixture or one hundred and twenty-four calories per equivalent of silicic acid formed.

Even if the heat were obtained, it would as the curves indicate be evolved not during a small period of time, but throughout the whole setting process. The necessary heat would therefore have to be of a far greater

magnitude than this to obtain a general deviation of the shape of the two curves in Figure 1.

In Figure 2, the same reasoning also applies, but in this case the temperature fluctuation would be of too small a magnitude to be observed by this means. This curve does show, however, that if there is any heat evolved or absorbed, it is of a very small magnitude and it is spread out during the whole time of set.

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