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Transmission and scattering of light by silicic acid gel-forming mixtures

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TRANSMISSION AND SCATTERING OF LIGHT

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SILICIC ACID GEL-FORMING MIXTURES

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TRANSMISSION AND SCATTERING OF LIGHT

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SILICIC ACID GEL-FORMING MIXTURES

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 Warren De Sorbo

Approved by Charles B. Hurd

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INTRODUCTION

In this investigation the transmission and scattering of light by the silicic acid gel forming mixtures have been studied during the process of gel formation in an effort to extend the work already done in this laboratory on the structure of silicic acid gels.

The intensity of the transmitted and scattered light has been measured in terms of galvanometer deflections using a photoelectric tube circuit. An attempt has been made to utilize these results in elucidating the changes in size and number of the colloidal particles which take place in gel formation.

HISTORICAL

The first mathematical expression for the intensity of light scattered by a colloidal solution at right angles to the incident beam was derived by Lord Rayleigh in 1871.

$$I = r \left(\frac{v^2}{d^2 \lambda^4} \right)$$

where I is the intensity of light scattered sidewise, v is the volume of the obstructing particle, d the distance between observer and particle, and λ the wave length of scattered light. An expression for the intensity of the transmitted beam, however, had been worked out as early as the middle of the 18th century by J. H. Lambert, and known as Lambert's law of absorption,

$$I = I_0 e^{-\epsilon t}$$

Comparatively little work has been done on the study of optical properties of silicic acid gel forming mixtures. Various investigators carrying on such investigations with various colloidal solutions have shown the importance of the study of optical properties as they help to reveal their structure without disturbing them.

Mie¹ has studied the absorption and scattering of light by colloidal solutions containing particles of various dimensions and has come to the conclusion that at constant concentration the intensity of the diffused light increases with the size of the particles and is proportional to their volume.

Krishnamurti² in studying the scattering of light by agar sols and gels has found that the micelles in the gels are much bigger than those in the sols. He has also studied the scattering and polarizing effect of light with aging sols, and has obtained an equation of the intensity curve for the scattered light³

$$I = C + \frac{K}{1 + b e^{at}}$$

Prasad and Hattiangadi⁴ have been able to determine a time of set by plotting the intensity of scattered light against time. This optical method of determining time of set will be referred to later.

Prasad, Mehta and Desai⁵ have measured the extinction coefficients of various gel-forming mixtures of silicic acid by means of Hilger-Nutting spectrophotometer.

In checking Von Smoluchowski's theory of flocculation, Freundlich and Ishizaka⁶ found the change in the number of particles indirectly; it was derived from such physical properties of the sol as the change in viscosity or the change in light absorption, which were thought to be a direct measure of the coagulation process.

APPARATUS

The photoelectric tubes used were the argon-filled tubes with cesium oxide cathode (PJ-23, G.E. model). A General Electric A.C. Sodium Vapor Lamp (60 watts) was used as a source⁷. The energy distribution in such a lamp lies

mostly in the sodium region, 5896 and 5890 \AA . The light source for such a study as this, and also where photo cells are used, should have a narrow band of the spectrum as possible. Day⁸ in making a spectrophotometric study of the transmission spectra in the visible range of wave lengths found that during gel formation the percent of light transmitted decreased with a decrease in wave length. The galvanometer used was a Leeds and Northrup type of wall galvanometer, no. 78638.

The gels were kept at a constant temperature (25° C.) by a water bath controlled by a De Khotinsky Thermoregulator and a knife type of immersion heater.

Quinhydrone potentiometer was used to measure the pH of the acid gels. The pH of the alkaline gels was not determined, but their alkalinity tested by means of litmus paper.

The rectangular glass cells which served as containers for the gel forming mixtures measured 8 x 8 x 3 cm.

EXPERIMENTAL

The gels were prepared by the reaction between acetic acid and sodium silicate. In a few cases sulfuric acid was used. The sodium silicate was the "E" Brand produced by the Philadelphia Quartz Company. The $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of this silicate is 1:3.19 by weight. This silicate upon dilution was titrated against standard sulfuric acid using methyl orange as an indicator. The apparent normality of the silicate solution used in all the runs was 1.328. Also the normality of the acetic acid used was 4.025 N.

In preparing the gel forming mixtures 150 c.c. of the silicate solution were always mixed with 150 c.c. of acetic acid solution containing varying

amounts of 4.025 N acetic acid. These were always mixed in the same manner in 400 c.c. beakers. A portion of this was placed in the rectangular cell, and the remainder was used to determine the pH and the time of set by the rod method.

In this investigation portions of the light scattered and transmitted were obtained simultaneously by using two photoelectric tubes of the same type.

The circuit is shown in the diagram on page 5.

A beam of light from S passes through a cell B containing water to remove most of the heat rays. The beam then passes through the cell A containing the gel-forming mixture. The cells P measure the transmitted and scattered light in terms of galvanometer deflections. The deflection of the galvanometer was measured on a scale of the wall galvanometer.

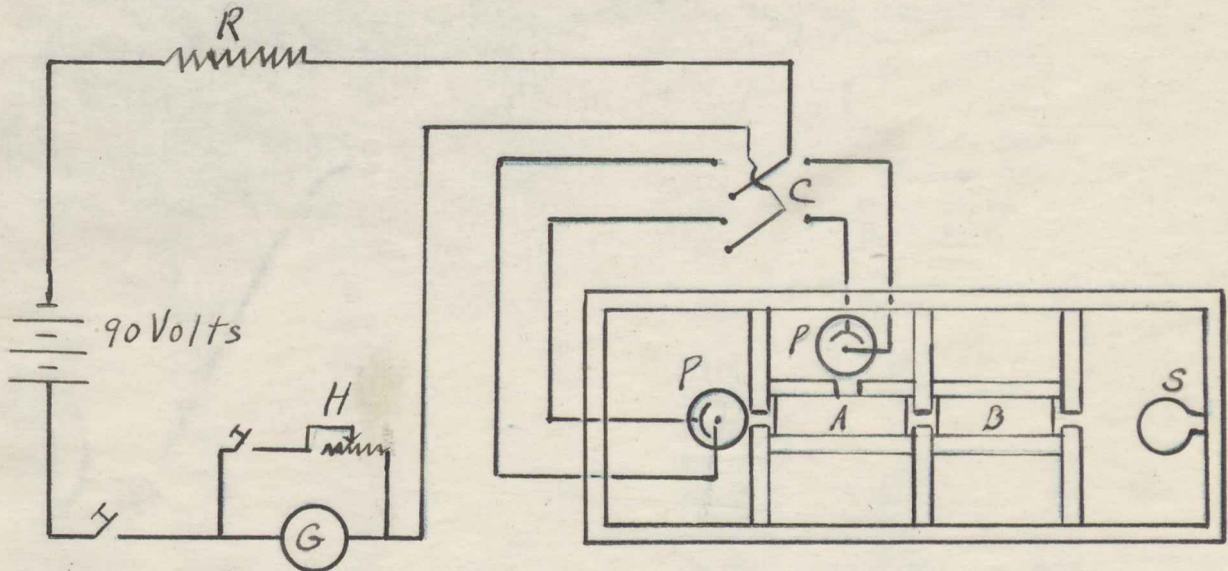
The deflection of the galvanometer due to each cell were measured at convenient intervals of time. The results obtained are given in Tables I and II in which the symbols used are the following:

D_t = deflection at time t in cm.

D_1 = deflection at initial time

T = time after mixing the solutions in minutes

To insure against any changes in the intensity of light due to variations in line voltage and also those due to rise in temperature of the sodium lab-arc the circuit was standardized several times during a run by means of resistance H and a jar containing a solution made up half of silicate and half water; thus D_1 is kept constant and D_t , the deflection due to the solution, is measured against the true initial galvanometer deflection. This would also take care of any variations in the photo tubes.



S- Sodium Lab-Arc

P- Photoelectric Cells

A- Cell Containing Mixture

B- Cell Containing Water

C-Double Pole Double Throw Switch

TABLE I - Galvanometer Deflections Due to the Transmitted Light

(150 c.c. Sodium Silicate, 1.328 N, mixed with 150 c.c. of acetic acid solution containing varying amounts of 4.025 N acetic acid.)

150 c.c. HAc 0 c.c. H ₂ O PH 4.21 D ₁ 29.0			125 c.c. HAc 25 c.c. H ₂ O PH 4.50 D ₁ 24.8		
D _t	D ₁ -D _t	I	D _t	D ₁ -D _t	I
29.0	0	-	24.8	0	-
29.0	0	14	24.8	0	4
29.0	0	16	24.8	0	9
28.8	.2	66	24.4	.4	42
28.7	.3	74	21.7	3.1	80
27.9	1.4	81	17.7	7.1	116
26.8	2.2	96	15.3	9.5	140
23.6	5.4	120	13.0	11.8	169
18.3	10.7	180	11.8	13.3	197
16.5	12.5	206	10.8	14.0	250
15.5	13.5	248	10.8	14.0	275
15.5	13.5	271			

100 c.c. HAc 50 c.c. H ₂ O PH 5.06 D ₁ 22.9			75 c.c. HAc 75 c.c. H ₂ O PH 5.30 D ₁ 24.0		
D _t	D ₁ -D _t	I	D _t	D ₁ -D _t	I
22.9	0	-	24.0	0	-
22.9	0	2	24.0	0	5
22.5	.4	14	22.7	1.3	18
22.2	.7	26	21.9	2.1	25
21.2	1.7	42	17.6	6.4	38
19.9	3.0	50	11.3	12.7	68
16.8	6.1	68	9.3	14.7	98
14.8	8.1	94	8.1	15.9	123
13.0	9.9	117	7.4	16.6	151
11.5	11.4	126	7.3	16.7	175
10.0	12.9	144			
9.6	13.5	159			
7.4	15.5	230			
7.6	15.3	245			

Table I - Continued

70 c.c. HAc 80 c.c. H ₂ O PH 5.42 D ₁ 25.1			55 c.c. HAc 95 c.c. H ₂ O PH 5.60 D ₁ 20.7		
D _t	D ₁ -D _t	T	D _t	D ₁ -D _t	T
25.1	0	-	20.7	0	-
25.1	0	13	19.3	1.4	5
23.0	2.1	21	18.3	2.4	7
18.2	6.9	28	16.1	4.6	8
16.6	8.5	36	13.4	7.3	10.5
11.3	13.8	58	11.1	9.6	12.5
10.3	14.8	70	9.7	11.0	14.5
9.6	15.5	87	7.4	13.3	21.5
8.6	16.5	104	5.3	15.4	35.0
7.7	17.4	124	4.4	15.9	52.0
7.4	17.7	193	4.0	16.7	57.5
7.3	17.8	237	2.3	18.4	150.

52 c.c. HAc 98 c.c. H ₂ O PH 5.78 D ₁ 20.0			25 c.c. HAc 125 c.c. H ₂ O PH (alk.) D ₁ 21.0		
D _t	D ₁ -D _t	T	D _t	D ₁ -D _t	T
20.0	0	-	21.0	0	-
18.7	1.3	1'15"	16.5	4.5	.25
17.9	2.1	2'45"	15.1	5.9	.75
14.0	6.0	4'40"	11.8	9.2	1.08
11.3	8.7	6'15"	4.4	16.6	1.75
8.95	12.95	11'20"	.1	20.9	2.33
5.20	14.80	13'30"	.1	20.9	10.0
3.50	16.5	20'			
2.50	17.5	40'			
1.20	18.8	80'			

Table I - Continued

23 c.c. HAc
127 c.c. H₂O
pH (alk.)
D₁ 21.0

D _t	D ₁ -D _t	T
21.0	0	-
18.6	1.6	1'10"
16.1	4.9	2'
12.4	8.6	3'
10.70	10.3	3'30"
4.70	16.3	5'
1.50	19.5	7'
.70	20.3	9'
.45	20.55	11'
.30	20.70	14'
.18	20.82	23'
.15	20.85	41'
.15	20.85	50'

19 c.c. HAc
131 c.c. H₂O
pH (alk.)
D₁ 20.6

D _t	D ₁ -D _t	T
20.6	0	-
20.5	.10	3
20.0	.60	6
17.8	2.80	19.5
12.7	7.90	30
5.8	14.80	42
3.9	16.7	48
2.0	18.6	52
.75	19.85	62
.40	20.20	70
.18	20.42	87
.15	20.45	110
.12	20.47	141
.1	20.50	210

18 c.c. HAc
132 c.c. H₂O
pH (alk.)
D₁ 21.5

D _t	D ₁ -D _t	T
21.5	0	-
19.2	2.2	51
11.4	10.1	70
9.8	11.7	74
5.65	15.85	86
2.30	19.20	101
1.00	20.5	116
.35	21.15	143
.25	21.25	155
.20	21.30	175
.15	21.35	222
.15	21.35	258

17 c.c. HAc
133 c.c. H₂O
pH (alk.)
D₁ 21.0

D _t	D ₁ -D _t	T
21.0	0	-
20.9	.1	5
20.5	.5	21
20.0	1.0	38
19.1	1.9	61
17.3	3.7	73
16.4	4.6	82
12.0	9.0	109
7.9	13.1	128
2.80	18.2	160
.50	20.62	206
.20	20.8	257
.15	20.85	285
.1	20.9	302

Table I - Continued

In the following 150 c.c. of sulfuric acid solution
were mixed with 150 c.c. sodium silicate (1.328 N)

66 c.c. H_2SO_4 (1.635 N)
84 c.c. H_2O
pH (alkaline)

122 c.c. H_2SO_4 (1.635 N)
28 c.c. H_2O
pH 5.41

D_t	$D_1 - D_t$	T
19.8	0	-
19.4	.4	2
18.4	1.4	6
17.5	2.3	9
15.7	4.1	12
14.1	5.7	19
12.3	7.5	24
10.0	9.8	32
6.6	13.2	43.5
4.6	15.2	56
2.2	17.6	82
1.2	18.6	155
.9	18.8	177

D_t	$D_1 - D_t$	T
21.0	0	-
21.0	0	5
20.5	.5	11
20.0	1.0	27
17.8	3.2	37
14.7	6.3	47
13.1	7.9	54
11.65	9.35	58
8.6	12.4	79
5.4	15.6	102
3.8	17.2	150

Table I - Continued

(100 c.c. of Sodium Silicate, 1.328 N, mixed with
50 c.c. of acetic acid solution)

50 c.c. HAc (app. 6 N)

no H₂O

PH 4.56

D₁ 27.5

D _t	D ₁ -D _t	I
27.5	0	-
27.3	.2	30
26.2	1.3	46
25.1	2.4	53
23.7	3.8	63
20.0	7.5	78
19.2	8.3	95
17.6	9.9	105
16.3	11.2	126
15.1	12.4	170
14.5	13.0	192
13.6	13.9	231

40 c.c. HAc (4 N)

10 c.c. H₂O

PH 5.51

D₁ 25.0

D _t	D ₁ -D _t	I
25.0	0	-
22.6	2.4	6
21.7	3.3	7
10.9	8.1	11
19.0	11.0	18
10.5	14.5	38
10.3	15.2	58
9.3	15.4	93
9.3	15.7	119
8.8	16.2	136

11 c.c. HAc

39 c.c. H₂O

PH (alk.)

D₁ 22.5

D _t	D ₁ -D _t	I
22.5	0	-
20.0	2.5	6
15.0	7.5	11
13.8	8.9	13
6.0	16.5	16
2.1	20.4	20
.3	22.2	26
.12	22.38	34
.12	22.58	48

TABLE II - Galvanometer Deflections Due to the Scattered Light

(150 c.c. Sodium Silicate, 1.328 N, mixed with 150 c.c. of acetic acid solution containing varying amounts of 4.025 N acetic acid.)

150 c.c. HAc no H ₂ O PH 4.21 D ₁ .50			125 c.c. HAc 25 c.c. H ₂ O PH 4.5 D ₁ .38		
D _t	D _t -D ₁	I	D _t	D _t -D ₁	I
.50	0.0	-	.38	0.0	-
.50	0.0	23	.45	.07	41
.52	0.02	40	.75	.27	89
.55	.05	39	1.10	.72	116
.60	.10	70	1.40	1.02	140
.78	.28	97	1.70	1.32	170
1.02	.52	122	1.80	1.42	198
1.30	.80	149			
1.52	1.02	172			
1.65	1.15	202			
1.78	1.28	229			

120 c.c. HAc 30 c.c. H ₂ O PH 4.75 D ₁ .32			110 c.c. HAc 40 c.c. H ₂ O PH 4.90 D ₁ .45		
D _t	D _t -D ₁	I	D _t	D _t -D ₁	I
.32	0	-	.45	0	-
.32	0	15	.45	0	15
.35	.03	24	.48	.08	21
.37	.05	40	.61	.16	48
.45	.13	45	.80	.35	65
.51	.19	63	1.52	1.07	110
.70	.38	78	1.90	1.45	139
1.00	.68	98	2.18	1.73	176
1.30	.98	127	2.33	1.88	212
1.50	1.18	145	2.33	1.88	245
1.90	1.58	204			
1.98	1.66	224			

Table II - Continued

100 c.c. HAc
50 c.c. H₂O
pH 5.06
D₁ .40

D _t	D _t -D ₁	I
.40	0	-
.41	.01	14
.70	.30	48
1.30	.90	86
1.55	1.15	106
1.80	1.40	118
2.00	1.60	138
2.24	1.84	160
2.48	2.08	200

85 c.c. HAc
65 c.c. H₂O
pH 5.20
D₁ .35

D _t	D _t -D ₁	I
.35	0	-
.41	.06	7
.47	.12	15
.72	.37	43
1.11	.75	63
1.89	1.54	100
2.35	2.00	135
2.73	2.38	189
2.75	2.40	200
2.75	2.40	230

75 c.c. HAc
75 c.c. H₂O
pH 5.50
D₁ .32

D _t	D _t -D ₁	I
.32	0	-
.52	0	5
.46	.14	19
.70	.38	27
1.12	.80	40
2.00	1.68	70
2.38	2.06	93
2.70	2.38	123
2.85	2.55	150
2.92	2.60	190

70 c.c. HAc
80 c.c. H₂O
pH 5.42
D₁ .32

D _t	D _t -D ₁	I
.40	0	-
.58	.18	7
1.02	.62	29
1.42	1.02	36
2.12	1.72	58
2.60	2.20	88
2.80	2.40	104
3.20	2.80	191
3.25	2.85	296

Table II - Continued

65 c.c. HAc
85 c.c. H₂O
pH 5.50
D₁ .30

D _t	D _t -D ₁	T
.30	0	-
.30	0	3
.52	.22	7
1.0	.70	23
1.45	1.15	31
1.72	1.42	37
2.35	2.05	59
2.60	2.30	73
2.80	2.50	88
3.20	2.90	150
3.20	2.90	160

55 c.c. HAc
95 c.c. H₂O
pH 5.60
D₁ .50

D _t	D _t -D ₁	T
.50	0	-
.70	.20	5.5
.85	.35	7
1.22	.72	9.5
1.32	1.32	13
2.20	1.70	17
2.50	2.00	21
3.12	2.62	36
3.25	2.75	44.5
3.40	2.90	68.5
3.58	3.08	82.5
3.75	3.25	137.5
3.80	3.30	166.0
3.80	3.30	191.0

52 c.c. HAc
98 c.c. H₂O
pH 5.78
D₁ .48

D _t	D _t -D ₁	T
.48	0	-
.58	.10	2'15"
.70	.22	3'10"
1.0	.52	4'15"
1.25	.77	5'
1.48	1.00	6'
1.95	1.47	8'
2.35	1.87	11'
2.75	2.27	16'
3.05	2.57	20'
3.68	3.20	51'
3.98	3.50	68'
4.03	3.55	96'
4.03	3.55	104

50 c.c. HAc
100 c.c. H₂O
pH 6.08
D₁ .40

D _t	D _t -D ₁	T
.40	0	-
.75	.35	2
1.90	1.50	3
2.40	2.00	4
2.70	2.30	5
3.28	2.88	8
3.45	3.05	10
3.55	3.15	12
3.70	3.30	16
3.82	3.42	21
4.28	3.88	32
4.28	3.88	82
4.30	3.90	116

Table II - Continued

25 c.c. HAc
125 c.c. H₂O
pH (alk.)
D₁ .58

D _t	D _t -D ₁	T
.58	0	-
.70	.12	35"
1.10	.42	1'15"
2.12	1.54	1'35"
3.40	2.82	2'
4.70	4.12	2'30"
6.00	5.42	3'
6.82	6.24	3'30"
7.50	6.92	4'
8.18	7.60	5'
8.80	8.22	7'
9.00	8.42	8'
9.28	8.68	12'
9.30	8.72	32'

23 c.c. HAc
127 c.c. H₂O
pH (alk.)
D₁ .40

D _t	D _t -D ₁	T
.40	0	-
.70	.3	1'30"
1.00	.6	2'30"
1.22	2.01	4'30"
3.31	2.91	5'30"
4.90	4.50	7'
5.50	5.10	8.5
7.08	6.68	11'30"
8.24	7.84	16'
9.00	8.60	30'
9.00	8.60	57'

22 c.c. HAc
126 c.c. H₂O
pH (alk.)
D₁ .48

D _t	D _t -D ₁	T
.48	0	-
.51	.03	1'35"
.58	.10	2'10"
.89	.41	3'50"
1.50	1.02	5'30"
1.90	1.42	6'30"
3.30	2.82	8'45"
4.50	4.02	10'25"
5.80	5.32	12'50"
6.80	6.32	16'
7.30	6.82	19'35"
8.13	7.65	24'
8.83	8.35	36'
9.18	8.70	50'

21 c.c. HAc
129 c.c. H₂O
pH (alk.)
D₁ .30

D _t	D _t -D ₁	T
.30	0	-
.48	.18	3'
1.80	1.50	7'30"
2.25	1.95	8'20"
4.80	4.50	12'40"
5.60	5.30	14'20"
6.30	6.00	16'30"
7.50	7.20	24'
7.70	7.40	38'
7.70	7.40	52'
7.92	7.62	95'
8.0	7.70	122'
8.8	8.50	147'

Table II - Continued

20 c.c. HAc
130 c.c. H₂O
pH (alk.)
D₁ .60

D _t	D _t -D ₁	T
.60	0	-
.70	.1	6
.92	.32	11
1.31	.71	15
1.78	1.18	19
2.19	1.59	20
3.45	2.85	25
5.60	5.0	32' 30"
6.95	6.35	37'
8.00	7.40	43' 30"
8.95	8.35	49'
9.32	8.72	55'
9.45	8.85	58'
9.45	8.85	72'

19 c.c. HAc
131 c.c. H₂O
pH (alk.)
D₁ .32

D _t	D _t -D ₁	T
.32	0	-
.32	0	3
.38	.06	7
.50	.18	14
.60	.28	19
1.40	1.08	31
2.90	2.58	41
4.90	4.58	53
5.75	5.43	58
6.60	6.28	66
7.40	7.08	78
8.27	7.95	93
8.77	8.45	113
9.02	8.70	145
9.07	8.75	206

18 c.c. HAc
132 c.c. H₂O
pH (alk.)
D₁ .38

D _t	D _t -D ₁	T
.38	0	-
.40	.02	3
.42	.04	20
.55	.17	31
.72	.34	42
1.02	.64	52
2.30	1.92	71
3.70	3.32	86
5.42	5.04	102
7.30	6.92	128
8.00	7.62	144
8.50	8.12	156
8.80	8.42	176
9.20	8.82	223
9.20	8.82	258

17 c.c. HAc
133 c.c. H₂O
pH (alk.)
D₁ .32

D _t	D _t -D ₁	T
.32	0	-
.32	0	5
.40	.08	15
.45	.13	38
.52	.20	51
.75	.43	73
1.08	.76	90
2.05	1.73	119
3.02	2.70	137
5.25	4.93	175
6.45	6.13	206
7.41	7.09	230
8.20	7.88	257
8.72	8.40	302

Table II - Continued

In the following sulfuric acid solution was used instead of acetic acid solution, with 150 c.c. of 1.328 N sodium silicate.

66 c.c. H_2SO_4 (1.635 N)
84 c.c. H_2O
pH (alk.)
 D_1 .52

E_t	$D_t - D_1$	T
.52	0	-
.58	.06	.3
.61	.09	5
.80	.28	10
1.20	.68	19
1.80	1.28	33
2.50	1.98	45
3.20	2.68	56
4.40	3.88	82
5.10	4.58	159
5.40	4.88	179
6.0	5.48	192
6.4	5.88	259
6.4	5.88	285

122 c.c. H_2SO_4 (1.635 N)
28 c.c. H_2O
pH (5.41)
 D_1 .40

D_t	$D_t - D_1$	T
.40	0	-
.40	0	3
.42	.02	11
.45	.05	18
.60	.20	27
.92	.52	37
1.30	.90	47
1.80	1.40	60
2.10	1.70	74
2.25	1.85	82
2.20	1.80	120
2.28	1.88	122

118 c.c. H_2SO_4
32 c.c. H_2O
pH 6.1
 D_1 4.0

D_t	$D_t - D_1$	T
.40	0	-
.70	.30	-
2.20	1.80	1
2.50	2.1	-
2.90	2.5	2.40
3.00	2.6	3'15"
3.50	3.1	5'
3.80	3.4	15'
3.80	3.4	28'
4.00	3.6	52'
4.10	3.7	65'
4.00	3.6	104'
4.00	3.6	124'

Table II - Continued

In the following the total volume of the gel-forming mixture is 150 c.c. containing 100 c.c. of sodium silicate (1.328 N) and 50 c.c. of acetic acid solution.

50 c.c. (approx. 6 N) HAc

No H₂O

pH 4.56

D₁ .35

40 c.c. HAc (4 N)

10 c.c. H₂O

pH 5.31

D₁ .30

D _t	D _t -D ₁	I	D _t	D _t -D ₁	I
.35	0	-	.30	0	-
.45	.10	5	.45	.15	6
.51	.16	16	1.00	.70	11
.62	.27	24	1.45	1.15	19
.76	.41	33	1.80	1.50	26
1.10	.75	57	2.00	1.70	38
1.25	.90	75	2.10	1.80	47
1.30	.95	96	2.10	1.80	64
1.50	1.15	122	2.35	2.05	99
1.58	1.23	140	2.40	2.10	109
1.62	1.27	162	2.40	2.10	126
1.70	1.35	176			
1.80	1.45	201			
1.80	1.45	211			

11 c.c. HAc

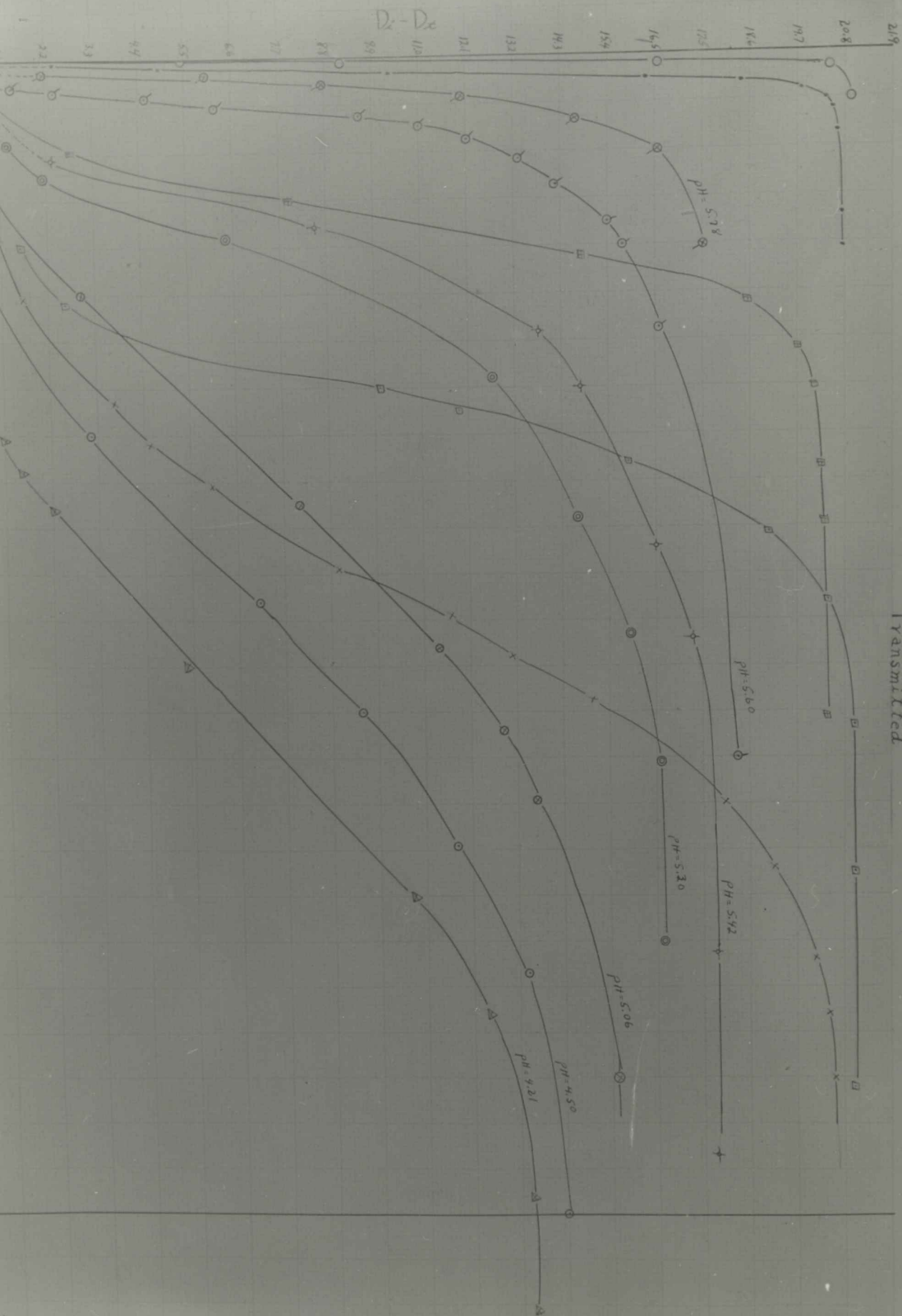
39 c.c. H₂O

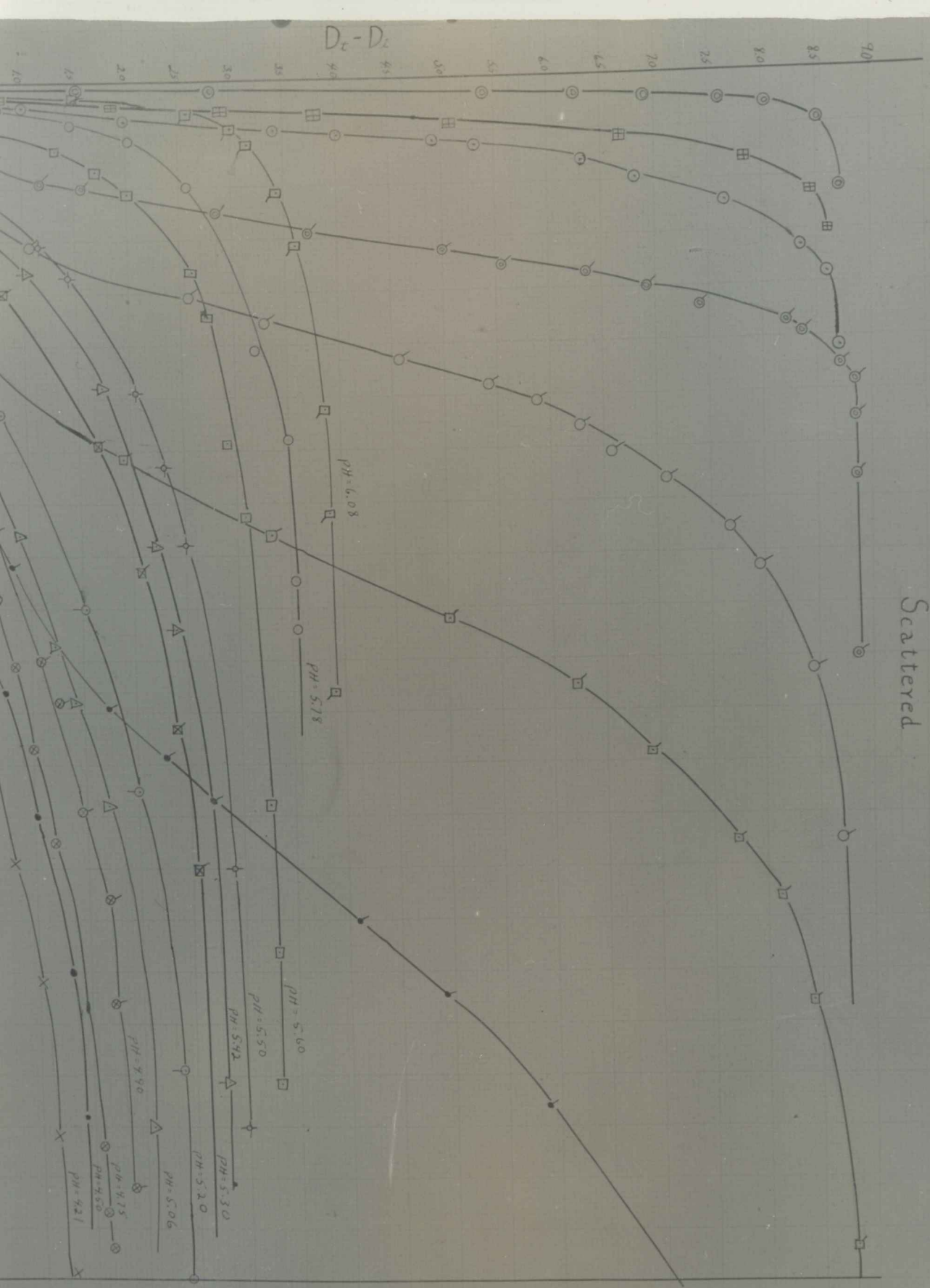
pH (alk.)

D₁ .40

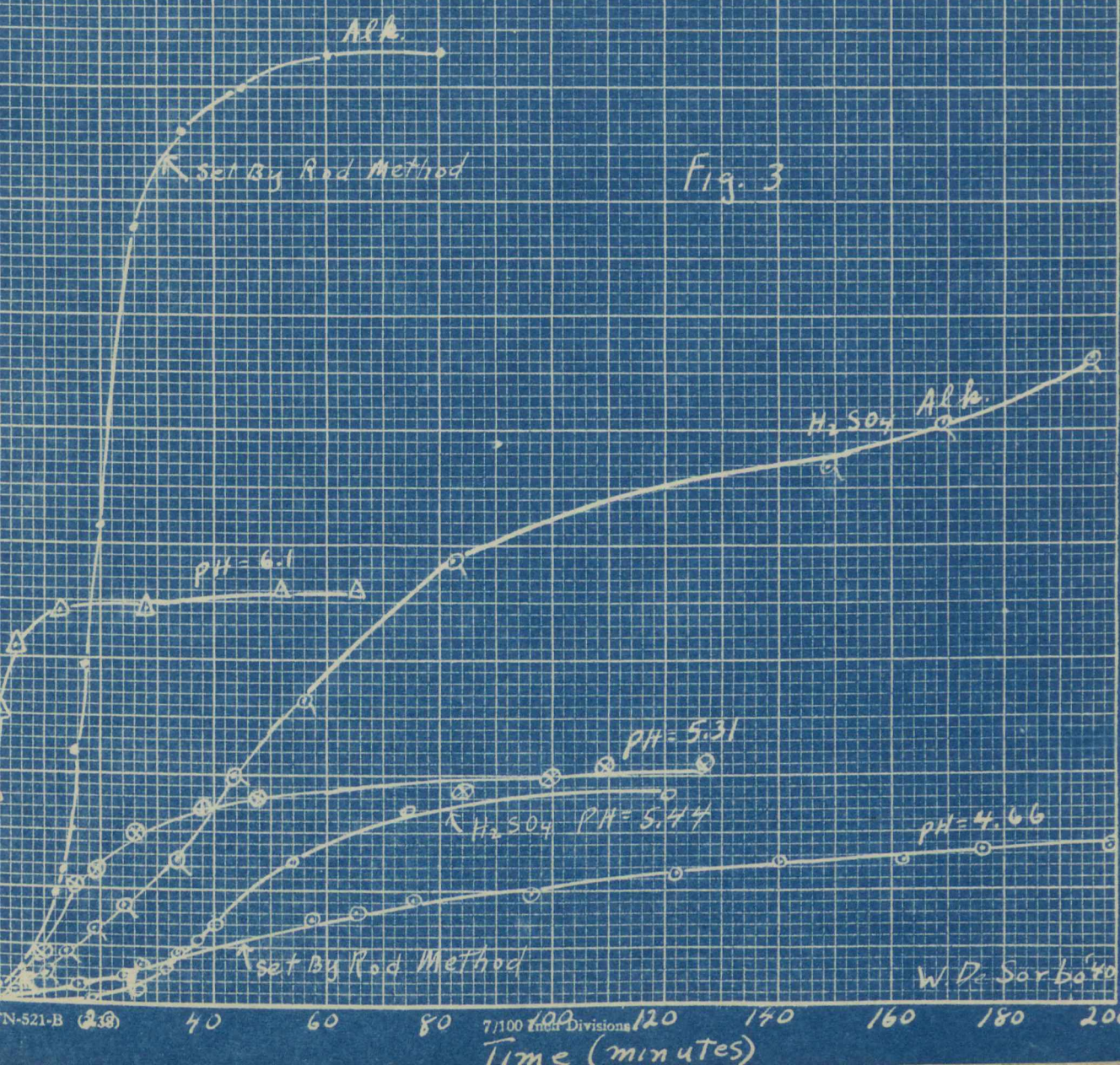
D _t	D _t -D ₁	I
.40	0	-
.52	.12	2
.70	.30	6
1.35	.95	12
2.60	2.20	15
4.55	4.15	20
7.20	6.80	26
8.00	7.60	34
8.40	8.00	45
8.70	8.30	60
8.70	8.30	80

Transmitted

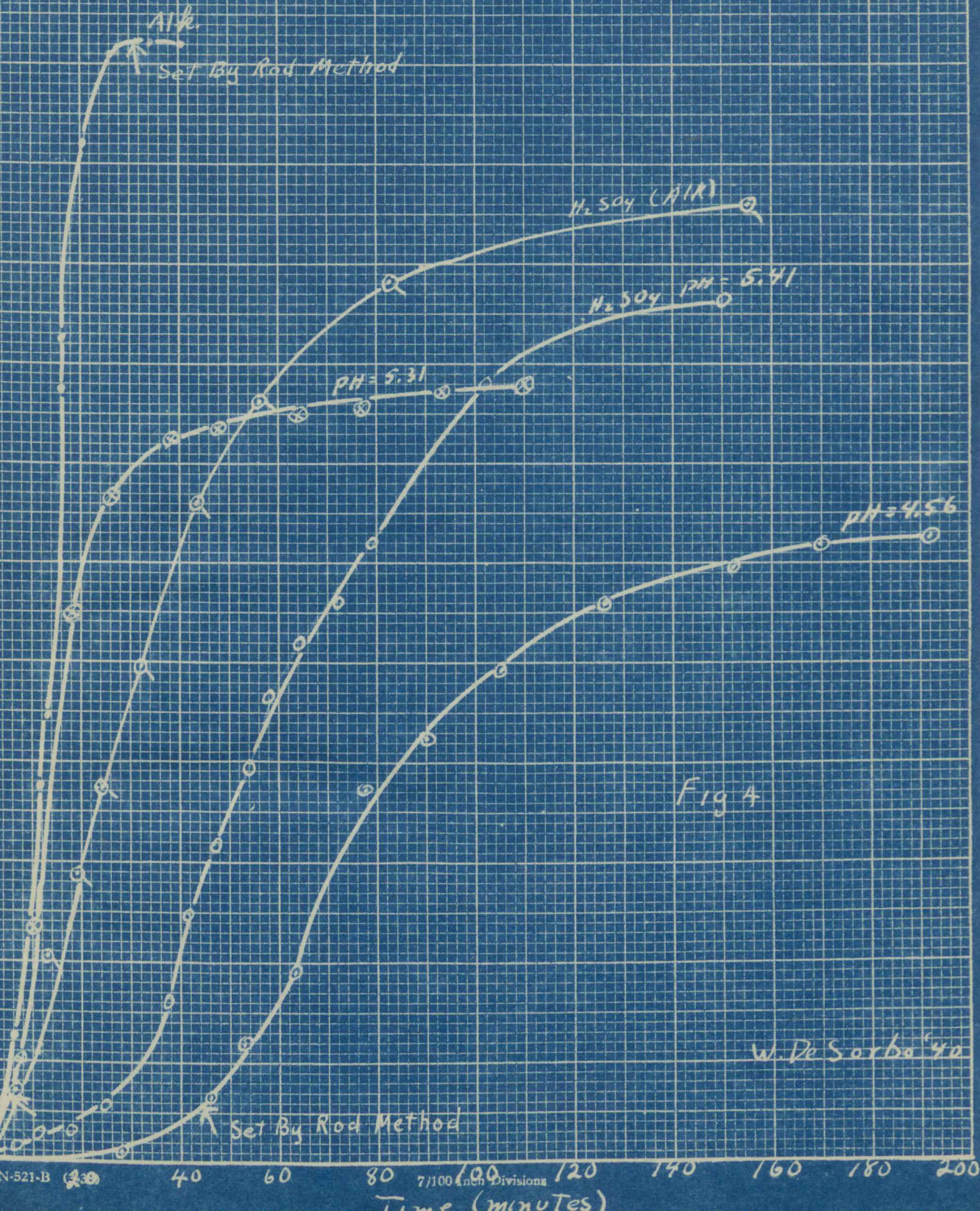




Scattered



Transmitted



It will be seen from the tables that in each case the galvanometer deflection decreases and at first rapidly and then more slowly approaching a constant value. The difference in deflection has been plotted against time giving the typical curves shown in Figures 1-4, inclusive. For scattered light the difference $D_t - D_i$ was plotted against time.

DISCUSSION OF RESULTS

The curves shown in Figures 1-4 inclusive are of sigmoid shape with a point of inflection. Since the deflection is proportional to the intensity it is obvious from the curves that the intensity of the transmitted light decreases and that of the scattered increases with time. These curves, therefore, represent the manner in which the size of particles or micelles of the gel increases during the process of gel formation.

In measuring the scattered light the first few readings indicate little if any change in the intensity of the light scattered. Light is scattered only when the size of the particles is comparable to the wave length of light. If one considers that after the gel forming constituents are mixed, a sol of silicic acid is first formed, then the gel forms from this sol by coagulation. The higher value for the intensity of scattered light in the gel than in the sols shows definitely that the particles in the gel forming mixtures are larger in size than in the sol. Several investigators have shown that silicic acid when first formed seems to be in the form of simple molecules of low molecular weight and this molecular weight has been found to increase rapidly with time reaching a value of over 8000¹². The period during which a gel is in the sol stage can be estimated from the curves. The continuous nature of the curves show that the process of gel formation - monosilicic acid to the final gel structure - is a continuous process.

Scattered

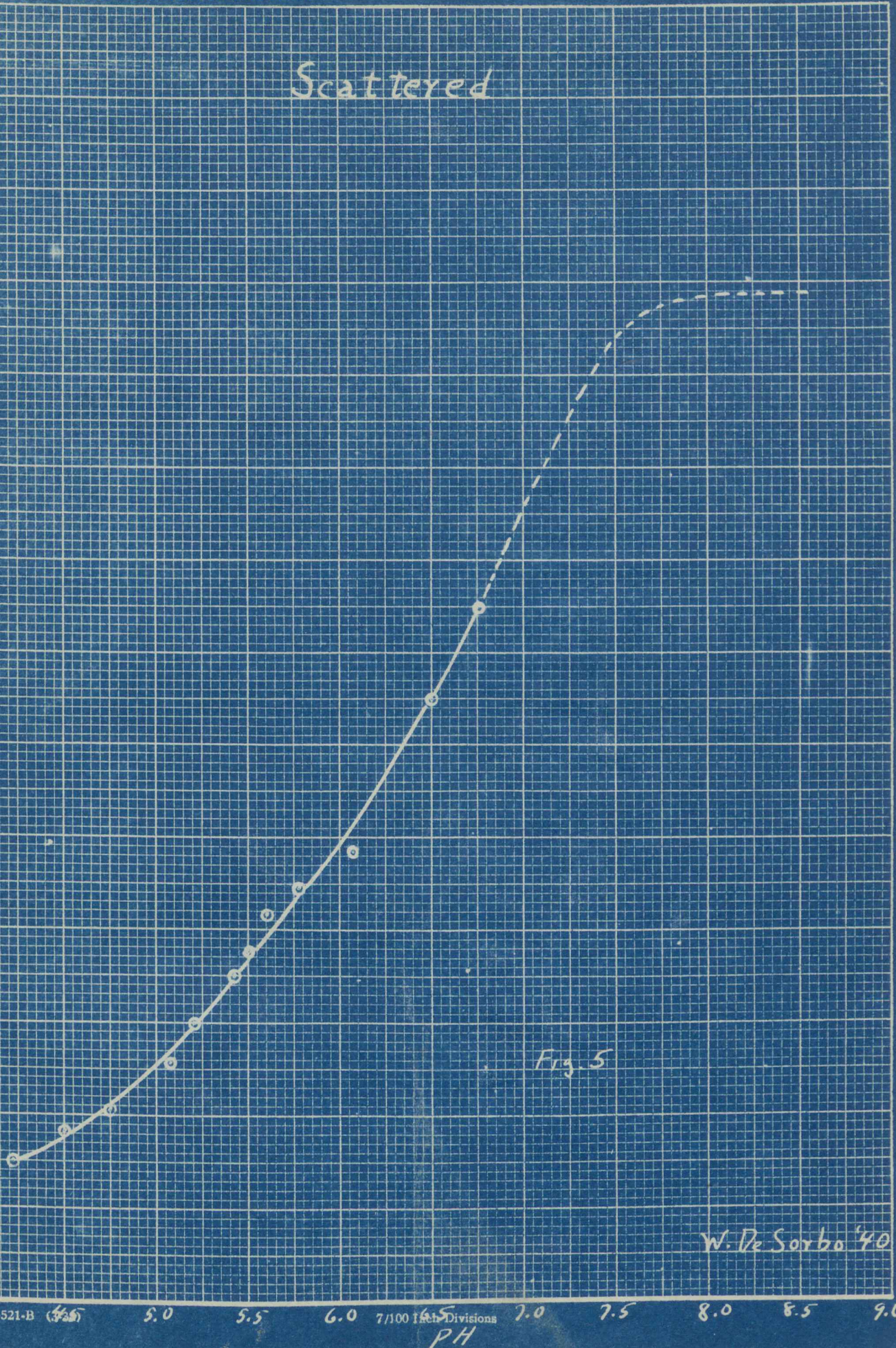


Fig. 5

W. De Sorbo '40

Transmitted

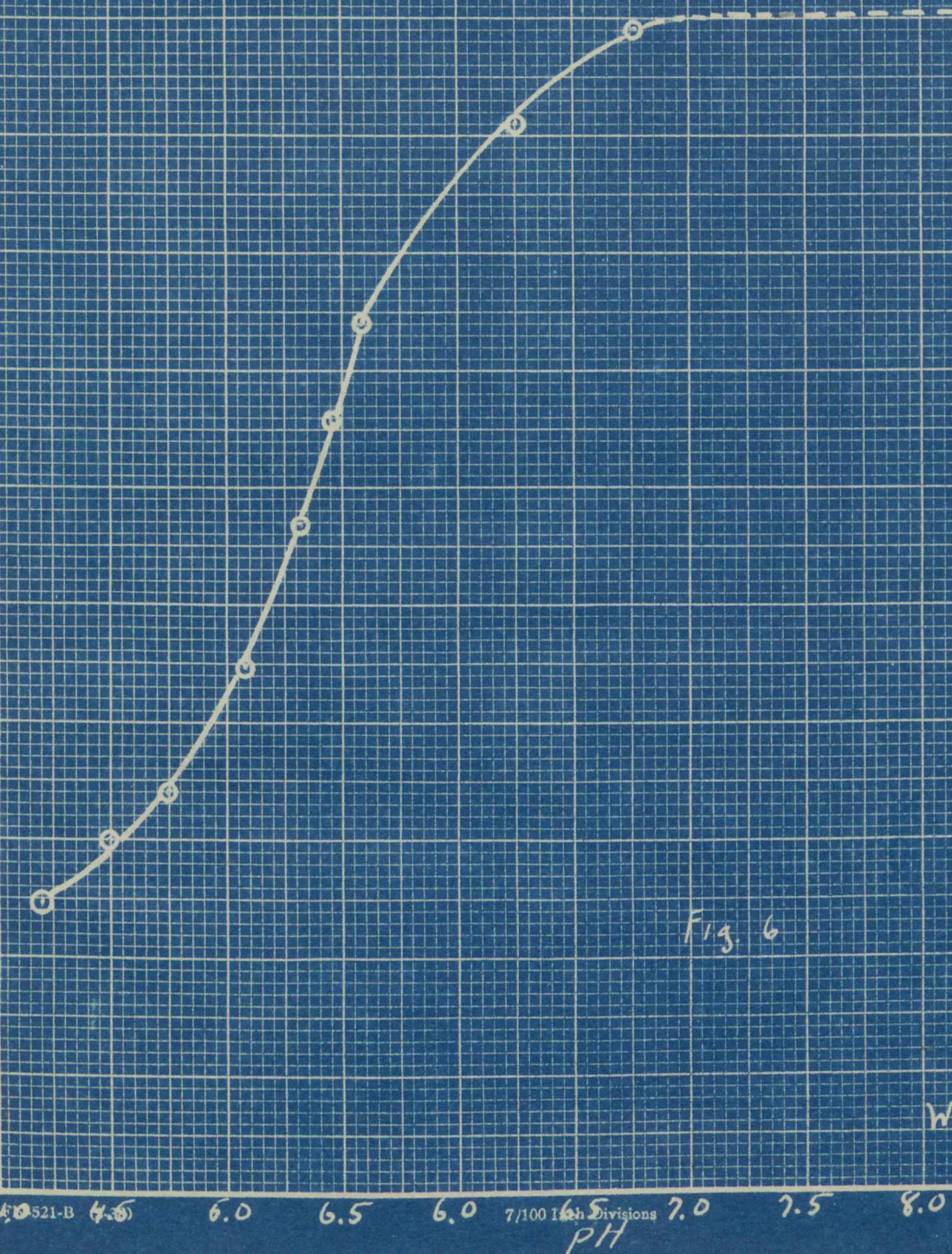


Fig. 6

W. De Sorbo '40

It can be seen from the tables and the curves represented by Figure 5 and 6 that for a constant concentration of silicate the value of the final intensity of the scattered light increases with a decrease in hydrogen ion concentration of the gel. It reaches a maximum with the alkaline gels. This maximum value seems to be constant for all the basic gels. This indicates that regardless of the pH of the alkaline gels, the size of particles which scatter the light must be about the same.

In the case of the transmitted light a similar curve has been obtained. Here the final intensity decreases with a decrease in hydrogen ion concentration, reaching a minimum for the basic gels. This minimum value of intensity corresponds to almost complete extinction of light with the size of the cells used.

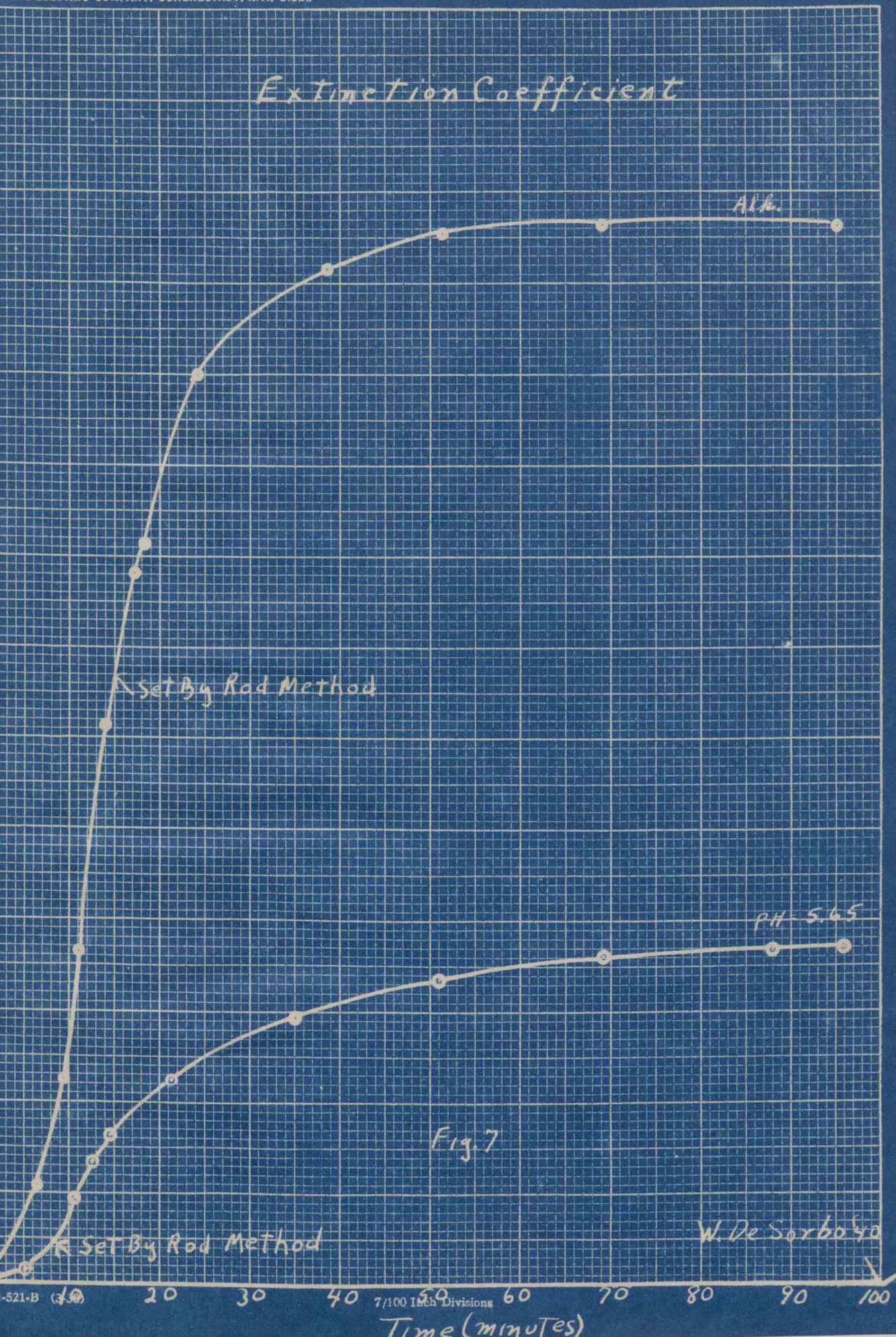
In order to study the effect of silicate concentration on the intensity of light, both scattered and transmitted, a few runs were made using a different concentration of sodium silicate (curves 3 and 4) and in a few cases sulfuric acid was used instead of acetic acid. The results seem to show that the final intensity of the transmitted and scattered light depends mostly on the hydrogen ion concentration. Limited time prevented a more extensive study in this direction.

TABLE III - Maximum Differences in Galvanometer Deflections
Due to the Transmitted and Scattered Light

(Total volume of solution is 300 c.c. containing
150 c.c. of Sodium Silicate (1.328 N)

<u>Volume of Acetic Acid (c.c.)</u>	<u>Volume of H₂O c.c.</u>	<u>pH</u>	<u>Transmitted D_t-D_t (max)</u>	<u>Scattered D_t-D_t (max)</u>
150	0	4.21	13.4	1.20
125	25	4.50	14.0	1.45
120	30	4.75	14.4	1.65
110	40	4.91	-	1.85
100	50	5.06	15.5	2.10
85	65	5.20	15.8	2.40
75	75	5.30	16.7	2.65
70	80	5.42	17.6	2.80
65	85	5.50	-	3.00
55	95	5.60	18.4	3.32
52	98	5.78	18.8	3.58
50	100	6.08	-	3.90
*45	105	6.50	20.6	5.20
*40	110	6.75	20.9	6.00
25	125	alk.	21.0	8.72
23	127	alk.	20.8	8.60
22	128	alk.	21.0	8.70
21	129	alk.	-	8.50
20	130	alk.	20.4	8.85
19	131	alk.	20.6	8.75
18	132	alk.	21.2	8.82
17	133	alk.	20.8	8.40

* Rapidly setting gels in which only the final readings were taken.



The data on transmitted light may be used in determining the extinction coefficient of silicic acid gel forming mixtures (Table 4). From Lambert's Law

$$I = I_0 e^{-Ed}$$

$$\begin{aligned} \text{Since } D_i &= kI_0 \\ D_t &= kI \end{aligned}$$

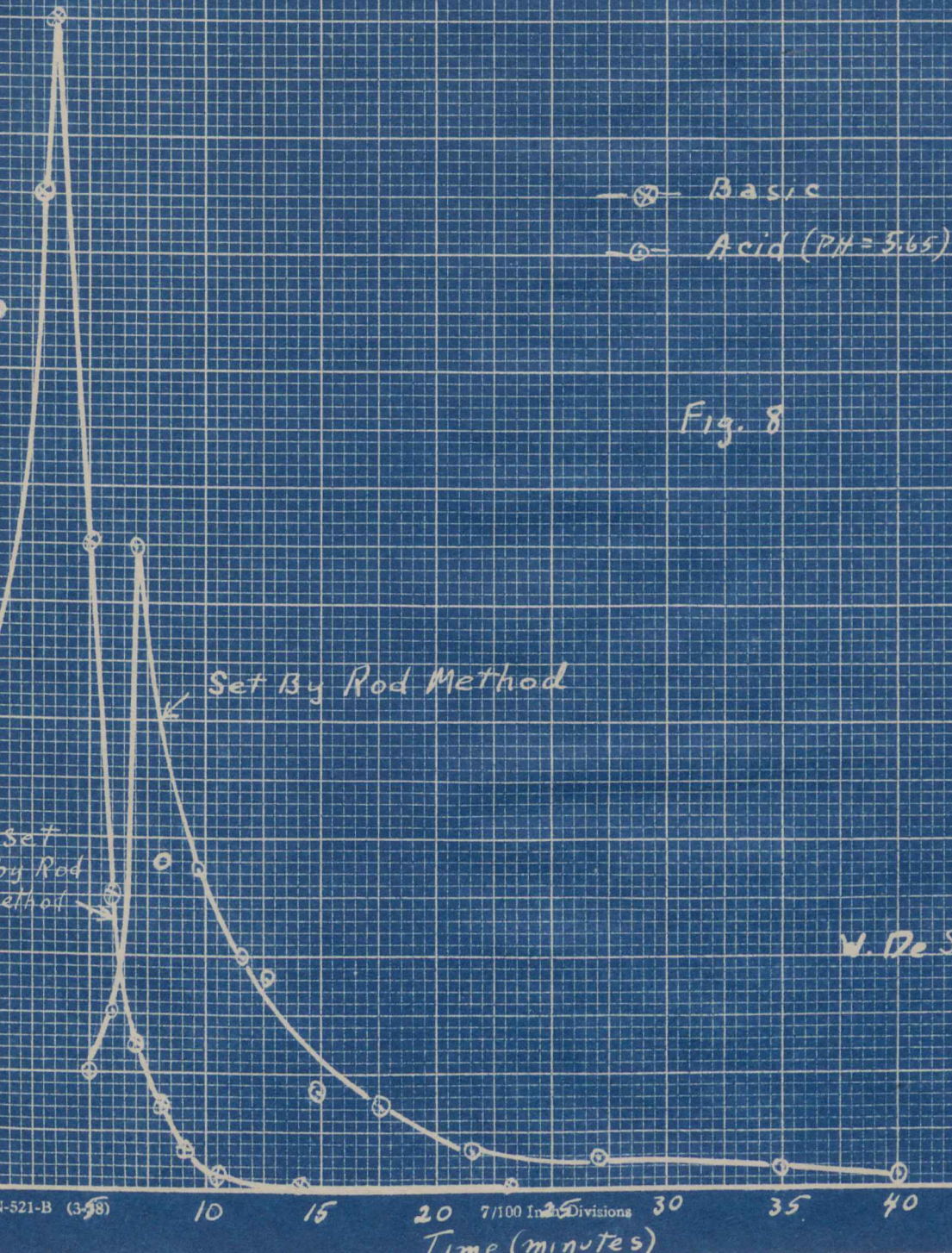
$$\text{then } D_t = D_i e^{-Ed}$$

Here E is the absorption coefficient since it is a measure of the rate of loss of light from the direct beam. However, some of the decrease of the intensity of light is in this case not due to a real disappearance of the light, but results from the fact that some is scattered to the sides by particles and thus removed from the direct beam.

True absorption represents the actual disappearance of the light, the energy of which is converted into heat motion of the particles of the absorbing material. In these gel forming mixtures this will occur to only a small extent so that the name absorption or extinction coefficient for E is not appropriate. In this case E must be regarded as made up of two parts, E_a due to the true absorption, and E_s due to the scattering. Typical curves of this extinction coefficient for a basic and acidic mixture are shown in Figure 7. Extinction coefficient for scattered light means nothing at all since Lambert's Law applies only to the decrease in intensity of the direct beam passing through the mixture.

Prasad and Hattiangadi have determined the time of set from the curves in which intensity of scattered light was plotted against time. The time of set was taken when the curves show a tendency of running parallel to the time axis. In Table 5 a comparison of this optical method and rod method of determining time of set has been arranged. It can be seen from the curves (Figures 1-4)

Transmitted



that the probable error in determining such a time of set is rather large, for in some of the curves it is difficult to determine when they begin to run parallel to the time-axis. The table is only of qualitative interest. However, it does show that the setting process continues after the gel has been pronounced set by the rod method.

Since each curve of Figures 1-4 shows a point of inflection, the slope of such a curve should have a maximum or a minimum when plotted against time. In many of these curves a maximum peak is obtained when the slope is plotted against time, but in a few cases the experimental errors are so greatly magnified that the peak is not obtained with certainty. However, with the new recording spectrophotometers, where the experimental errors are less than one-tenth of one percent, no difficulty at all should be encountered in obtaining these curves which may be of some value as described in the following paragraphs.

Figure 8 shows two such curves. The time of set by the rod method does not coincide with the peak of the curve; for the acid gels it more nearly coincides with the peak. This peak of the curve could be arbitrarily called the time of set of a gel; but such a method would undoubtedly be much more tedious and time consuming than the more simple rod method. However, it is a possible method, especially if the new spectrophotometers are used. The method could be used in studying silicic acid gels in which the concentration of the silica is insufficient to render the gel its strength or rigidity required to support the rod. There are numerous examples of gels having a weak gel structure, for example, strongly alkaline silicic acid gels, some of zirconia gels, and titania gels.

TABLE IV - Extinction Coefficient

150 c.c. Sod. Sil. (1.328 N)
 55 c.c. HAc (4.025 N)
 95 c.c. H₂O
 pH 5.65

150 c.c. Sod. Sil. (1.328 N)
 21 c.c. HAc (4.025 N)
 129 c.c. H₂O
 pH (alk.)

<u>D_t</u>	<u>T(min.)</u>	<u>E</u>
20.7	-	0
19.3	5.0	.0037
18.9	6.0	.0049
18.3	7.0	.0066
16.1	8.0	.0136
14.5	9.5	.0193
13.4	10.4	.0235
11.1	12.5	.0338
9.7	19.5	.0411
7.4	21.5	.0558
5.3	35.0	.0739
4.4	51.0	.0840
3.9	69.0	.0906
3.7	88.0	.0934
3.7	96.0	.0934

<u>D_t</u>	<u>T(min.)</u>	<u>E</u>
20.5	-	-
20.0	2.0	.0013
19.6	2.7	.0024
12.65	6.7	.0262
9.90	7.8	.0395
7.15	9.0	.0572
4.20	10.5	.0860
3.80	11.0	.0915
1.60	13.2	.1384
1.20	14.0	.1540
1.00	14.7	.1639
.70	16.0	.1833
.58	17.0	.1935
.48	18.0	.2038
.20	24.5	.2514
.12	38.5	.2790
.10	51.0	.2889
.10	74.0	.2889
.10	95.0	.2889

TABLE V - Determining Time of Set

150 c.c. of 1.328 N Sodium Silicate
150 c.c. of Acetic Acid Solution

<u>Volume of HAc (c.c.)</u>	<u>Volume of H₂O (c.c.)</u>	<u>pH</u>	<u>Rod Method</u>	<u>Optical Method Transmitted</u>	<u>Scattered</u>
150	0	4.21	112	250	190
125	25	4.50	88	220	184
120	30	4.75	75	-	170
100	50	5.06	71	200	160
85	65	5.20	60	-	157
75	75	5.30	37	150	140
70	80	5.42	28	130	140
65	85	5.50	22	-	130
55	95	5.60	8'45"	58	82
52	98	5.78	3'45"	40	70
50	100	6.08	2'	-	62
25	125	alk.	3'	6	10
23	127	alk.	6'	10	24
22	128	alk.	12'30"	-	40
20	130	alk.	33	-	58
19	131	alk.	135	70	135
18	132	alk.	155	140	210
17	133	alk.	240	220	380

H₂SO₄

66	84	alk.	37	-	-
122	28	5.41	39	-	94
118	32	6.1	less 1'	-	13

100 c.c. of 1.328 N Sodium Silicate
50 c.c. of Acetic Acid Solution

HAc

50 (6 N)	0	4.56	45	-	180
11	39	alk.	31	-	60
40	10	5.31	5	-	50

TABLE VI - Determining Time of Set by Plotting
Slope of the Curves of Figure 1

150 c.c. of Sodium Silicate (1.328 N)

25 c.c. of 4.025 N Acetic Acid

127 c.c. of H₂O

<u>D_t</u>	<u>D₁-D_t</u>	<u>T</u>	<u>Δ (D₁-D_t)</u>	<u>Δ T</u>	<u>$\frac{\Delta (D_1-D_t)}{\Delta T}$</u>
20.2	-	-	-	-	-
19.4	1.6	35"	.8	35" (appr.)	1.87
18.6	1.6	1' 10"	2.5	50"	3.03
16.1	4.9	2'	3.7	1'	3.70
12.4	8.8	3'	1.7	30"	3.40
10.7	10.3	3' 30"	6.0	1' 30"	4.00
4.7	16.3	5'	2.2	1'	2.20
2.5	18.5	6'	1.0	1'	1.00
1.50	19.5	7'	.50	1'	.50
1.00	20.0	8'	.30	1'	.30
.70	20.3	9'	.15	1'	.15
.55	20.45	10'	.10	1'	.10
.45	20.55	11'	.05	1'	.05
.40	20.60	12'	.05	1'	.05
.35	20.65	13'	.05	1'	.05
.30	20.70	14'	.05	3'	.018
.25	20.75	17'	.05	6'	.008
.18	20.82	23'	.05	11'	.003
.15	20.85	34'	-	-	-

150 c.c. of Sodium Silicate (1.328 N)

55 c.c. of HAc (4.025 N)

95 c.c. H₂O

20.7	-	-	-	-	-
19.3	1.4	5	.4	1.0	.40
18.9	1.8	6	.6	1.0	.60
18.3	2.4	7	2.2	1.0	2.20
16.1	4.6	8	1.6	1.5	1.06
14.5	6.2	9' 30"	1.1	1.0	1.10
13.4	7.3	10' 30"	1.5	1.0	1.50
11.9	8.8	11' 30"	.8	1.0	.80
11.1	9.6	12' 30"	.75	1.0	.75
10.35	10.35	13' 30"	.65	1.0	.65
9.70	11.0	14' 30"	1.1	3.0	.36
8.60	12.1	17' 30"	1.2	4.0	.30
7.40	13.3	21' 30"	.9	6.5	.14
6.50	14.2	27'	1.2	8.0	.15
5.30	15.4	35'	.4	5.0	.08
4.90	15.8	40'	.9	17.5	.05

In all the intensity-time curves of both the transmitted and scattered light, the time of set of the acid gels as determined by the rod method falls on the lower part of the curves (Figures 3-4), while for basic gels the time of set falls on the upper part of the curve.

Similarity of curves 1-4 fulfills somewhat the conditions of Smoluchowski's theory of coagulation⁹. Prasad, Mehta and Desai, considering the process of gel formation as one of coagulation of the sol, applied this theory to the case of silicic acid gel formation. They found that for a certain range of extinction coefficients of scattered light the gel formation of silicic acid approximates to the case of an ideal coagulation assumed by Smoluchowski's theory, but the variations obtained for low and high extinction coefficients were considerable.

In applying the theory here a particular value of D_1-D_t of the various curves (Figures 1-4) at time $t_1, t_2, t_3 \dots$ etc., represent a definite stage of coalescence.

Following the same procedure as Prasad, Mehta and Desai, we have that the change in the total number of particles Σn for each gel should have a constant value, then the ratio of any two time units should be constant:

$$t_1:t_2:t_3:\dots:t_n = T_1:T_2:T_3:\dots:T_n$$

$T_1, T_2 \dots$ are constants and their ratio must be independent of the value of D_1-D_t for transmitted light, or of D_t-D_1 of the scattered light. These ratios have been obtained from the curves of Figures 1-2, and are shown in Tables 7 and 8. The variations in ratios are not small enough to be neglected. The gelation of silicic acid although it may approximate the case of ideal coagulation assumed by Smoluchowski at certain stages of coagulation does not do so throughout. A different type of coagulation must take place since the particles possess a high degree of hydration which alters the probability of adhesion as assumed by the theory.

HAC 23 c.c. 19 c.c. 18 c.c. 17 c.c. 52 c.c. 55 c.c. 70 c.c. 100 c.c. 125 c.c. 150 c.c.

D ₁ -D _t	t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉	t ₁₀	t ₁₁
2.2	.9	16.9	48.4	59.1	2.90	6.7	21.0	25.5	45.2	70.0	96.0
3.3	1.3	21.1	55.8	70.0	3.40	7.7	25.8	30.0	53.0	82.2	107.8
4.4	1.7	24.3	59.8	80.1	4.00	8.5	27.0	33.3	62.8	93.0	118.0
5.5	2.0	28.4	65.0	88.0	4.20	9.7	28.8	36.3	72.4	103.0	129.2
6.6	2.20	28.0	65.2	95.0	4.60	10.4	30.9	39.0	82.0	112.2	140.0
7.7	2.50	29.5	66.8	102.0	5.30	11.2	33.2	42.6	91.9	122.0	151.2
8.8	2.90	31.6	68.0	107.8	5.60	12.0	36.2	46.8	101.8	133.3	162.2
9.9	3.20	33.4	69.6	111.8	6.40	12.9	39.6	51.2	111.8	145.8	172.9

Ratios

D ₁ -D _t	$\frac{T_1}{T_2}$	T_2	$\frac{T_3}{T_2}$	$\frac{T_4}{T_2}$	$\frac{T_5}{T_2}$	$\frac{T_6}{T_2}$	$\frac{T_7}{T_2}$	$\frac{T_8}{T_2}$	$\frac{T_9}{T_2}$	$\frac{T_{10}}{T_2}$	$\frac{T_{11}}{T_2}$
2.2	.053	1	2.86	3.49	.112	.396	1.24	1.51	2.55	4.14	5.68
3.3	.061	1	2.64	3.32	.161	.364	1.22	1.42	2.51	3.90	5.10
4.4	.069	1	2.46	3.29	.164	.349	1.11	1.37	2.58	3.82	4.85
5.5	.075	1	2.40	3.3	.159	.367	1.10	1.34	2.74	3.90	4.89
6.6	.078	1	2.33	3.39	.164	.371	1.11	1.39	2.92	4.00	5.00
7.7	.084	1	2.27	3.45	.179	.379	1.12	1.44	3.08	4.13	5.13
8.8	.091	1	2.15	3.41	.177	.379	1.14	1.48	3.22	4.21	5.13
9.9	.095	1	2.10	3.34	.190	.386	1.18	1.53	3.36	4.30	5.17

HAc	25 c.c.	19 c.c.	13 c.c.	17 c.c.	52 c.c.	55 c.c.	70 c.c.	75 c.c.	100 c.c.	125 c.c.	150 c.c.
D _t -D _i	t ₁	t ₂	t ₃	t ₄	t ₅	t ₆	t ₇	t ₈	t ₉	t ₁₀	t ₁₁
.4	2.8	21.8	45.0	22.2	3.3	7.3	22.0	27.0	57.0	99.0	111.0
.5	2.9	23.5	48.0	73.2	4.8	8.2	25.0	30.2	65.0	105.0	120.0
.7	3.0	26.5	53.6	87.0	5.0	9.5	30.1	36.6	73.5	115.0	138.0
1.0	3.2	30.2	59.5	99.0	6.0	10.6	35.5	45.6	91.5	130.0	168.0
1.2	3.5	31.5	61.1	102.2	6.1	11.2	38.0	48.6	97.0	146.0	179.0
1.5	4.0	35.4	66.8	113.4	7.8	14.5	48.3	62.0	121.5	-	-
1.6	4.1	36.2	67.8	116.0	9.2	15.5	51.8	65.8	127.5	-	-
2.0	4.8	38.5	72.5	124.0	10.8	21.0	72.0	85.5	168.0	-	-
2.5	5.2	40.8	78.0	132.8	18.0	32.3	109.5	135.0	-	-	-

Ratios

D _t -D _i	$\frac{T_1}{T_2}$	T_2	$\frac{T_3}{T_2}$	$\frac{T_4}{T_2}$	$\frac{T_5}{T_2}$	$\frac{T_6}{T_2}$	$\frac{T_7}{T_2}$	$\frac{T_8}{T_2}$	$\frac{T_9}{T_2}$	$\frac{T_{10}}{T_2}$	$\frac{T_{11}}{T_2}$
.4	.128	1	2.06	1.01	.151	.334	1.01	1.25	2.70	4.54	5.09
.5	.123	1	2.04	3.32	.204	.348	1.06	1.28	2.76	4.46	5.10
.7	.113	1	2.02	3.28	.189	.358	1.17	1.38	2.88	4.34	5.20
1.0	.102	1	1.97	3.27	.196	.350	1.19	1.51	3.02	4.49	5.56
1.2	.111	1	1.94	3.25	.193	.355	1.20	1.54	3.08	4.63	5.68
1.5	.112	1	1.89	3.20	.220	.409	1.37	1.75	3.43	-	-
1.6	.113	1	1.87	3.20	.254	.426	1.43	1.81	3.52	-	-
2.0	.124	1	1.88	3.22	.280	.545	1.67	2.22	4.36	-	-
2.5	.127	1	1.91	3.25	.250	.790	2.68	3.30	-	-	-

SUMMARY

1. The intensity of the scattered and transmitted light has been measured by means of photoelectric cells. The data shows that the particles or micelles in the gel are larger than those in the sol. Also the particles in the alkaline gels are larger than those in the acid gels.
2. Using Lambert's Law, the extinction coefficient of silicic acid gel-forming mixtures could readily be calculated.
3. The optical method of determining time of set has been discussed. It has been suggested for use where the gel structure is of such a strength that it will not support the rod.
4. Von Smoluchowski's kinetic theory of flocculation has been applied to the silicic acid gels.

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TABLE VIII - Index to Curves of Figure 1

For Transmitted Light (See Table 1)

150 c.c. Sodium Silicate, 1.328 N, mixed with
150 c.c. of Acetic Acid Solution containing vary-
ing amounts of 4.025 N Acetic Acid.

<u>Volume of HAc (c.c.)</u>	<u>Volume of H₂O (c.c.)</u>	<u>pH</u>	<u>Symbol</u>
150	0	4.21	△
125	25	4.50	○
100	50	5.06	⊗
75	75	5.30	⊙
70	80	5.42	⋈
55	95	5.60	⊖
52	98	5.78	⊗
25	125	alk.	○
23	127	alk.	•
19	131	alk.	⊞
18	132	alk.	⊠
17	133	alk.	×

TABLE IX - Index to Curves of Figure 2

For Scattered Light (See Table 2)

<u>Volume of HAc (c.c.)</u>	<u>Volume of H₂O (c.c.)</u>	<u>pH</u>	<u>Symbol</u>
150	0	4.21	×
125	25	4.50	•
120	30	4.75	⊗
110	40	4.90	⊗
100	50	5.06	△
85	65	5.20	⊙
75	75	5.30	⊗
70	80	5.42	△
65	85	5.50	⊕
55	95	5.60	□
52	98	5.78	○
50	100	6.08	□
25	125	alk.	⊙
23	127	alk.	⊕
22	128	alk.	⊙
20	130	alk.	⊙
19	131	alk.	⊙
18	132	alk.	⊕
17	133	alk.	•