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## A Study of the Effect of Temperature Upon Reactions Between Stannous and Arsenate Ions in Silicic Acid Gels

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A STUDY OF THE  
"   
EFFECT OF TEMPERATURE UPON REACTIONS  
BETWEEN  
STANNOUS AND ARSENATE IONS  
IN  
SILICIC ACID GELS

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5838 J  
Thesis

By  
Ellis Elder  
June, 1932

5838 J  
Thesis



A Thesis  
Submitted to the Department of Chemistry  
College of the Pacific

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In partial fulfillment  
of the  
Requirements for the  
Degree of Master of Arts

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## CHAPTER I

### STATEMENT OF THE PROBLEM

The purpose of this investigation was to determine to what extent the reaction between stannous and arsenate ions in silicic acid gels is influenced by temperature.

This was to be done by observing (1) the rate of crystal growth; and (2) the appearance of the crystal growth in sets of gels identical in composition but kept at different temperatures throughout the process of crystal growth.

## CHAPTER II

### HISTORICAL BACKGROUND

Numerous studies have been made on the subject of gels made by the addition of acid to sodium silicate solution. The resulting gel has many peculiar and interesting properties. By mixing an ionizing substance with the components of the gel and allowing a solution of another ionizing substance to diffuse through the gel after it has set large crystal growths of varied patterns may be obtained.

The reaction between stannous and arsenate ions in silicic acid gels results in very interesting crystal growths. This particular reaction has been studied by W. Farr; the results of this study are embodied in a thesis submitted for the Master of Arts degree to the College of the Pacific, June, 1931. These results definitely show that the acidity of the gels influences this reaction to a very great extent. The rate of growth, amount of growth, and appearance of crystals are all markedly affected by changes in the acidity of the gel. Farr concludes:

The chemical action within the gels is apparently controlled to a greater extent by the amount and strength of the

acid used than by the kind of acid.<sup>1</sup>

It seemed reasonable that the temperature at which the gels are kept during the crystallizing reaction might also be a factor affecting the development of the crystals. So it remained to determine by experiment whether or not this reaction is affected by temperature, and, if so, in what way and to what extent.

Nothing was found in the chemical literature which would indicate that this particular phase of the problem has ever been investigated.

C. B. Hurd and H. A. Letteron call attention to the fact that the time of setting of silica gels is greatly influenced by temperature;<sup>2</sup> but nothing is included about any such effect on ionic reactions within the gels.

<sup>1</sup> Farr, W., Master of Arts Thesis, College of Pacific, 1931.

<sup>2</sup> Hurd, C. B., Letteron, H. A., "Studies on Silicic Acid Gels", Journal Physical Chemistry, 36: 604.

### CHAPTER III

#### APPARATUS AND MATERIALS

Two air baths, and one ice-water bath were used in keeping the gels at constant temperatures. Large (40x56 x40 cm., 58x48x40 cm.), specially made wooden boxes with glass windows served as air baths. Toluene tube regulators were used with these air baths. A sawdust-insulated 11.4 liter (3 gal.) crock was used as an ice-water bath. By keeping the ice-water bath well iced the temperature was kept very constant. One set of gels was kept at room temperature as indicated by a mercury thermometer of 0-150 degrees C range, suspended near this set of gels. During the course of the experiment, the room temperature varied between the limits of 16.5 degrees C to 24.8 degrees C, but most of the readings were made near 20 degrees C.

The gels were made in test tubes of approximately 17.8x2.5 cm. dimensions. The bores of these test tubes were found to be not exactly uniform.

Pipettes were used in measuring out all solutions--in making the gels, and in adding the diffusing agent. Neither the pipettes nor the burettes used in standardizing were recalibrated, inasmuch as the errors likely to

be present would be smaller than those involved in other parts of the procedure.

All chemicals used were of C. P. quality, except the sodium silicate solution, which was made up by diluting the 40 degree Baumé, grade N, water glass; the undiluted solution was found to contain 17.4 percent  $\text{Na}_2\text{O}$ .



## CHAPTER IV

## PROCEDURE

The following plan of gel preparation was used: Four sets of gels, each set to be of identical composition and to consist of duplicate gels made with sulphuric acid of approximately the following normalities: 0.2 N, 0.4 N, 0.6 N, 0.8 N, 1.0 N, and 1.2 N; a total of twelve gels to a set.

The acid of approximate normality of 0.4 was carefully standardized against anhydrous  $\text{Na}_2\text{CO}_3$ , using methyl red as the indicator. A NaOH solution was made up to approximately 0.6 N, and this was compared with the standardized acid (0.4291 N). The normalities of the other acid solutions were determined by comparison with this NaOH solution.

The sodium silicate solution was made by diluting the 40 degree solution to a specific gravity of 1.06 as determined by a float hydrometer. This solution was found to be 0.5775 N as a base by titration with acid. The sodium silicate solution was diluted 1 to 10 (volume) of water before titration with acid in order to prevent the formation of a gel which would have almost immediately

resulted if it were titrated without dilution. Methyl red was used as indicator.

The stannous chloride solution was made up by adding 85 c. c. of concentrated HCl solution to 54.4 grams of  $\text{SnCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  q. s. 1000 c. c. This solution is approximately 0.5 N stannous ion. The acidity of this solution was found to be 1.465 by comparison with 0.5845 N NaOH solution, using phenolphthalein as indicator.

The test tubes in which the gels were made were cleaned with a warmed solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  in concentrated  $\text{H}_2\text{SO}_4$ , washed repeatedly with distilled water, and dried.

The following procedure was used in making up all the gels. To each tube of one set 20 c. c. of acid was added. To this was added 5 c. c. of the stannous chloride solution. Then 20 c. c. of sodium silicate solution, was slowly added, whereupon the tube was shaken to thoroughly mix the contents, tapped to remove all bubbles, and tightly stoppered.

The gels were allowed to set at room temperature for 19 days after which 5 c. c. of the diffusing agent, sodium arsenate, was added. The sodium arsenate solution was made up at this time by addition of  $\text{H}_2\text{O}$  q. s. 1000 c. c. to 141.4 grams of crystalline sodium arsenate.

After the addition of the sodium arsenate the tubes were tightly stoppered, sealed with sealing wax, and placed in the constant temperature baths.

It has been found that the rate of setting of silica gels is greatly affected by temperature,<sup>1</sup> also, that the process of setting of gels does not abruptly discontinue at the time when the gel first appears to be set, but changes continue to take place within the gel for some time after apparent setting. If the diffusing agent had been added, and the gels placed at different temperatures as soon as the gels had first appeared to be set then the rates at which these additional physical changes would take place within the gels would be different for each set of gels because these changes are influenced by temperature. It was in order to eliminate this complication that the gels were allowed to set for such a long time before placing them at different temperatures.

At frequent intervals, measurements of the amount of crystal growth in the different gels were made with a millimeter scale. In making these measurements the gels were taken out of the temperature baths. The time

<sup>1</sup> "Studies on Silica Acid Gels", Journal Physical Chemistry, 36: 604.

required for measurements was about ten to fifteen minutes per set each time the measurements were made.

Temperature readings and such thermostat adjustments as were necessary were made twice a day.

All gels were taken from the temperature baths 188 hours after placing them in the baths; and were allowed to remain at room temperature for two hours while being photographed. After 1218 hours the gels were again photographed. No further measurements were taken after this time.

## CHAPTER V

### OBSERVATION OF CRYSTAL GROWTH

Measurements of crystal growths were made with decreasing frequency during the course of the experiments. The time intervals between successive measurements became greater as the rate of crystal growth decreased.

All measurements which were made are shown in the tables which follow. Tables I to VI inclusive show the rate of advance of the crystal growth in the gels at the different temperatures used (one table for each normality). Tables VII to XII show the amount of crystal growth at different intervals.

For the sake of clearness the data contained in tables I to VI are summarized in graphs I to VI. The relation between temperature and amount of crystal advance is shown in graphs VII to XII.

It was noted that the upper limit of the crystal band moves downward only very slowly, while the lower boundary moves down rapidly.

TABLE I

Showing the rate of advance of the crystal growth in gels identical in composition kept at the temperatures

indicated. The distance from the meniscus of gel to the farthest point of advance of the white crystalline band is given in millimeters.

The gels contained 0.2077 N  $\text{H}_2\text{SO}_4$ . The resultant normality as a base of the entire content of this gel was calculated to be 0.0016 N.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00		22	24	25
35.08	32	33	36	40
43.58	34	37	41	46*
58.50	38	43	47	53
67.08	40	45	51	57
82.33	43	50	55	65
89.58	44	52	58	67
108.75	47	57	63	72
114.33	48	59	64	74
131.58	51	62	69	81
157.08	54	67	75	91
179.33	57	72	80	96
202.50	60	75	84	100
250.25	66	84	92	113**
300.75	71	92	100	113

\* Indicates point at which evidence of cracking of gel was first noticed.

\*\* Indicates point at which it was first observed that the white band had reached the bottom of the tube.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
349.00	76	99	109	113
419.75	82	107	115**	113
541.00	91	119**	115	
708.00	101	119	115	
924.00	113**	119		
1212.00	113			

TABLE II

Showing the rate of advance of the crystal growth in gels identical in composition kept at the temperatures indicated. The distance from the meniscus of gel to the farthest point of advance of the crystal growth is given in millimeters.

These gels contain 0.4291 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of this gel was calculated to be 0.0968 N.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00		18	19	20
35.08	23	25	27	31
43.58	25	28	30	34*
58.50	28	32	34	39
67.08	29	34	36	41
82.33	30	37	39	45
89.58	31	38	41	45
108.75	33	41	43	50
114.33	34	41	44	52
131.58	36	44	47	54
157.08	39	47	51	49
179.33	40	49	54	62

\* Indicates point at which cracking was first noticed.



Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	42	51	56	66
250.25	46	56	59	73
300.75	49	61	65	79
349.00	53	64	69	86
419.75	56	70	76	88
541.00	63	78	82	94
708.00	68	85	88	100
924.00	73	90	93	104
1212.00	78	94	96	107

TABLE III

showing the rate of advance of the crystal growth in gels identical in composition kept at the temperatures indicated. The distance from the meniscus of gel to the farthest point of advance of the crystal growth is given in millimeters.

These gels contain 0.6436 N  $H_2SO_4$ . The resultant acid normality of the entire content of this gel was calculated to be 0.1922 N.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00		13	15	17
35.08	18	20	22	25
43.58	20	23	25	30
58.50	23	27	29	34
67.08	24	28	31	36
82.33	26	30	34	40
89.58	27	31	35	41
108.75	28	34	38	45
114.33	29	35	39	46
131.58	31	38	42	48
157.08	33	40	45	52
179.33	35	42	47	55

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	36	44	49	57
250.25	39	48	52	63
300.75	41	51	57	68
349.00	44	55	61	71
419.75	48	59	65	75
541.00	53	64	71	79
708.00	58	70	79	83
924.00	63	75	84	89
1212.00	68	81	87	93

TABLE IV

Showing the rate of advance of the crystal growth in gels identical in composition kept at the temperatures indicated. The distance from the meniscus of gel to the farthest point of advance of the crystal growth is given in millimeters.

These gels contain 0.8548 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of this gel was calculated to be 0.2149 N.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00		13	14	15
35.08	17	19	21	25
43.58	18	22	24	28
58.50	21	25	27	32
67.08	22	26	30	33
82.33	23	28	32	36
89.58	24	29	33	37
108.75	25	32	35	40
114.33	26	33	36	41
131.58	28	34	38	44
157.08	30	36	40	47
179.33	31	38	42	49

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	32	39	44	51
250.25	35	43	48	56
300.75	37	45	52	59
349.00	38	49	56	62
419.75	40	51	59	65
541.00	43	56	65	69
708.00	46	62	69	73
924.00	50	66	72	78
1212.00	53	72	73	80

TABLE V

Showing the rate of advance of the crystal growth in gels identical in composition kept at the temperatures indicated. The distance from the meniscus of gel to the farthest point of advance of the crystal growth is given in millimeters.

These gels contain 1.0774 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of this gel was calculated to be 0.3850 N.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00				15
35.08	16	18	20	23
43.58	18	20	22	26
58.50	19	23	26	29
67.08	20	24	27	31
82.33	21	26	29	34
89.58	22	27	30	35
108.75	23	29	32	38
114.33	24	30	33	38
131.58	26	31	35	40
157.08	27	33	37	44
179.33	28.	35	39	46

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	29	36	41	47
250.25	31	39	43	49
300.75	33	43	46	51
349.00	35	45	48	53
419.75	37	49	50	55
541.00	40	53	53	58
708.00	43	57	55	61
924.00	46	59	57	63
1212.00	50	61	59	64

TABLE VI

Showing the rate of advance of the crystal growth in gels identical in composition kept at the temperatures indicated. The distance from the meniscus of gel to the farthest point of advance of the crystal growth is given in millimeters.

These gels contain 1.2937 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of this gel was calculated to be 0.4811 N.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00				14
35.08			19	22
43.58	16		22	24
58.50	18	21	23	27
67.08	19	22	25	28
82.33	20	24	27	31
89.58	20	25	28	32
108.75	21	27	30	33
114.33	21	28	30	34
131.58	22	28	32	36
157.08	23	30	34	39
179.33	24	31	36	41



Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	25	32	37	43*
250.25	26	35	38	44
300.75	28	37	41	46
349.00	29	39	43	47
419.75	30	41	45	48
541.00	32	43	46	48
708.00	35	46	49	48
924.00	38	48	52	48
1212.00	40	49	54	48

\* Indicates point at which evidence of gel cracking was first noticed.

TABLE VII

Showing the width (in millimeters) of the white crystalline band in gels of identical composition kept at the temperatures indicated.

These gels contain 0.2077 N  $\text{H}_2\text{SO}_4$ . The resultant normality as a base of the entire content of the gel was calculated to be 0.0016 N. (These gels are the same ones referred to in table I.)

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00		5	6	6
35.08	11	9	11	12
45.58	11	10	13	15*
58.50	11	13	14	18
67.08	11	13	17	20
82.33	11	15	18	23
89.58	11	16	19	24
108.75	12	18	21	26
114.33	12	18	21	27
131.58	13	19	23	29
157.08	13	21	25	35
179.33	14	23	27	36

\* Indicates point at which evidence of cracking of gel was first noticed.

Hours	0° C. (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	14	24	29	37
250.25	16	27	31	43**
300.75	16	30	35	35
349.00	18	33	40	30
419.75	20	37	41**	19
541.00	22	40**	33	
708.00	24	30	19	
924.00	27**	16		
1212.00	13			

\*\* Indicates point at which it was first observed that the white band had reached the bottom of the tube.

TABLE VIII

Showing the width (in millimeters) of the crystal band in gels of identical composition kept at the temperatures indicated.

These gels contain 0.4291 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of the gel was calculated to be 0.0968 N. (These gels are the same ones as referred to in table II.)

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00		11	12	13
35.08	11	17	20	21
43.58	13	19	21	23*
58.50	16	23	25	28
67.08	17	24	26	31
82.33	18	27	29	35
89.58	19	28	31	35
108.75	21	30	33	39
114.33	22	31	34	40
131.58	24	34	36	43
157.08	27	37	40	48
179.33	28	39	43	51

\* Indicates point at which evidence of gel cracking was first noticed.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	30	41	45	54
250.25	34	46	51	61
300.75	37	51	55	67
349.00	41	54	59	74
419.75	44	60	66	75
541.00	51	68	72	82
708.00	56	76	78	88
924.00	61	80	83	92
1212.00	66	84	85	95

TABLE IX

Showing the width (in millimeters) of the crystal band in gels of identical composition kept at the temperatures indicated.

These gels contain 0.6436 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of the gel was calculated to be 0.1922 N. (These gels are the same ones referred to in table III.)

Hours	30° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00		8	10	13
35.08	9	15	17	21
43.58	13	18	20	26
58.50	15	22	24	31
67.08	16	23	26	33
82.33	17	25	29	37
89.58	18	26	30	38
108.75	19	29	33	41
114.33	20	30	34	42
131.58	22	33	37	44
157.08	24	35	40	49
179.33	26	37	42	52

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	27	39	44	54
250.25	30	45	47	60
300.75	32	46	52	65
349.00	35	50	56	67
419.75	39	54	60	70
541.00	44	59	65	76
708.00	49	65	72	76
924.00	54	68	75	82
1212.00	59	74	77	84

TABLE X

Showing the width (in millimeters) of the crystal band in gels of identical composition kept at the temperatures indicated.

These gels contain 0.8548 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of the gel was calculated to be 0.2149 N. (These gels are the same ones referred to in table IV.)

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00			8	13
35.08	13	15	16	22
43.58	14	17	19	24
58.50	17	20	23	29
67.08	18	21	25	30
82.33	19	23	27	33
89.58	20	24	28	33
108.75	21	26	30	37
114.53	22	27	31	38
131.58	24	29	33	40
157.08	26	31	35	43
179.33	27	33	37	46



Hours	0° C (mm.)	Room T. (mm.)	0° C (mm.)	40° C (mm.)
202.50	28	34	39	47
250.25	31	39	43	50
300.75	33	40	47	52
349.00	34	43	51	54
419.75	35	45	54	55
541.00	38	49	60	59
708.00	41	55	63	62
924.00	44	57	63	65
1212.00	46	62	61	65

TABLE XI

Showing the width (in millimeters) of the crystal band in gels of identical composition kept at the temperatures indicated.

These gels contain 1.0774 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of the gel was calculated to be 0.3850 N. (These gels are the same ones referred to in table V.)

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00				13
35.08	11	12	15	20
43.58	12	14	17	23
58.50	13	18	20	26
67.08	14	19	22	28
82.33	15	21	24	31
89.58	16	22	25	32
108.75	17	23	27	35
114.33	18	25	28	35
131.58	20	26	30	37
157.08	21	28	32	39
179.33	22	30	35	41

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	23	31	36	42
250.25	25	33	39	43
300.75	27	36	41	44
349.00	29	38	42	45
419.75	31	42	44	46
541.00	33	45	47	48
708.00	35	48	47	49
924.00	38	49	47	48
1212.00	41	50	46	45

TABLE XII

Showing the width (in millimeters) of the crystal band in gels of identical composition kept at the temperatures indicated.

These gels contain 1.2937 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of the gel was calculated to be 0.4811 N. (These gels are the same ones referred to in table VI.)

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
14.00				12
35.08			14	18
43.58	xxx		17	20
58.50	xxx	16	19	24
67.08	xxx	17	21	25
82.33	xxx	19	23	28
89.58	13	20	23	29
108.75	14	22	25	30
114.33	14	23	25	30
131.58	15	23	27	32
157.08	16	25	30	34
179.33	17	26	32	36

xxx Indicates presence of crystals, but of no definite band.

Hours	0° C (mm.)	Room T. (mm.)	30° C (mm.)	40° C (mm.)
202.50	18	27	33	37*
250.25	19	30	34	37
300.75	21	31	36	38
349.00	22	33	37	39
419.75	23	34	38	39
541.00	25	35	39	38
708.00	27	37	41	36
924.00	29	38	43	35
1212.00	30	37	45	35

\* Indicates point at which evidence of gel cracking was first noticed.



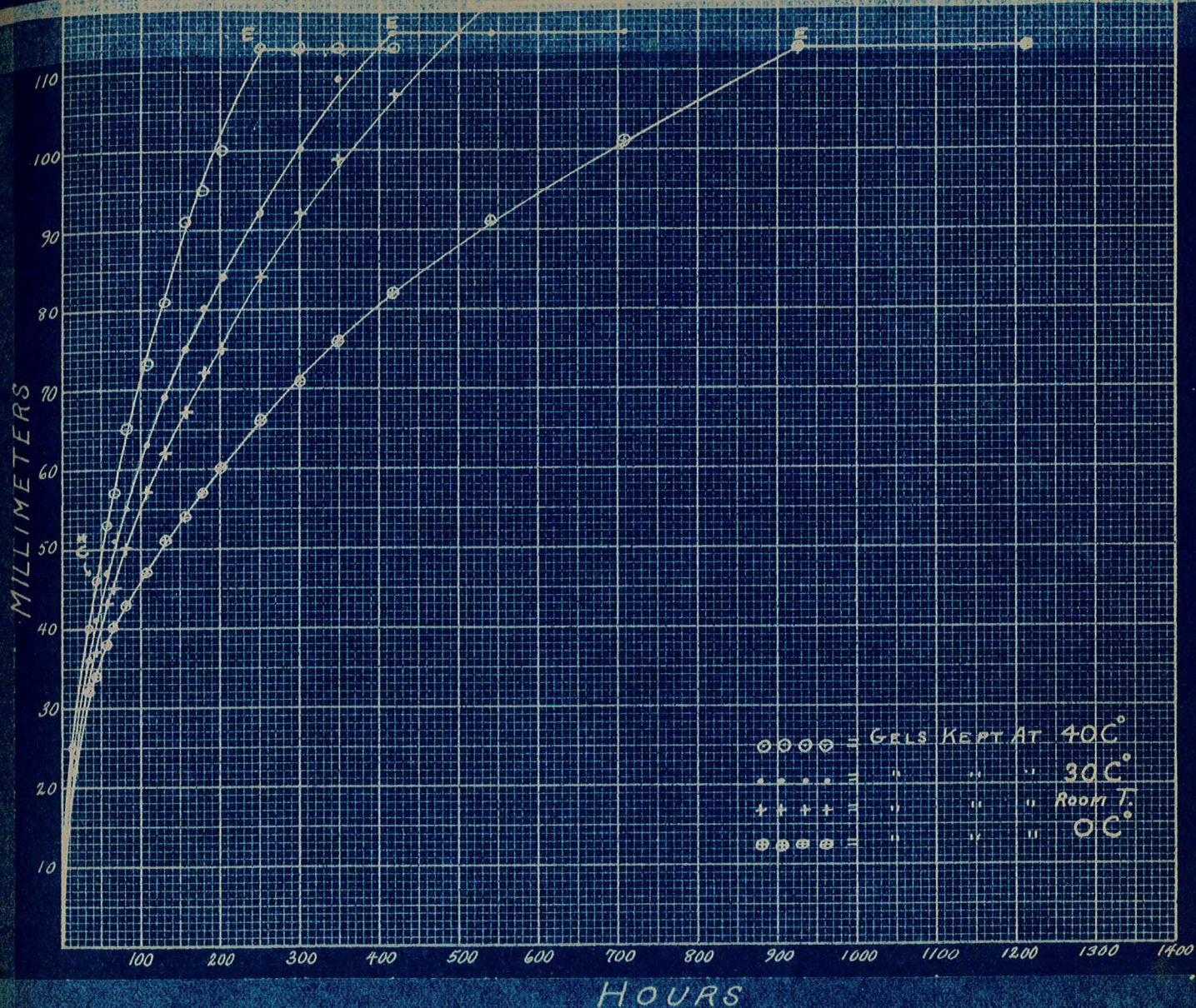


Fig. 1

Showing the rate of advance of the white band in gels of identical composition kept at the temperatures indicated by the legend. The ordinates correspond to the distances from the meniscus of the gel to the farthest point of downward advance of the white band.

The gels contain .2077 N.  $\text{H}_2\text{SO}_4$ . The resultant normality of the entire content of this gel was calculated to be .0016 N. in the base range.



(Referring to Fig. 1)

\*  
C Indicates point at which evidence of cracking of the gel was first noticed.

The white band has reached the bottom of the tube at the points indicated by the letter E.



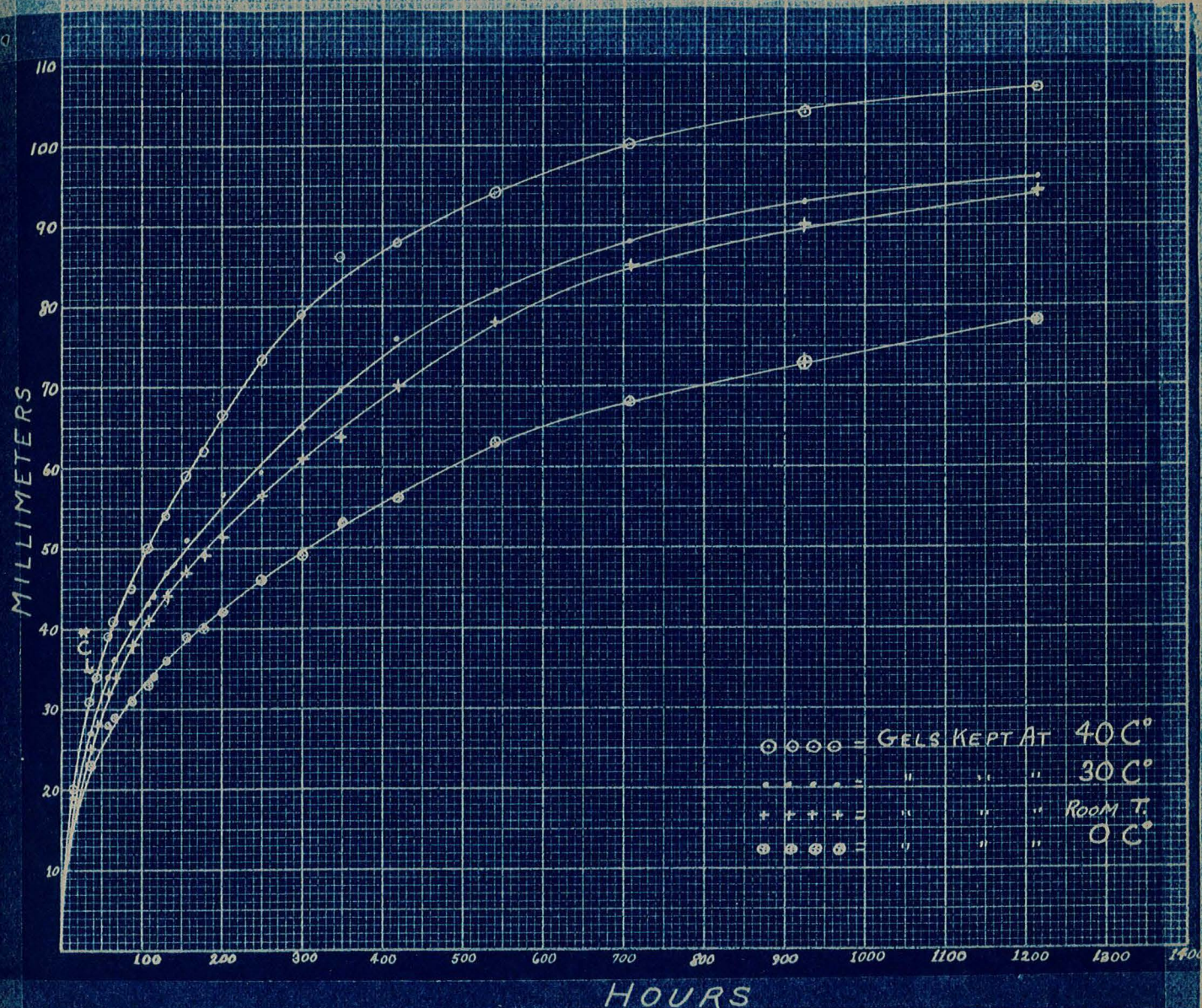


Fig. 2

Showing the rate of advance of the crystal growth in gels of identical composition kept at the temperatures indicated by the legend. The ordinates correspond to the distances from the meniscus of the gel to the farthest point of downward advance of the crystal growth.

The gels contain .4291 N.  $H_2SO_4$ . The resultant normality of the entire content of this gel was calculated to be .0968 N. in the acid range.



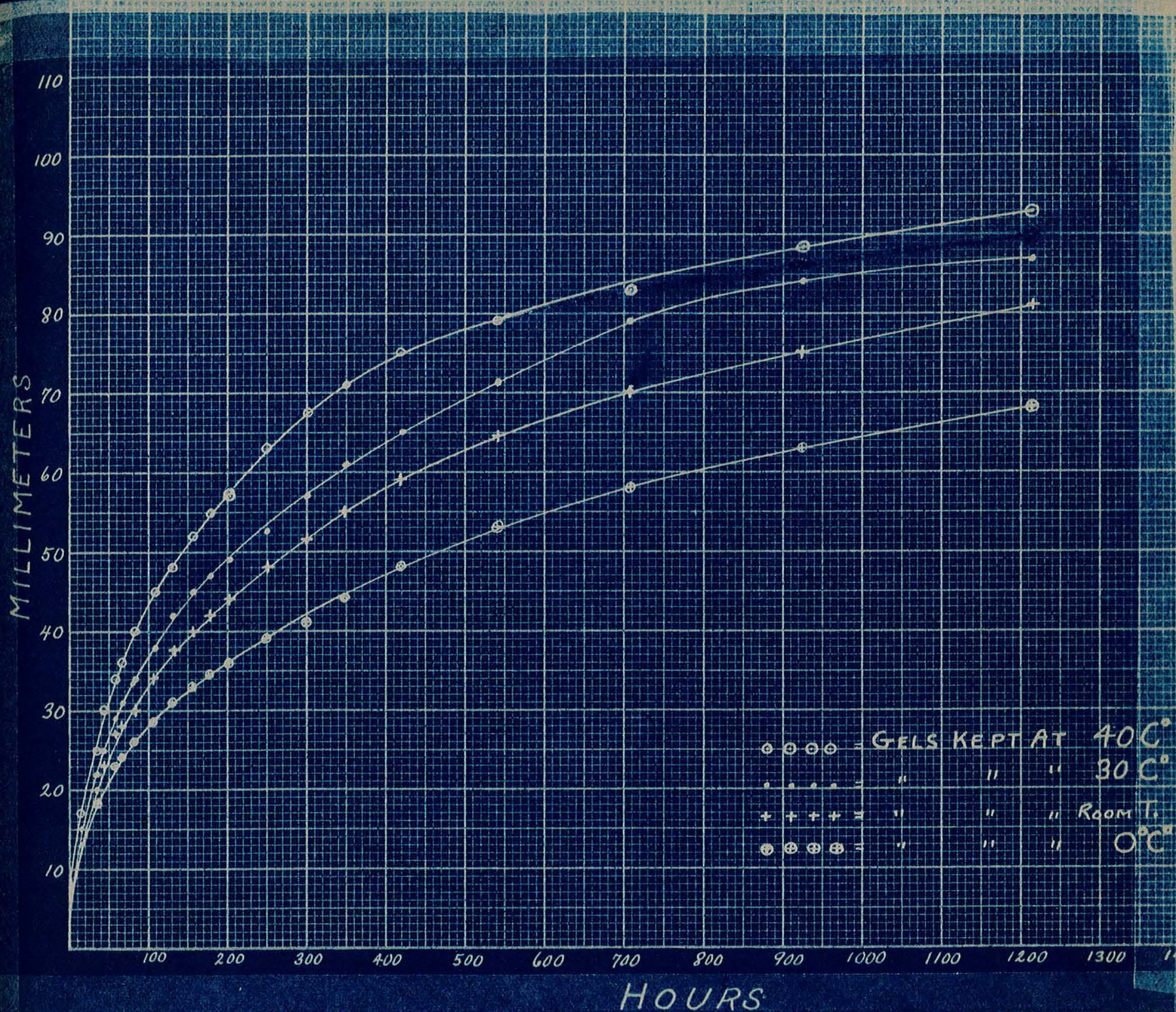


Fig. 3

Showing the rate of advance of the crystal growth in gel of identical composition kept at the temperatures indicated by the legend. The ordinates correspond to the distances from the meniscus of the gel to the farthest point of downward advance of the crystal growth.

The gels contain .6436 N.  $\text{H}_2\text{SO}_4$ . The resultant normality of the entire content of this gel was calculated to be .1922 N. in the acid range.



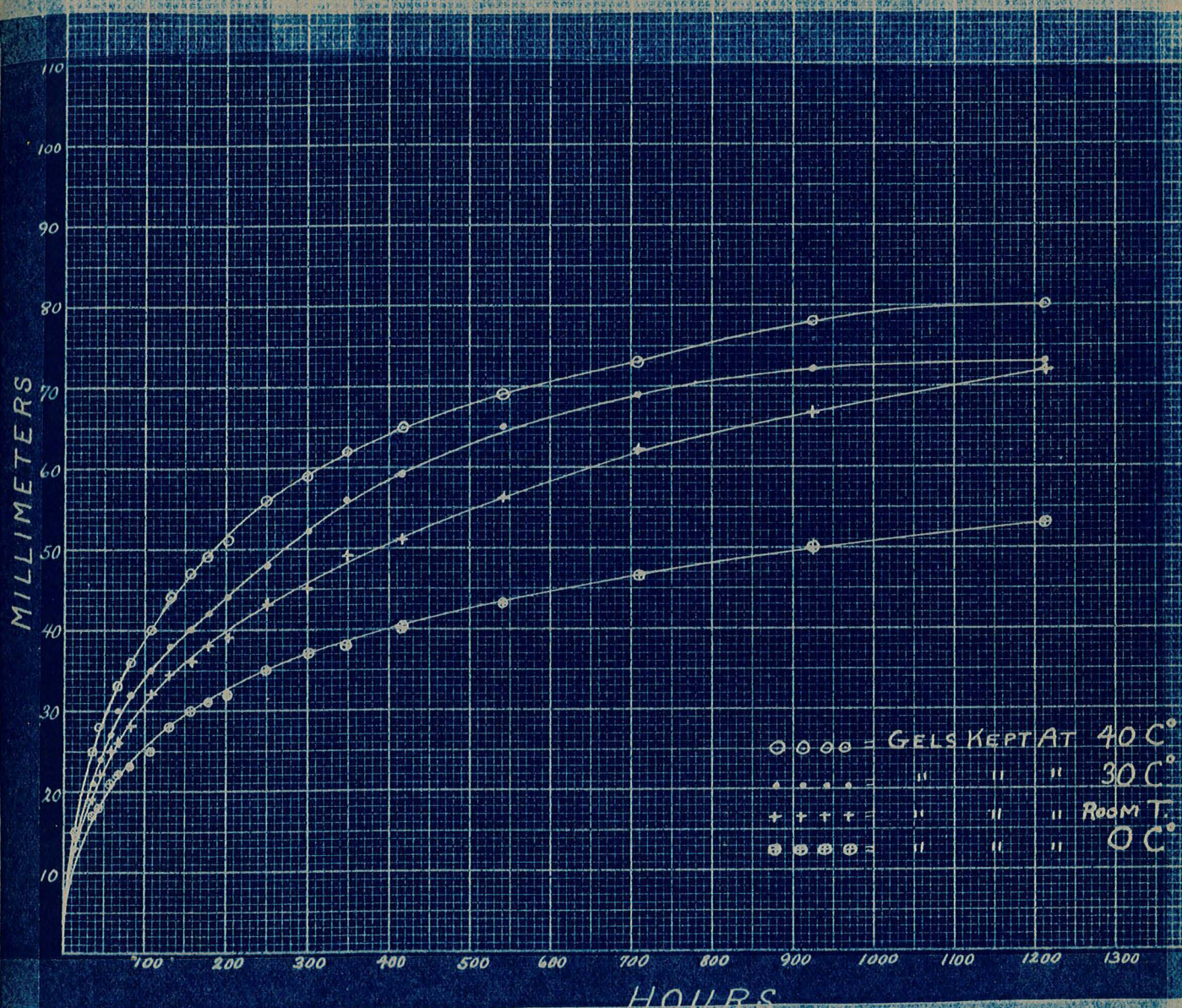


Fig. 4

Showing the rate of advance of the crystal growth in gels of identical composition kept at the temperatures indicated by the legend. The ordinates correspond to the distances from the meniscus of the gel to the farthest point of downward advance of the crystal growth.

The gels contain .8548 N.  $\text{H}_2\text{SO}_4$ . The resultant normality of the entire content of this gel was calculated to be .2149 N. in the acid range.



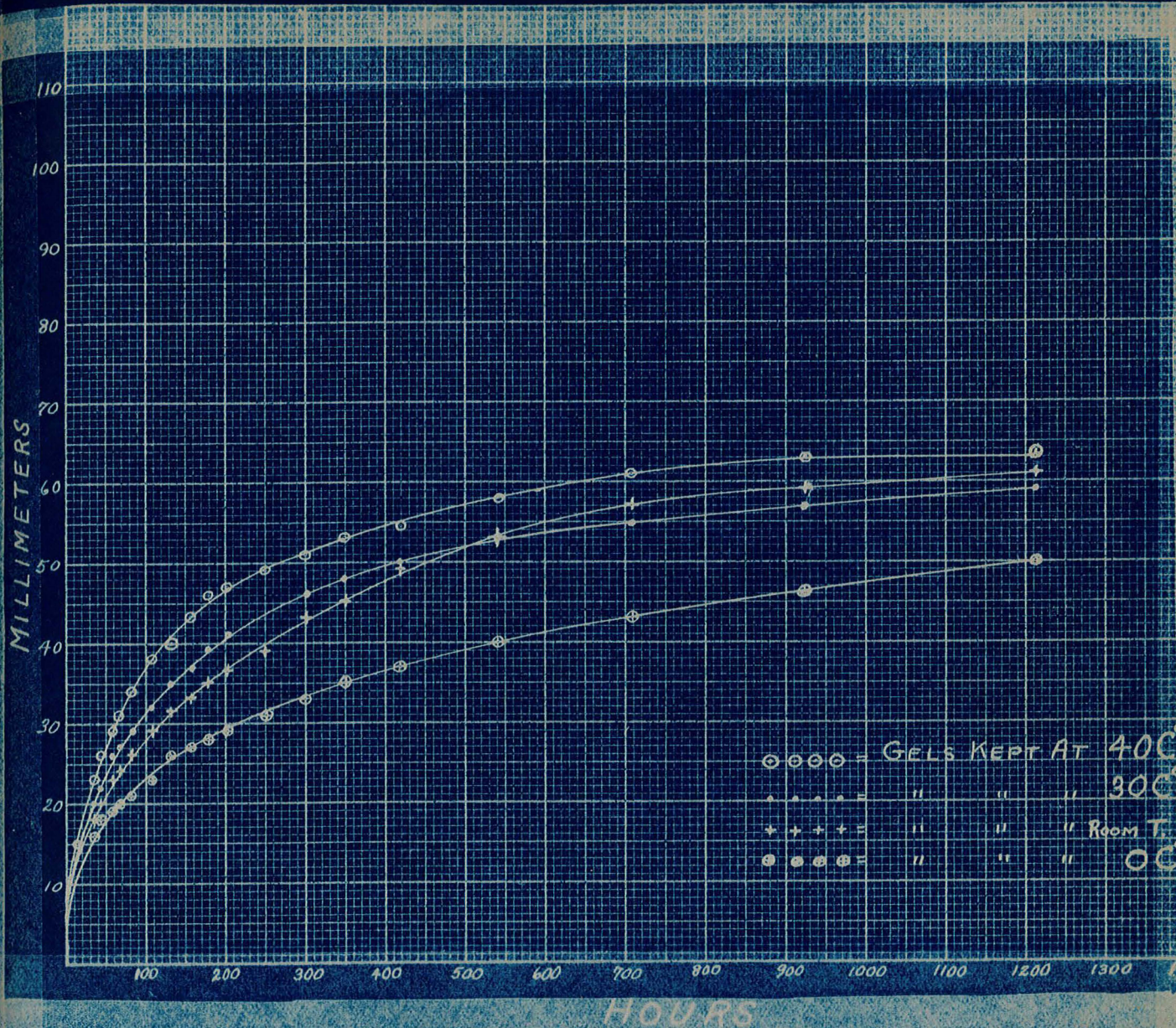


Fig. 5

Showing the rate of advance of the crystal growth in gels of identical composition kept at the temperatures indicated by the legend. The ordinates correspond to the distances from the meniscus of the gel to the farthest point of downward advance of the crystal growth.

The gels contain 1.0774 N.  $H_2SO_4$ . The resultant normality of the entire content of this gel was calculated to be .3850 N. in the acid range.



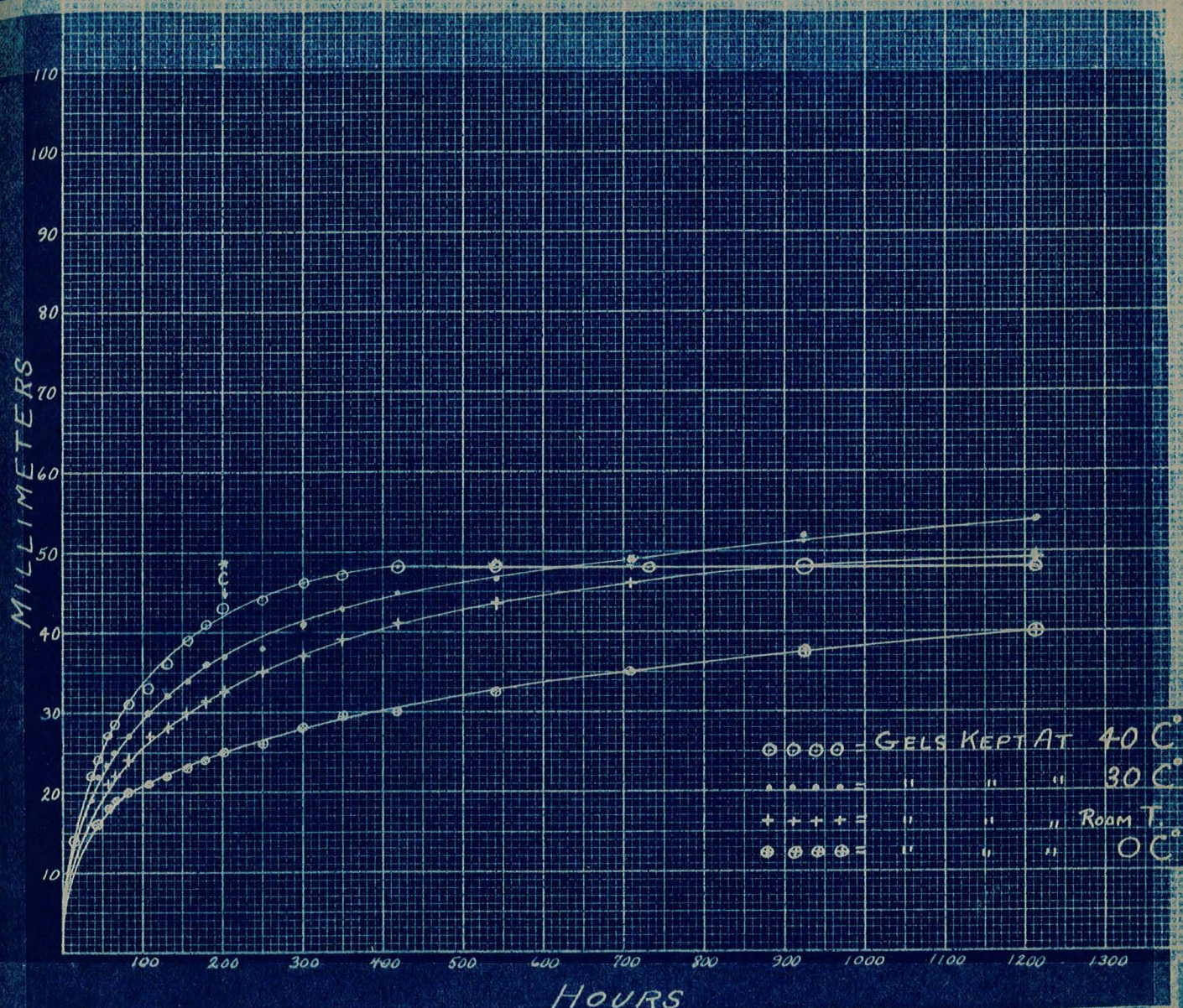


Fig. 6

Showing the rate of advance of the crystal growth in gels of identical composition kept at the temperatures indicated by the legend. The ordinates correspond to the distances from the meniscus of the gel to the farthest point of downward advance of the crystal growth.

The gels contain 1.2937 N.  $H_2SO_4$ . The resultant normality of the entire content of this gel was calculated to be .4811 N. in the acid range.



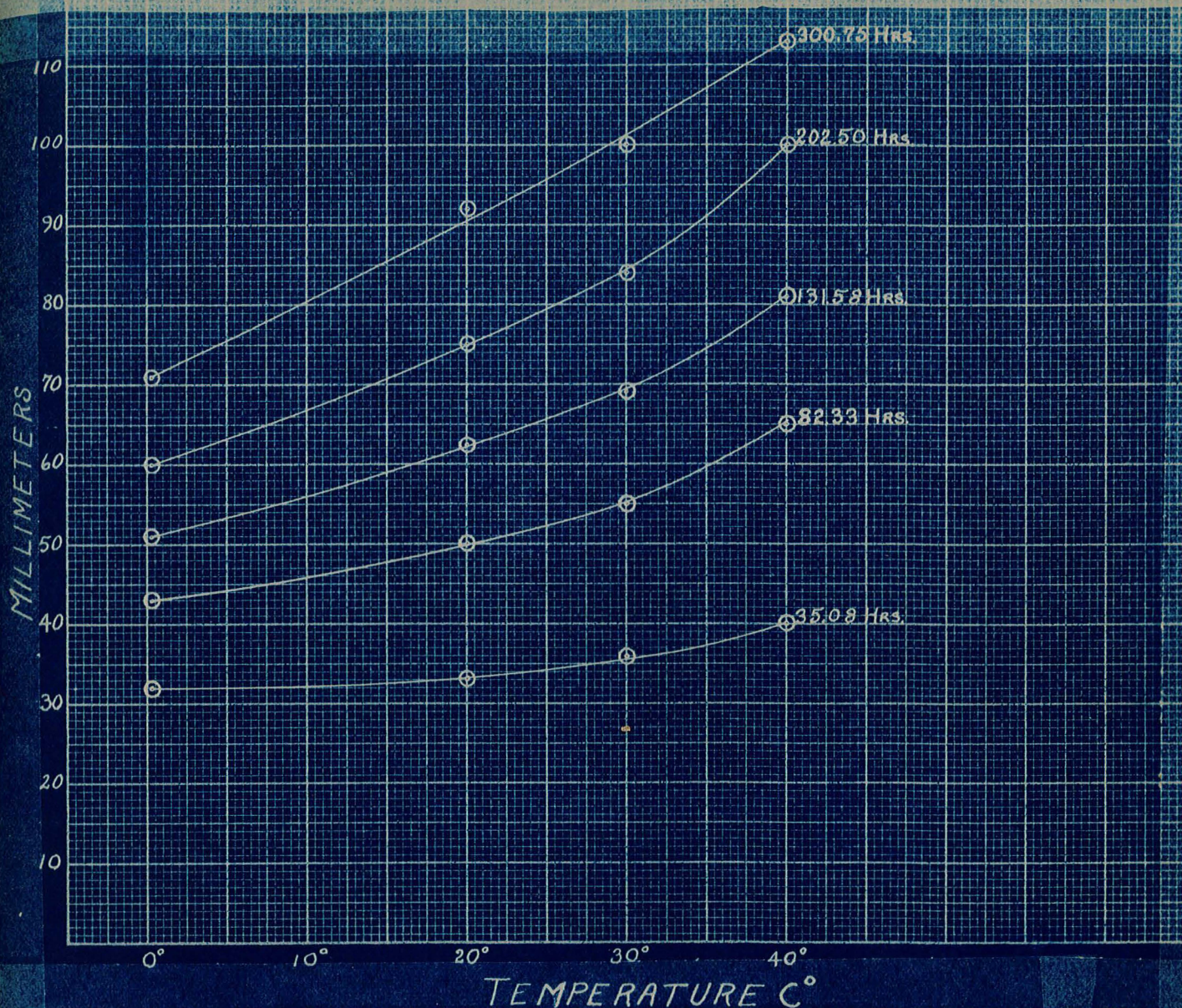


Fig 7

Showing the relation between temperature and amount of crystal advance (distance from meniscus of gel to farthest point of downward progress of the white band) in gels containing .2077 N  $\text{H}_2\text{SO}_4$ . The resultant normality of the entire content of this gel was calculated to be .0016 N. in the base range.

Room temperature is plotted as 20 C°.



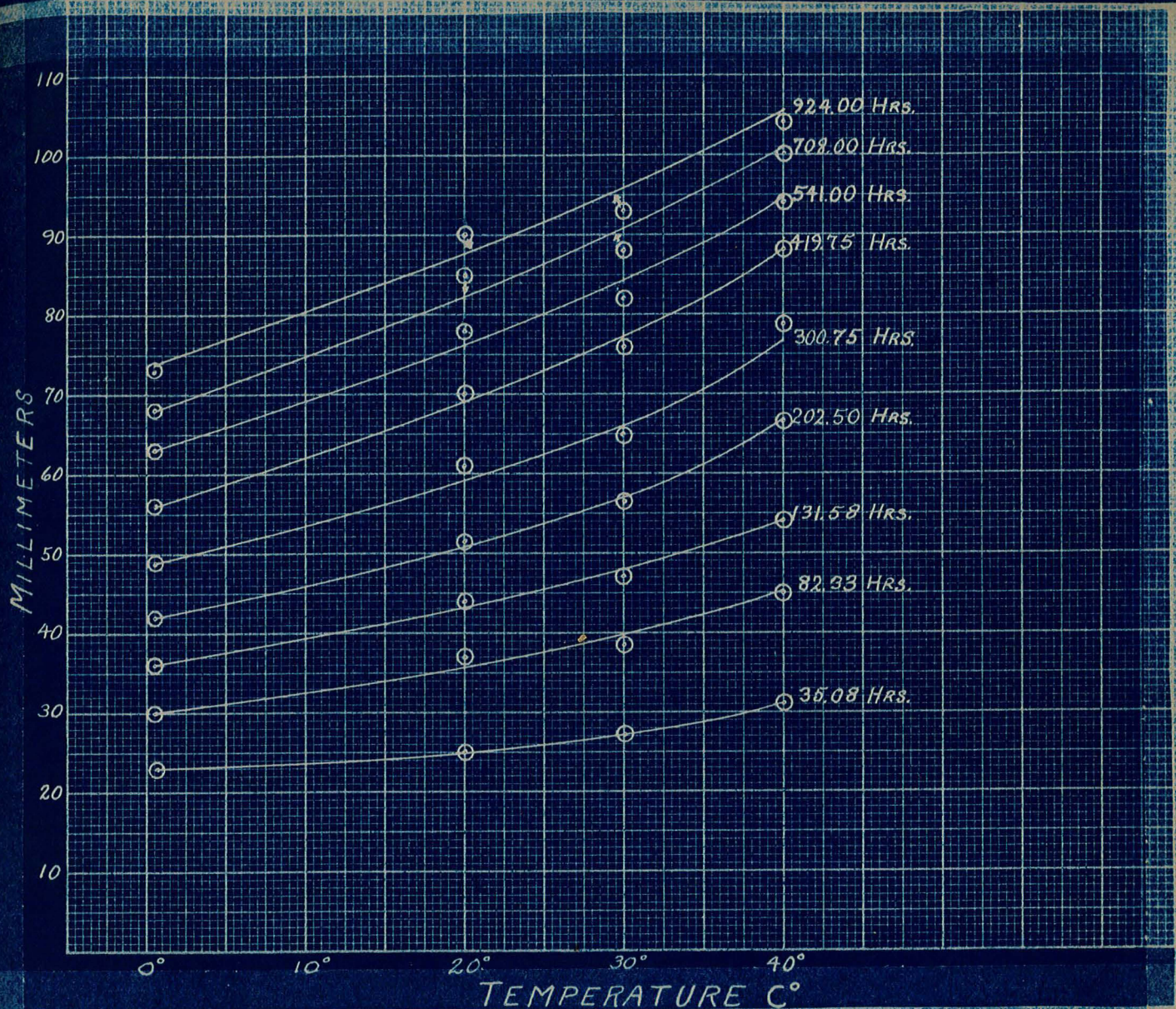


Fig. 8

Showing the relation between temperature and amount of crystal advance (distance from meniscus of gel to farthest point of downward progress of crystal growth) in gels containing .4291 N.  $\text{H}_2\text{SO}_4$ . The resultant normality of the entire content of this gel was calculated to be .0968 N. in the acid range.

Room temperature is plotted as 20 C°.



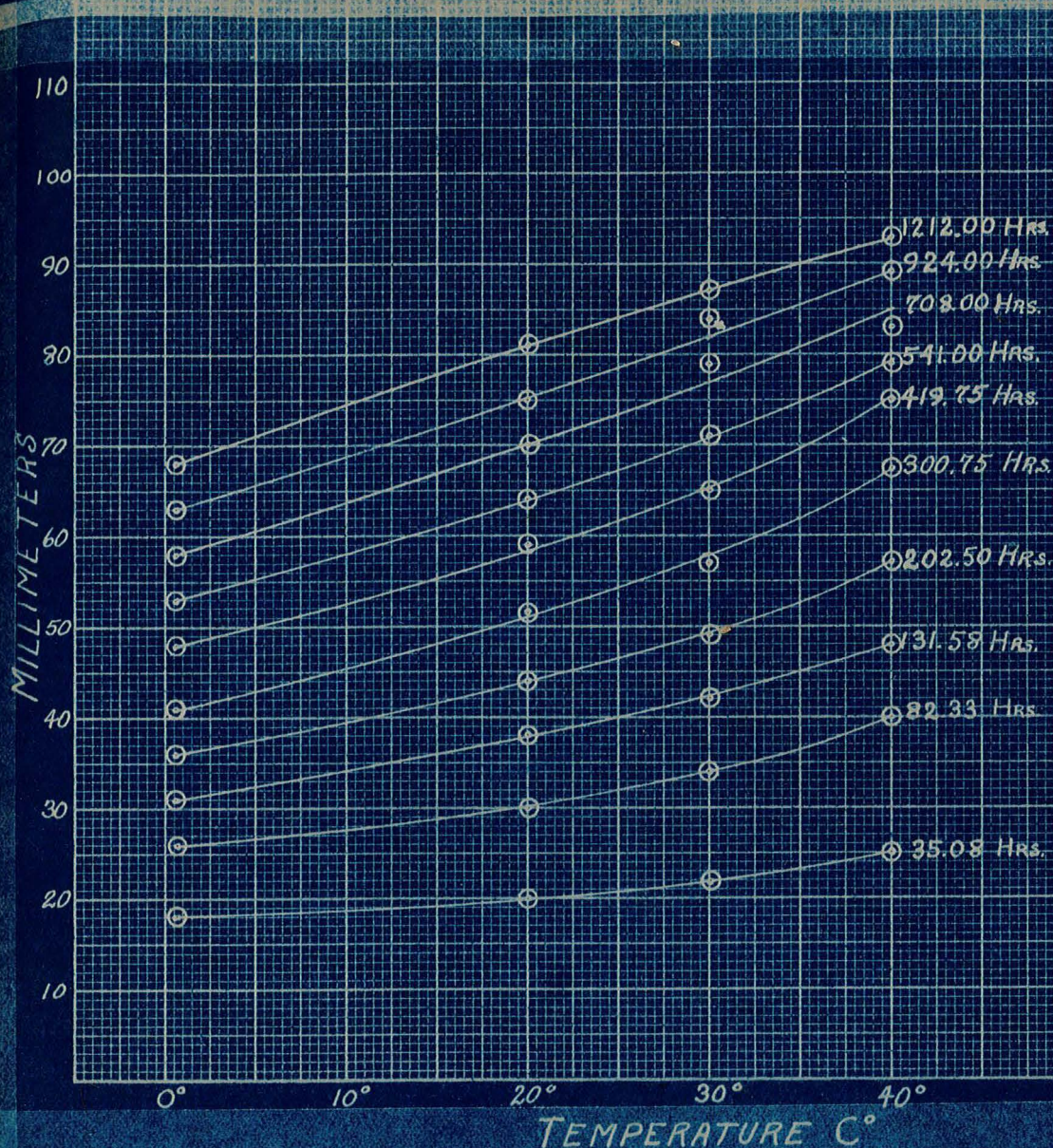


Fig. 9

Showing the relation between temperature and amount of crystal advance (distance from meniscus of gel to farthest point of downward progress of crystal growth) in gels containing .6436 N.  $\text{H}_2\text{SO}_4$ . The resultant normality of the entire content of this gel was calculated to be .1922 N. in the acid range.

Room temperature is plotted as 20 C.



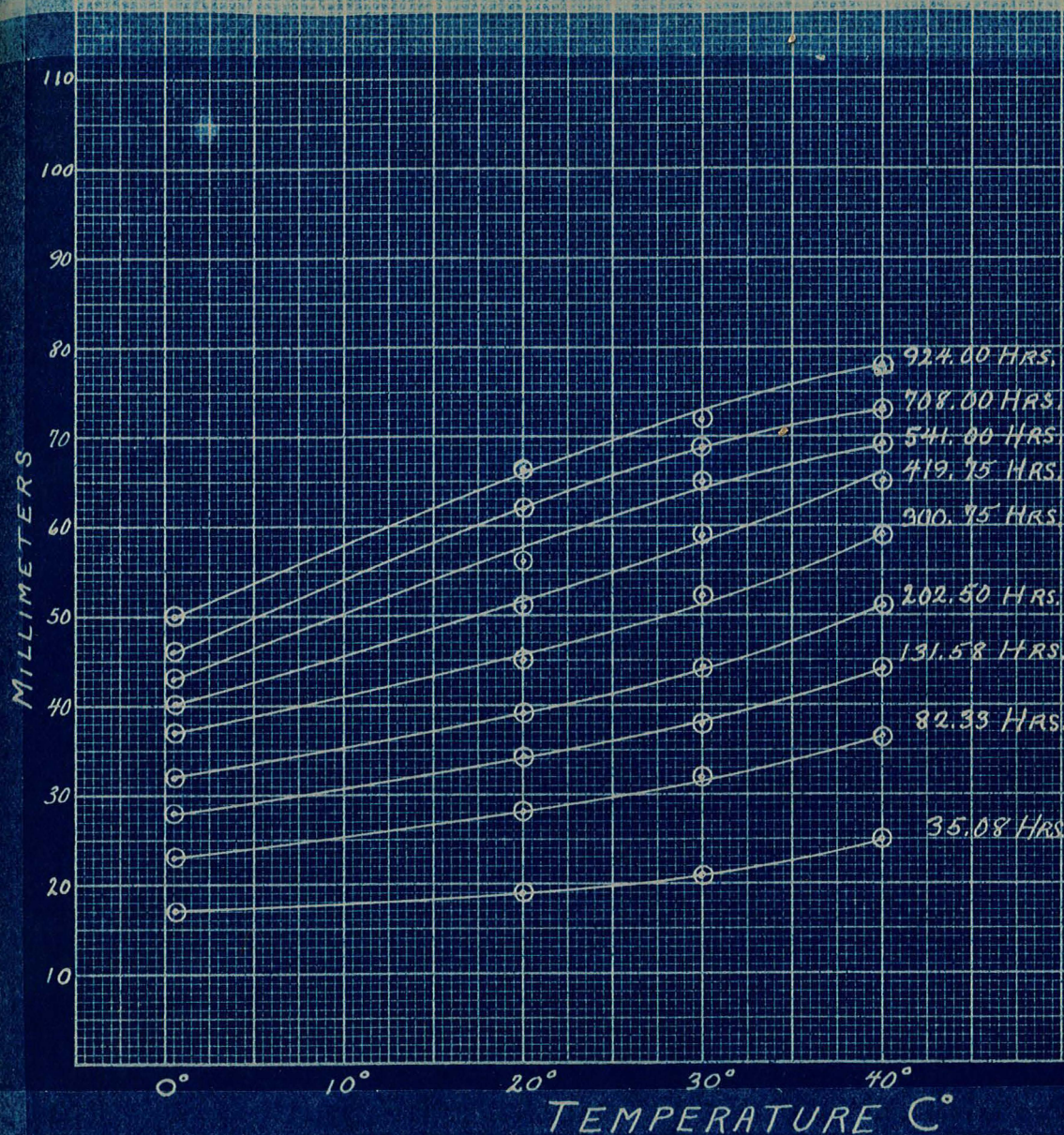


Fig. 10

Showing the relation between temperature and amount of crystal advance (distance from meniscus of gel to farthest point of downward progress of crystal growth) in gels containing .8548 N.  $\text{H}_2\text{SO}_4$ . The resultant normality of the entire content of this gel was calculated to be .2149 N. in the acid range.

Room temperature is plotted as 20 C°.



MILLIMETERS

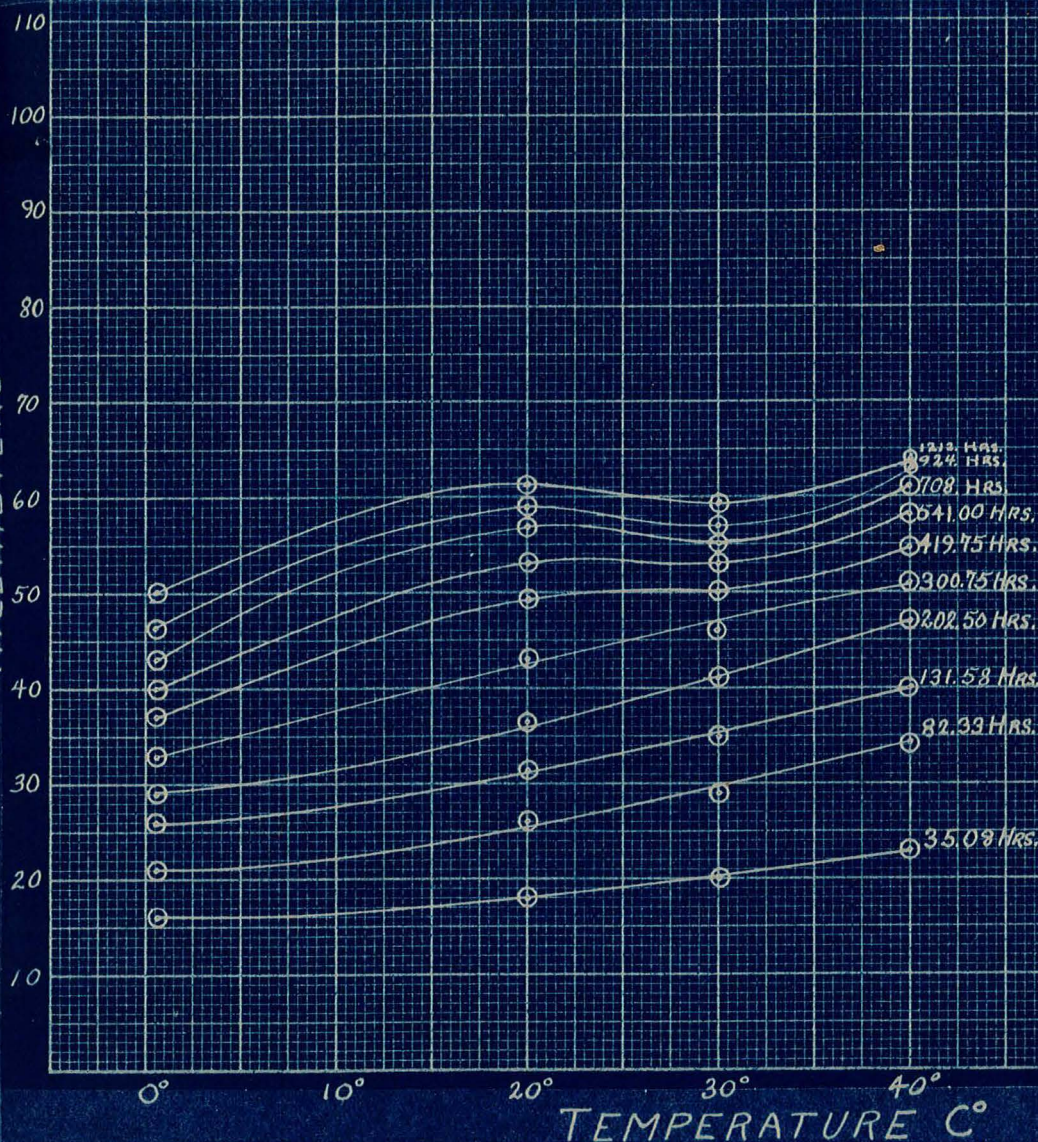


Fig. 11

Showing the relation between temperature and amount of crystal advance (distance from meniscus of gel to farthest point of downward progress of crystal growth) in gels containing 1.0774 N.  $\text{H}_2\text{SO}_4$ . The resultant normality of the entire content of this gel was calculated to be .3850 N. in the acid range.

Room temperature is plotted as 20 C°.



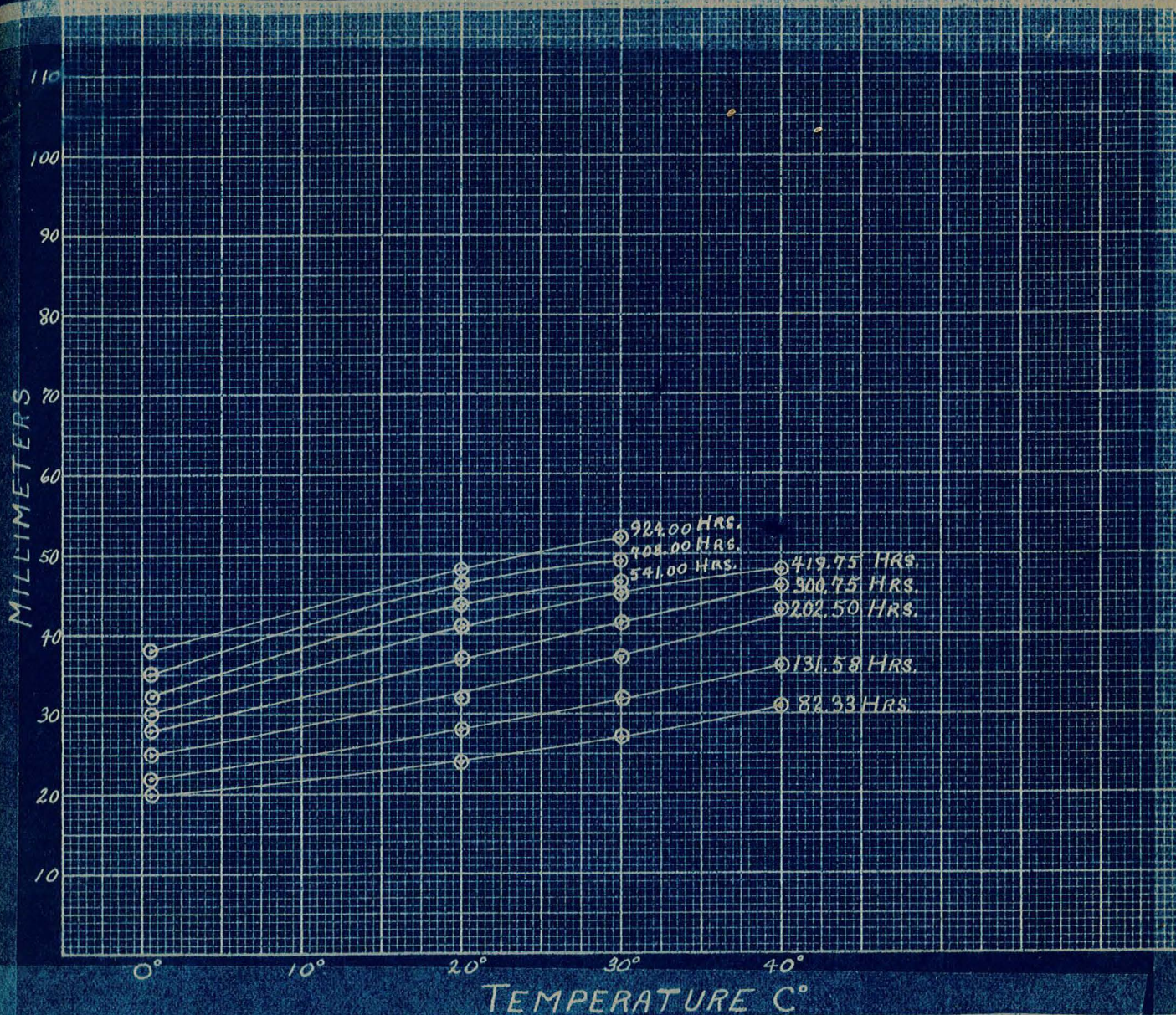


Fig. 12

Showing the relation between temperature and amount of crystal advance (distance from meniscus of gel to farthest point of downward progress of crystal growth) in gels containing 1.2936 N. H<sub>2</sub>SO<sub>4</sub>. The resultant normality of the entire content of this gel was calculated to be .4811 N. in the acid range.

Room temperature is plotted as 20 C°.



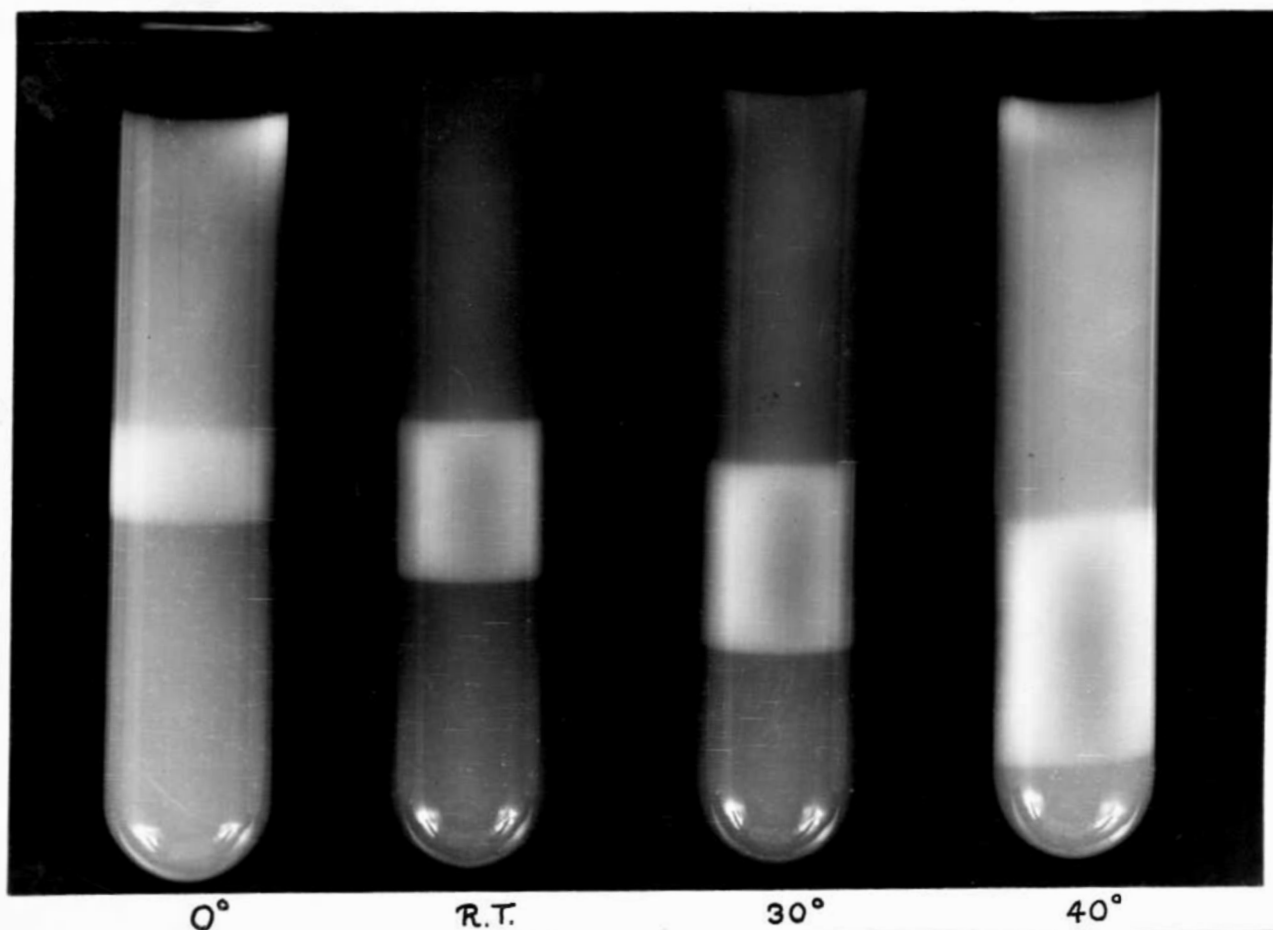


Fig. 13

Showing growths after 188 hours (since addition of diffusing agent) in gels containing .2077 N  $\text{H}_2\text{SO}_4$ . The resultant normality as a base of the entire content of this gel was calculated to be .0016 N. The above gels are of identical composition, but were kept at the following temperatures: 0° C, room temperature, 30° C, and 40° C, respectively.

The white bands are composed a very fine particles; no individual crystals could be discerned with the naked eye in any of the gels of this normality.

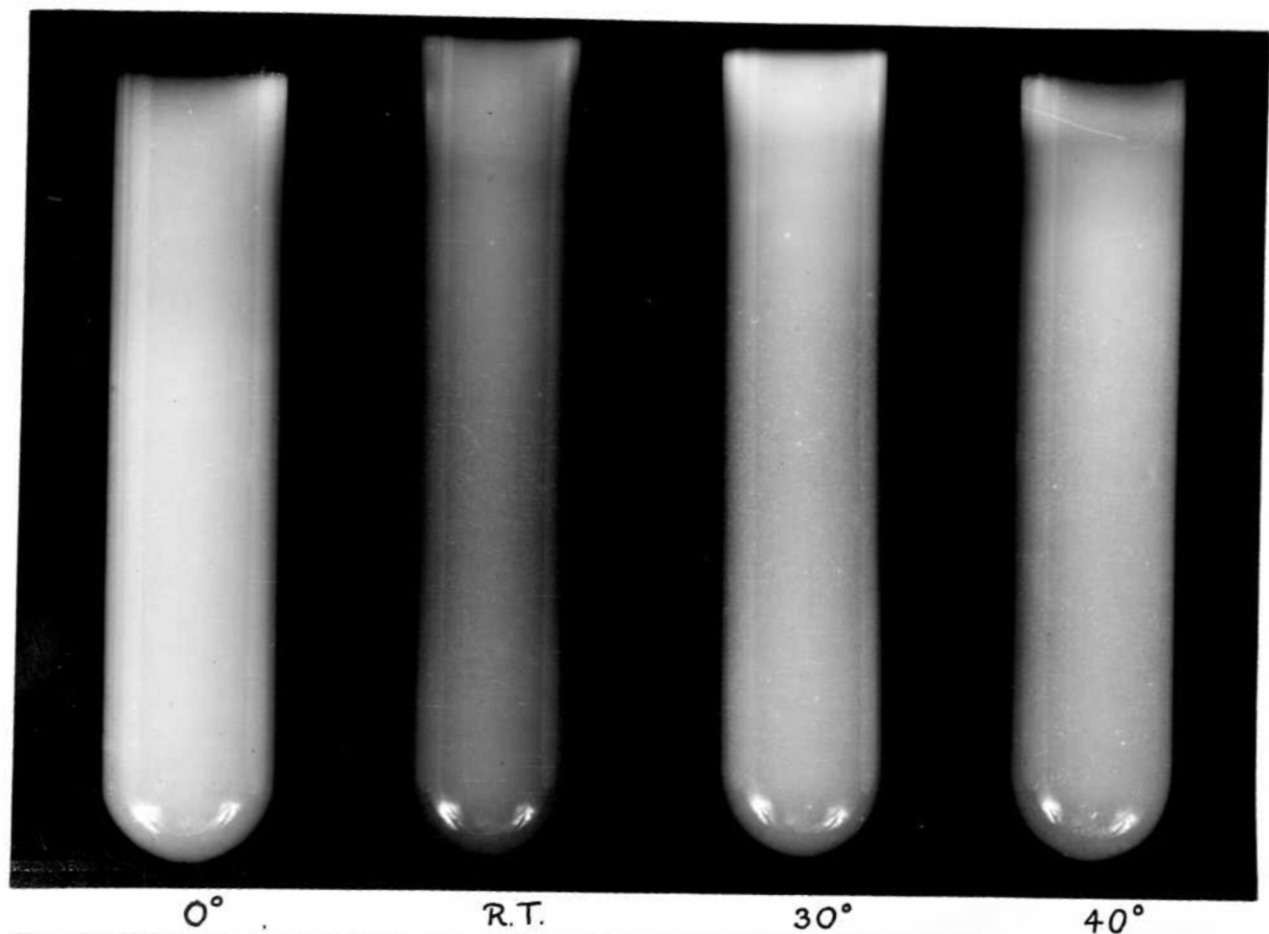


Fig. 14

The above are the same gels as shown in Fig. 13; but after 1218 hours of growth.

The white bands have entirely disappeared. Many minute spherical particles are present in all the gels except the one farthest to the left (one kept at  $0^{\circ}\text{C}$ ). This gel appears in the photograph to be filled with fine white particles; this is due to reflection of light by the surface of the tube, as this gel was really clear.

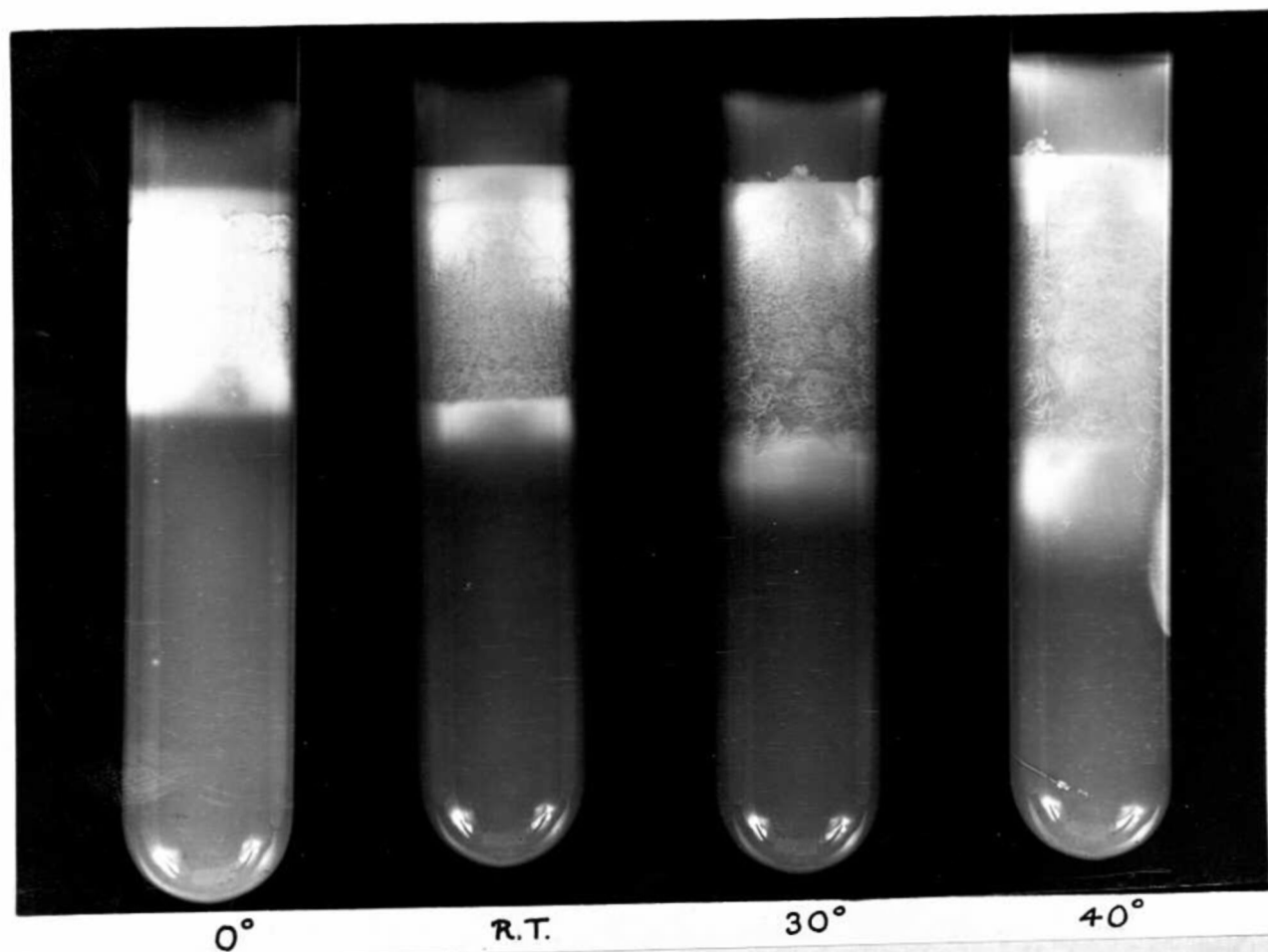


Fig. 15

Showing growths after 188 hours ( since the addition of the diffusing agent) in gels containing .4291 N  $H_2SO_4$ . The resultant acid normality of the entire content of this gel was calculated to be .0968 N. The above gels are of identical composition, but were kept at the following temperatures: 0°C, room temperature 30°C, and 40°C, respectively.

The shape of the crystals is quite different from that of any of the growths in gels of other normalities. It can be seen that the crystals are larger in gels kept

at higher temperatures; also, it appears that the higher the temperature the greater the amount of crystal growth as determined by the amount of crystal advance and width of band. The succeeding photographs show this to be true of all other crystal growths studied.

The gel farthest to the right had cracked after 44 hours of growth.

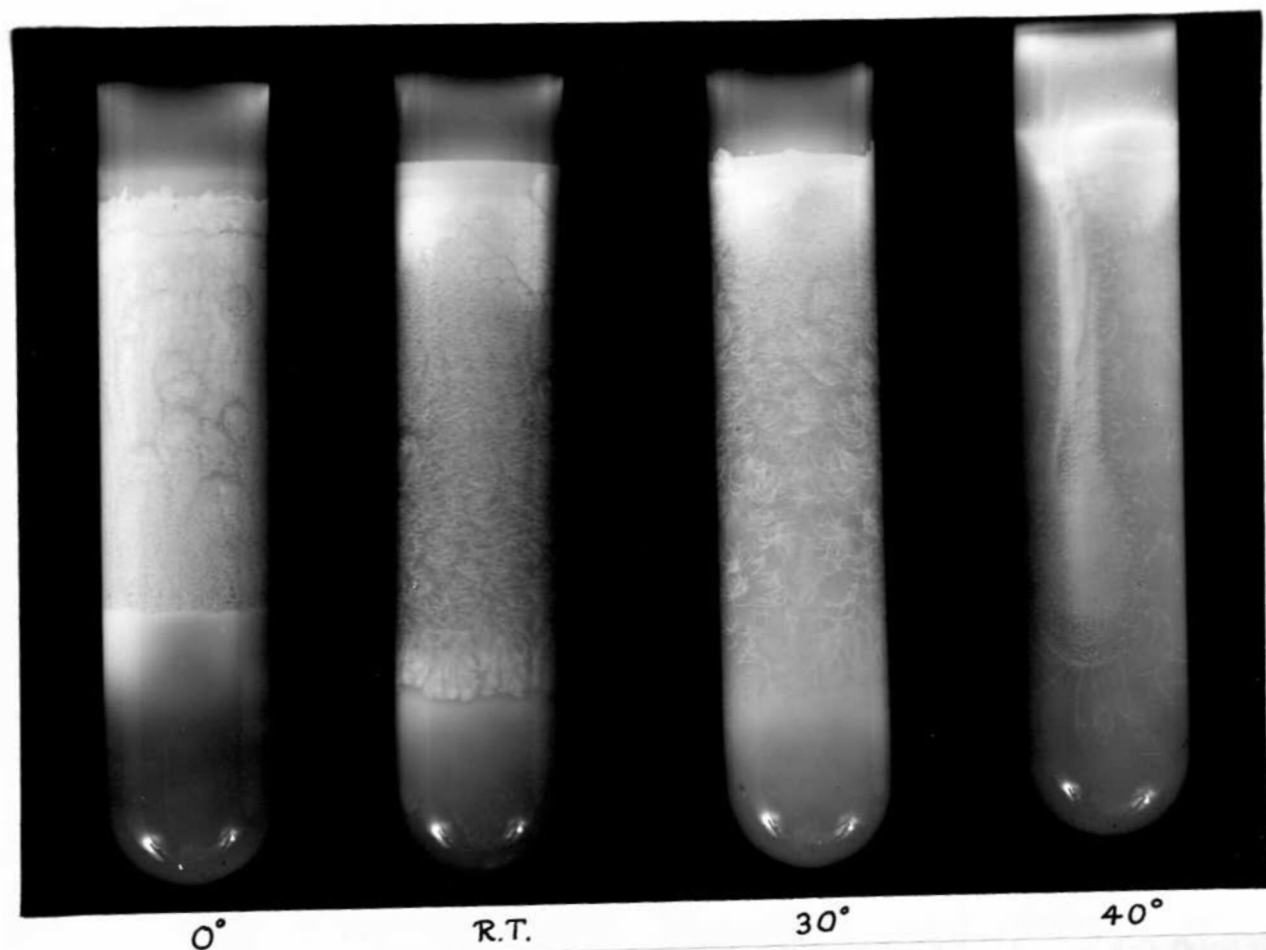


Fig. 16

The above are the same gels as shown in Fig. 15; but after 1218 hours of growth.

The crystals toward the top of the gels are smaller than those lower in the tube. This fact is shown by the succeeding photographs to be true also of all other crystal growths.

The effect of cracking can be clearly seen in the gel farthest to the right.

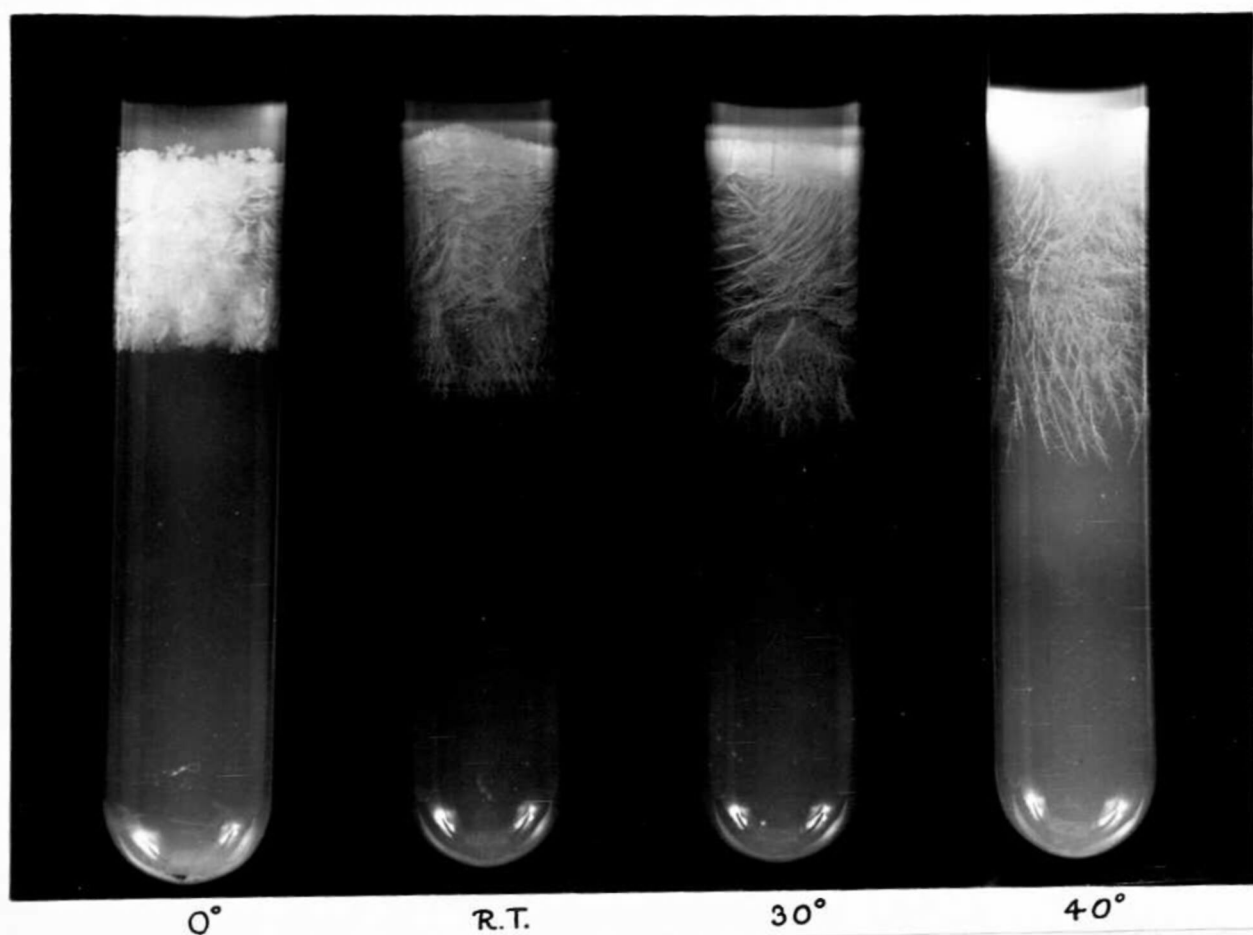


Fig. 17

Showing growths after 188 hours (since the addition of the diffusing agent) in gels containing .6436 N  $\text{H}_2\text{SO}_4$ . The resulting acid normality of the entire content of this gel was calculated to be .1922. The above gels are of identical composition, but were kept at the following temperatures:  $0^\circ\text{C}$ , room temperature,  $30^\circ\text{C}$ , and  $40^\circ\text{C}$ , respectively.

Note the effect of temperature upon the size and shape of crystals, amount of advance, and width of band.



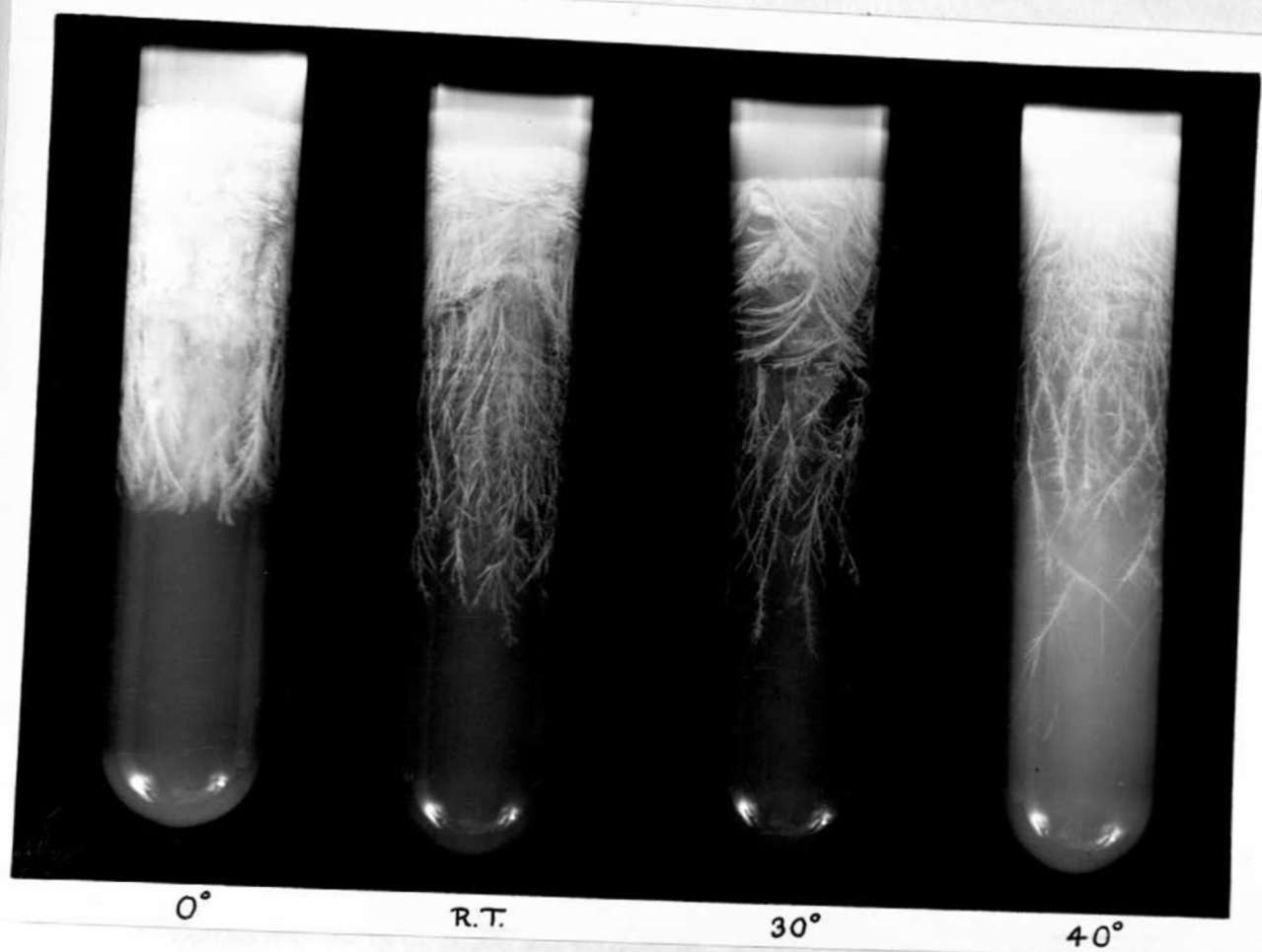


Fig. 18

The above are the same gels as those shown in Fig. 17; but after 1218 hours of growth.

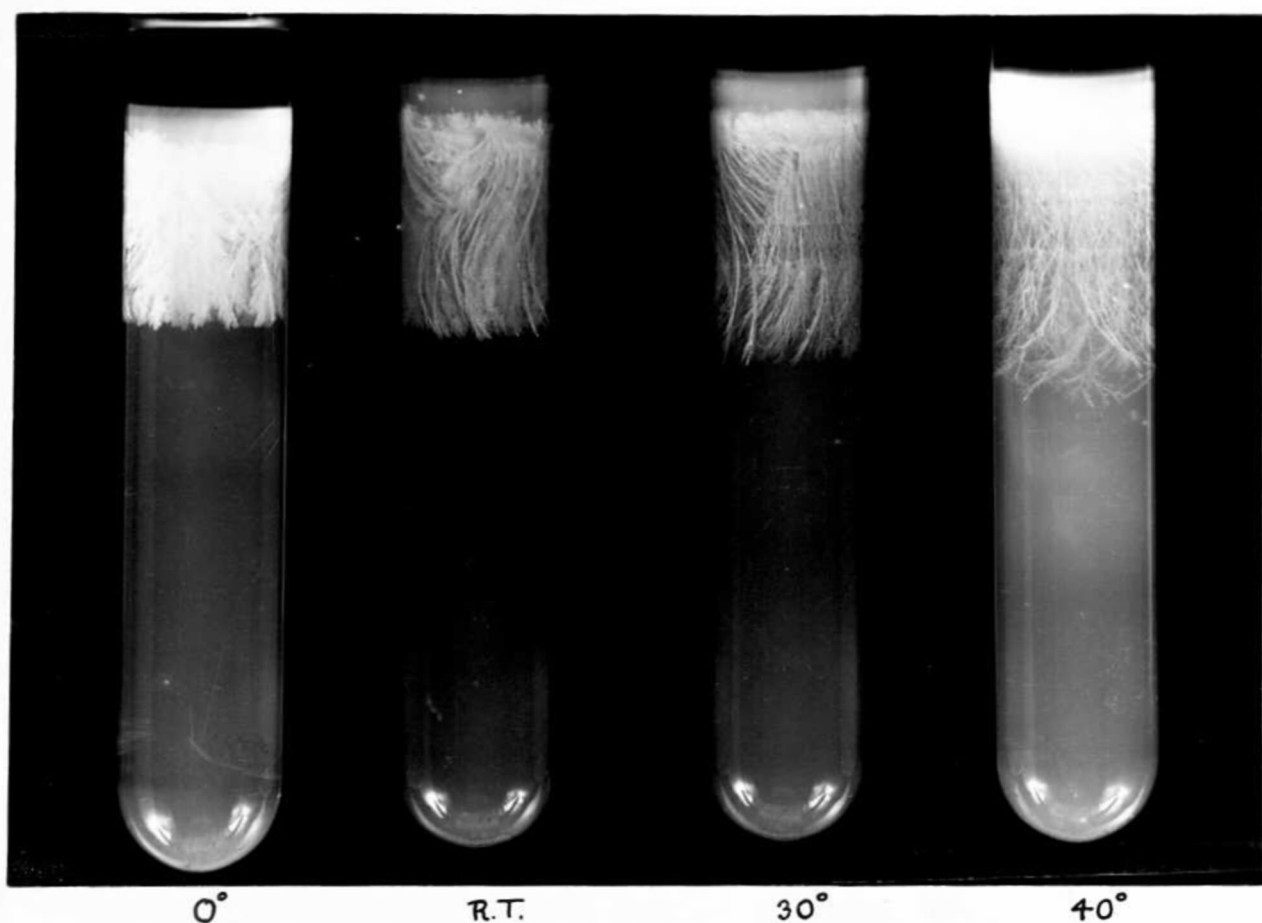


Fig. 19

Showing growths after 188 hours (since the addition of the diffusing agent) in gels containing .8548 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of this gel was calculated to be .2149 N. The above gels are of identical composition, but were kept at the following temperatures:  $0^\circ\text{C}$ , room temperature,  $30^\circ\text{C}$ , and  $40^\circ\text{C}$ , respectively.

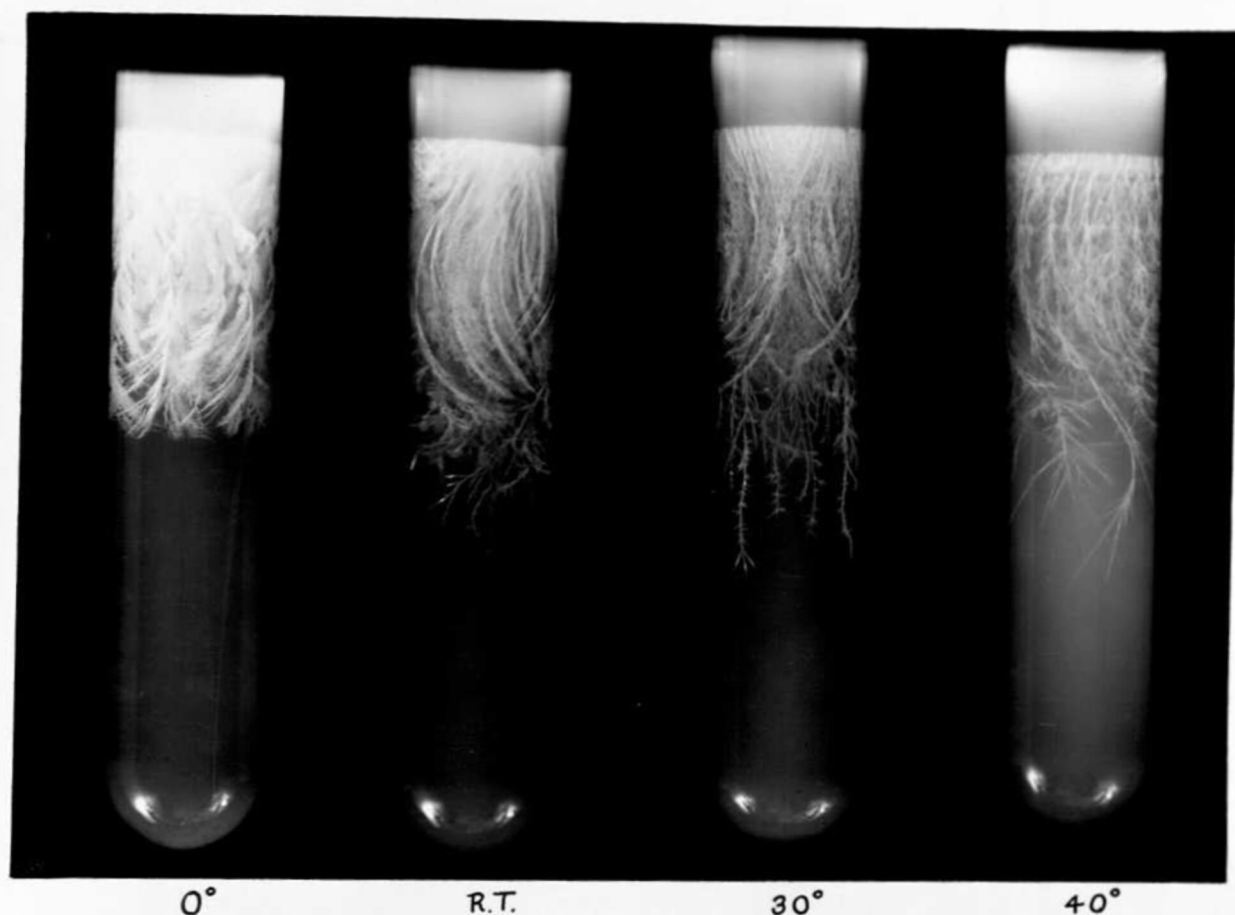


Fig. 20

The above are the same gels as those shown in Fig. 19; but after 1218 hours of growth.

Note that the upper boundaries of crystal growths have moved farther downward in the gels kept at the higher temperatures. Although the amount of advance (distance from meniscus of gel to farthest point of advance of crystal growth) increases with temperature it can be seen that the compactness of the growths decreases with temperature. This is true of all the crystal growths studied.

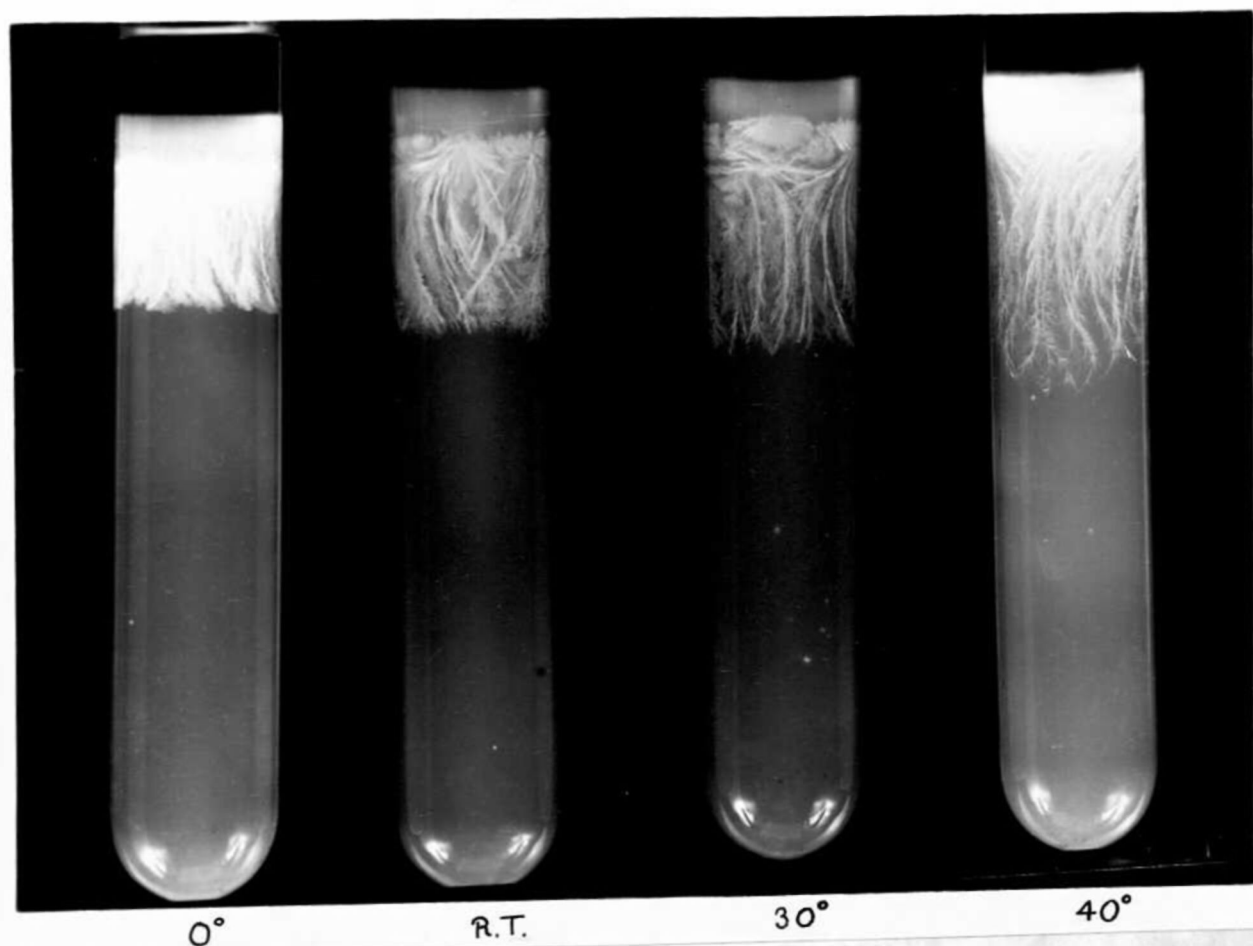


Fig. 21

Showing growths after 188 hours (since the addition of the diffusing agent) in gels containing 1.0774 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of this gel was calculated to be .4811 N.

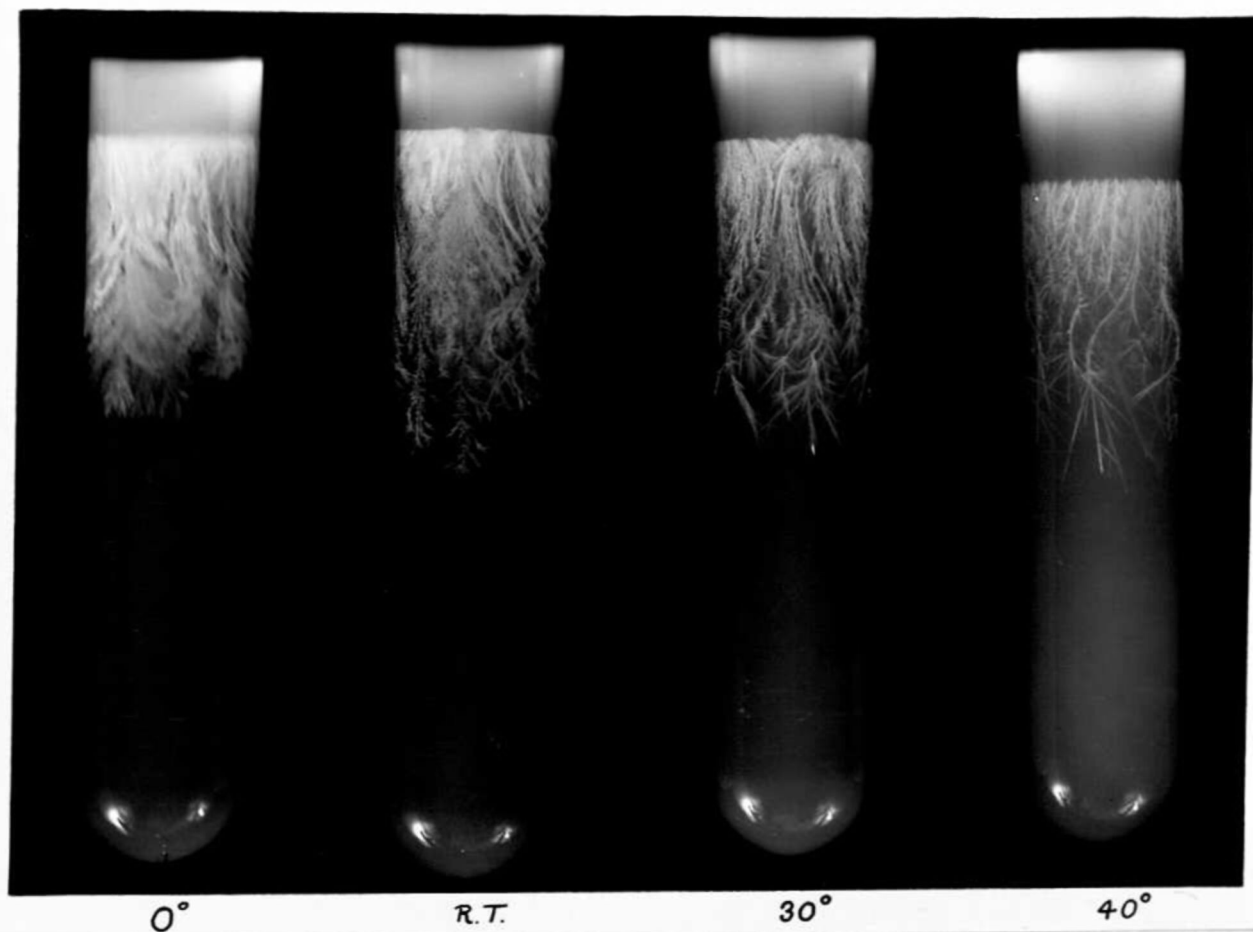


Fig. 22

The above are the same gels as those shown in Fig. 21; but after 1218 hours of growth.

The downward migration of the upper boundary of the crystal growth has been greater in this set of gels than in the gels shown in Fig. 20.

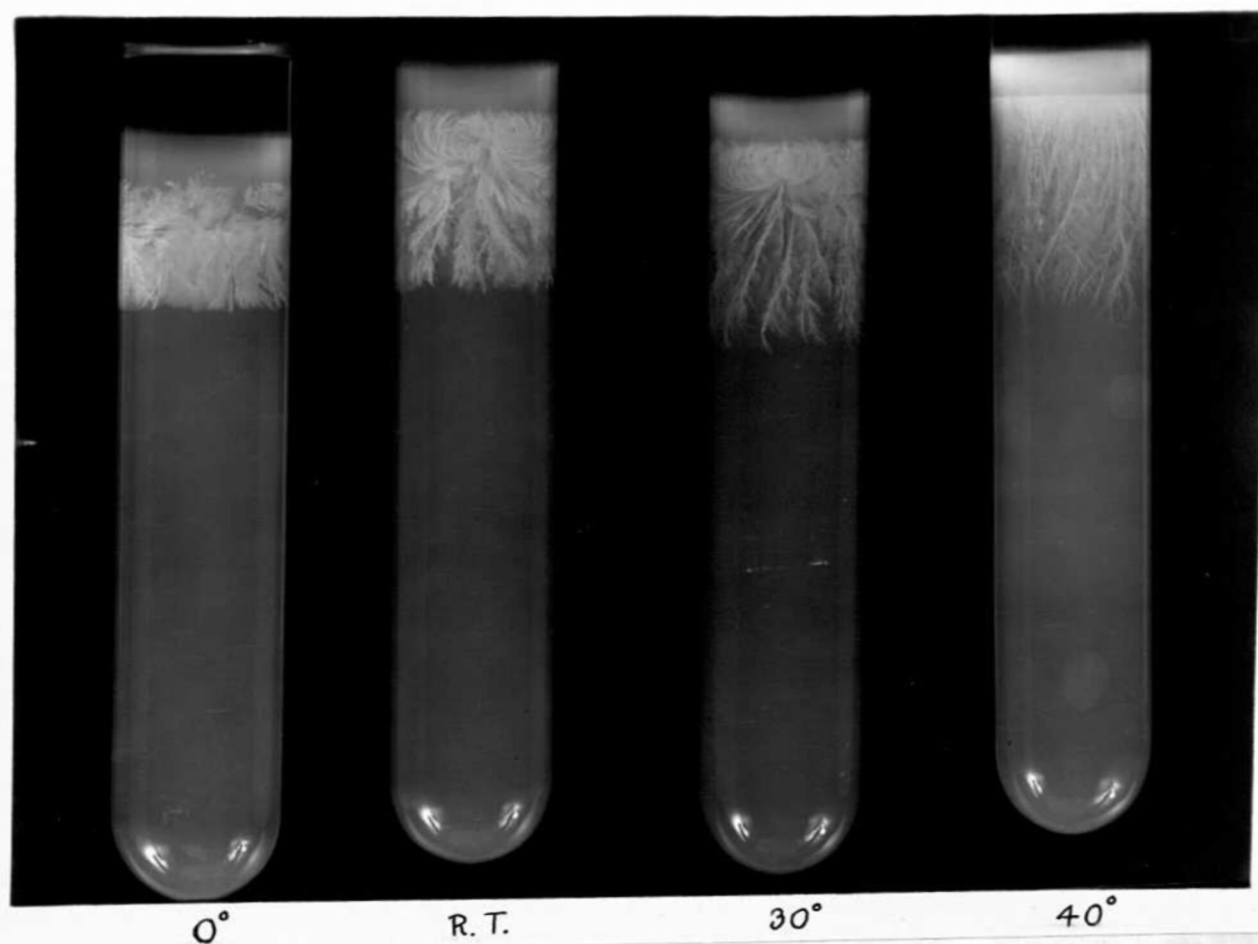


Fig. 23

Showing growths after 188 hours (since the addition of the diffusing agent) in gels containing 1.2937 N  $\text{H}_2\text{SO}_4$ . The resultant acid normality of the entire content of this gel was calculated to be .4811 N.

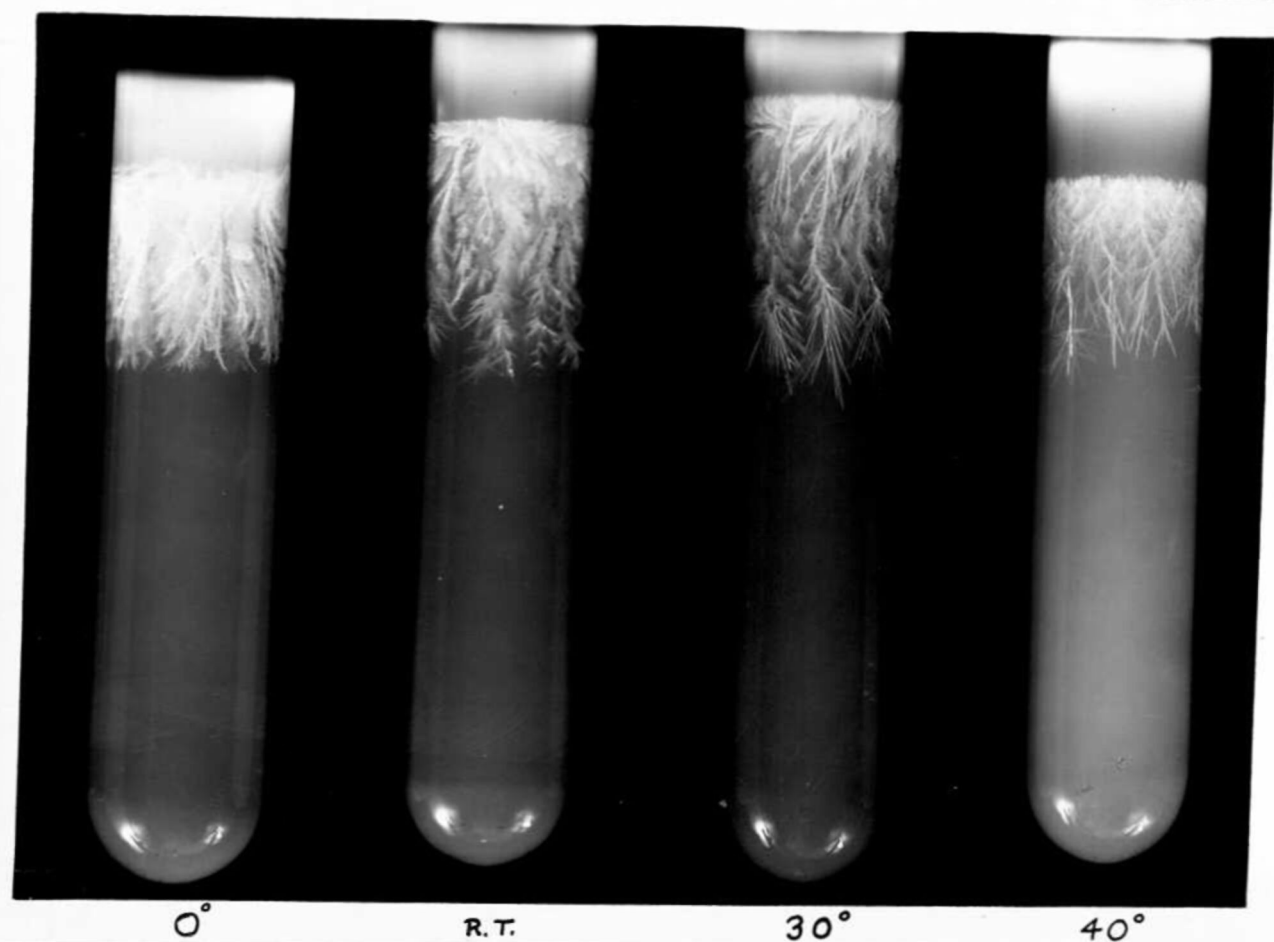


Fig. 24

The above are the same gels as those shown in Fig. 23; but after 1218 hours of growth.



## CHAPTER VII

## SUGGESTIONS FOR FUTURE WORK ON THE PROBLEM

Temperature recording devices could be used to advantage in work of this nature.

Water baths are definitely superior to air baths for maintaining constant and uniform temperatures.

The test tubes used in this study were not of uniform diameters. More accurate results should be possible with tubes of uniform bore.

The error involved in measuring the extent of crystal growths could be reduced by use of more refined methods of measurement. Very accurate results could be obtained by use of a cathetometer, but the additional time required might not justify its use. A system of measurement whereby the position of the crystal band might be ascertained without removing the gels from the temperature baths or otherwise disturbing them would be preferable to the method used in this study. This might be done by the attachment of millimeter scales at the side of each tube with provision for adequate illumination to facilitate the taking of readings from without the temperature baths.

If gels are to be kept at temperatures higher than 35° C it would be well to use a method of sealing other than by sealing wax. Sealing wax becomes soft at these



temperatures; this results in imperfect sealing. Cellophane well cemented around the sides of the tube with an appropriate cement is suggested in preference to wax.

It might be better to use a water glass solution of greater purity than the commercial grade.

In determining the effect of temperature upon any chemical action it would be well to regulate all other conditions which might affect the reaction in question. It may be that crystal growths in gels are affected differently by light of different intensities and frequencies. It would be better in a study of this nature to provide uniform conditions of illumination for all the gels. The easiest way of doing this would be by keeping all gels in the dark except when making measurements.

There are several other possible factors which remain to be fully investigated in the study of the reaction between stannous and arsenate ions in silicic acid gels. A few of these are suggested in the paragraphs to follow.

It is likely that the concentration of the stannous chloride in the gel is an important factor in crystal growth; also, varying the concentration of the sodium arsenate might produce changes in crystal growth.

A determination of the effect of gravity upon the diffusion of sodium arsenate through the gel could be made

by inverting one set of gels, and allowing an identical set to remain upright. Some arrangement would have to be made so as to keep the diffusing agent always in contact with the gel. By uniformly distributing the diffusing agent within a gel in contact with the gel containing the  $\text{Sn Cl}_2$  this condition could be realized. The sodium arsenate could be mixed with sodium silicate solution and acid of such quantity and concentration as to form a quick setting gel. The resulting solution could be poured on top of the gel containing the  $\text{Sn Cl}_2$ ; when the solution has set to a gel the tube could be inverted without removing the contact of the diffusing agent with the gel containing the  $\text{Sn Cl}_2$ .

It may be that this reaction is affected by electromagnetic waves. This could be determined by observation of crystal growth in sets of gels kept at different conditions of electromagnetic illumination. The effect of varying the frequency or the intensity or both could thus be determined. It would be necessary in such a study to keep all the gels at the same temperature.

The exact chemical composition of the crystals formed under the conditions of this study has never been determined. The problem of analyzing these crystal growths presents the experimental difficulty of obtaining pure samples of the crystals free from the gel.

## CHAPTER VIII

## CONCLUSIONS

1. The rate of crystal formation in silicic acid gels by the reaction between stannous and arsenate ions is greatly influenced by temperature.

2. The shape, crystal pattern, and size of crystals are dependent upon the temperature at which the gels are kept during the process of crystal growth.

3. Differences in rate of crystal formation, in shape and size of crystals due to differences in temperature are produced in gels of all acid normalities used in this study.

4. Differences in temperature were found to have little if any significant effect upon the position of the upper boundary of the crystal growth in all gels except those containing 0.2077 N.  $\text{H}_2\text{SO}_4$ . The position of the upper boundary of the crystal growth in gels of this acid content, and of the lower boundary of growth in all the gels is greatly affected by differences in temperature.

5. These differences due to variations in temperature are of greater magnitude in gels of certain acidity than in others.

6. The growth of crystals is not a process of the first or of the second degree; it probably involves simultaneous processes, one a first order process, that of the diffusion of sodium arsenate through the gel, another a second order reaction between the stannous and the arsenate ions.

7. Changes in temperature produce definite and abrupt changes in the shape and size of the crystals in the same gels. This conclusion is a result of observations made after the gels were finally taken from the temperature baths and placed at room temperature.

8. Cracking of silicic acid gels takes place in gels kept at 40 degrees C sooner than in ones kept at lower temperatures.

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