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The effect of pH on the setting of silicic acid gels

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MS 1958
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THE EFFECT OF pH ON THE

SETTING OF SILICIC ACID GELS

by

Ella Rose Kunes

MS 1958

I wish to express my sincere thanks to Dr. George H. Hurd, who has given me encouragement and help, and who has given of his time generously in order that I might finish my research.

I would also like to thank Dr. George H. Hurd, who has been most gracious in his help and Dr. Howard L. Hurd, who has been helpful to me.

A thesis presented to the Department of
Chemistry of Union College in partial fulfillment
of the requirements for the degree of Master of
Science in Chemistry.

By Ella R. Kunes

Approved by Charles B. Hurd

June, 1958

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ACKNOWLEDGEMENT

I wish to express my sincere thanks to Dr. Charles B. Hurd who has given me encouragement and inspiration and who has given of his time generously in order that I might finish my research.

I would also like to thank Dr. George H. Reed, who has been most gracious in answering my questions and granting my requests, and Dr. Howard E. Sheffer whose guidance and advice have been very helpful to me.

Gift of Author October 6, 1958

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INTRODUCTION

The purpose of this investigation was to determine the effect of pH on the time of set of silicic acid gels and to find out how the pH changes as the sol stands, during the setting process. Several theses and papers on the effect of pH on the setting of silicic acid gels have already been written by C.B. Hurd and students at Union College (2, 30, 33-35, 38, 42, 70). This time we were particularly interested in getting accurate results for the alkaline region. The silicic acid gels were made by reaction of sodium silicate and acetic acid. The pH was varied first by using different amounts of acetic acid, keeping the amount of sodium silicate and the total amount of solution constant, and secondly by using different amounts of silicate, keeping the ratio of silicate to acetic acid constant and the total volume of solution constant.

When reading the literature I found that there was some confusion in terminology. In general, the terms " colloidal silicic acid " and " sol of hydrated silica " were used to refer to fluid mixtures containing hydrated silica. The term " silicic acid gel " was used to designate the gel after it had set. The term " silica gel " was used to designate the harder, partially dehydrated gel.

HISTORICAL

A. Preparation

One method used for preparing silicic acid hydrosols is the mixing of sodium silicate with acid. Graham (18) was one of the earliest investigators to work with silicic acid, using this method of preparation. He prepared them by mixing a ten per cent solution of sodium silicate with a ten per cent solution of hydrochloric acid, obtaining a solution of silicic acid which formed a firm elastic gel on standing (12). Others who used this method of preparation include Bradfield (5), Mylius and Groschuff (63), Hurd (28-46), Kraut (50), Weitz, Franck, and Schuchard (90), Holmes (25), Jordis (48) and Tschermak (87). Ray and Ganguly (75,76) made a quantitative study of the best pH range for the formation of gels at each concentration of silicate.

Hydrolysis of various silicon compounds is another method used for preparing silicic acid hydrosol. Some of the compounds which have been used are SiCl_4 (91,21), tetraethyl orthosilicate and methyl orthosilicate (7,8).

Sols of silicic acid can also be prepared by electrolyzing solutions of sodium silicate using a Hg cathode and an inert anode (53). When a 1.5% solution of silicate was used the resulting sol, which was neutral to litmus, set in four weeks. When a 30% solution of silicate was used SiO_2 separated on the anode and prevented further electrolysis.

Other methods of preparation which have been used include hydration of SiO_2 in bomb at 400°C , oxidation of SiH_4 , and peptization of silicic acid gel by potassium hydroxide.

To obtain a silicic acid gel from the sol, merely let the sol stand.

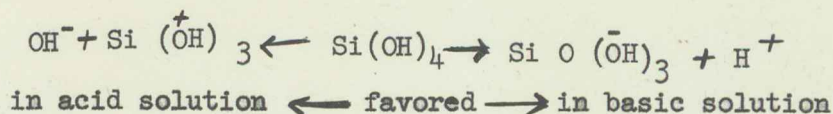
B. Mechanism of Setting

Pappada (67,68) studied the mechanism of coagulation using electrolytes. He postulated that the silicic acid structure behaves as if it is made up of capillary vessels between the walls of which water establishes a double electric layer. As the ions of the electrolyte diffuse into these membranes the charge on the membranes is neutralized by the ions of opposite sign and the gel sets.

Modern theory postulates that the process of setting of the gel involves condensation of Si (OH)₄ groups to form Si-O-Si bonds and elimination of water (29) Monomeric orthosilicic acid condenses to form polyorthosilicic acid. Molecular weight determinations and pH measurements substantiate this theory. A molecular weight of 147 has been determined for the sol particles when first prepared (84). This molecular weight gradually increases, and continues to increase even after the gel is set, up to about 8000. For most silicic acid gels the hydrogen ion concentration is higher at first than it is after some time has elapsed. This decrease in hydrogen ion concentration could be caused by polymerization because some of the hydrogen atoms in the polymerized compound are not able to ionize as easily as in the monomer. Decreasing solubility as the gel sets also substantiates the polymerization theory.

The cause of this polymerization has been a subject of study. Treadwell and Wieland (86) advanced the theory that the tetravalent silicon is still unsaturated in coordinate valence. Another cause of polymerization is found in the amphoteric character of the silicic acid sol (85,91), the value for the acid ionization constant being about 2×10^{-10} . Particles of the sol are positive in strongly acid solution and negative in weakly acid, neutral, and basic solution.

The isoelectric point changes slightly with the age of the sol (19). The following equation represents the equilibrium between the ions:



Efremov and Nerpin (11) have recently written an article comparing the setting of a gel to the conversion of a liquid molecular structure into a solid. The shear stress involved suggests an analogy between the two mechanisms.

Sen and Ghosh (78) developed an equation for the gelation time t , assuming that t of silicic acid sols is inversely proportional to the velocity constant of gelation. The Arrhenius equation $\frac{d \ln k}{dt} = \frac{E}{RT^2}$

was applied by putting $k = \frac{K}{t}$ where K is a constant. The equation becomes $\frac{d \ln t}{dt} = \frac{-E}{RT^2}$ or $\log t = \frac{E}{2.303RT} + \text{constant}$.

For sols of a single type of acid system the gelation time at one temperature and pH were inversely proportional to the square of SiO_2 concentration.

Yadova and Ghosh (92) found that the times of set of pure silicic acid gels and of gels formed by the interaction of sodium silicate with iron and chromium chlorides obey the equation $\frac{1}{t} = \frac{Bc}{Ae}$,
 t = time of set, c = concentration of SiO_2 and A and B are constants.

C. Factors Influencing the Time of Set

The effect of temperature on the time of set was investigated by C.B. Hurd and his co-workers (28, 40, 41, 70). Solutions of sodium silicate were treated with varying amounts of acids.

Some of the acids used were acetic, tartaric, and succinic. The initial concentration of the SiO_2 was kept constant. The setting of a silicic acid gel is a chemical reaction and in general, it is hastened by raising the temperature. However, above pH 10.5 raising the temperature increases the time of set. A rise in temperature at these higher pH values increases the dissolving of the gel more than it increases the rate of gel formation. The average heat of activation for the reaction taking place during the setting of the gel was found to be 16,640 calories.

Hurd and his co-workers (2, 30, 33-35, 38, 42 70) and Prasad (71) have studied the effect of hydrogen ion concentration on the time of set. A flat minimum time of set was found near the neutral point. Between pH 4.2 and 5.5 the time of set was a linear function of the pH. With strong acids, such as HNO_3 , HCl , H_2SO_4 and H_3PO_4 , the pH varied as setting proceeded. These solutions were not well buffered.

The effect of varying the soda-silica ratio of the original silicate on the time of set has also been studied (32, 40). The ratio was varied from 1:2.00 to 1:3.85. No effect upon time of set was found. The time of set was discovered to be inversely proportional to the square of the silica concentration at a fixed temperature and pH (43).

Another factor which has been studied is the effect of electrolytes on the time of set (24, 72, 79). The presence of neutral salts decreases the time of set, but not to the extent that they decrease it for a hydrophobic salt like As_2S_3 . Anions decrease the time of set in the order $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$. According to Laskin (55) the coagulating action of electrolytes is due chiefly to the dehydrating action of the strongly hydrated ions on the colloid particles.

Non-electrolytes have some effect on the time of set, but not as much as electrolytes do (57, 59, 60, 61). When the system is acidic all the alcohols act as retarders. When it is alkaline only the higher polyhydric alcohols act in this manner. The monohydric alcohols and glycol change from accelerators to retarders between pH 7.4 and 8.5 (60). The longer-chain alcohols are more effective than the shorter-chain ones. The organic anions decrease the time of set in this order: tartaric > formic > trichloroacetic > acetic > citric (73)

Solutes such as amyl alcohol, methylamine, dimethylamine, trimethylamine, pyridine, and phenylamine decrease the time of set, mainly by increasing the pH of the mixture (31).

Some other substances which have been investigated are diacetone alcohol, propionaldehyde, xylose, and rhamnose (61). These all showed curves similar to those obtained for the alcohols. Hexoses decreased the time of set throughout the pH range. Ethyl acetate increased the time of set, probably because acetic acid was formed. Benzene showed little effect.

The time of set varies slightly with the commercial brand of sodium silicate which is used.

D. Structure of the Gel

There are three general theories of gel structure (29): the emulsion theory, the cellular theory, and the fibrillar theory.

The emulsion theory (65,66) assumes that the gel has an emulsoid structure. This theory is refuted by viscosity and elasticity measurements and stress-strain curves calculated by Hatschek (22).

The cellular theory was proposed by Bütschli (9). It states that droplets of liquid are held in a "honey-comb" structure. Bütschli's observations, which were made by aid of a microscope, seem to

be refuted by Anderson (3) and Zsigmondy (93), who showed that the pores in silicic acid gel are too small to be seen with a microscope. The cellular theory explains the retention of water by a gel and the elasticity of the gel, but does not explain syneresis or evaporation of water from a gel or the fact that there is very little increase in the electrical conductivity as the gel sets (45).

The theory which most people believe now is the fibrillar theory (64). This theory states that the gel structure consists of solid fibers containing liquid in the pores, both solid and liquid phase continuous. Pappada and Sadowsky (68) and Prasad and Hattiangadi (72-74) believed that the gel was formed by simple agglomeration but insensitivity to electrolytes and the fact that sodium sulfate is less effective than sodium chloride in causing the sol to set indicates that the gelling process is not simple coagulation.

This fibrous structure might consist of a mat of crystals. Krejci and Ott (51) found a cristobalite structure in the gel by x-ray analysis. Pascal (69) failed to find any ortho-, meta- or pyro-silicic acid molecules in the gel but did find silica and water. The failure of silicic acid gels to exhibit thixotropy is strong evidence against this explanation of the fibrillar theory.

Other workers have suggested that the fibrous structure is like a "brush-heap" made up of large polysilicic acid molecules with the spaces filled with liquid. When a gel sets, condensation takes place (48), water being split out between 2 simpler silicic acid molecules (32). This structure best explains the insensitivity to electrolytes, the increase in molecular weight on setting, decreasing solubility on setting, absence of increase in electrical resistance, diameter of pores, syneresis, lack of thixotropy, evaporation of liquid, and elasticity.

Later studies by Serikov (81) using X-ray analysis show SiO_2 gel structure to be characterized by ordered regions of atoms joining regions with disordered distribution of atoms. The pores seem to be spherical and their dimensions about 20A. The whole polysilicic acid structure is greatly solvated.

E. Properties

1. Properties of the Sol of Hydrated Silica

The molecular weight of silicic acid when first formed was found to be 60 by Gruner and Elöd (20) and 149 by Treadwell (84). It increases to a value of about 8000. The presence of electrolytes in solution complicates the measurement of molecular weight.

When first formed silicic acid sol passes easily, with the electrolyte, through membranes used for dialysis (6,39,44). As time elapses the silicic acid becomes unable to go through the membrane, indicating that polymerization is taking place.

The electrical charge on the particles is positive in strongly acid solution and negative in other solutions (56). The sol is amphoteric in character and ionization gives the particles their charge.

The sols are transparent when first formed, but become opaque on setting. They show a Tyndall cone after they have stood a while (52). No optical activity has been found (10).

2. Properties of the Gel

One of the most interesting properties of silicic acid gels is the property of exhibiting syneresis (17,26, 27, 58). The gel contracts, squeezing out water. The shrinkage continues even after the gel has set and is probably caused by the continuing process of polymerization.

Silicic acid gels show characteristic resonance frequencies upon excitation by electric waves (27). This resonance can be

detected by the nature of a light beam reflected by the surface of the gel. This property has value in following the progress of polymerization and structure of the gel. Another property which has been useful in following the progress of gelation is surface tension (37).

Silicic acid gels do not show thixotropy (46). When they are broken up and beaten into fine particles, acidic mixtures will reset eight times. Basic mixtures will not reset at all.

Spittle (82) undertook research to determine whether a silicic acid gel could be made which would be reversible with respect to temperature, that is a gel which could be liquefied by heating or cooling. He was unsuccessful in attempts to find reversibility.

Other properties exhibited by silicic acid gels are elasticity (54), vibration when their container is struck a sharp blow (26), and ease of migration of ions through the gels.

EXPERIMENTAL

The sodium silicate used was "E" brand purchased from the Philadelphia Quartz Co., and was prepared by diluting 330 cc of the commercial product with distilled water to make a liter of solution. This silicate solution was 1.41 N when standardized against 1.221 N standard sulfuric acid, using methyl orange as an indicator. The sulfuric acid had been standardized against sodium carbonate.

The acetic acid solution was prepared by diluting 120 cc of glacial acetic acid to make 1 liter of solution. This solution was 2.58 N when standardized against 1.34 N sodium hydroxide using phenolphthalein as an indicator. The sodium hydroxide had been standardized against the 1.221 N standard sulfuric acid, using methyl orange as an indicator. All water used in mixing solutions was freshly distilled so that there wouldn't be too much carbon dioxide in it. Carbon dioxide has a coagulating effect of silicic acid sols.

A simplified form of the reaction which was studied could be represented in this way: $\text{Na}_2\text{SiO}_3 + 2\text{HAc} \rightarrow \text{H}_2\text{SiO}_3 + 2\text{NaAc}$

When the silicate and acetic acid were mixed together there was a heating effect so that the mixture obtained was 2° higher in temperature than the silicate and acetic acid were. For all our experiments we wanted the temperature of the mixture to be 25°C. To correct for the 2° rise in temperature we set up a water bath thermostat consisting of a large tank of water in which the heat was electrically controlled. A shelf of wire mesh was placed about three inches down from the top of the tank and fastened securely with wire to the sides of the tank. When the water bath was in use it was filled with water up to about two inches over the wire mesh shelf. The temperature was set at 23° and beakers containing measured amounts of silicate and acetic acid (in separate

beakers) were placed on the wire mesh shelf and were allowed to remain in the water bath for at least a half hour. Then proceeding with the experiment, the silicate and acid were mixed and temperature of the mixture obtained was 25°C . For the remainder of the experiment the mixture was kept in a pan of water, the temperature of the water being kept at 25°C by adding warm or cold water as needed.

The Beckmann pH meter was used for measuring the pH during the experiments. When using this meter a cell consisting of a glass electrode and a calomel electrode are connected to it. The glass electrode has a thin membrane of glass at the lower end. This membrane separates a .1N HCl solution inside the membrane from the mixture being tested which is outside the membrane. A potential is created which can be measured and which depends on the hydrogen ion concentration of the mixture.

For determining the time of set a number of small glass rods 10 cm. long and 3 mm. in diameter were made. In preparing them a long glass rod was held in the flame until it softened. Then the rod was drawn out and the small 10 cm. rod was cut from the long rod in such a way that the small rod had one end which was tapered to a blunt point. Both ends of the small rod were firepolished. The time of set of a mixture was determined by inserting one of these rods, tapered end first, into the mixture at an angle of about 10° - 20° . If the mixture supported the rod at that angle, the mixture had set.

A typical experiment was conducted in this way: the desired amount of silicate was measured by a pipette and placed in one 100 cc beaker. The desired amount of acetic acid was measured out by a burette into another 100 cc beaker. Water from another burette was added to the acetic acid in sufficient quantity so that later in the experiment, when the acetic acid and silicate were mixed together, the total amount of

mixture would be 80 cc. In all our experiments the total amount of mixture used was 80 cc. The two beakers were covered with watch glasses to prevent evaporation and lead weights were placed on top of the watch glasses so that the beakers wouldn't tip over when put into the water bath thermostat. Then the two beakers were placed on the wire mesh shelf in the water bath thermostat, the temperature of the water being set at 23°C . After they had been there a half hour they were taken out of the bath and the silicate was poured into the beaker containing the acetic acid and water. The mixture was poured back and forth from one beaker to the other seven or eight times to assure adequate mixing. The mixture was then placed in a pan of water, the temperature of the water being kept at 25°C . for the remainder of the experiment. A stop watch was started at the moment the silicate was poured into the acetic acid and water solution and the time was measured up to the time the mixture set, as ascertained by inserting the small glass rod. When the mixture supported the rod at 10° - 20° , it had set, and the time which had elapsed was recorded as the time of set. pH measurements were started on the same sample as soon as the solutions had been mixed and a study was made of the change of pH as the setting process took place.

RESULTS AND DISCUSSION

The results of all the experimental work are summarized in the graphs and the accompanying tables. Most of the work was done on samples containing 25 c.c. of silicate, but some work was done on samples containing 20 c.c., 30 c.c., and 35 c.c. of silicate. In all cases enough distilled water was added to the acetic acid so that the total volume of sample was 80 c.c. after the acetic acid solution and the silicate were mixed.

A commercial brand of silicate was used and when a new silicate solution had to be made up some difficulty was encountered in trying to duplicate exactly the composition of the old silicate solution. The composition of the commercial silicate in one drum can differ slightly from the composition of the silicate in another drum and this difference is a source of error.

The Beckmann pH meter was found to be a satisfactory instrument for measuring the pH. The silicate has a tendency to coat the glass electrode. In the later experiments the electrode showed signs of becoming insensitive, the needle on the pH meter taking a longer time to come to rest. However, the electrode gave satisfactory service for a year.

Little difficulty was encountered in determining the time of set by using the "tilted-rod" method. An erroneous time of set is obtained if the surface of the sample is disturbed too much. To avoid this error several duplicates of each sample were made. From the first samples an approximate time of set was obtained by testing at short intervals after the sample began to assume a milky-white color. This color indicates that the sol is beginning to set. The continuous testing of these first samples disturbed the surface so that only an approximate

time of set was obtained. From the remaining samples an exact time of set was determined by leaving them undisturbed until nearly time for them to set and then testing them with the glass rod.

Curves 1-19 show the change in pH with passage of time, the time of set being indicated by a vertical line. A stop-watch was started at the moment the silicate was poured into the acetic acid and that moment was used as the zero-reference point for measurement of time of set and for all measurements of time intervals indicated on the graphs, in the tables, and in the text. The first pH reading which could be recorded was always taken at the one-minute interval because time had to be allowed for mixing the solutions, inserting the electrodes, and waiting for the needle of the pH meter to come to rest. The acid sols showed very little change in pH with lapse of time. The basic sols, on the other hand, showed a fairly rapid rise in pH the first five or ten minutes. From then on the pH rose slightly, but didn't change very much. In some cases, as shown on the graphs, a downward trend was noticed after the initial rise. Possibly all of the basic gels would have shown a downward trend in pH eventually if time had permitted a thorough investigation and readings could have been taken for each sample after a lapse of several hours from the time of mixing.

Curves 20-23 show the initial pH plotted against the log time of set. Curve 20, for samples containing 25 c.c. of silicate, shows a minimum time of set near pH 7. Insufficient data had been accumulated to show a minimum time of set on curves 21, 22, and 23, which are for samples containing 20, 30, and 25 c.c. of silicate respectively, but in the alkaline range they show increasing length of time of set with increase in pH.

Curve 24 shows the change in time of set with addition of different amounts of acetic acid. All samples represented on this curve

contained 25 c.c. of silicate. This graph shows a minimum time of set when the sample contained 12 c.c. of acetic acid. This sample had an initial pH of 7.13.

Curves 25-27 show the change in time of set with addition of different amounts of silicate, keeping the ratio of silicate to acetic acid constant. Samples containing a higher concentration of silicate took less time to set. It is interesting to note that the curves become nearly parallel as the amount of silicate is decreased.

Curve 28 shows the amount of change of pH (Δ pH) plotted against the initial pH. An extrapolated value for the initial pH was obtained by extending curves 1-9 to the abscissa, where time equals zero. The initial pH values were read from the points where these curves meet the abscissa. The Δ pH used in the graph was calculated by subtracting this extrapolated value of the initial pH from the pH at the time of set. More data should be accumulated to show the exact shape of this curve, but the graph shows that Δ pH increases sharply in the alkaline region. From this graph a rough approximation can be made of the pH rise to be expected for a mixture having a particular initial pH.

The rise in Δ pH substantiates the theory that the gel sets by a polymerization process. There is a decrease in the acidic type of ionization as polymerization proceeds. Basic gel mixtures, when made from acetic acid and silicate, reveal this decrease in ionization because they are not well buffered.

TABLE I

CHANGE OF pH WITH TIME - DATA FOR CURVES 1-9*

Temperature 25°C. 25 c.c. of silicate

pH Readings with Lapse of Time (in minutes)

Curve	c.c.HAc	c.c.H ₂ O	1	3	5	7	10	15	20	30	40	Time of Set (in minutes)
1	16	39	4.40						4.45		4.40	40.17
2	15	40	4.80				4.85		4.83	4.80	4.85	24.25
3	14	41	5.35		5.38		5.40	5.42	5.41			5.67
4	13	42	6.30	6.32	6.32	6.32	6.33					1.33
5	12	43	7.13	7.27	7.33	7.39	7.42	7.48				.88
6	11	44	7.90	8.20	8.19	8.23	8.29	8.34				1.50
7	10	45	9.00	9.15	9.22	9.28	9.33	9.40				3.08
8	9	46	9.59	9.82	9.88		9.90	9.92	10.02	10.08	10.10	28.33
9	8	47	10.22		10.47		10.56	10.57	10.59	10.56	10.56	324.00

* The time of set is indicated by a vertical line.

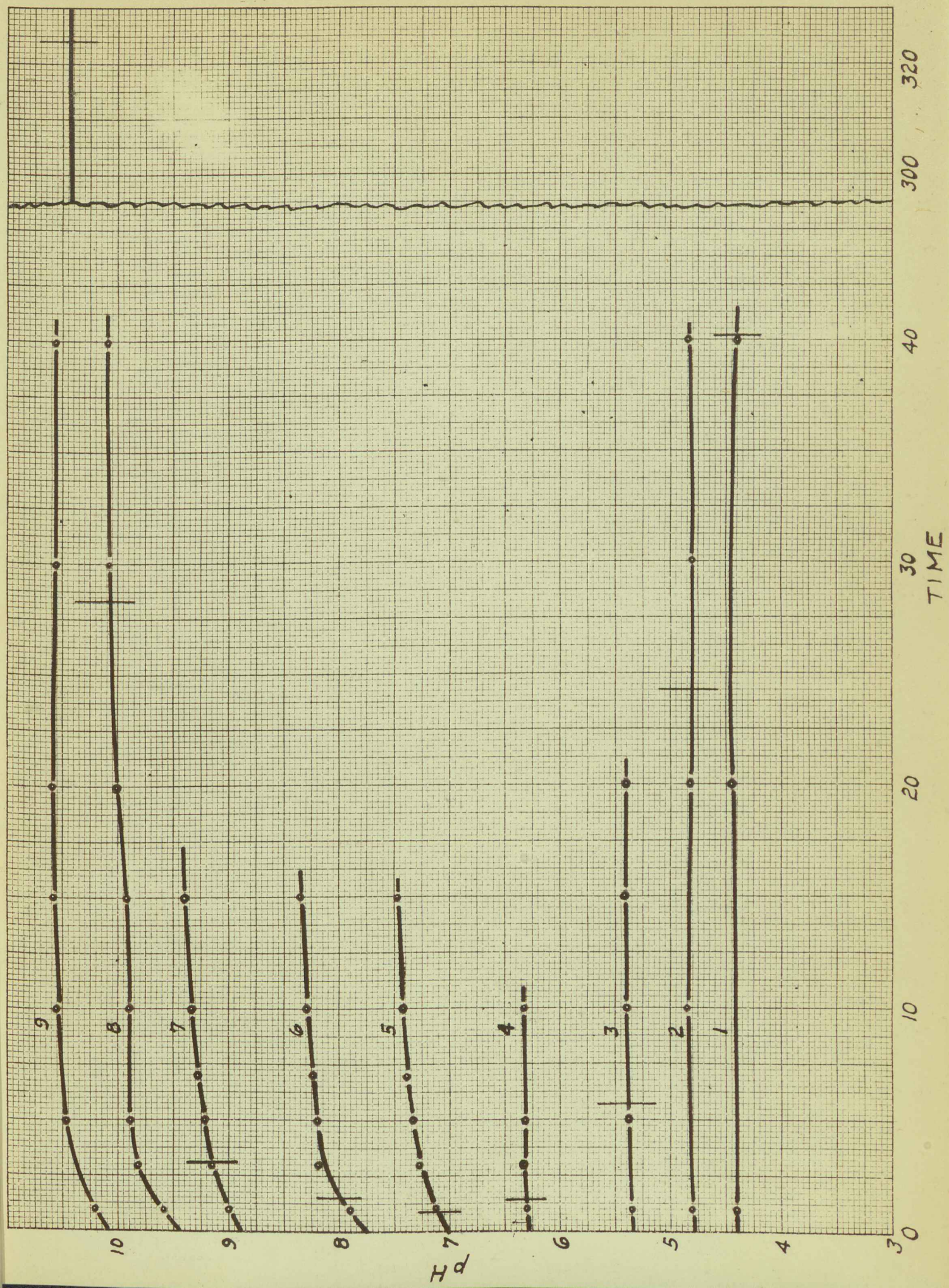


TABLE II

CHANGE OF pH WITH TIME - DATA FOR CURVES 10-12*

Temperature 25°C. 20 c.c. of silicate

pH Readings with Lapse of Time (in minutes)

<u>Curve</u>	<u>c. c. HAc</u>	<u>c. c. H₂O</u>	<u>1</u>	<u>5</u>	<u>10</u>	<u>15</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>60</u>	<u>Time of Set</u>
10	9.6	50.4	8.40	8.52	8.59		8.70			8.85	2.16
11	8.8	51.2	9.02	9.20	9.31		9.35		9.45	9.55	6.75
12	8.0	52.0	9.40	9.68	9.80	9.85	9.88	9.88			41.08

-17-

* The time of set is shown by a vertical line.

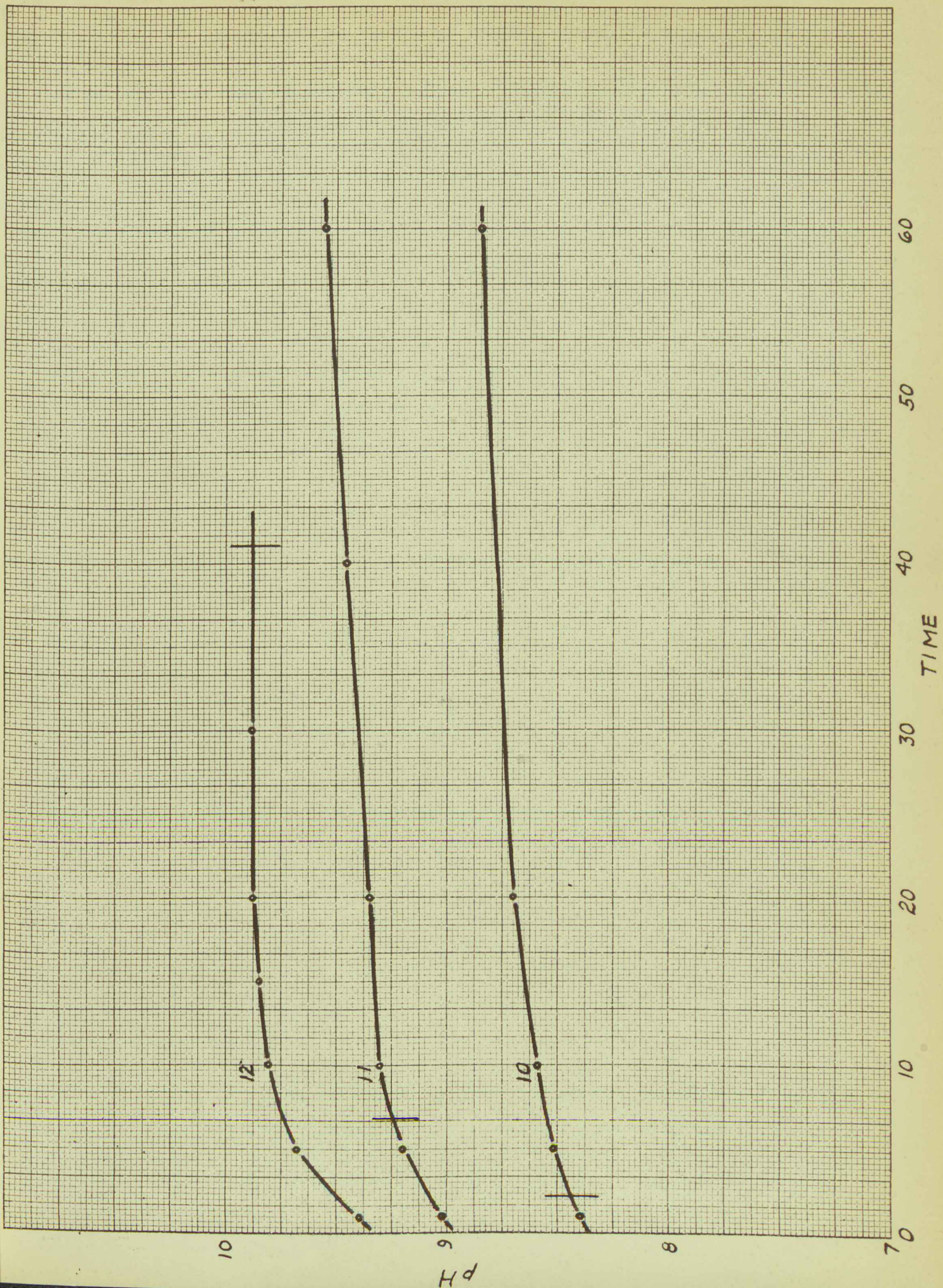


TABLE III

CHANGE OF pH WITH TIME - DATA FOR CURVES 13-16*

Temperature 25°C. 30 c.c. of silicate

Curve	ccHac	ccH ₂ O	<u>1</u>	<u>3</u>	<u>5</u>	<u>7</u>	<u>10</u>	<u>15</u>	<u>20</u>	<u>30</u>	<u>190</u>	<u>220</u>	Time of Set (in minutes)
13	12	38.0	9.65			9.90	9.96	10.02		10.12			1.00
14	10.8	39.2	9.70	9.90	10.02	10.08	10.10	10.19					3.08
15	9.6	40.4	9.80	10.13	10.24		10.29	10.32	10.39	10.41			29.42
16	8.4	41.6	10.26	10.56	10.67	10.69	10.69	10.69	10.69	10.62	10.55	10.57	200.00

* The time of set is indicated by a vertical line.

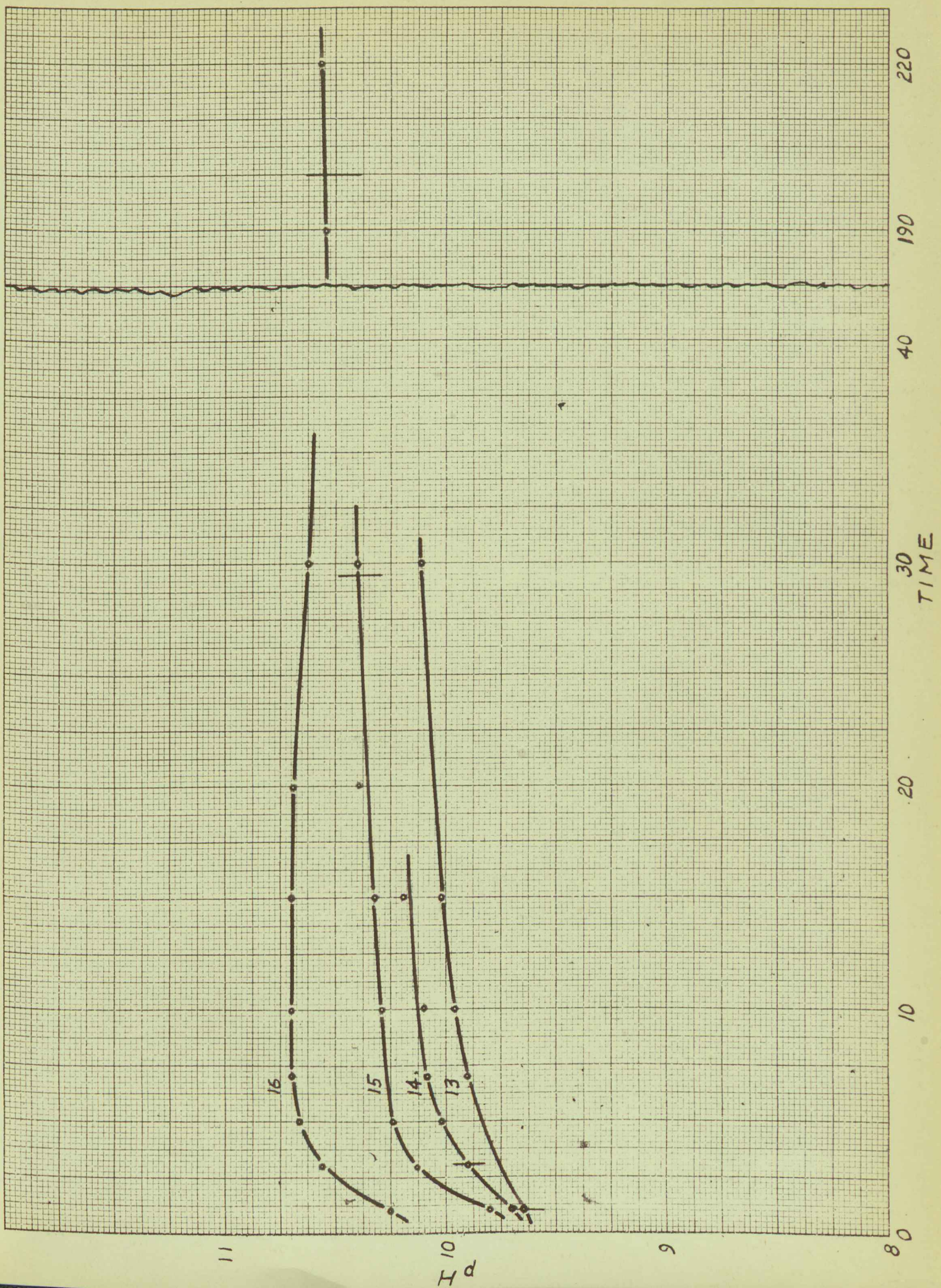


TABLE IV

CHANGE OF pH WITH TIME - DATA FOR CURVES 17-19 *

Temperature 25°C. 35 c.c. of silicate

pH Readings with Lapse of Time

Curve	c.c. HAC	c.c. H ₂ O	<u>1</u>	<u>5</u>	<u>10</u>	<u>15</u>	<u>20</u>	<u>30</u>	<u>40</u>	Time of Set (in minutes)
17	12.6	32.4	9.95	10.25	10.27		10.35			1.00
18	11.2	33.8	10.22	10.51	10.57		10.58	10.62	10.62	4.17
19	9.8	35.2	10.70	10.79	10.87	10.89	10.93	10.99	10.95	33.17

-19-

* Time of set is indicated by a vertical line.

40

30

20

10

0

TIME

11

H_{d10}

9

8

19

18

17

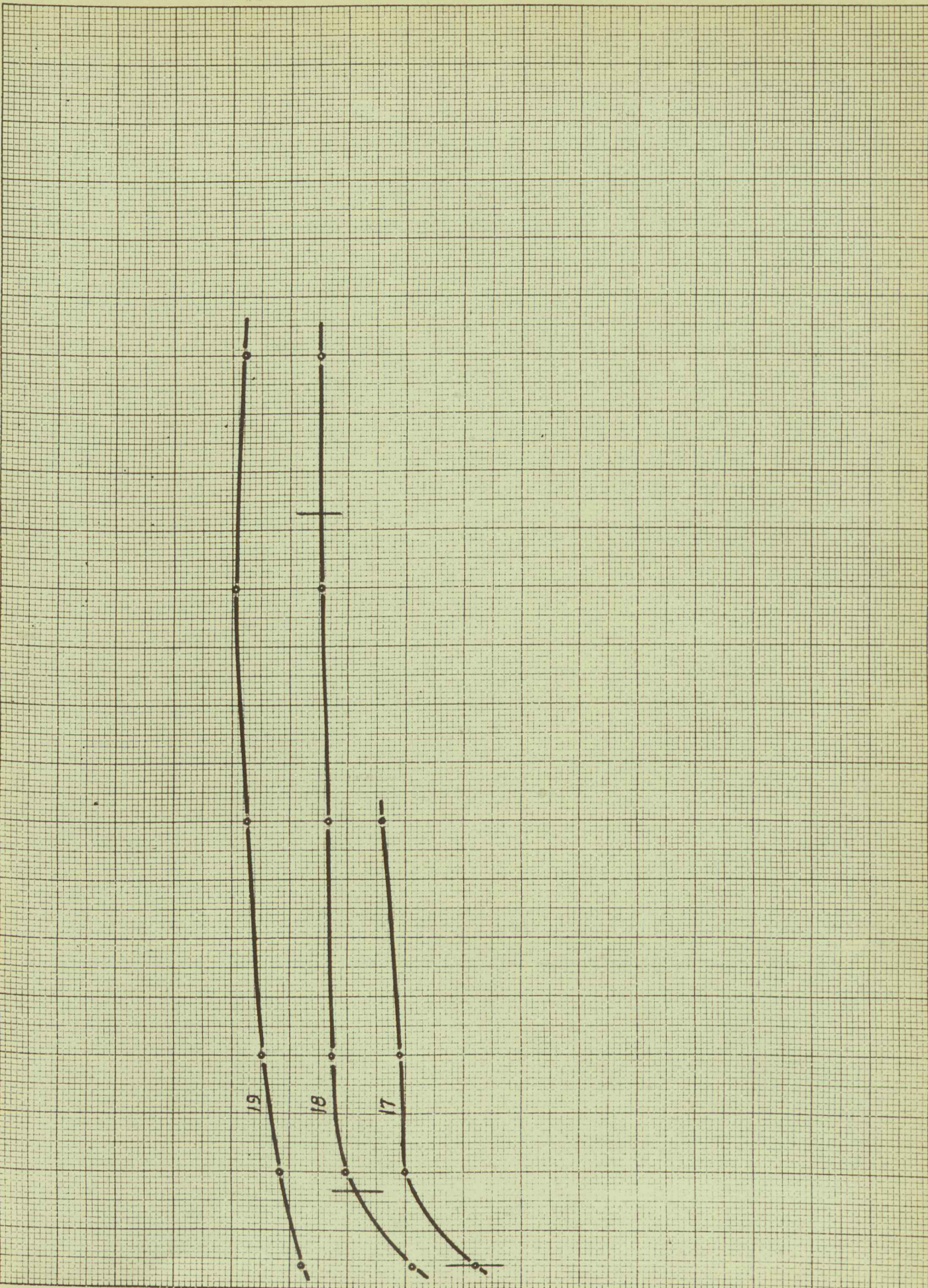


TABLE V

CHANGE OF LOG TIME OF SET WITH CHANGE IN INITIAL pH - DATA FOR CURVE 20

Temperature 25°C. 25 c.c. of silicate, amount of acid was varied

<u>c.c. HAc</u>	<u>c.c. H O</u> 2	<u>Initial</u> <u>pH</u>	<u>Time of Set</u> <u>(in seconds)</u>	<u>Log time of Set</u>
16	39	4.40	2410	3.38
15	40	4.80	1455	3.16
14	41	5.35	340	2.53
13	42	6.30	80	1.90
12	43	7.13	53	1.72
11	44	7.90	90	1.95
10	45	9.00	185	2.27
9	46	9.59	1700	3.23
8	47	10.22	19440	4.29

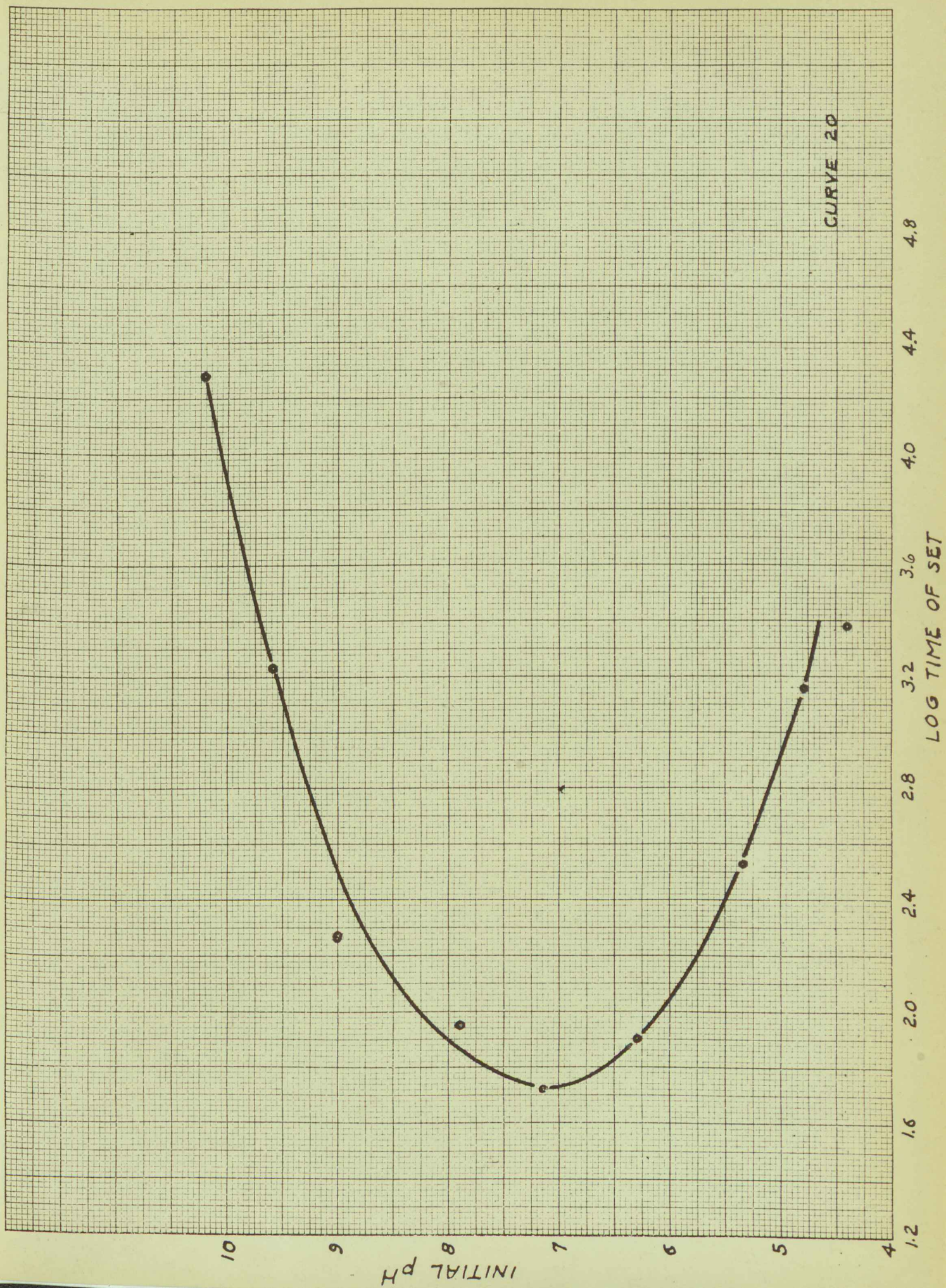


TABLE VI

CHANGE IN LOG TIME OF SET WITH CHANGE IN INITIAL pH - DATA FOR CURVE 21

Temperature 25°C. 20 c.c. of silicate, amount of acid was varied

<u>c.c. HAC</u>	<u>c.c. H O</u> <u>2</u>	<u>Initial pH</u>	<u>Time of Set</u> <u>(in seconds)</u>	<u>Log Time of Set</u>
9.6	50.4	8.40	130	2.11
8.8	51.2	9.02	395	2.60
8.0	52.0	9.40	2465	3.39

9.6

9.4

9.2

9.0

8.8

8.6

8.4

8.2

INITIAL pH

1.8

2.0

2.2

2.4

2.6

2.8

3.0

3.2

3.4

3.6

LOG TIME OF SET

CURVE 21

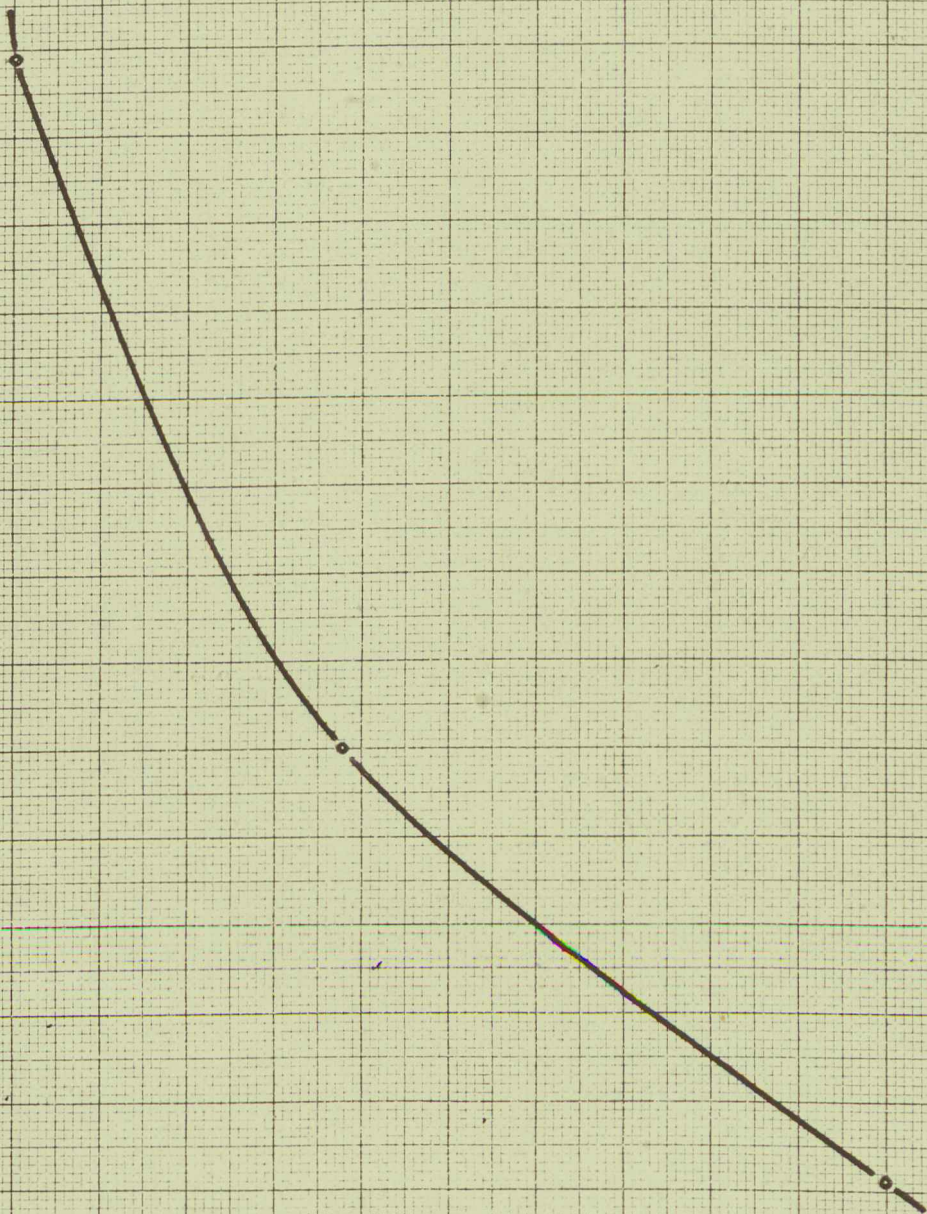


TABLE VII

CHANGE IN LOG TIME OF SET WITH CHANGE IN INITIAL pH - DATA FOR CURVE 22

Temperature 25°C. 30 c.c. of silicate, amount of acid was varied

<u>c.c. HAC</u>	<u>c.c. H O</u> <u>2</u>	<u>Initial pH</u>	<u>Time of Set</u> <u>(in seconds)</u>	<u>Log Time of Set</u>
12.0	38.0	9.65	60	1.78
10.8	39.2	9.70	185	2.27
9.6	40.4	9.80	1765	3.25

LOG TIME OF SET

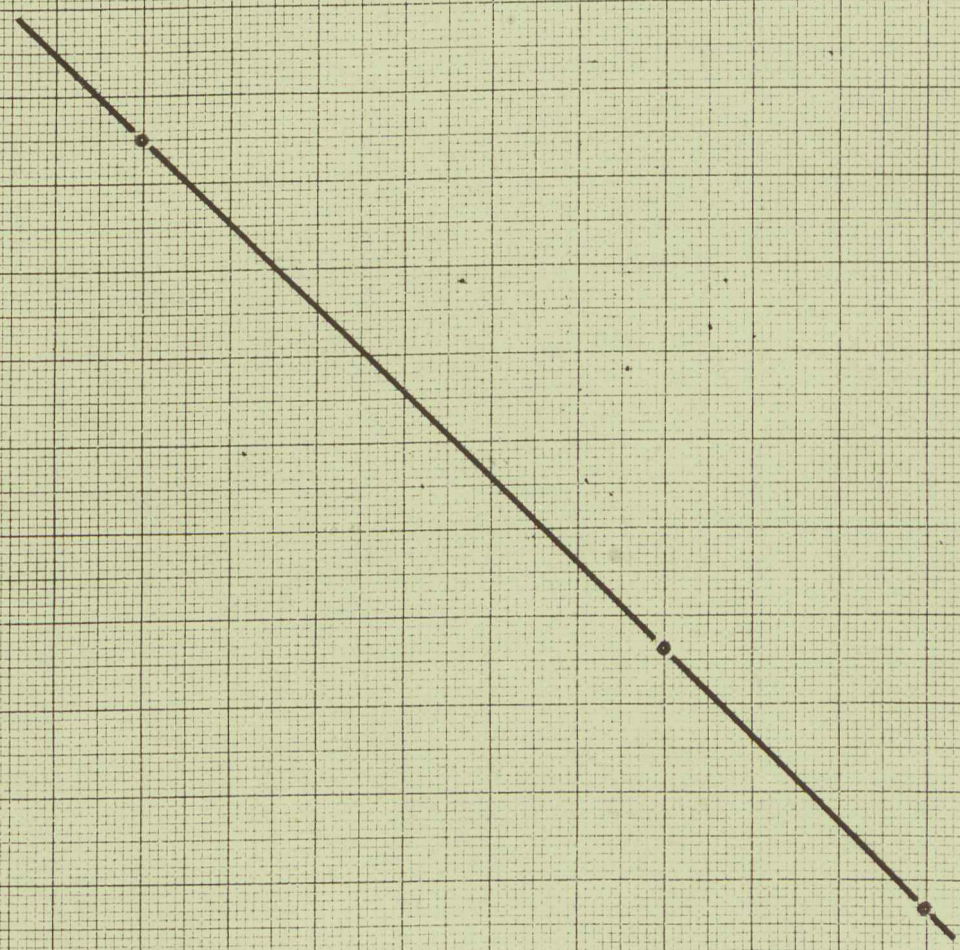
4

3

2

1

CURVE 22



INITIAL pH

9.7

9.8

TABLE VIII

CHANGE IN LOG TIME OF SET WITH CHANGE IN INITIAL pH - DATA FOR CURVE 23

Temperature 25°C. 35 c.c. of silicate, amount of acid was varied

<u>c.c. HAC</u>	<u>c.c. H₂O</u>	<u>Initial pH</u>	<u>Time of Set</u>	<u>Log time of Set</u>
12.6	32.4	9.95	60	1.78
11.2	33.8	10.22	250	2.40
9.8	35.2	10.70	1990	3.30

LOG TIME OF SET

4

3

2

1

CURVE 23

INITIAL pH

10.8

10.6

10.4

10.2

10.0

9.8

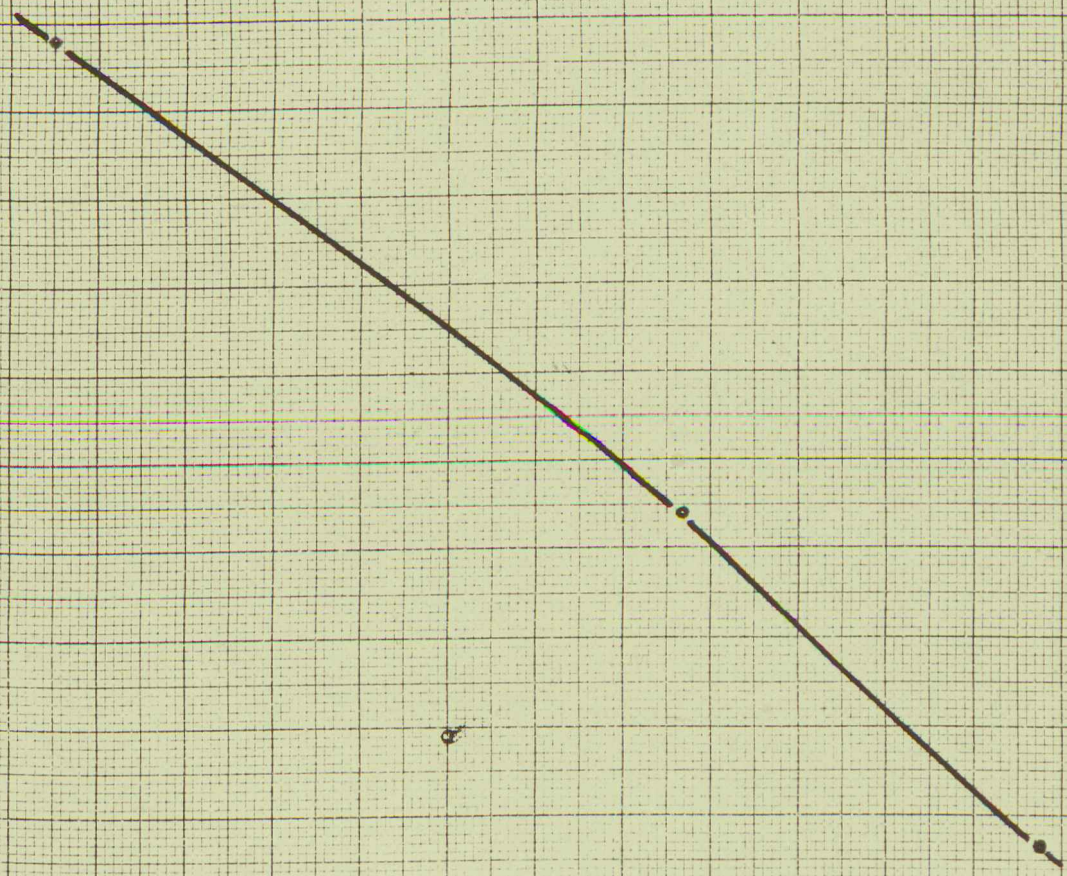


TABLE IX
CHANGE IN TIME OF SET WITH CHANGE IN AMOUNT OF ACID - DATA FOR CURVE 24
Temperature 25°C 25 c.c. of silicate

<u>c.c. HAc</u>	<u>c.c. H O</u> 2	<u>Time of Set</u> (in minutes)
16	39	40.17
15	40	24.25
14	41	5.67
13	42	1.33
12	43	.88
11	44	1.50
10	45	3.08
9	46	28.33
8	47	324.00

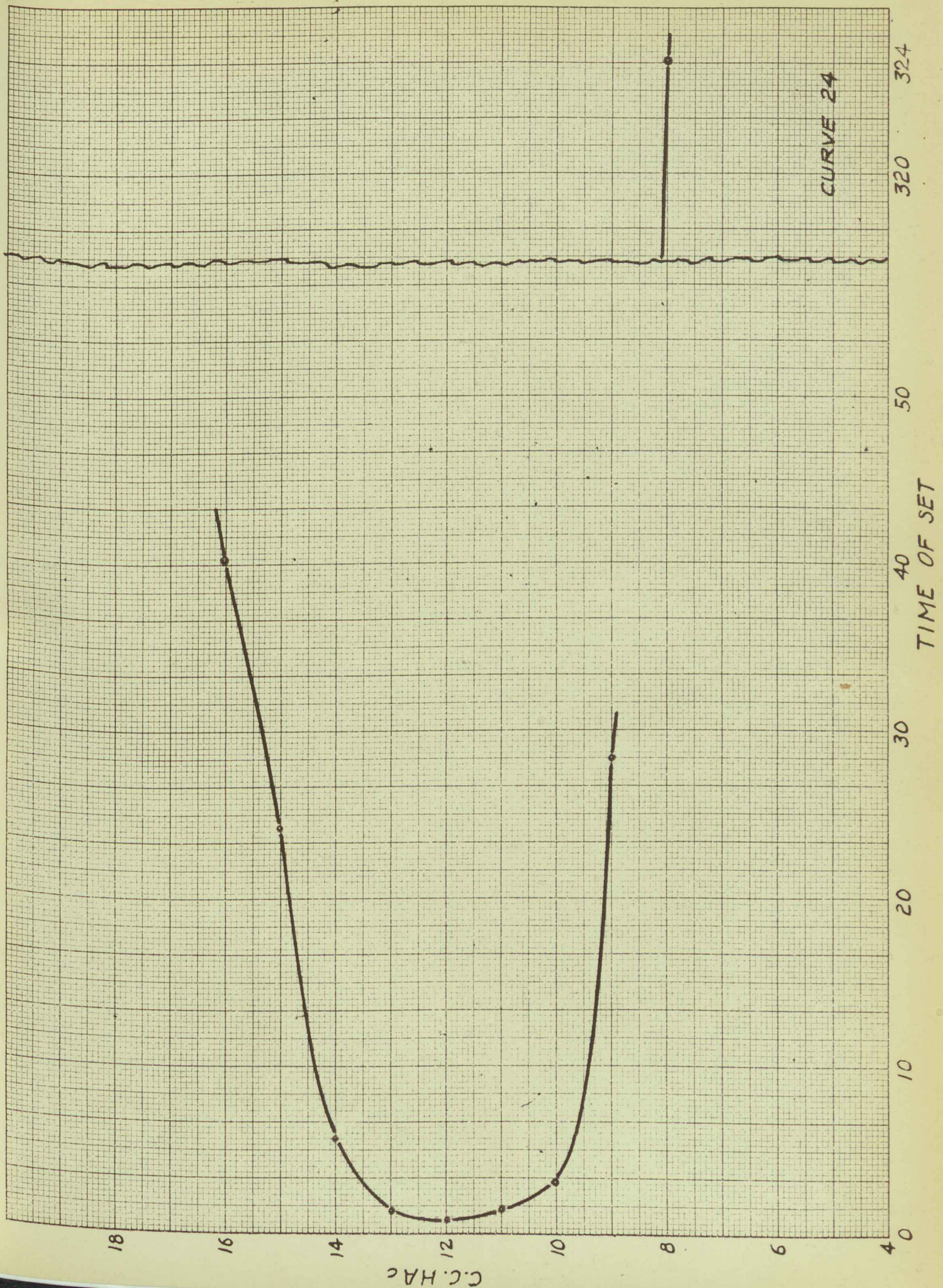


TABLE X

CHANGE IN TIME OF SET WITH CHANGE IN AMOUNT OF SILICATE - DATA FOR CURVES 25-27

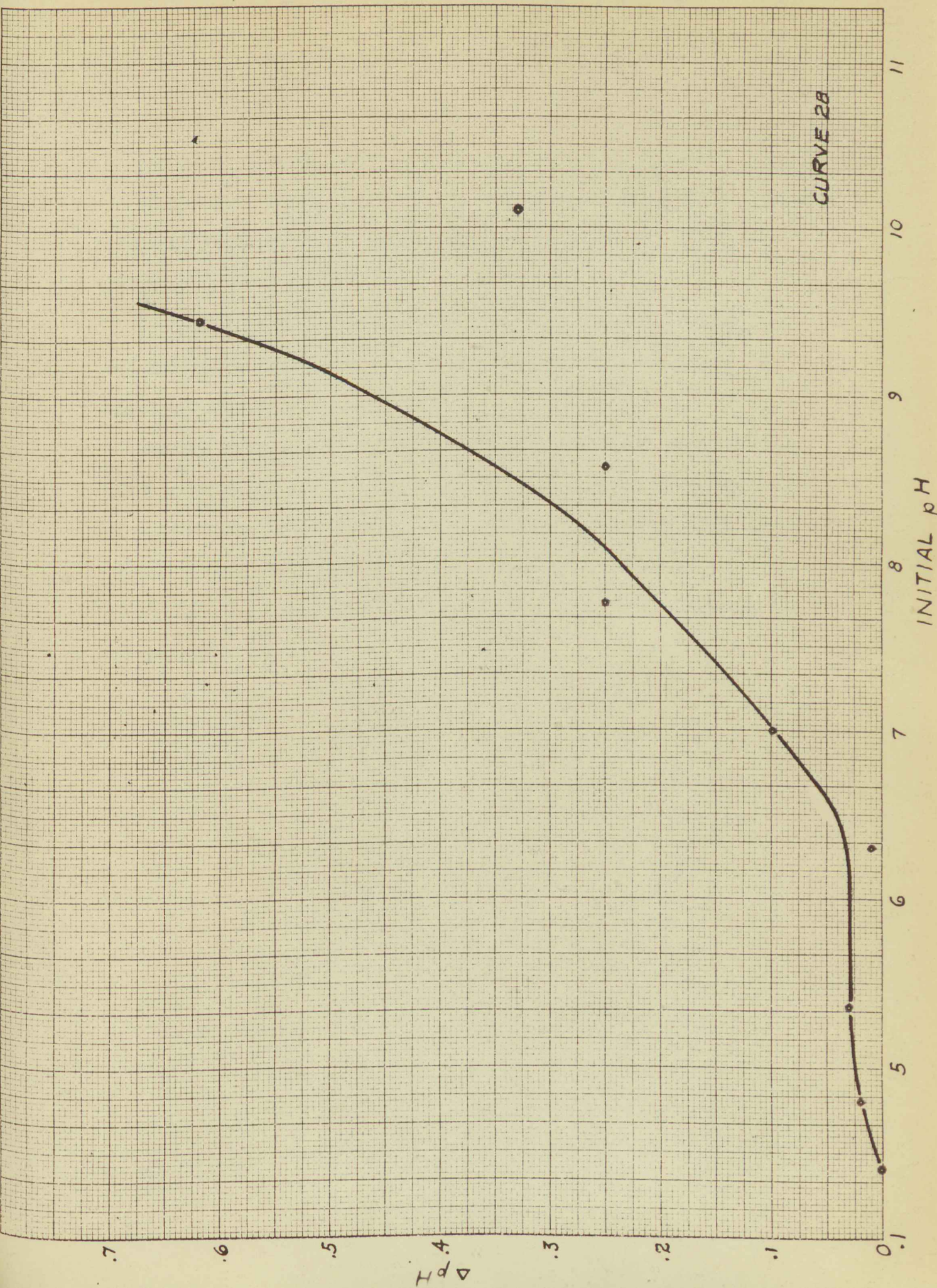
Temperature 25°C. ratio of silicate to acid constant for each curve

<u>Curve</u>	<u>c.c. Silicate</u>	<u>Ratio of Silicate to HAc</u>	<u>c.c.H O 2</u>	<u>Time of Set (in minutes)</u>
25	20	25:10	52.0	41.08
	25	"	45.0	3.08
	30	"	38.0	1.00
26	25	25:9	46.0	28.33
	30	"	39.2	3.08
	35	"	32.4	1.00
27	25	25:8	47.0	324.00
	30	"	40.4	29.42
	35	"	33.8	4.17



TABLE XI
CHANGE IN THE AMOUNT OF pH DRIFT WITH CHANGE IN INITIAL pH - DATA FOR CURVE 28
Temperature 25°C. 25 c.c. of silicate

<u>c.c.HAc</u>	<u>Initial pH (t= 0)</u>	<u>pH at Time of Set</u>	<u>Δ pH</u>
16	4.40	4.40	.00
15	4.80	4.82	.02
14	5.35	5.38	.03
13	6.30	6.31	.01
12	7.00	7.10	.10
11	7.75	8.00	.25
10	8.90	9.15	.25
9	9.45	10.07	.62
8	10.10	10.43	.33



The effect of pH on the time of set of silicic acid gels was studied. The gels were made by mixing acetic acid and sodium silicate.

For samples containing 25 c.c. of silicate in 80 c.c. of solution a minimum time of set, as the amount of acid was varied, was found a little above pH 7.

An increase in the concentration of silicate in the silicic acid sol, keeping the ratio of silicate to acid constant, resulted in a decrease in the time of set.

Little change in pH was noted for acidic sols with lapse of time, but a drift toward higher pH values was noted for samples having initial pH values in the alkaline range. The change in pH, Δ pH, when plotted against initial pH, showed a sharp increase for mixtures having initial pH values above 6.30. The polymerization mechanism of setting was substantiated.

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