

1929

I. The quinhydrone electrode and the soil reaction;  
II. The gravimetric method for the determination of  
carbonates in soils; III. Application of the  
quinhydrone electrode to investigations on base  
exchange in soils

Emerson R. Collins  
*Iowa State College*

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Agriculture Commons](#), and the [Soil Science Commons](#)

### Recommended Citation

Collins, Emerson R., "I. The quinhydrone electrode and the soil reaction; II. The gravimetric method for the determination of carbonates in soils; III. Application of the quinhydrone electrode to investigations on base exchange in soils " (1929). *Retrospective Theses and Dissertations*. 14233.

<https://lib.dr.iastate.edu/rtd/14233>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact [digirep@iastate.edu](mailto:digirep@iastate.edu).

## INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

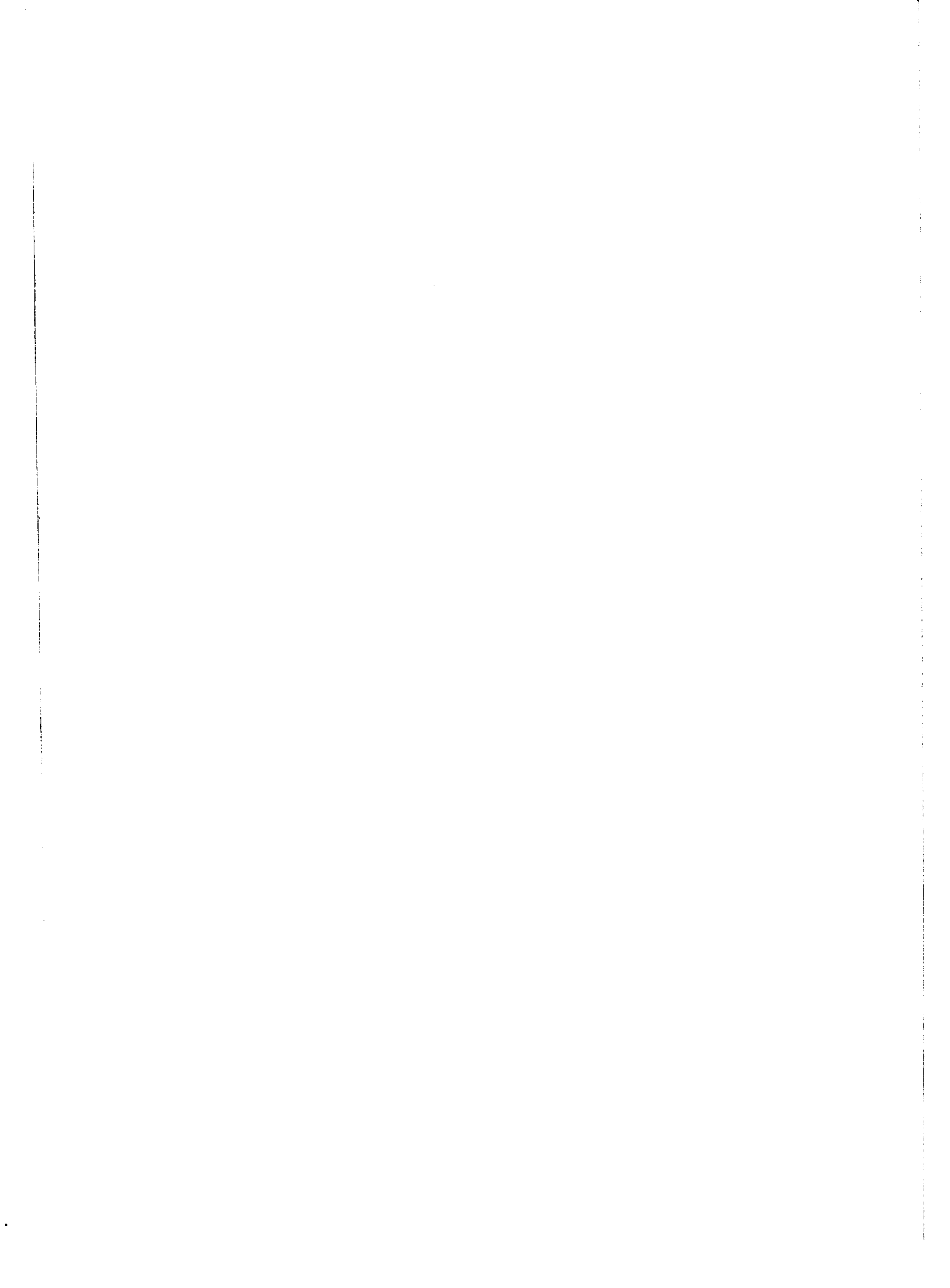
**The quality of this reproduction is dependent upon the quality of the copy submitted.** Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning  
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA  
800-521-0600

**UMI<sup>®</sup>**



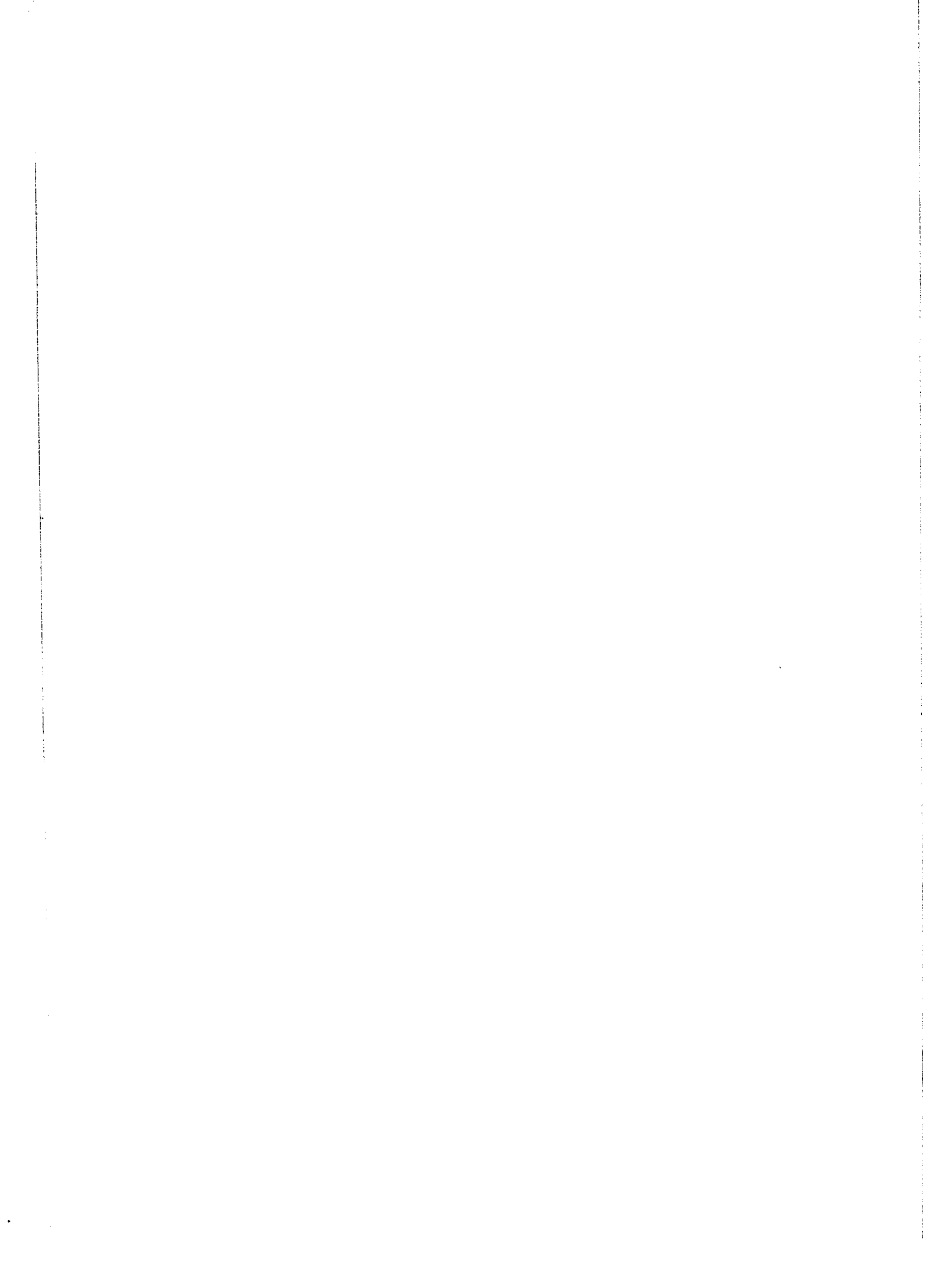
## **NOTE TO USERS**

**Page(s) missing in number only; text follows.  
Microfilmed as received.**

**Page 27**

**This reproduction is the best copy available.**

**UMI**



- I. THE QUINHYDRONE ELECTRODE AND THE SOIL REACTION.
- II. THE GRAVIMETRIC METHOD FOR THE DETERMINATION OF CARBON-ATES IN SOILS.
- III. APPLICATION OF THE QUINHYDRONE ELECTRODE TO INVESTIGATIONS ON BASE EXCHANGE IN SOILS.

BY

Emerson R. Collins

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Soil Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1929

UMI Number: DP14423

UMI<sup>®</sup>

---

UMI Microform DP14423

Copyright 2006 by ProQuest Information and Learning Company.  
All rights reserved. This microform edition is protected against  
unauthorized copying under Title 17, United States Code.

---

ProQuest Information and Learning Company  
300 North Zeeb Road  
P.O. Box 1346  
Ann Arbor, MI 48106-1346

ACKNOWLEDGMENT

The writer wishes to express his appreciation and thanks to Dr. Norman A. Clark for the suggestion of these problems and for his encouragement and helpful advice given during the work.

T 3101



I. THE QUINHYDRONE ELECTRODE AND THE SOIL REACTION.

This part of the thesis was published jointly with Dr. Norman A. Clark in Soil Sci. 24:453-463, December 1927. A reprint of this paper is inserted for convenience.

THE QUINHYDRONE ELECTRODE AND THE SOIL  
REACTION

BY

NORMAN ASHWELL CLARK AND EMERSON R. COLLINS

*Iowa State College*

REPRINTED FROM  
SOIL SCIENCE, VOL. XXIV, No. 6, December, 1927

## THE QUINHYDRONE ELECTRODE AND THE SOIL REACTION

NORMAN ASHWELL CLARK AND EMERSON R. COLLINS

*Iowa State College*<sup>1</sup>

Received for publication August 22, 1927

The application of the quinhydrone electrode to soil investigations was made by Biilmann (4) and by Christensen and Tovborg-Jensen (10) in 1924. This method for the determination of pH in soils proved to have several advantages over the hydrogen electrode as well as over the colorimetric method; for example, in the first case the necessity for coating the electrodes with platinum black is removed; and in the second, turbidity in solutions is no longer a factor. Because of the speed with which determinations can be made, due to the quickness of the quinhydrone electrode to attain equilibrium, and to the fact that it is not "poisoned" by soils or affected by nitrates (6, 8), it is rapidly coming into general use. Further investigations on methods and accuracy are therefore desirable.

The theory of the quinhydrone electrode has been given by Biilmann (2, 3, 6), LaMer and Parsons (22), and by Kolthoff and Furman (21). The solid quinhydrone which is added to the soil-water mixture, dissolves and dissociates into equi-molecular quantities of hydroquinone and quinone. From the equation:

$$\pi \text{ (E.M.F.)} = \frac{RT}{2F} \ln \frac{(\text{quinone})}{(\text{hydroquinone})} + \frac{RT}{F} \ln (\text{H}^+) + K \dots \dots \dots \text{(A)}$$

the first term is zero when the concentration of quinone is the same as the concentration of hydroquinone, and therefore

$$\pi = \frac{RT}{F} \ln (\text{H}^+) + K \dots \dots \dots \text{(B)}$$

If the activity of the ions is disregarded (21, p. 1) K is  $\pi$  (or  $\pi_0$ ) when the concentration of the hydrogen ion is 1.

Biilmann (2), by checking the quinhydrone electrode against a hydrogen electrode in solutions of the same  $\text{H}^+$  concentration, found that at 25°C.  $\pi_0 = 0.6990$  and at 18°C., 0.7044, the platinum of the quinhydrone electrode being positive to the hydrogen electrode. Thus at 18°

$$\pi = 0.0577 \log (\text{H}^+) + 0.7044 \dots \dots \dots \text{(C)}$$

and at 25°

$$\pi = 0.0591 \log (\text{H}^+) + 0.6990 \dots \dots \dots \text{(D)}$$

---

<sup>1</sup> Contribution from the Department of Chemistry.

When the quinhydrone electrode has been used in soil determinations, the second half cell has been either one of the calomel electrodes or a special half cell of 0.01 *N* HCl and 0.09 *N* KCl, introduced by Veibel (27). The pH of this mixture is 2.03 (6), or of a similar mixture of 0.01 *N* HCl and 0.09 *N* NaCl, 2.038 (25, p. 24). Biilmann and Tovborg-Jensen prefer this electrode to the calomel half cell because it is easily made up and has a comparatively high pH value. It has the drawback, however, that a fresh one must be made each day. The equation for this (6) is

$$\text{pH} = 2.03 + \frac{\pi}{0.0001984T} \dots \dots \dots (\text{E})$$

Veibel compared it with the normal and 3.5 normal calomel half cells for the amount of variation, and found that it could be reproduced without greater change than the calomel cells, but that it was not markedly more accurate.

Hissink and Van der Spek (19) use the normal calomel electrode as the half cell, whereas Baver (1) favors the saturated calomel cell. Both of these have the advantage over Veibel's cell, that once made up, they will not vary for a considerable time. It is necessary, however, to reverse the poles of electrodes for some readings, e.g., with the normal calomel electrode as the half cell, at 18°. With the half cell instead of the normal hydrogen electrode the E.M.F. is 0.2864 too low (11, p. 456), and equation (C) becomes:

$$\pi + 0.2864 = 0.0577 \log (\text{H}^+) + 0.7044 \dots \dots \dots (\text{F})$$

or  $\text{pH} = 7.24 - \frac{\pi}{0.0577}$ . If the pH is greater than 7.24 the E.M.F. is negative; if the pH is less than 7.24, the E.M.F. is positive. It is, however, a simple matter to place a double switch in the circuit and, when necessary, reverse the poles without touching the electrodes. Veibel's electrode has the advantage that the change would occur at 2.03, so that for the soil work the potential would rarely alter its sign.

#### TEMPERATURE

There is a considerable amount of confusion with regard to temperature corrections. Biilmann and Krarup (5) found that the potential of the quinhydrone electrode, in a 0.1 *N* hydrochloric acid, against the hydrogen electrode, followed the equation:

$$\pi_t = 0.7175 - 0.00074t \text{ between } 0^\circ \text{ and } 37^\circ \text{C.}$$

The calculated and determined results fell within 0.4 of a millivolt. This equation, however, does not take into account the temperature coefficient of a calomel half cell, and where one of these is used, it is not correct to state that "the temperature factor as determined in Biilmann's investigations is 0.77 millivolts per degree deviation from 25°C."

The temperature coefficient of the whole cell varies with the half cell used. Büllmann and Tovborg-Jensen (6) have noted the temperature effects with Veibel's electrode. For the calomel cells corrections may be made as follows:

Sørensen and Linderstrøm-Lang (26) give the temperature coefficients

0.1 <i>N</i> Cal. electrode— <i>N</i> Hyd. electrode.....	0.00006
1.0 <i>N</i> Cal. electrode— <i>N</i> Hyd. electrode.....	0.00024
3.5 <i>N</i> Cal. electrode— <i>N</i> Hyd. electrode.....	0.00039

Kolthoff and Furman (21, p. 141) give the saturated calomel electrode—*N* Hyd. electrode 0.00065. From these figures and the value 0.00074 above, the temperature coefficient for the quinhdrone electrode with the 0.1 *N* calomel electrode is 0.00006–0.00074 = –0.00068; with the *N* calomel electrode –0.00050; with the 3.5 *N* –0.00035; and with the saturated –0.00009.

From equation (F) at 18°C.:

$$\pi + 0.2864 = 0.0577 \log (H^+) + 0.7044 \text{ for the quinhdrone}$$

compared to the normal calomel electrode

$$\text{or } \text{pH} = \frac{0.4180 - \pi}{0.0577}$$

With the temperature coefficient –0.00050, as shown above, Kolthoff (20) gives the formula

$$\text{pH} = \frac{0.4181 - 0.00050 (t - 18) - \pi}{0.0577 + 0.0002 (t - 18)} \dots\dots\dots (G)$$

This is the formula used by Hissink (19). It can be checked for 25°C. by using formula (D) with the value 0.2848 (11, p. 456) added to  $\pi$ ; the agreement is good.

For the saturated calomel and the normal hydrogen electrodes at 18° the value is 0.2506 (11, p. 456). Ewing (15) prefers 0.2504. In the same way as before at 18°C.:

$$\text{pH} = \frac{0.4538 - 0.00009 (t - 18) - \pi}{0.0577 + 0.0002 (t - 18)} \dots\dots\dots (H)$$

Calculated from this at 25°,  $\text{pH} = \frac{0.4532 - \pi}{0.0591}$ .

Equation (D) is used to check this, with the value 0.2464 (11) for the saturated calomel electrode. At 25°,

$$\text{pH} = \frac{(0.6990 - 0.2464) - \pi}{0.0591} = \frac{0.4526 - \pi}{0.0591} \dots\dots\dots (I)$$

This is fair agreement: the pH values differ only from 0.01 to 0.02.

From equation (I) a table can be made for the pH at 25°, or Bayer's table (1) can be used. Bayer's figures are slightly higher than those from equation

(I), but agree within 0.04 pH. By the use of figure 1 the amount of change in the pH for temperatures between 20° and 30° can be obtained directly for any given  $\pi$ . Corrections are *added* to the calculated pH if the temperature is *below* 25°, and subtracted if the temperature is higher. For example, if  $\pi$  is + 0.0313, from equation (I) the pH is 7.13 (Baver's table gives 7.15); but if the temperature of the experiment was 29°C., the corrected pH is 7.03, as the graph gives a correction of 0.10 pH at 29°, when  $\pi = 0.313$ . It will be seen

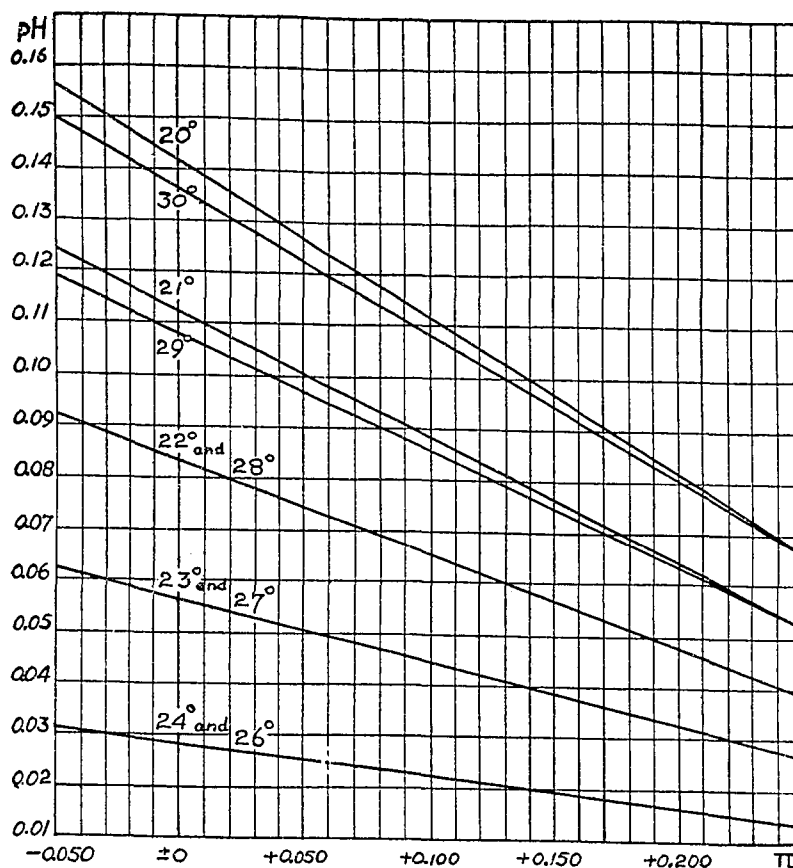


FIG. 1. pH CORRECTIONS AT TEMPERATURES OF 20° TO 30°C. FOR VARYING VALUES OF  $\pi$

that the temperature corrections are more important on the alkaline side. The following formula may also be used instead of the tables and graph:

$$pH = \frac{0.4526 - 0.00009 (t - 25) - \pi}{0.0591 + 0.0002 (t - 25)} \dots\dots\dots (J)$$

Dawson (14) by taking the average value per degree (0.0006) of the Michaelis figures (11, p. 200), obtains 0.00014 for the temperature coefficient of the

quinhydrone and the saturated calomel electrodes. Kolthoff and Furman (21) give the value 0.00065 per degree, which give 0.00009 for the coefficient. This seems to be more nearly correct, as the value is 0.00085 for the normal hydrogen electrode (26) and 0.00020 for the saturated calomel electrode (16, 15); this, however, would make only a small alteration in Dawson's table.

#### EXPERIMENTAL

In the experiments following, the quinhydrone electrode was prepared as described by Biilmann (3). The saturated KCl calomel half cell was used as the standard electrode. Connection was made by an agar bridge dipping into a closed solution of saturated KCl, in order to prevent diffusion and to keep down junction potentials.

The use of the KCl bridge with 5 per cent agar as suggested by Biilmann and Tovborg-Jensen (6) was found more satisfactory and caused less "drifting" of readings than bridges with a smaller percentage. Five grams of agar were placed in 100 cc. of the saturated KCl and the whole was weighed. The mixture was then boiled until the agar dissolved (heating below boiling produced very slow solution) and made up to the original weight with water. This prevented crystallization on cooling. It was found better to bring the solution almost to the solidification temperature before filling the tube by suction, in order to prevent contraction and the consequent drawing away from the sides of the tube. This contraction was further hindered by etching the inside of the glass tube with hydrofluoric acid containing a small amount of ammonium chloride, especially where much strain was put on the bridge, e.g., when it was being pushed into a thick soil suspension.

The electrode used for the soil suspensions with the quinhydrone was of flattened platinum wire. This was rather more durable than the usual flag when thrust into settled soil, particularly in the case of sand, and was much more convenient where stirring by motor was used to keep the soil in suspension.

Three types of soil were compared: a sandy soil, 13A, from the Miami series; a loam, 25A, from the Carrington, and a slightly heavier loam, 40A, from the low-lying soils of the Wabash series. Conductivity water (the laboratory distilled water redistilled over alkaline permanganate) was used in all cases.

The problems relating to the pH of a soil obtained by means of the quinhydrone electrode have been divided into two classes: first, preparation of the soil, e.g., soil water ratio, shaking, equilibrium; and second, measurement of the pH. The ratio of soil to water has not yet been standardized, some investigators have used 1:5 as with the hydrogen electrode (8), but there are reports (1) to show that a ratio of 1 soil to 5 water with the hydrogen electrode gives a pH value very close to the figures obtained with the quinhydrone electrode when the ratio is 1:1. A uniform method would prove valuable even though it had to be altered for special cases, e.g., for peat soils which would not give a suspension with an equal weight of water.

Biilmann and Tovborg-Jensen point out that an equilibrium between the soil and the water is desired, and that this is attained most rapidly if small amounts of water are used, they therefore advise a 1:1 ratio and recommend that the electrode should not be placed in the supernatant liquid, but lowered until entirely surrounded by soil, because the water nearest to the soil should come to equilibrium most quickly. They also suggest that if the substances causing the pH are more or less insoluble, there will be a saturated solution of these at both 1:1 and 1:5 ratios: but if they are fairly soluble, the solution at 1:1 may be much more concentrated than at 1:5. The pH would be altered by the increase of water with the more soluble but not with the comparatively insoluble substances.

Biilmann and Tovborg-Jensen further draw attention to the fact that the quinhydrone attains equilibrium instantaneously, so that if successive measurements show "drift," then either equilibrium between soil and water is not attained, or absorption of a component of the quinhydrone has taken place. In the second case a measurement immediately after mixing would be more nearly correct. In their experiments they found that the paste quickly

TABLE 1  
*Equilibrium reaction of three soils*

TIME AFTER SHAKING	SOIL 40A		SOIL 25A		SOIL 13A	
	½ minute	10 minutes	½ minute	10 minutes	½ minute	10 minutes
<i>ratio</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>
1:1	5.74	5.71	5.57	5.57	5.89	6.23
1:5	5.97	5.95	5.86	5.75	6.26	6.36

attained the final value, and that usually no drift occurred at dilutions of 1:1 up to 1:10. They concluded that after shaking for a few seconds and measuring with the electrode submerged, the equilibrium reaction is measured. The method that was recommended, therefore, is to shake for a few seconds with a ratio of 1:1, stand half a minute for the soil to settle, and measure the pH with the electrode in the settled soil.

This method was checked by the writers in the three soils mentioned, and the results are shown in table 1. Each figure is the average of three measurements which agree closely.

Soils 40A and 25A show no drift at 1:1 ratio. The soil should then be at equilibrium with the water in the paste, and no adsorption is indicated. The sandy soil, 13A, showed drift at both 1:1 and 1:5 ratios, indicating either no equilibrium or adsorption of one of the compounds of the quinhydrone. In all cases, with an increase of water, there is a change of pH, pointing to soluble substances which affect the acidity. If this suggestion is correct, increasing dilution should give a continual change of pH in the same direction, up to a maximum or minimum, when the pH would move towards the pH of



the water used. Hissink and van der Spek (19) show very clearly that this turning point is reached in some soils.

## EQUILIBRIUM SOIL:WATER

In order to test this equilibrium between soil and water, the three soils 40A, 25A, and 13A were treated as follows:

1. Shaking a few seconds, settling  $\frac{1}{2}$  minute and 10 minutes—electrode in paste.
2. Stirring with motor. A small stirrer at the bottom of the wide-mouth test tube, arranged to give a slight upward throw. Measurement taken while stirring; electrode in suspension.

TABLE 2  
Results of test of equilibrium between soil and water, on three soils

	RATIO 1:1			RATIO 1:5		
	40A	25A	13A	40A	25A	13A
	pH	pH	pH	pH	pH	pH
1. Shake 2-3 seconds stand $\frac{1}{2}$ minute.....	5.74	5.57	5.89	5.95	5.86	6.26
Shake 2-3 seconds stand 10 minutes.....	5.71	5.57	6.23	5.95	5.75	6.36
2. Stir with motor—just to mix.....	5.72	5.54	5.95	6.00	5.67	6.07
Stir with motor— $\frac{1}{2}$ hour.....	.....	.....	.....	6.13	5.72	.....
Stir with motor—3 hours.....	.....	.....	.....	6.16	6.22	.....
3. Rotating 2 hours.....	5.81	5.86	6.22	6.23	6.82	.....
Rotating 6 hours.....	5.84	5.90	6.15	.....	.....	.....
Rotating 20 hours.....	6.06	6.00	6.13	.....	.....	.....
Rotating 24 hours.....	.....	.....	.....	6.26	6.82	6.56
Rotating 36 hours.....	6.12	5.96	.....	.....	.....	.....
4. Colloid Mill 0.07 inch.....	.....	.....	.....	7.42	*	7.03
0.014 inch.....	.....	.....	.....	.....	.....	7.23
0.002 inch.....	.....	.....	.....	.....	.....	7.39

\* Alkaline.

3. Rotating machine. Soil and water rotated over and over, with speed slow enough to let mixture fall from one end of container to the other. Settle—electrode in paste.

4. Colloid Mill. The soil-water mixture passed through a colloid mill, cone type, with clearances from 0.07 to 0.002 inch. The particles did not settle out for a long time on standing—electrode in suspension.

The results show that there is no definite soil-water equilibrium in these soils, even in the 1:1 ratio. With 40A and 25A, which did not change when shaken a few seconds and allowed to stand 10 minutes, there is a progressive change toward the alkaline side on stirring or rotating, and a very decided rise in the pH value when sent through the colloid mill. The sandy soil, 13A, which showed a drift in the 10 minutes, did not change much by rotation at

1:1 ratio, but it also showed alkalinity through the colloid mill, and the finer the grinding the more alkaline the suspension became.

These figures are in accord with Fisher's suggestion (17) of a difference between the composition of the inside of the particle and the outside. Brown and Johnson (7) found indications of this when measuring the lime requirements of Iowa soils, while Cook (13), with New Jersey soils, obtained more acidity by grinding, indicating a more acid center of the soil particle.

#### FILTRATES AND SUSPENSIONS

Differences in the pH of the supernatant liquid, the paste and the suspension, emphasize the variations which may be expected in filtrates or centrifugates of soil suspensions. Carlton (9), working with 50 centrifuged extracts, found a difference in 16 soils ranging from 0.55 pH to 0.10. Similarly Gillespie and Hurst (18) found many differences when comparing the colorimetric pH of the centrifuged extracts with the suspensions electrometrically determined.

TABLE 3  
*Results of a comparison of filtrates with suspensions for various treatments of soils*

SOIL	TREATMENT—RATIO 1:5	SUSPENSION	FILTRATES SUCCESSIVE 10-CC. PORTIONS					
			1	2	3	4	5	6
		pH	pH	pH	pH	pH	pH	pH
13A	Rotation 24 hours	6.56	6.95	7.13	6.93	6.98	6.89	....
25A	Rotation 24 hours	6.82	7.51	7.56	7.55	7.60	....	....
40A	Stir $\frac{1}{2}$ hour	6.13	6.78	6.76	6.89	7.09	7.07	....
40A	Stir 3 hours	6.26	7.38	7.32	7.39	6.90	....	....
40A	Colloid Mill	7.42	5.88	6.67	7.05	6.83	6.78	7.22

Pierre (23), who prefers filtering to centrifuging, obtained fairly good agreement between the pH of the soil suspension and the filtered extract. He used a method of filtration with suction and washed filter papers, designed by Truog, and he considers that the differences usually found may be due to the effect of the CO<sub>2</sub> in the air on the little buffered filtrate. Sharp and Hoagland (24) with a CO<sub>2</sub> content of 10 per cent introduced into the electrode vessel, found small effect on any except alkali soils.

The larger part of these comparisons have been with colorimetric determinations and the hydrogen electrode. They are open to a number of objections mentioned by Pierre (23), but with the quinhydrone electrode the difficulties disappear. The figures in table 3 show some of the results of comparing filtrates with suspensions for various treatments of the soils. The Truog filtration method was used as described by Pierre. Each 10 cc. of the filtrate was tested for the pH; only a small amount of suction was used except on the last of the filtrate, when the soil was sucked dry.

The figures show that with these treatments there is a considerably larger

difference between the filtrates and the suspensions than has been generally recorded. The variation in the successive portions of the filtrates is also marked.

In the soils used, the differences in the pH of the supernatant liquid and the paste became greater as the soil was made finer. If a soil-water mixture 1:5 is passed several times through the colloid mill and allowed to settle without stoppering, the suspension should be in equilibrium with air. A settling tube was prepared 9 feet long, with outlets every foot, so that samples at various heights could be drawn off. Table 4 shows a large increase in the pH value at the lower levels.

These differences can possibly be explained by the Donnan equilibrium—if two solutions are separated by a membrane, and there is a non-diffusible ion on one side, the concentration of the diffusible ion is greater on the side of the non-diffusible ion. No membrane is actually required, however, as long as an

TABLE 4  
*Soil pH values at different levels of settling tube*

SOIL	13A	25A	40A
	pH	pH	pH
Suspension.....	7.39	Alkaline } >8.5 }	7.42
Top of liquid.....	6.83	6.64	6.55
Liquid above paste.....	6.84	6.61	6.51
Top of paste.....	8.25	Alkaline } >8.5 }	7.60
Middle of paste.....	Alkaline } >8.5 }	Alkaline } >8.5 }	7.75
Bottom of paste.....	Alkaline	Alkaline	7.59

ionized part of the system is unable to diffuse. Comber (12) has pointed out that when a soil is treated with acid, certain non-diffusible (or slowly diffusible) ions, chiefly aluminum, come into solution. When the soil settles, these produce the Donnan equilibrium, the aluminum accumulates in the pore spaces and causes a lower concentration of the anion in the supernatant liquid. Similarly, soils treated with alkalis cause various slowly diffusible anions (e.g., silicates, aluminates) to be held in the pore spaces, and these produce lower cation concentration in the supernatant liquid. Hydrolysis of alkaline particles could cause the same phenomenon and would account for lower acidity in the paste.

If there is no equilibrium in the paste between the soil and the water, or at most a semi-stable equilibrium, the method adopted for the measurement of the pH must be empirical, but at the same time should give a reproducible value, characteristic of the particular soil. As there is a distinct difference in the pH values of the supernatant liquid and the paste, the mixture kept in

suspension might be expected to be more representative of the soil. When the particles were brought into motion by stirring and the electrode was placed in the suspension, the readings either did not change from the simple shaking method (as in soil 40A, table 1) or more often the E.M.F. altered but failed to remain approximately constant. This did not hold out advantages over the electrode in the paste.

The stirring was applied in another manner, and one which proved more satisfactory. The soil sample was placed in the wide-mouth test tube and stirred for  $\frac{1}{2}$  minute; this mixed the water thoroughly with the soil without a grinding effect. The quinhydrone was then added to the mixture, which was shaken for a few seconds and allowed to stand for a half a minute as outlined. The electrode was placed in the paste. This method gave results varying slightly from the simple shaking and settling, but they were reproducible. Over 1000 measurements were taken on a number of soils with very different treatments, and in only a few cases the electrode failed to attain a comparatively constant E.M.F. In these measurements the agar bridge was placed near the electrode in the paste; there is sometimes a slight difference in the potential if the bridge is in the supernatant liquid.

#### SUMMARY

Further investigations have been made in the application of the quinhydrone electrode to the measurement of pH in soils.

1. Temperature corrections have been worked out for the quinhydrone electrode with the saturated KCl calomel half cell.

2. Biilmann and Tovborg-Jensen's method—mixing the soil and water by shaking for a few seconds—has been compared with stirring by motor, by rotary shaker, and by passing through a colloid mill, in order to investigate the equilibrium of the soil-water mixture. No definite equilibrium was found on the soils used.

3. By the use of a long settling tube, it was found that soil passed through the colloid mill increased the differences between the supernatant liquid and the settled soil. The Donnan equilibrium may account for the variation between the pH of the soil suspension, the supernatant liquid, and the paste. It is pointed out that there is still the question as to which of these should be measured for the soil reaction.

4. Reproducible values have been found by stirring the soil with water, using a 1:1 ratio, followed by the few seconds shaking and settling for a half minute, as described by Biilmann and Tovborg-Jensen.

#### REFERENCES

- (1) BAVER, L. D. 1926 The use of the quinhydrone electrode for measuring the hydrogen-ion concentration of soils. *Soil Sci.* 21: 167-179.
- (2) BIILMANN, E. 1921 Sur l'Hydrogénation des Quinhydrones. *Ann. Chim.* 15: 109-157.
- (3) BIILMANN, E. 1924 Oxidation and reduction potentials of organic compounds. *Trans. Faraday Soc.* 19: 676-691.
- (4) BIILMANN, E. 1924 On the measurement of hydrogen-ion concentration in soil by means of the quinhydrone electrode. *Jour. Agr. Sci.* 14: 232-239.
- (5) BIILMANN, E., AND KRARUP, I. 1924 The temperature coefficient of the quinhydrone electrode. *Jour. Chem. Soc.* 125: 1954-1956.

- (6) BIILMANN, E., AND TOVBORG-JENSEN, S. 1927 On the determination of the reaction of soils by means of the quinhydrone electrode. *Trans. 2nd Comm. Internat. Soc. Soil Sci.* B: 236-274.
- (7) BROWN, P. E., AND JOHNSON, H. W. 1915 The effect of grinding the soil on its reaction as determined by the Veitch method. *Jour. Amer. Soc. Agron.* 7: 216-220.
- (8) BURGESS, P. S. 1926 Report on reaction value of soils. *Jour. Assoc. Off. Agr. Chem.* 9: 138-141.
- (9) CARLTON, E. A. 1923 A comparison of the Jones calcium acetate method for lime requirement with hydrogen-ion concentration of some Quebec soils. *Soil Sci.* 16: 79-90.
- (10) CHRISTENSEN, H. R., AND TOVBORG-JENSEN, S. 1924 Investigations of methods used for determining the soil reaction. *Internat. Mitt. Bodenk.* 14: 1-25 (*Chem. Abs.* 1925: 369-370).
- (11) CLARK, W. M. 1925 The Determination of Hydrogen Ions. Baltimore, Md.
- (12) COMBER, N. M. 1926 The action of non-diffusible ions in soil phenomena. *Trans. 2nd Comm. Internat. Soc. Soil Sci.* B: 43-45.
- (13) COOK, R. C. 1916 Effect of grinding on the lime requirement of soils. *Soil Sci.* 1: 95-98.
- (14) DAWSON, L. E. 1926 The pH with quinhydrone electrode. *Sugar* 28: 211-214; 262-264; 310-312; 369-370.
- (15) EWING, W. W. 1925 The preparation of electrolytic mercurous chloride in saturated potassium chloride for use in the calomel electrode. *Jour. Amer. Chem. Soc.* 47: 301-305.
- (16) FALES, H. A., AND MUDGE, W. A. 1920 A study of the saturated potassium chloride calomel cell. *Jour. Amer. Chem. Soc.* 42: 2434-2453.
- (17) FISHER, E. A. 1921 Studies of soil reactions: II. The colorimetric determination of the hydrogen-ion concentration in soils and aqueous soil extracts. *Jour. Agr. Sci.* 11: 45-65.
- (18) GILLESPIE, L. J., AND HURST, L. A. 1918 Hydrogen-ion concentration—soil type—common potato scab. *Soil Sci.* 6: 219-236.
- (19) HISSINK, D. J., AND VAN DER SPEK, J. 1926 Die pH Bestimmung des Bodens nach der Biilmann'schen Chinhydrone-methode. *Trans. 2nd Comm. Internat. Soc. Soil Sci.* B: 29-40.
- (20) KOLTHOFF, J. M. 1925 Die Zuverlässigkeit der Chinhydrone-elektrode für die Messung der Wasserstoffionenkonzentration in verschiedenen Lösungen. *Ztschr. Physiol. Chem.* 144: 259-271.
- (21) KOLTHOFF, J. M., AND FURMAN, N. H. 1926 Potentiometric Titrations. New York.
- (22) LAMER, V. K., AND PARSONS, T. R. 1923 The application of the quinhydrone electrode to electrometric acid-base titrations in the presence of air, and the factors limiting its use in alkaline solution. *Jour. Biol. Chem.* 57: 613-31.
- (23) PIERRE, W. H. 1925 The H-ion concentration of soils as affected by carbonic acid and the soil-water ratio, and the nature of soil acidity as revealed by these studies. *Soil Sci.* 20: 285-305.
- (24) SHARP, L. T., AND HOAGLAND, D. R. 1916 Acidity and adsorption in soils as measured by the hydrogen electrode. *Jour. Agr. Res.* 7: 123-145.
- (25) SØRENSEN, S. P. L. 1909 Études Enzymatiques. II Sur la mesure et l'importance de la concentration des ions hydrogène dans les réactions enzymatiques. *Compt. Rend. Lab. Carlsberg* 8: 1-168.
- (26) SØRENSEN, S. P. L., AND LINDERSTRØM-LANG, K. 1924 On the determination and value of  $\pi_0$  in electrometric measurements of hydrogen ion concentrations. *Compt. Rend. Lab. Carlsberg* 15: (6) 1-40.
- (27) VEIBEL, S. 1923 The quinhydrone electrode as a comparison electrode. *Jour. Chem. Soc.* 123: 2203-2207.

SOIL SCIENCE  
VOLUME XXIV, NUMBER 6, DECEMBER, 1927

CONTENTS

Studies on the Transformations of Iron in Nature. II. Concerning the Importance of Microorganisms in the Solution and Precipitation of Iron. R. L. STARKEY AND H. O. HALVORSON .....	381
A Study of Base Exchange in Soils with the Aid of the Quinhydrone Electrode. F. O. ANDEREGG AND R. P. LUTZ .....	403
Cross Inoculation with Cowpea and Soybean Nodule Bacteria. O. H. SEARS AND W. R. CARROLL .....	413
The Relation of Organic Matter and Nitrogen Content to Series and Type in Virgin Grassland Soils. J. C. RUSSEL AND WM. G. McRUER .....	421
The Quinhydrone Electrode and the Soil Reaction. NORMAN ASHWELL CLARK AND EMERSON R. COLLINS .....	453
Retention of Phosphorus by Soil Colloids. C. A. ROSZMANN .....	465
The Fate of Fractional Incorporations of Burnt Lime in Two Soil Zones. W. H. MACINTIRE .....	475
Index .....	487

II. THE GRAVIMETRIC METHOD FOR THE DETERMINATION OF CARBONATES  
IN SOILS.

This second part of the thesis was published jointly with  
Dr. Norman A. Clark in Soil Sci.:27:407-414. A reprint of this  
paper is inserted for convenience.

THE GRAVIMETRIC METHOD FOR THE DETERMINATION OF  
CARBONATES IN SOIL

BY

NORMAN ASHWELL CLARK AND EMERSON R. COLLINS

*Iowa State College*

REPRINTED FROM  
SOIL SCIENCE, VOL. XXVII, No. 5, May, 1929



## THE GRAVIMETRIC METHOD FOR THE DETERMINATION OF CARBONATES IN SOIL

NORMAN ASHWELL CLARK AND EMERSON R. COLLINS

*Iowa State College*<sup>1</sup>

Received for publication January 28, 1929

Of the three methods generally used for the determination of carbonates in the soil—titrimetric, volumetric, and gravimetric—the gravimetric has fallen to a certain extent into disfavor and has received little attention for some time. Cain (5) cited many of the difficulties encountered in the absorption of carbon dioxide and the weighing of the absorbent, and soil chemists have not made any serious effort to improve the process, although it is generally accepted that the method gives very accurate results if precautions are observed (16).

The procedure can be stated briefly as the production of carbon dioxide from the carbonates by the action of dilute acid on the soil; the purification, drying, and absorption of the resulting gas, by drawing it through a "train" by aspiration; and the final weighing of the absorbing material. The chief precautions needed are: 1. the preliminary sweeping out of all traces of carbon dioxide from the apparatus; 2. the decomposition of all the carbonates in the soil without an attacking of the organic matter—a difficulty shared with the gas-volumetric and titrimetric methods; 3. the removal of the air from the absorption bulb with the same water content as it has on entering. Errors may also be incurred by the variation in the amount of moisture on the surface of the absorbing bulb. In the apparatus described hereafter, we have made an adaptation which shortens the time needed for sweeping out the carbon dioxide; the decomposition of the carbonates has been accelerated; the time taken both for the absorption and for the weighing has been materially reduced.

The old method of heating the soil with strong acid in order to set free the carbon dioxide was abandoned because of the action on the organic matter. Marr (10) at Rothamsted, after trying a variety of methods, finally distilled the soil with dilute HCl under reduced pressure at 50°C. for 20 minutes. He claimed that under these conditions no decomposition of organic matter took place, and carbonates were readily decomposed. Marr at the same time confirmed the conclusion of Amos (2) that occlusion of carbon dioxide in air-dry soil did not take place to any extent; this is also in accordance with our observations. MacIntire and Willis (8) suggested H<sub>3</sub>PO<sub>4</sub> for the acid, but re-

<sup>1</sup> Contribution from the Department of Chemistry,

turned later to HCl (9) as the phosphoric acid failed to give complete decomposition of all carbonates in 30 minutes. 1:10 HCl was recommended by them for most soils and 1:5 for soils with greater than 15 per cent  $\text{CaCO}_3$ . They state "We have found that the action of 1:10 HCl on soil organic matter at room temperature is altogether negligible upon 5, 10, 20 gm. charges of the average soil." They also observe that if residual magnesite occurs in a soil "neither boiling for 1 minute, or several minutes, nor the Marr method, nor the Tennessee Station method will effect the complete decomposition of the mineral magnesium carbonate." Such soils are of rare occurrence, but they needed boiling for 30 minutes to get complete decomposition.

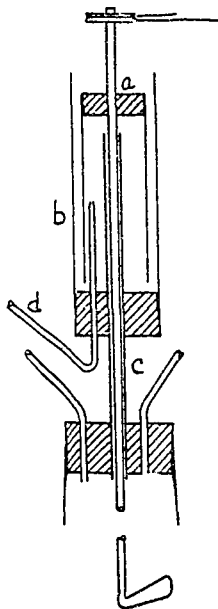


FIG. 1. STIRRER WITH MERCURY SEAL

MacIntire and Willis noted the necessity for shaking the soil with the acid and devised a multiple shaking apparatus which was later adopted by the Association of Official Agricultural Chemists. Truog (17) avoided the shaking by bubbling the  $\text{CO}_2$ -free air through the soil solution. In a previous report (6) we have noted the fineness to which soil is brought by continuous stirring, and in place of shaking we therefore introduced a stirrer combined with the mercury seal.

The stirrer with mercury seal was described by Brühl (4) and has become increasingly useful to the organic chemist (1). It can be applied frequently to soil problems. Figure 1 shows the stirring rod attached by a stopper (a) to the inverted tube which revolves with it. This tube is sealed to the passage of gas by the mercury in the outer tube (b). The tube (c) connects the seal

with the flask; the stirring rod, slightly greased, fits fairly closely into this. It is convenient to attach one of the small 1/8 H.P. stirring motors directly to the stirring rod to avoid vibration. An innovation is the presence of the extra inlet (*d*) which passes inside the revolving tube and terminates above the level of the mercury; this enables air to be drawn through the seal, effectively preventing any carbon dioxide from staying in the air spaces.

Preliminary stirring is unnecessary: a soil which was stirred with water free from carbon dioxide for 5 hours before adding the HCl, did not give any increase in the final amount of carbon dioxide compared to the same soil when stirred only during the time of aspiration. The speed of evolution of the gas without preliminary stirring was equal to the rate of production from the soil which had been previously stirred, indicating that the stirring during aspiration allows the acid to attack the carbonates with rapidity, as well as holding to a minimum the solution of carbon dioxide in the liquid (8). We have used a concentration of acid sufficient to make a 1:10 HCl in the flask when added to the soil and water. For soils with a high concentration of carbonates, or for lime materials, we have included sufficient acid to obtain approximately 1:10 HCl in the flask after the reaction, and have added the acid slowly.

A solution of potassium hydroxide is effective when used as the absorbent for the carbon dioxide but it necessitates slow aspiration. In order to accelerate the passage of the air, ascarite has been utilized. This sodium hydroxide, asbestos mixture was introduced in work on steel by Stetser and Norton (15) who found that the ascarite retained the water produced by the absorption of the carbon dioxide. Marsh (11), however, reported against its use for soils. He states that gases must be drawn or forced through the absorbing medium for periods varying from 12 to 48 hours or more, and as the ascarite lost water after 5 hours, he concluded that "where long runs are necessary as in the determination of CO<sub>2</sub> production from soil, ascarite because of loss of moisture, can not be successfully used."

A possible means of adapting ascarite for soils was pointed out by Underwood (18). In the direct determination of carbon dioxide in limestone Underwood passed the gas over phosphorus pentoxide before it entered a Midvale absorption bulb containing the ascarite, and again over the pentoxide before it left the bulb. In this way he took care of any excess moisture which was not absorbed by the ascarite. We have used a U tube with glass stopcocks for the absorbing materials. Approximately one-half inch of phosphorus pentoxide is placed on glass wool on the ascarite where the gases emerge from the tube. This allows of much faster aspiration than if a potassium hydroxide solution is used, and it is easy to see when the material should be renewed.

A drying agent, which compares well with phosphorus pentoxide in absorptive capacity and has several advantages, is magnesium perchlorate trihydrate, sold under the name "dehydrite." This was tested by Willard and Smith (19) and has been used by a number of investigators for carbon determinations

(3, 14); it has been applied by Lee and Brown (7) to biological processes. The dehydrite can be used until it increases in weight 20 to 25 per cent, and does not become sticky when charging the tubes. It gives little resistance to the gas and when used shrinks so that it does not stick or clog. This can replace the phosphorus pentoxide, but we have used a somewhat larger quantity of the dehydrite in the weighing tube.

In order to facilitate the removal of the tube from the train, the arms may be ground to make glass joints, instead of being attached with rubber connec-

TABLE 1  
*Weight of U tubes without aspiration*

	MINUTES IN BALANCE CASE		
	5	15	25
Wiped with alcohol, etc.....	82.8876	82.8877	82.8880
Repeated.....	82.8876	82.8879	82.8880
Repeated.....	82.8876	82.8876	82.8881
Wiped with alcohol, etc.....	82.8879	82.8881	82.8882
Repeated.....	82.8878	82.8881	82.8882
Wiped with alcohol, etc.....	34.8027	34.8028	34.8029
Repeated.....	34.8026	34.8028	34.8029
Repeated.....	34.8026	34.8028	34.8029

TABLE 2  
*Weight of U tubes with aspiration*

TREATMENT	HOURS ASPIRATED	MINUTES IN BALANCE CASE			
		5	10	15	20
Preliminary.....	1.25	60.2356	60.2358	60.2360	60.2360
	1.25	60.2683	60.2682	60.2682	60.2683
HCl added.....	1.5	60.2685	60.2685	60.2688	60.2688
	4.5	60.2696	60.2695	60.2696	60.2696
	1.0	60.2696	60.2698	60.2699	60.2699
CaCO <sub>3</sub> per cent.....		0.515	0.515	0.514	0.514

tions. The U tube is wiped off with an alcohol-dampened cloth and afterwards with a dry cloth: it is then placed in the balance case for a few minutes before weighing. We have found, even with a large U tube weighing 80 gm. when filled, that the original weight rarely changes more than 0.2 to 0.3 mgm. when it is left in the laboratory air for the five or six hours necessary for aspiration. Tubes weighing from 40 to 60 gm. when packed with the ascarite and P<sub>2</sub>O<sub>5</sub> or dehydrite give a volume of sufficient size for a large number of

soil determinations; weighing with a tare is generally unnecessary if tubes are wiped off and weighed at the beginning of the run, although the weight will alter on long standing. Table 1 gives figures for both large and small tubes after being wiped with alcohol. Weights were standardized and weighings made as outlined by Richards (13) and are reported to the nearest 0.1 mgm.

From the figures given it will be seen that the gain in weight is very slow after 5 minutes in the balance case. Table 1 shows that consistent results can be obtained by wiping with the alcohol-dampened cloth, followed by a dry cloth and weighing after 5 minutes. Pregl (12) suggests the final wiping should be with chamois skin in microanalytical work in order to prevent electrification, and this procedure can be recommended. Table 2 gives figures for an actual series of weighings during a run on soil, with the  $\text{CO}_2$  calculated as  $\text{CaCO}_3$ . A sample of Iceland Spar gave the following results: weight after

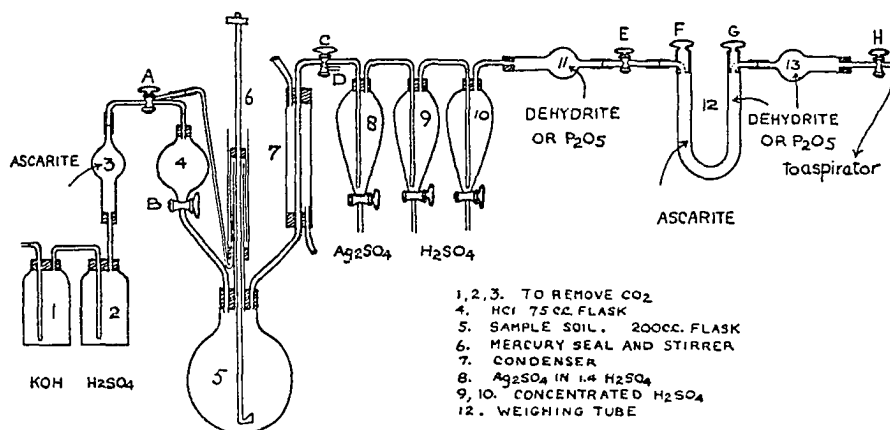


FIG. 2. APPARATUS FOR CARBON DIOXIDE DETERMINATION IN SOILS

5 minutes, 99.85 per cent  $\text{CaCO}_3$ ; after 10 minutes, 99.84; 15 minutes, 99.85; 20 minutes, 99.86.

In figure 2, numbers 1, 2, and 3 serve to remove carbon dioxide from the air. The dropping funnel 4 is fitted with a rubber stopper, and is filled completely with the hydrochloric acid. A small water condenser, made of two glass tubes, has been found satisfactory for substances which do not need boiling; this protects from too much dilution the silver sulfate which is to catch the hydrochloric acid. When a silver precipitate forms it is easily removed through the stopcock at the bottom, and by creating a slight vacuum, a fresh solution is sucked up. The concentrated sulfuric in the following funnels can be replaced in the same way. The glass tubes in these are drawn to fine points, as in numbers 1 and 2, to decrease the size of the bubbles. Under the conditions the phosphorus pentoxide or dehydrite in 11 lasts for a long time without renewal. If the absorption tube 12 is fastened with rubber connections instead of ground glass joints, care must be taken that small

particles of rubber do not get inside the arms. Other joints may be wiped with benzene saturated with equal parts of paraffin and beeswax.

## PROCEDURE

From 5 to 20 gm. of soil which has been passed through a 1-mm. sieve, is placed in flask 5 and washed down with a little CO<sub>2</sub>-free water. Air is then drawn through the apparatus by running water from the aspirator; by the use of the three-way stopcock at *A* the CO<sub>2</sub>-free air can be taken through the

TABLE 3  
*Carbon dioxide from soil, calcium carbonate and mixtures*

SAMPLE	TEMPERATURE	WEIGHT OF SOIL <i>gm.</i>	WEIGHT OF CaCO <sub>3</sub> <i>gm.</i>	ASPIRATION TO CONSTANT WEIGHT		WEIGHT OF CO <sub>2</sub> <i>gm.</i>	CaCO <sub>3</sub> IN SAMPLE		CaCO <sub>3</sub> IN SOIL <i>per cent</i>
				<i>hours</i>	<i>liters</i>		<i>per cent</i>	<i>per cent</i>	
Iceland spar.....	Room	.....	1.8171	5	15	0.7978	99.85	.....	
Iceand spar.....	Room	.....	1.9912	4	13	0.8748	99.92	.....	
Iceland spar.....	Room	.....	1.2210	4.5	14	0.5373	100.00	.....	
Iceland spar.....	Room	.....	1.9414	3.75	14	0.8534	99.98	.....	
						Average	99.94		
Soil 10.....	Room	5.0000	.....	5.25	14	0.1305	5.94	.....	
Soil + spar.....	Room	5.0000	1.6219	4.5	19	0.8431	.....	5.93	
Soil 10.....	50°	5.0000	.....	3.25*	9	0.1318	6.00	.....	
Soil 22c.....	Room	10.0000	.....	4	13.5	0.4898	11.14	.....	
Soil 22c + spar.....	Room	10.0000	1.2430	6	17	1.0357	.....	11.13	
Soil 22c.....	50°	10.0000	.....	4*	12	0.4942	11.24	.....	
Soil 22c + spar.....	50°	10.0000	1.2430	1.25*	5	1.0373	.....	11.17	
CaCO <sub>3</sub> .....	Room	.....	0.3276	5.5	24	0.1398	97.05	.....	
Soil 32.....	Room	15.0000	.....	7.25	20	0.0340	0.52	.....	
Soil 32 + CaCO <sub>3</sub> .....	Room	15.0000	0.2757	5.75	32	0.1511	.....	0.51	
Soil 32.....	50°	15.0000	.....	7.25*	16	0.0356	0.54	.....	
Soil 32 + CaCO <sub>3</sub> .....	50°	15.0000	0.2757	3.00*	14	0.1520	.....	0.53	

\* After aspiration at room temperature as above. Final figures were the same when soil was run at 50° from the time of adding acid.

† Total in mixture minus amount in CaCO<sub>3</sub> as found at room temperature.

stirrer or through the funnel 4. If there are no leaks, when the inlet at 1 is closed for a few minutes, the water will cease to flow. Stopcocks are then closed and tube 12 is weighed as described, and the aspiration repeated until the weight is constant. The tube is replaced in the train and funnel 4 filled with the dilute hydrochloric acid. Before opening *B* stirring and aspiration are started, and then *A* and *B* turned to allow a few drops at a time to pass into flask 5. When all the acid is in the flask, aspiration proceeds slowly at first, and is gradually increased and continued until no change in weight in

the absorption bulb occurs. The  $\text{CO}_2$ -free air is drawn through the mercury seal or through funnel 4 as desired. Between runs the stopcocks are closed, so that the drying parts of the system 8, 9, 10, and 11 are kept free from the outside air. After the introduction of the soil into 5, the three-way stopcock may be opened at *D* and air drawn through from 1 to *D*; this materially accelerates the preliminary removal of the  $\text{CO}_2$  from the apparatus.

The three soils reported contain very widely differing amounts of carbonate. It will be seen from table 3 that in the mixture of soil and carbonate, when the  $\text{CO}_2$  in the Iceland spar is subtracted from the mixture, the recovery of the  $\text{CO}_2$  from the soil is almost identically the same as it is when the soil only is used. At  $50^\circ$  there is a slight increase in the amount of  $\text{CO}_2$  given off. MacIntire and Willis ascribe this to a decomposition of the organic matter at the higher temperature (8), and this seems to be the case. Saturated  $\text{CO}_2$  water with  $\text{HCl}$  was aspirated and all the  $\text{CO}_2$  was removed in about 2 hours at room temperature. No increase in weight was found by raising the temperature to  $50^\circ$ . Similarly the Iceland spar showed no increase in the weight of  $\text{CO}_2$  on running at  $50^\circ$ . The indication is that the increase when soil is present is due to the action on the soil and not to any  $\text{CO}_2$  dissolved in the water.

During the time of aspiration little or no attention is needed—five to seven hours has been found long enough in almost all cases for the U tube to come to constant weight.

#### SUMMARY

1. An improved method for the gravimetric determination of soil carbonates has been outlined.
2. The method makes use of ascarite and either dehydrite or phosphorus pentoxide as absorbents.
3. The soil mixture is stirred instead of shaken, and the mercury seal is adapted for this purpose.
4. One to ten hydrochloric acid is used at room temperature. At  $50^\circ$  there is a slight increase in the amount of  $\text{CO}_2$  given off.
5. Figures are given for determinations on three soils containing widely differing amounts of carbonates, both alone and mixed with calcium carbonate.

#### REFERENCES

- (1) ADAMS, R. ET AL. 1921 Organic Synthesis. New York.
- (2) AMOS, A. 1905 A method for the determination of carbonates in soils. *Jour. Agr. Sci.* 1: 322-326.
- (3) AVERY, S. 1928 Carbon and hydrogen determinations using a metal tube. *Indus. and Engin. Chem.* 20: 1232-1244.
- (4) BRÜHL, J. W. 1904 Ueber einen Schüttel- und Rühr-Apparat. *Ber. Deut. Chem. Gesell.* 37: 918-924.
- (5) CAIN, J. R. 1914 Determination of carbon in steel and iron by the barium carbonate titration method. *Jour. Indus. and Engin. Chem.* 6: 465-468.
- (6) CLARK, N. A., AND COLLINS, E. R. 1927 The quinhydrone electrode and the soil reaction. *Soil Sci.* 24: 453-463.

- (7) LEE, M. O., AND BROWN, J. B. 1927 A note on the use of magnesium perchlorate trihydrate (dehydrite) and asbestos-sodium hydroxide (ascarite) in gravimetric metabolism determinations. *Jour. Biol. Chem.* 73: 69-72.
- (8) MACINTIRE, W. H., AND WILLIS, L. G. 1913 Soil Carbonates. A new method of determination. *Tenn. Agr. Exp. Sta. Bul.* 100.
- (9) MACINTIRE, W. H., AND WILLIS, L. G. 1915 The determination of soil carbonates. A modification. *Jour. Indus. and Engin. Chem.* 7: 227-228.
- (10) MARR, F. S. 1908 Estimation of calcium carbonate in soils. *Jour. Agr. Sci.* 3: 155-160.
- (11) MARSH, F. W. 1925 A test of ascarite, a carbon dioxide absorbent as its own drier. *Jour. Assoc. Off. Agr. Chem.* 8: 442-444.
- (12) PREGL, F. 1917 *Die Quantitative Organische Mikroanalyse*, p. 38-39. Berlin.
- (13) RICHARDS, T. 1900 Note on a method of standardizing weights. *Jour. Amer. Chem. Soc.* 22: 144-149.
- (14) SMITH, G. F., BROWN, M., AND ROSS, J. F. 1924 Magnesium perchlorate trihydrate—its use as a drying agent for steel and organic combustion analysis. *Indus. and Engin. Chem.* 16: 20-22.
- (15) STETSER, J. B., AND NORTON, R. H. 1918 Combustion train for carbon determination. *Iron Age* 102: 443-445.
- (16) TRUOG, E. 1915 Methods for the determination of carbon dioxide and a new form of absorption tower adapted to the titration method. *Jour. Indus. and Engin. Chem.* 7: 1045-1048.
- (17) TRUOG, E. 1916 A new apparatus for the determination of soil carbonates and new methods for the determination of soil acidity. *Jour. Indus. and Engin. Chem.* 8: 341-345.
- (18) UNDERWOOD, J. E. 1926 Apparatus for the direct determination of carbon dioxide. *Indus. and Engin. Chem.* 18: 1069-1070.
- (19) WILLARD, H. H., AND SMITH, G. F. 1922 The preparation and properties of magnesium perchlorate and its use as a drying agent. *Jour. Amer. Chem. Soc.* 44: 2255-2259.



# SOIL SCIENCE

VOLUME XXVII, NUMBER 5, MAY, 1929

## CONTENTS

Detection and Significance of Manganese Dioxide in the Soil. W. O. ROBINSON .....	335
An Efficient Soil Tube Jack. C. A. TAYLOR AND HARRY F. BLANEY .....	351
Some Influences of the Development of Higher Plants upon the Microorganisms in the Soil: II. Influence of the Stage of Plant Growth upon Abundance of Organisms. ROBERT L. STARKEY .....	355
The Botanical Composition and Morphological Features of "Highmoor" Peat Profiles in Maine. A. P. DACHNOWSKI-STOKES.....	379
Contribution to the Chemical Composition of Peat: IV. Chemical Studies of Highmoor Peat Profiles from Maine. SELMAN A. WAKSMAN AND KENNETH R. STEVENS.....	389
The Effect of Sweet Clover and Alfalfa Roots and Tops on the Fungous Flora of the Soil. THOMAS L. MARTIN.....	399
The Gravimetric Method for the Determination of Carbonates in Soil. NORMAN ASHWELL CLARK AND EMERSON R. COLLINS.....	407

TABLE OF CONTENTS

	Page
INTRODUCTION. . . . .	6
DESCRIPTION OF THE SOILS USED . . . . .	8
QUINHYDRONE ELECTRODE . . . . .	10
FACTORS INFLUENCING HYDROGEN ION CONCENTRATION. . . . .	13
A. Soil to Water Ratio . . . . .	13
B. Method of Preparing the Soil. . . . .	14
C. Time of Equilibrium . . . . .	18
THE EFFECT OF ELECTROLYTES IN THE SOIL SUSPENSION . . . . .	28
A. Influence upon the Colloidal Fraction of Soils. . . . .	28
1. Coagulation of soil particles. . . . .	28
2. Factors influencing the coagulating power of electrolytes . . . . .	30
a. Size of particles . . . . .	30
b. The reaction of the soil. . . . .	30
c. Different replaceable cations present . . . . .	30
d. Time factor . . . . .	30
e. The effect of different cations of the electrolyte . . . . .	31
f. The effect of different anions of the electrolyte . . . . .	32
g. The effect of mixtures of electrolytes. . . . .	32
B. Influence on the Hydrogen Ion Concentration . . . . .	36
C. Influence on Base Exchange. . . . .	38
SOIL ACIDITY AND LIME REQUIREMENT . . . . .	45
A. Intensity Factor of Soil Acidity. . . . .	45
B. Quantitative Factor of Soil Acidity . . . . .	48
C. Buffer Capacity . . . . .	96
CONCLUSIONS . . . . .	101
SUMMARY . . . . .	104
LITERATURE CITED. . . . .	105

APPLICATION OF THE QUINHYDRONE ELECTRODE TO INVESTIGATIONS  
ON BASE EXCHANGE IN SOILS

INTRODUCTION

When a soil is treated with a solution containing an electrolyte, there is an exchange of the positive and negative ions between the electrolyte and the complex of the soil. The exchange of the positive ion is usually referred to as "Base Exchange". This term should not give the idea that only metallic ions take place in the reaction, as it is known that hydrogen has a greater replacing activity than any of the positive metallic ions.

The relative amount of hydrogen compared to the kind and quantity of other replaceable ions on the complex determines the quantitative factor of soil acidity or the lime requirement. The pH or the intensity factor of soil acidity does not necessarily indicate the amount of lime needed to neutralize the acidity of the soil. Different soils show varying increases in pH due to the addition of the same quantity of base to equal amounts of soil. The observed property of retarding the increase in pH upon the addition of a base is known as the buffer capacity of the soil.

Methods for measuring the hydrogen ion concentration are of increasing importance. While some work has been done with the antimony electrode, it has not been advanced far enough to be used without some question as to its applicability to soil suspensions. The quinhydrone method is more satisfactory for this work and

it has been carefully studied and is applied here to the investigation of the buffer action of a considerable number of Iowa soils.

DESCRIPTION OF SOILS USED

For the experimental results in this paper we have collected 21 soil types of Iowa from the counties indicated.

Their description, location, origin, color, drainage and lime requirement are tabulated in Table I. This information has been taken from the soil survey reports of the respective counties. Story County does not have a soil survey report so the table has been filled in as fully as possible from observation.

TABLE I  
DESCRIPTION OF SOILS

No.:	Series	Class	County:	Origin and Location	Color	Drainage	Lime Requirement
1	:Bremer	:Silt Loam	:Dallas:	:Terrace	:Dark Brown	:Poor	: 3,000
2	:Buckner	:Fine Sandy Loam	:Dallas:	:Terrace	:Brown	:Good	: 6,000
3	:Cairington	:Loam	:Story:	:Drift	:Brown	:Satisfactory:	
4	:Clarion	:Loam	:Story:	:Drift	:Light Brown	:	
6	:Clyde	:Silty Clay Loam	:Hardin:	:Drift	:Black	:Poor	: 2,000
7	:Conover	:Silt Loam	:Boone:	:Drift	:Grayish Brown	:Fair	: 8,000
8	:Fargo	:Silty Clay Loam	:Hardin:	:Terrace	:Brownish Black	:Poor	: 3,000
9	:Fayette	:Silt Loam	:Hardin:	:Loess	:Grayish Brown	:Slow	: 8,000
10	:Lamoure	:Silty Clay Loam	:Dallas:	:Swamp and Bottomland:	:Dark Brown	:Poor	: 0,000
11	:Lindley	:Fine Sandy Loam	:Dallas:	:Drift	:Grayish Brown	:Excellent	: 3,000
12	:Millsdale	:Loam	:Hardin:	:Terrace	:Brown	:Good	: 6,000
13	:Muscatine	:Silt Loam	:Hardin:	:Loess	:Black	:Poor	: 8,000
14	:O'Neil	:Sandy	:Story:	:Terrace	:Brown	:Good	:
15	:Peat	: --	:Boone:	: --	:Black	:Poor	: 0,000
16	:Sarpy	:Fine Sandy Loam	:Dallas:	:Swamp and Bottomland:	:Brown	:Good	: 2,000
17	:Shelby	:Loam	:Dallas:	:Drift	:Brown	:Good	: 8,000
18	:Sioux	:Sandy	:Story:	:Terrace	:Brown	:Good	:
19	:Tama	:Silt Loam	:Hardin:	:Loess	:Dark Brown	:Good	: 8,000
20	:Wabash	:Silt Loam	:Story:	:Bottomland:	:Dark Brown	:	:
21	:Waukusha	:Loam	:Boone:	:Terrace	:Brownish Black	:Adequate	: 2,000
22	:Webster	:Silty Clay Loam	:Story:	:Drift	:Dark Brown	:	:

Data taken from soil survey map of the respective counties.

## QUINHYDRONE ELECTRODE

Considerable attention has been directed during the last few years to the quinhydrone electrode as a means of determining the hydrogen ion concentration of soils.

This electrode has been widely used in replacing the colorimetric method and the hydrogen electrode. A large amount of work has been done to determine the accuracy of the electrode and the factors influencing the observed results.

Snyder (52) found a close agreement between the quinhydrone electrode and the hydrogen electrode between pH 4.0 and pH 9.0 with soils. The potential, however, drifted gradually from pH 8 to pH 9.

Kolthoff (37) found that in all cases at 18° good results were obtained at less than pH 8.0. In protein solutions having a good buffer action reproducible results could be obtained as high as pH 9.0.

Baver (5) using electrodes of platinum cone, platinum foil, platinum gauze and gold foil, showed some differences in the observed pH. He suggests the use of a solution of definite pH or a control soil to check the accuracy of the electrode.

Nicklas and Hoch (44) state that it is necessary to add at least 500 mgs. of quinhydrone for 100 grams of soil. Baver suggests 0.05 grams for every 15 cubic centimeter of solution. From our observation there is no exact amount that must be added, but it is necessary to have a saturated solution.

### Procedure Used

We have used the quinhydrone electrode in connection with the Schollenberger electrode (Schollenberger (49)) to prevent diffusion of potassium chloride.

Since a soil suspension shows a different pH in the supernatant liquid and in the settled soil, it was thought advisable to keep the soil in suspension with a mechanical stirrer. This is arranged in the manner shown in Figure I. It will be observed that the electrode (11) and the stirrer (10) are placed lower than the ground glass joint (9). This allows contact between the soil and the platinum electrode so that equilibrium may be reached before immersing (9). This also cuts down any excess diffusion for with practically every soil the reading was constant.

Under the proper conditions with a good ground glass joint at (9) there was no diffusion from the calomel electrode noticeable when immersed in distilled water and held to the light. Another test for the diffusion of potassium chloride was made by placing a solution of silver nitrate in the electrode vessel (12) and starting the stirrer as in a pH measurement. Not even a trace of cloudiness appeared in the silver nitrate solution until after several minutes of stirring.

One to five ratio of soil to water was used in every case. Sufficient quinhydrone was added to the solution and placed in contact with the platinum electrode while stirring. After a few seconds, the electrode vessel (12) was pushed up so that (9) was in contact with the solution and the E.M.F. reading was taken at once.



- ① Rubber policeman
- ② Rubber stopper
- ③ Saturated KCl
- ④ Calomel
- ⑤ Mercury
- ⑥ Pt. wire
- ⑦ Rubber stopper
- ⑧ KCl crystals
- ⑨ Ground glass seal
- ⑩ Stirrer
- ⑪ Pt. wire hammered flat
- ⑫ Electrode vessel
- ⑬ Hg connection
- ⑭ Rubber stopper

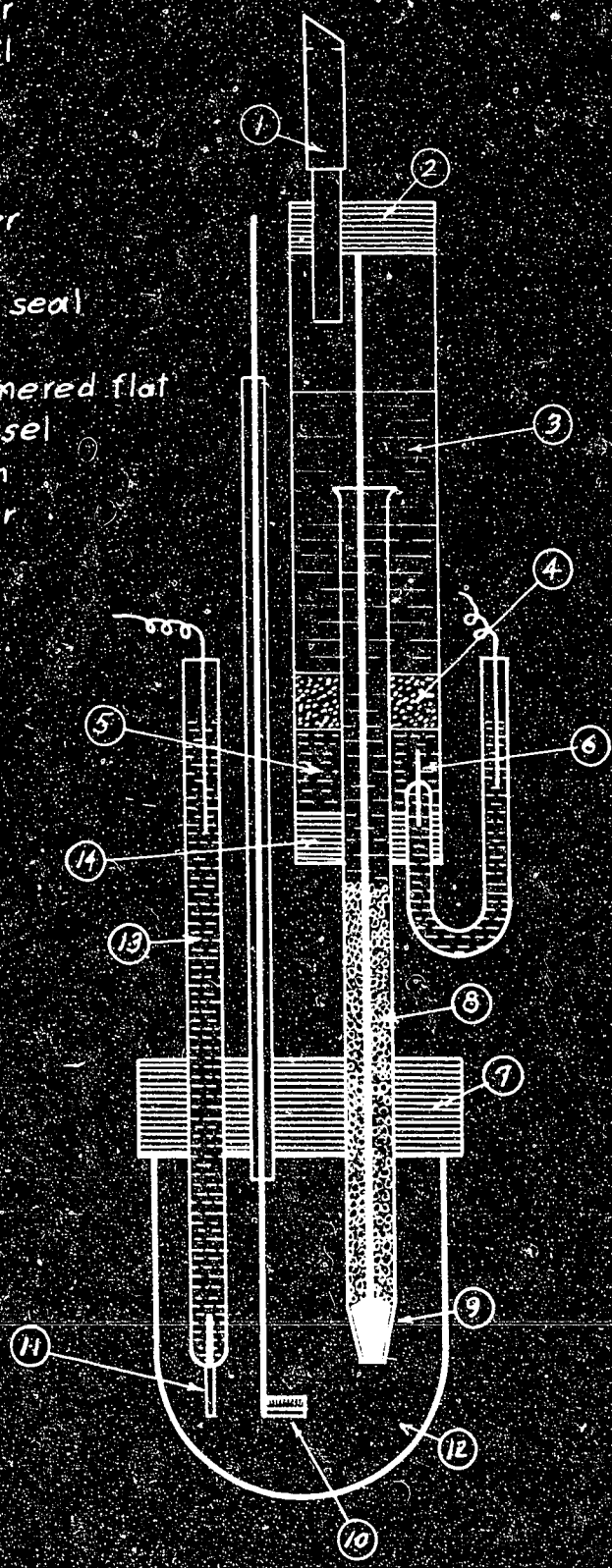


Fig. 1 Quinhydrone Electrode

## FACTORS INFLUENCING HYDROGEN ION CONCENTRATION.

The factors influencing hydrogen ion concentration in soils are considered under the following headings:-

- A. Soil to Water Ratio.
- B. Method of Preparing the Soil.
- C. Time of Equilibrium.

### Soil to Water Ratio

Considerable discussion has taken place in the literature regarding the correct ratio to be used in determining the hydrogen ion concentration of soils. This ratio has ranged from 1:1 to 1:5 for soil to water, and a few workers have even exceeded the latter ratio.

Druschinin (20) indicates little influence of soil to water ratio on the hydrogen ion concentration of soil suspensions. On unlimed soils the hydrogen ion concentration decreases slightly with increased water, while limed soils give the opposite effect. Joseph and Snow (35) suggest 1 to 5 ratio, as the ratio has an important influence on the results. They show that the hydrogen ion concentration decreased as the soil to water ratio increased. Similarly Burgess (1)(12) recommends 1 to 5 ratio and shows a slight but gradual decrease in acidity with dilution. He supports his suggestion by saying that greater dilutions have nothing to recommend them, while less water with certain mucks and clays may give too thick a magma. Furthermore 1 to 5 ratio is almost universally used.

Hissink and Van der Spek (30) give an explanation for the variation with dilution. Soil particles are negatively charged in aqueous suspensions. It is assumed that they carry a double electric layer, the inner consisting of aluminosilicates or humic acid anions and the negative outer layer of H, K, Na, Ca, and Mg. ions. The hydrogen of the double layer and that of the molecularly dispersed acids determine the acidity of the soil. Clay acids are weak, humic acids mostly weak, although occasionally they are moderately strong. Decrease of acidity with dilution is explained by the assumption that each unit volume contains a smaller number of colloidal particles with a double layer. This interpretation was supported by the fact that centrifugates or filtrates give a lower hydrogen ion concentration than the original suspensions.

In order to get results comparable with those of other investigators, a ratio of 1:5 for soil to solution has been used in all cases.

#### Method of Preparing the Soil

Cook (17) using New Jersey soils found an increase in lime requirement (Veitch method as by Brown and Johnson) in every case due to grinding. Brown and Johnson (19), however, found that certain sandy Iowa soils showed a decrease in lime requirement with grinding. Sharp and Rouillard (30) using six soils from four American states, found generally that pH was unaltered by grinding, although in one case the pH increased from 6.4 to 7.15.

Fisher (21) states that the difference is due to the variation between the chemical structure of the interior and the partially weathered exterior part of the crumb structure. He finds consistently lower pH for 100 mesh samples than for 3 m.m. sieved soils shaken for the same time. However, the 3 m.m. sample shaken for thirty hours gave a much lower pH than either of the others. Sharp and Hoagland (50) explain the difference as a slow rate of solubility possessed by acid constituents. Comber (16) points out that there is no justification for assuming that the hydrogen ion concentration of a given soil sample is uniform throughout. This is supported by the fact that the hydrogen ion concentration of a suspension differs as the soil settles out or is shaken up. This points to a difference between the supernatant liquid and that in the pore spaces. Similarly there may be a difference between the concentration of the hydrogen ions and other ions in the liquid outside the soil crumb and inside. If this is true, then we should expect a difference before and after grinding.

Tidmore (54) explains the fact that a soil suspension will invert more sugar than a soil extract of the same hydrogen ion concentration, on the supposition that there may be a higher hydrogen ion concentration at the surface of the soil particle than in the solution.

Fisher (21) gives another explanation for change in lime requirement and pH value due to shaking. He noticed that the longer shaking and the more finely ground, the greater the

turbidity even after centrifuging. He thought the variation might be due to some action of suspended clay. Baver (2), and Clark and Collins (14), have shown the efficiency of a stirrer in breaking up the soil crumb. Therefore an apparatus has been devised as shown in Figure 2, in order to obtain as uniform a suspension as possible. The procedure is described in detail under the following heading.

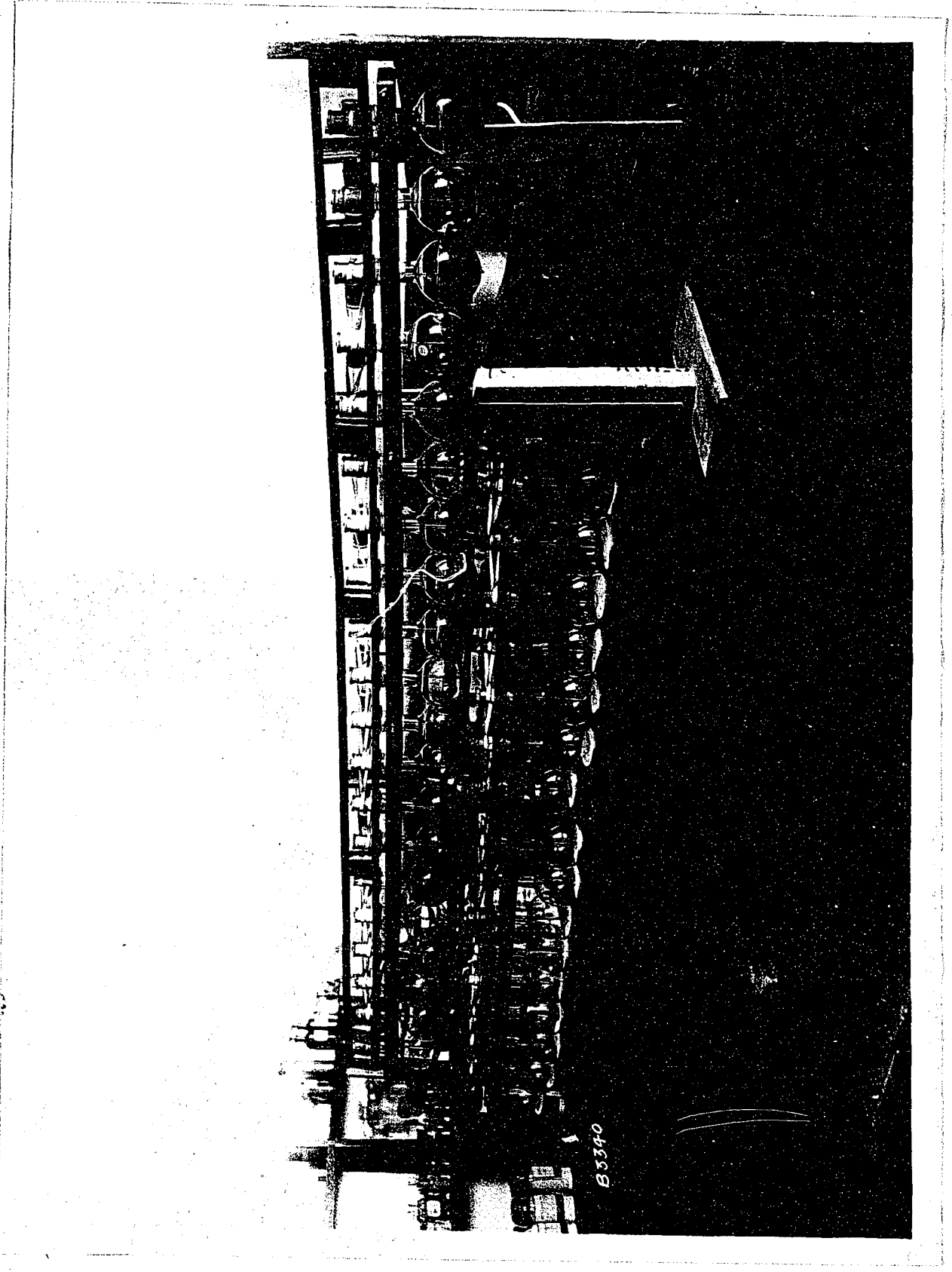


Fig. 2. Stirring Apparatus

### Time of Equilibrium

We will consider here the time of equilibrium between soil and electrolyte solutions, as well as soil and water. This is justified by the fact that soils contain soluble salts and the difference is a factor of concentration.

Burgess (11) shows that variation in the time of shaking from 15 to 45 minutes makes but little difference in the case of soil and water, although acid soils become more acid on shaking. Burgess (12) further shows that the optimum time of shaking the suspension before taking the reading appears to be thirty minutes. He states that intermittent shaking is as good as continuous. Sharp and Hoagland (50) found that equilibrium is obtained in acid soils in a few minutes but a longer time is required for soils that are approximately neutral. This is explained as the slow rate of solubility possessed by the acid constituents of the soil.

Hardy and Lewis (29) have found no appreciable difference in the majority of cases in the titration value obtained for soil in calcium chloride solution, whether it is titrated at once or allowed to stand to develop acidity. This indicated a rapid equilibrium between soil and calcium chloride solutions, but in the case of free lime a rather lengthy period of contact was thought advisable. They added 0.03 N. calcium hydroxide, five cubic centimeters at a time and determined the reaction after vigorous and continuous shaking. Only a slight change in reaction was observed after a three minute shaking period, but

additions above five cubic centimeters necessitates a longer agitation.

Maiwald (38) states that approximately constant values are obtained, for titration curves, only after more than one day of reaction. Similarly Hissink and Van der Spek (31) find that equilibrium is slow and that about three days are required in the case of direct titration with sodium hydroxide, calcium hydroxide or barium hydroxide. Crowther (18) shows that the equilibrium with alkaline solutions is most rapid when shaken with finely divided samples, and that approximately constant values are obtained after a few hours when the final solution is still on the acid side. Brioux (9) found that with three times the theoretical amount of calcium oxide the pH gradually decreased to slightly less than pH 7.0 in a few months. If exactly the theoretical amount is added the pH may fall below the original value. Nitrate nitrogen determinations showed that in no case could nitrification account for the neutralization of all the calcium oxide.

#### Experimental Results on Time of Equilibrium.

Many of the results obtained for time of equilibrium have been obtained by methods consisting of shaking by hand or of intermittent shaking. Since different fractions settle out at different rates, all fractions may not be in contact with the solution of the same concentration. As Comber (16) and others have pointed out, there may be a difference between the concentration of the hydrogen ions and the other ions in the liquid

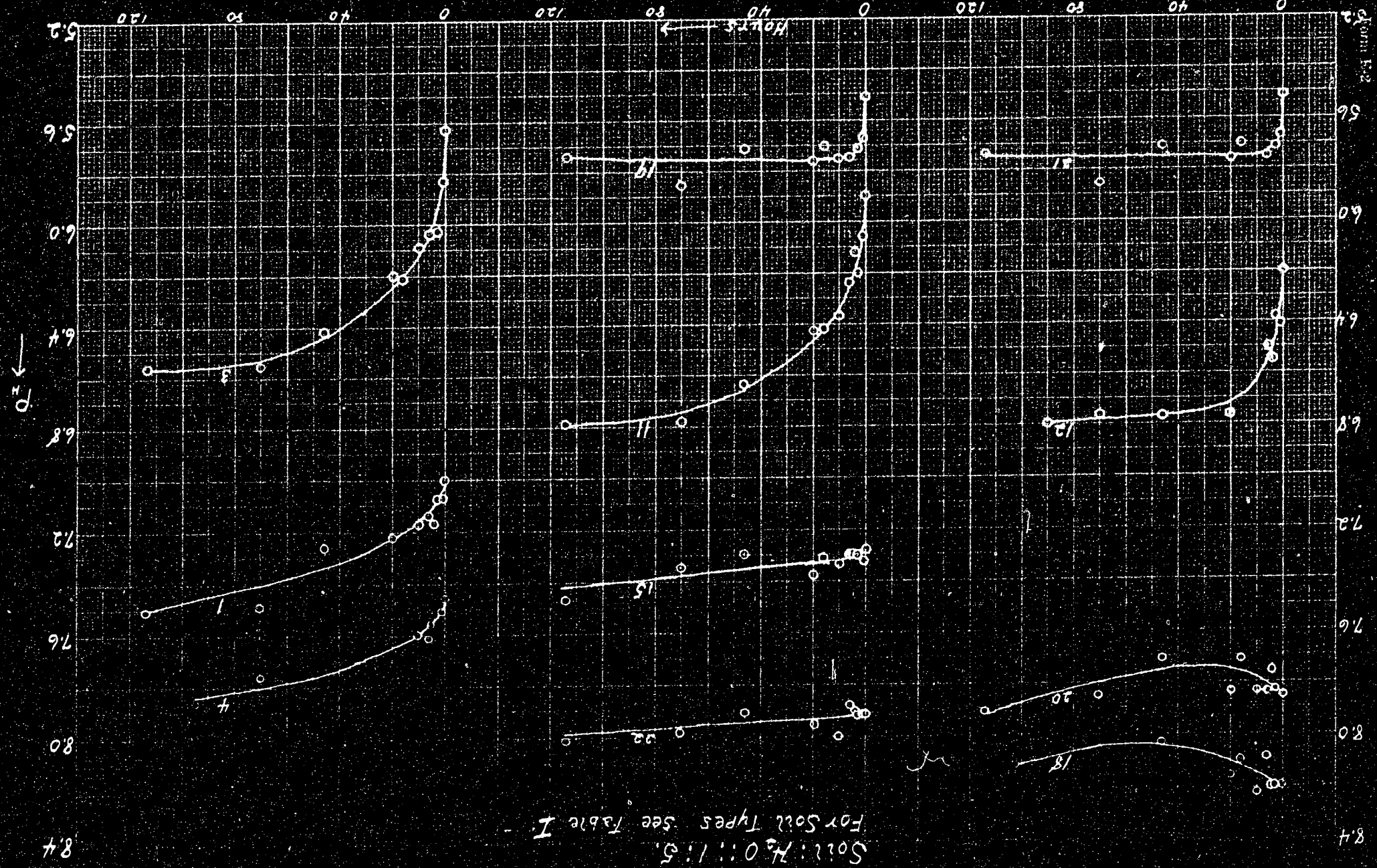


outside and inside the soil crumb. Therefore the apparatus described previously, and shown in Figure 2, has been used to keep the soil in intimate contact with the solution and to break up the soil crumb structure.

Figures 3 and 4 show the results obtained for variation of pH with time of stirring with water. Figures 5 and 6 show the same type of curves for the soils in calcium hydroxide solution, and Figures 7 and 8 for the soils in 0.4 normal calcium chloride solution brought to pH 7.0 with calcium oxide. Samples were removed from the flasks shown in Figure 2 by means of a twenty five cubic centimeter pipette with a small piece of rubber tubing attached to the end. These samples were removed while the stirrer was in motion in order to get as uniform a sample as possible. The pH was then determined, on this solution, with the electrode shown in Figure 1.

From these curves obtained with twenty one Iowa soils, it is difficult to draw any definite conclusion as to the optimum time of stirring necessary for equilibrium. It is easy to see that any definite time stated to be necessary for equilibrium would not hold for all soils. It is therefore suggested that, with these soils, the only way to determine equilibrium with water or admixed reagents is to stir each soil until approximately no change in pH is observed.

Soil: H<sub>2</sub>O :: 1:5  
 For Soil Types see Table I  
 7.28.3.



Soil Reaction in Water

1:5 Ratio  
For Soil Types see Table I



Hours →  
Fig. 4.

Soil Reaction in  $\text{Ca}(\text{OH})_2$  0.0055%  
 Soil:  $\text{Ca}(\text{OH})_2$  0.055% = 1:5 Ratio  
 For Soil Types See Table I.

9.4

9.0

8.6

8.2

7.8

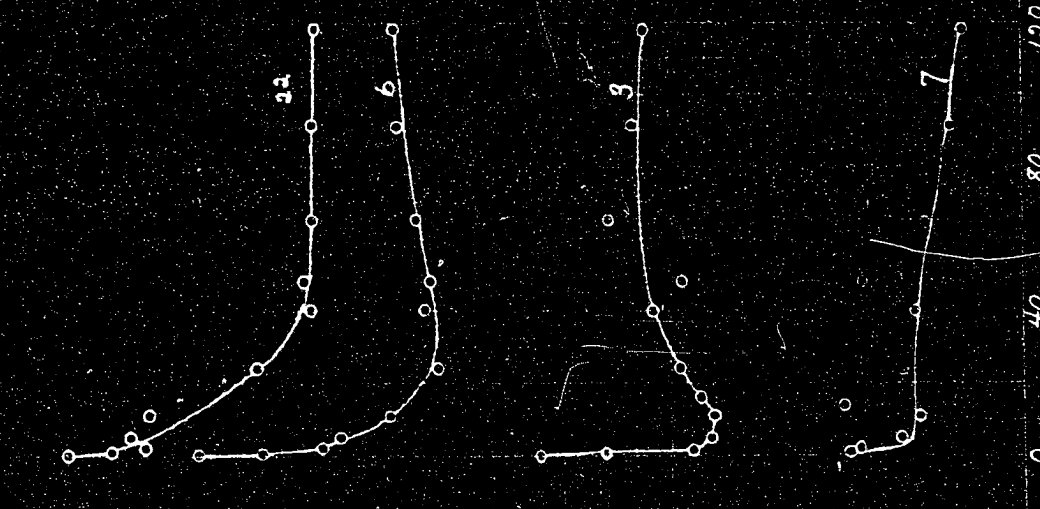
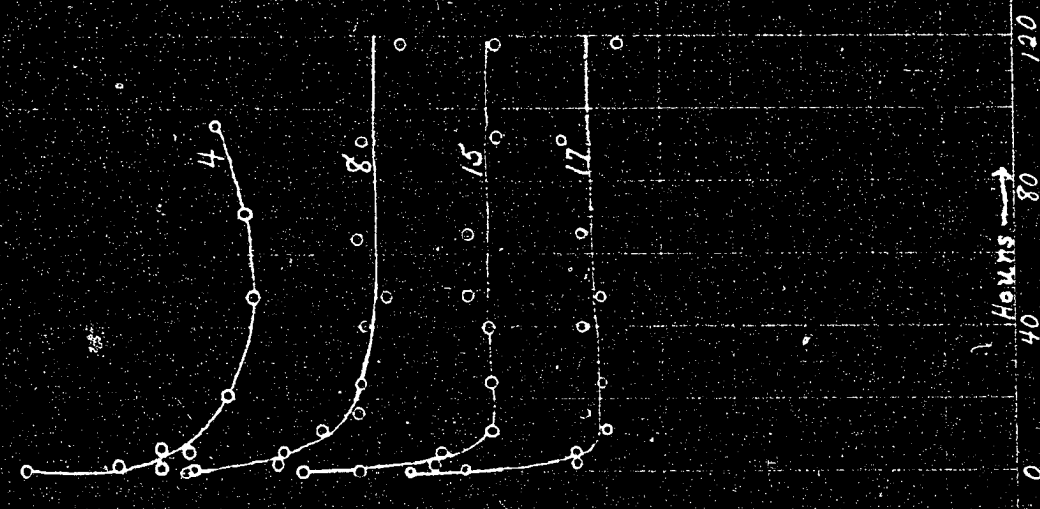
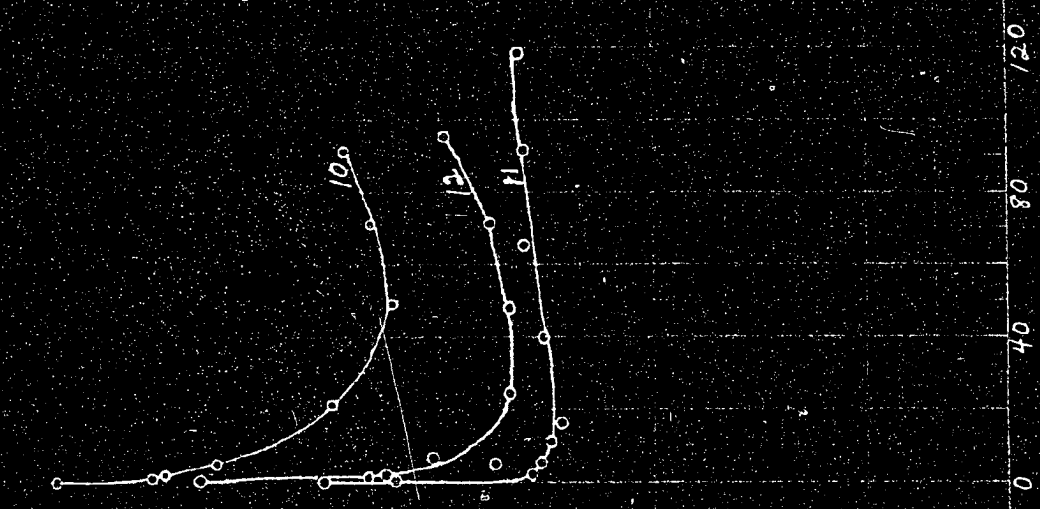
7.4

7.0

6.6

6.2

$\text{pH}$  ↑



9.4

9.0

8.6

8.2

7.8

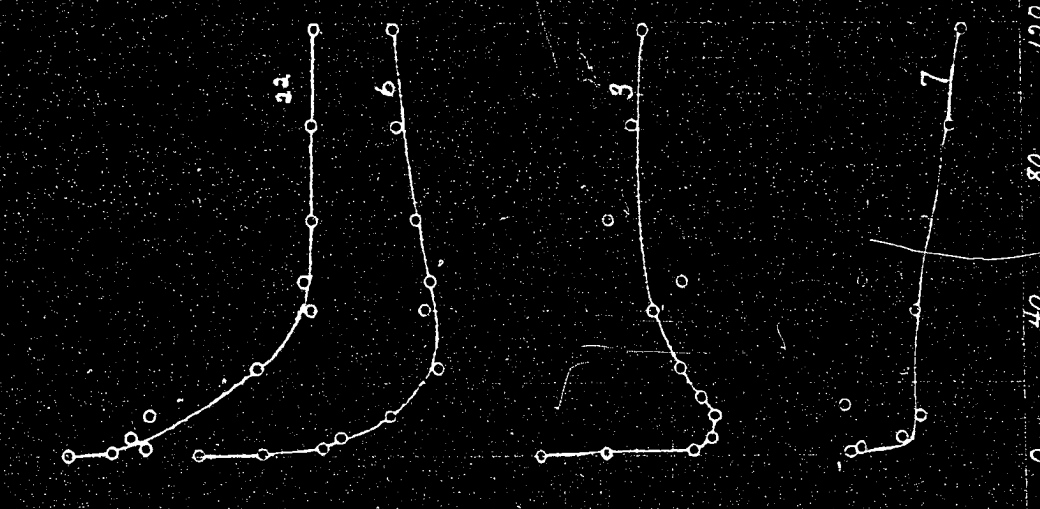
7.4

7.0

6.6

6.2

$\text{pH}$  ↑



Hours →

Fig. 5.

Soil Reaction in  $Ca(OH)_2$  0.0055N

Soil:  $Ca(OH)_2$  0.0055N = 1:1.5 Ratio  
For Soil Types see Table I



Hours → 80  
Fig. 6.

Soil Reaction in  $\text{CaCl}_2$  0.4N.  $\text{P}_H$  70

1:5 Ratio.

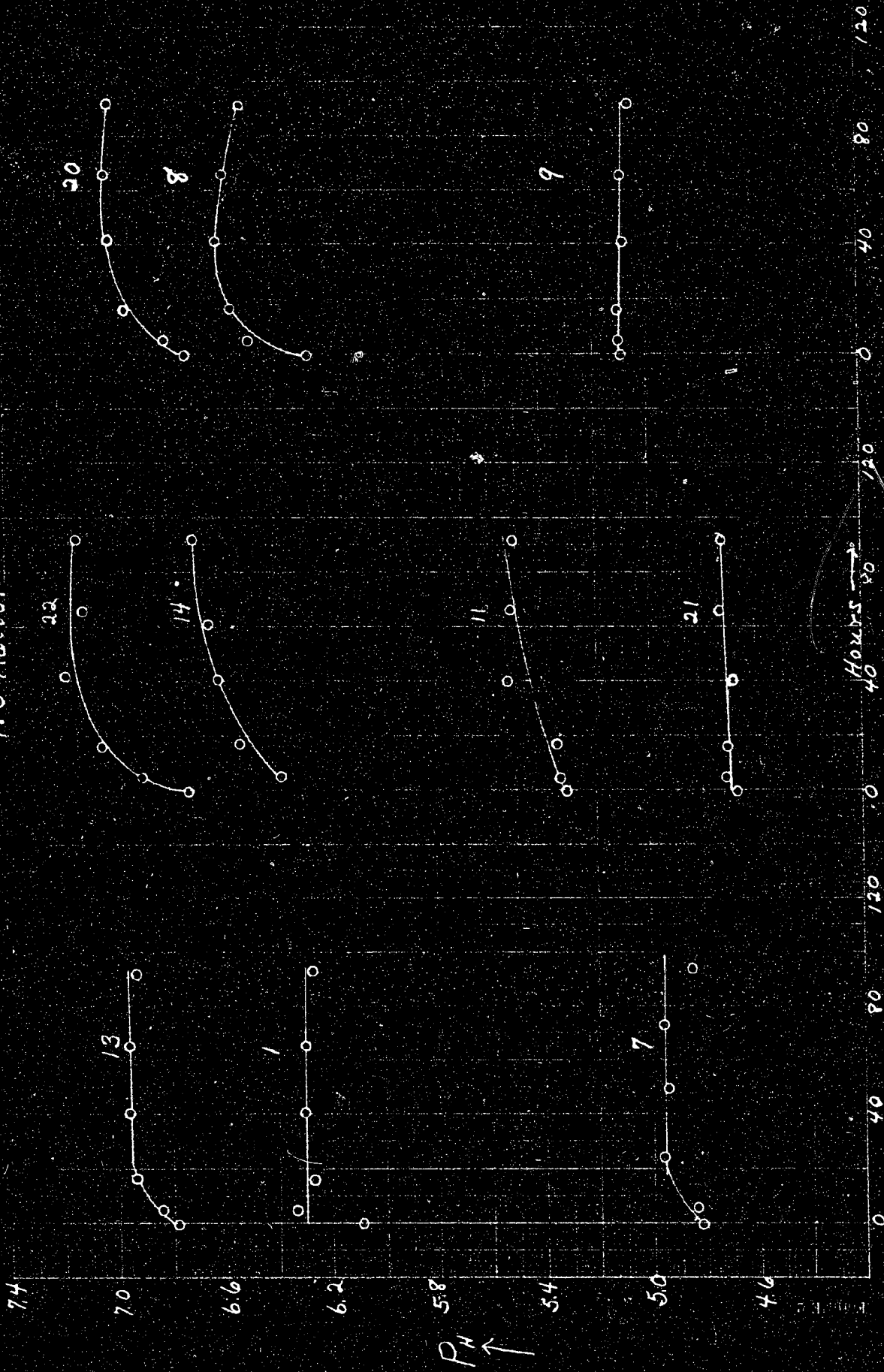
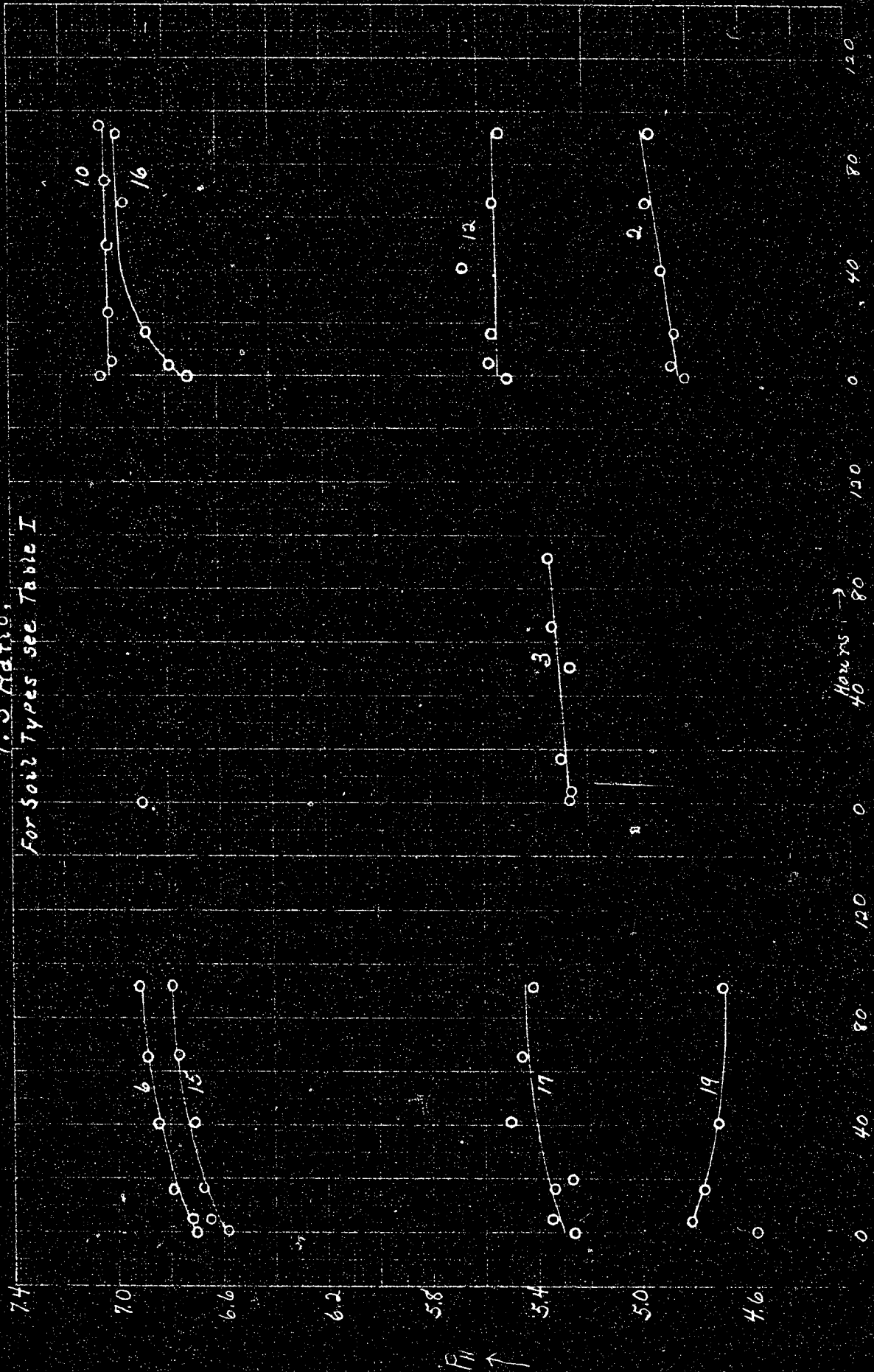


Fig. 7

Soil Reaction in  $\text{CaCl}_2$  0.4N. P. 7.0

1:5 Ratio,  
For Soil Types see Table I



Hours →

Fig. 8

THE EFFECT OF ELECTROLYTES IN THE SOIL SUSPENSION.

A. Influence upon the Colloidal Fraction of Soils.

1. Coagulation of soil particles.

In the smaller fractions of the soil, including clay, silt and humus, we are dealing with colloids and such properties must be considered in the explanation of various treatments.

Marshall (39) has made a very complete review of the researches on soil colloids, and we will only bring out a few of the points given.

Freundlich (23) found that according to the amount of electrolyte added (or in dealing with soils, present in the suspension) a sol may be brought into the region of slow coagulation or of rapid coagulation. In the region of slow coagulation the particles still retain a portion of their original charge and the rate at which they coalesce shows a very sensitive variation with the amount of electrolyte present. Curves connecting the time taken to reach a given stage of coalescence with the amount of electrolyte are hyperbolic. Mattson (40) and Gallay (24) obtain curves of this type for clay, in which an increase of the amount of electrolyte brings us to the region of rapid coagulation. We are then on the arm of the curve which runs parallel to the time axis. The rate of coagulation thus becomes independent of the amount of electrolyte.

Oden (45) has shown that in the case of clays, coagulation



THE EFFECT OF ELECTROLYTES IN THE SOIL SUSPENSION.

A. Influence upon the Colloidal Fraction of Soils.

1. Coagulation of soil particles.

In the smaller fractions of the soil, including clay, silt and humus, we are dealing with colloids and such properties must be considered in the explanation of various treatments.

Marshall (39) has made a very complete review of the researches on soil colloids, and we will only bring out a few of the points given.

Freundlich (23) found that according to the amount of electrolyte added (or in dealing with soils, present in the suspension) a sol may be brought into the region of slow coagulation or of rapid coagulation. In the region of slow coagulation the particles still retain a portion of their original charge and the rate at which they coalesce shows a very sensitive variation with the amount of electrolyte present. Curves connecting the time taken to reach a given stage of coalescence with the amount of electrolyte are hyperbolic. Mattson (40) and Gallay (24) obtain curves of this type for clay, in which an increase of the amount of electrolyte brings us to the region of rapid coagulation. We are then on the arm of the curve which runs parallel to the time axis. The rate of coagulation thus becomes independent of the amount of electrolyte.

Oden (45) has shown that in the case of clays, coagulation

is much less simple, owing to particles varying in size. Large particles reach the region of slow coagulation at a lower electrolyte concentration than the smaller ones. Three critical concentrations can be distinguished corresponding to (a) the point at which the larger, primary particles are slowly coagulated, (b) that at which the secondary particles have united to form aggregates of approximately equal size 2 - 5  $\mu\mu$  and (c) that at which the sol as a whole shows rapid coagulation. Galloway (24) has shown that the phenomenon of partial coagulation and precipitation in layers is due to wide variation in particle size in association with high concentrations.

We can not assume from this discussion that clay alone shows these properties, as Oden (45) working with mixtures of Clay and neutral humate, also clay and humic acid, found a strong protective action in the order of that of protein. Mattson (40) points out that the action consists not only in a protection of the clay by the humus, but also a sensitisation of the humus by the clay. Mixtures of humic acid and clay are coagulated at concentrations of electrolytes intermediate between those necessary for each separately. Comber, working with salts in the order of their coagulating power, finds that the order is completely reversed in the case of the silt fraction compared to the clay. He found that silica gel showed the same behavior as clay while silicic acid sol resembles silt. This variation in

different fractions is explained in his theory by regarding all small soil particles as consisting of two parts, a hard mineral kernel and a gel-like coating. The differences between silt and sand are due to the different proportions of these. The relative amount of gel increases as the particles diminish in size.

2. Factors influencing the coagulating power of electrolytes.

a. Size of particles as shown above.

b. The reaction of the soil.

Bradfield (8) found that different acids coagulate clay at pH 5.8. The amount of potassium chloride needed to flocculate the soil increased gradually with the pH up to the neutral point where it rose rapidly to a constant value.

c. Different replaceable cations present.

Wiegner (57) and Gallay (24) studied coagulations of clays with different replaceable cations and found that sodium, potassium and ammonium clays are approximately equally sensitive to electrolytes. The calcium clay was much more sensitive, being coagulated by N/100 calcium chloride while the potassium clay required N/10.

d. Time factor.

Gallay (24) followed the coagulation of clay using the Oswald viscosimeter and found that during coagulation the viscosity rose, reaching a maximum when coagulation was completed. This observed effect was due in part to the fact that the sols were relatively concentrated so

that the particles influenced each others motion, and in part to the hydration of the particles. The effect of hydration was seen in the gradual decrease of viscosity with time after coagulation.

The coagulum was shrinking and giving up the water which it had enmeshed during coagulation.

e. The effect of different cations of the electrolyte.

Gedroiz (25) and Wiegner (57) have shown that the flocculating power of alkali cations increased in the series, Li, Na, K, Rb and also in the series Mg, Ca, Sr and Ba. Wiegner (57) and Gallay (24) found that in all cases bivalent cations are better precipitants than univalent, but that the difference became less as the concentration of the suspension increased. Using a potassium clay the effect of the alkali cations increased from lithium to cesium. Wiegner has shown that the effect of different cations was due to the difference in hydration of these ions, and this effect was the same whether the clay was prepared in the usual way or whether it was saturated with any of these cations. Gedroiz (26) saturated clay with various mono and bi valent cations and then subjected the product to mechanical analysis. He found a great variation in the amount of clay fraction according to the cations used. Monovalent cations, including hydrogen which had only a small effect, increased the dispersion in the order H, K,  $\text{NH}_4$ , Na and Li.

f. The effect of different anions of the electrolyte.

Hall and Mouson (28) working with Kaolin suspensions have shown that there were appreciable differences in the effect of various calcium compounds on coagulation.

The hydroxide has a much lower flocculating power than the salts. This is usually ascribed to the peptizing tendency of the hydroxyl ion. Gedroiz (25) showed that for true clay the flocculating power of calcium hydroxide was superior to that of the sulfate, nitrate and bicarbonate but equal to that of the chloride. Comber has verified this work of Gedroiz but shows that the order is completely reversed in the case of the silt fraction. This does not disagree with Hall and Mouson because, as stated above, they worked with a comparatively coarse suspension of kaolin.

g. The effect of mixtures of electrolytes.

Freundlich points out that care must be used in drawing conclusions based on results obtained in mixed electrolytes, for the interpretation of such experiments is very difficult. The addition of small amounts of alkali hydroxides to calcium salts has been shown by Gedroiz, Comber and Mattson to increase their power of precipitation. Gedroiz found the same for sodium chloride and sodium hydroxide within certain limits. Mattson showed conclusively that in the case of clay a very small amount of calcium hydroxide showed a stabilizing effect, as did

also low concentrations of alkali in the presence of calcium salts. He showed that quartz and humic matter did not show this behavior, but only the increased coagulating power shown by Clay in higher concentrations. Adsorption experiments showed that adsorption of calcium ions was much increased by the alkali. The coagulation in the presence of hydroxyl took place while the particles still carried a much higher charge than was found for the coagulum produced by simple salts. The action of caustic soda, at a concentration of 0.0002 N, on clay particles was to increase the charge to double that in pure water. At higher concentrations the charge was decreased. Calcium sulfate always decreased the charge. When caustic soda was added in increasing concentrations to calcium sulfate, the charge was increased even at greater concentrations of caustic soda than 0.0002 N.

Mattson explained these facts by assuming that there was a preferential adsorption of the hydroxyl ion which tended to raise the charge. Opposed to this tendency was the discharging effect of cations. However since each cation could be attached to more than one hydroxyl the particles could be held together by the poly valent cations. This would occur when the number of poly valented cations was not nearly sufficient to cause coagulation by the usual discharging effect. Gedroiz found that sodium hydroxyde and sodium chloride showed a similar effect with regard to clay, namely, that in

low concentrations of salts the addition of sodium hydroxide reduced the precipitating power, while at higher concentrations an enhanced power of coagulation was observed. This would not follow with univalent ions, from Mattson's explanation, unless he assumes that auxiliary valencies are the cause of the binding and not merely the primary valencies. Comber supposes that this anomalous flocculation is a property of the gel coating of the soil particles and that the mineral core does not possess this phenomenon. Mattson, however, used suspensions that had been ignited before use, so that he was dealing with a true suspensoid when he proved the increased adsorption of calcium in the presence of the hydroxyl ion.

Mattson (40) has shown that this property of alkali in enhancing the sensitivity towards calcium salts is true of humic acid as well as clay. The addition of alkali to humic acid enhanced the sensitivity towards calcium salts until the concentration of the alkali became equivalent to that of the calcium, when the hydroxyl ion began to have a peptizing action. In the case of humic acid this latter was supposed to be due to the formation of sodium humate.

Summarizing these results for the effect of electrolytes on the colloidal fraction of the soil, we find:

1. Coagulation of the soil may be slow or rapid depending upon the amount of electrolyte.
2. The same is true of clay, silt and humus, but is much less simple because of the variation in the size of particles. Large particles precipitate first.
3. The factors influencing the coagulating power of electrolytes divide into the following headings.
  - a. The size of the particle influences coagulation as the larger particles precipitate first.
  - b. The reaction of the soil determines the amount of potassium chloride required to flocculate the particles. The higher the pH the more potassium chloride is required.
  - c. Different replaceable cations present in the complex show varying sensitivity to electrolytes. Na, K and  $\text{NH}_4$  clays approximately equally sensitive. Calcium clays are much more sensitive.
  - d. The time factor is important because of the changes taking place accompanying the slow coagulation, such as changes in viscosity and hydration.
  - e. The effect of different cations of the electrolyte has an important significance, as the flocculating power increases in the series Li, Na, K, Rb, also in the series Mg, Ca, Sr, and Ba. With saturated clays the different cations increased the dispersion of the clay fraction in the order H, K,  $\text{NH}_4$ , Na and Li. This difference between cations is explained as a hydration



effect.

- f. The effect of different anions of the electrolyte were found to vary with different fractions. Calcium hydroxide was found superior to other calcium salts in the coagulation of clay. This order is reversed in the case of silt.
- g. Coagulation by mixtures of electrolytes is difficult to interpret. The addition of small amounts of alkali hydroxides to calcium salts increases the precipitating power. The same is true of sodium hydroxide added to sodium chloride. Very small amounts of calcium or alkali hydroxides show a stabilizing effect as did low concentrations of alkali in the presence of calcium salts. Quartz and humic matter show only the increased coagulating power even at low concentrations.

#### B. Influence on the Hydrogen Ion Concentration.

In the study of the effect of neutral salts on soils as determined by the hydrogen ion concentration, it is noticed that all salts show the same type of reaction, differing only in degree. This observed effect is shown by an increase in acidity. Crowther (18) shows that potassium and barium gave the greatest increase, ammonium salts only slightly less, and sodium much smaller except at the highest concentration. Potassium oxalate gave the highest pH caused by the precipitation of exchange calcium and the formation of the highly hydrolysed potassium

clays and humates. Anderegg and Lutz (1) determined the ionization constants of clay by preparing the acid clay by dialysis and titrating with salt solutions. They found that clay acts like a monobasic acid in contact with the solutions of the neutral salts used. The ionization constants were found to be as follows:

Na Clay $1.70 \times 10^{-5}$	Mg Clay $0.73 \times 10^{-5}$
K Clay $1.15 \times 10^{-5}$	Ca Clay $0.76 \times 10^{-5}$

Joseph (32) explains the effect of neutral salts on clay on a purely chemical basis. He found that the acidity developed on treating various clays with sodium chloride solution increased as the ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$ , reaching a maximum for pure silica. Different salts bring different amounts of silica into solution, the order of cations being Na K Ba Ca. He supposed that the solubility of the silicates or complexes decrease in this order. Kappen and Breidenfeld (34), however, have failed to observe acidity on treating purified silica with potassium chloride. Mukherjee (42) using purified silica and Ghosh (27) using hydrated manganese dioxide have concluded from their experiments that the adsorption theory alone can account for all the facts.

Because of the varied concentrations of salts used by different workers, as well as soils consisting of varying fractions or particle size and containing different replaceable ions, it is hardly possible to make a close comparison between the precipitating or coagulating power of salt solutions and the increase in acidity noticed when treating soils with salt solutions. However, it is worth while to compare the results of a number of workers.

The flocculating power increases in series Li, Na, K, Rb also in the series Mg, Ca, Sr and Ba (Wiegner and Gallay).

The greatest increase in acidity given by K and Ba for the salts studied.  $\text{NH}_4$  slightly less and Na much smaller except at higher concentrations (Crowther).

The replacing activity is given by Kelly and Brown as  $\text{H} > \text{Ca} > \text{Mg} > \text{K} = \text{NH}_4 > \text{Na}$ .

Thus it appears that those ions having the greatest flocculating power have the greatest replacing activities, which seems very logical if we consider that a reaction goes to completion when a precipitate is formed. This would seem to favor the theory of Joseph considering that different salts bring different amounts of silicates into solution, the order of cations being Na K Ba Ca. Calcium causing the greatest precipitation and gives the highest increase in acidity.

Another suggestion that might be offered is that the coagulation decreases the buffer action by removing the soil particles from suspension and thus shows a greater intensity of acidity or decrease in pH.

Another cause for the increased acidity due to the addition of a neutral salt will be noticed under base exchange reactions. The hydrogen is forced off the complex by the mass action of the cation of the salt added.

### C. Influence on Base Exchange.

When a soil is treated with the solution of an electrolyte an exchange takes place between the ions of the solution and the

absorbed ions of the dispersed soil particles. This exchange of the positive ions, including hydrogen, is known as base exchange. The exchange capacity of a soil can be determined by leaching the soil with a neutral salt solution and analyzing the leachings. Bobko and Askinaze (4) have summarized some of the necessary conditions for methods of determining the absorption capacity of soils by adding a neutral salt.

1. The neutral salt must be easy to estimate analytically.
2. It must not be present in the soil.
3. It must be active in replacing bases.
4. It must not act destructively on the absorbing complex.

There will be no attempt made to summarize the various methods of determining this exchange reaction but a few methods will be presented for the sake of comparison. Barium chloride has been used by many workers; Bobko and Askenaze (4), Burgess and Breazeale, Gedroiz, Hissink, etc. Others, using ammonium chloride for the electrolyte, are Kelly and Brown (35), Smith (51), Joffe and McLean, etc. This salt is recommended because it can easily be removed from the solution by evaporating to dryness and igniting. Schollenberger (48) recommends ammonium acetate because the salts of weak acids are better replacing agents than the salts of strong acids. Taranor (53), Bradfield (6), Mattson (41), Oden (46) and Wilson (59) have compared methods of extraction with electrolytes to the method of electro dialysis of the soil. They have found that the amounts of bases brought into solution by the two methods compare very favorably. The electro dialysis

of the soil brings about a replacement of the bases with hydrogen. Therefore the dialyzed soil is similar to the product obtained after leaching with a dilute acid. Since hydrogen is the most active of the replacing ions, dilute acids have been used to a great extent and found to give results comparable to those obtained with neutral salts (Kelly and Brown (36) and others.)

Most of the methods developed for the use of electrolytes in leaching the soil can be used only in the case of carbonate free soils. Page and Williams (47) have suggested a modified method that can be used with soils containing carbonates. The rostersed soil is intimately mixed with excess calcium carbonate and the mixture finally leached with normal sodium chloride. The reaction for total exchange goes to completion with continuous leaching with fresh sodium chloride solution. Turner (56) objects to this method because of the following:

1. The reaction may not go to completion due to calcium in solution as calcium carbonate.
2. Two liters for the volume of leaching solution are insufficient.
3. The unreliability of the factor for the solubility of calcium carbonate in the sodium chloride solution used for leaching.

Because of these objections to the method of Page and Williams as given by Turner, a modified method of procedure will be presented for the Williams' method in the following experimental work.

Carbonate determinations, on the twenty one Iowa soils described were made using the method of Clark and Collins (15).

In these determinations both 1 to 10 hydrochloric acid and 0.5 normal acetic acid were used with the results shown in Table II. It will be observed that the majority of these soils show a carbonate content and any method of base exchange using salt solutions or weak acids will show too high a value according to the solubility of the carbonate in the solution used.

Because 0.5 N acetic acid reacts slowly with the carbonate found in some soils, it was found necessary to modify the method of Williams as follows: Twenty five grams of air dried soil ( 1 mm.) were placed in a three hundred cubic centimeter erlenmeyer flask with two hundred cubic centimeters of 0.05 normal acetic acid. This solution was stirred vigorously for fifteen minutes with an efficient mechanical stirrer. Glass rods were extended into the solution to break up the particles as suggested by Bayer (2). The suspension was then allowed to stand over night and the supernatant liquid poured onto a filter. Two hundred cubic centimeters more 0.5 normal acetic acid were added and stirred again for fifteen minutes. This solution was poured onto the filter and the soil leached with 0.5 normal acetic acid until one liter had been collected. The calcium was estimated by the method given by Williams (58) and checked with the results obtained from a complete analysis of the remaining solution. In order to prove that this treatment was sufficient to decompose all of the carbonates, the soils from the above experiment were dried and sieved. The soil was weighed up and carbonate determinations made by the method of Clark and Collins (15) using 1 to 10 hydrochloric acid. The results obtained showed that within

TABLE II.

CALCIUM CARBONATE DETERMINED BY THE USE OF THE APPARATUS DESCRIBED BY CLARK AND COLLINS (15).

Soil Number	:HCl 1:10	:HAc .5N
1	.58%	.54%
2	.04	.02
3	.05	.01
4	.53	.36
6	.27	.02
7	.01	.02
8	.10	.07
9	.02	.01
10	5.94	5.70
11	.07	.02
12	.05	.00
13	.36	.33
14	.55	.52
15	.94	.86
16	7.52	7.69
17	.04	.01
18	10.68	11.94
19	.03	.01
20	3.94	3.63
21	.04	.03
22	11.18	11.28

experimental error all the carbonates had been decomposed.

The original soils show slight variations in carbonate content depending upon the acid used but this is thought to be due to the long period necessary for decomposition of the carbonate with 0.5 normal acetic acid. As shown by Clark and Collins (15) the bulb used for weighing the carbon dioxide evolved may change weight during such a long period required for 0.5 normal acetic acid. In some cases twenty four hours were necessary to completely decompose the carbonate.

Using the suggestion of Bollen and Neidig (5) and expressing the results in equivalent parts per million ( $\text{Eq p.p.m.} \times \frac{1}{\text{eq. wt}}$ ) we can calculate the total base exchange of calcium and magnesium by subtracting the equivalent parts per million of carbon dioxide from the total equivalent parts per million of calcium and magnesium obtained by the modified Williams method. These results are tabulated in Table III.



TABLE III.

BASE EXCHANGE DATA FOR THE SOILS DESCRIBED

Soil:	:	:	:	:	:	:
No.:	A	B	C	D	E	:
1	424.8	39.6	464.4	115.9	348.5	:
2	56.8	23.6	80.4	8.0	72.4	:
3	112.0	17.6	129.6	10.0	119.6	:
4	183.2	33.2	216.4	106.0	210.4	:
6	520.8	56.8	577.6	53.9	523.7	:
7	98.0	2.8	100.8	2.0	98.8	:
8	342.8	48.0	390.8	20.0	370.8	:
9	94.8	10.4	105.2	4.0	101.2	:
10	1050.4	182.0	1232.4	1186.8	45.6	:
11	90.4	11.6	100.2	14.0	86.2	:
12	81.6	9.6	91.2	10.0	81.2	:
13	396.0	53.6	449.6	72.0	377.6	:
14	173.6	36.0	209.6	110.0	99.6	:
15	951.2	662.4	1613.6	188.0	1425.6	:
16	1070.0	266.8	1336.8	1502.5	--	Δ:
17	96.0	14.8	110.8	8.0	102.8	:
18	1376.0	278.8	1654.8	2133.9	--	Δ:
19	106.8	3.2	110.0	6.0	104.0	:
20	628.4	142.4	770.8	787.2	0.0	:
21	144.0	18.8	162.8	8.0	154.8	:
22	2350.8	439.6	2790.4	2233.8	556.6	:

Δ These soils required about two days for the carbonate determination with 0.5 N acetic acid and the time given for leaching with this acid was probably insufficient.

Results expressed as equivalent parts per million

$$\text{Eq. p.p.m.} = \text{p.p.m.} \times \frac{1}{\text{eq. wt}}$$

Column A. Base Exchange Ca + Ca in the form of carbonates.

Column B. Base Exchange Mg + Mg in the form of carbonates.

Column C. Base Exchange Ca and Mg + Ca and Mg in the form of carbonates.

Column D. Eq. p.p.m. carbon dioxide or Ca + Mg in the form of carbonates.

Column E. C - D = Base Exchange Ca and Mg.

## SOIL ACIDITY AND LIME REQUIREMENT.

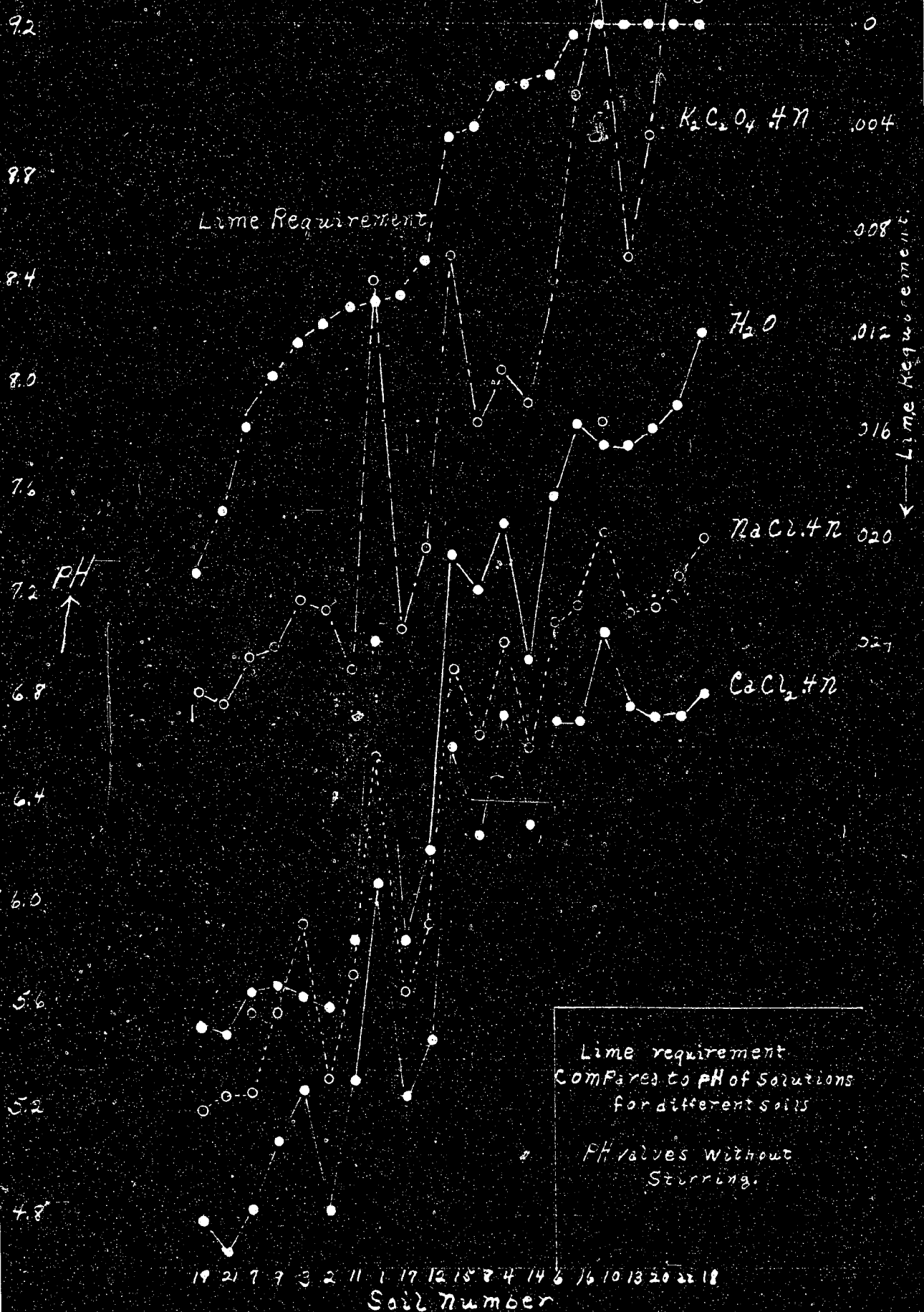
### Intensity Factor of Soil Acidity

The intensity factor of soil acidity is measured by colorimetric or electrometric methods and expressed as pH or hydrogen ion concentration. It is generally accepted that pH expresses only the intensity factor of soil acidity and gives us no indication of the power of neutralizing acids or bases. Several attempts have been made to correlate the pH of a soil with the lime requirement, but from the fundamental conception one would not expect any such correlation except by chance. Investigators that have reported such a correlation always show several exceptions if they have used a reasonable number of soils.

The term "lime requirement" is itself unsatisfactory. Generally it may be defined as the amount of lime necessary to be added to the soil in order to bring the pH of the soil to a reaction suitable for good growth of crops. This reaction may vary for different plants, but as a rule a pH near the neutral point is desirable. A large number of methods has been used to determine the best amount of lime to apply but with only slight agreement. The early procedures were empirical as the conception of pH did not exist; later methods have attempted to find the amount of base to be added to the soil to bring it to a pH of approximately 7.0.

Figure 9 show these Iowa soils arranged in the order of decreasing lime requirement, determined by the method of Hardy and Lewis (29) as the amount of calcium hydroxide required to bring the soil to pH 7.0 in calcium chloride 0.4 normal. The accompany-

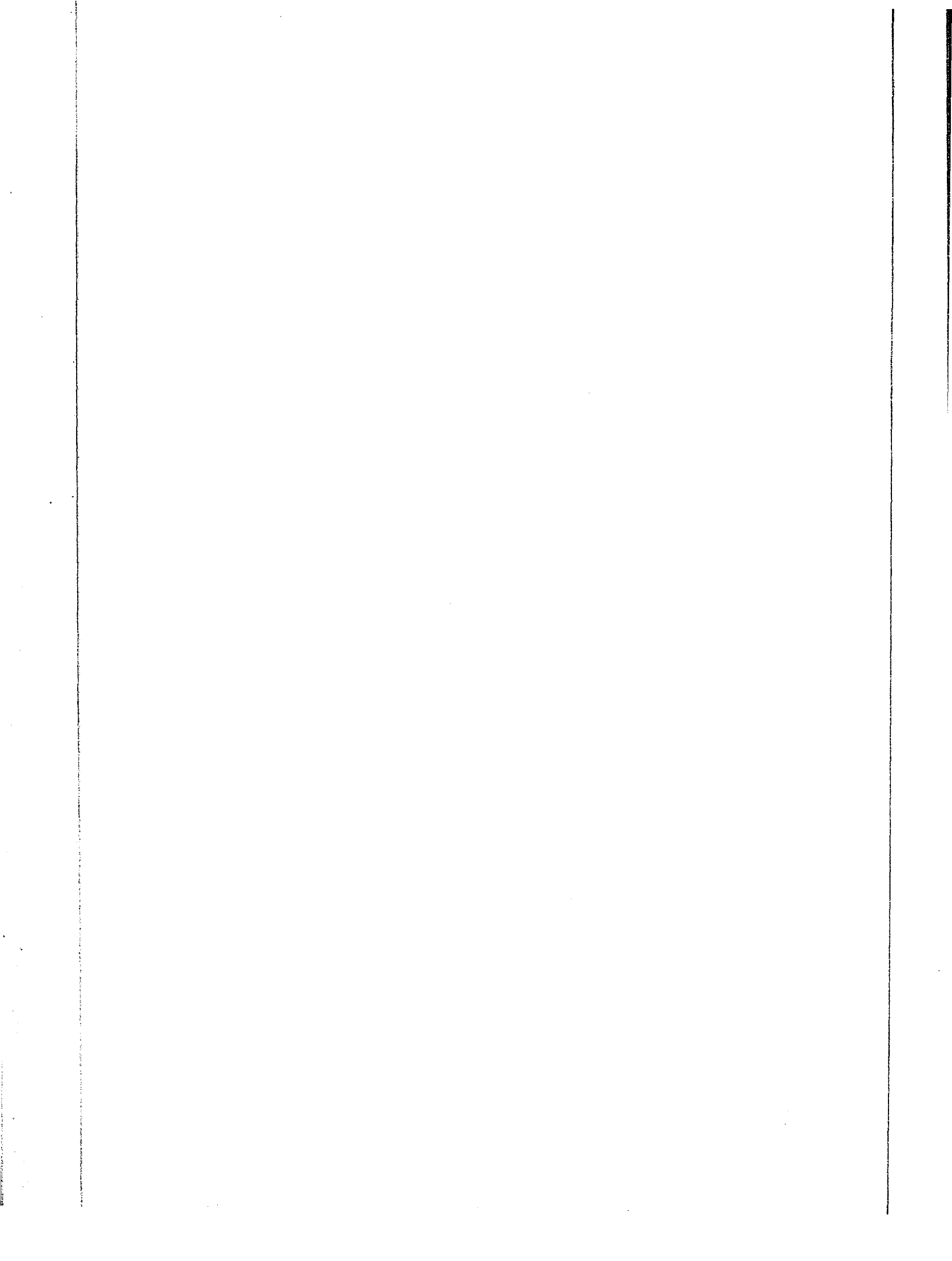
ing points show the pH of the 21 soils in water, sodium chloride, calcium chloride and potassium oxalate. It will be observed that the pH in any of these solutions shows very little correlation with the lime requirement determined by this method.

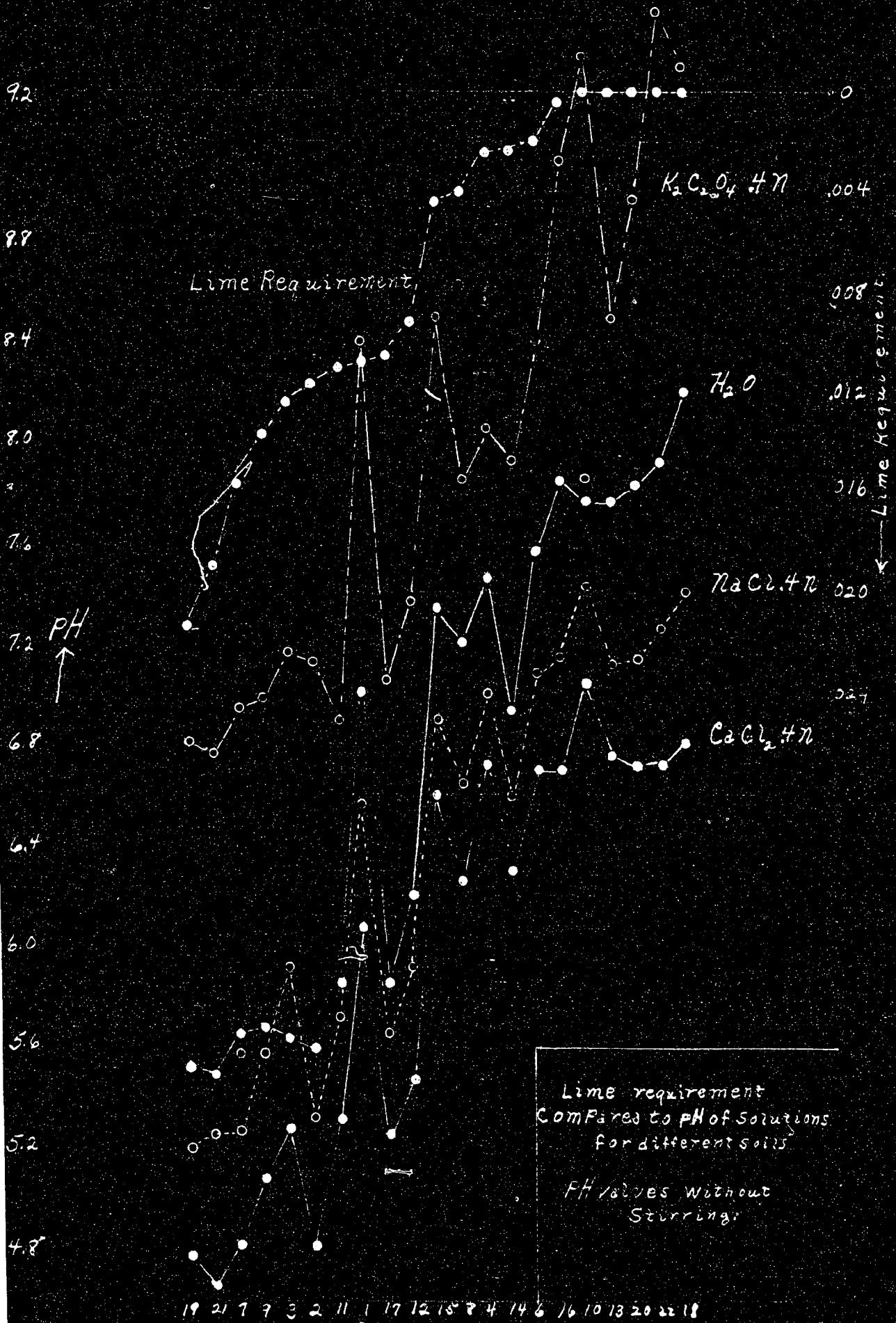


Lime requirement compared to pH of solutions for different soils

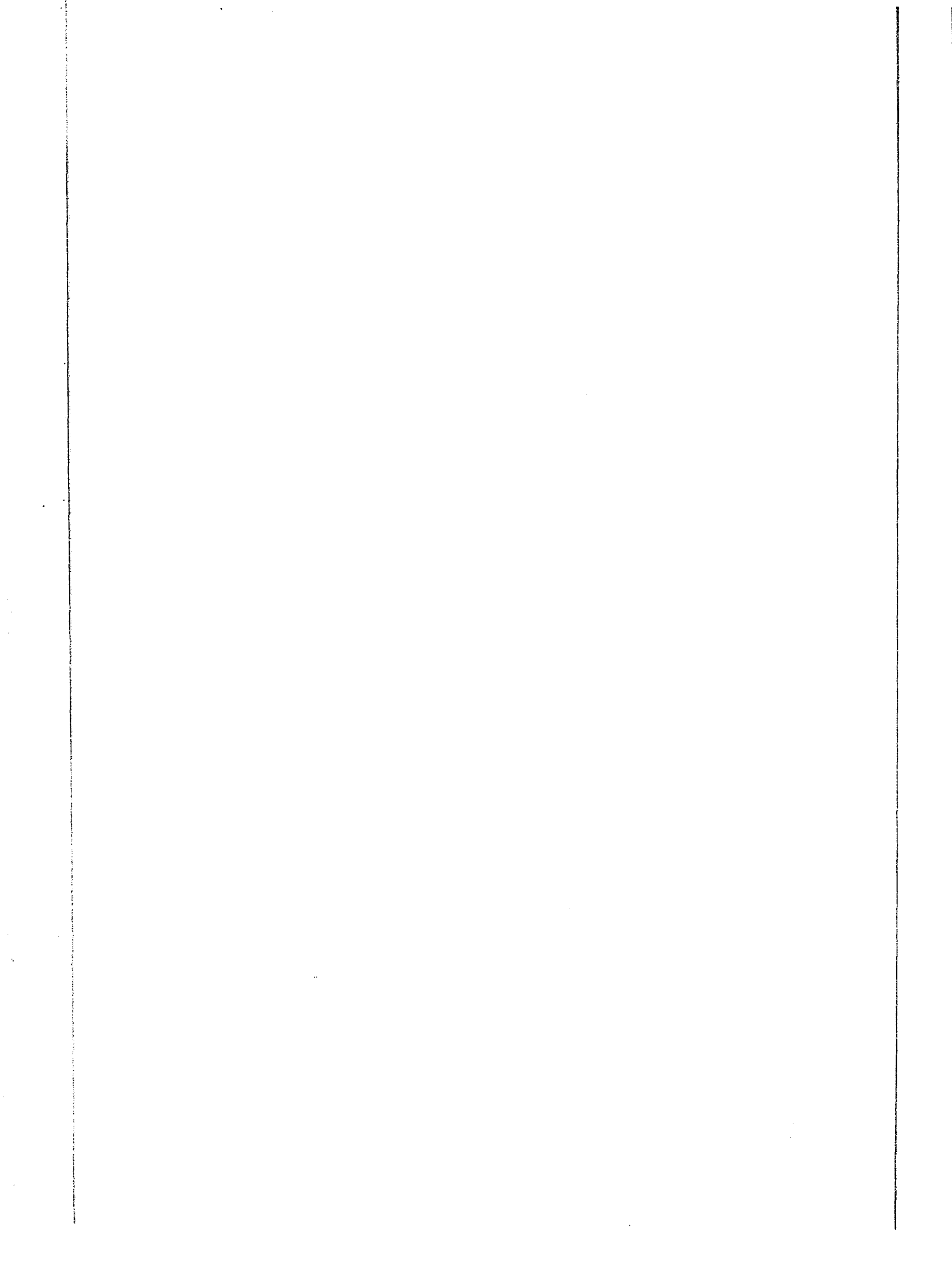
pH values without stirring.

Fig. 9.





Lime requirement compared to pH of solutions for different soils  
 pH values without stirring.



Quantitative Factor of Soil Acidity

The quantitative factor of soil acidity can be determined by electrometric titration of the soil suspension, either before or after adding a neutral salt. It has been shown by Crowther (18) Maiwald (38) Brioux (9) as well as others that soils possess a considerable degree of buffer action and therefore give small and regular changes in pH values upon the addition of base or acid. Hissink and Van der Spek (31) found a great difference between the amounts of sodium calcium and barium hydroxide required to bring the soil to pH 7.0. Since the sodium hydroxide gave results too low for the lime requirement of a soil, they recommend the use of calcium hydroxide to determine the amount of lime necessary to bring the soil to pH 7.0. Brioux (9) compared the Hutchinson-MacLennan method, (shaking fifteen grams of soil with three hundred cubic centimeters of 0.02 N calcium bicarbonate and determining the calcium in solution before and after shaking) with the electrometric method which consists of plotting pH values against increasing amounts of lime water. He showed that the two methods give results of the same order generally within 0.01 to 0.02%, except with soils having a high humus content.

Hardy and Lewis (29) state that Fisher (22), Crowther and Martin (19) and Christensen and Jensen (13) have demonstrated that titration with alkaline solutions does not furnish a suitable method for the determination of lime requirement. This is because a titration mainly determines by neutralization, the quantitative factor of soil acidity and only very partially the capacity of the



soil for exchange with calcium. They have therefore suggested that the titration should be carried out in a salt solution, because in particular the addition of a neutral salt noticeably increases the capacity of the reagent for displacing the hydrogen ion from the complex and makes it possible to titrate the hydrogen directly.

Trénel (55) used potassium chloride and titrated with sodium hydroxide as a means of determining the lime requirement. Other investigators have used different salts and various bases, but Hardy and Lewis (29) suggest that it is better to use calcium chloride and titrate with calcium hydroxide in order to prevent confusion of ions. Their procedure consists of the development of exchange acidity by treating a known mass of soil with a solution of calcium chloride accurately neutralized to pH 7.0 and then titrating the mixture directly with dilute standard lime water until the pH of the suspension equals 7.0, using the quinhydrone electrode for the measurements.

On account of the difficulty encountered in comparing the different electrometric methods by using data from varied sources, it has been deemed advisable to make a comparison of three common procedures. The methods studied are:

1. Titration of the soil suspension with calcium hydroxide.  
Hissink and Van der Spek (31) Brioux (9) and others.
2. Titration of the suspension in calcium chloride solution with calcium hydroxide. Hardy and Lewis (29), Crowther (18) and others.
3. Titration of the suspension in sodium chloride solution

with sodium hydroxide. Trénel (55) titrated potassium chloride solution with sodium hydroxide. Sodium chloride has been used here to prevent confusion of ions.

Figures 10 to 31 inclusive show the experimental results obtained on the 21 soils described. These curves were obtained by using 1 to 5 ratio soil to solution and stirring in the apparatus shown in Figure 2. Samples were removed at the times indicated on the curves and the  $p^H$  determined by the quinhydrone electrode shown in Figure 1.

These titration values are plotted,  $p^H$  against the normality of the base used, in Figures 31 to 51 inclusive, and from these graphs we can calculate the amount of base required to bring the soil to  $p^H$  7.0.

Figure 52 shows the variation in the value obtained for the lime requirement, by the method of titrating the calcium chloride suspension with calcium hydroxide to  $p^H$  7.0, for zero, ten and ninety hours stirring. The other two methods compared in this paper show the same variation, so the value for ninety hours is taken because this seems to be closer to the equilibrium value. The time taken is rather arbitrary as any period chosen for equilibrium will not hold for all cases. Maiwald (38) has chosen seventy two hours while Hardy and Lewis (29) say that a few minutes are sufficient.

A comparison of the three electrometric methods of lime requirement are given in Figure 53 at ninety hours stirring. It will be observed that the three methods give results approximately in the same order but varying in intensity.

It is difficult to make a definite conclusion as to the best or the most accurate method of the three studied for the determination of the quantity of lime necessary to be added to the soil to produce the best reaction for plant growth. However it should be pointed out, as suggested by Hardy and Lewis (29), that titration with a base only determines the quantitative factor of soil acidity and only partially the capacity of the soil for exchange. The presence of a neutral salt increases the capacity of the base for replacing the hydrogen ion from the complex and therefore gives us a better index to the potential acidity of the soil.

The salt and base used have been shown to have an influence on the actual value obtained for the lime requirement, so it is suggested here that calcium chloride be used as the salt and calcium hydroxide as the base. The lime requirement is then defined as the amount of calcium hydroxide required to bring the soil to pH 7.0 in a calcium chloride suspension. While the optimum amount of calcium chloride is not known, there are indications that above 0.4 N the salt error is appreciable in the measurement of pH.

Soil Reaction in Bases, Soil No. 1.  
 Ratio Soil: Solution = 1:5

$\text{NaCl}$  0.4N

$\text{CaCl}_2$  0.4N

$\text{H}_2\text{O}$

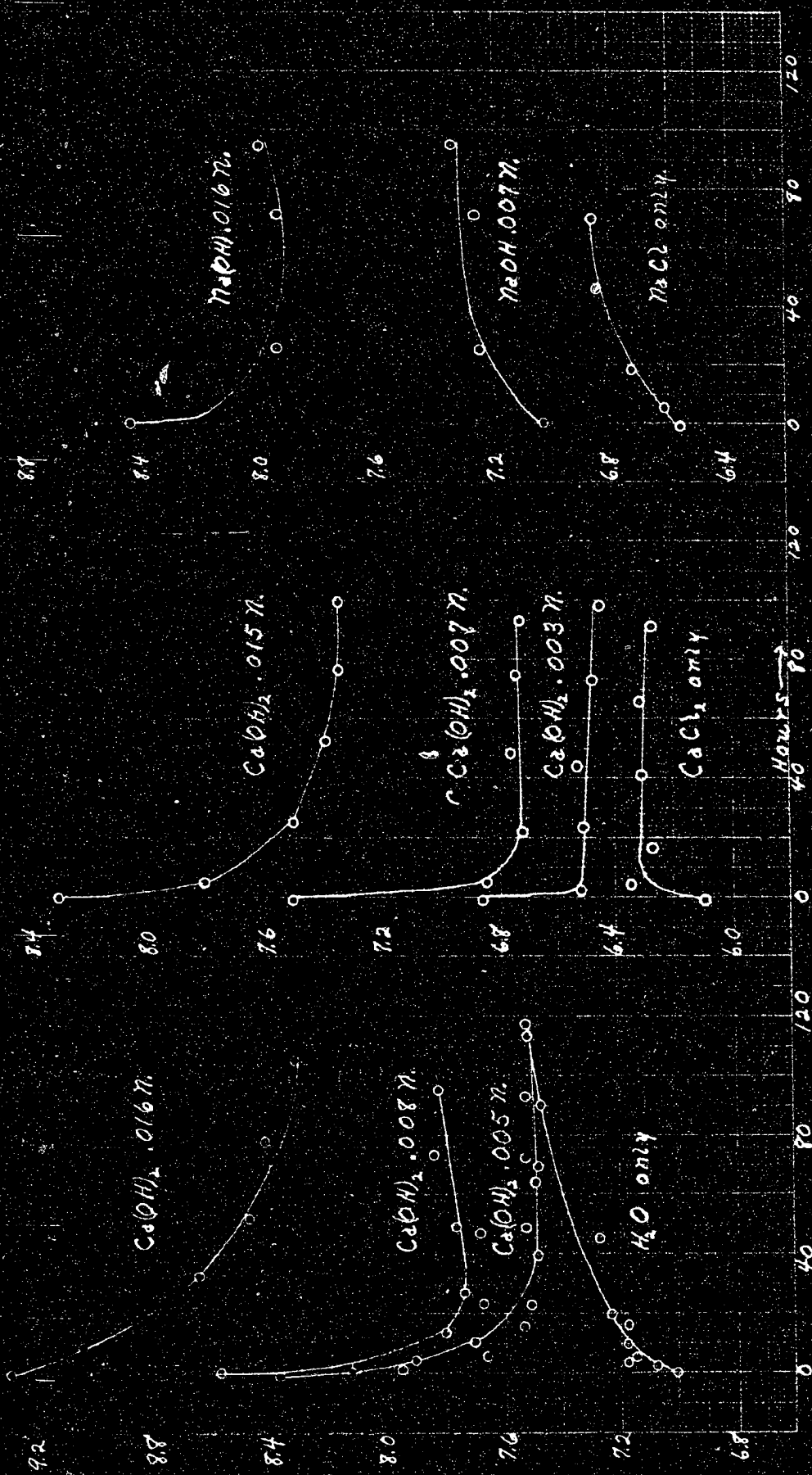
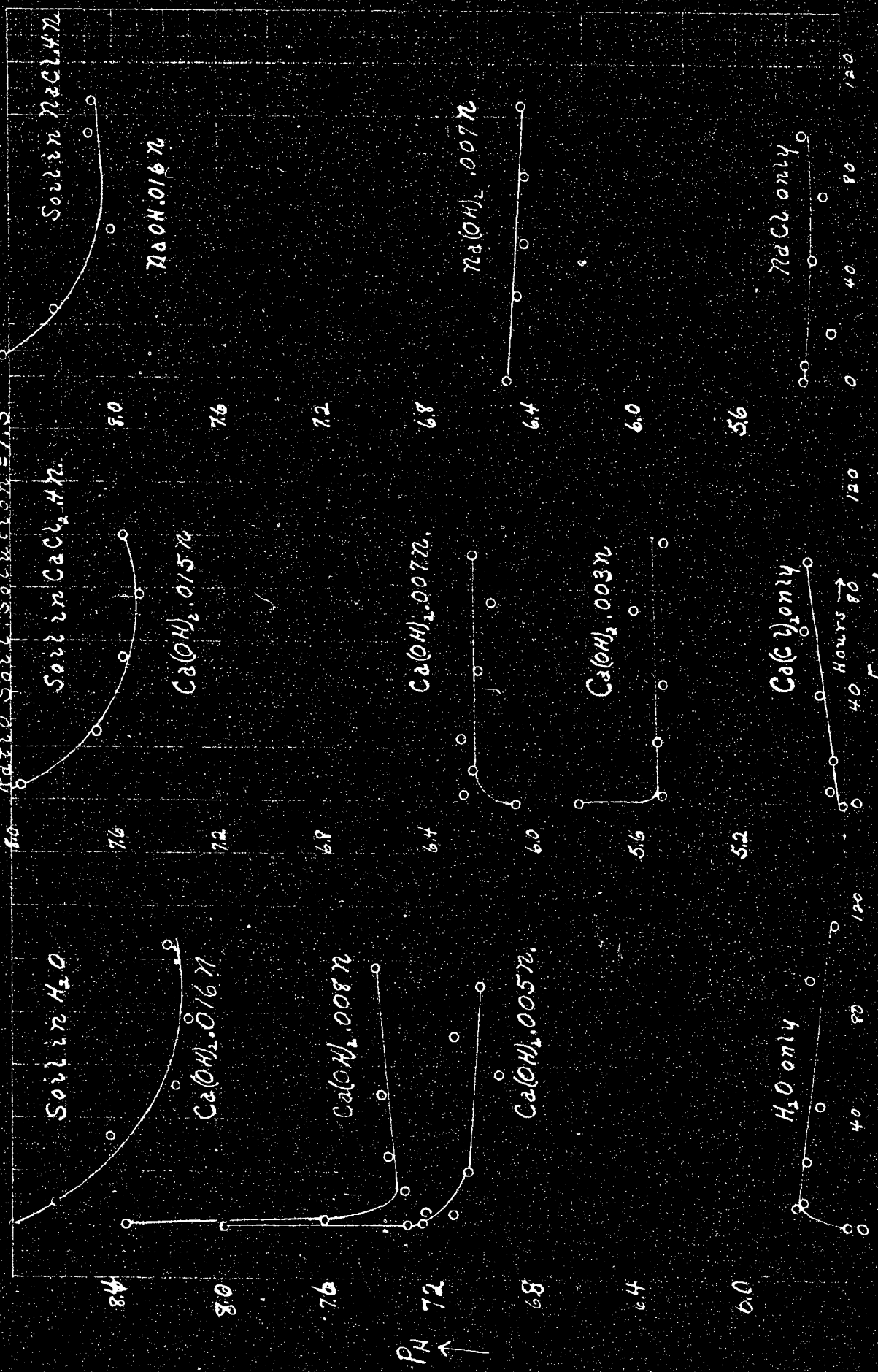


Fig. 10.

Soil Reaction with Bases. Soil No. 2

Ratio Soil: Solution = 1:5



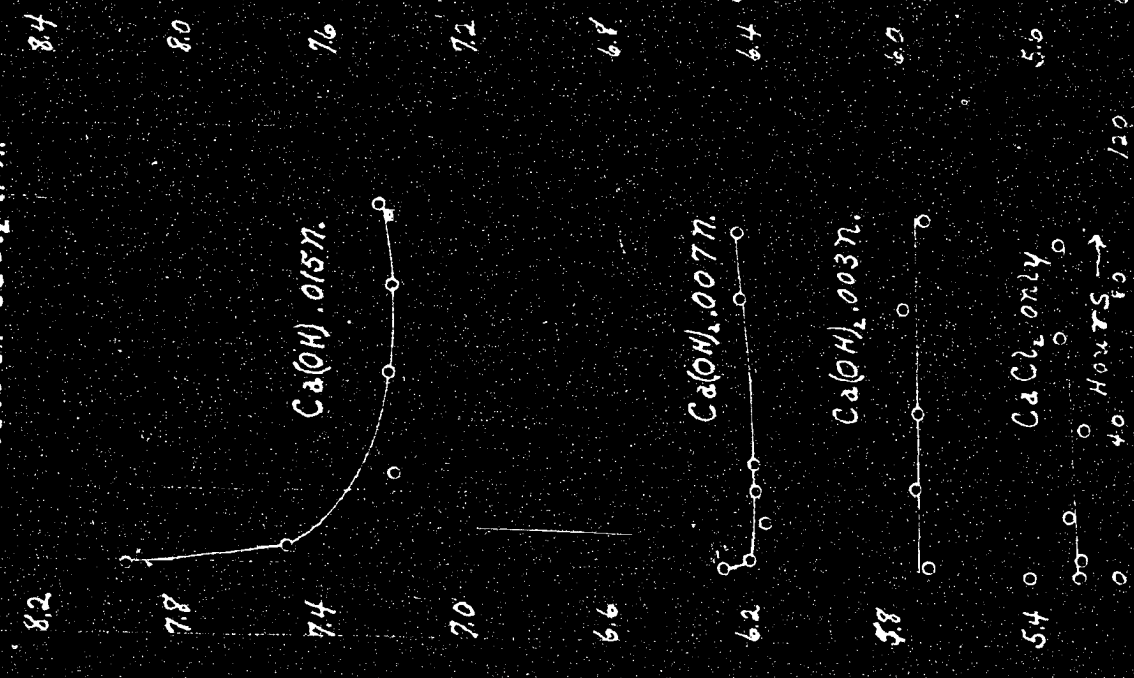
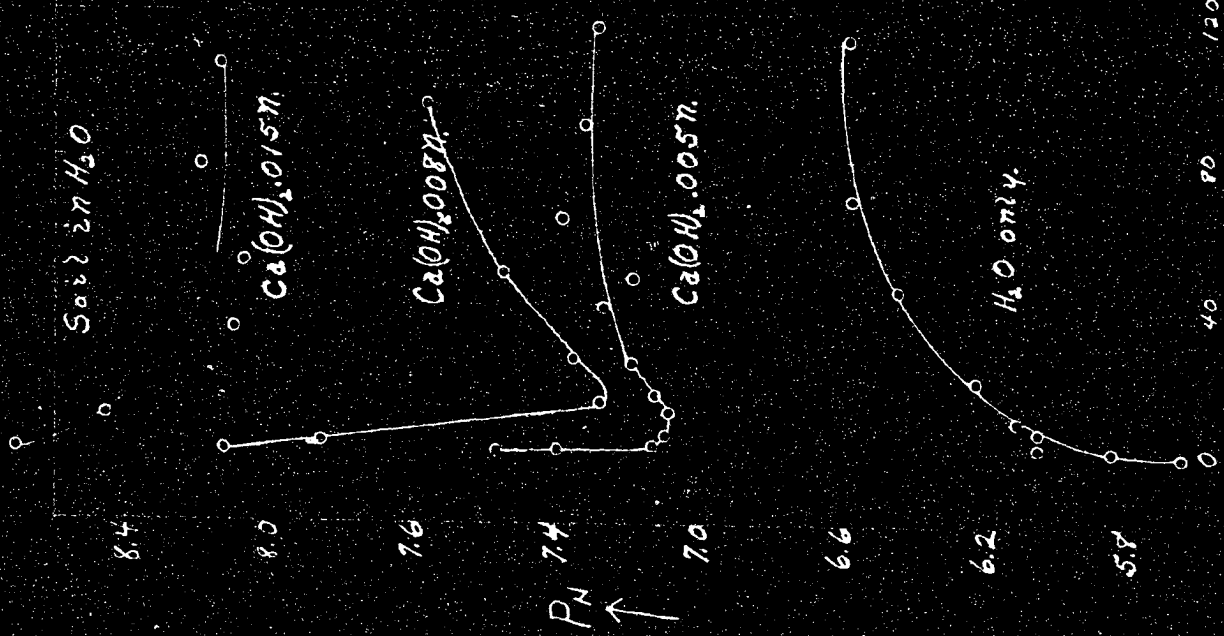
Ca(OH)<sub>2</sub> only  
40 Hours →  
Fig. 11

Soil Reaction in Bases Soil No. 3

Ratio Soil: Solution = 1:5

Soil in  $\text{CaCl}_2$  4N

Soil in  $\text{NaCl}$  4N



PH ↑

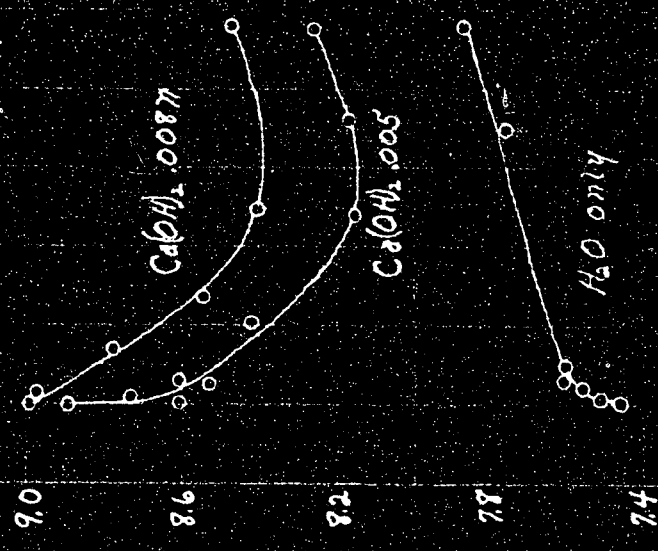
Hours →

Fig. 12.

Soil Reaction with Bases Soil No. 4

Ratio, Soil: Solution = 1:5

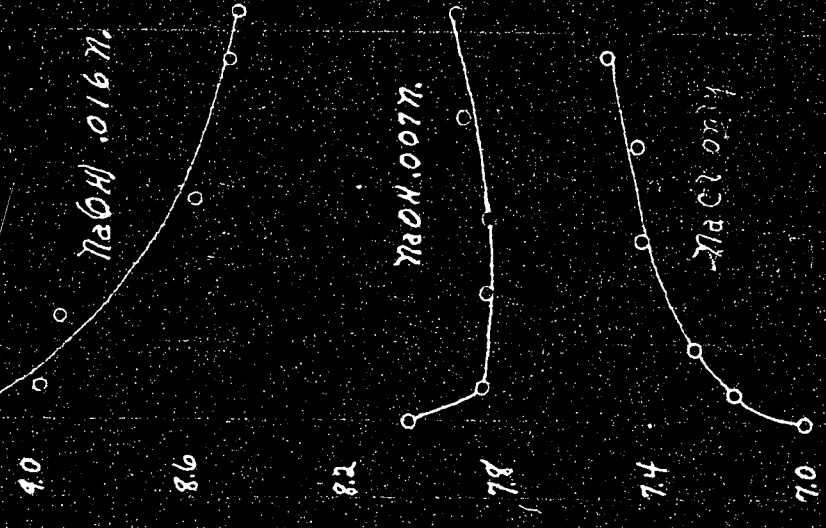
Soil in H<sub>2</sub>O



Soil in CaCl<sub>2</sub> 4N



Soil in NaCl 4N



Hours → 0 40 80 120  
Fig. 13.

Soil Reaction with Bases  
 Ratio Soil Solution = 1:5  
 Soil No. 6

Soil with H<sub>2</sub>O

Soil in CaCl<sub>2</sub> 4N

Soil in NaCl 4N

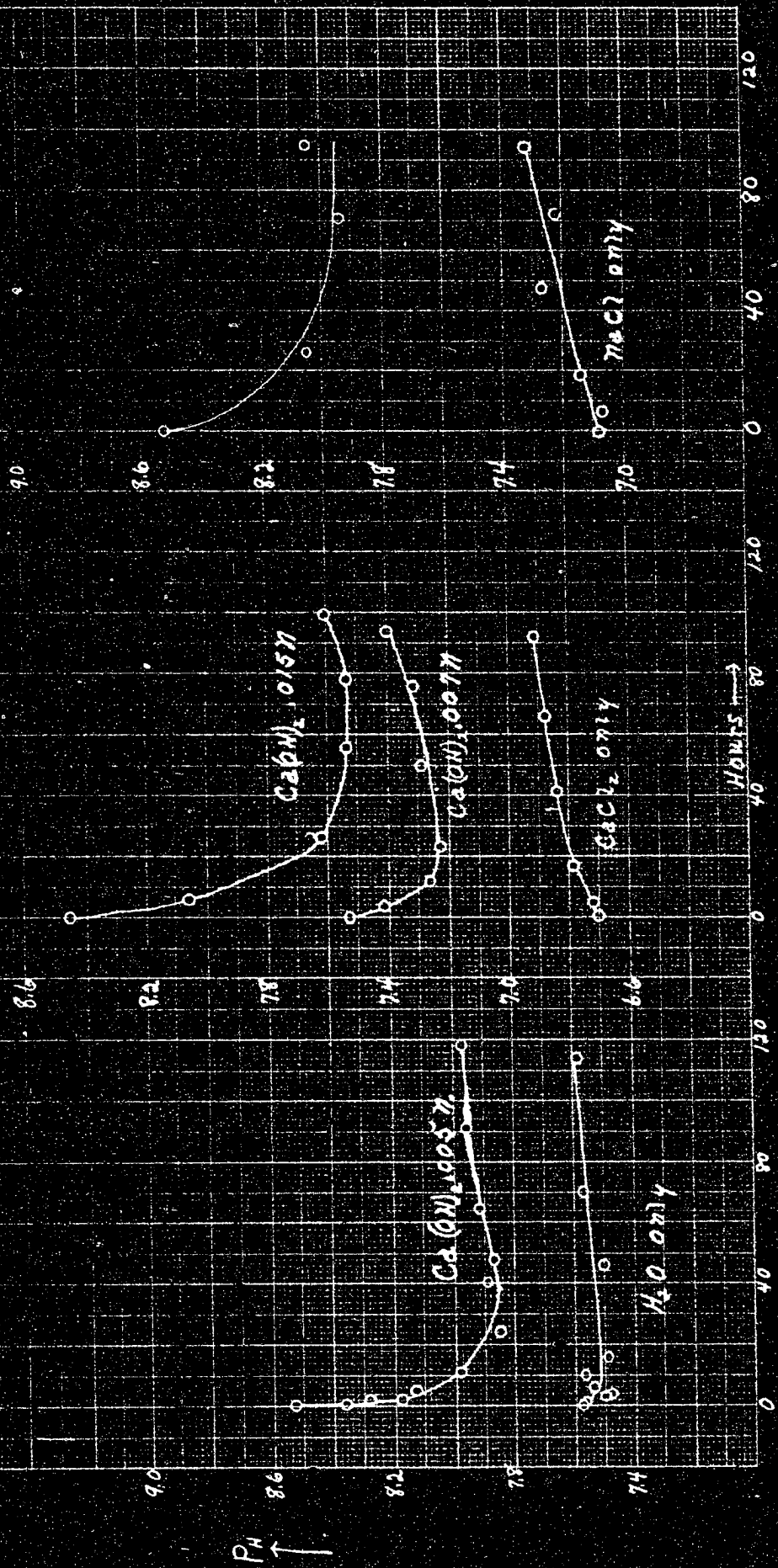


Fig. 14.



Soil Reaction with F<sub>255</sub>.  
 F<sub>255</sub> 1:0.02:Solution = 1:5

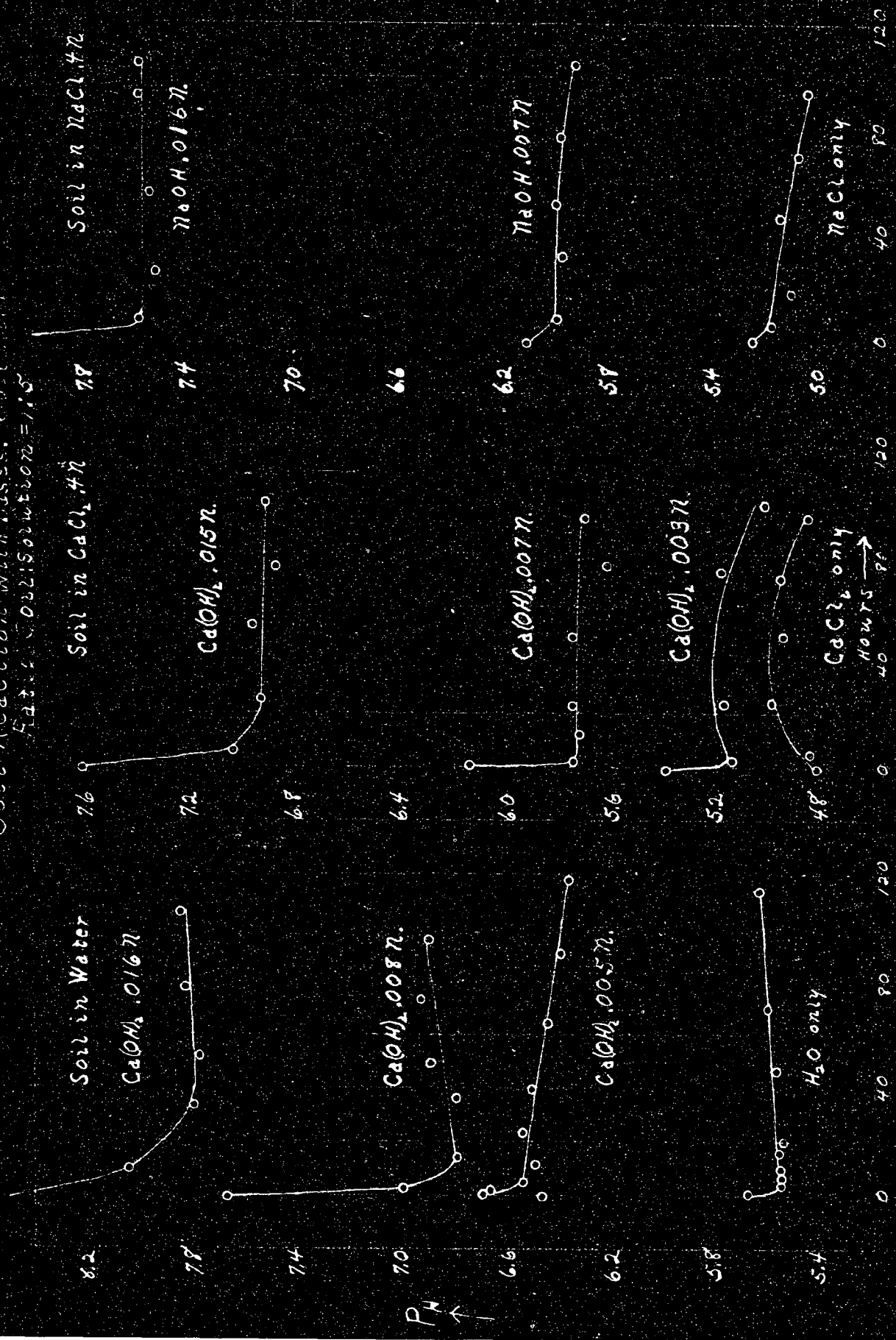


Fig. 15.

Soil Reaction with Bases. Soil No. 8  
 Ratio Soil: Solution = 1:5

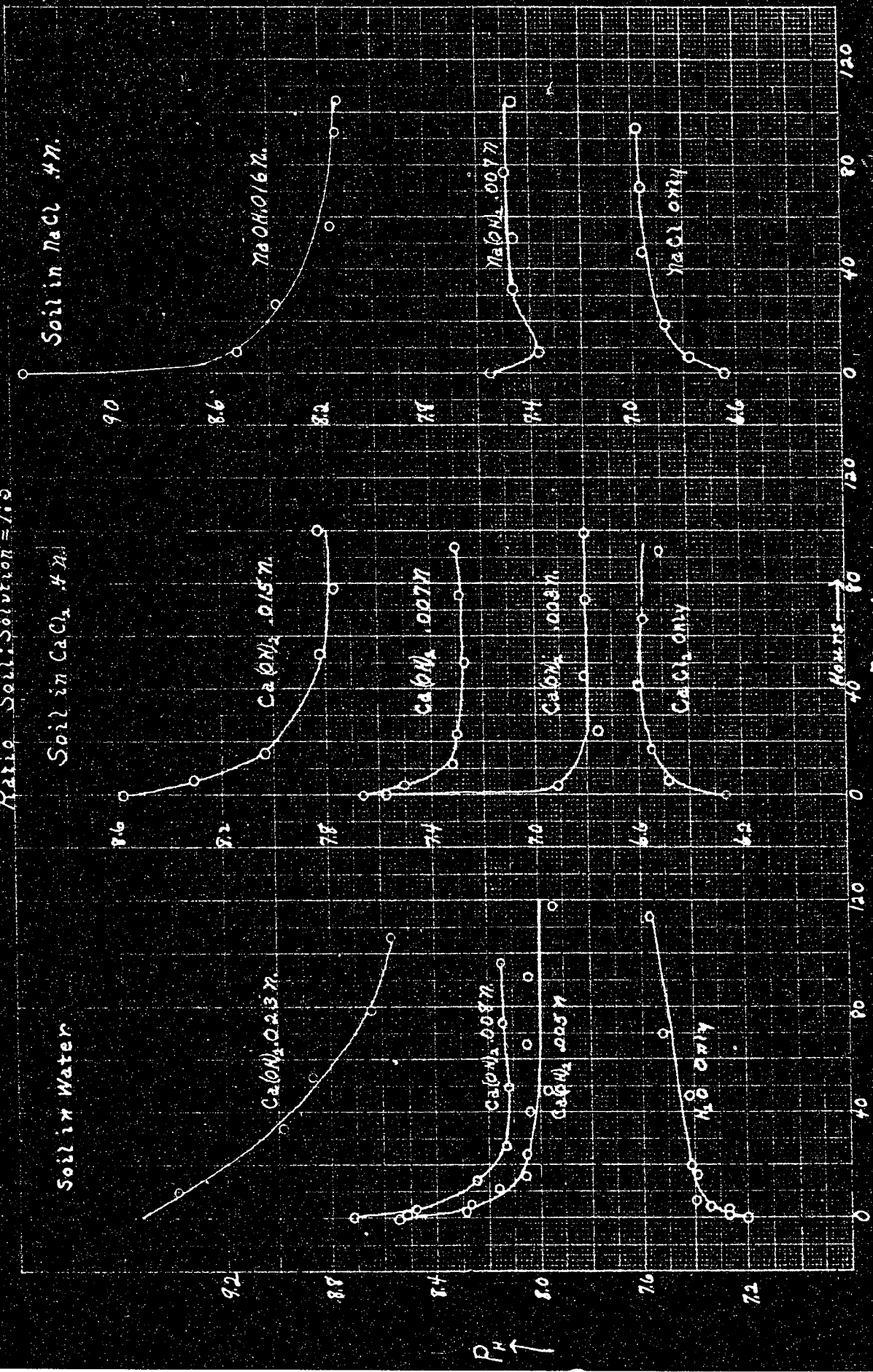


Fig. 16.

Soil Reaction with Bases Soil No. 9  
 Soil: Solution = 1:15 Ratio

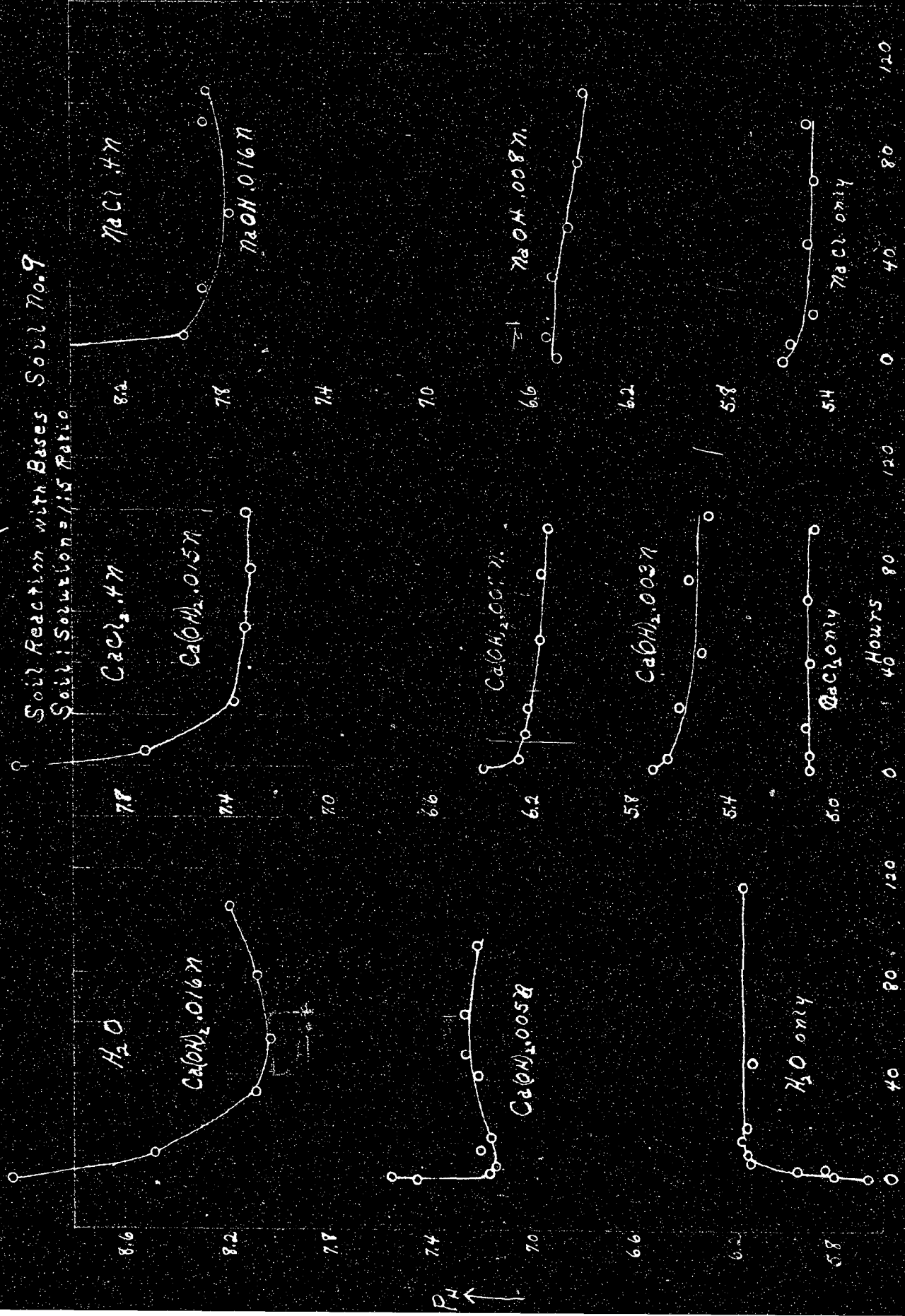


Fig. 17.

Soil No. 10

Soil in Water

Soil in  $\text{CaCl}_2$  4%

Soil in  $\text{NaCl}$  4%

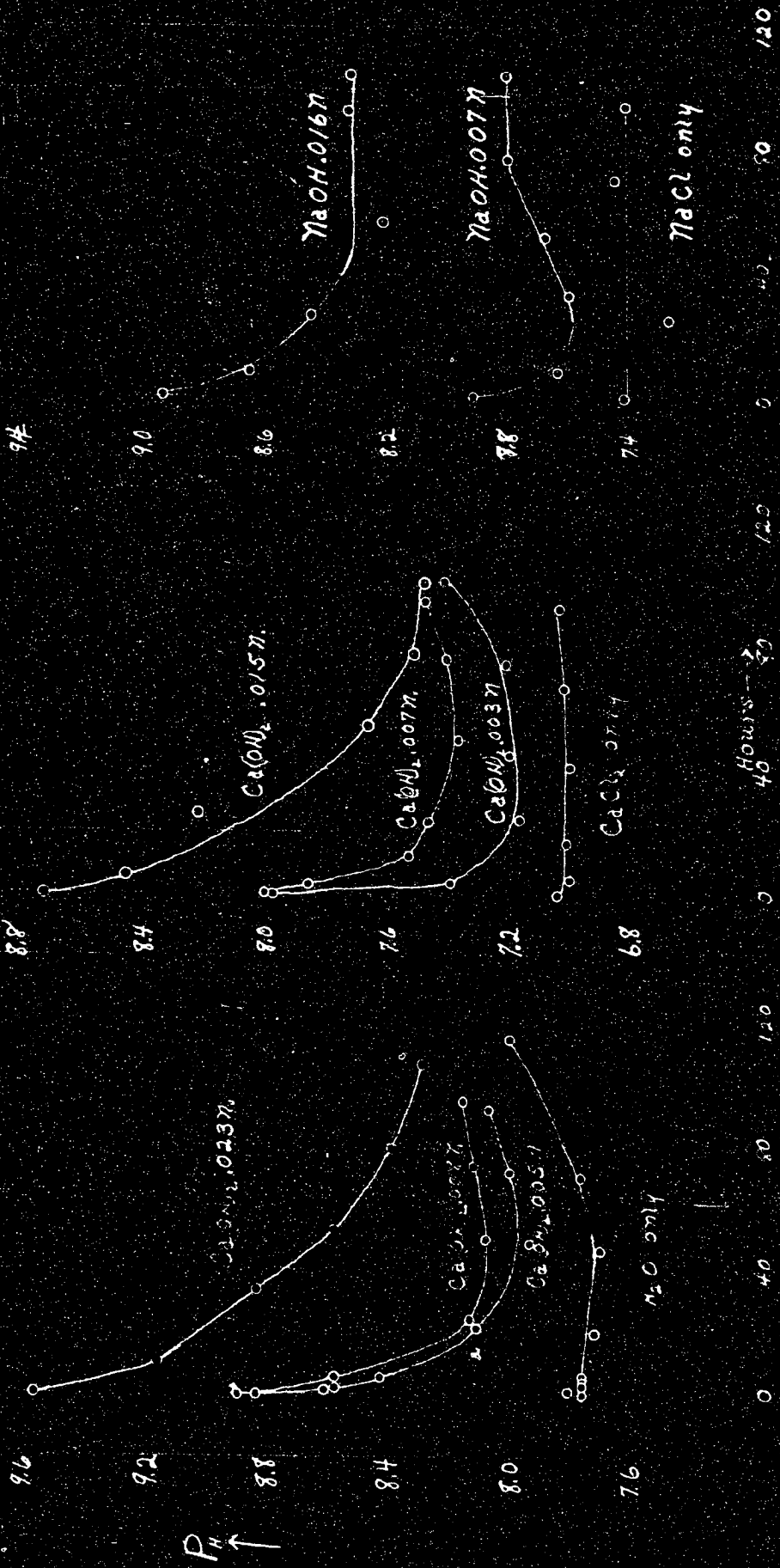


Fig. 18.

Soil No. 11  
 Ratio Soil: Solution = 1:2

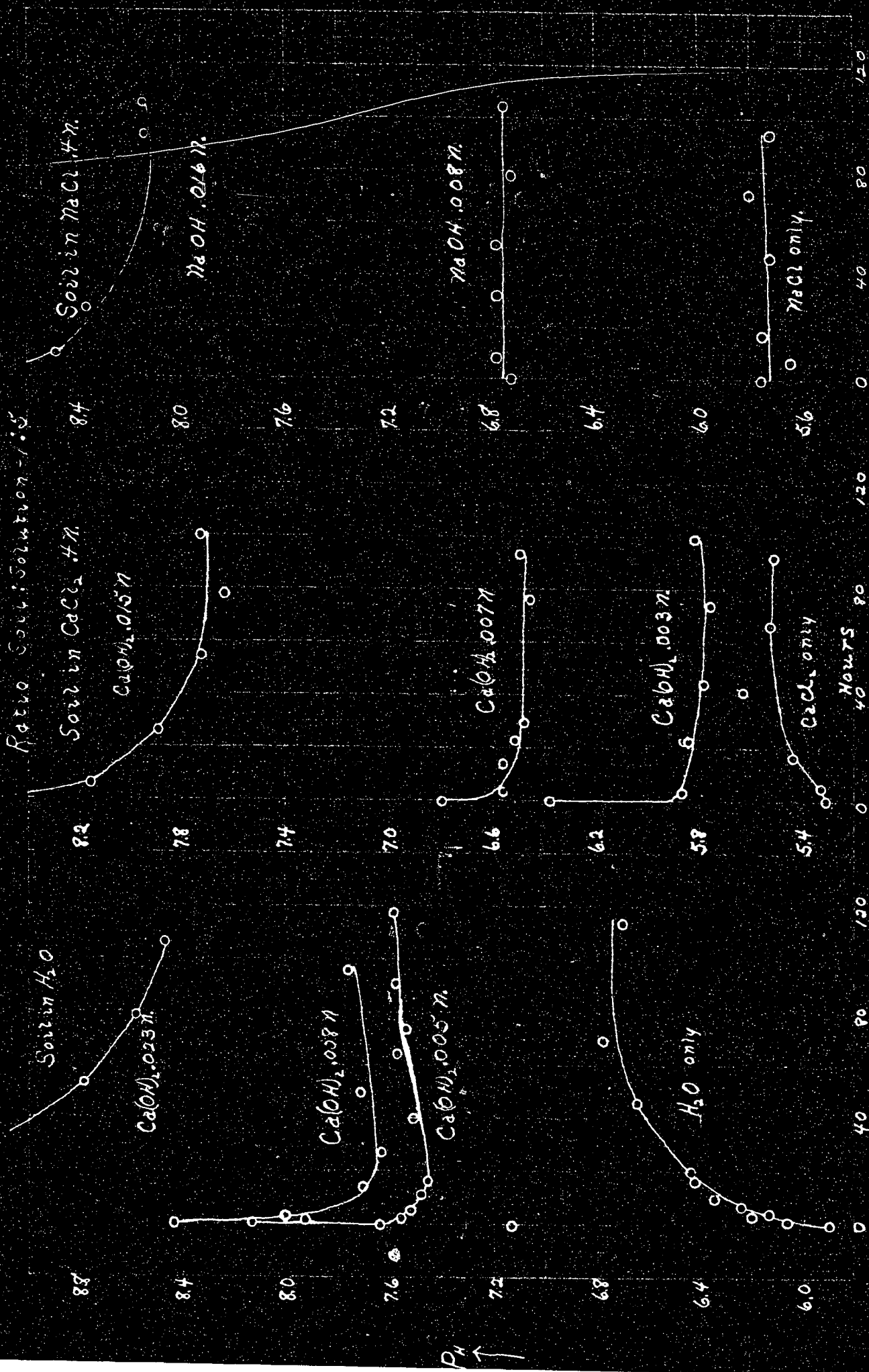


Fig. 19

Soil Reaction with Bases - Soil No. 12  
 Rate Soil: Solution = 1:5

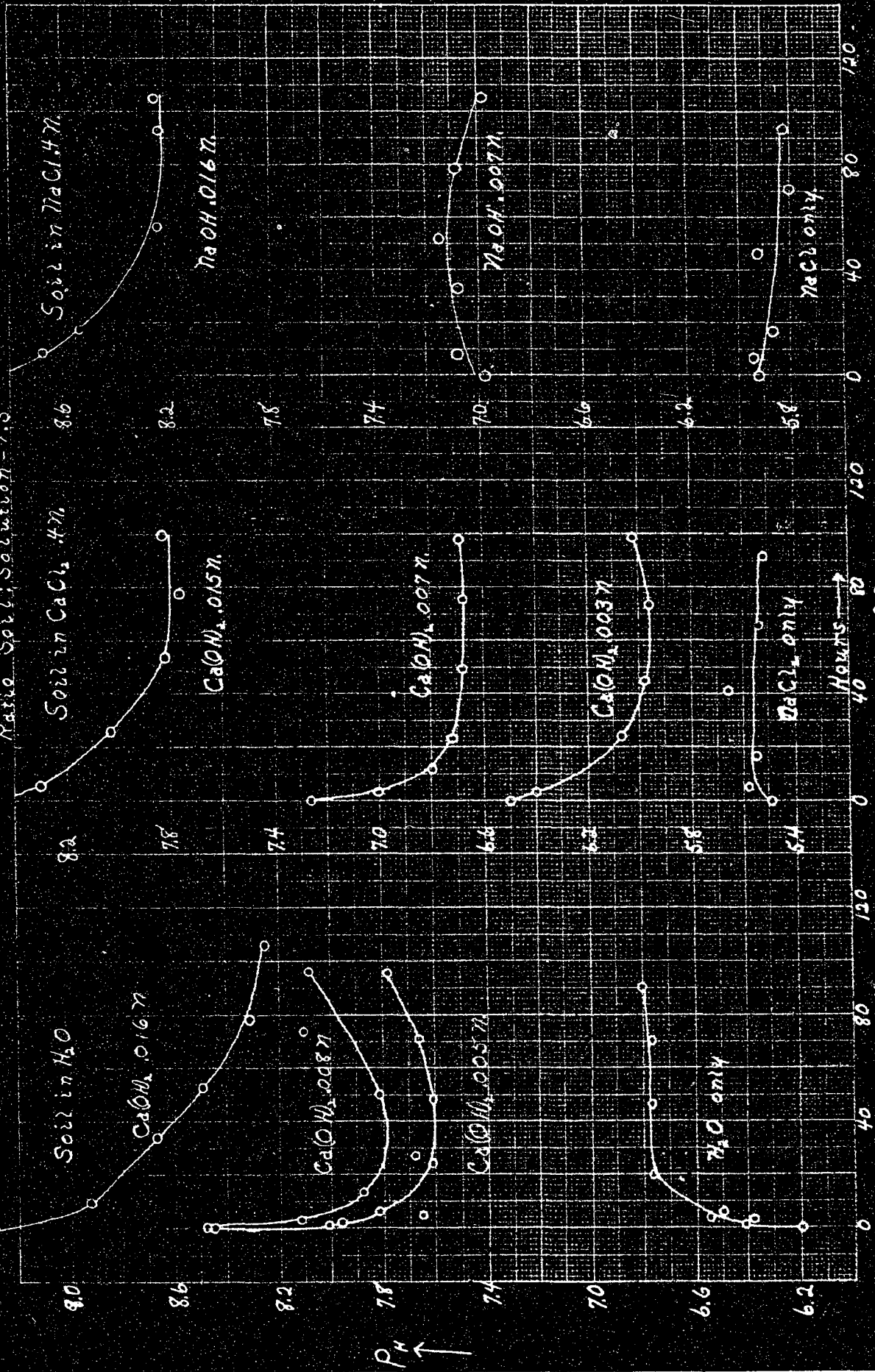


Fig. 20.

Soil Reaction with Bases Soil No. 13  
 Ratio Soil: Solution = 1:5

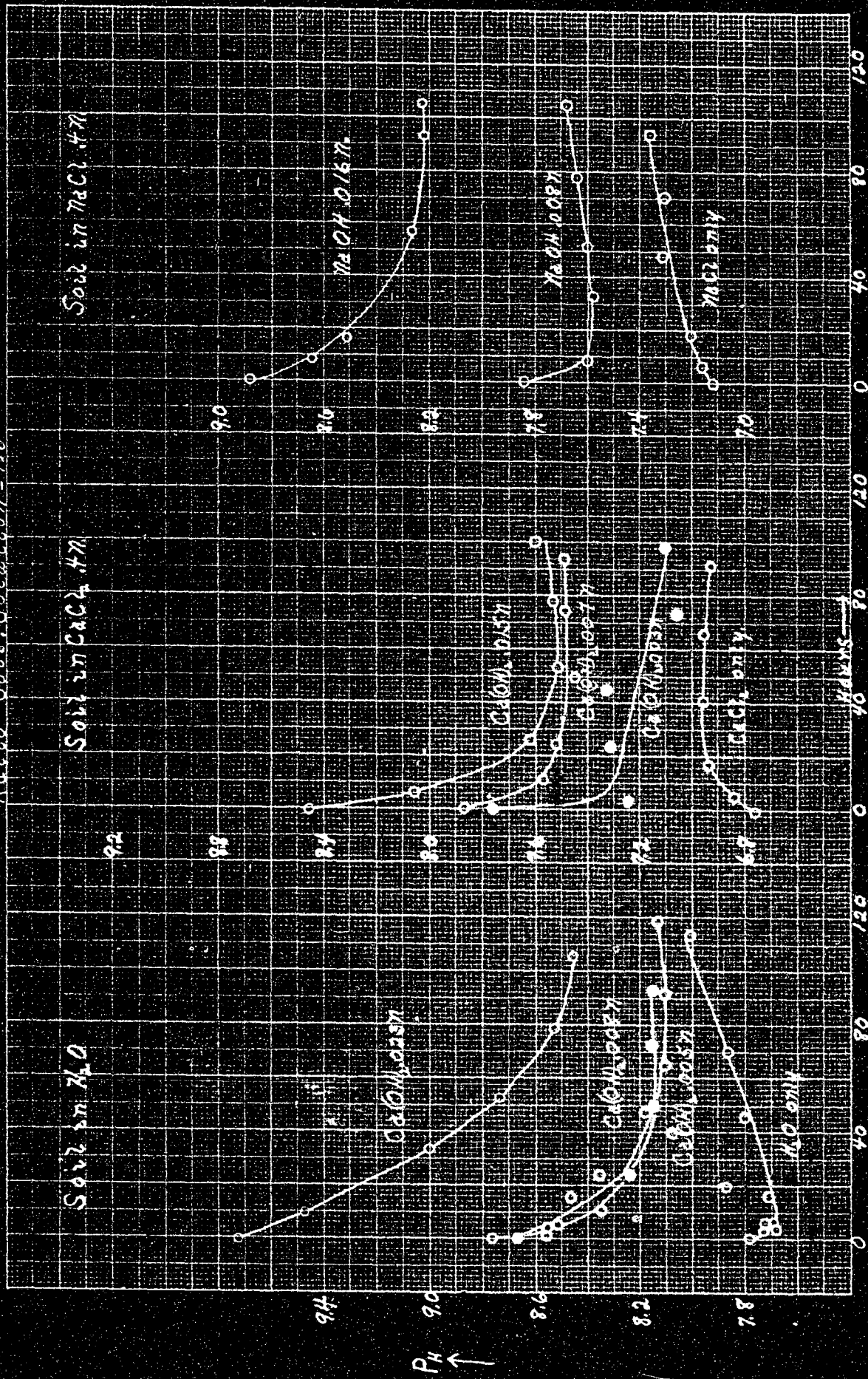


Fig. 2f.

Soil Reaction with Bases. Soil No. 14  
 Ratio Soil: Solution = 1:5

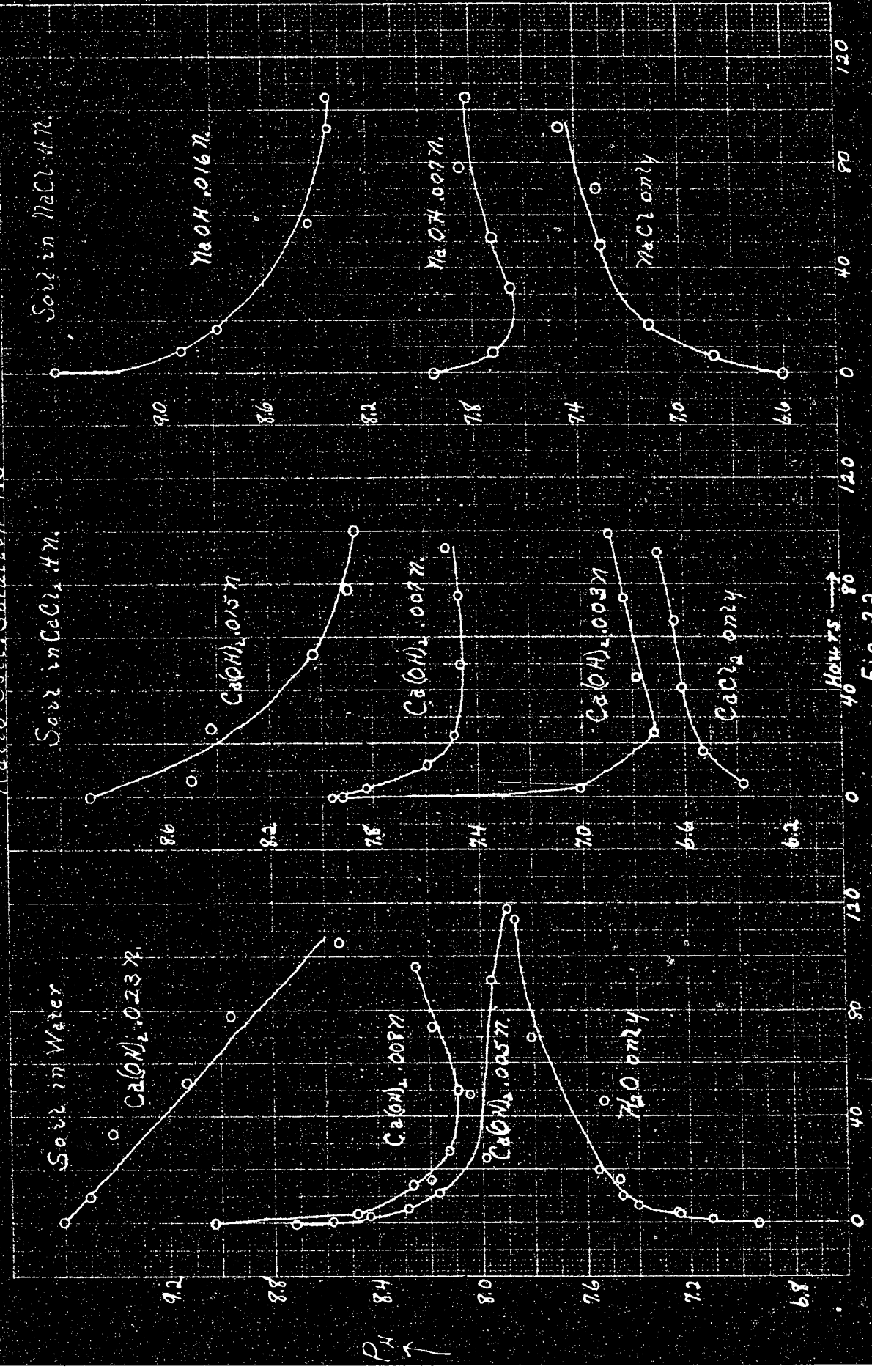
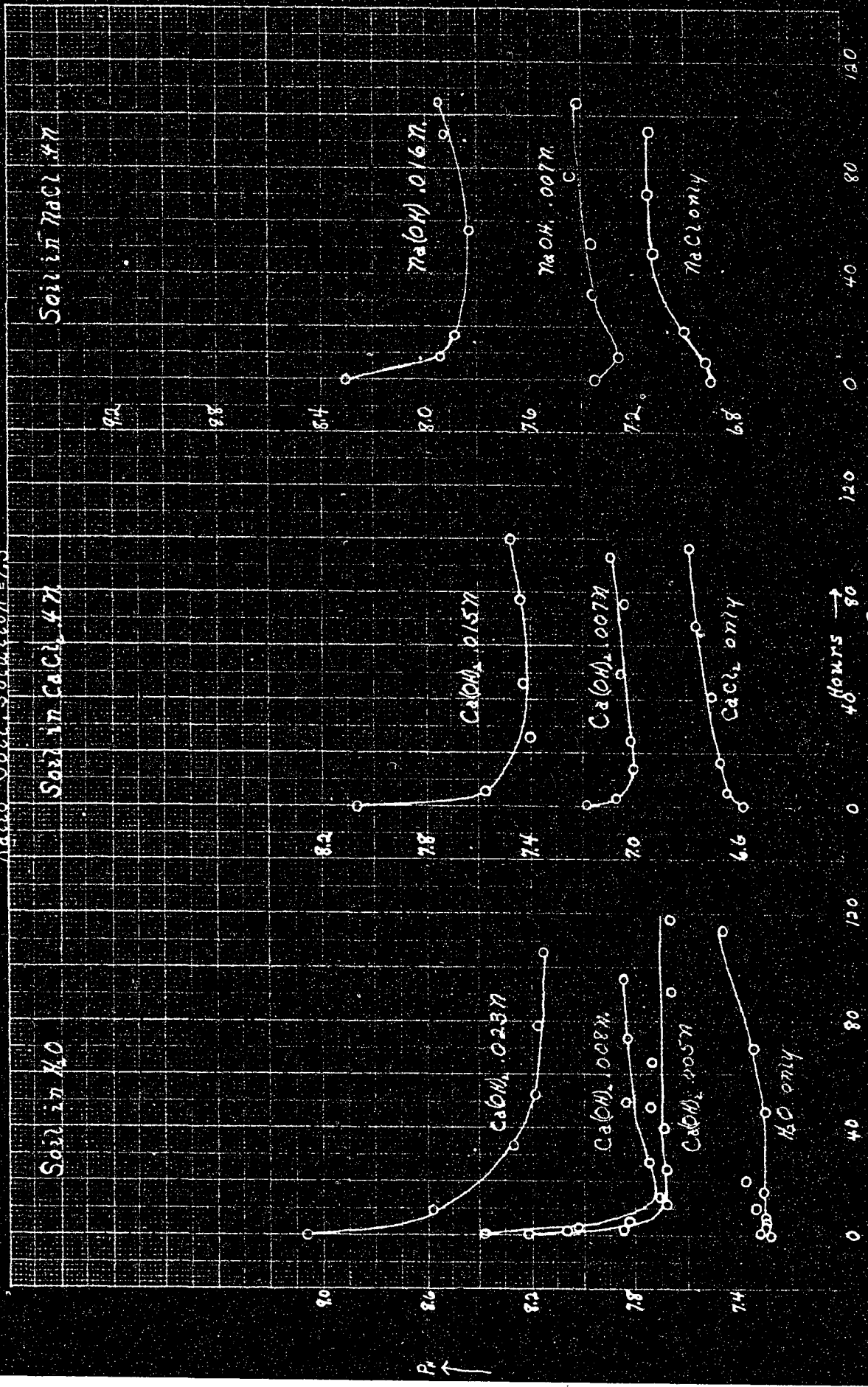


Fig. 22



Soil Reaction with Bases Soil No. 15

Ratio Soil Solution = 1:5



Hours →  
Fig. 23.

Soil Reaction with Bases Soil No. 15  
 Ratio Soil:Solution = 1:5

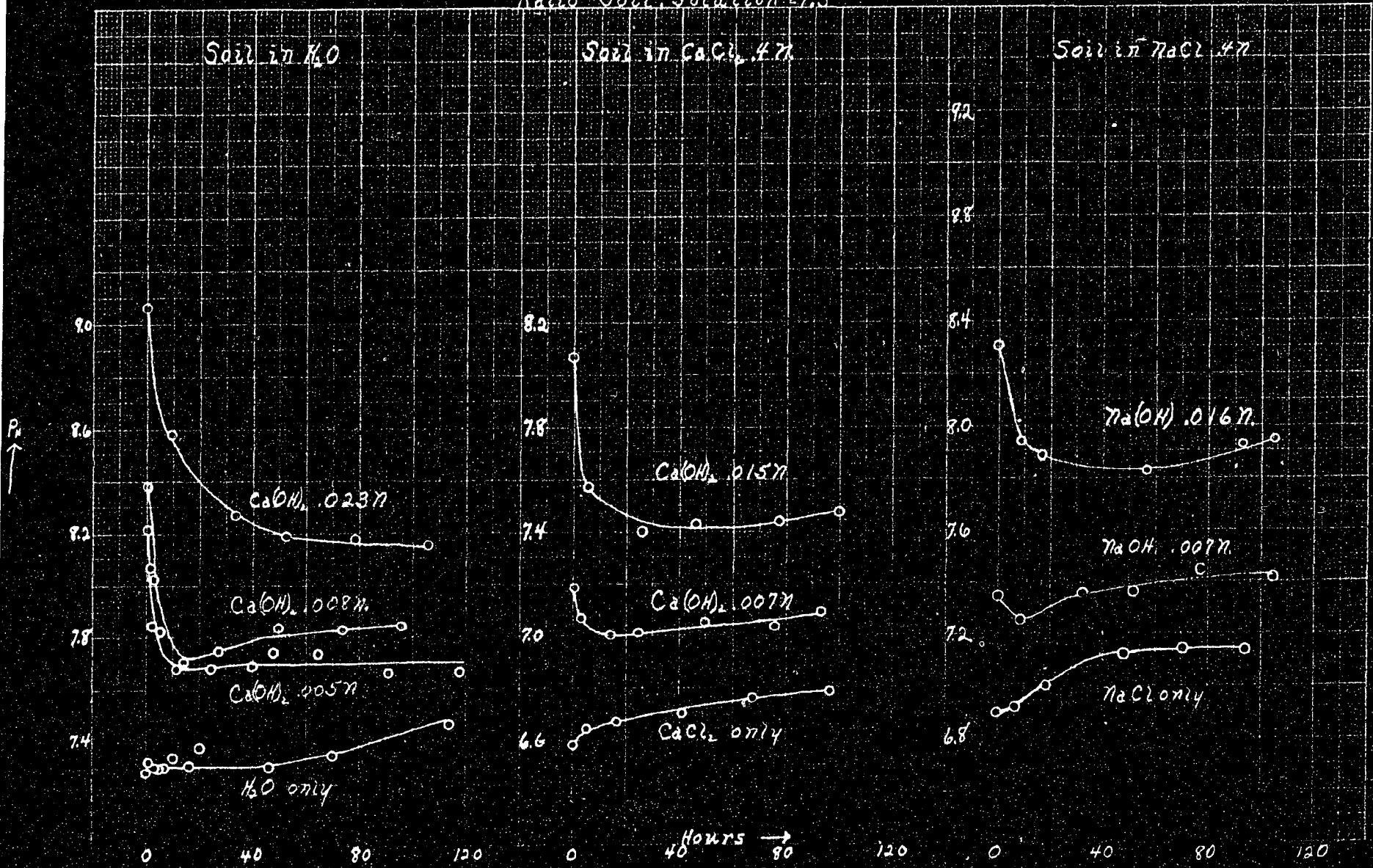
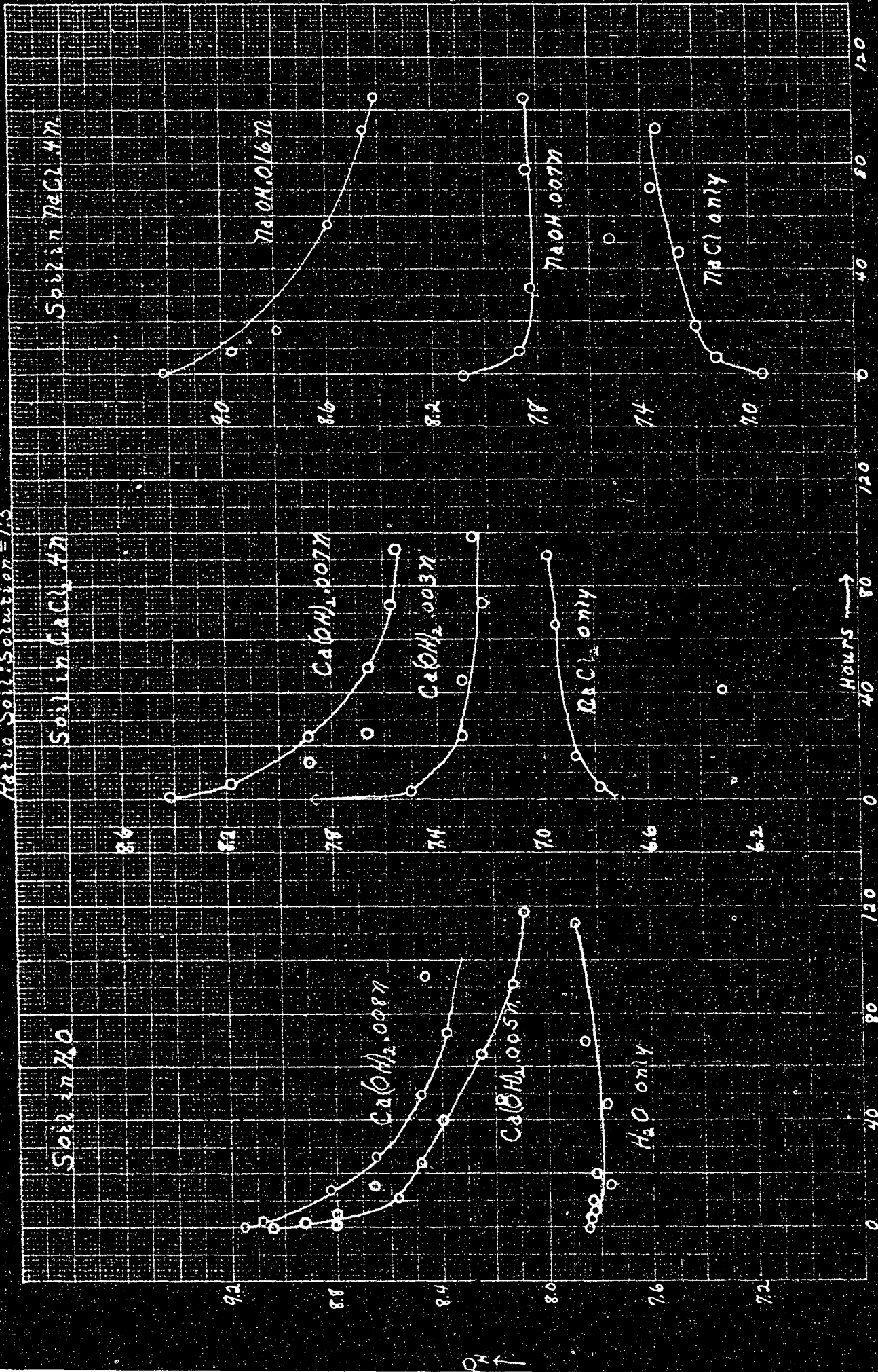
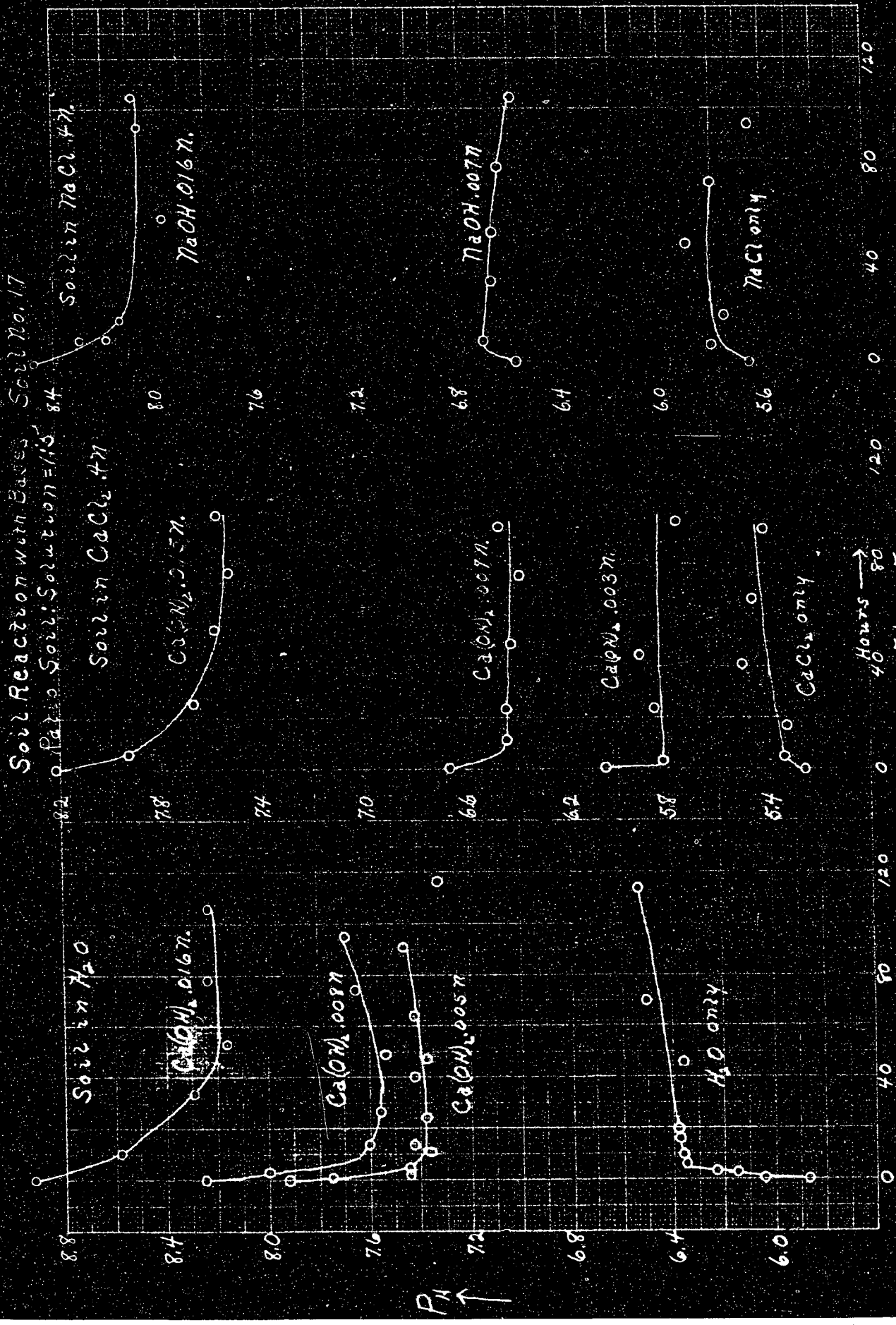


Fig. 23.

Soil Reaction with Bases Soil No. 16  
 Ratio Soil: Solution = 1.5



Hours →  
 Fig. 24.



Hours → 40 80 120  
Fig. 25

Soil Reaction with Bases. Soil No. 18.  
Ratio Soil: Solution = 1/5

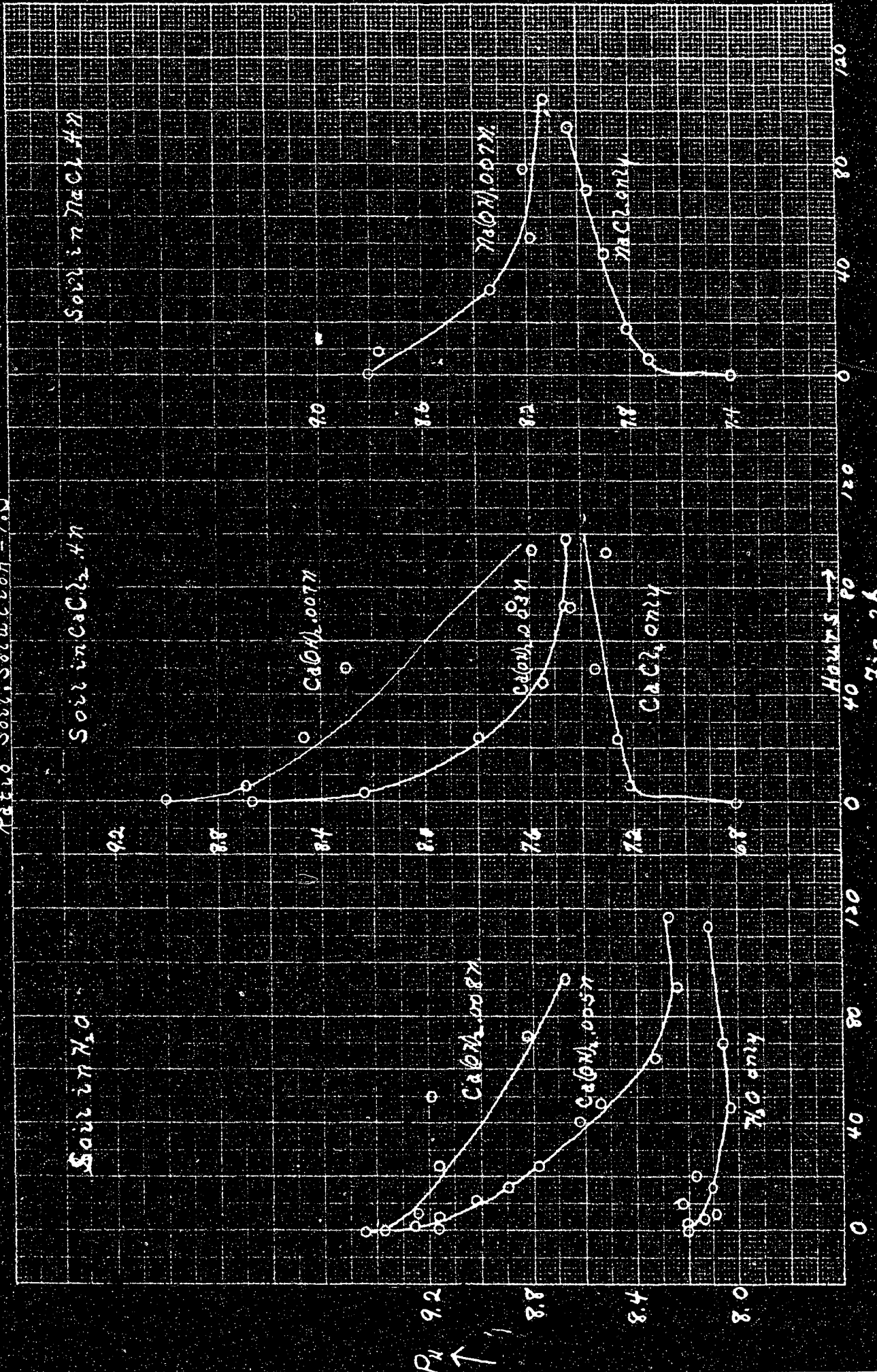


Fig. 26.

Soil Reaction with Bases. Soil No. 18.  
 Ratio Soil: Solution = 1/10

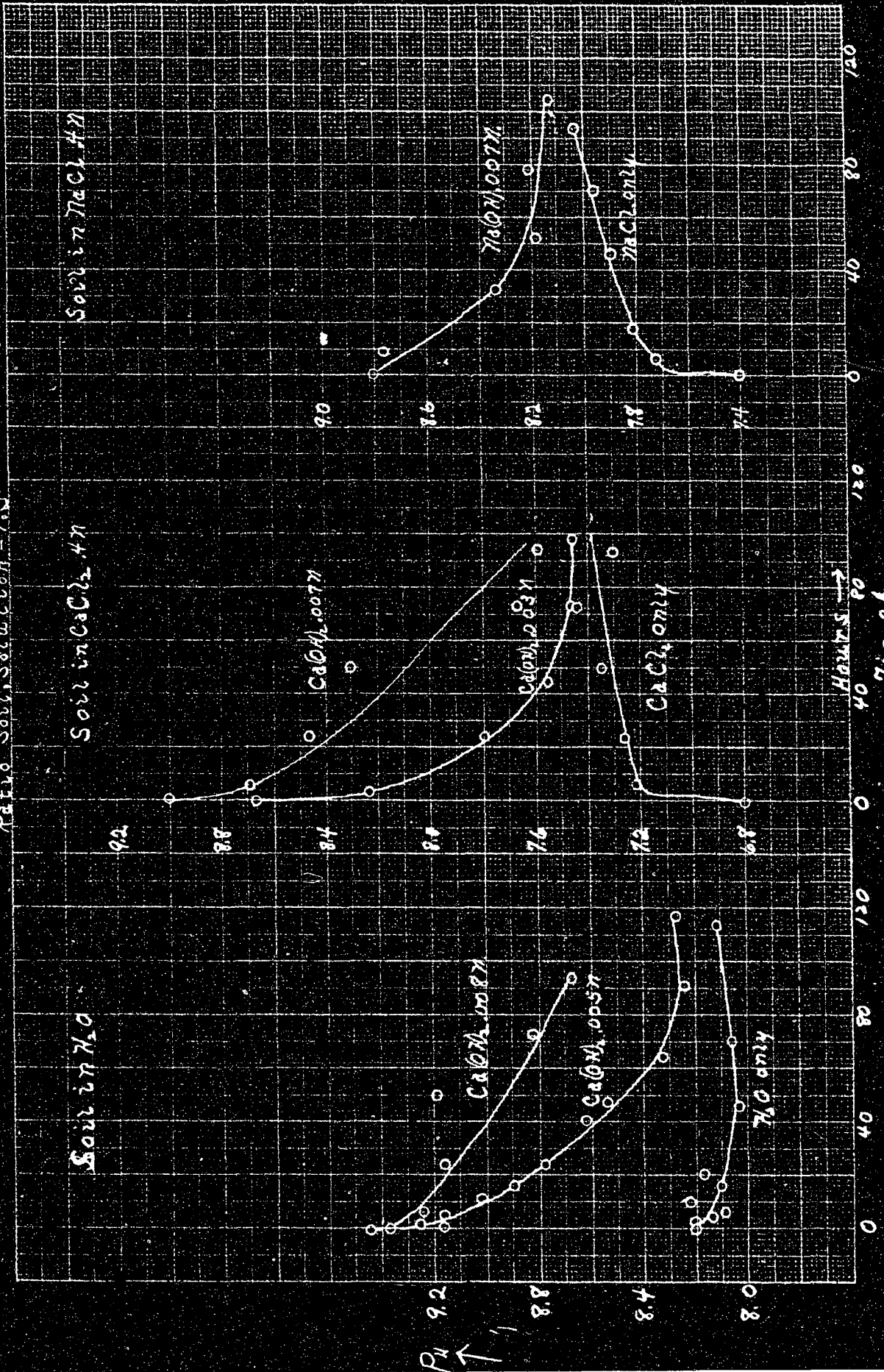
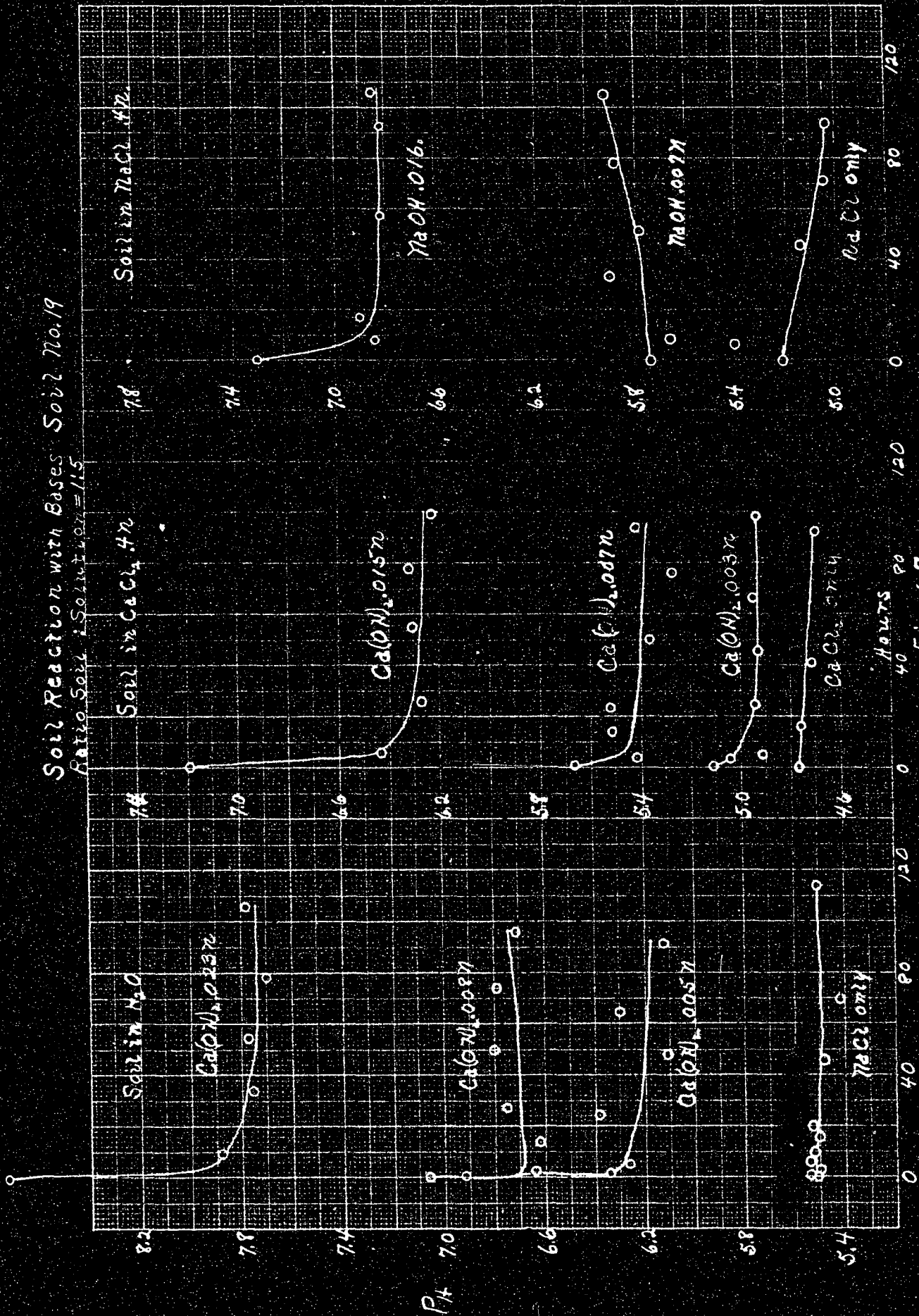


Fig. 26.

Soil Reaction with Bases Soil No. 19

Ratio Soil i Solution = 1/5



Hours 0 40 80 120  
Fig. 27

Soil Reaction with Bases Soil No. 20  
 Ratio Soil: Solution = 1:5

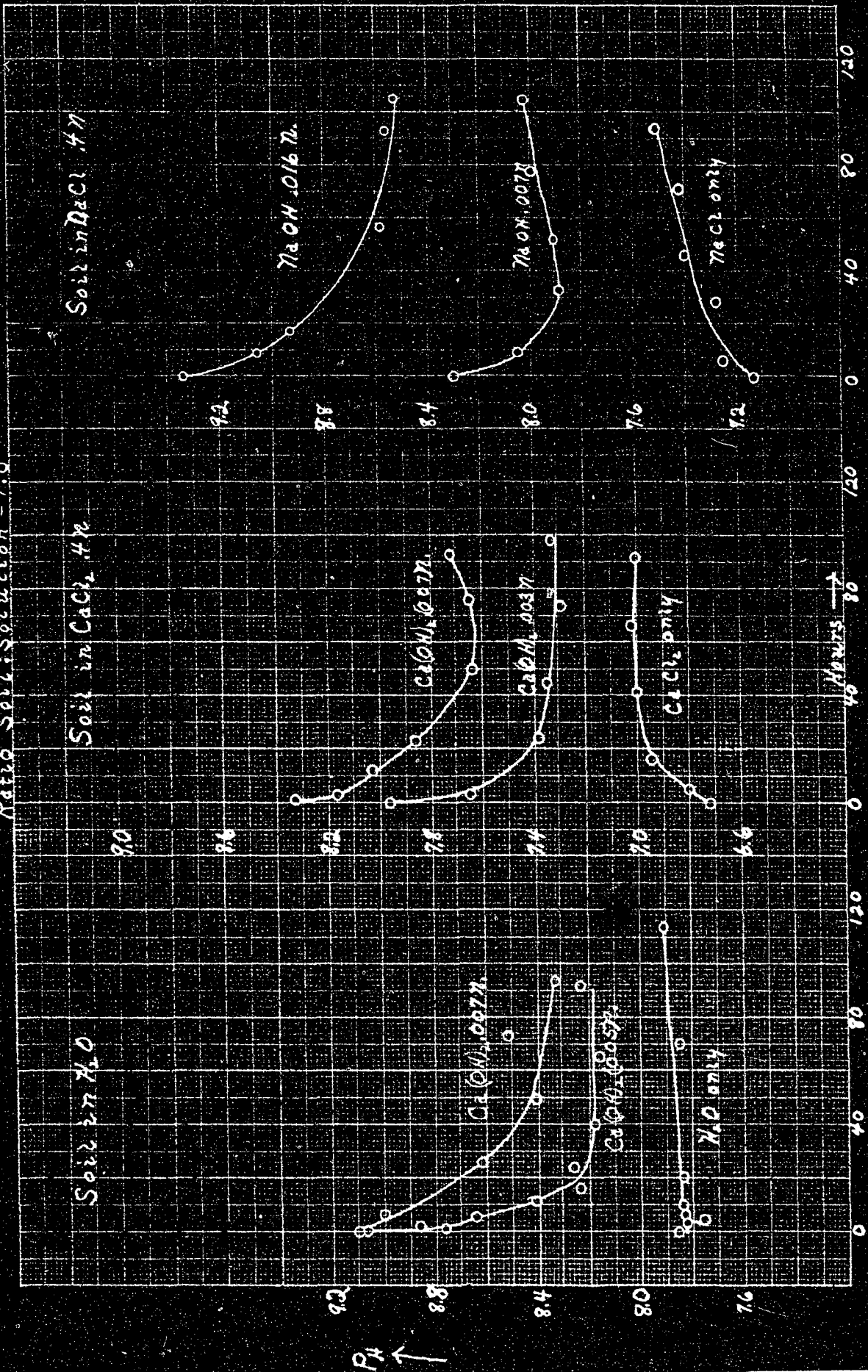


Fig. 28.



Soil Reaction with Bases. Soil No. 21.

Ratio Soil: Solution = 1:5

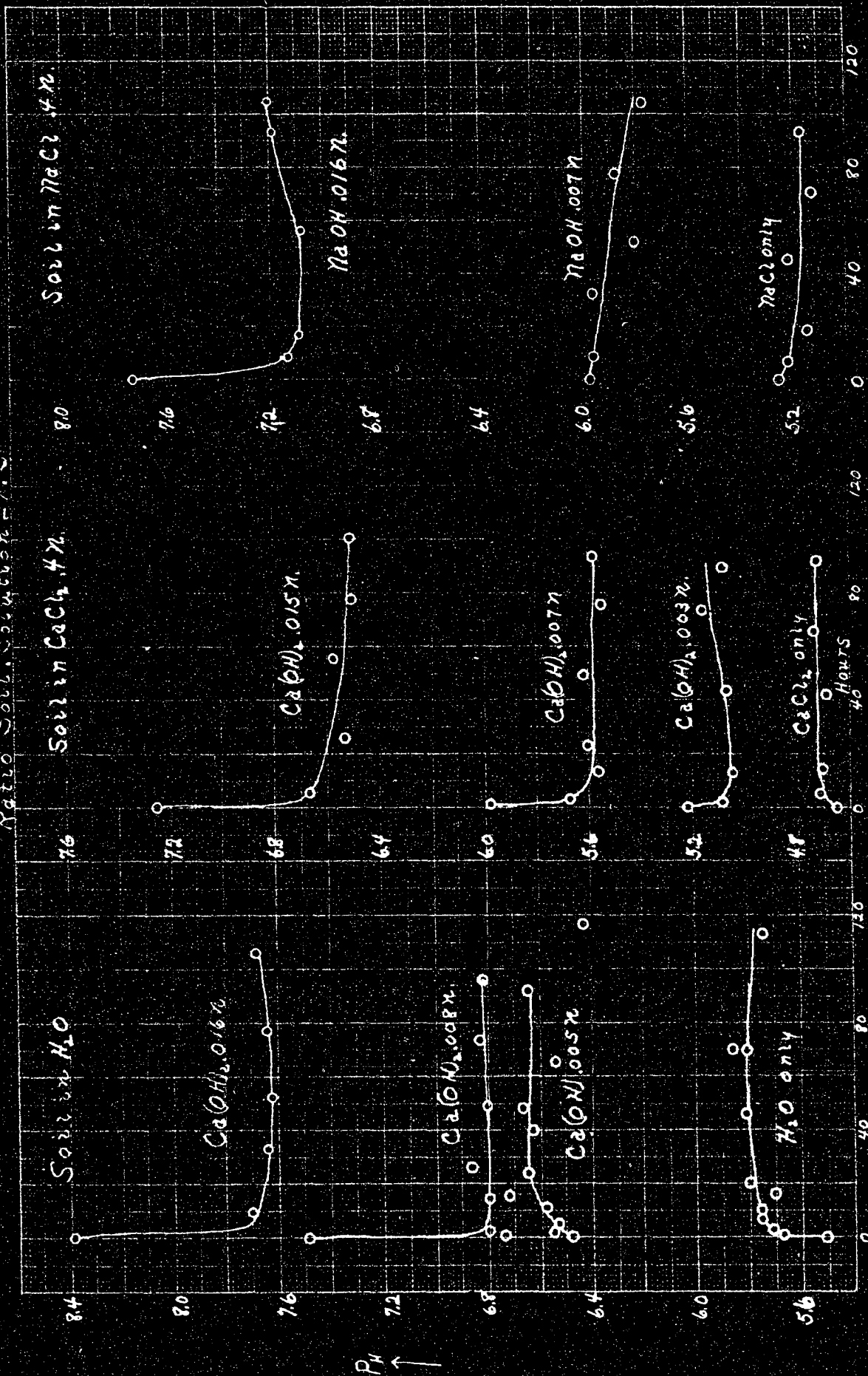
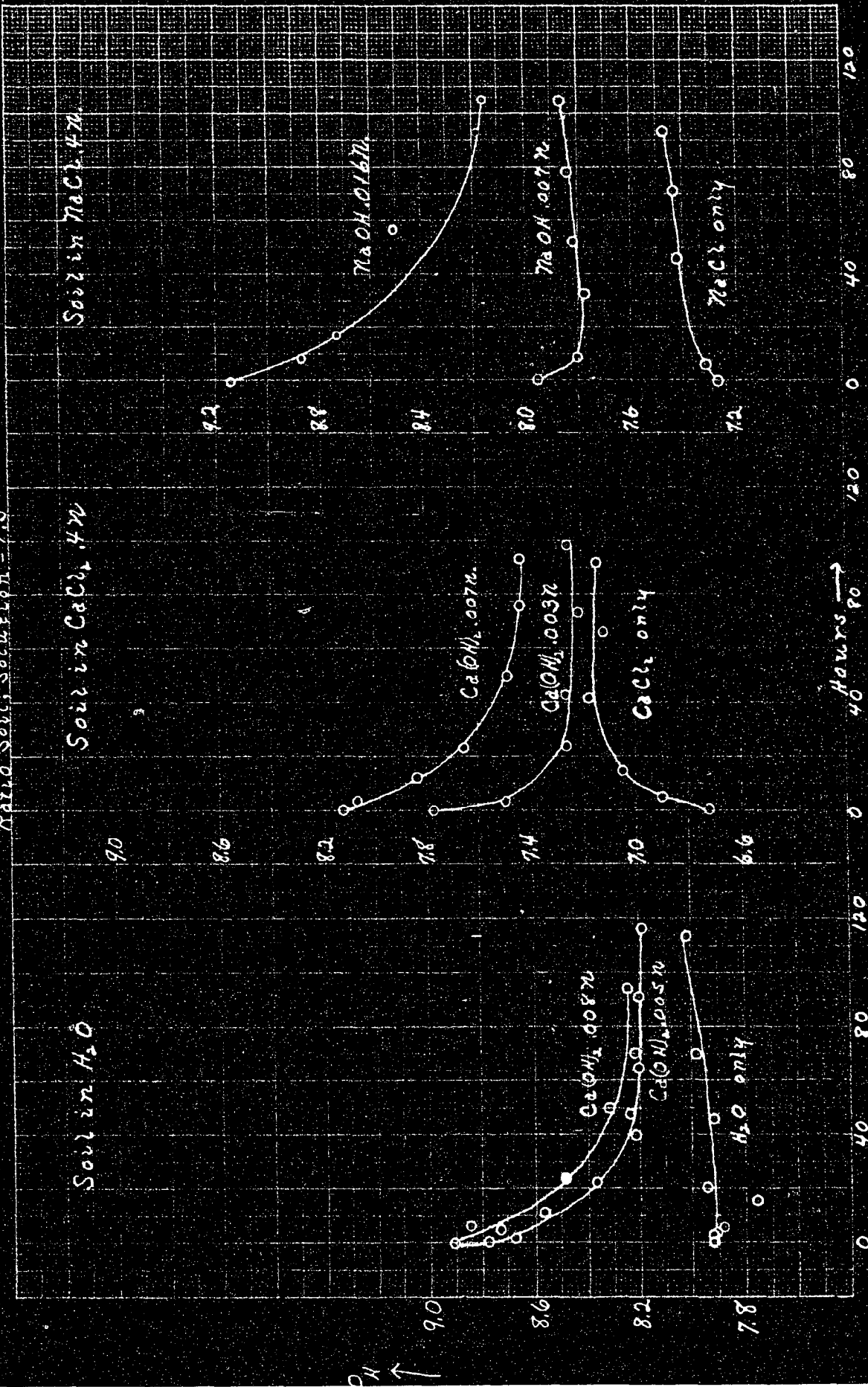


Fig. 29.

Soil No. 22.

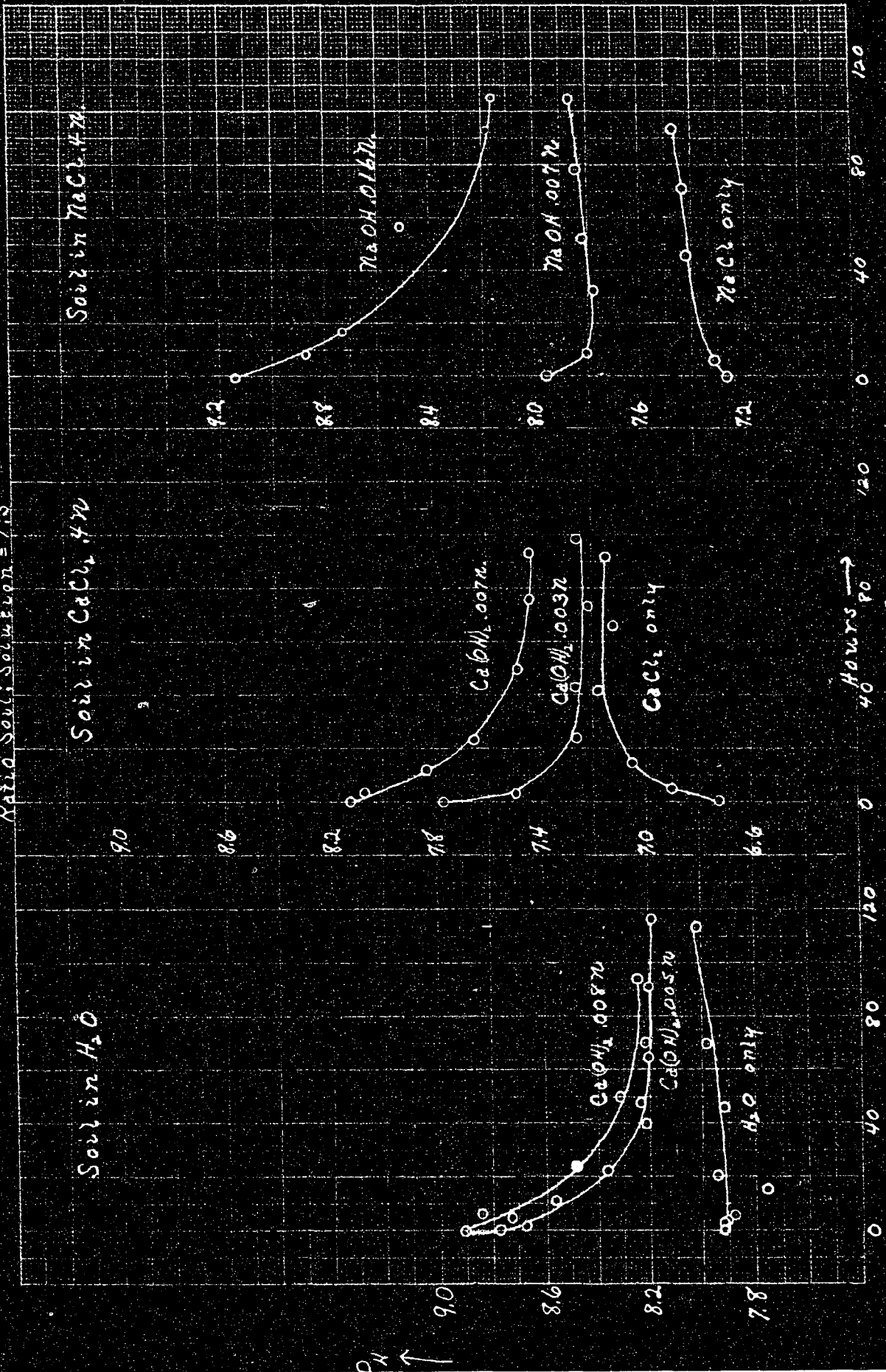
Soil Reaction with Bases  
Ratio Soil: Solution = 1:5



Hours →  
Fig. 30.

Soil No. 22.

Soil Reaction with Bases  
Ratio Sol: Solution = 1:5



Hours →  
Fig. 30.

Buffer Action. Solid Sol. 1:5 Ratio

H<sub>2</sub>O

CaCl<sub>2</sub> 4%

NaOH 4%

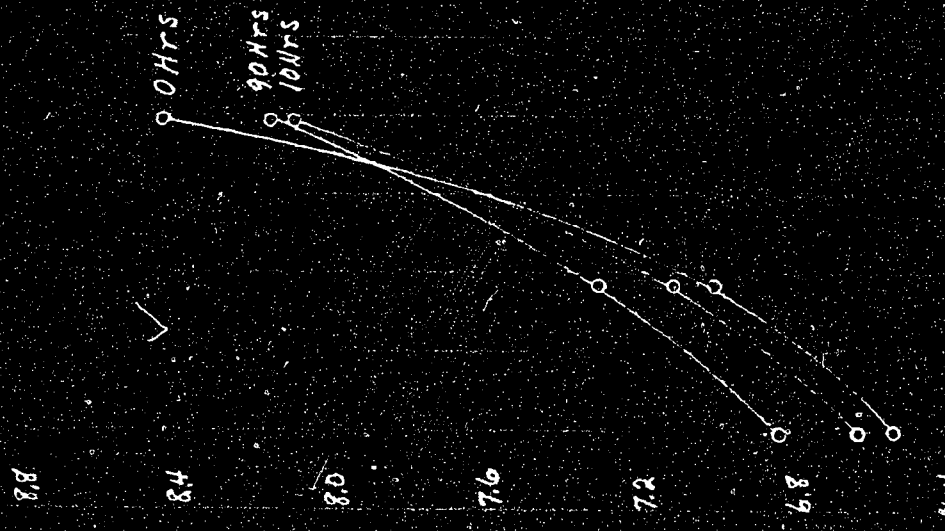
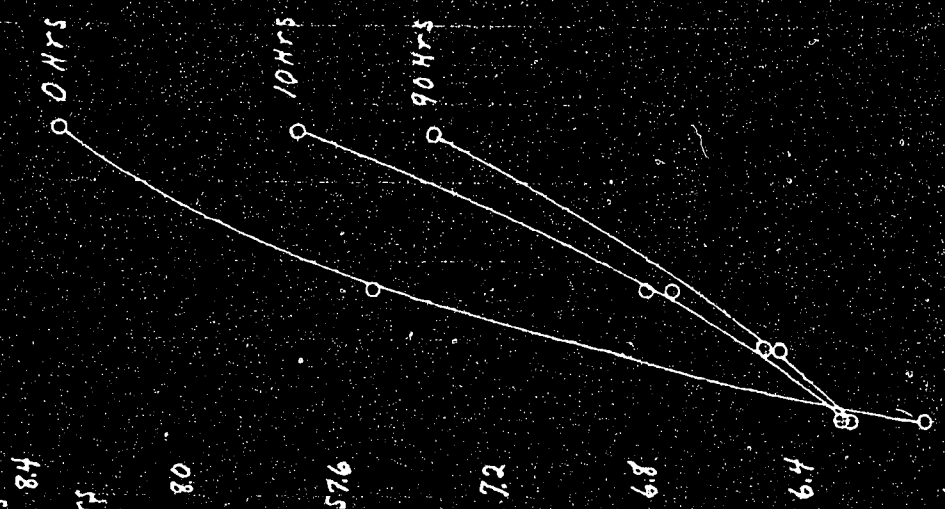
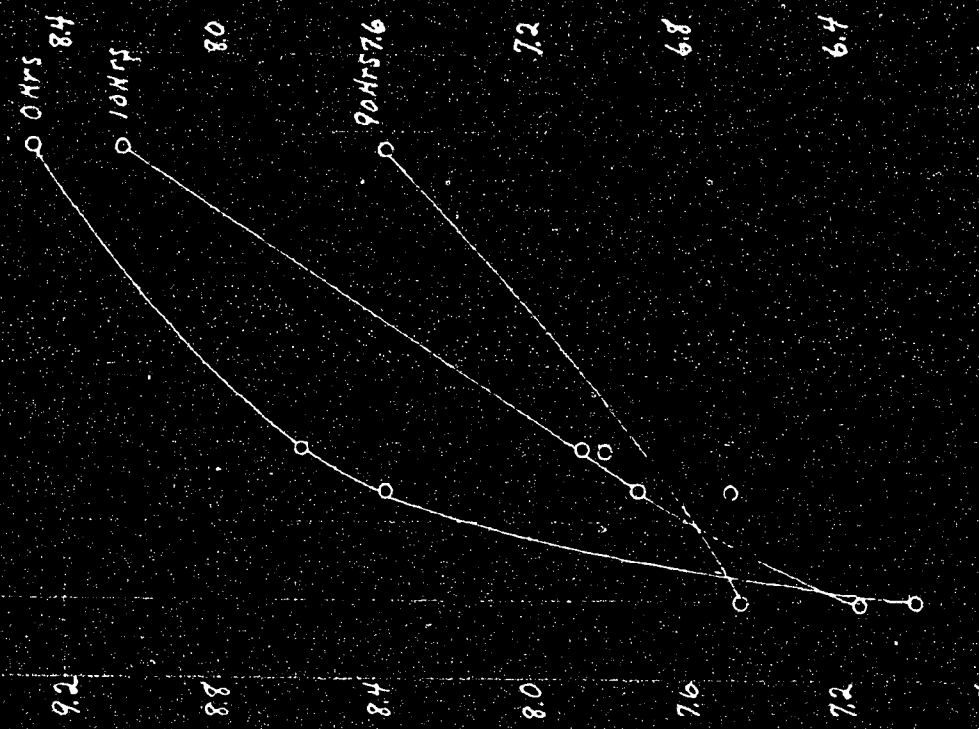


Fig. 31

Butter Action Soil No. 2  
1:5 Ratio

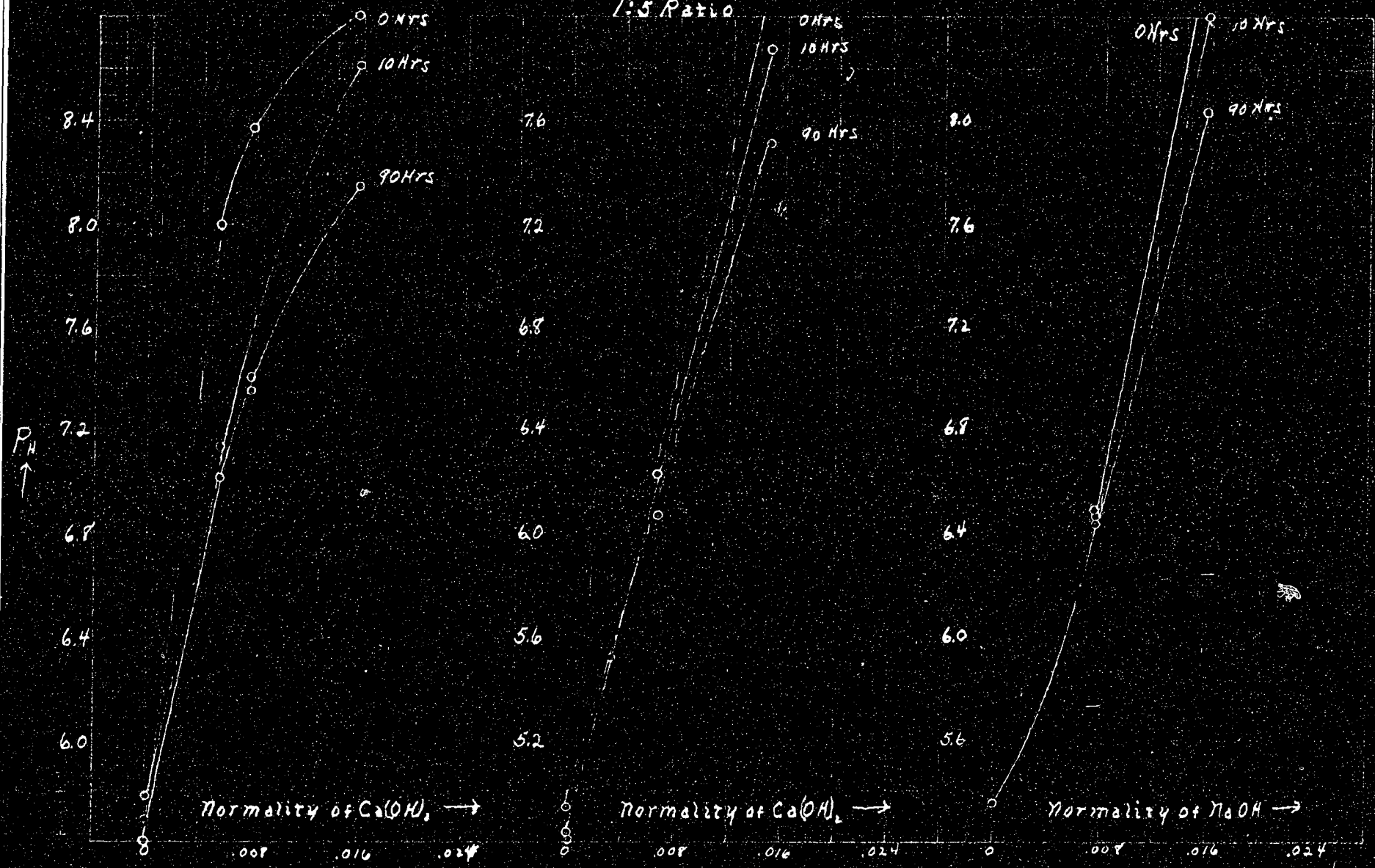
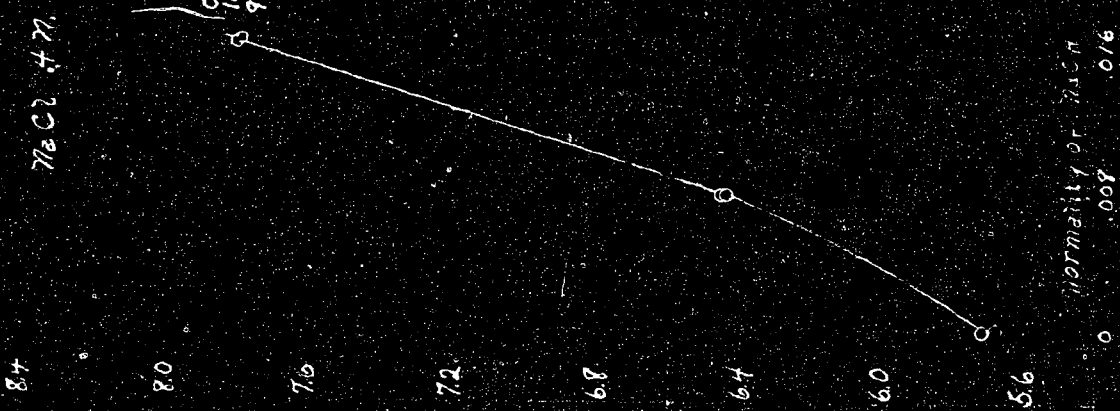


Fig 32

Buffer Action Soil 77a3  
1:5 Ratio



Normality of Ca(OH)<sub>2</sub> →  
0.008 0.016 0.024

Normality of Ca(OH)<sub>2</sub> →  
0.008 0.016 0.024

Normality of Ca(OH)<sub>2</sub> →  
0.008 0.016 0.024

Fig. 33

P\* <

Buffer Action, Soil No. 4.  
 11.5. 1930

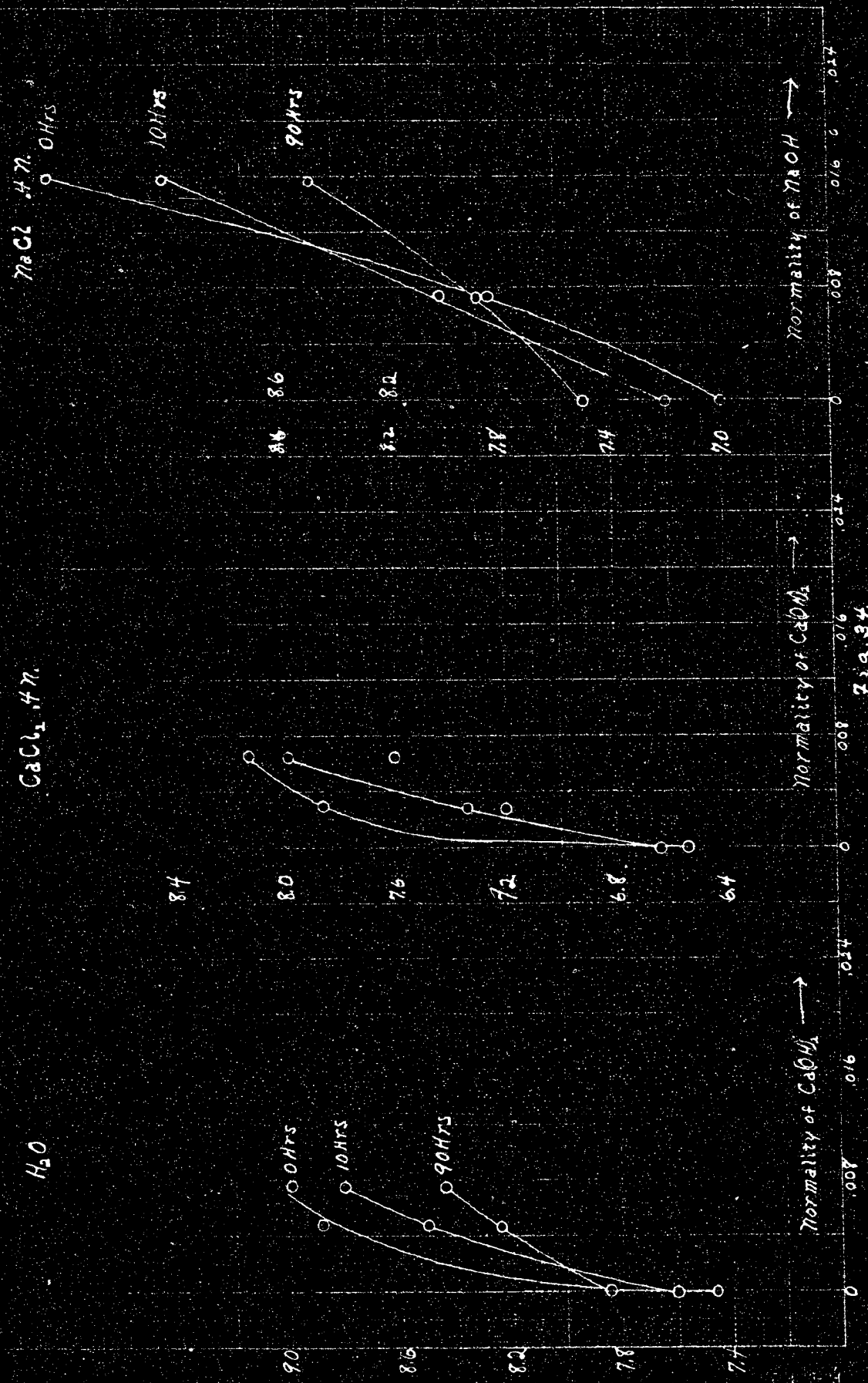


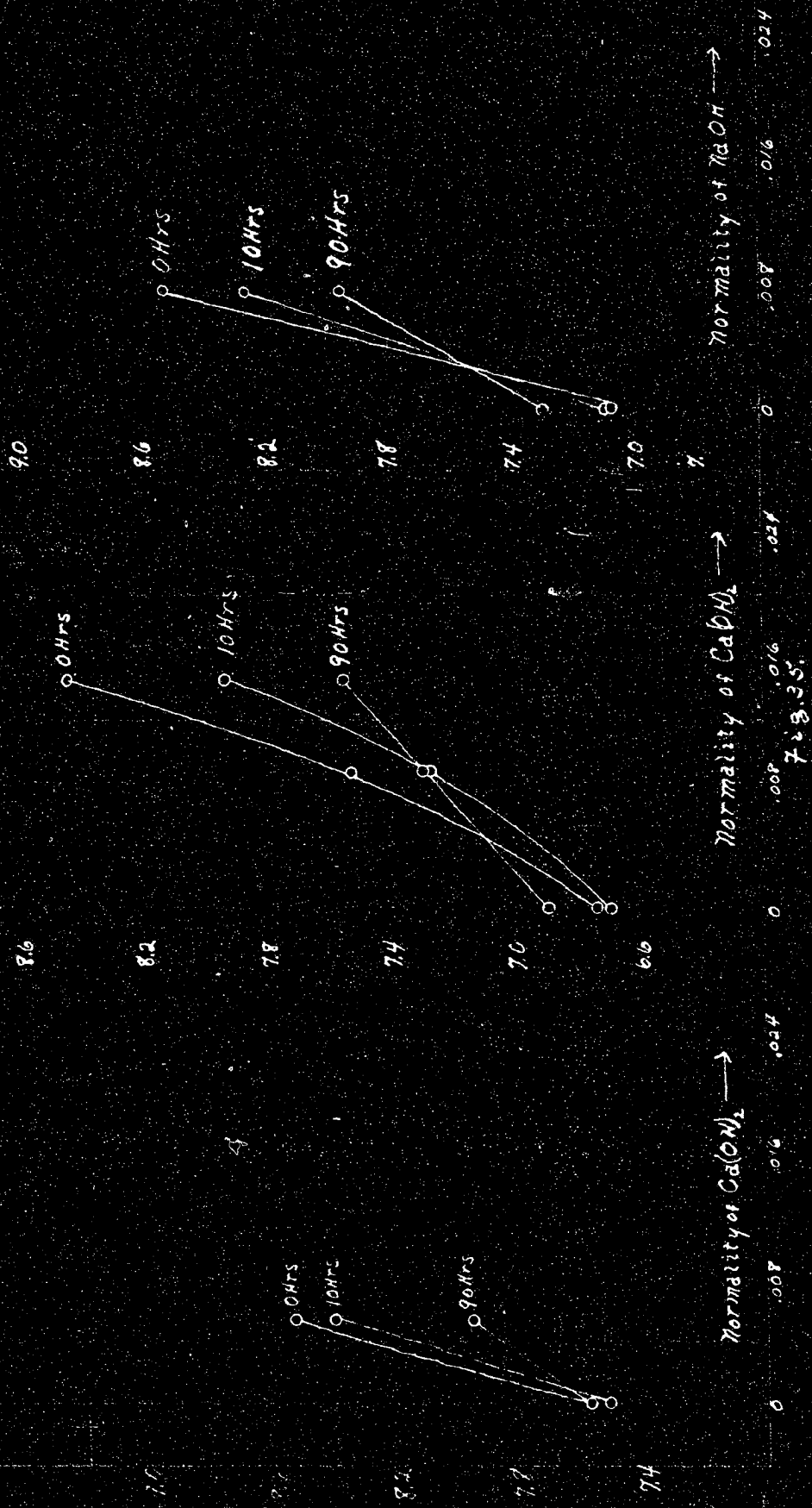
Fig. 34.

Buffer Action. Soil no. 6  
1:5 Ratio

$\text{NaCl}$  .4N.

$\text{CaCl}_2$  .4N.

$\text{H}_2\text{O}$



Normality of  $\text{NaCl}$  →

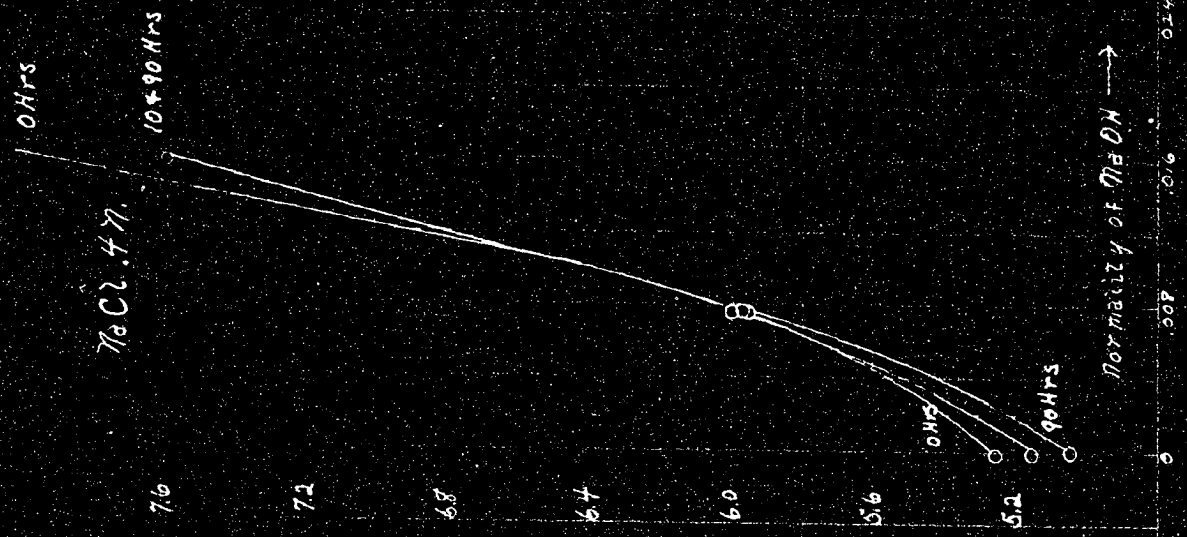
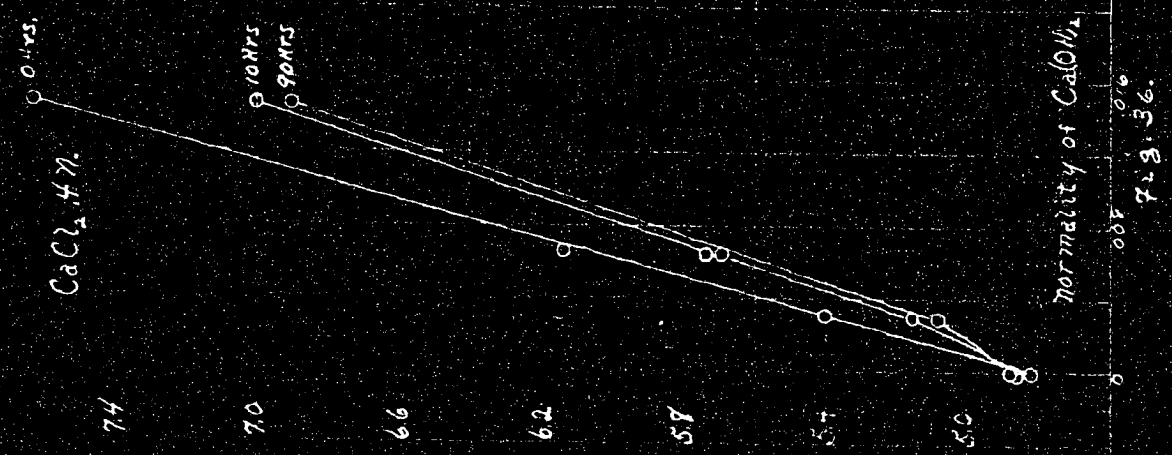
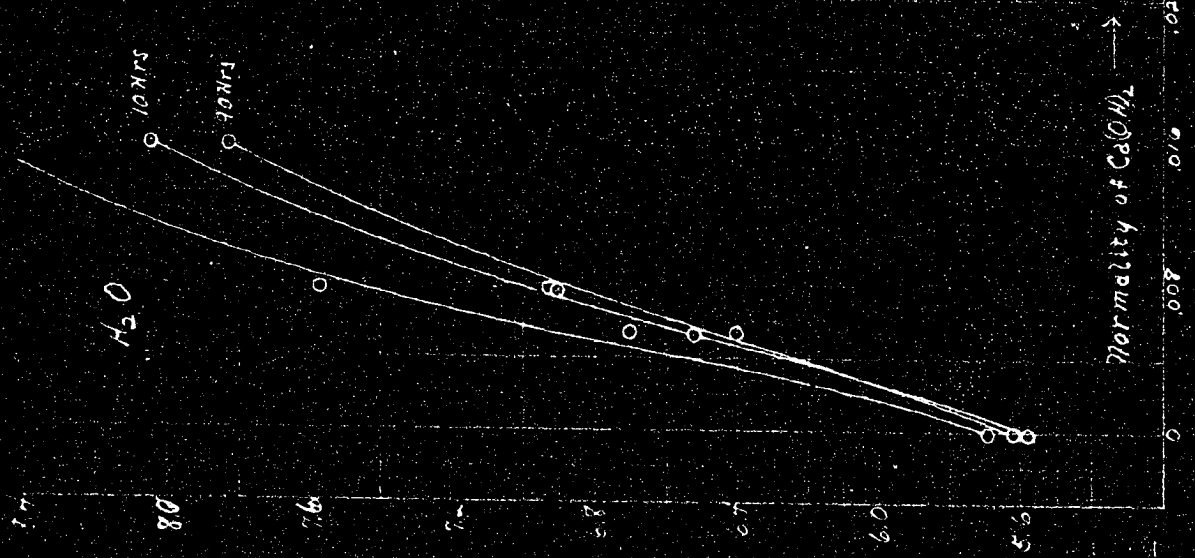
Normality of  $\text{CaCl}_2$  →

Normality of  $\text{Ca}(\text{OH})_2$  →

72.3.35.



Buffer Action Soil No. 7  
1:5 Ratio



7.9.56.

1:5 Ratio Buffer Action. Soil No. 8

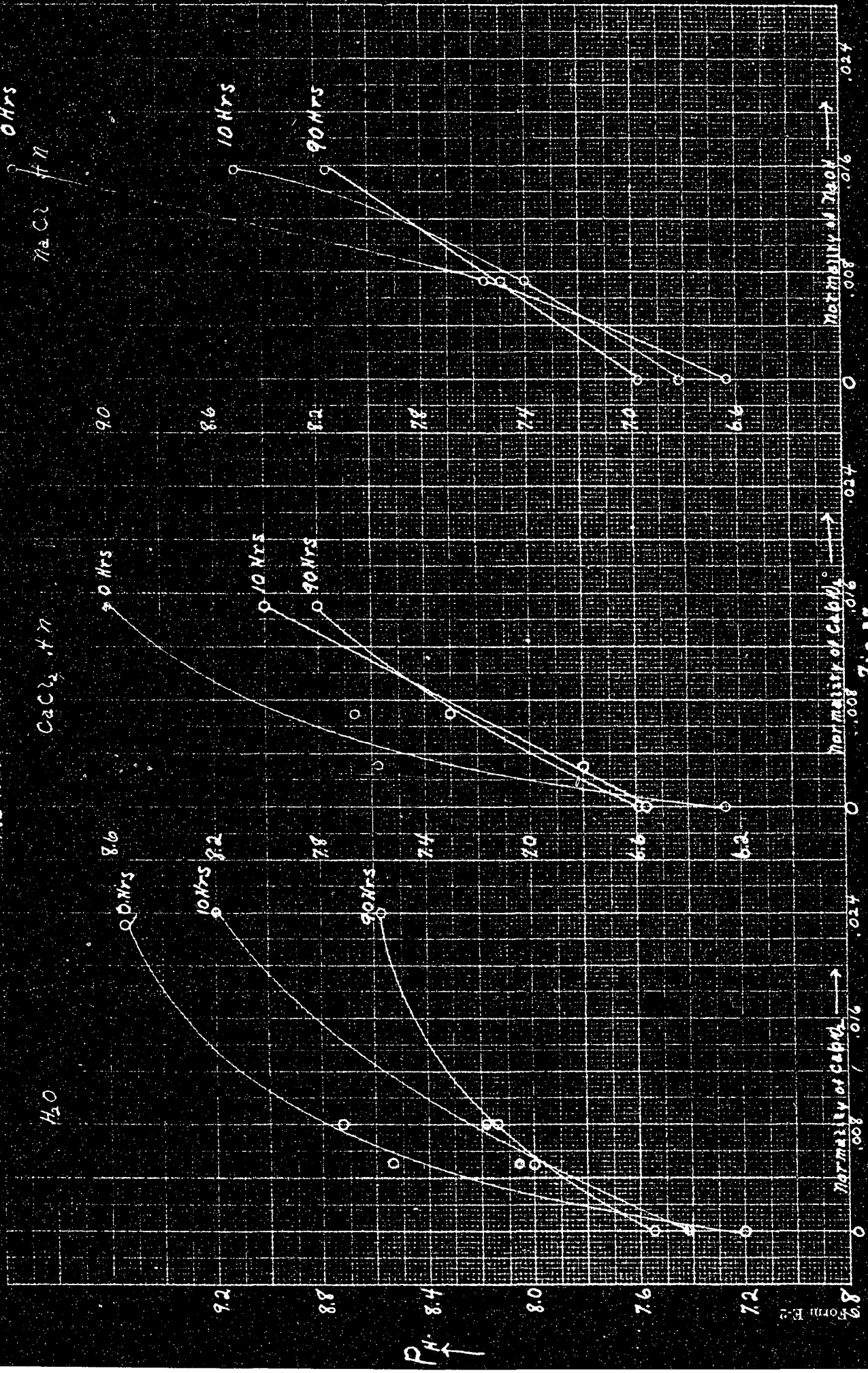


Fig. 37

Buffer Action Soil no. 9.  
1:5 Ratio

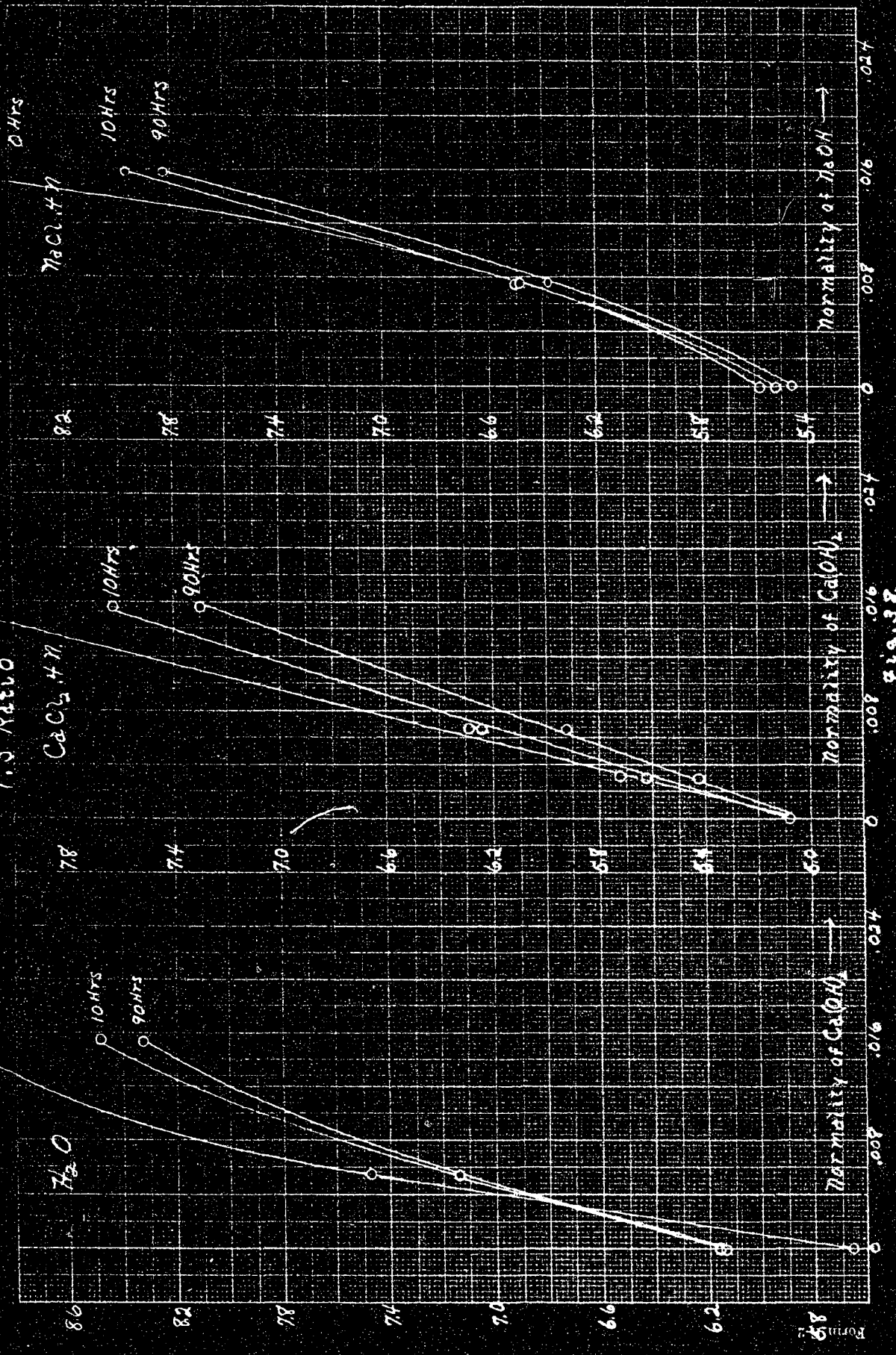


Fig. 38

Butter Action, Soil No. 10  
1:5 Ratio.

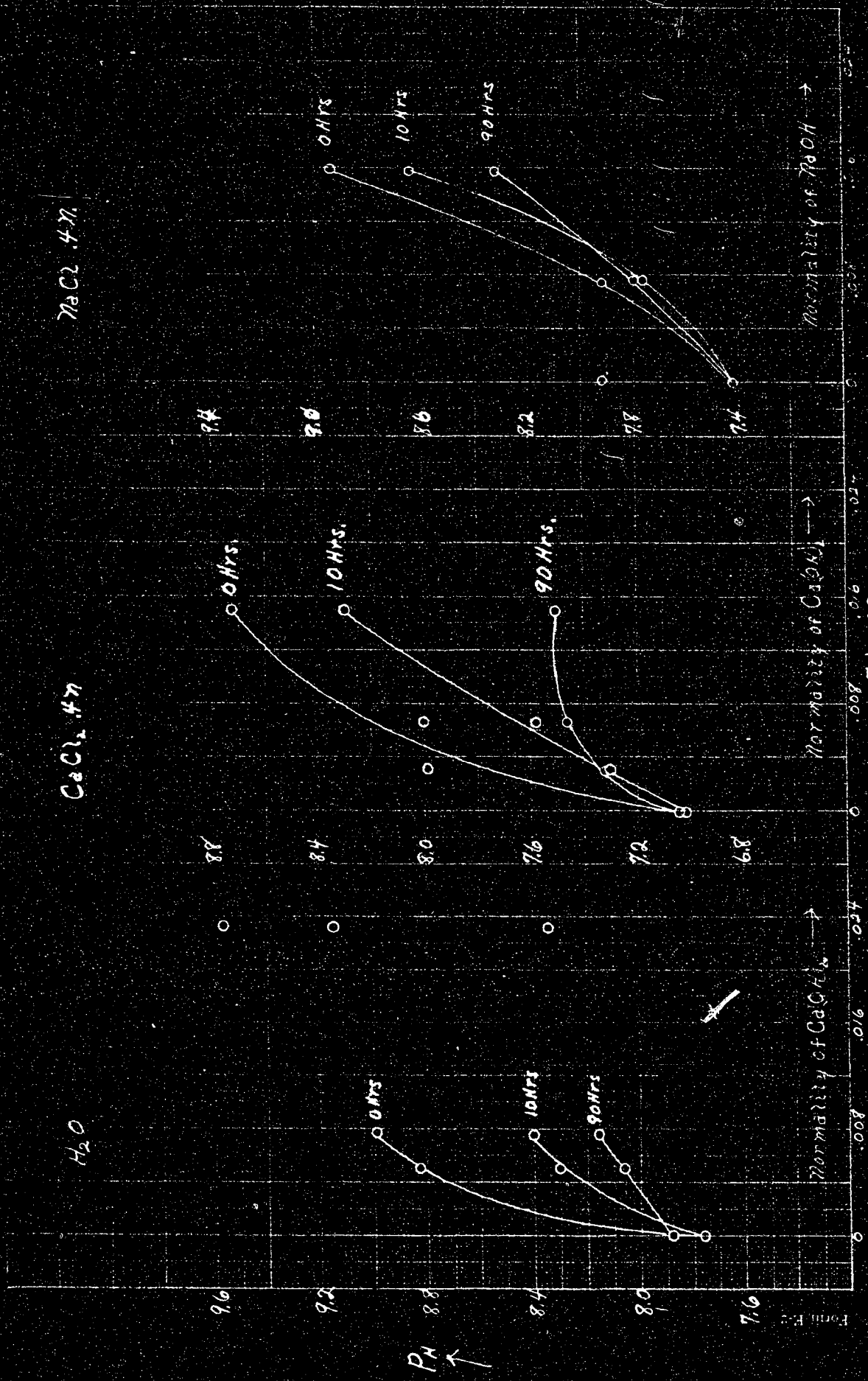


Fig. 39

Buffer Action Soil No. 11.  
1:5 Ratio

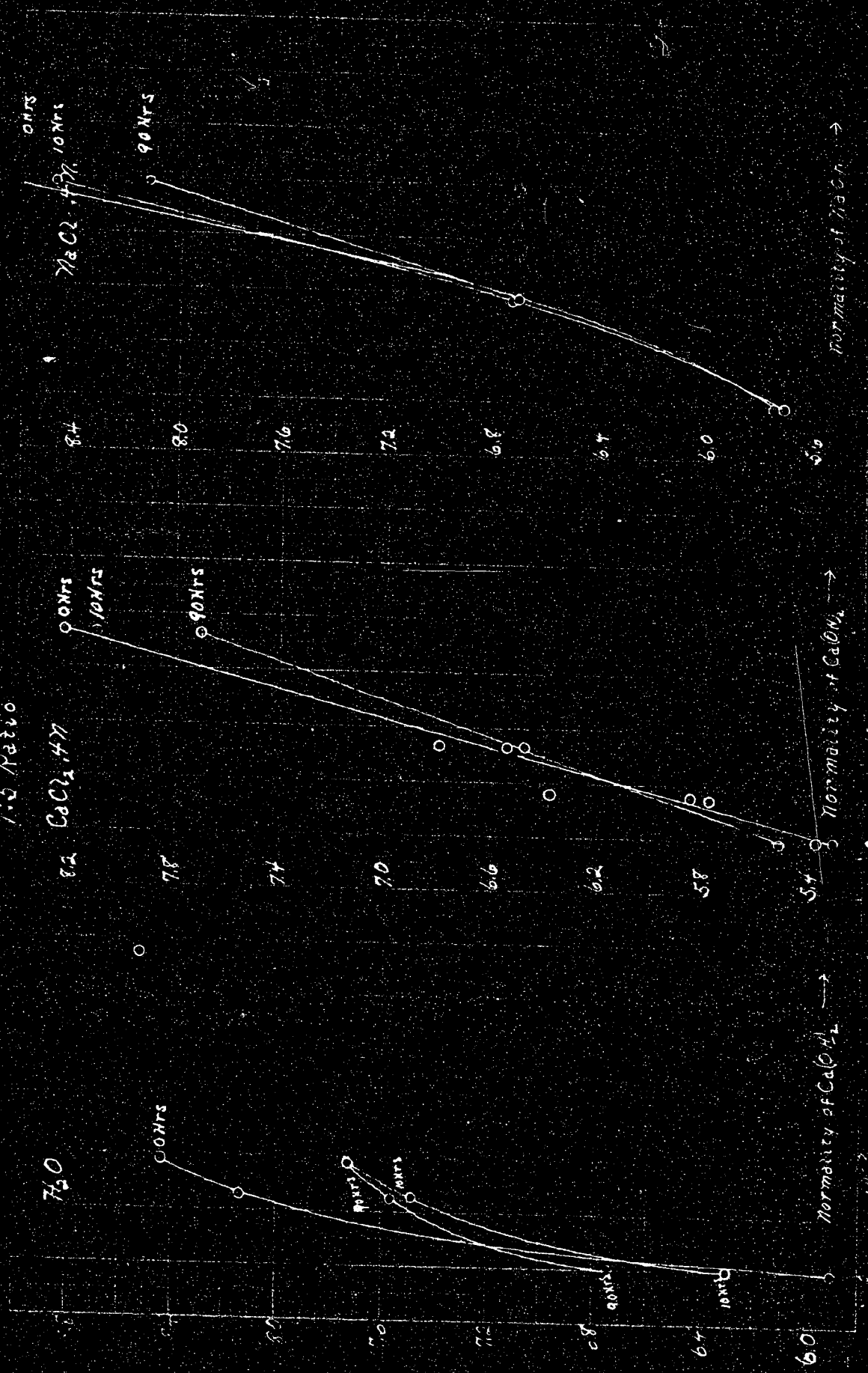


Fig. 40.

Buffer Fraction, Soil No. 12.

Ratio 1:5

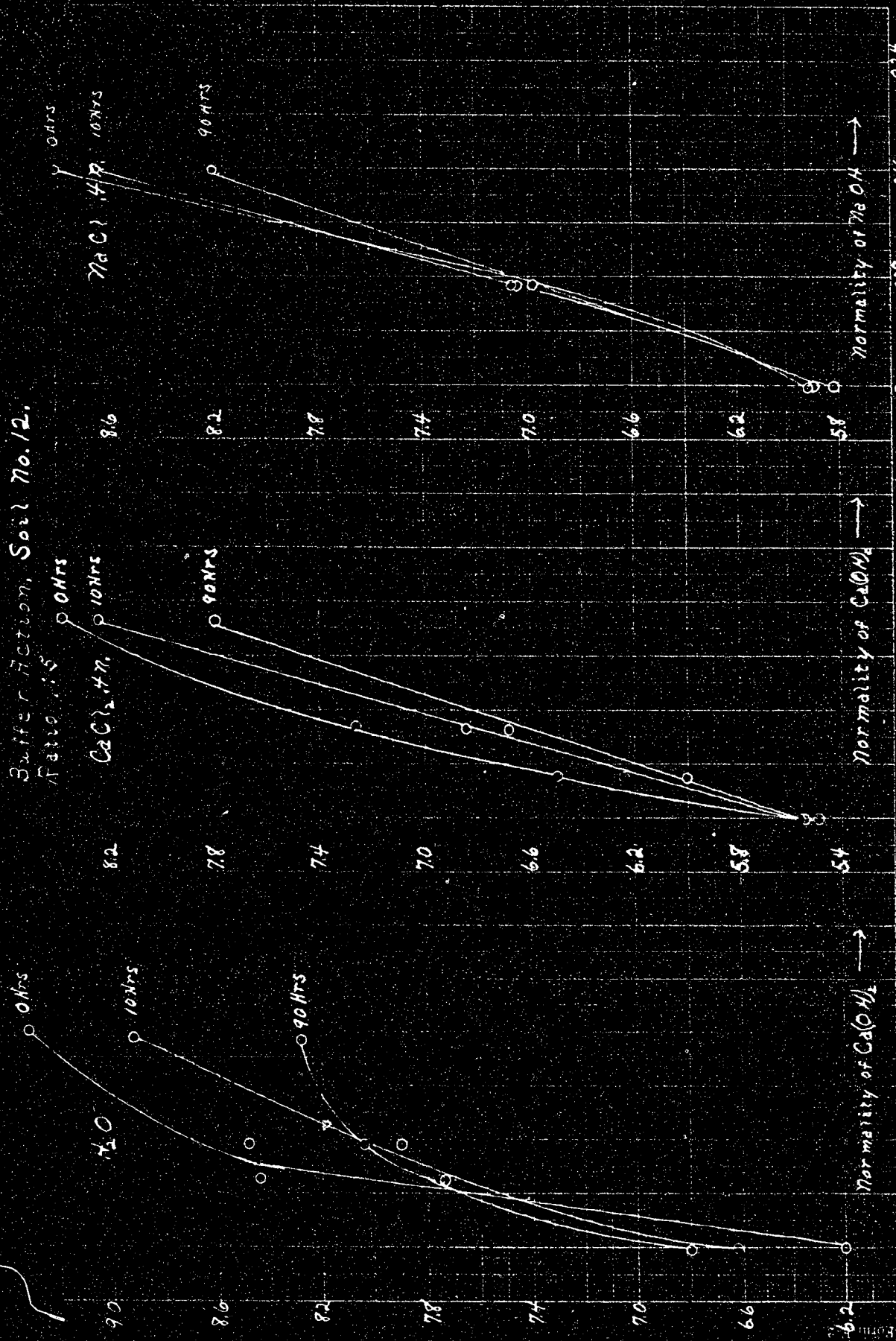


Fig. 41.



Buffer Action Soil No. 14  
1:5 Ratio

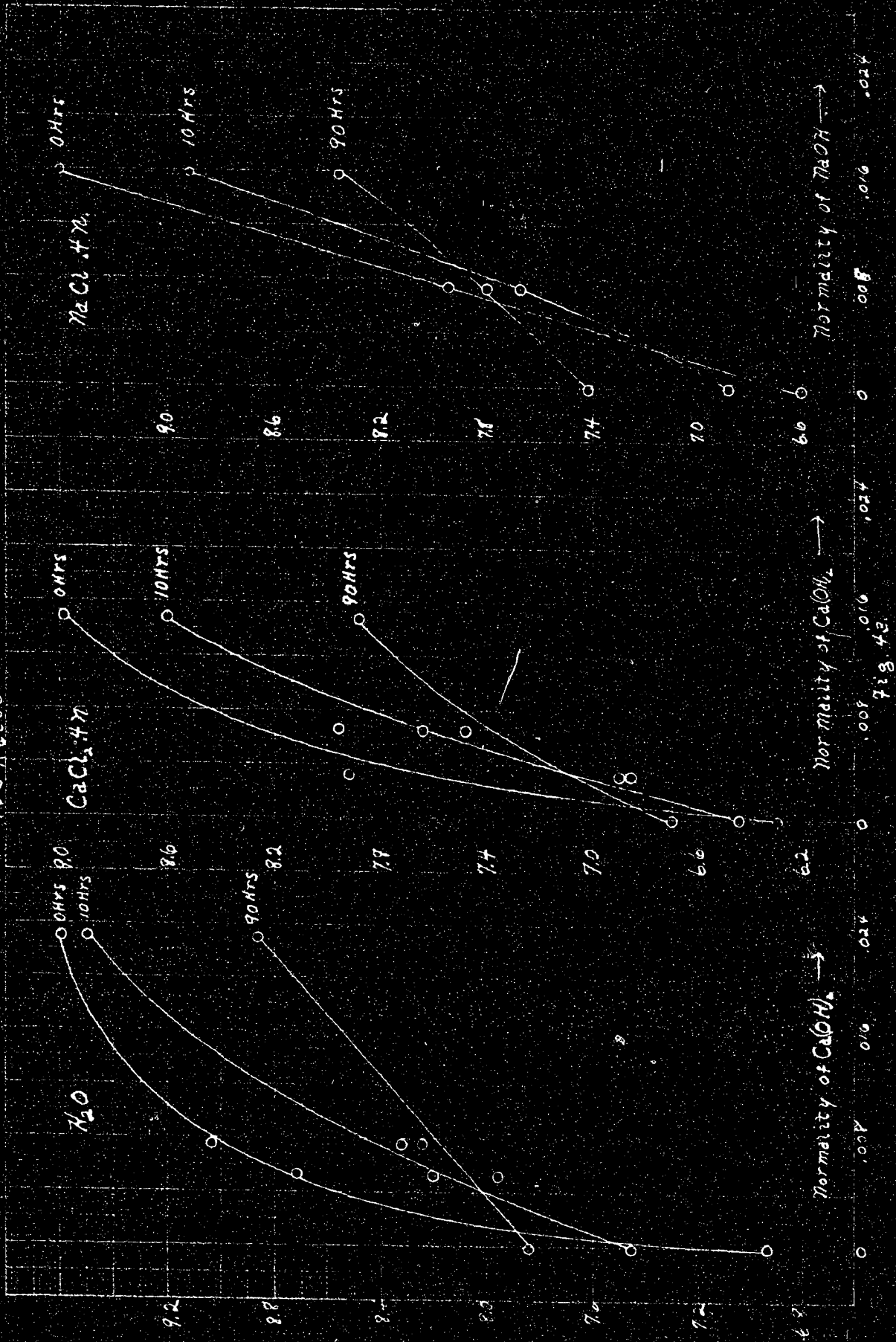


Fig. 42

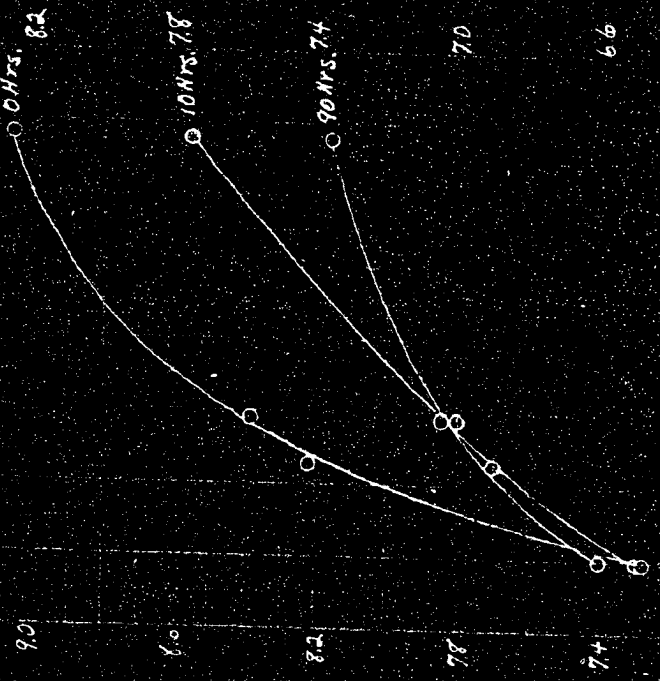


Buffer Action, Soil No. 15,  
1:5 Ratio

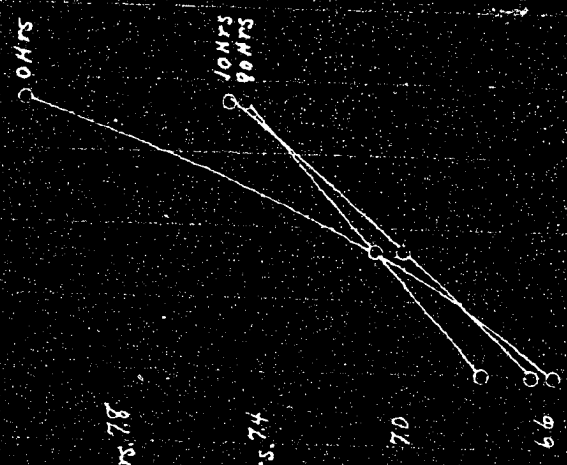
H<sub>2</sub>O

CaCl<sub>2</sub> .4N

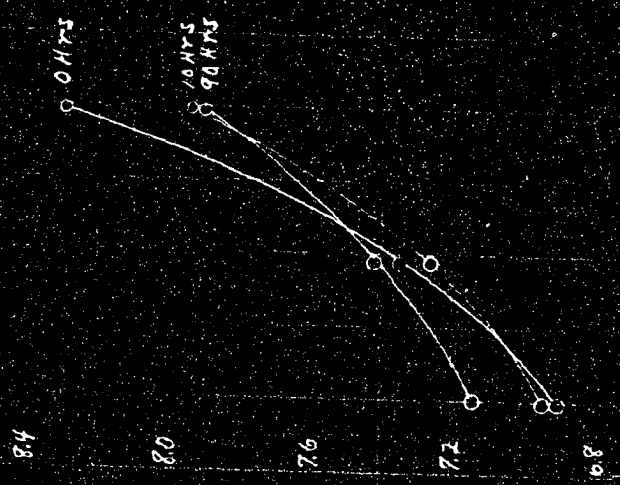
NaCl .4N



Normality of Ca(OH)<sub>2</sub> →



Normality of Ca(OH)<sub>2</sub> →



Normality of NaOH →

7.8, 7.4

Buffer Action Soil No. 16  
1:5 Ratio

H<sub>2</sub>O

CaCl<sub>2</sub> 4M

NaCl 4M

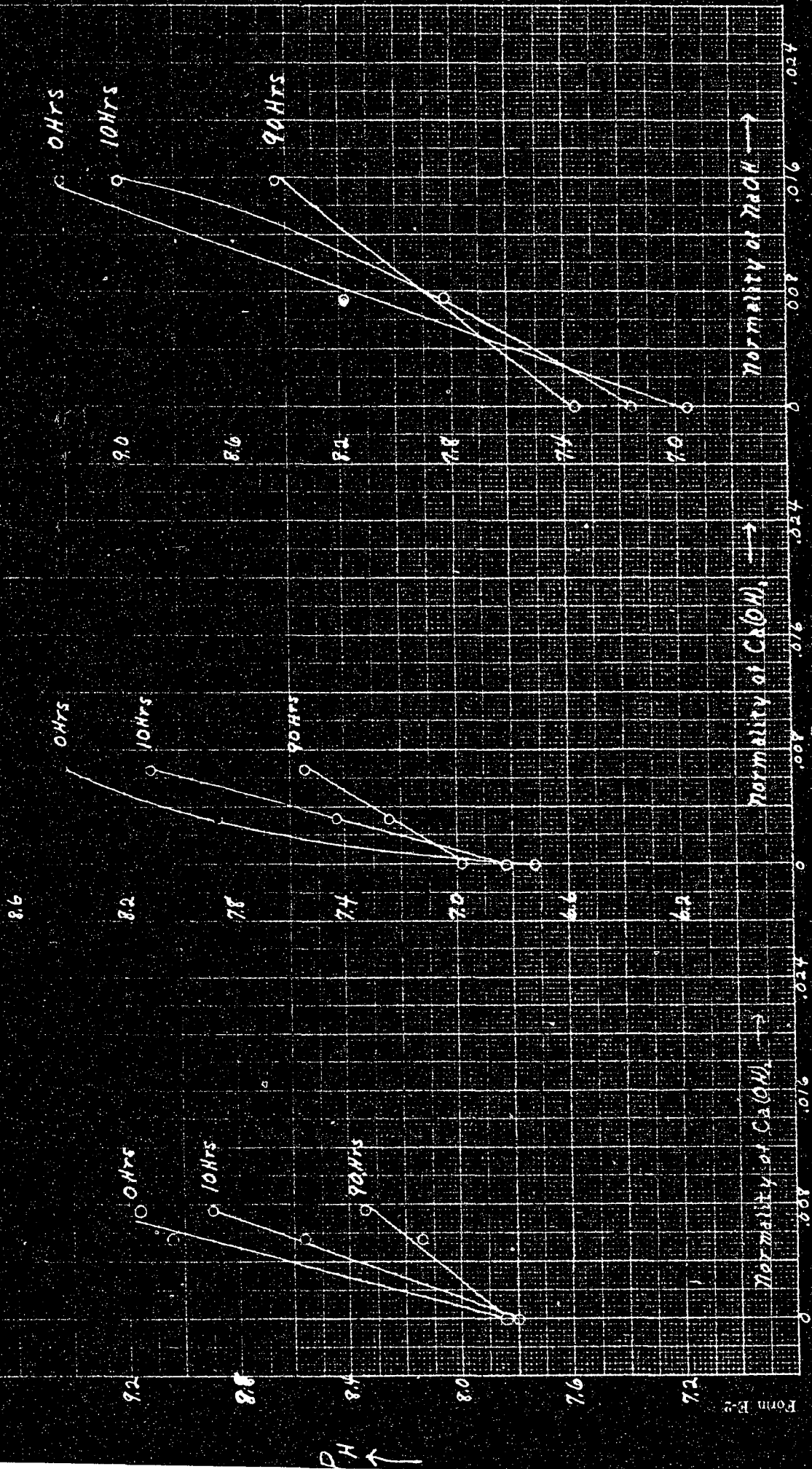


Fig. 45.

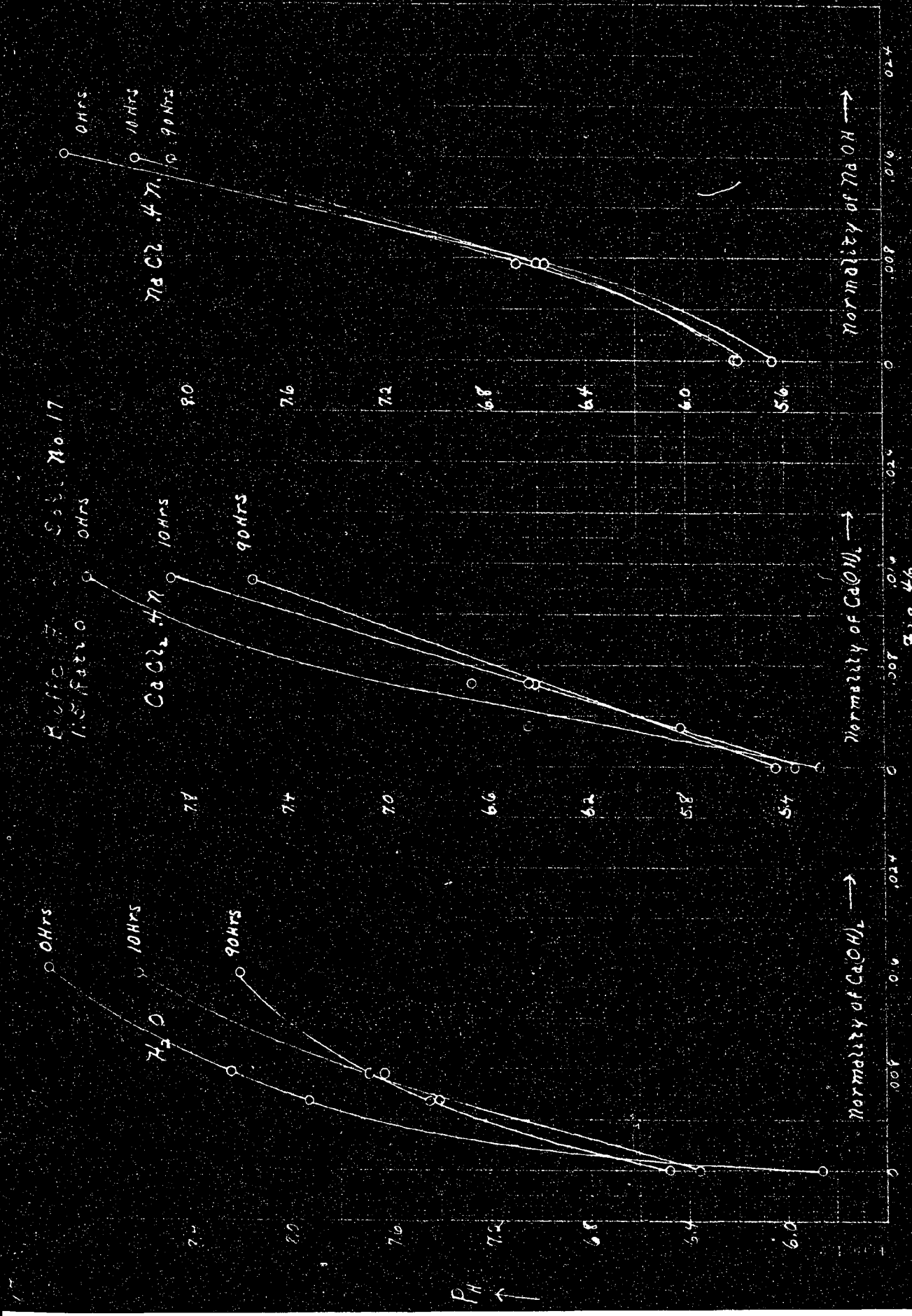


Fig. 46

Buffer fraction Soil No. 18  
1.5 M NaCl

H<sub>2</sub>O

CaCl<sub>2</sub> 0.1

NaCl 0.1

7.1

8.8

8.7

8.0

7.9

7.2

6.8

7.2

8.8

8.7

8.0

9.6

8.6

8.2

7.8

7.7

0 HRS

10 HRS

90 HRS

Normality of CaCl<sub>2</sub> →

Normality of Ca(OH)<sub>2</sub> →

Normality of NaOH →

0 .008 .016 .024 .032 .040 .048 .056 .064 .072 .080 .088 .096 .104 .112 .120 .128 .136 .144 .152 .160 .168 .176 .184 .192 .200

0 .008 .016 .024 .032 .040 .048 .056 .064 .072 .080 .088 .096 .104 .112 .120 .128 .136 .144 .152 .160 .168 .176 .184 .192 .200

0 .008 .016 .024 .032 .040 .048 .056 .064 .072 .080 .088 .096 .104 .112 .120 .128 .136 .144 .152 .160 .168 .176 .184 .192 .200

0.008 0.016 0.024 0.032 0.040 0.048 0.056 0.064 0.072 0.080 0.088 0.096 0.104 0.112 0.120 0.128 0.136 0.144 0.152 0.160 0.168 0.176 0.184 0.192 0.200

Fig. 47

Buffer Action Soil No. 19.  
1:5 Ratio

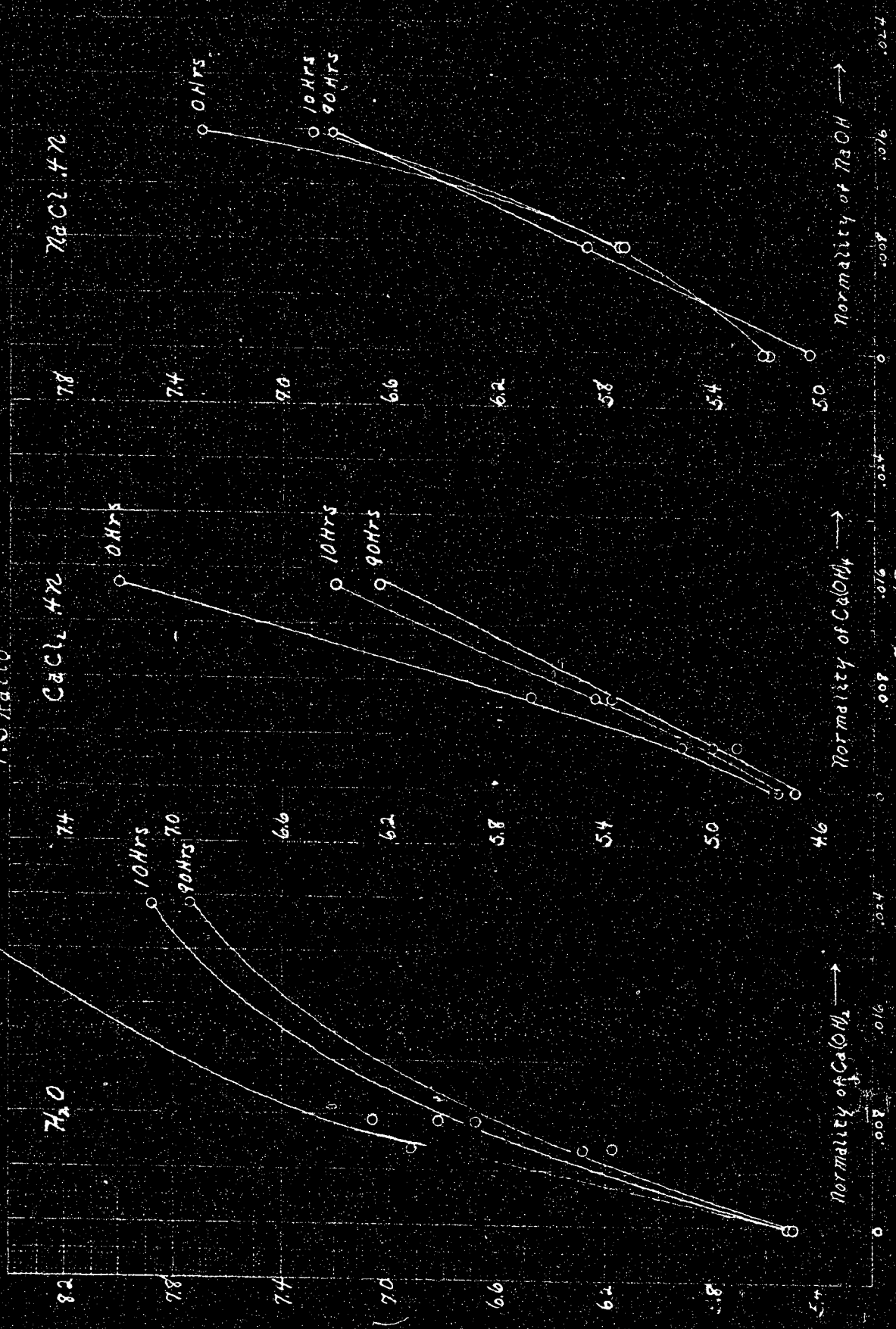


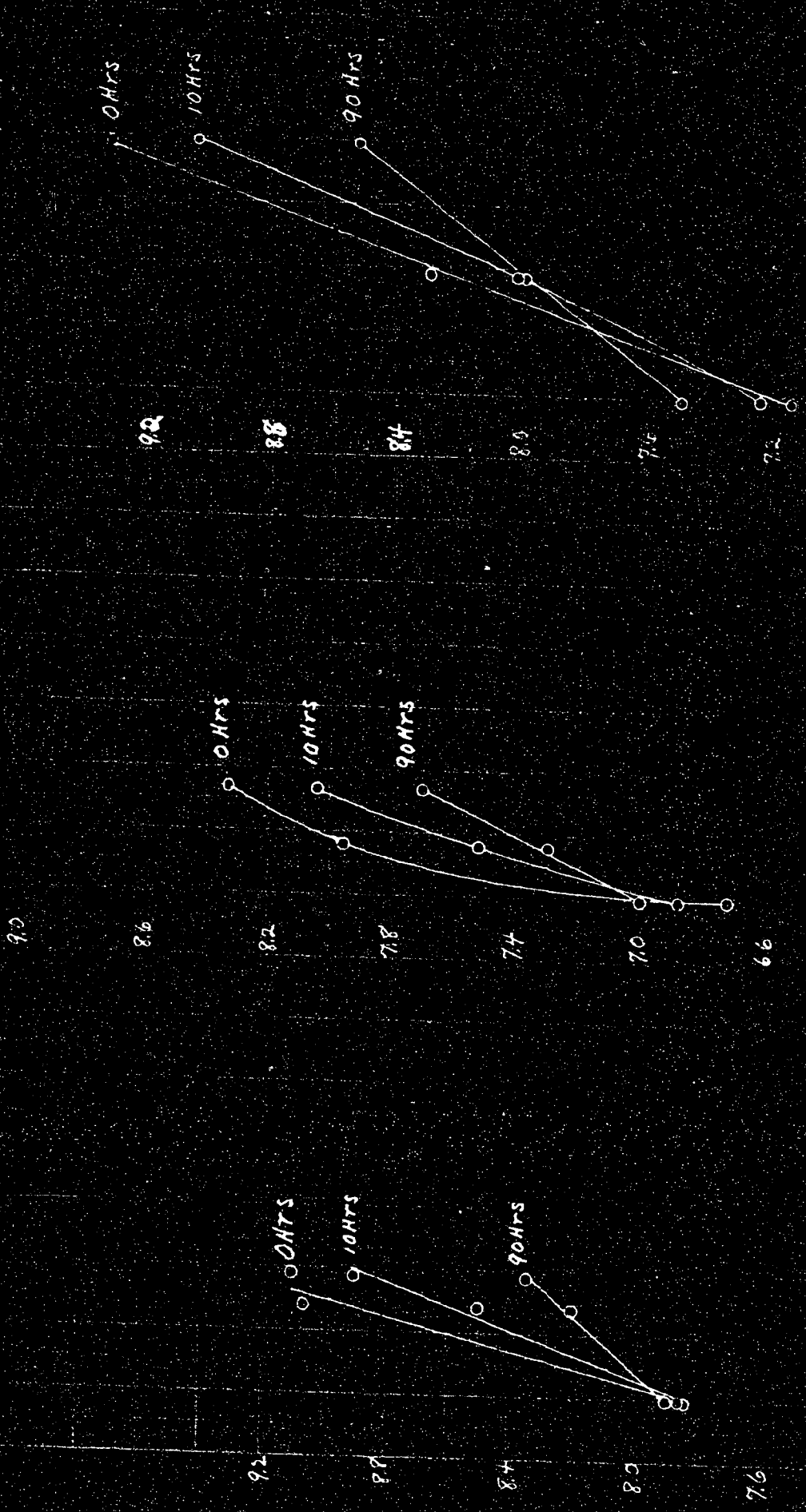
Fig. 48.

Buffer Action Soil No 20  
1:1 Ratio

H<sub>2</sub>O

C=Cl<sub>2</sub>H<sub>2</sub>

NaCl #2



Normality of Ca(OH)<sub>2</sub> →

Normality of Ca(OH)<sub>2</sub> →

Normality of NaOH →

Fig. 3.7.7

Equilibrium Soil Moisture

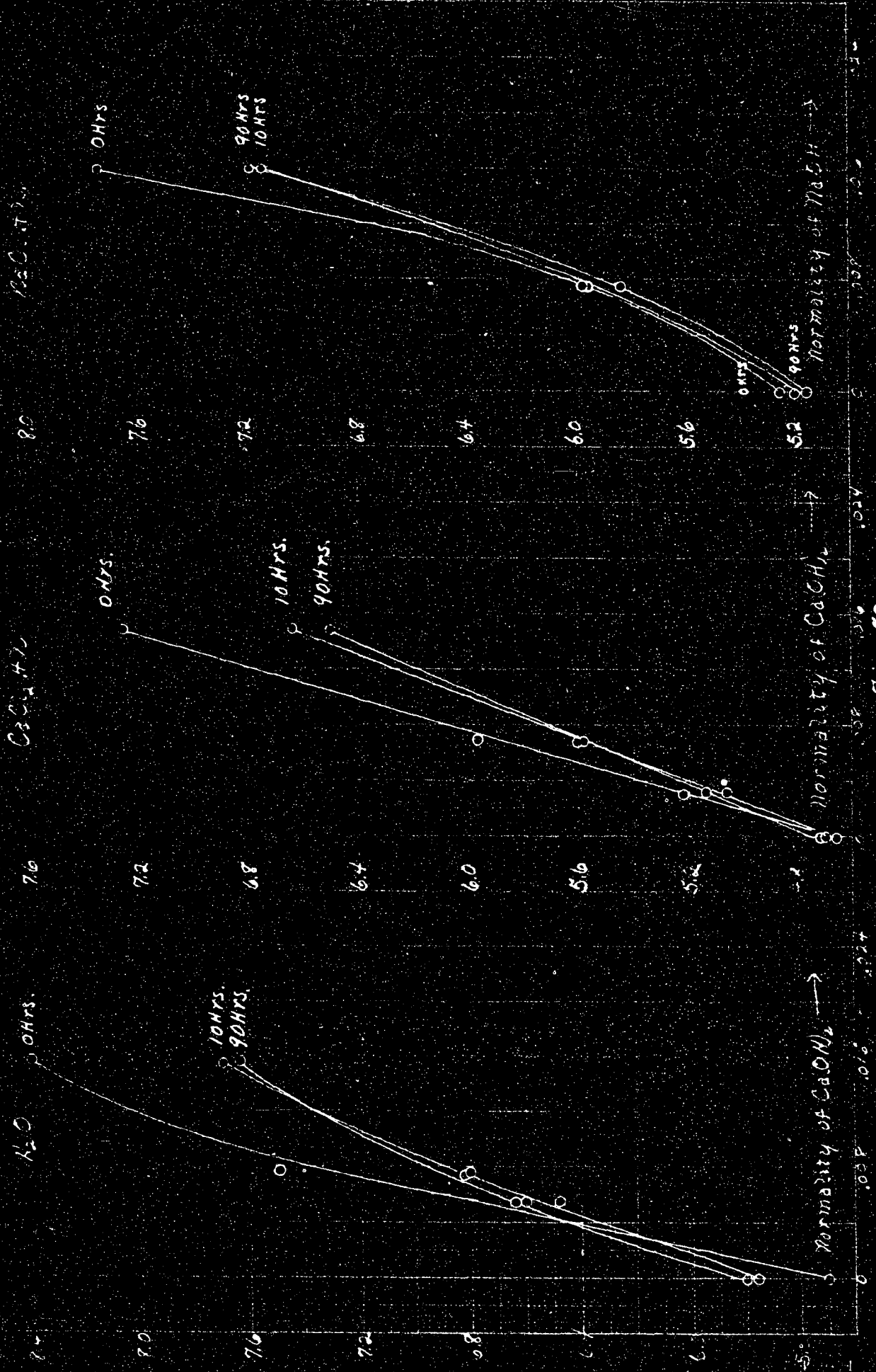


Fig. 50

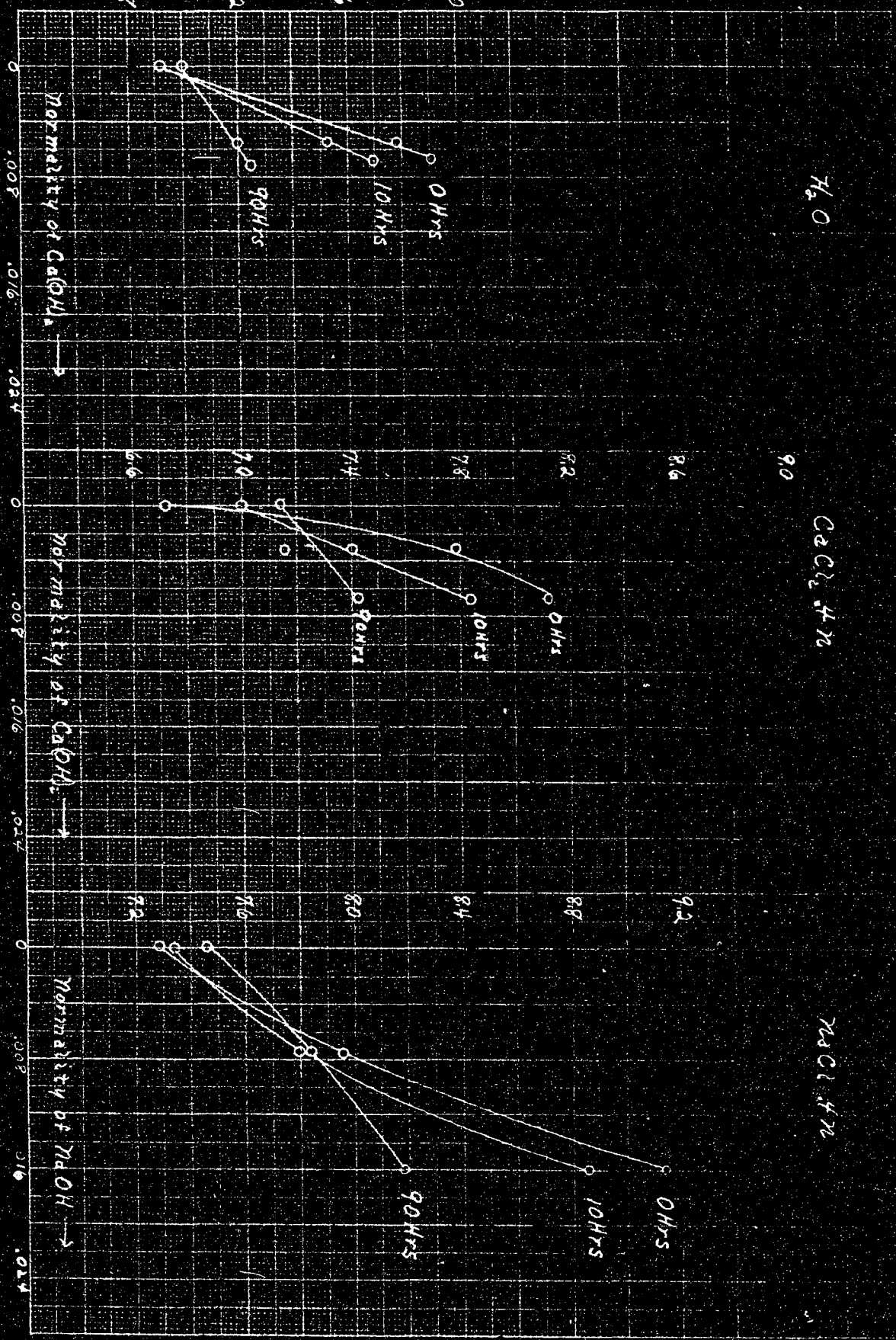
Buffer Action Soil No. 22  
1:5 Ratio

H<sub>2</sub>O

CaCl<sub>2</sub> M

MgCl<sub>2</sub> M

Form E-2



729.51

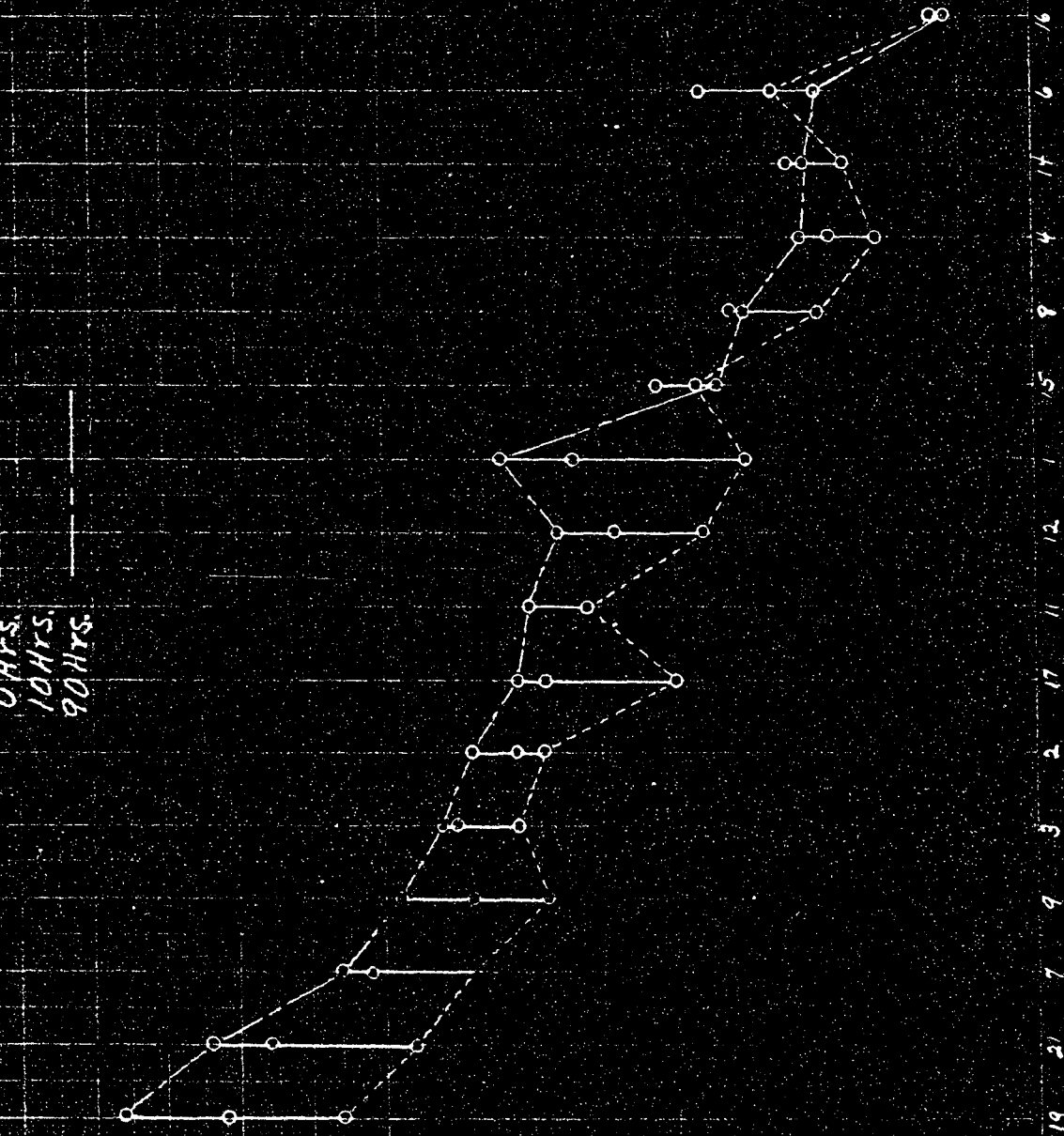


Lime Requirement with Various Times of Stirring.

Titration with  $\text{Ca}(\text{OH})_2$  in  $\text{CaCl}_2$  Solution 4%.

0 Hrs. ———  
 10 Hrs. ———  
 90 Hrs. ———

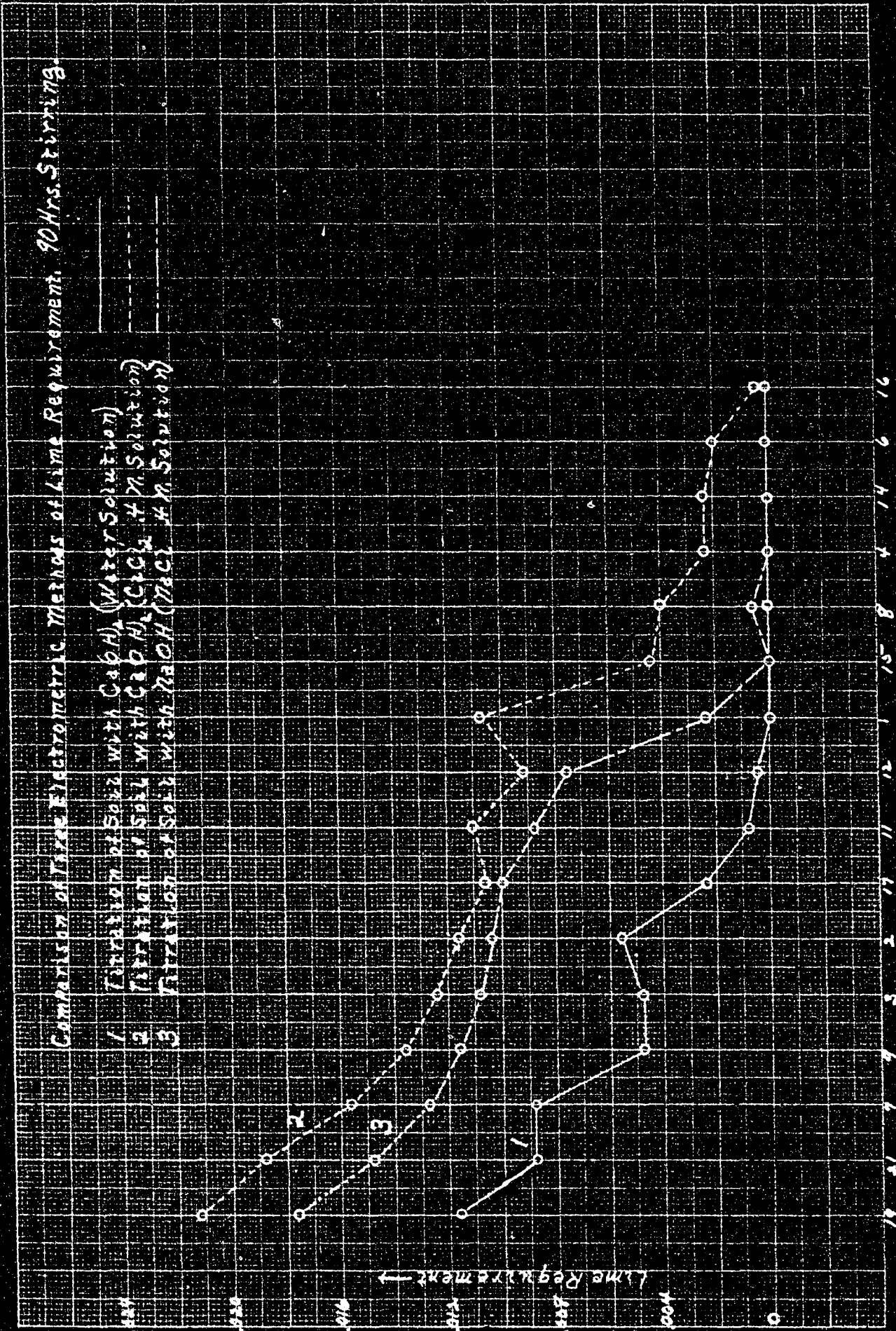
Lime Requirement →



Soil Number.  
 72952

Comparison of Three Electrometric Methods of Lime Requirement. 90 Hrs. Stirring.

- 1 Titration of Soil with  $\text{CaO}$  (Water Solution)
- 2 Titration of Soil with  $\text{CaO}$  (4% Solution)
- 3 Titration of Soil with  $\text{NaOH}$  (2% Solution)



Soil Number  
Fig. 53.

### Buffer Capacity

The term buffer action, which refers to the property of certain substances to retard the normal change in pH upon the addition of an acid or a base, has been used to some extent during the last few years by soil investigators. Crowther (18) has defined the buffer capacity of soils in terms of the slope of the titration curves. On account of their curvature, he suggests some definite range should be selected, as pH 6.0 to 7.0. He shows that the buffer action varies with the content of organic matter and clay.

Maiwald (38) gives six factors upon which he considers the degree of buffering and the form of the titration curve depends.

1. The chemical character of the colloidal complex as determined by the absolute base binding capacity of anions.
2. The saturation condition of the colloid complex as indicated by  $x$  in the formula  $XR^+ + (100-x)H^+$ .
3. The absolute content of substances capable of reaction.  
(The colloidal content or better the sum of  $R^+ + H^+$  per gram of soil.)
4. Degree of division of the colloid and the change in the titration range.
5. The character and composition of exchangeable bases.
6. Character of admixed reagents.

Numbers 1 and 2 are considered material factors while 3 and 4 are concentration factors depending on the mass law. Numbers

5 and 6 are secondary factors. The combined effect of the six factors give a smooth flat titration curve with a wide buffer action. In carbonate poor soils he considers that it is probable that the colloidal complex of humus and clay give almost all the buffer action.

Meyers and Gilligan (43) attribute buffer action to impurities held by the colloidal fraction. Their theory is that the buffer action is not due to the colloidal properties but to salts, metallic or acid radicals that are held by the colloidal fraction.

Maiwald (38) Crowther (18) and Brioux (9) have found smooth curves for the titration reaction, while Bradfield (7) found a sudden increase in pH at the neutral point incase of acid soils. He interpreted this as an indication that the alkaline mixture must first neutralize the acid clay and then flocculate the resulting salt of the clay. He therefore concluded that there should be no increase at the neutral point in the case of neutral soils, and this was found to be the case.

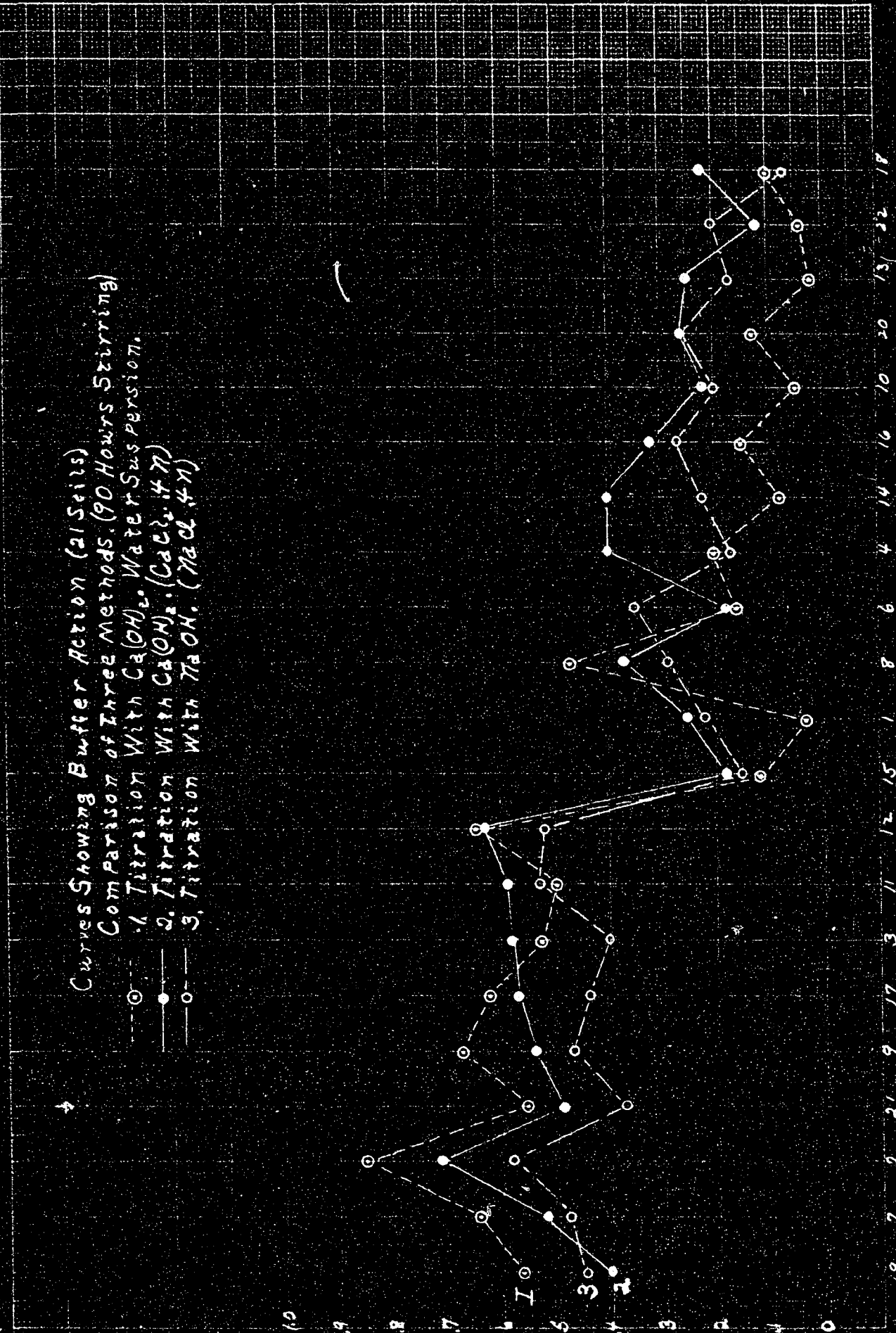
The buffer action curves for the twenty one Iowa soils described as obtained, with calcium hydroxide in a water suspension and in a calcium chloride suspension, as well as sodium hydroxide in a sodium chloride suspension, are given in Figures 31 to 51 inclusive. These curves give the relative buffer action only, for the absolute buffer capacity of the soil it would be necessary to find the pH values of the different solutions without the soil added. Several points, however, can be seen from a study of the curves.

Smooth curves are obtained with no indication of a sudden increase at the neutral point as found by Bradfield. The effect of the time of stirring on the buffer action is very noticeable. This effect is summarized in Figure 54 which gives a graphic presentation of the increase in pH due to the addition of calcium hydroxide 0.008 N to the twenty one soils in the ratio soil to solution of 1:5. The relative buffer capacity without stirring will be the difference between the pH taken immediately in a water suspension and the corresponding pH in the calcium hydroxide suspension. Similarly the relative buffer capacity can be determined for the ninety hour stirring period. Since the buffer capacity of a soil has been defined as the tendency of a soil to retard the normal increase in pH, it can be seen that the relative buffer capacities are compared in Figure 55. The soils are arranged in the order of increasing pH in order to make the comparison as clear as possible. The pH of the soil may of course influence the actual buffer capacity. The results show that the three methods while differing more than can be ascribed to experimental, give after ninety hours stirring a fair degree of coordination on all the different types of soils.



Curves Showing Buffer Action (21 Soils)  
 Comparison of Three Methods (90 Hours Stirring)  
 1. Titration With  $\text{Ca}(\text{OH})_2$  Water Suspension.  
 2. Titration With  $\text{Ca}(\text{OH})_2$  (CaCl<sub>2</sub> 4N)  
 3. Titration With  $\text{NaOH}$  (NaCl 4N)

---○ Titration With  $\text{Ca}(\text{OH})_2$  Water Suspension.  
 —● Titration With  $\text{Ca}(\text{OH})_2$  (CaCl<sub>2</sub> 4N)  
 —○ Titration With  $\text{NaOH}$  (NaCl 4N)



Soil Number.  
 Figure 50.

### CONCLUSIONS.

The subject of base exchange and hydrogen ion concentration is being studied by many workers in the field of soil science and progress can be observed from year to year. A problem of this complex nature cannot be solved until sufficient data is collected from varied sources to establish facts upon which explanations can be based.

While the factors studied, as outlined above, could be expected to influence the various properties of the soils which have been investigated, correlation of these factors, both from the work reported here and from that of other investigators, has not been altogether definite. For example, the study of the different soil fractions gives us no correlation with increase in pH on stirring, as these increases occurred in soils ranging from a sand to the smaller particles of a clay. No correlation is apparent from base exchange data as increase occurred in soils both with high and low exchange calcium and magnesium.

On the other hand it can be seen that the time of equilibrium is a variable factor depending as much upon the electrolyte used as upon the particular soil. It may require several days for the pH to become constant in water, while with a salt solution frequently no appreciable change is observed after a short time of contact between the soil and the solution. Compare curves 3, 4, 6 and 8. It seems hardly likely that this condition would exist if the factor were one of crumb structure as suggested by



Fisher, as the same crumb structure is originally present in both cases, and it is improbable that complete disintegration would be instantaneous.

A further suggestion by the same worker seems to have more justification and to be supported by the results here obtained. Fisher noticed that soils shaken with water for a considerable time showed greater turbidity than at first, and indicated that the change in pH might be influenced by the suspended clay particles. In view of the colloidal properties of clay, silt and humus as shown under the discussion of the effect of electrolytes in the soil suspension, an explanation based on these properties can be considered.

When water is added to a soil, there is a tendency for the formation of a colloidal suspension and this is observed by the turbidity of the solution even after centrifuging. With lengthening time of contact between the soil and water the turbidity increases, showing that more particles are coming into colloidal suspension. The observed effect upon the pH is dependent upon the chemical nature of the colloid and the kind of ions in the Helmholtz double layer. Usually the effect is observed as an increase in pH (a decrease in acidity) and this would be accounted for by the fact that the colloids coming into suspension act as a buffer thus lowering the observed acidity. In cases of increase of acidity as reported by Cook using New Jersey soils it is possible that the double layer ionizes with the liberation of sufficient hydrogen ions to more than counterbalance the buffer

action of the colloid itself.

In further support of this theory it can be pointed out that salts have a coagulating or flocculating power on soil colloids and therefore, in a salt solution of sufficient strength to keep the colloids coagulated, there should be no appreciable increase in pH with stirring. This is observed to be true in all cases and is outstanding in soil numbers 3, 11, 12, 14 and 17 (Figures 3, 4, 6 and 8) which gave large increases in pH due to stirring with water but not with 0.4 normal calcium chloride solution.

If the colloids coming into solution thus act as a buffer, the next step would be to compare the buffer capacity of a soil before and after adding a neutral salt; this has been done in Figure 55. Conclusions here, however, can be drawn only with caution as it has been pointed out that calcium chloride has an effect in base exchange and by mass law will force hydrogen off the complex or colloid. This hydrogen will enter into the reaction with a base and increase the apparent buffer capacity, thus masking the other factor.

Further investigations into the buffer capacities of soils, and the various factors which determine their buffering effects are needed.

### SUMMARY

1. The quinhydrone electrode is modified so that it can be used with a stirrer to keep the soil in suspension while the reading is taken.
2. A stirring apparatus has been devised to keep a large number of soils in intimate contact with the solution and to hasten the time of equilibrium.
3. Equilibrium conditions have been studied for 21 Iowa soils and the conclusion reached that no definite time can be given for equilibrium which will hold for all the soils studied.
4. A modified procedure is given for the Williams method of determining base exchange in order that it may be applied to soil containing carbonates.
5. The quinhydrone electrode is applied to the determination of lime requirement and buffer capacity of the soil.
6. A comparison is made of three electrometric methods for determining lime requirement.

Titration is made with calcium hydroxide in a water suspension and in a 0.4 normal calcium chloride solution, and also titration in a 0.4 normal sodium chloride suspension with sodium hydroxide.

The lime requirement is taken as the amount of base required to bring the soil to pH 7.0.

The three methods give results approximately in the same order but differing in intensity.

7. A comparison is given for the buffer capacity of the soils de-

terminated by the three methods of titration given above.

LITERATURE CITED

1. Anderegg, F. O. and Lutz, R. P. 1927. A study of base exchange in soils with the aid of the quinhydrone electrode. *Soil Sci.* 24:403-412.
2. Bayer, L. D. 1928. Mechanical dispersion as an aid in chemical study of soils. *Jour. Amer. Soc. Agron.* 20:403-410.
3. Bayer, L. D. 1928. The drift in the potential of the quinhydrone electrode. *Jour. Amer. Soc. Agron.* 20:1125-1140.
4. Bobko, E. V. and Askinazi, D. L. 1925. Contributions to the question concerning the method of estimating the adsorption capacity and the condition of unsaturation of soils (trans. title) *Trudy Nauch. Inst. Udobr. (Trans. Inst. Fert.) (Moscow), No. 25 (1925).* 1-42. (*Expt. Sta. Rec.* 1925. 53: 616) (Original article not seen).
5. Bollen, W. B. and Neidig, R. E. 1927. A suggestion for uniformity and utility of data in soil solution analysis. *Soil Sci.* 24:69-70.
6. Bradfield, R. 1927. A simplified cell for determining the electrolysable base content of soils and permutits. *Jour. Amer. Soc. Agron.* 19:1015-1020.
7. Bradfield, R. 1924. The importance of hydrogen ion concentration control in physico-chemical studies of heavy soils. *Soil Sci.* 17:411-422.
8. Bradfield, R. 1923. The relation of hydrogen ion concentration to the flocculation of a colloidal clay. *Jour. Amer. Chem. Soc.* 45:1243-1250.
9. Brioux, Ch. 1928. The lime requirements of acid soils. (Trans. title) *Chimie et industrie. Special No., 889-903 (April 1928).* *Chem. Abs.* 1929. 23:229. (Original article not seen)
10. Brown, P. E. and Johnson, H. W. 1915. The effect of grinding the soil on its reaction as determined by the Veitch method. *Jour. Indus. and Engin. Chem.* 7:776-777.
11. Burgess, P. S. 1926. Report on (the determination of the) reaction value of soils. *Jour. Assoc. Off. Agr. Chem.* 9: 138-141.
12. Burgess, P. S. 1927. Report on (the determination of the) reaction value of soils. *Jour. Assoc. Off. Agr. Chem.* 10: 167-171.

13. Christensen, H. R. and Jensen, S. T. 1926. The determination of the lime requirement of the soil. Trans. 2nd Comm. Internatl. Soc. Soil Sci. A:94-115.
14. Clark, N. A. and Collins, E. R. 1927. The quinhydrone electrode and the soil reaction. Soil Sci. 24:453-463.
15. Clark, N. A. and Collins, E. R. 1929. The gravimetric method for the determination of carbonates in soil. Soil Sci. 27:407-414.
16. Comber, N. M. 1926. The action of non-diffusible ions in soil phenomenon. Trans. 2nd Comm. Internatl. Soc. Soil Sci. B:43-45.
17. Cook, R. C. 1916. Effect of grinding on lime requirement of soils. Soil Sci. 1:95-98.
18. Crowther, Edward M. 1925. Studies on soil reaction. III. The determination of the hydrogen ion concentration by means of the hydrogen electrode. Jour. Agr. Sci. 15:201-220.
19. Crowther, E. M. and Martin, W. S. 1925. Studies on soil reaction. VI. The interaction of acid soils, calcium carbonate and water, in relation to the determination of "Lime Requirement". Jour. Agr. Sci. 15:237-255.
20. Druschinin, D. W. and Bobko, E. W. Einfluss einzelner faktoren auf die reaction der bodenlösung. Ztschr. Pflanzeneinahr. u. Dungung 5A:345-369.
21. Fisher, E. A. 1921. Studies of soil reactions. II. The colorimetric determination of the hydrogen ion concentration in soils and aqueous soil extracts. Jour. Agr. Sci. 11:45-65.
22. Fisher, E. A. 1921. Studies on soil reaction. I. Jour. Agr. Sci. 11:19-44. A résumé.
23. Freundlich, H. 1922. Kapillarchemie. Akadem. Verlagsgesellschaft, Leipzig, p. 591.
24. Gallay, R. 1926. Beitrag zur kenntnis der tonkoagulation. Kolloidchem. Beihefte. 21:431-489.
25. Gedroiz, K. K. 1914. Colloid chemistry in the study of soils. (Trans. title) Zhur. Opytn. Agron. (Russ. Jour. Expt. Landw.), 15:181-216. (Expt. Sta. Rec. 1915. 33:118-119; Original article not seen).
26. Gedroiz, K. K. Cited in Zsigmondy (1920). Friedr. Vieweg. and Sohn., Leipzig, p. 287.

27. Ghosh, B. 1926. Parallelism between the effect of neutral salts on the electrical charge of hydrated manganese oxides and the concentration of hydrogen ions liberated. Jour. Chem. Soc. (London) 129:2605-2614.
28. Hall, A. D. and Mouson, C.G.T. 1907. The flocculation of turbid liquids by salts. Jour. Agr. Sci. 2:244-256.
29. Hardy, F. and Lewis, A. H. 1929. A rapid electrometric method for measuring "Lime Requirement" of soils. Jour. Agr. Sci. 19:17-25.
30. Hissink, D. J. and Van der Spek, J. 1925. Het wezen van den zuurgraad van den grond. Chem. Weekbl. 22:500-501.
31. Hissink, D. J. and Van der Spek, J. 1926. Titration curves of humus soils. Trans. 2nd Conn. Internatl. Soc. Soil Sci. A:72-93.
32. Joseph, A. F. and Hancock, J. L. 1924. The composition and properties of clay. Jour. Chem. Soc. (London) 125:1888-1895.
33. Joseph, A. F. and Snow, O. W. 1929. The dispersion and mechanical analysis of heavy alkaline soils. Jour. Agr. Sci. 19:106-110.
34. Kappen, H. and Breidenfeld, J. 1926. Zur kenntnis der säurewirkungen der kieselsäure und gewisser silikate. Ztschr. Pflanzenernähr. u. Düngung. A7:174-190.
35. Kelly, W. P. and Brown, M. S. 1924. Replaceable bases in soils. Calif. Agr. Exp. Sta. Tech. Paper, 15.
36. Kelly, W. P. and Brown, S. M. 1925. Ion exchange in relation to soil acidity. Soil Sci. 21:289-302.
37. Kolthoff, J. M. 1925. Die zuverlässigkeit der chinhydronelektrode für die messung der wasserstoffionenkonzentration in verschiedenen lösungen. Ztschr. Physiol. Chem. 144:259-271.
38. Maiwald, K. 1928. Untersuchungen zur bestimmung und deutung des puffervermögens karbonatarmer böden. Kolloidchem. Beihefte, 27:251-346.
39. Marshall, C. E. 1927. Some recent researches on soil colloids. A review. Jour. Agr. Sci. 17:315-333.
40. Mattson, S. E. 1922. Die beziehungen, adsorption und teilchenladung mit besonderer berücksichtigung. Kolloidchem. Beihefte. 14:227-313.

41. Mattson, Sante. 1926. Electrodialysis of the colloidal soil material and exchange bases. Jour. Agr. Sci. 33:553-567.
42. Mukherjee, J. N. 1925. The nature of the hydrolytic adsorption with reference to the adsorption of electrolytes and of water. I. General and theoretical introduction. Quart. J. Indian. Chem. Soc. 2:191-224.
43. Myers, P. B. and Gilligan, G. M. 1927. Mechanism of buffer action in soils. Science N.S. 66:302.
44. Nicklas, H. and Hock, A. 1925. Zur frage der austauschazidität der boden und des zusammenhanges zwischen titrations-und aktueller azidität. Ztschr. Pflanzenernähr. u. Düngung. 5A:370-392.
45. Odén, S. 1919. Die koagulation der tone und die schutzwirkung der humussäure. Jour. Landw. 67:177-208.
46. Odén, S. 1927. The acidity buffering capacity and liming of the soil. (Trans. title) Medd. Centralanstalt. försöksväsendet jordbruks No. 318, Avdel Lantbruksbotan No. 37:1-84 (Chem. Abs. 1928. 22:1003) (Original article not seen).
47. Page, H. J. and Williams, W. 1925. Studies on base exchange in soils. Faraday Soc. Trans. 20:573.
48. Schollenberger, C. J. 1927. Exchangeable hydrogen on soil reaction. Science N.S. 65:552-553.
49. Schollenberger, C. J. 1925. An improved calomel electrode. Jour. Indus. and Engin. Chem. 17:649.
50. Sharp, L. T. and Hoagland, D. R. 1916. Acidity and adsorption in soils as measured by the hydrogen electrode. Jour. Agr. Res. 7:123-145.
51. Smith, A. M. 1925. The exchangeable bases in some Scottish soils. Jour. Agr. Sci. 15:466-475.
52. Snyder, E. F. 1927. A comparative study of the quinhydrone and hydrogen electrode for determination of hydrogen ion concentration of soils. Jour. Agr. Res. 35:825-834.
53. Taranov, K. N. 1928. Electrodialysis of soils (Trans. title) Ukrainskü. Khem. Zhurnal. 3:89-112 (Chem. Abs. 1929. 23:460) (Original article not seen).
54. Tidmore, J. W. and Parker, F. W. 1924. Methods of studying strength of soil acids. Soil Sci. 18:331-338.



55. Trénel, M. 1925. Can the lime requirement of the soil be determined from the reaction of soil suspensions containing potassium chloride? Proc. Internatl. Soc. Soil Sci. 1:199.
56. Turner, P. E. 1928. Investigations of method of Page and Williams for the determination of the saturation capacity of soils. Jour. Agr. Sci. 18:257-265.
57. Wiegner, G. 1925. Dispersion and interchange (ionic) of bases. (Trans. title) Kolloid Ztschr. Special number, April 1, 1925, 341-369; (Chem. Abs. 1925. 19. 3402-3403) (Original article not seen).
58. Williams, R. J. 1928. The determination of exchangeable calcium in carbonate free soils. Jour. Agr. Sci. 18: 439-445.
59. Wilson, B. D. 1928. Exchangeable cations in soils as determined by means of normal ammonium chloride and electro-dialysis. Soil Sci. 26:407-422.