

## FACTORS AFFECTING SOIL REACTION I—THE SOIL-WATER RATIO

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BY ROBERT M. SALTER AND M. FRANCIS MORGAN\*

Many attempts have been made in recent years to correlate biological processes with reaction. Positive relations have been established between the germination of seeds, the growth of plants, the ecological distribution of plants, the development of both pathogenic and non-pathogenic soil organisms and the reaction of the growth medium.

Both electrometric and colorimetric procedures for measuring reaction are in common use, the former being employed for soil suspensions, the latter more frequently for solution cultures, liquid media, and soil extracts. In the application of most of this work to soil conditions the tacit assumption has been made that the reaction of soils under normal field conditions is not far different from the values obtained in measurements upon soil suspensions and soil extracts. The possible effects of wide differences in moisture content, of drying, or of time of standing in contact with water have in general been neglected in spite of the fact that the value of much of this work depends necessarily upon how accurately it applies to soils under normal growth conditions. The present work is an attempt to discover the nature of any possible relationship between the ratio of soil to water and the hydrogen-ion concentration of the soil suspension.

A review of the literature fails to reveal any consistency of opinion among soils workers as to the effect of variable moisture content upon reaction. Sharp and Hoagland, (18) working with a modification of the hydrogen electrode procedure found no significant differences in hydrogen-ion concentrations of soil suspensions over quite wide ranges of soil-water ratios. They state:

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\* From the Department of Soils, The Ohio State University.

"An inspection of the data indicates comparatively insignificant changes in the H-ion concentration when widely varying proportions of water to soil are used. Most of these small fluctuations can be ascribed to the limitations of the apparatus. Hence it is reasonable to assume that the H-ion concentration of the soil suspensions approximates those of the soil solutions. This argument is theoretically sound, since, in all the larger proportions of soil employed it is probable that the solution is saturated with respect to the acid-forming constituents."

Gillespie and Hurst (6) in reporting upon the H-ion concentration of two soil types, the Caribou Loam and the Washburn Loam, make the following comment:

"The average difference obtained by varying the ratio from 1:1 to 1:2 was 0.14 in the value of the exponent for nine soils. This indicates that at optimum moisture content the acidity may be more intense, but to what extent cannot be calculated. Only results between the same ratios of water to soil should be compared."

In later work the same investigators obtained a mean value of 0.04 for the difference between the exponent of the H-ion concentration when the dilution was increased for a soil-water ratio of 1:1 to a ratio of 1:2. This positive difference means that the soil extract was less acid when more water was used.

Rice and Osugi<sup>16</sup> measured the inverting power of acid soils for cane sugar at soil-water ratios varying from 1 to 32 grams of soil to 100 cc of water. They found greatly increased hydrolysis with the higher amounts of soil but since they were unable to observe any difference in the reaction of the extracts from such soils, determined colorimetrically, they concluded that the solid phase is the active factor in inverting cane sugar. It should be mentioned however, that, although these investigators were undoubtedly working with acid soils, all determinations of reaction on the extracts from these soils gave results indicating almost exact neutrality. Since this work is so completely at variance with the results of other workers in this respect it seems highly probable that the results of Rice

and Osugi may be in error due to some fault in the technique of the colorimetric procedure employed, and that the greater hydrolysis of sugar at higher soil-water ratios may well have been due to a higher concentration of hydrogen-ions in solution.

Plummer<sup>14</sup> found that the film water obtained by the oil pressure method from soils of approximately optimum moisture contents was more highly acid in the case of acid soils and more highly alkaline in the case of alkaline soils than the soil suspensions determined at a much lower soil-water ratio. Thus the film water from a Porter's loam soil at 25% moisture content (dry basis) showed a H-ion concentration of  $0.25 \times 10^{-4}$  as compared to  $0.9 \times 10^{-6}$  for a suspension of the same soil containing 10 grams of soil to 100 cc of water. The film water from a Chickamauga limestone soil showed a reaction of  $0.8 \times 10^{-11}$  compared with  $0.1 \times 10^{-9}$  for the suspension. If such differences as these actually exist between the reaction of soils at normal moisture contents and those commonly employed in H-ion measurements it would appear that a study such as herein reported may be of value.

More recently Hudig and Sturm,<sup>10</sup> working with both soil solutions and soil suspensions found that the H-ion concentration varies with the soil-water ratio.

### **Experimental Methods**

In measuring the variations in hydrogen-ion concentration under different moisture conditions the following procedures were followed:

1. Electrometric Method, using the Hydrogen-Electrode.—This method has come into very general use in soil acidity investigations. Its high degree of accuracy at any dilution at which the soil is actually in suspension makes it especially applicable to this work. In this respect it is superior to the colorimetric procedure employed by Wherry and others.

A type "K" Leeds and Northrup potentiometer was used, measurements being made against a normal KCl-Calomel electrode. A platinum-coated glass electrode of the Luther

type was used in a hydrogen cell of about 10 cc capacity. Hydrogen was passed over the electrode at the rate of about two small bubbles per second. It was found that with the small quantity of liquid used (1 to 5 cc) the bubbling of the gas made sufficient provision for keeping the soil in suspension. The temperature was kept near 25° C and any unavoidable deviation from this point was corrected for in calculating the results.

As it seemed advisable to cover a rather wide range of dilution, it was decided to vary the ratio of soil to water from 1:1 to almost infinite dilution in steps such that the degree of dilution was each time multiplied by 5. Experimental work developed the need for intermediate ratios in order to more accurately establish the systematic variation observed, hence ratios representing logarithmic means were also included. As finally developed, the following soil-water ratios were used:

Grams soil per 1000 cc water	In electrode vessel	
	Cc water	Gram soil
1000.0	1	1.0000
447.0	2	.8940
200.0	2	.4000
89.4	5	.2000
40.0	5	.4470
17.88	5	.0894
8.0	5	.0400
3.58	5	.0179
1.6	5	.0080
.716	5	.0036
.32	5	.0016

2. *Sucrose Hydrolysis Method.*—The velocity of sucrose hydrolysis has been quite generally employed as a measure of the H-ion concentration of solutions. Hanley<sup>7</sup> and Rice and Osugi<sup>16</sup> have used the method to indicate soil reaction. It seemed advisable to correlate the H-electrode method with determination of the soil's capacity to produce inversion of cane sugar at varying moisture contents. This method possesses the advantage of indicating reaction with moisture contents

closely approaching those of field soils. On the other hand, it is recognized that no direct measurement of hydrogen-ion concentration can be made by this means, the velocity of sucrose hydrolysis serving only as an index of the relative reaction.

The soil to which varying quantities of 15% sucrose solution had been added was digested in an autoclave steam bath kept at atmospheric pressure for two hours. The soil suspensions were kept in constant agitation since preliminary work indicated that this was necessary to uniformity of results. After digestion the amount of invert sugar was determined by a combination of the Munson and Walker and Bertrand methods in which  $\text{Cu}_2\text{O}$  is finally determined by reduction of ferric iron and titration with standard  $\text{KMnO}_4$ .

Velocity constants were calculated for each dilution from the usual formula for mono-molecular reactions:

$$K = \frac{2.30}{t} \log_{10} \frac{a}{a - x}$$

where "a" is initial amount of sugar present, and "x" is amount inverted in time "t."

Dilutions were made upon the same basis as for hydrogen-ion determinations. In this case successive steps of moisture content approaching normal field conditions could be added.

The following amounts of soil and sucrose solution were used:

Grams soil per 1000 cc water	Sucrose solution	Soil, gm
11180	2	22.36
7480	4	29.92
5000	4	20.00
1000	15	15.00
200	25	5.00
40	25	1.00
8	25	.20
3.58	50	.179
1.6	50	.08

In the first three cases the amount of liquid was not sufficient to permit of soil suspension. To insure thorough incorporation of sucrose solution at these low moisture contents the air-dry soil was ground in an agate mortar with the required quantity of the liquid. Even with this precaution, results were found to be quite irregular, and as shown later by the tabulated data and graph serve only to show approximate relations. With all other dilutions an accuracy of about one percent was obtained.

In these investigations nine soils were studied by the electrometric method. Four of these were compared as to sucrose hydrolysis. The soils used were acid, showing calcium carbonate requirements of from two to three and one-half tons per 2,000,000 pounds, by both Veitch and Jones methods. With the exception of the one designated 1WS the soils used were taken from the collection of the West Virginia Experiment Station. Their chemical analysis is reported in Bulletin 168 of that station.

The soils studied were as follows:

Soil	Series	Type	Color
No. 171A	Dekalb	Sandy loam	Yellow-brown
No. 357A	Dekalb	Silt loam	Yellowish gray
No. 149A	_____	Sandy loam	Dark gray
No. 152A	_____	Silt loam	Light gray
No. 44A	_____	Silty clay loam	Dark gray
No. 1WS	Elk	Silt loam	Medium gray
No. 78A	Moshannon	Clay loam	Red
No. 154A	Huntington	Sandy clay	Reddish brown
No. 59A	Upshur	Clay	Indian-red

### Experimental Data

For the sake of brevity complete data for the H-ion concentration as determined electrometrically is given for only one soil, No. 357. (See Table I.)

The condensed results of the electrometric measurements for all soils is given in Table II.

Complete data used in calculating the sucrose hydrolysis velocity constants are shown in Table III, for soil No. 171A only. The sucrose hydrolysis velocity constants for all soils studies are given in Table IV.

TABLE I  
Complete Hydrogen-ion Data for Soil No. 357A

Soil, gm per 1000 cc H <sub>2</sub> O	Potentiometer reading, m-volts			Average	pH	H-ion con- centration
	(a)	(b)	(c)			
1000	518.0	518.1	517.3	518	3.983	.0001040
447	525.0	525.3	524.9	525	4.091	.0000811
200	532.8	533.1	533.1	533	4.226	.0000594
89.4	546.5	546.2	546.0	546	4.446	.0000358
40.0	557.3	557.0	557.1	557	4.632	.0000233
17.88	568.7	568.3	567.9	568	4.818	.0000152
8.00	581.2	581.0	580.9	581	5.038	.0000092
3.58	602.3	602.5	601.8	602	5.393	.0000041
1.6	625.1	625.7	624.9	625	5.782	.0000016

### Discussion of Results

From an inspection of the data it is at once apparent that the H-ion concentration increases as the soil-water ratio increases. It is also seen that the increase in H-ion concentration is not a linear function, but increases at a slower rate than the soil-water ratio. The fact that such a variation is observed immediately discredits any theory of soil acidity which assumes that the acid reaction is due to highly insoluble acids, either organic or inorganic which must under conditions of equilibrium form a saturated solution and give an approximately constant H-ion concentration. Reference has already been made to Hoagland's statement suggesting that the constancy of H-ion concentration which he observed at varying soil-water ratios could be taken as supporting such a theory.

The distribution of H-ions between soil and solution at varying soil-water ratios suggests the possibility that we are here dealing with a phenomenon similar to adsorption. To test out the validity of this assumption, it seemed desirable to determine to what extent the data might be made to satisfy

TABLE II  
Relation of pH of Soil Suspensions to the Soil-water Ratio

Soil gm per 1000 cc H <sub>2</sub> O	171A pH	357A pH	149A pH	152A pH	44A pH	154A pH	1WS pH	59A pH	78A pH
1000	3.787	3.983	4.023	4.176	4.210	4.581	4.446	4.649	4.514
447	3.999	4.091	4.159	4.210	4.243	4.598	4.514	4.734	4.615
200	4.193	4.226	4.277	4.260	4.311	4.666	4.632	4.852	4.767
89.4	4.446	4.446	4.429	4.412	4.412	4.767	4.801	4.987	4.953
40	4.734	4.632	4.598	4.548	4.548	4.920	4.936	5.156	5.122
17.88	4.970	4.818	4.818	4.717	4.683	5.089	5.055	5.258	5.224
8	5.292	5.038	5.038	4.953	4.869	5.292	5.173	5.342	5.342
3.56	5.664	5.393	5.376	5.325	5.089	5.596	5.342	5.410	5.511
1.6	5.917	5.782	5.697	5.697	5.444	5.866	5.596	5.495	5.697
.716	—	—	—	6.340	5.765	—	5.985	5.596	5.968
.32	—	—	—	—	5.985	—	6.272	5.697	—



TABLE III  
Complete Sucrose Hydrolysis Data for Soil No. 171A

Soil gm per 1000 cc H <sub>2</sub> O	Total mgm sucrose	Aliquot used	KMnO <sub>4</sub> titration cc .05 N		Average titrations	Cu mgm	Sucrose in aliquot mgm	Total sucrose hydrolyzed mgm	Velocity K
			(a)	(b)					
11180	300	.5	65.5	65.2	65.35	205.7	100.88	201.76	.009316
7480	600	.2	50.3	50.3	50.30	158.4	75.9	379.5	.008066
5000	600	.2	51.9	51.2	51.55	162.2	78.0	390.0	.008500
1000	2250	.1	69.3	69.2	69.25	218.0	107.4	1074.0	.006166
200	3750	.1	79.1	79.0	79.15	249.2	123.16	1231.16	.003308
40	3750	.1	48.8	49.6	49.20	156.0	74.86	748.6	.001858
8	3750	.1	21.2	20.9	21.05	66.4	29.64	296.4	.000683
3.58	15000	.05	25.4	25.6	25.50	80.3	36.28	725.6	.000408
1.6	15000	.05	16.8	16.7	16.75	52.9	22.40	448.0	.000268

TABLE IV  
Sucrose Hydrolysis Velocity K

Soil-grams per 1000 cc H <sub>2</sub> O	171A ( $\times 10^{-4}$ )	357A ( $\times 10^{-4}$ )	154A ( $\times 10^{-4}$ )	1WS ( $\times 10^{-4}$ )	78A ( $\times 10^{-4}$ )
11180	93.16	47.83	50.33	43.58	24.92
7480	80.66	37.33	38.91	35.00	21.50
5000	85.00	34.19	34.50	30.33	19.75
1000	61.66	27.75	26.00	24.91	22.25
200	33.08	19.16	15.41	17.41	17.16
40	18.58	10.66	8.50	10.91	10.83
8	6.83	6.00	5.00	4.42	6.08
3.58	4.08	4.33	3.75	2.25	5.08
1.6	2.68	3.41	2.25	1.00	3.75

the well-known adsorption isotherm of Freundlich. To do this, however, necessitates a somewhat modified statement of Freundlich's equation, since in varying the soil-water ratios, we not only vary the mass of the adsorbent, but at the same time vary the total amount of acidity (H-ions) present.

The following procedure illustrates the development of the modified equation from the usual method of statement.

General formula for adsorption:

$$(1) \frac{x}{m} = \beta C^d \text{ where } x = \text{amt. adsorbed}$$

C = concn. in solution

m = mass of adsorbent

$\beta$  and d are constants.

For the purpose of present study, let

C = concn. of H-ions in soln.

x = amt. of H-ions adsorbed

$x + C$  = total H-ions present (adsorbed and free).

Since the total number of H-ions present is presumably a function of the total mass of the soil, m, it follows that

$$(2) X + = Km, \text{ where } K \text{ is a constant.}$$

or

$$(3) x = Km - C$$

by substituting in (1)

$$(4) \quad \frac{Km - C}{m} = \beta Cd$$

from which

$$(5) \quad K - \beta Cd = \frac{C}{m}$$

Equation (5) contains three unknowns, viz: the constants  $K$ ,  $\beta$  and  $d$ . By selecting from the data for any one soil three known concentrations:  $C_1$ ,  $C_2$ ,  $C_3$ , corresponding to three known amounts of soil:  $m_1$ ,  $m_2$ , and  $m_3$ , it should be possible to calculate mathematically the values of the above constants. The extent to which these same constants may be used in predicting the H-ion concentrations at still other soil-water ratios forms a measure of the degree of conformity of the concentrations observed to the usual adsorption distribution. The details of the mathematical procedure involved in the calculation of the constants is given in the footnote.<sup>1</sup>

<sup>1</sup> Methods of calculating constants  $d$ ,  $\beta$  and  $K$ .

From the observed values of  $C$  at three different soil-water ratios, we have

$$K - \beta C_1 d = \frac{C_1}{m_1} \quad (1)$$

Similarly

$$K - \beta C_2 d = \frac{C_2}{m_2} \quad (2)$$

Similarly

$$K - \beta C_3 d = \frac{C_3}{m_3} \quad (3)$$

Subtracting (2) from (1)

$$(C_2 d - C_1 d) = \frac{C_1}{m_1} - \frac{C_2}{m_2} \quad (4)$$

Subtracting (2) from (3)

$$(C_3 d - C_2 d) = \frac{C_3}{m_3} - \frac{C_2}{m_2} \quad (5)$$

Dividing (4) by (5)

$$\frac{C_2 d - C_1 d}{C_3 d - C_2 d} = \frac{\frac{C_1}{m_1} - \frac{C_2}{m_2}}{\frac{C_3}{m_3} - \frac{C_2}{m_2}} \quad (6)$$

TABLE V  
Comparison of Actual with Calculated Soil-water Ratios corresponding to pH Values given in Table II

Actual quantity soil per 1000 cc water, gm	Calculated quantity of soil per 1000 cc required to give observed H-ion concentrations						
	Soil Number						
	171A gms.	357A gms	149A gms	152A gms	44A gms	154A gms	1WS gms
1000	1000	1000	947	1015	995	1120	1000
447	424	453	429	426.4	449.6	630	249
200	214	207	205	215.4	190.3	204	86.3
89.4	94.2	81.05	95.6	73.78	94.3	87.2	34
40	40	42.15	58.74	39.99	40.1	38.1	17.6
17.88	19.9	23.31	20.6	21.9	21.9	19.25	12.0
8	8.3	12.18	9.92	10.6	10.52	9.63	8
3.56	3.56	4.59	3.52	4.01	3.77	4.43	4.4
1.6	1.6	1.66	1.40	1.6	1.6	1.87	2.1
.716	—	—	—	.35	.626	—	.74
.32	—	—	—	—	.338	—	.32

Table V shows a comparison for seven of the soils studied of the grams soil per 1000 cc of water actually employed with the quantities of soil calculated to produce the H-ion concentration observed. It was not possible to give the calculated H-ion concentration for the variable amounts of soil used, since equation (5) does not lend itself readily to the calculation of "C."

The agreement of the calculated amounts of soil per 1000 cc required to produce the observed H-ion concentrations and the amounts actually used are in general very good for work of this nature. For six soils there is an almost exact agreement. Some discrepancies are apparent in the data for soils 154A and 1WS, while for soils 59A and 78A the data did not permit of calculation of the constants of the adsorption isotherm. These apparently abnormal soils will be discussed later.

### Graphic Representation of Results

To facilitate visualization of the variation of reaction with varying soil-water ratios as well as to bring out the degree of conformity of observed and theoretical values, it seemed de-

Let

$$\frac{C_1}{m_1} - \frac{C_2}{m_2} = a$$

and

$$\frac{C_3}{m_3} - \frac{C_2}{m_2} = b$$

Then

$$b(C_2d - C_1d) = a(C_2d - C_3d) \quad (7)$$

From which

$$(a - b)C_2d = a C_3d - b C_1d \quad (8)$$

This equation cannot be solved directly, but  $d$  can be calculated by a method of approximation where assumed values for  $d$  (between 0 and 1) are substituted until a value is found which satisfies (8).

From (4)

$\beta = \frac{a}{C_3d - C_1d}$  from which  $\beta$  can be calculated by substituting the determined value of  $d$ .

By substituting known values of  $d$  and in (1), (2) or (3),  $K$  can be calculated.

sirable to express the data in graphic form. Figure 1 shows the direct plotting of H-ion concentration against the soil-water ratio (Curve I) and also the same data plotted against

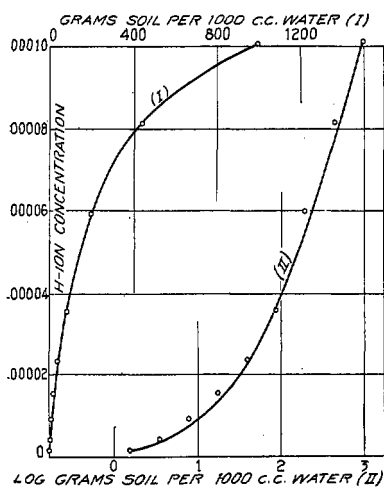


Fig. 1

Soil No. 357 A  
 $K = 1.319 \times 10^{-5}$   
 $\beta = 2.322 \times 10^{-4}$   
 $\delta = 0.32$

the logarithm of the soil-water ratio (Curve II) for soil 357A. In this and subsequent graphs with the exception of Curve IX and X in Fig. 3, and of Figs. 4 and 5, the curve itself connects values which satisfy the calculated isothermal constants, while the points representing experimentally determined values are enclosed by small circles. It will be observed that by this method of plotting, the curve approaches neutrality with increasing dilution at such a rate as to make significant differences between the logarithmically increasing soil-water ratios employed. The

plotting of H-ion concentration against the logarithm of the soil-water ratio overcomes this objection. Data for all soils are shown plotted in this way in Figs. 2-3 inclusive.

Both tabular and graphic representation of the data emphasize the fact that there is a close conformity of the observed values and the theoretical values calculated on the assumption that we are dealing with an adsorption phenomenon. With the soil designated as IWS, data shown graphically Curve VIII in Fig. 3, the observed H-ion concentrations are considerably below calculated values for the range of concentration from 17.88 gm to 1000 gm per liter. With soils 78A and 59A Curves IX and X in Fig. 3, the depression of H-ion concentration values over this same range of dilution is so great that it becomes impossible to calculate an ad-

sorption isotherm which will satisfy any three points on the curve.

The apparent abnormality over this range of dilution is more clearly shown by plotting the logarithm of the soil-water ratio against the logarithm of the pH values as shown in Fig. 5 for soils 78A, 152A, 171A and 1WS. Of these four

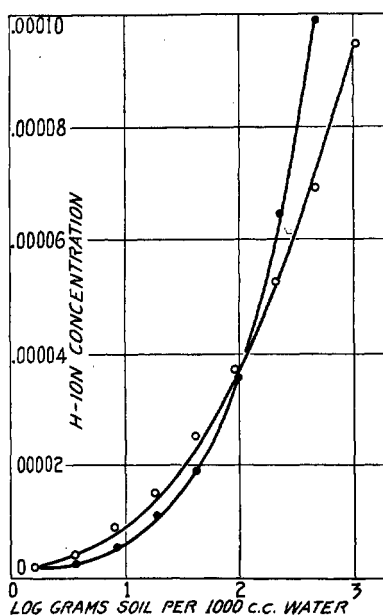


Fig. 2

Dots	Circles
Soil No. 171 A	Soil No. 149 A
$K = 1.690 \times 10^{-5}$	$K = 5.430 \times 10^{-5}$
$\beta = 3.650 \times 10^{-4}$	$\beta = 1.140 \times 10^{-4}$
$\delta = 0.10$	$\delta = 0.08$

soils, 152A and 171A, while conforming quite closely to the theoretical adsorption isotherm (See Curves V in Fig. 3, and Fig. 2), are seen to show this abnormal tendency to a slight extent at corresponding degrees of dilution. Curve IX in Fig. 3 for 78A and Curve VIII in Fig. 3 for 1WS on the other hand are seen to be decidedly depressed at these ranges as

compared to the former soils. The other five soils studied show similar tendencies, but to avoid complexity were not included in the graph. If we are actually dealing with an adsorption phenomenon it would appear that over the range of dilution noted there is a slight increase in the adsorptive ca-

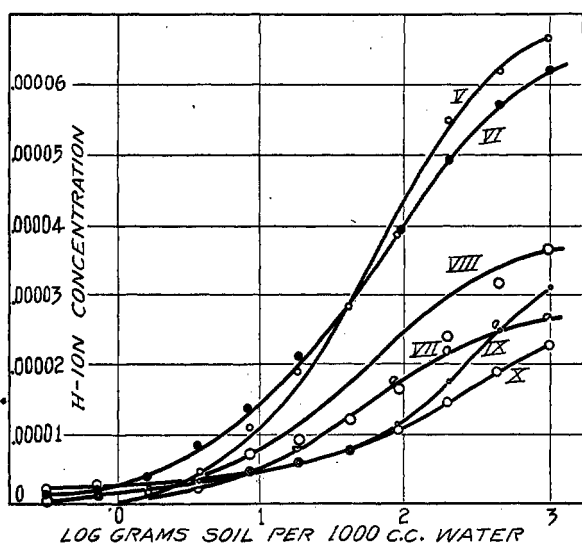


Fig. 3

V  
Soil No. 152 A  
 $K = 1.3257 \times 10^{-5}$   
 $\beta = 3.681 \times 10^{-2}$   
 $\delta = 0.83$

VI  
Soil No. 44 A  
 $K = 1.2177 \times 10^{-4}$   
 $\beta = 2.388 \times 10^{-4}$   
 $\delta = 0.07$

VII  
Soil No. 154 A  
 $K = 9.423 \times 10^{-6}$   
 $\beta = 1.617 \times 10^{-3}$   
 $\delta = 0.49$

VIII  
Soil No. 1 WS  
 $K = 2.8818 \times 10^{-5}$   
 $\beta = 2.206 \times 10^{-4}$   
 $\delta = 0.2$

IX  
Soil No. 78 A

X  
Soil No. 59 A

capacity of the soil, possibly due to an increased peptization of colloidal materials with increased specific surface. In this connection it is interesting to note that Bradfield<sup>2</sup> found a considerable increase in the relative amounts of colloidal



material present when a highly colloidal subsoil was suspended in increasing amounts of water. This increase was most rapid over a range of soil-water ratios in general similar to that noted above.

The highest soil-water ratio used in the H-ion measurements was 1:1 or a moisture content of 100% on a dry basis. This is of course considerably above moisture conditions for optimum growth relations.

It is especially desirable to be able to predict the reaction at lower moisture ranges. Where H-ion concentration is plotted against the logarithm of the soil-water ratio the theoretical adsorption curve is an S-shaped line asymptotically approaching neutrality at infinite dilution on one end and asymptotically approaching some definite H-ion concentration at infinitely high soil-water ratios on the other. Curves V-VIII in Fig. 3 show the S-shape of the typical

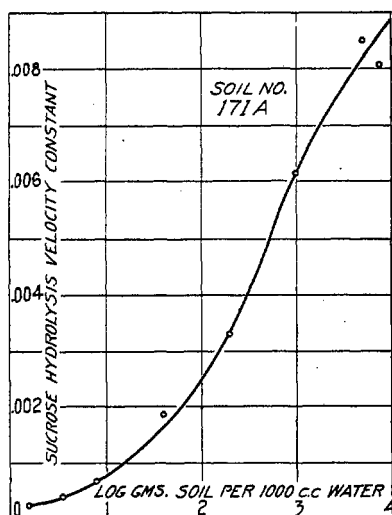


Fig. 4

isotherm. In the two curves of Fig. 2 the bending of the curve at high soil-water ratios is not observed, and by the extrapolation of the theoretical curve it can be shown that this flexing of the curve should appear at soil-water ratios which are considerably higher than can be employed experimentally. Figure 2 shows at the highest soil-water ratio a slight tendency for this flex to appear.

It was hoped that by the sucrose-hydrolysis method it would be possible to investigate the higher soil-water ratios to better advantage. While over the range of dilution covered by both H-ion and sucrose-hydrolysis methods the two procedures appear to give results showing close correlation, as

shown by Table IV, the experimental error in the sucrose hydrolysis method at moisture contents below a 1:1 ratio was found to be so great that only a very general idea of the probable trend of the reaction could be obtained. This is apparent from Fig. 4 which shows graphically the sucrose-

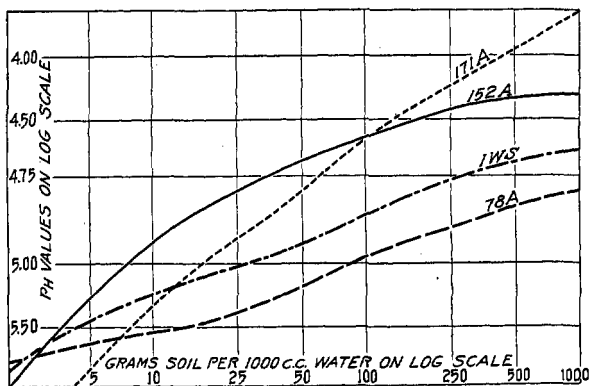


Fig. 5

hydrolysis data for soil 171A. The graph does show, however, that the flexing of the curve actually begins at a point beyond the highest soil-water ratio used in the electrometric H-ion measurements.

### Adsorption and Soil Acidity

Van Bemmelen<sup>1</sup> first suggested that the combination of bases with humus were not true chemical compounds but instead "mixtures of base and of various colloid substances held together by some sort of surface attraction." Later since the general theory of surface adsorption has been developed by Willard Gibbs, J. J. Thomson, Freundlich and Wo. Ostwald, it has been applied to soil processes by Cameron,<sup>3</sup> Parker,<sup>13</sup> Harris,<sup>9</sup> Russell,<sup>17</sup> Prescott,<sup>15,17</sup> Fisher<sup>5</sup> and numerous other workers. The term "adsorption" can at present be most satisfactorily described as the concentration of a solute on a

surface (in the case of soils at the interphase solid-liquid surface), due to interatomic attraction of a truly chemical nature, designated by Irving Langmuir<sup>11</sup> as secondary valence. That such surface concentration is rather definitely related to changes of surface tension and electrical potential has long been known. According to the ideas of Langmuir,<sup>11</sup> Harkins<sup>8</sup> and other workers on surface forces, the question as to whether surface concentration is a physical or chemical phenomenon would seem to be no longer pertinent.

On account of the high specific surface of soils, particularly those of finer types due both to their macroscopic and colloidal components it appears that they should offer unusual opportunity for surface phenomena in general. Under soil conditions the various soil colloids, due to mutual adsorption, probably form adsorption compounds of high complexity. This fact makes any prediction as to their adsorptive capacity, precipitation or physical properties very difficult. Since the colloidal material of most soils when suspended in water migrate in an electrical field to the anode, negative colloids must predominate at the normal reaction of such suspensions.

In general it can be said that a theory of surface concentration of adsorption which supposes the existence of a specific adsorptive relation between the surface of the adsorbent and the individual ions (including H and OH ions) of electrolytes, dependent upon the attraction of secondary valence of the atoms of the adsorbent and of the particular ions, can be made to explain most of the properties of soil acidity, basic exchange and precipitation phenomena in soils. The presence of an electrical charge on the surface of the adsorbent due either to certain production of ions in solution or to adsorption of ions from the solution opposes but does not necessarily prevent the adsorption of ions of like charge. The adsorption of oppositely charged ions neutralizes the electrical charge of a colloidal particle, decreases the electrostatic repulsion between such particles, and increases the interphase surface tension, all tending to decrease the stability of the colloid and favoring flocculation. The adsorption of ions of like charge

increases the charge of the colloid, thereby lowering the inter-phase surface tension and stabilizing the colloid thus necessitating the adsorption of more of the ion of opposite charge for precipitation. The H and OH ions have much greater adsorbability than most of the common ions, which fact explains the sensitivity of colloidal solutions to changes in reaction, also the fact that the iso-electric point of colloids generally can be stated in terms of pH in spite of the presence of other ions. Judging from the slope of the electrometric titration curve of soils above and below neutral the soil colloids have a stronger preferential adsorption for the OH than for the H ion. Basic exchange in soils can be looked upon as the substitution of one adsorbed cation by another, although Parker's work<sup>13</sup> would indicate that in the action of neutral salts on acid soils the replacement of adsorbed H-ions by the base of the salt is the primary action. Since equivalent quantities of various ions carry equal amounts of electrical energy it is not surprising that replacement of ions should take place in equivalent amounts. According to the adsorption theory the reaction of an acid soil with an alkali is a combination process involving both the neutralization of the H-ions present and the adsorption of the base. This agrees with Fisher's<sup>5</sup> conclusion from his study of the adsorption of CaO from calcium bicarbonate solutions by soils that "there would appear to be little doubt therefore that the lime requirement of a soil is the sum of two quantities: (1) the lime required to neutralize soil acids, and (2) the lime actually adsorbed by the soil complex, and it is impossible at present to differentiate between these." In this connection it should be mentioned that the value of "K" of the adsorption isotherm used in the present work gives a measure of the total amount of acidity in the soil in the form of adsorbed and unadsorbed H ions. The values obtained by this method, however, are so small as to indicate that either a relatively large fraction of the base adsorbed is used up in satisfying the adsorptive capacity of the soil or that the factors of ionization or solubility of unionized

acids are of considerable importance in determining soil reaction.

Loeb<sup>12</sup> has recently applied the theory of "Donnan Equilibrium" to the adsorption of electrolytes from colloidal solutions of the emulsoid colloids, gelatin, egg albumen and casein, and finds that it offers a very satisfactory explanation of the change in physical properties including viscosity, swelling and osmotic pressure with varying concentration of electrolyte, or varying pH. While this theory has never been applied to soils it would appear that a study of soil acidity and the physical properties of soils from the viewpoint of "Donnan Equilibrium" might be highly profitable. Donnan<sup>4</sup> has shown on thermo-dynamic grounds that when a membrane separates ions to some of which it is permeable and to others impermeable an equilibrium is set up between the ions which are free to pass through the membrane whereby they are unequally distributed on either side. Loeb has shown that the ultimate particles in colloidal solutions of gelatin, etc., are true ions and molecules. Since these are unable to penetrate the colloid proper, he assumes that each colloidal particle acts as if it were surrounded by a membrane impermeable to these ions and molecules, resulting in an unequal distribution of any electrolytes present between the solution within and without the colloidal particle. He has shown that the physical properties of such colloidal solutions are very definitely related to the potential difference which arises from such an unequal distribution of electrolyte. This distribution, which is logarithmic over a certain range of concentration, is in certain respects similar to the usual adsorption distribution.

### Summary

1. A study has been made of the H-ion concentration of nine acid soils at soil-water ratios varying from 1:1 to 1:3125, employing the hydrogen-electrode method.
2. The velocity of sucrose hydrolysis at a range of soil-water ratios from 1:0.0894 to 1:625 has been determined for five of the same soils.

3. The electrometric and sucrose hydrolysis methods were found to agree in indicating a systematic variation of H-ion concentration with variations in soil-water ratio, the highest H-ion concentration occurring at high soil-water ratios, with a progressive decrease as dilution is increased.

4. In general, the changes in H-ion concentration at varying soil-water ratios agree with the distribution of H-ions between soil and solution which could be expected if controlled by an adsorption mechanism.

5. A slight tendency was noted with all soils to deviate from the theoretical adsorption values over a restricted range of dilution. With two of the nine soils studied, this deviation was sufficient to prevent the determination of a theoretical equation which would describe the variations in H-ion concentration observed.

6. On the basis of the results obtained, it appears that the reaction of a soil is dependent upon: first, the total dissociated acid present; second, the adsorptive capacity of the soil for the H-ion; and third, the soil-water ratio.

### Conclusion

In view of the fact that the effective hydrogen-ion concentration of a soil is not a constant, but varies significantly and systematically when the soil-water ratio is changed, it must be recognized that the reaction of a soil as ordinarily determined by either electrometric or colorimetric procedures is not an exact indication of the reaction of the same soil at normal field moisture contents. For the soils included in the present study, the calculated reaction at a field moisture content of 20% varies from .10 to .85 pH below the reaction at a soil-water ratio of 1:5. Part of the difficulty of interpreting work involving measurements of soil reaction might perhaps be eliminated if workers in this field would agree to accept some standard soil-water ratio for measurements of this kind. The authors would suggest a soil-water ratio of 1:5 as being well suited to both colorimetric and electrometric procedures. Where a more accurate idea of the reaction at low moisture

contents is desired this can be obtained by extrapolation of the graph connecting the H-ion concentration determined at three soil-water ratios, preferably 1:5, 1:25 and 1:125. Plotting the pH values against the logarithm of the soil-water ratios lends itself best to this treatment.

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