The application of this type of apparatus for other processes, involving simple heat effect, or where the filament is covered with catalytic material such as oxides, etc., is now under investigation.

Summary

1. A filament support has been described which eliminates all previous difficulties in the preparation of diphenyl, such as local heating and short circuiting due to expansion and sagging.

2. Very good yields of diphenyl can be obtained from benzene by maintaining the Nichrome filament at a yellowish-red heat.

3. The benzene used was commercially pure and not anhydrous. The addition of more water did not hasten the reaction.

DURHAM, NEW HAMPSHIRE

[CONTRIBUTION FROM THE SOILS LABORATORY, AGRICULTURAL EXPERIMENT STATION, UNIVERSITY OF MISSOURI]

THE NATURE OF THE ACIDITY OF THE COLLOIDAL CLAY OF ACID SOILS

BY RICHARD BRADFIELD

RECEIVED MAY 11, 1923

The problem of soil acidity has probably been investigated more than any other one soil problem, but in spite of the vast amount of work that has been done there is still considerable doubt as to its real nature.

Fisher[1] in his excellent résumé of the subject concludes: "It cannot be said that the enormous amount of work done has either solved the practical problem or clarified our ideas as to what exactly soil acidity means."

The earlier chemists believed with Sprengel[2] that soil acidity was due to the accumulation of complex insoluble organic acids. Recent work by Odén,[3] using electrochemical methods, has established the validity of Sprengel's contention when applied to soils high in organic matter. Some of our most acid soils, however, are very low in organic matter and their acidity must be due to some other cause. If aqueous extracts of most acid soils are boiled to expel the carbon dioxide they will not as a rule be sufficiently acid to redden litmus paper even though the moist soil itself may change it almost immediately. This and similar observations led to some doubt as to the existence of real acids in soils and to the idea of "negative acidity." The conception of "negative acidity" had its origin in the work of Van Bemmelen who found that certain colloids and soils exhibited a preferential absorption for bases when treated with neutral salts, leaving the solution acid. This idea was developed into the selective adsorption theory of soil acidity by Cameron, Parker, Harris and others.[4] Ramman discarded the expression

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[1] Fisher, *J. Agr. Sci.*, **11**, 20 (1921).

[2] Sprengel, *Archiv. Ges. Naturl.*, **8**, 145 (1826).

[3] Odén, *Trans. Faraday Soc.*, [2] **17**, 288 (1922).

[4] Cameron, *J. Phys. Chem.*, **14**, 320, 393 (1919). Parker, *J. Agr. Res.*, **1**, 179 (1913). Harris, *Mich. Expt. Sta. Tech. Bull.*, 19 (1914). Ramman, "Bodenkunde," J. Springer, Berlin, **1911**.

"acid soils" using instead "absorptively unsaturated soils." Salter and Morgan[5] in a recent study of the effect of the soil-water ratio on the Sörensen value of acid soils, found that the relationship was logarithmic and could be expressed by the usual absorption isotherm. They concluded that their data "discredit any theory of soil acidity which assumes that the acid reaction is due to highly insoluble acids, organic or inorganic which must under conditions of equilibrium form a saturated solution and give a constant P_H."

A great number of the recent workers on soil acidity believe, nevertheless, in the existence of highly complex insoluble alumino-silicic acids. This theory proposed by Loew in 1913 has been substantiated by the work of Ashley, Mellor and Clark[6] on the constitution of pure clays, and by Truog[7] who worked with agricultural soils. Soil chemists are practically unanimous in the opinion that the condition called "soil acidity" is due to a removal of the soluble bases by prolonged leaching. Since soils are composed of complex minerals, which are salts of strong bases and weak acids, it is to be expected that they would hydrolyze slowly, producing soluble bases which would be leached away by the rains and the insoluble acid residue would remain *in situ* to accumulate as the weathering proceeded. MacIntire[8] points out that the degree of acidity of a soil is closely correlated with its degree of hydration.

The principal arguments against the true acid theory are (1) that equivalent quantities of different bases are not taken up by soils, (2) that the titration curves of soils by bases show no breaks corresponding to neutral points but are almost linear. Truog[7] found however that, if experimental conditions were adjusted so as to keep side reactions at a minimum, equivalent quantities of bases were taken up by soils. The absence of breaks in the titration curves may be due, as will be shown later, to the fact that such titrations are usually made by adding increments of the standard base to a definite quantity of the acid soil. This is quite contrary to the teachings of physical chemistry. If a sharp end-point is desired the weak acid should be added to the strong base.

A survey of the literature on soil acidity shows that the following points are very well established regardless of the nature of the underlying causes.

1. Natural soils vary in Sörensen (P_H) value from about 3.5 to 9.5.
2. Aqueous extracts of acid soils when freed from carbon dioxide are usually acid-free.
3. Extracts of acid soils made with neutral salt solutions show a higher Sörensen value than the soil, and also considerable titrable acidity.
4. Titration curves, made by adding increments of bases to a fixed weight of soil and determining the corresponding Sörensen values show no definite breaks to indicate end-points, but are almost linear.
5. The slope of the curve varies widely with soil type. It is usually inversely proportional to the content of colloidal material. In other words the buffer action of a soil is some direct function of its colloid content.

Principles Underlying the Present Investigation

Soils are complex systems with particles ranging from a few millimeters in diameter down to molecular dimensions. The rate at which a

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[5] Salter and Morgan, *J. Phys. Chem.*, **27**, 123 (1923).

[6] Loew, *Porto Rico Agr. Expt. Sta. Bull.*, **13** (1913). Ashley, *Bur. Standards. Tech. Paper*, **23** (1913). Mellor and Holdcroft, *Pot. Gaz.*, **36**, 680 (1911). Clark, *U. S. Geol. Surv. Bull.*, **588** (1914).

[7] Truog, *J. Phys. Chem.*, **20**, 457 (1916).

[8] MacIntire, *J. Am. Soc. Agron.*, **13**, 157 (1921).

chemical reaction proceeds increases with a decrease in the size of the reacting particles. It is to be expected then that the more finely divided colloidal material in soils would reach an equilibrium much more quickly than the non-colloidal fraction. The situation is probably complicated still more in soils by the fact that the colloidal fraction forms a coating over the coarser particles which would tend to protect them. Because of this complexity of the soil system it would seem logical to use a physically homogeneous fraction for studies of the nature of the acidity. Since the buffer action of soils is closely correlated with their colloid content, the colloid fraction would seem to be the one best adapted for such studies. It has the additional advantages of having a high specific surface and of being accurately measurable by means of ordinary pipets and burets, which greatly facilitates titrations.

The end-point in the titration of colored solutions can readily be determined by conductivity measurements. The conductivity is at a minimum at the neutral point in the case of the titration of a strong base by a strong acid, and it makes little difference in that case whether the acid is added to the base or the reverse. If, however, a strong base is being neutralized by a weak acid the conductivity curve shows no increase after the neutral point is reached, but remains practically constant. If the process is reversed, and the strong base added to the weak acid, which is the method usually followed in soil investigations as pointed out by Findlay,[9] "The minimum will not be sharp owing to the fact that the change in conductance is not due so much to the disappearance of the fast-moving hydrion (which is present in comparatively small concentration) as to the replacement of the un-ionized acid molecules by the ions of the salt formed."

A similar situation exists in making a titration curve by means of the hydrogen electrode. In order to obtain distinct breaks at the end-points of the titration the amount of buffering substances should always be kept at a minimum. This can be done by titrating the strong base with the weak soil acid. In the work of Knight, Spurway, and Stevenson,[10] increments of the standard alkali solution were added to fixed quantities of soils. Under such conditions a maximum amount of either the weak soil acid or its salt is always present, exerting so great a buffer action that these investigators find an almost linear relationship between the amounts of base added and the increase in Sörensen value produced.

In this investigation standard solutions of sodium hydroxide and calcium hydroxide were titrated with the colloidal material from four acid

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[9] Findlay, "Practical Physical Chemistry," Longmans, Green and Company, London, **1911**, p. 180.

[10] Knight, *J. Ind. Eng. Chem.*, **12**, 465 (1920). Spurway, *Mich. Agr. Expt. Sta. Tech. Bull.*, 57 (1922). Stevenson, *Soil Science*, **12**, 145 (1921).

soils and the end-points located by both conductivity and hydrogen-ion concentration measurements.[11]

Experimental Part

The colloidal clay was extracted from the heavy sub-soils of the Marion, Cherokee, Putnam and Robertsville silt loams, each of which is very acid and very low in organic matter, by the method developed in this Laboratory. The solutions used contained 1 g. of oven-dried material per 100 cc. except in the case of the Robertsville, which contained 2 g.

Preliminary trials indicated that the basic solutions should have a normality of the order of 0.01 *N*. Ten cc. of 0.01 *N* base was placed in a 100cc. graduated flask by means of a pipet and the desired quantity of the 1% colloidal clay solution added. Enough neutral distilled water was added to bring the volume up to 100 cc. (except in the case of the additions of 100 cc. or over). After the solutions were thoroughly mixed, they were poured into 100cc. florence flasks which were kept stoppered to minimize contamination by carbon dioxide. About 15 minutes after mixing, a portion of the mixture was used for a hydrogen-ion determination. These determinations were made with a standard potentiometer, using the saturated potassium chloride calomel electrode and a modification of the Hildebrand type of hydrogen electrode. The temperature varied only slightly from 25°.

The conductivity measurements were made by the usual bridge method, using a Washburn Type B cell, a microphone hummer as a source of alternating current and a tunable telephone receiver to indicate the point of balance. The resistance was kept constant at 9999 ohms and the results are reported as bridge readings. The potentiometer was used as a bridge. The bridge wire was 1100 units long. The temperature was maintained at 25° ± .02 by a small thermostat.

Experimental Results.—The 1% stock solutions of the colloidal clays gave the conductivities and Sörensen values shown in Table I.

TABLE I

CONDUCTIVITY AND SÖRENSEN VALUES OF 1% COLLOIDAL CLAY SOLUTIONS

Soil	E.m.f.	P_H	Bridge reading
Putnam	0.498	4.30	935
Cherokee	.520	4.65	990
Marion	.506	4.42	1007

The rate of reaction between the colloidal solutions and the bases was studied by mixing the two in the desired proportions as usual, then determining the conductivity at frequent intervals. Equilibrium was attained almost instantly. Bridge readings taken as soon after mixing as possible were almost identical with those taken after standing overnight.

[11] THIS JOURNAL, **45,** 1245 (1923).

The titration curves for the Putnam and Cherokee clays obtained by both the conductivity and hydrogen electrode methods are given in Fig. 1. The curve for the Marion clay was almost identical in type with the Putnam and is for that reason omitted. About twice the usual quantity of base was used in the curve for the Robertsville clay (III) in order to place more points on the slanting portions of the curve. (A 2% solution of the Robertsville clay was used and the results plotted on the 1% basis.) The conductivity curves are all of the type commonly obtained in the titration of a strong base by a weak acid. As the strong base is neutralized and replaced by the comparatively insoluble salt of the alumino-silicic acid, the conductivity decreases linearly. After all of the base has been neutralized, the conductivity becomes constant and the addition of an excess

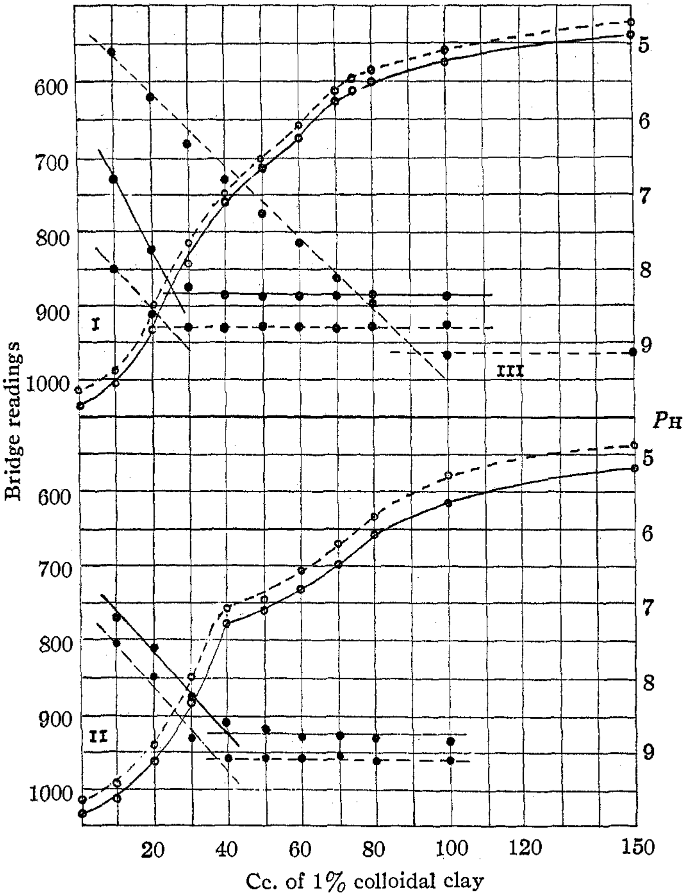

Fig. 1.—Titration curves of Putnam clay (I), Cherokee clay (II), and Robertsville clay (III). Circles represent hydrogen-electrode curves; dots, conductivity curves. Broken lines denote that $Ca(OH)_2$ was the base used; continuous lines, NaOH

of the weak colloidal acid has no effect. If we were dealing with an adsorption of the type expressed by Freundlich's isotherm instead of a neutralization, we should expect the curve to continue to drop in a logarithmic fashion until the value of the colloidal clay was approached. The curves obtained with calcium hydroxide approach this point, as would be expected from the low solubility of the calcium silicates and from the differences in the mobilities of the calcium and hydrogen ions but the minimum conductivity obtained with sodium hydroxide was in every case considerably higher than that of untreated clays; increasing the amount of clay almost four times after this minimum had been obtained failed to reduce the conductivity further. This would seem to indicate that in this case either we have an ordinary neutralization with the formation of the sodium salt of the acid which is more soluble than the acid itself, or from the adsorption point of view the colloidal clay regardless of the amount present is unable to adsorb the sodium beyond a certain critical concentration. Adsorptions are usually characterized by the lack of stoichiometric relations between the quantities of different bases taken up. In the conductivity curves of all the clays studied the two linear portions of the curves intersect at a point (the end-point) which corresponds to approximately the same amount of acid regardless of the nature of the base, which would seem to be rather conclusive evidence of the stoichiometric character of the reaction.

The curves obtained with the hydrogen electrode are also of the type commonly obtained in the neutralization of a strong base by a weak acid. The flatter portion of the curves in the most alkaline region is not as pronounced as in most titration curves, probably due largely to the great dilution of the standard alkali used (0.001 *N* after dilution). There is in each case a slight change in the slope of the curves at about P_{H} 7. This break is especially marked in the case of the Cherokee and indicates that there may be at least two distinct dissociation constants involved. The curves gradually flatten as an excess of the colloidal acids is added and approach the Sörensen value of the pure acids. The curves for sodium hydroxide follow those for calcium hydroxide very closely, confirming the conductivity curves, but show always slightly more alkalinity. This is doubtless due partly to differences in the solubility and hydrolysis of the salts formed and partly to a slight difference in the concentration of the basic solutions used. The sodium hydroxide solution was slightly over 0.01 *N* (0.0105) and the calcium hydroxide solution was not quite 0.01 *N* (0.0099). This difference when calculated to equivalents of the colloidal acids makes a difference of about 1.8 cc. of the 1% solutions.

The end-points of the titration obtained by the two methods (the intersection of the linear portions in the case of the conductivity curves and the midpoint of the steep portion of the curve in the case of the P_{H} curves) lie as close together as could be expected with a weak acid of this type.

About 37 cc. of 1% Cherokee, 27 cc. of 1% Putnam, and 37 cc. of 1% Marion soil were required to neutralize 10 cc. of the 0.01 *N* bases. This gives the 1% solutions of the acids about the following normalities, Cherokee 0.0027, Putnam 0.0037 and Marion 0.0027.

Discussion of Results

The chief objections to the chemical theory of soil acidity are (1) no one has ever been able to isolate an undeniable acid from a soil in quantities commensurate with the soil's "sourness;"[12] (2) acid soils do not absorb bases in equivalent quantities; (3) titration curves made by titrating a comparatively large mass of soil with a base are practically linear, showing no break such as is characteristic of true neutralizations.

The results obtained in this investigation tend to show that the colloidal material of an acid soil is itself an acid which ionizes to produce a definite Sörensen value and which shows a definite titrable acidity or normality on titration with strong bases. The fact that the acid is colloidal explains why it is not found in colloid-free aqueous extracts. Soils investigators have as a rule been expecting to obtain a negative ion of the soil acid which would be of the same dimensions as the ordinary crystalloid ion. This could hardly be expected if we consider the great complexity of the minerals which are found in soils. It would seem much more logical to expect the anion of the soil acid to be very large and complex, even reaching colloidal dimensions.

It has long been known that clay particles when suspended in water and placed in an electrical field migrate to the anode. Recent measurements in this Laboratory show that the velocity of migration of the colloidal particles is of the same order of magnitude as that of the average slow moving ion of crystalloids. This shows that the particles have an electric charge of the same order of magnitude as that of the crystalloid ion. This charge has commonly been ascribed to the preferential adsorption of hydroxyl ions by the colloidal particle. If the excess of hydrogen ions in the colloidal clays studied is due to the ionizing of the colloidal particles themselves, as this work indicates, then an equal negative charge must remain on the residual colloidal particle. These charged colloidal particles would be in reality very large complex negative ions, as the cataphoresis experiments indicate. This view is in harmony with the findings of Loeb, Pauli, Michaelis, Sörensen and others in their investigations of colloidal protein solutions and with the work of McBain on colloidal electrolytes.

The results obtained by Salter and Morgan[5] which are discussed above would be expected if they were dealing with a colloidal acid. Their argument in favor of the adsorption theory is based on their belief that

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[12] Russell, "Soil Conditions and Plant Growth," Longmans, Green and Co., London, **1921**, p. 110.

they were dealing in all the soil-water ratios studied, with a saturated solution. This fundamental assumption is not necessarily true. Their belief that they were dealing with a saturated solution was apparently based upon the fact that there always remained a certain amount of the solid phase undissolved. A considerable portion of most soils is made up of rather coarse particles of minerals such as quartz which are very inactive. The amount of colloidal material is in most cases comparatively small, so small as to make it seem highly improbable that the solution was saturated even with a ratio of 1 part of soil to 1 part of water. Their curves began to flatten, however, in the most concentrated mixtures, which indicates that they were probably approaching a concentration in which the Sörensen value would become constant. Any weak acid will yield a logarithmic curve for certain concentrations when its hydrogen-ion concentration is plotted against its concentration. The curve becomes linear only when the acid is completely dissociated at infinite dilution. The curve of Salter and Morgan becomes practically linear at the point corresponding to 100 g. of soils to 1000 cc. of water which indicates that they have reached a concentration corresponding to infinite dilution at that ratio. Instead of discrediting a colloidal acid theory of soil acidity, their results would seem to be exactly what would be expected from such a theory.

The second objection to the true acid theory of soil acidity is that equivalent amounts of bases are not removed. As pointed out above such results have usually been attained when a relatively large ratio of soil to reacting base was used. Such conditions favor complex side reactions in which the solubilities of the resulting salts play a role. Truog has shown that if a small sample of soil is treated with a large excess of the base or salt, conditions favoring the direct action and unfavorable to the side reactions, approximately equivalent quantities of bases are taken up. In this investigation the same end was accomplished by adding small increments of the colloidal acid to a definite quantity of strong bases. The titration curves for calcium and sodium hydroxides in each case lie so close together that if we take into consideration the differences in the solubilities of the alumino-silicates which are indicated in the conductivity curves, there can be little doubt that equivalent quantities of the two bases are neutralized by the colloidal acid.

The third objection, that soil titration curves do not exhibit definite breaks, has been shown to be unfounded provided that the strong base is titrated with the weak soil acid. With the reverse procedure, which is usually followed in soil investigations, an excess of the weak acids and their salts, the substances responsible for the high buffer action are present from the start and tend to obscure the breaks normally expected. The end-points found by the conductivity method are as sharp as those commonly obtained with weak acids.

The curves obtained by the hydrogen-electrode method are also of the type usually obtained with very weak acids. There are no sharp breaks, but the slope changes gradually, showing the least buffer action between *P*H 9.5 and 7. At the latter point there is a slight flattening of the curve with all clays studied. This flattening is more marked with the Cherokee soil than with any of the others (Fig. 1, II). It seems to be as pronounced as that observed in the titration of certain weak crystalloidal acids such as phthalic acid[13] and would seem to be evidence that at least a dibasic acid was involved. It would be difficult to account for such a change by the adsorption theory but it is exactly what would be expected if we were dealing with a true neutralization of a base by a weak polybasic acid.

There yet remains the possibility that the acidity neutralized is due to acids other than alumino-silicic. As pointed out above, the colloids used in this study were extracted from the sub-soils of four soils very low in organic matter. They were likewise very low in phosphate and sulfate. The percentages of these substances were so low and the quantity of colloidal acid used so small as to render it inconceivable that the acidity found was due either to organic acids or to traces of the more common strong inorganic acids.

In spite of the strong acidity of the soil colloids and of the fact that the colloid content of soils is much higher than is commonly believed, as has been shown by the recent work of Moore, Fry and Middleton[14] and confirmed in this Laboratory, it is not believed that such acidity accounts for all the acidity of sour soils. The exteriors of the larger non-colloidal particles of such soils have doubtless lost considerable of their bases. The work of Brown and Johnson, Truog[15] and others indicates that the interior of such particles when freshly exposed to the solvent action of water after thorough grinding may contain enough soluble bases to render the solution alkaline in reaction. Such particles are probably responsible for most of the so-called latent acidity, since the results obtained in this investigation indicate that the reaction of the colloidal material is very rapid.

Additional evidence in favor of the true acid nature of acid colloidal clays is found in the studies previously reported,[16] in which it was found that the concentration of potassium ions required for complete flocculation of the acid clay increased about 10-fold when the Sörensen value was raised from 6.5 to 8.5, and then became constant, indicating that after a sufficient concentration of hydroxyl ions to neutralize the acid has been added further increases (almost a thousand-fold) are without effect.

[13] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, **1920**, p. 191.

[14] Moore, Fry and Middleton, *J. Ind. Eng. Chem.*, **13**, 527 (1921).

[15] Brown and Johnson, *ibid.*, **7**, 776 (1915). Ref. 7, p. 478.

[16] Bradfield, THIS JOURNAL, **45**, 1243 (1923).

Other studies on the variation of the hydrogen-ion concentration of the acid clays upon dilution gave curves apparently identical in type with those obtained with weak acids such as acetic acid.[17]

Summary

1. Solutions of calcium and sodium hydroxides were titrated with 1% solutions of four subsoil colloidal clays. The end-points found by both the conductivity method and the hydrogen electrode were fairly definite and the curves were of the type usually obtained in titrating a strong base with a weak acid.

2. The same amounts of the colloidal acids were required to neutralize equivalent quantities of the two bases.

3. Definite breaks were found in the conductivity curves, indicating the neutralization of definite acids which in 1% solutions had concentrations ranging from 0.0027 to 0.0037 *N*.

4. The reaction between acid colloidal clays and strong bases seems to be an ordinary neutralization. Recourse to the adsorption theory seems unnecessary.

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[Contribution from the Laboratory of Physiological Chemistry, University of Iowa]

STUDIES ON ENZYME ACTION. THE RELATIONSHIP BETWEEN THE CHEMICAL STRUCTURE OF CERTAIN COMPOUNDS AND THEIR EFFECT UPON THE ACTIVITY OF UREASE

By Elbert W. Rockwood and William J. Husa

Received June 29, 1923

Various organic compounds have been reported as influencing the activity of urease.[1] Lövgren[2] gives a rather full review of the general properties of urease and includes a bibliography containing over 200 references. From his review of the literature Lövgren concludes that all the promoters[3] are weak acids of amphoteric electrolytes, and that their accelerating influence lies in their checking of the P_H increase.

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[17] Bradfield, paper to appear in *J. Phys. Chem.*, **1923**.

[1] (a) Armstrong and Horton, *Proc. Roy. Soc.*, **85B,** 109 (1912). (b) Armstrong, Benjamin and Horton, *ibid.*, **86B,** 328 (1914). (c) Marshall, *J. Biol. Chem.*, **17,** 351 (1914). (d) Van Slyke and Zacharias, *ibid.*, **19,** 181 (1914). (e) Falk, *Biochem. Z.*, **59,** 298 (1914). (f) Jacoby and Umeda, *ibid.*, **68,** 23 (1915). (g) Jacoby, *ibid.*, **74,** 105 (1916); **84,** 358 (1917); **85,** 358 (1918). (h) Bayliss, *Arch. Néerland. physiol.*, **2,** 621 (1918); through *C. A.*, **13,** 1077 (1919). (i) Rona and György, *Biochem. Z.*, **111,** 115 (1920). (j) Wester, *Pharm. Weekblad,* **59,** 173 (1922); through *C. A.*, **16,** 1253 (1922).

[2] Lövgren, *Biochem. Z.*, **119,** 215 (1921).

[3] Pease and Taylor, *J. Phys. Chem.*, **24,** 241 (1920).