VOL. XXXV. JULY, 1913. NO. 7

THE JOURNAL

OF THE

American Chemical Society

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.]

SOME APPLICATIONS OF THE HYDROGEN ELECTRODE IN ANALYSIS, RESEARCH AND TEACHING.[1]

BY JOEL H. HILDEBRAND.

Received May 5, 1913.

With the development of theoretical chemistry various principles and methods have been suggested from time to time as applicable to the problems of the practical chemist. Many of these have remained unused, however, due possibly to the fact that they have appeared too complicated, either in mathematics or in apparatus required, to appear feasable to the man not specially trained in physical chemistry. Among these is the possibility of following changes in concentration of ions by means of changes in potential of suitable electrodes. The hydrogen electrode especially has been used for some time in physico-chemical research,[2] but its possibilities for solving many of the problems of the analytical and technical chemist seem to be but little recognized. The writer has been consulted about so many problems whose solution lay in the use of the hydrogen electrode, that it has seemed to him that many chemists might welcome a description of a simple form of apparatus, together with the illustrations we have thus far accumulated of its applicability to problems arising in analysis, research and teaching.

[1] Presented at the general meeting of the Society at Milwaukee, March 25. The part relating to the titration of magnesium in limestone was published by Joel H. Hildebrand and Herbert S. Harned in the *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 1, 217.

[2] Cf. Loomis and Acree, *Amer. Chem. J.*, 46, 585, 621 (1911). An extensive bibliography is here given.

Principles of Method.

If two electrodes of the same metal are placed into solutions containing the ion of the metal in different concentrations, c_1 and c_2, respectively, and these solutions are placed in electrical contact, either through a porous partition or by means of a siphon, or even separated by gravity alone, then there exists between the two electrodes a difference of potential expressed fairly closely by the formula

$$E = 0.000198\ T/n \log c_1/c_2,$$

where E denotes the difference of potential, T the absolute temperature, and n the valence of the ions of the metal in solution. At room temperatures, about 18°, the formula becomes

$$E = 0.058/n \log c_1/c_2.$$

For example, if the metal is silver, when $n = 1$, and if c_1 and c_2 are 0.1 and 0.001 normal, respectively, then $\log c_1/c_2 = \log 100 = 2$, and $E = 0.116$. Conversely, when E is measured either concentration can be easily calculated if the other is known. For example, if $c_1 = 0.1$ and the measured value of E is 0.216, then

$$\log 0.1/c_2 = 0.216/0.058 = 3.62,$$

and

$$0.1/c_2 = 7.9 \times 10^3, \text{ whence } c_2 = 1.3 \times 10^{-5}.$$

It is thus possible to determin quite accurately even very small ionic concentrations, whence such things as the solubility of the silver halides may be determined very easily.

Now the same principle can be applied to the determination of hydrogen-ion concentration (acidity or alkalinity), if for electrodes we use a noble metal, like platinum or palladium, saturated with hydrogen under a definit pressure. Thus if we use such an electrode dipping into a solution containing normal hydrogen-ion so that $c_1 = 1$, and measure the difference of potential between it and another similar electrode dipping into a solution in which the hydrogen ion concentration c is unknown, the two solutions being connected, say, by a siphon containing concentrated potassium nitrate or chloride solution, then the unknown concentration and the difference of potential are related by the expression

$$E = 0.058 \log 1/c.$$

In practice it is more convenient to use a calomel electrode than the normal hydrogen electrode. Since the latter is 0.28 volt more positive than the former (we are considering a calomel electrode containing normal potassium chloride) the difference of potential between the unknown hydrogen electrode and the calomel electrode will be 0.28 volt more than that between the former and the normal hydrogen electrode, so that the above formula becomes, when the normal calomel electrode is used,

$$E = 0.058 \log 1/c + 0.28.^1$$

Before describing the apparatus by which the e. m. f. can be measured, we will consider for a moment the significance of the hydrogen-ion concentration of solutions. It was found by Kohlrausch and Heydweiller[2] that the purest water that they could prepare showed an electrical conductivity. Since this could be ascribed only to hydrogen- and hydroxyl-ions from the water itself, and since the conductivity of these ions when present in normal concentration was known from measurements with acids and bases, it was a simple matter to calculate the amount of these ions present in pure water. Assuming that they were produced in equal amount as given by the equation

$$H_2O = H^+ + OH^-,$$

the concentration of each expressed in mols per liter became 10^{-7}, approximately, at ordinary temperatures. According to the law of mass action, if the concentration of either of these ions is increased by the addition of acid or alkali that of the other is diminished according to the equation

$$\text{conc. of } H^+ \times \text{conc. of } OH^+ = 10^{-14}.$$

Thus if we have a solution containing 0.01 normal OH^- (which can be gotten approximately by using 0.01 N KOH), the solution will contain H^+ at a concentration of 10^{-12}.

Now the neutralization of acids and bases, the precipitation of hydroxides, the precipitation of salts of weak acids from their solution in strong acids, etc., are accompanied by changes in the concentration of the hydrogen- and hydroxyl-ions which it is often important and usually very instructive to follow; this can easily be done by the aid of the hydrogen electrode, as above described.

The first application of these principles to analysis was made by Böttger,[3] who titrated a number of acids and bases, including several reproduced in this paper. The purpose of this communication is to call attention to the value of his work, to show how the manipulation may be simplified and thus made available to the practical chemist, and to ascribe some new applications, including its use in choosing indicators, preparing normal salts, and the study of the precipitation and separation of metals.

---

[1] In addition to the e. m. f. given by this formula there is a smaller e. m. f. at the surface of contact between the two liquids of different concentration. For comparative purposes this can be ignored. It is considerably diminished if a neutral salt, best potassium chloride, is added to the solution around the hydrogen electrode. The same end is attained by using saturated potassium chloride in the arm of the siphon of the calomel electrode.

[2] *Wied. Ann.*, **53**, 209 (1894).

[3] *Z. physik. Chem.*, **24**, 253 (1897).

Apparatus.

The hydrogen electrode used in this work is shown in Fig. 1. A platinum foil about 8 × 25 mm. is welded to a short piece of platinum wire, which is in turn fused to a stiff copper wire. The latter is thrust into a glass tube just wide enough to receive it, which is fused around the platinum wire just above the foil. The copper wire is fastened in the tube at the top with marine glue. This electrode is contained in a slightly wider tube having a side arm near the top for the admission of hydrogen, and a bell-shaped enlargement at the bottom to protect the foil and to confine the hydrogen which must bathe its upper half. A wide notch is cut in the bottom of the bell to allow the liquid to rise enough to cover the lower half of the foil. After adjusting the inner tube carrying the electrode to the proper height it is fastened to the outer tube by means of marine glue. The platinum foil has been previously bent into an S-shape so as to pass into the bell. This arrangement of the foil exposes a sufficient line of contact between the phases solution-platinum-hydrogen to prevent the electrode from becoming unsaturated by the currents likely to be taken from it. Before use the electrode must be covered with platinum black by the usual process.[1] This platinizing should be repeated after some dozens of titrations in order to secure the most satisfactory readings.

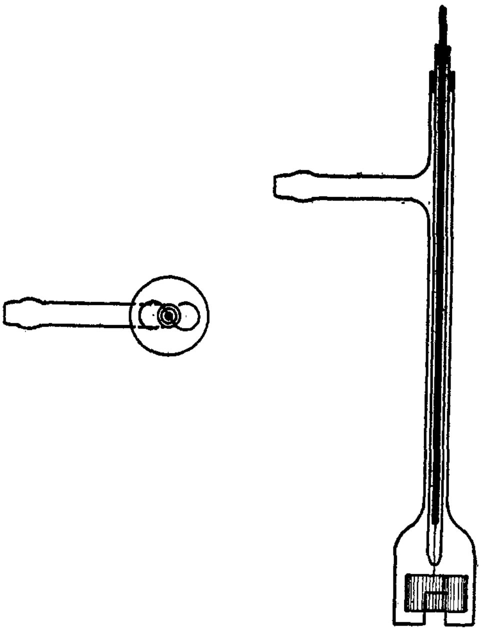

Fig. 1.

The arrangement of the rest of the apparatus is shown in Fig. 2. C is a calomel electrode which furnishes a constant potential to compare with the hydrogen electrode *h*. These two electrodes together form a cell whose e. m. f. is to be measured so that we can determin the hydrogen-ion concentration in the solution around the hydrogen electrode *c* in equation (1).

---

[1] For this as well as other information concerning the principles and use of the various pieces of apparatus described later, see works such as Ostwald-Luther, *Physiko-Chemische Messungen;* or Findlay, *Practical Physical Chemistry.*

Probably the greatest obstacle to the use of the hydrogen electrode for analytical purposes has been the fact that the above e. m. f., as originally determined by Böttger, required the use of a potentiometer, and the loss of some time in making adjustments and calculations. To avoid this difficulty we have made use of a voltmeter instead of a potentiometer, as Sand[1] has done in his apparatus for the separation of the metals by graded potential. A rather laborious and time consuming task to the analyst is thus made quite rapid and simple.

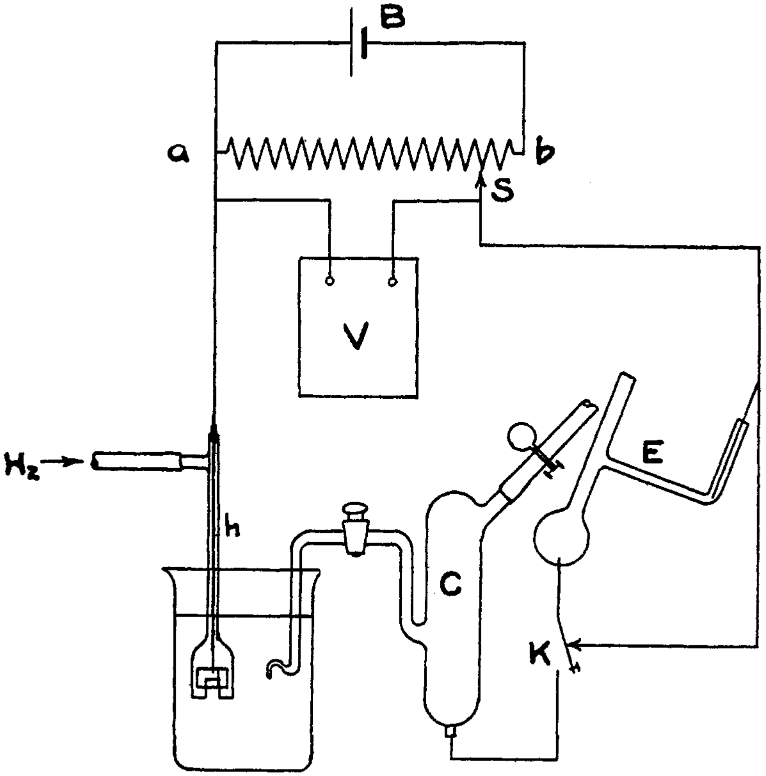

Fig. 2.

The e. m. f. of the cell, hydrogen electrode-calomel electrode, is balanced against a variable fraction of the e. m. f. of the battery B. The latter causes a fall of potential along the rheostat *a–b*, and by adjusting the position of the sliding contact *s*, any desired fraction of the e. m. f. of B can be shunted between *a* and *s*. When this is just equal to the e. m. f. of the cell composed of the hydrogen and calomel electrodes, connected so that the two e. m. fs. will oppose each other,[2] then no cur-

---

[1] *J. Chem. Soc.*, 91, 374 (1907).

[2] The calomel electrode will always be positive in this work and should therefore be connected to the positive pole of the battery B.

rent will pass through the electrometer or galvanometer E on pressing the key K. The measurement consists, therefore, in sliding *s* along until, on pressing the key, there is no deflection at E. The fall of potential from *a* to *s* is then read on the voltmeter V also shunted across these points.

Since the differences of potential used in this work range up to a little over one volt, the battery B may be any fairly constant cell, such as a storage, dry, sal-ammoniac, or gravity battery. If a lead accumulator is used, it is better to put in series with it a resistance approximately equal to that of the rheostat *a–b*, so that the fall of potential through the latter shall be about one volt, and its whole length may be utilized. The rheostat should have a sufficient number of turns to admit of an adjustment of the voltmeter to 0.01 volt, otherwise almost any length and resistance will suffice. An ordinary slide-wire such as is used in Wheatstone-bridge measurements will do very well if its resistance is sufficient to prevent the too rapid discharge of the battery.

The voltmeter should have a range of 1.1 volt, and should be readable to 0.01 volt. Greater accuracy is not necessary for this purpose. If it is provided with a key the latter should be pressed while adjusting the slider as well as when making a reading. This is necessary as the fall of potential from *a* to *s* is changed by throwing the voltmeter in or out of the circuit.

The Lippmann electrometer is less expensive and in some respects more satisfactory as a zero indicator at E than a galvanometer, although it may require some attention to keep in order. It has the advantages that it is dead beat, easy to observe, and is practically a static instrument, therefore not discharging the hydrogen electrode, and allowing the stopcock (not greased) of the calomel electrode to remain closed during the observations, thus preventing diffusion between the beaker and the calomel electrode. As shown in the figure, the electrometer must be short-circuited between observations by a suitable connection at the key.

In making a titration the solution to be titrated is put into a beaker, the hydrogen electrode immersed in it, and connection with the calomel electrode made through the siphon of the latter. Hydrogen gas, washed, say, with permanganate, but not dried, is run into the hydrogen electrode at, roughly, such a rate that the bubbles escape once every second or two. About ten minutes are required before the electrode becomes saturated, though only about a minute is necessary if the electrode has been previously saturated in a beaker of distilled water. As soon as the e. m. f. has become constant, determined as previously described, the titration may proceed. The readings become constant almost immediately after the titrating solution has been thoroughly stirred into the solution after each addition. The readings may be plotted on cross-section paper directly as taken, saving time and also enabling one to see approaching changes. The time of ordinary titrations need take only a few minutes. Where precipitates are produced, more time is required to get the solution and precipitate in equilibrium.

The results here described are best discussed by reference to the curves.

In order to understand the full significance of these curves it is necessary to remember that changes in the e. m. f. (ordinates) correspond to changes in the acidity or alkalinity, *i. e.*, hydrogen- and hydroxyl-ion concentration, and that the higher the e. m. f. the less is the hydrogen-ion concentration. On the curves are shown corresponding hydrogen-ion concentrations in even powers of ten. The ordinates corresponding to these were calculated by means of the formula (1). The "neutral point," where the concentration of both hydrogen and hydroxyl-ion is 10^{-7}, corresponding to an e. m. f. of 0.69 volt, is indicated by a line, below which the solution becomes increasingly acid, and above which it becomes increasingly alkaline.

By referring to the curve for hydrochloric acid it will be seen that the e. m. f. changes very little for the first additions of alkali, but as the amount of acid becomes less a relatively greater amount is removed by further additions of alkali, until suddenly the e. m. f. rises almost vertically, a drop or two changing the solution from strongly acid to strongly alkaline. Further additions of alkali naturally produce relatively less and less increase in the alkalinity.

Acetic acid shows an initial e. m. f. much greater than hydrochloric acid, corresponding to a smaller hydrogen-ion concentration. This brings out the well-known fact that acetic acid is a relatively weak acid. It will be noticed further that the first additions of alkali cause a marked decrease in the acidity. This shows the effect of the acetate-ion in diminishing the acidity of the acetic acid. We have the equilibrium

$$CH_3COOH = CH_3COO^- + H^+,$$

and since the concentration of the CH_3COO^-, originally small due to the slight dissociation of acetic acid, is greatly increased by the addition of some alkali, the concentration of the H^+ must be correspondingly diminished, as expected by the law of mass action. This effect is sufficient to decrease the acidity *gradually* almost to the neutral point before the jump to alkaline reaction takes place. It is easy to show mathematically that the point of inflection, or the middle of this jump, corresponds to the normal salt, when the acid and the base are present in equivalent amounts. It will be noticed that this point at which the acid and base are equivalent does not give a neutral but an alkaline solution, corresponding to the well-known fact that sodium acetate solutions are alkaline due to hydrolysis. An interesting problem for a student in this connec-

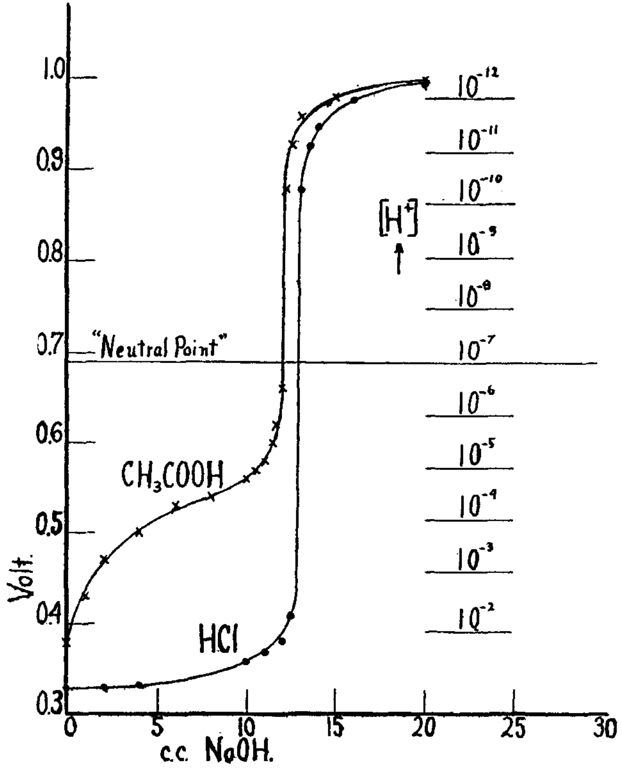

Fig. 3.—Titration of hydrochloric and acetic acids with sodium hydroxide.[1]

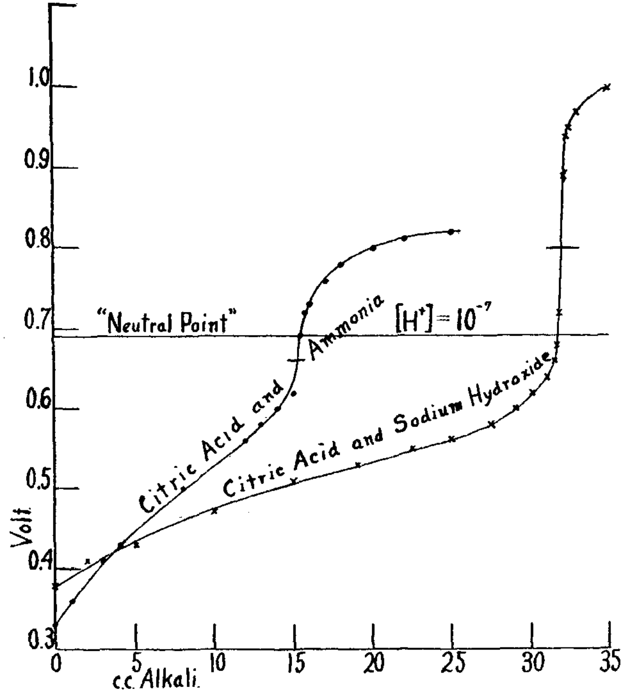

Fig. 4.—Titration of citric acid with sodium hydroxide and with ammonia.

---

[1] Titrations of both of these acids were made by Böttger, *loc. cit.*

tion is to calculate from this curve the degree of hydrolysis and also the dissociation constant of acetic acid.

There are doubtless few tasks which confront the practical chemist more frequently and pressingly than the proper choice of indicators. Those who have confronted this problem from a pedagogical standpoint appreciate the difficulty of bringing dissociation constants out of the realm of mathematical abstraction, as well as that of finding the particular dissociation constants desired. Curves such as these, however, enable one to choose the proper indicator with certainty and also to make clear to students the principles involved as has no other method which the writer has been able to discover.

It is well known that the various indicators may behave very differently; thus a mixture of monosodium and disodium hydrogen phosphate reacts alkaline according to methyl orange and acid according to phenolphthalein. Again, the former indicator can be used in titrating ammonia but not in titrating acetic acid, whereas with the latter the reverse is true. The reason for this difference is that indicators do not necessarily change color at the neutral point but rather at a definit hydrogen-ion concentration peculiar to each indicator. (This may alter with the temperature and with the presence of certain salts, etc.) This color change is produced by a change in ionization, indicators being weak acids or bases, accompanied, doubtless, always by a tautomeric change.[1] If the dissociation constant of the indicator is known the hydrogen ion concentration at which it changes color can be calculated.[2] Since, however, the latter is easier to determin than the former and since it is the thing we wish to know in using an indicator, there is little use, for our present purpose, in complicating matters by the discussion of dissociation constants. Moreover, these are known in but few cases, whereas the hydrogen-ion concentration at which the color-change takes place is known for a large number of indicators. Measurements of this quantity have been made by Friedenthal,[3] Salessky,[4] Fels,[5] Salm,[6] and Sörensen.[7] The measurements of Salm cover the largest number of indicators, and since his results are not known or accessible to many American chemists it will doubtless not be unwelcome to have some of them reproduced here, in view of the importance of such data in the light of the method here described. Table I, accordingly, shows the hydrogen-ion concentration at which some

---

[1] cf. Stieglitz, THIS JOURNAL, **25**, 1112 (1903).

[2] For a very full discussion and references on this subject cf. A. A. Noyes, THIS JOURNAL, **32**, 815 (1910).

[3] *Zeit. Elektrochem.*, 10, 113 (1904).

[4] *Ibid.*, **10**, 204 (1904).

[5] *Ibid.*, **10**, 208 (1904).

[6] *Z. physik. Chem.*, **57**, 471 (1907).

[7] *Compt. rend. Lab. de Carlsberg*, **8**, 1 (1909).

TABLE I.

Concentration of H^+	1.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.	10^{-6}.	10^{-7}.	10^{-8}.	10^{-9}.	10^{-10}.	10^{-11}.	10^{-12}.	10^{-13}.	10^{-14}.
Alizarin	....	....	....	....	....	....	yellow	lilac	....	....	....	....	violet	....	blue
Alizarin green B	red	....	....	....	....	....	....	....	....	....	....	red	yellow	green	....
Benzopurpurin B	....	....	....	violet	rose	yellow	....	....	....	....	....	....	....	....	rose
Cochineal	....	....	....	....	yellow	yellow-pink	lilac	....	....	....	....	....	....	....	....
Congo red	....	....	....	blue	violet	red-violet	orange	orange red	....	....	....	....	....	....	....
Crocein	....	....	....	....	....	....	....	....	....	....	....	....	rose	violet	....
Cyanin	....	....	....	....	....	colorless	....	trace blue	blue	....	....	....	....	....	....
Dimethylamidoazobenzene	....	cherry	red	flesh color	yellow	....	....	....	....	....	....	....	....	....	....
Guaiacum tincture	....	....	....	....	....	....	colorless	....	greenish	yellow	....	....	....	....	....
Heliantin II	....	....	....	....	....	....	....	....	....	....	....	....	....	yellow	lilac
Litmus	....	....	....	....	....	red	red-violet	violet	blue	....	....	....	....	....	....
Mauvein	green	greenish blue	blue	violet	....	....	....	....	....	....	....	....	....	....	violet red
Methyl red	....	....	....	red	....	pink-	yellow	....	....	....	....	....	....	....	....
Methyl orange	rose red	....	....	....	orange	yellow	....	....	....	....	....	....	....	....	....
α-Naphtholbenzoin	....	...	....	....	....	....	....	....	....	yellow	green	greenish blue	....	....	....
Neutral red	violet	cherry red	....	....	....	....	....	rose red	orange	yellow	....	....	....	....	....
p-Nitrophenol	....	....	....	....	....	colorless	light green	yellow	....	....	....	....	....	....	....
Phenacetolin	....	....	....	....	yellow	brown-red	rose red	....	....	....	....	violet-red	slowly lighter	colorless	....
Phenolphthalein	....	....	....	....	....	....	....	....	colorless	red	....	....	....	....	colorless
Rosolic acid	....	....	....	....	....	....	yellow	rose	red	....	....	....	....	....	....
Sodiumalizarin sulfonate	....	...	....	....	yellow-green	brown	red	...	....	....	....	lilac	violet	....	....
Tetrabromphenolphthalein	....	....	....	....	....	....	....	....	colorless	violet	....	....	....	....	colorless
Thymolphthalein	....	....	....	....	....	....	....	....	....	colorless	blue	....	....	....	....
Tropaolin	flesh color	yellow	....	....	....	....	....	....	flesh color	rose red	....	....	....	....	....
Tropaolin 0	....	....	....	....	....	....	....	....	....	....	....	greenish yellow	orange	....	....
Tropaolin 00	....	cherry red	flesh color	yellow	....	....	....	....	....	....	....	....	....	....	....
Tropaolin 000	....	....	....	....	....	....	....	....	....	....	....	yellow	orange	....	....
Trintrobenzene	....	....	....	....	....	....	....	....	....	....	....	....	colorless	orange	....

of the well-known indicators change color. The table is based on that of Salm with some omissions and changes.[1]

If we refer again to Fig. 3 it is evident that any indicator except those in the extreme end columns will do for the titration of the strong acid, hydrochloric, with the strong base. A very slight addition of alkali at the end point is sufficient to change the hydrogen-ion concentration through a range great enough to include all of the color changes of the table. With acetic acid, however, the rapid change in acidity, shown by the jump in the curve, is approximately between hydrogen-ion concentrations of 10^{-7} and 10^{-10}. It is thus quite evident that phenolphthalein, changing between 10^{-8} and 10^{-9}, will give a sharp end point, while methyl orange, changing between 10^{-4} and 10^{-5}, will change color gradually, and long before the equivalent amount of base has been added, and hence, as is of course in this instance well known, is unsuitable in this titration. It may be noted that an indicator changing color nearest the middle of the jump in the curve will, in general, give the sharpest end point.

There is a very important but little-known fact that should be emphasized in this connection, *i. e.*, that the hydrogen-ion concentrations at which indicators change color may be very different from the values given by Salm and others when certain substances are present.[2] Particulars regarding this fact will be published later; it is mentioned now to show that calculations such as are given by A. A. Noyes[3] for choosing the proper indicator may lead to incorrect results, and that *the only safe method is to have the supposedly correct indicator present while making a titration with the hydrogen electrode, and see if the color change actually does take place at the point of inflection of the curve.*

Although citric acid is tribasic, the dissociation constants are not different enough to give distinct end points. The neutralization of the second and third hydrogen-ions commence before the preceding one is completely neutralized. It is evident also from the curve that normal sodium citrate reacts alkaline, due to hydrolysis and that an indicator changing color at about 10^{-9} would be the best for titrating this acid.

On account of the importance of normal ammonium citrate to the fertilizer chemists, and the difficulty that has been encountered in its preparation, we were led to titrate citric acid with ammonia. The curve represents the action of concentrated ammonia on a nearly saturated solu-

---

[1] See also papers by Washburn, *Proc. Ill. Water Supply Assoc.*, **1910**, 93, and Thiel, *Der Stand der Indikatorenfrage, Ahren's Sammlungen*, **16** (1910–11).

[2] Cf. Hildebrand, THIS JOURNAL, 30, 1914 (1908); Rosenstein, *Ibid.*, 34, 1117 (1912). The writer has noticed "salt effects" enormously greater than those described by Rosenstein, throwing the color change off whole powers of ten from the tabulated values.

[3] *Loc. cit.*

tion of the acid. Evidently the normal salt has a hydrogen-ion concentration between 10^{-6} and 10^{-7}, and its presence is shown by an indicator changing in this interval. The best indicator for this purpose is now being studied in this laboratory.

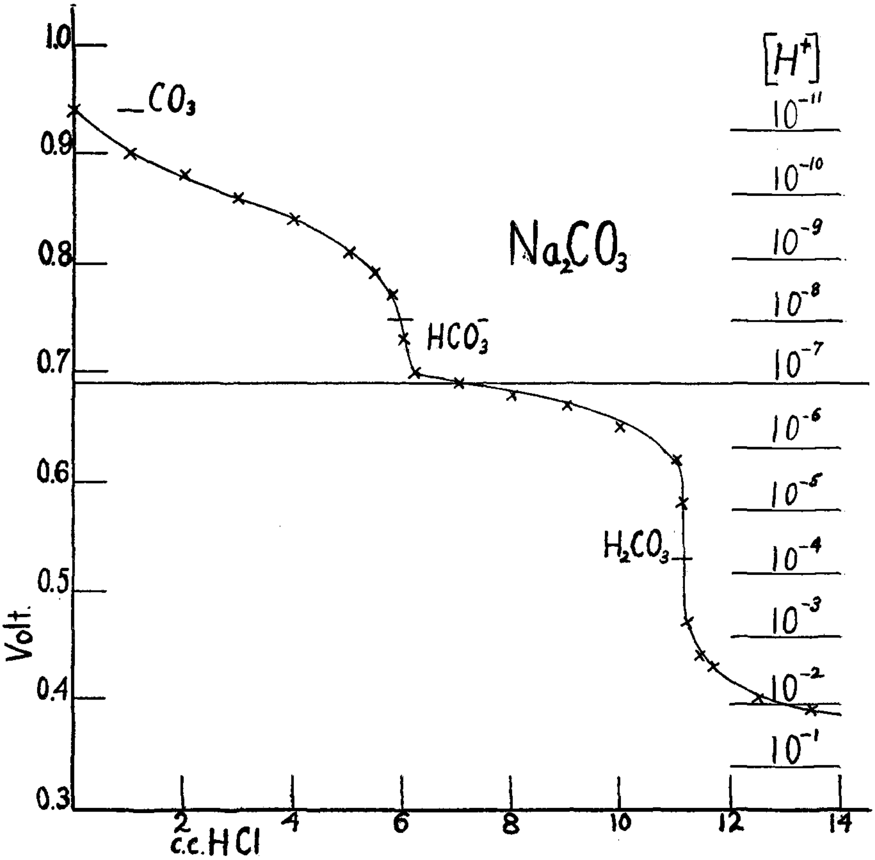

Fig. 5.—Sodium carbonate with hydrochloric acid.

We see in this curve first the strong alkaline reaction of sodium carbonate, due to hydrolysis. As acid is added we have the reaction

$$CO_3^{--} + H^+ = HCO_3^-.$$

This is accompanied by a decrease in alkalinity of the solution, becoming more rapid when the reaction is completed. The familiar use of phenolphthalein to indicate the end of the change from carbonate to acid carbonate is justified by this curve, although it is evident that as sharp an end point cannot be expected here as is obtained on the completion of the next stage of the titration, corresponding to the reaction

$$HCO_3^- + H^+ = H_2CO_3.$$

The second and more pronounced drop in the curve indicates the end of this reaction and we can see the justification for the use of methyl-orange to give this point.

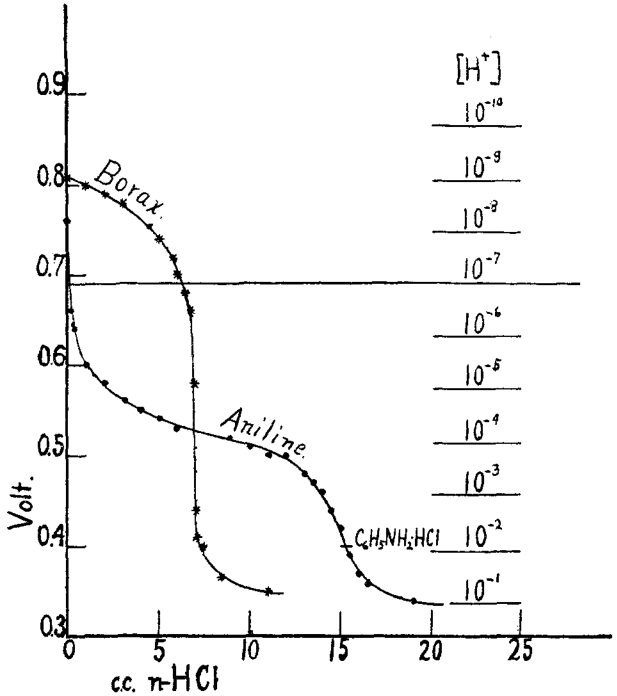

Fig. 6.—Borax and aniline with hydrochloric acid.[1]

Turning our attention first to the curve for borax we see the alkaline reaction of borax solutions and the gradual liberation of boric acid as the titration proceeds. This is so weak that as long as borax is present in any considerable amount the solution remains alkaline, the hydrolysis of the borax overcoming the acidity of the free acid liberated. When the borate-ion is all removed there remains nothing to unite with the hydrogen ion of the hydrochloric acid added and the solution increases rapidly in acidity. Methyl-orange, as is evident, indicates the end of this titration.

The curve for aniline shows first weak basic character and then the rapid change to an acid solution when even a small quantity of aniline hydrochloride is produced, due to the strong hydrolysis of the latter. When the equivalent amount of acid has been added we do not find a very marked drop in the curve, which shows that no indicator would give very ac-

---

[1] Aniline was titrated by Böttger, but the curve he gives is much inferior to the one here given. No end point is apparent in the former.

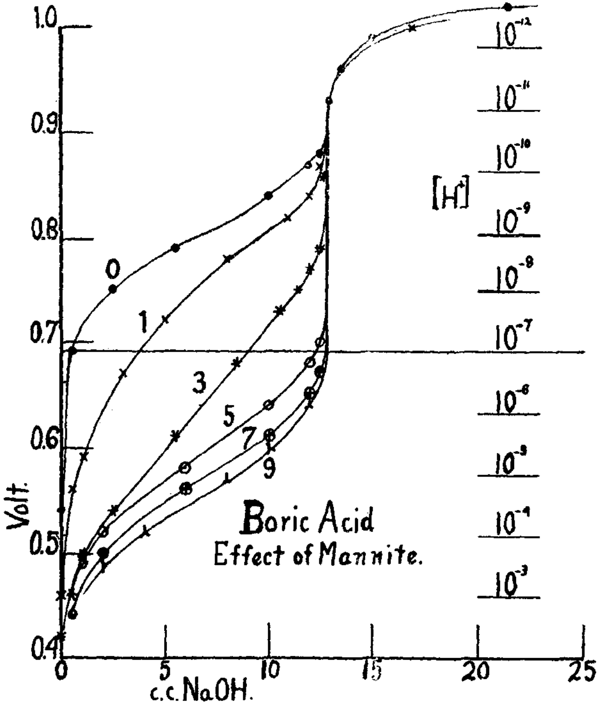

Fig. 7.—Boric acid. Effect of mannite.[1]

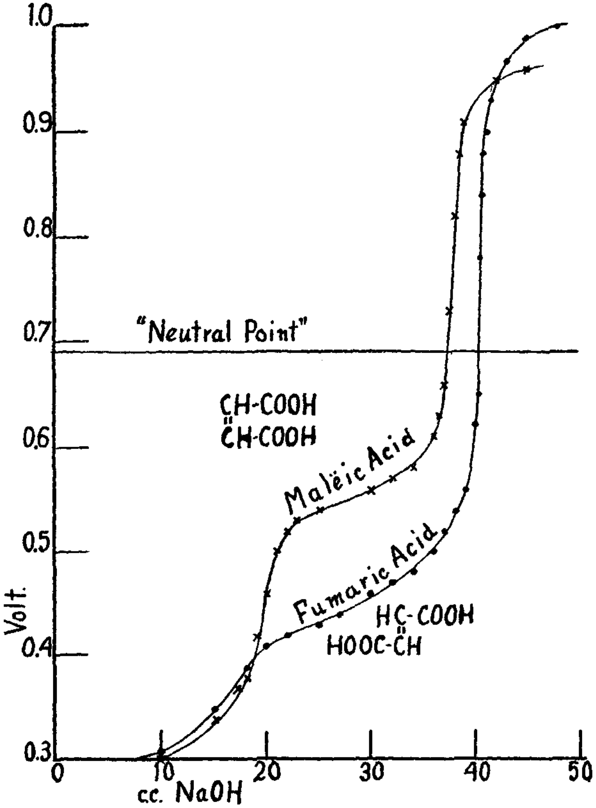

Fig. 8.—Maleic acid and fumaric acid.

---

[1] Titrations made by Mr. H. S. Harned.

curate results; we do find, however, a well-defined point of inflection, so that an accurate titration is possible by the use of the hydrogen electrode. Where the e. m. f. at such a point of inflection has been once determined it is possible to make a very rapid titration of any solution by setting the voltmeter at this value of e. m. f. and titrating till the electrometer gives no deflection on pressing the key. This procedure may prove very useful in cases where an indicator cannot be used, as, for example, with dark-colored solutions.

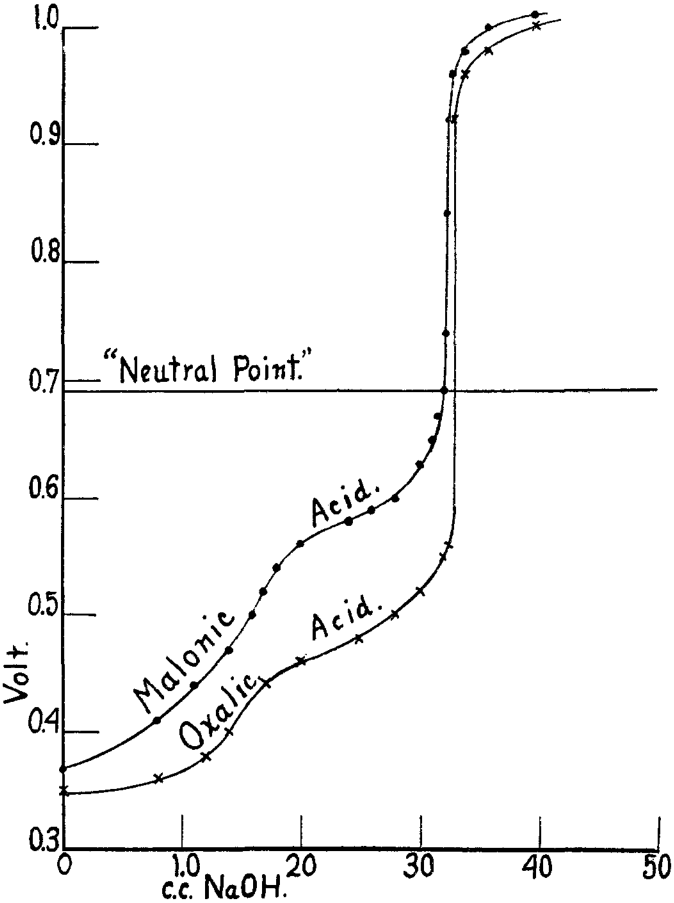

Fig. 9.—Oxalic acid and malonic acid.

These curves represent the effect of mannite in the titration of boric acid. The first, boric acid alone, has been determined previously by Böttger,[1] and later by C. L. A. Schmidt and C. P. Finger.[2] The other

---

[1] *Loc. cit.*

[2] *J. Phys. Chem.*, 12, 406 (1908).

curves represent the results of adding to 0.812 gram of boric acid 1, 3, 5, 7 and 9 grams of mannite successively, the last addition corresponding to 3 mols of mannite to 1 mol of boric acid. We see from the curves why phenolphthalein, changing at about 10^{-8}, does not give the end point in titrating boric acid alone, but that the addition of mannite produces a great increase in the strength of the acid permitting its titration with this indicator. We see further how we might choose an indicator changing at 10^{-11} to titrate without the addition of the mannite. The reason for this increase in the strength of boric acid in the presence of mannite is being investigated further in this laboratory.

These curves show the effect of structure on the dissociation of the two hydrogen-ions of these acids. Proximity strengthens the first but weakens the second, so that the first dissociation of maleic acid is greater than that of fumaric acid, while the reverse is true of the second. Moreover, there is a much greater difference between the two ions of maleic acid than of fumaric acid. This has all been pointed out before by means of dissociation constants, but visualizing the difference in this way may prove of interest to teachers, at least.

The ionization relations of these acids are evident in these curves, and time need not be consumed in their discussion. It is interesting to

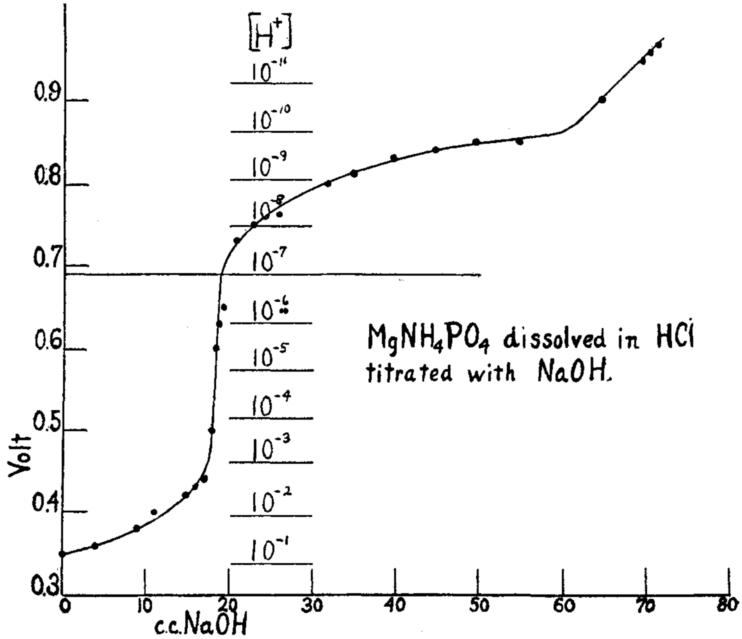

Fig. 10.—The volumetric determination of magnesium ammonium phosphate precipitate.[1]

---

[1] Titration by Mr. Philip S. Gunion.

note the curve for oxalic acid in connection of the work of Wm. Blum[1] of the Bureau of Standards on the preparation of pure normal sodium oxalate. The middle of the abrupt rise in this curve corresponds very closely to the turning point of phenolphthalein, the indicator selected by Blum. The ease with which such a problem is solved by these curves deserves special emphasis.

The determination of this precipitate volumetrically is a well-known procedure, and although the indicator is known in this case it will serve to illustrate the choice of an indicator in a case that would naturally be rather confusing. The presence of the ions of the weak bases, ammonia and magnesia, and of the tribasic weak phosphoric acid makes the choice of an indicator by the usual criteria very uncertain. The curve, however, makes it quickly evident that the solution of the precipitate in hydrochloric acid can be accurately titrated back with strong alkali by the use of methyl-orange.

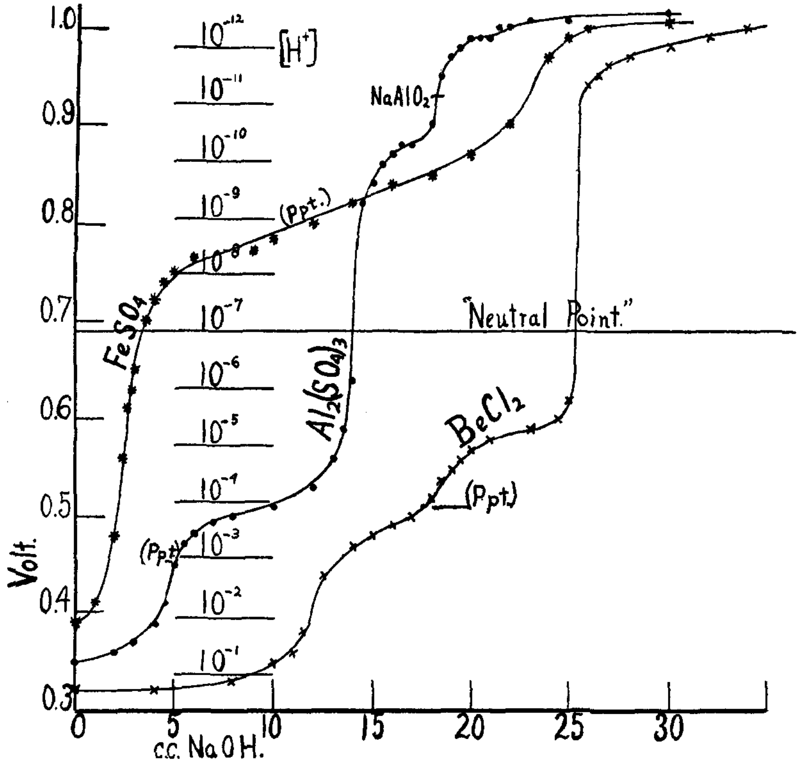

Fig. 11.—Action of sodium hydroxide on salts of aluminium, beryllium and ferrous iron.

---

[1] *J. Phys. Chem.*, 12, 406 (1908).

Much of interest and importance is brought to light by titrations of this type. If we notice first the curve for ferrous sulfate we see that the (acidulated) solution must be made alkaline before ferrous hydroxide is precipitated. Aluminium hydroxide, however, is precipitated while the solution of aluminium sulfate is still strongly acid, the hydrogen-ion concentration during the precipitation varying roughly between 10^{-3} and 10^{-5}. This is of interest in connection with the separation of iron from easily hydrolyzed metals. Ferric salts cannot be investigated with the hydrogen electrode because they are reduced by it, but there is every reason to believe that they would behave very much like aluminium salts, hence we see the value of keeping iron in the ferrous state when separating, *e. g.*, from titanium. We see also why ferrous hydroxide is not precipitated by boiling with sodium thiosulfate whereas those of aluminium, ferric iron, etc., are precipitated by this reagent.

The recognition of normal aluminium sulfate is a problem of considerable importance both to the maker and to the buyer of this salt. It is very easy to see what point in the curve corresponds to the normal salt, so that the hydrogen electrode could easily be used for this purpose. One of the students in this laboratory will soon have ready for publication an indicator method, worked out by the aid of this curve, by which the ratio of SO_3 to Al_2O_3 can be very rapidly and simply determined by one to whom the use of the hydrogen electrode might appear too formidable.

The solution of aluminium hydroxide in an excess of alkali is indicated by the final portions of the curve. It will be seen that the proportion of alkali used corresponds to the formation of $NaAlO_2.nH_2O$. There seems also to be a slight break in the curve corresponding to the addition of another equivalent of base. This cannot be regarded as certain until confirmed by more accurate measurements. We believe, however, that the curve here given supports the theory of the solution of aluminium hydroxide as an acid rather than as a colloid, as claimed by Mahin, Ingraham and Stewart.[1] The ultramicroscope, which these investigators seem not to have applied and which should give rather decisive evidence for or against a colloid theory fails to show the presence of a colloid in this solution, although the ordinary solutions of aluminium hydroxide produced by dialysis show submicrons very plainly in the ultramicroscope.

The curve for beryllium chloride seems to show the formation of a soluble basic salt before the precipitation of the hydroxide. The solution of the latter in alkali cannot be seen from the curve, as the alkali was not concentrated enough for that purpose. We see, on comparing the curves for aluminium and beryllium, that the hydroxide of the former is precipitated in a more acid solution than that of the latter. Hence aluminium

---

[1] THIS JOURNAL, 35, 30 (1913).

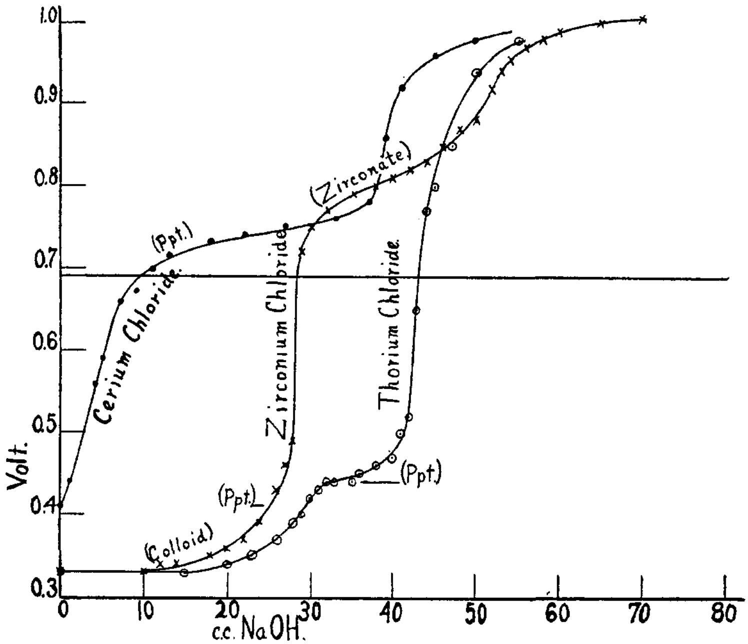

Fig. 12.—Action of sodium hydroxide on chlorides of cerium, zirconium and thorium.

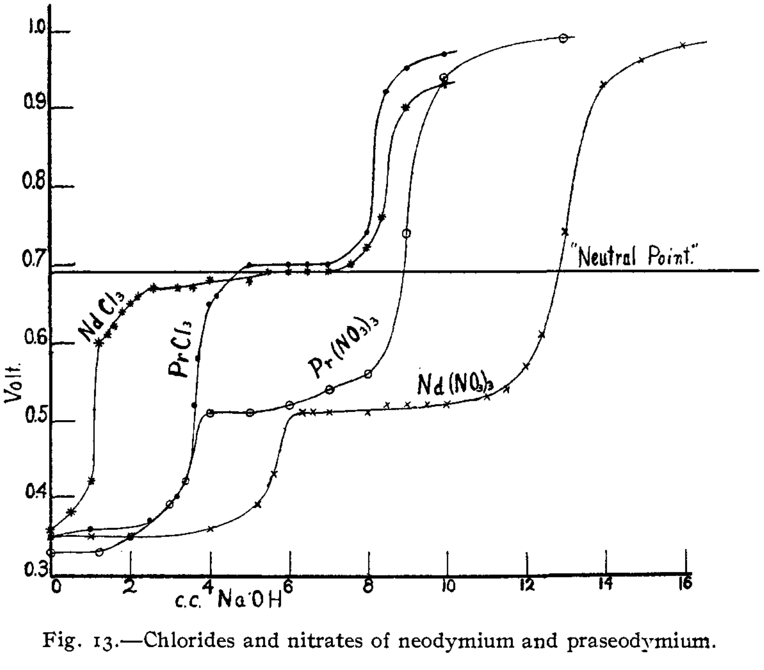

Fig. 13.—Chlorides and nitrates of neodymium and praseodymium.

hydroxide would be more readily precipitated by such a reagent as sodium thiosulfate, but since the difference between the two hydroxides is not very great no very good results can be expected from such a separation. Similar considerations apply to the reprecipitation of the hydroxides from their solutions in alkalis.

Considerations similar to those just discussed apply to these curves. It is evident that the separation of zirconium and thorium from cerium by salts yielding small amounts of hydroxyl by hydrolysis is very effective. The action of potassium azide as a precipitant for thorium is to be explained in this way. It is evident that its virtues, of which we learn in the literature, are not at all peculiar. There are a great number of salts of weak acids which might be used for the same separations by proper adjustment of the hydrolysis, if necessary, by the addition of an excess of the acid. Basic acetate separations are a familiar example of the principle involved. The feasibility of such separations could be quite readily predicted by means of this kind of curves.

Attention should be called to the evidence shown by the curve for the formation of the insoluble alkali zirconate.

The zirconium hydroxide seems to be formed first as a colloidal solution and then suddenly coagulated when a certain concentration of hydroxyl-ion is reached. Thorium hydroxide, on the other hand, seems to be precipitated as it is formed.

The possibility of predicting separations by this means invited its application to this difficult separation. All that we can do just now is to illustrate the method of attack and show proof that one conceivable method of separation is impossible. It will be seen from the curve that the hydroxides are precipitated at almost the identical concentration of hydroxyl-ion, hence a separation or even a fractionation of the hydroxides by any reagent is hopeless. We were somewhat excited by a difference originally observed which we show here to be due to the different hydrogen-ion concentration required for precipitation when nitrates are used. If the same salts of both metals are used then no difference is to be found. It is important to note the different behavior of the nitrates and chlorides, the former evidently giving less soluble basic nitrates. This may account for some of the trouble that arises in certain reactions. An author may work out a separation on the hydrolysis principle, and if he uses chlorides, the next investigator, who may use nitrates or sulfates, may be quite unable to reproduce the results of the other.

This separation is to receive further study by precipitating compounds other than the hydroxides. The salts of a weak acid may be dissolved in hydrochloric acid and titrated with alkali, when a difference in solubility would become apparent and could be used as the basis for a separation. The chromate separation of barium and strontium by proper adjustment of acidity is an illustration of the type of reaction we hope to discover for the separation of didymium into its constituents.

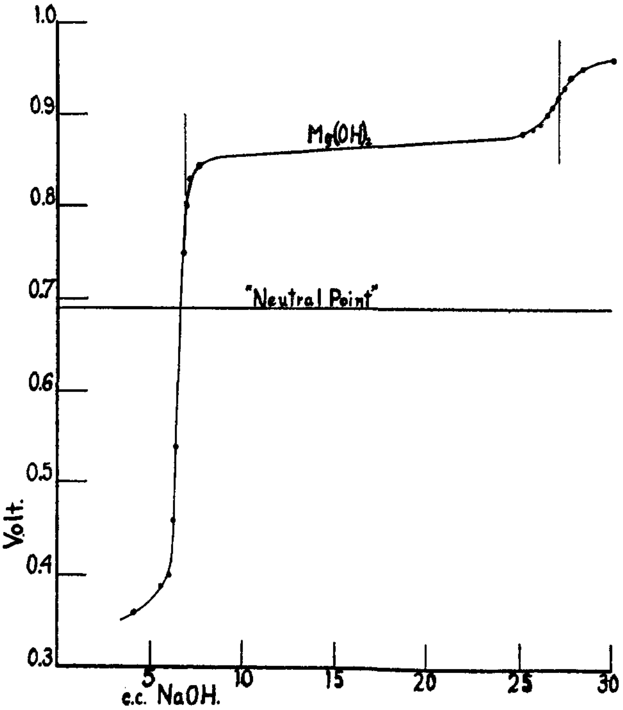

Fig. 14.—The titration of magnesium in the presence of calcium.[1]

If hydroxyl-ion is added to a solution containing both calcium and magnesium-ion, the smaller solubility of magnesium hydroxide causes it to be precipitated before calcium hydroxide, and a smaller concentration of hydroxyl-ion is necessary to precipitate the former than the latter. Furthermore, as long as magnesium-ion is present in the solution in any quantity the concentration of the hydroxyl-ion cannot increase very much as the latter is attacked and precipitated by the former. As soon, however, as magnesium-ion is practically all removed from the solution, the concentration of hydroxyl-ion can then increase to a value sufficient to precipitate the calcium-ion present. This increase, although not very great, is enough to show the end of the first reaction. Fig 14 shows the type of curve obtained by titrating a sample of dolomite dissolved in hydrochloric acid and boiled free from carbon dioxide. As soon as the excess of acid is neutralized the e. m. f. rises abruptly till the precipitation of magnesium hydroxide begins. It then rises very slowly until this reaction is finished, and then more rapidly till the precipitation of calcium

---

[1] Already published (*loc. cit.*) by Hildebrand and Harned, *loc. cit.*

hydroxide begins. The point of inflection here indicates the amount of alkali necessary for the precipitation of the magnesium hydroxide.

With the hydrogen electrode as an indicator it is possible to make this titration very rapidly. The detrimental effect of magnesia in limestone makes its estimation a matter of considerable importance. Unfortunately, however, the ordinary method of determining magnesium in the presence of calcium requires the preliminary precipitation of iron, calcium, etc., before the separation of the magnesium. The skill and experience necessary to make a good separation of calcium and magnesium, and the time necessary to complete both of these precipitations are disadvantages which the technical man would doubtless often be glad to overcome. The method here described allows the determination of magnesia in lime to be made with an accuracy more than adequate for all technical purposes, and in a very short time.

To carry out a determination, the sample, say, of limestone, is first weighed out, the quantity depending upon the magnesia content and the accuracy desired. The end point of the titration can be determined to about 0.2 cc., using normal alkali, which corresponds to 0.004 gram MgO. Therefore, a sample containing about 0.4 gram MgO, and requiring 20 cc. for its precipitation, could have its magnesia content determined with an accuracy of about 1 part per 100. Greater accuracy is, of course, offset by slightly greater time, so that the amount of the sample must be determined according to the conditions.

The sample having been weighed out, with an accuracy of 1 part per 100, it is transferred to a small round-bottomed flask, sufficient dilute hydrochloric acid added to effect its solution, and the last traces of carbon dioxide expelled by boiling for a moment under reduced pressure by the aid of a filter pump. A safety trap should be inserted between the flask and the pump. As soon as the solution of the sample is complete and the carbon dioxide expelled, the contents of the flask are washed out into a beaker for titration. The gang does not interfere and need not be filtered out.

The hydrogen electrode and the siphon of the calomel electrode are next inserted into the solution, and the titration begun. Time is saved if the hydrogen electrode has been previously saturated while dipping into distilled water. A moment is necessary for the readings to become constant due to the contact of the electrode with the air in transference. The normal alkali, free from carbonate, is added until the e. m. f. begins to rise. The neutralization of the excess of hydrochloric acid may be quickly effected if methyl-orange is present and the alkali added until it just turns yellow. This will indicate the beginning of the rapid rise in the curve, before which e. m. f. readings are unnecessary. The readings of e. m. f. from now on should be plotted directly as they are taken on cross-section paper. The parts of the curve to be observed carefully are the end of the first rise and the final rise from the precipitation of magnesium hydroxide to that of calcium hydroxide. Along this portion readings should be taken every 0.2 cc. The point of inflection of the smooth curve drawn through these points is taken as the end of the reaction. Iron (ferric) and aluminium, if present, should not interfere as they are precipitated while the solution is still acid, before the magnesium comes down.

TABLE II.

Wt. sample.	Cc. N/NaOH.	Wt. MgO.	% MgO.
1.297	12.1	0.242	18.7
1.297	12.2	0.244	18.8

Gravimetric 18.75

TABLE III.

Wt. sample.	Cc. N/NaOH.	Wt. MgO.	% MgO.	Time.
0.524	5.4	0.109	20.8	$2^1/_2$ hours
0.535	5.4	0.109	20.4	
0.471	4.8	0.097	20.6	
0.485	5.1	0.103	21.2	
2.048	20.7	0.418	20.4	2 hours
2.012	20.1	0.406	20.2	
		Mean	20.6	
		Gravimetric	20.82	

The results obtained by Harned are shown in Tables II and III. Those in Table II represent the first quantitative experiments made, so that it is evident that no special experience is necessary beyond an understanding of the manipulation. The first four results in Table III were obtained simultaneously. Each sample was weighed out and its solution started successively, so that by the time the fourth was in the flask the first was ready for titration. The time required, two and one-half hours, includes the initial weighing and the final calculation of the results. The next two determinations were made with larger samples and no great effort for speed was put forth.

This titration does not, strictly speaking, belong under the title of this communication, as it is not a hydrogen electrode that is used but simply a platinum electrode. The curve, therefore, represents not the acidity of the solution but the oxidizing power. Such an electrode is charged more positively the greater the oxidizing power of the solution, and therefore undergoes a rapid change of potential when the last traces of a reducing substance are oxidized by an added oxidant, and *vice versa*. This method of determining the end point in such reactions was proposed by Crotogino.[1]

The disadvantages of titrating iron with permanganate in the pres-

---

[1] *Z. anorg. Chem.*, **24**, 225 (1900).

ence of hydrochloric acid are well known, as is also the greater ease, on the other hand, with which hydrochloric acid solutions can be obtained in most cases. The substitution of bichromate for permanganate requires the use of the time-consuming external indicator. This is obviated by determining the oxidation potential of the solution with the apparatus here described.

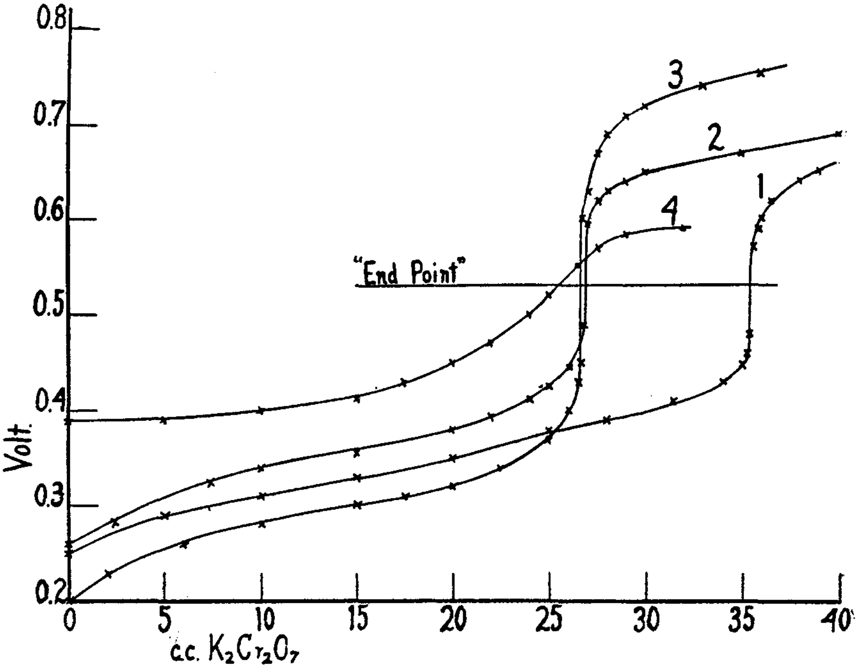

Fig. 15.—Titration of iron with potassium bichromate.[1]

Fig. 16 gives typical curves obtained by titrating ferrous-ammonium sulfate in this way. The quantities involved are given in Table IV. It will be seen that concentrated hydrochloric acid would be present in order to get a sharp end point. Curve 4, with the acid dilute, was quite unsatisfactory, whereas the others gave very sharp end points. In making a determination of iron it is not necessary to construct a curve. It is sufficient to set the voltmeter at the middle of the rise in the curve, about 0.53 volt, and add bichromate solution until, on pressing the key, the electrometer or galvanometer reverses its deflection. As the end point is approached the deflections become less marked. This results in a saving of time over the "spot-plate" indicator, besides making it easier to avoid running past the end point. The greatest variations found in making titrations in this way have been one part in three hundred.

---

[1] Experimental work by Mr. Edward J. Pugh.

TABLE IV.

Curve.	Acid.	Water.	Wt. Mohr's salt.	Gr. Fe = 1 cc. KCrO.
1	50 cc. conc. HCl	100 cc.	1.40	0.00560
2	50 cc. conc. HCl	100 cc.	1.05	0.00559
3	100 cc. conc. HCl	50 cc.	1.05	0.00560
4	25 cc. c *n*/5 HCl	125 cc.	1.05	—

The writer desires to express his thanks to Messrs. Herbert S. Harned, Edward J. Pugh, and Philip S. Gunion, for some of the titrations reproduced in this paper.

Summary.

In this paper attention is called to the value of the hydrogen electrode as an indicator in titrations, as first proposed by Böttger, and apparatus is described whereby titrations can be made with the ease and rapidity required for practical use.

Curves are given representing titrations of a number of acids, bases and salts. By the aid of these curves many interesting facts are made clear, such as the differences between acids and bases of different strengths, the distinction between normal and neutral salts, and the phenomena of hydrolysis. A reliable method is shown for preparing normal salts.

The use of these curves in choosing indicators is explained, and attention is called to the fact that they offer the most reliable method we have for that purpose. The large effect of certain salts and other substances on the color change of many indicators makes it unsafe to rely solely on calculations from dissociation constants, even where these are known, and the selection of the indicator from tables such as those of Salm. In difficult cases the only sure method is to have the probable indicator present while titrating with the hydrogen electrode, and see if the indicator changes color at the point of inflection of the curve.

The hydrogen electrode can be used alone for titrations where some circumstance such as the color of the liquid prevents the use of an indicator.

A number of precipitations have been studied by this means, and illustrations given to show how separations of metals may be predicted and controlled.

A method is described for the rapid determination of magnesium in the presence of calcium.

If instead of a hydrogen electrode an unattackable electrode is submerged in the liquid, the rest of the apparatus being the same, it is posible to follow oxidation and reduction reactions, and not be limited to the ordinary cases where color changes occur. As an example is given the titration of ferrous iron with bichromate, where it is shown that the method is superior in speed and accuracy to the use of an external indicator.