VOLUMETRIC ANALYSIS OF METALS IN GLACIAL ACETIC ACID

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE in the Department of Chemistry

We accept this thesis as conforming to the standard required from candidates for the degree of MASTER OF SCIENCE.

Members of the Department of Chemistry.

THE UNIVERSITY OF BRITISH COLUMBIA
April, 1953
ABSTRACT

Recent work has demonstrated that certain metal salts of inorganic acids may easily be titrated with perchloric acid in glacial acetic acid. To test the accuracy of the method, a series of titrations was run on the acetates of twenty-three representative metals. The resulting curves show that accurate reproducible end points may be obtained for the acetates of the more electropositive metals, while those of aluminum, chromium and iron yield anomalous results. An explanation for this is offered. The acetates of tin, bismuth, antimony, uranium and copper are too weak to be determined by this method.

Metals, oxides, or other more difficultly soluble compounds may be conveniently introduced into acetic acid solution by first dissolving in nitric acid (or in certain cases aqua regia), followed by the addition of sufficient acetic anhydride to react with all the water and decompose all the nitrate present. Quantitative analytical separations may be effected using such common reagents as oxalic, nitric, and tartaric acid, hydrogen iodide and hydrogen sulphide. They were used in analysing eleven metal mixtures, with accuracy comparable to the more lengthy gravimetric process often required in aqueous solution.
ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to my research director, Dr. K. Starke, for his invaluable aid and encouragement during the course of this investigation.

I also wish to thank the International Nickel Company for financial support of this work, and Major Aluminum Products of Vancouver for a sample of aluminum-magnesium alloy.
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I. INTRODUCTION

Until recently, water has been the solvent employed for most analyses, both qualitative and quantitative. However, it is impossible to carry out reactions, such as neutralization, involving acids (or bases) appreciably weaker than water, since water, being a stronger acid (base), will react preferentially with the added reagent. For this reason, in the last three decades, non-aqueous solvents have become increasingly important in analysis, particularly in quantitative determinations, since acid-base titrations in these media possess the accuracy, speed, and simplicity required for good analytical methods.

In order to characterize the properties of interest in nonaqueous solutions, it is useful to review the particular properties of water which are responsible for the unique position it occupies among solvents (34). Water, available in large quantities, is an excellent solvent for most classes of substances, both electrolytes and non-electrolytes. The pure solvent is a poor conductor of electricity, but aqueous solutions of electrolytes have high conductivities. Moreover, water has the ability to convert potential electrolytes into true electrolytes. Many substances, such as sulphur dioxide, ammonia, hydrogen chloride, and tertiary amines, which by themselves are non-electrolytes, react with water to give solutions which are excellent conductors. Neutralization reactions between strong acids yielding hydronium
ions and bases yielding hydroxyl ions occur easily in water, a process made possible by its limited self-ionization. The phenomenon of hydrolysis is a characteristic reaction of water. Not only do dissolved salts undergo hydrolysis, but many substances such as acyl chlorides, esters, and salts of very weak acids react chemically with the solvent in such a way that the original solutes cannot be recovered directly.

The superiority of water as a general solvent is reflected more precisely through its exceptional and anomalous physical properties. The high values of its melting point, boiling point, heat of vaporization, and dielectric constant, and its low viscosity, distinguish it as a solvent of the highest general utility. However, there are properties of nonaqueous media which indicate that they are, in certain specialized circumstances, superior to water as a solvent.

One of the most striking of these properties is the high acidity displayed by solutions of $\text{HClO}_4$, $\text{H}_2\text{SO}_4$, and $\text{HCl}$, for example, in aprotic liquids such as benzene or chloroform, or in acid solvents, such as glacial acetic acid. These compounds are strongly acidic and completely ionized in aqueous solution, but are even more acidic in solvents of lesser ionizing power. Moreover, the acid strengths of $\text{HClO}_4$, $\text{H}_2\text{SO}_4$, and $\text{HCl}$ differ widely in these media, whereas in water they are indistinguishable for equal concentrations. That such phenomena occur may at first seem surprising, but, as the ensuing discussion shows, they arise as a logical
consequence of the Brönsted-Lowry concept of acids and bases.

The concept of electrolytic dissociation has dominated the field of acid-base chemistry for over half a century. Until 1926 it was considered to be the full explanation of acid-base phenomena, although it was realized that the theory could not be applied to solvents other than water. There were scattered reports of titrations in nonaqueous media (19,20,21), but it was not until Hantsch (30) published his series of investigations that a departure from the prevailing theory became evident. The appearance of the Brönsted-Lowry theory (2, 3, 4, 5, 42, 43) and the classic investigations by Conant, Hall, and Werner (7, 8, 26, 27, 28) on acidity in glacial acetic acid, put the following analysis on a sound experimental and theoretical basis.

It has been shown by Brönsted that a logically consistent general measure of acidity is the hydrogen-ion potential, or the closely related hydrogen-ion activity. It has been found that the use of activities instead of potentials is convenient, but it should be noted that this does not imply any knowledge of the concentration. Hydrogen-ion activity is defined as an exponential function of the hydrogen-ion potential, which represents the work concerned in the reversible removal of hydrogen ions from a given system, or their addition to it. High activity means loosely bound hydrogen ions; low activity implies strongly bound hydrogen ions. A reaction proceeds by the transfer of hydrogen ions
from higher to lower activity, although hydrogen ions as such do not exist to a measurable extent in the solution.

Since only the ratios of activities may be measured, one must always set up an arbitrary scale of numerical values. Usually different conventions are adopted for different solutions such that the activity coefficient approaches unity at infinite dilution, but this is not satisfactory when solutions of the same solute in various solvents are considered. If the same scale is used for a set of solvents, then two solutions with the same hydrogen-ion potential (i.e. the same true acidity) will have the same hydrogen-ion activity, no matter what the solvent, but it also follows that the activity coefficient will not approach unity for infinitely dilute solutions.

With this understanding, following Hammett (29) we may consider a mathematical approach to the effect of solvent upon acidity. Let HX be the acid concerned; S the solvent; C the concentration; a the activity; f the activity coefficient; and C_a the stoichiometric concentration of HX. Regardless of the solvent, we have

\[ a_{H^+} = K_{HX} \frac{a_{HX}}{a_{X^-}} = K \frac{C_{HX}}{C_{X^-}} \frac{f_{HX}}{f_X} \quad (1) \]

but if the solvent is basic we also have

\[ a_{H^+} = K_s \frac{a_{SN^+}}{a_s} = K_s \frac{C_{SN^+}}{C_s} \frac{f_{SN^+}}{f_s} \quad (2) \]
If, as seems probable, $C_{H^+}$ may be considered negligibly small

$$C_a = C_{HX} + C_{X^-} = C_{HX} + C_{SH^+}$$  \hspace{1cm} (3)$$

since the reaction between the acid and the solvent is $HX + S \rightleftharpoons X^- + SH^+$. A combination of 1, 2 and 3 gives

$$a_{H^+} = \frac{K_{HX}}{2} \left\{ -1 + \sqrt{1 + 4 \frac{C_a K_S}{K_{HX}} \frac{S_{SH^+} S_{X^-}}{S_a S_{HX}}} \right\}$$  \hspace{1cm} (4)$$

Since $a_{H^+}$ increases with increasing $K_y$ this equation records the principle that decreased basicity of the solvent (greater $K_y$) means greater acidity, although it means less ionization.

In order to see more clearly the effect of changes of the dielectric constant, we may consider two limiting cases of 4. When the second term under the radical sign is large compared with one, we obtain

$$a_{H^+} = \frac{\sqrt{C_a K_S K_{HX} S_{SH^+} S_{HX}}}{S_a S_{X^-}}$$  \hspace{1cm} (5)$$

This is the case for a weak acid or weakly basic solvent; the reaction $HX + S \rightleftharpoons X^- + SH^+$ is incomplete and the acidity depends on both $K_y$ and $K_{HX}$, i.e. upon the properties of both acid and solvent. On the other hand, when the same term is small the radical may be expanded and using only the linear term we have

$$a_{H^+} = \frac{C_a}{S_a} \frac{K_S S_{SH^+}}{S_{X^-}}$$  \hspace{1cm} (6)$$

Here ionization is large and the acidity depends only on
the properties of the solvent. This represents the levelling effect of the solvent, mentioned by Hantsch and by Conant and Hall.

It is now possible to make at least a qualitative prediction of the effect of the dielectric constant from the known effect of this property upon the activity coefficients. The activity coefficient of an ion is greater in solvents of low than of high dielectric constants, as demonstrated by the extremely low solubility of true salts in such media. This is predicted by the interionic attraction theory of electrolytes. The changes in activity coefficients of uncharged molecular species from solvent to solvent are much smaller than the changes of the ionic activity coefficients. Therefore, it follows that ratios such as $\frac{f_{HX}}{f_X}$ or $\frac{f_S}{f_{SH}^+}$ will decrease with decreasing dielectric constant. Now, as an admittedly rough approximation, assume that the change in this ratio between two different solvents is independent of the acid or base concerned. There is some reason for believing that specific effects upon the ratio will be considerably smaller than on the individual activities, corresponding to the impression that acids and bases very soluble in organic liquids will have salts which are soluble in organic liquids.

It then follows that the ratio $\frac{f_{SH}^+ f_{HX}}{f_S f_X}$ in equation 5 will be approximately unity for all solvents; that the hydrogen ion activity of a weakly ionized acid is independent
of the dielectric constant of the medium. It follows from equation 6 that the hydrogen ion activity of a highly ionized acid will be greater in solvents of low than in solvents of high dielectric constant. For intermediate cases, a decrease in the dielectric constant will result in a more or less large increase in the hydrogen-ion activity.

From the work of Conant and Hall, and from the above discussion, it appears that there are three principal influences affecting the apparent strength of an acid in a given solvent. The first is the "intrinsic strength" of the acid, the general tendency of the molecule to liberate a proton. The constant expressing this tendency may be regarded as fixed and equal for all solvents at any given temperature. Next, there is the basic strength, or protophilic tendency, of the solvent, which determines to what extent the true strength of the acid can manifest itself. Finally there is the dielectric constant of the solvent which determines the extent to which the ions, products of the reaction of the acid with the solvent, can exist independently of each other. Water is a basic solvent of high dielectric constant. Therefore, strong acids react completely with it, and the products exist as separate ions.

\[ \text{HClO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^- \]

The acidity of a dilute solution in water can never be very high, however, because the acid molecules all react to pro-
duce hydronium ions, whose proton activity is not very great.

In a non-basic solvent, such as acetic acid or benzene, the acid molecules will combine with the solvent to a much less extent, so that the proton activity of their individual molecules may give a high acidity to the solution, although, because of the low dielectric constant there will be few (unassociated) ions. Although as yet no method exists to compare the acidities of solutes in different solvents in a completely rigorous manner, it has become evident that these predictions are fulfilled. Thus it may well be possible to prepare a series of solutions containing only moderate concentrations of the strongest acids in suitable solvents whose true acidities range well into the million fold values of those obtainable in water solution at the same concentration. As indicators can be found which are sensitive in the range of high absolute acidity, it should be possible to develop a "pH technique" which will extend to high negative values. One must always remember, however, that the true measure of acidity is to be taken as the hydrogen ion activity as measured with a suitable electrode, and not other less precise effects.

These conclusions may be amplified by an illustrative example. Many very weak anhydro bases, which do not form salts in aqueous solutions, are neutralized by perchloric or sulphuric acid in glacial acetic acid solution. This is shown by the titration curves obtained by Conant and Hall
It should be noted that in the formation of salts from anhydro bases, no water is eliminated, and so the water activity is not involved. Their results confirm experimentally that, whether acid strength is defined in terms of the relative hydrogen ion activities of their equimolal solutions, or in terms of salt formation with anhydro bases, perchloric and sulphuric acids are stronger in acetic acid than in water.

At present we have some information about the behavior of acids in a wide variety of solvents, of which ammonia, water, and glacial acetic acid may be considered as representative examples. In each medium, evidence points to the proton being completely solvated. In comparing the three solvents, one is led to consider that the essential difference between glacial acetic acid and water is the same as that between water and ammonia. The acetic acid molecule has less affinity for a proton than the water molecule; the \( \text{CH}_3\text{COOH}^+ \) ion gives up its extra proton more readily than \( \text{H}_3\text{O}^+ \).

The formation of a salt from an anhydro base is the reverse of the dissociation of the acid. The anhydro base \( (B) \), the anion of the acid \( (X^-) \) and the solvent molecule \( (S) \) may all be regarded as competing for the proton \( \text{H}^+ \). Therefore the following equations may be written:

\[
\begin{align*}
X^- + \text{H}^+ & \rightleftharpoons \text{HX} \quad \text{(7)} \\
B + \text{H}^+ & \rightleftharpoons \text{BH}^+ \quad \text{(8)} \\
S + \text{H}^+ & \rightleftharpoons \text{SH}^+ \quad \text{(9)}
\end{align*}
\]
Probably in most solvents the amount of unsolvated proton is small, but we may still formulate the reaction of salt formation of B:

\[
SH^+ + B \rightleftharpoons BH^+ + S
\]

in terms of the competing reactions 8 and 9 on Page 9. A very weak base B (corresponding to a very strong acid BH\(^+\)) will only form stable salts in a solvent which has considerably less affinity for the proton than B itself. Also it is obvious that salt formation can only occur with an anion (X\(^-\)) which will release the proton to B. The interrelation of these three competing reactions is illustrated in Fig. 1, due to Conant and Hall (7).

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<tr>
<th>Acid Ion</th>
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<tr>
<td>(C_6H_5O^-)</td>
<td>NH(_3)</td>
<td>RNH(_2)</td>
</tr>
<tr>
<td>RCOO(^-)</td>
<td></td>
<td>C(_6)H(_5)NH(_2)</td>
</tr>
<tr>
<td>CCl(_3)COO(^-)</td>
<td>H(_2)O</td>
<td></td>
</tr>
<tr>
<td>(C_7H_7SO_3^-)</td>
<td>AcOH</td>
<td>NH(_2)CONH(_2)</td>
</tr>
<tr>
<td>HSO(_4)^-</td>
<td></td>
<td>CH(_3)CONH(_2)</td>
</tr>
<tr>
<td>ClO(_4)^-</td>
<td></td>
<td>C(_6)H(_5)NHCOCH(_3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C(_6)H(_5))^(_3)N</td>
</tr>
</tbody>
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**FIG. I**

Relative Basic Strengths of Certain Acid Ions Solvents and Organic Bases
The position of some common acids, anhydro bases and three solvents are indicated by the formulas. The scale is arbitrary; lack of data still makes it impossible to evaluate exact relationship.

Acids are strong only in the solvents lying above them in the diagram, e.g. perchloric is strong in all three solvents; sulphuric and hydrochloric in water and ammonia; and RCOOH only in ammonia. Anhydro bases are neutralized by one equivalent of any acid which is stronger than their "onium" ions, provided that the action occurs in a solvent lying below the position of the ions on the scale. Thus RCONH₂ is neutralized only in acetic acid and only by perchloric acid. If any solvent is found in which triphenylamine may be titrated, it will lie beneath acetic acid on the diagram.

Since perchloric acid is very strong in acetic acid, and since the acidic nature of the medium prevents solvolysis of salts of strong acids and weak bases, one may conclude that acetic acid is an excellent solvent for the analysis of substances weakly basic in nature. The work of Conant and Hall provided the basis for all subsequent investigations, but it has only been in the past fifteen years that sufficient interest has arisen in the method to yield practical dividends. In this period, procedures have been published for the determination of pyridine and various pyrimidines (48); amines (1, 22, 23, 44, 61), amino acids and alcohols (38, 44, 47, 58, 59, 60); oxazolines (44);
quinine and nicotine (31, 35); alkylene oxides (1); sulphonamides (61); basic nitrogen in oils (71); and choline salts of carboxylic acids (45). More closely related to the subject of this paper was the determination of the solubilities of certain inorganic salts in acetic acid by Davidson and his co-workers (9-17, 24, 25) and by Kolthoff (40), followed by the successful analysis of metal salts of carboxylic acids and of strictly inorganic salts by Pifer and Wollish (50, 51, 53), Higuchi and Concha (32, 33), and Markunas and Riddick (44). Since Davidson has shown (9) that metathetical reactions may proceed as easily in acetic acid as in water, these last results indicate that rapid and accurate quantitative analyses could be carried out on one or more metal compounds provided they could be easily introduced into acetic acid solution and that methods of separation could be found. It was the object of this investigation to begin developing such methods.

II. EXPERIMENTAL

A. Materials and Apparatus

For every titration, the sample was dissolved in anhydrous acetic acid. The ordinary C.P. grade of commercial acid was purified by the method of Kendall and Gross (37), that is, by adding the calculated amount of acetic anhydride to react with the water present, then distilling twice using a thirty-inch helix type column. The fraction boiling at 117-118°C. was collected; samples melted at 16.5°C. (lit.
Two solvents were used for the titrating solution of perchloric acid: glacial acetic acid and 1, 4-dioxane. The latter was reagent quality solvent, purified according to Vogel (63), and distilled twice. The fraction boiling between 100.5°C. and 101.5°C. was collected; samples had a melting point of 11.8-11.9°C. (lit. 12°C. (63)).

The titrant used in all cases was an approximately tenth normal solution of perchloric acid in either glacial acetic acid or dioxane. These were prepared as follows:

(a) Acetic acid solution.

Approximately thirty-one ml. of a 60% aqueous solution of perchloric acid were mixed with glacial acetic acid (500 ml.), chilled acetic anhydride (33 ml.) was added, and the solution diluted to two liters. It was necessary to allow the solution to stand overnight (or preferably two to three days) to allow the anhydride to react with the water present. This solution could be used with both indicator and potentiometer.

(b) Dioxane solution.

This solution was prepared in a similar manner except that no acetic anhydride was added. Occasionally the solution had a brown color, but this did not influence the acid strength. The solution contained a small amount of water and so could only be used for potentiometric titrations.
Indicator

A 0.5% solution of crystal violet in glacial acetic acid was found to be satisfactory. One drop was sufficient for a fifty-five ml. solution. The color change of crystal violet is not sharp, passing from blue-violet through various shades of blue and green to yellow. The blue-green end point was especially difficult to detect when the titration produced a white precipitate, as with potassium or ammonium salts. The best procedure was to titrate a sample to the end-point potentiometrically, add the indicator and use this solution as a standard.

Potentiometer

Two instruments were used:

(a) A Beckman model G pH meter, serial number 1996, equipped with a glass saturated aqueous calomel electrode system. To obtain maximum sensitivity, the latter was of the sleeve type. The solution inside the electrode was changed frequently to prevent contamination by acetic acid diffusing in.

The calomel electrode could not be used to titrate solutions of lead or silver, since precipitates of the chloride froze the ground glass surface of the electrode. This difficulty was overcome by using a salt bridge consisting of a U-tube, with ground glass stoppers at each end, filled with a supersaturated solution of lithium acetate in acetic acid, with a little added gelatin to prevent crystallization of
the salt. The U-tube connected the solution being analysed to a saturated aqueous solution of potassium chloride, into which the calomel electrode dipped. A less cumbersome arrangement involved the use of a silver-silver chloride electrode as a reference electrode in place of the calomel electrode.

(b) A Fisher senior titrimeter was used when a series of analyses to the same end point was to be run. The same electrode systems as described above were employed.

**Standardization of the Titrant**

Sodium carbonate, or preferably potassium acid phthalate (57), may be used as a primary standard. Approximately six tenths of a gram were dissolved in glacial acetic acid (55 ml.) and titrated either potentiometrically, or with crystal violet indicator to a blue-green end-point.

Water acts as a weak base in acetic acid. Its presence in the solution when titrating potentiometrically can be tolerated up to 1.5% (44) but it causes erroneous results when using an indicator. To minimize absorption from the atmosphere, it was convenient to use a lipless beaker closed by a thin rubber stopper through which a small hole was punched to admit the burette tip.

One must remember that organic liquids generally have a high coefficient of cubical expansion and hence temperature changes will have an appreciable effect on the normality of the solution. Allowance was made for this by assuming that
the N/10 solution in acetic acid or dioxane had the same coefficient as the pure solvent.

The metals and acetates were of the best obtainable purity, and were used without further purification. Other compounds were prepared as described.

B. Titration of Metal Salts

The metals studied were to be titrated as acetates, so, to determine the sensitivity and accuracy of the method, series of titrations were carried out on metal acetates as described below. To check the accuracy each salt was analysed by the method indicated, according to the instructions in Vogel's "Quantitative Analysis" (64). The results of all the determinations are listed in Table 1.

Sodium Acetate

The anhydrous salt was dried for one hour at 110°C. A convenient solution for titration contained three milliequivalents of the salt in forty milliliters of acetic acid. This concentration was used in all subsequent analyses. It was necessary to warm the mixture to effect rapid solution; the solution was then quickly chilled and titrated immediately, either potentiometrically or to the blue-green crystal violet end-point. The gravimetric check was as sodium magnesium uranyl acetate.

Acetates of Potassium, Lithium, Barium, Strontium, and Ammonium

These were analysed in the same manner as sodium acetate.
Since ammonium acetate is so hygroscopic, it had to be re-crystallized. This is best done from methanol or acetic acid, followed by washing with ether and drying in a vacuum desiccator at one centimeter pressure. All gave equally good results with indicator or potentiometer methods. The salts were analysed gravimetrically as follows:

- potassium as perchlorate
- lithium as sulphate
- barium as sulphate
- strontium as sulphate
- ammonium (volumetrically) by treating with strong base, distilling into excess standard acid and titrating the excess.

**Magnesium Acetate**

Visual determinations with the indicator gave poor results, since the end-point occurs at an ill-defined yellow-green shade. The end point may be determined by comparing the sample being analysed with a solution of indicator + magnesium perchlorate in acetic acid in a Coleman spectrophotometer. However, it was easier and quicker to use the potentiometric method. The gravimetric check was as magnesium ammonium phosphate.

**Acetates of Calcium, Manganese, and Cadmium**

These may be titrated potentiometrically but not with the indicator. The gravimetric checks were as follows:

- calcium as the oxide,
- manganese as manganese ammonium phosphate,
- cadmium as the pyridine thiocyanate complex.

**Acetates of Cobalt and Nickel**

For reasons unexplained, no satisfactory end-point
could be obtained when titrating with the acetic acid solution of perchloric acid. However, reproducible, but poorly-defined, end-points were obtained with a solution of perchloric acid in dioxane. Both cobalt and nickel were determined gravimetrically as the pyridine thiocyanate complex.

**Zinc Acetate**

Zinc acetate is quantitatively insoluble in acetic acid, and so cannot be determined directly. It may be easily analysed by adding a measured excess of HClO₄ solution, and back titrating with standard sodium acetate solution. The gravimetric check was as the pyridine thiocyanate complex.

**Acetates of Lead and Silver**

The calomel electrode could not be used in either determination for reasons described before, so both analyses were carried out using a silver-silver chloride electrode. In addition, silver acetate is only partly soluble in acetic acid, and had to be determined by the back titration method described for zinc acetate. As a check, lead was determined as the molybdate and silver as the chloride.

**Acetates of Iron, Chromium and Aluminum**

Although reproducible end-points were obtained, they yielded anomalous results, so that the method could not be applied directly. The results are discussed further in the next section.

**Acetates of Tin, Antimony, Copper, Bismuth and Uranium**

These acetates behave as if they were essentially
undissociated in acetic acid, and could not be titrated by this method. Since tin (II) usually occurs as the chloride, which interferes with the titration, it was removed by adding the required amount of a standard solution of lead acetate.

**Titration of Chloroacetates**

Several chloroacetates were prepared according to the method of Kastle and Keiser (57). They were all soluble in acetic acid, and, except for the ammonium salt, were analysed by the same method described previously for acetates. Each was also estimated gravimetrically by the same method as for the corresponding acetates, except for ammonium chloroacetate. Its solution in acetic acid and in water changed strength continuously, possibly as a result of conversion into glycine, and could not be titrated.

**Titration of Chlorides**

The presence of the chloride ion interfered with the titration, a difficulty which was overcome by a method due to Pifer and Wollish (50, 52). A slight excess of a solution of mercuric acetate in acetic acid (6 gm. per 100 ml.) was added to the solution to be titrated. The halide was removed as HgX₂, and the acetate ion liberated could then be determined. Mercuric acetate is essentially undissociated in acetic acid (46) and the excess therefore did not interfere. However, on standing, or on the addition of acetic anhydride, a complex mercuric compound is formed (46)
preventing the desired reaction. Hence the solution should be freshly prepared, and appreciable amounts of acetic anhydride must not be present in the solution to be titrated. (The amount of acetic anhydride present may easily be determined (6, 41, 49).)

C. Separation and Analysis of Metal Acetate Mixtures

Solubilities of Metal Salts in Acetic Acid

Zinc acetate was found to be quantitatively insoluble in acetic acid, and could be separated from other salts which were completely soluble by dissolving the mixture in water, adding the requisite amount of acetic anhydride, and filtering.

Various common reagents were tested as precipitating agents with twenty-one representative metals as outlined below. Whenever the metal acetate was only partly soluble in acetic acid, the precipitate was filtered off and the residual solution tested. In all cases, a solution of one milliequivalent of metal acetate in twenty milliliters was used.

Whenever a precipitate was produced upon the addition of one of the test reagents, it was removed by centrifuging and the liquid tested for completeness of precipitation as follows: The solution was evaporated almost to dryness twice with excess concentrated nitric acid to remove all organic matter, and the residue taken up in dilute nitric acid. The solution was then tested for the presence of the
appropriate ion according to the methods outlined in Treadwell-Hall (62).

**Hydrochloric, Hydriodic, and Hydrosulphuric Acids**

In each case the dried gas was passed through the solution until the latter was saturated.

**Sulphuric Acid**

Sufficient chilled acetic anhydride was added to chilled reagent grade acid to react with all the water present. The mixture was allowed to stand out of contact with air for twenty four hours to allow the reaction to go to completion, resulting in a yellow-tinged very viscous liquid. Enough of this was added to each test solution to give a five-fold excess. Those which did not react were allowed to stand for two days, after which a portion of each was diluted with 5% water.

**Nitric Acid**

Reagent grade fifteen molar acid was added to each test solution to give a five-fold excess.

**Phosphoric Acid**

Reagent grade 85% acid was added to each solution to give about a five-fold excess.

**Benzoic, Oxalic, Salicylic, Tartaric Acids**

These are not very soluble in acetic acid at room temperature, so a saturated solution at 100°C. was used, the test solutions also being maintained at this temperature. About a five-fold excess was added in each case.
The results of these two hundred ten tests are summarized in Table 2. Since the results with the sulphuric acid were at variance with those of Davidson (9) in that only three metals gave precipitates, the following additional tests were carried out.

The sulphates of Mg, Mn(II), Cr(III), Fe(III), Ca, Co, Nr and Sn(II) were refluxed with glacial acetic acid for four hours, after which the liquid was tested for the presence of the appropriate ion in the manner described before. Then the sulphates were dissolved in water, and sufficient acetic anhydride added to react with all of it, producing the same anhydrous medium as in the first set of tests. The results of these experiments are given in Table III.

Separations Effected

On the basis of the foregoing tests, the following analytical separations were carried out:

Zinc and Magnesium

Three milliequivalents each of the two metals were mixed and dissolved in dilute nitric acid (5 ml.). The solution was diluted with acetic acid (15 ml.) and heated to boiling. Acetic anhydride (33 ml.) was added cautiously, the mixture being boiled until the yellow color disappeared. The beaker was covered with aluminum foil, the suspension digested on a steam bath for ten minutes, chilled in ice-water, and centrifuged. The magnesium solution was titrated immediately. The zinc may be determined as described above, or by difference.
Zinc and Copper

The metals were separated by the same procedure as above. The zinc was determined as described before, and the copper obtained by difference.

Barium and Calcium

Three milliequivalents of each metal were dissolved in nitric acid (5 ml.), the solution diluted with acetic acid (15 ml.), heated to boiling, and acetic anhydride (33 ml.) cautiously added. The solution was boiled until the yellow color disappeared, then chilled in ice water. Concentrated nitric acid (2 ml.) was added, and the solution vigorously stirred. The precipitate of barium nitrate was removed by centrifuging, and the calcium solution immediately titrated. The barium may be determined by difference, or by decomposing the nitrate with acetic anhydride, and titrating in the usual way.

Silver and Aluminum

Three milliequivalents each of the two metals were brought into solution as above, except that concentrated nitric acid was used. The solution was chilled and saturated with dried H₂S gas. The silver sulphide was removed by centrifuging, dissolved in dilute nitric acid, and the solution boiled to expel the liberated H₂S. Sufficient acetic anhydride was added to react with the water and decompose the nitrate. Thirty-five milliliters of standard perchloric acid solution were added, and the excess back-titrated with
standard sodium acetate solution, using silver-silver chloride and glass electrodes.

**Lead-Tin**

The procedure was exactly the same as in the preceding separation; great care had to be exercised not to allow any water to enter the system until the separation was complete, since stannous sulphide would precipitate if water was present. The lead sulphide was removed by centrifuging, treated and analysed as the silver sulphide above.

**Magnesium and Antimony; Magnesium and Lead; Magnesium and Copper**

The lead, antimony, and copper were removed with hydrogen sulphide; the procedure being exactly the same as in the preceding case, except that aqua regia was required to dissolve the antimony. Sufficient mercuric acetate reagent (6 gm. per 100 ml.) was added to the magnesium solution, after removing the sulphide, to react with all the chloride present. The magnesium may then be determined in the usual manner.

If accuracy greater than four percent is not required, the magnesium may be titrated directly in the presence of the antimony. These results were generally of the order of 4% too high.

Similarly, magnesium may be titrated directly in the presence of copper; the results were of the order of 8% too high.
Nickel-Chromium

About three milliequivalents of each metal were mixed and dissolved in dilute hydrochloric (5 ml.) acid (since nitric acid renders chromium passive). The solution was heated to boiling and acetic anhydride (30 ml.) cautiously added. A five-fold excess of a hot solution of oxalic acid in acetic acid was added, the beaker covered and chilled in ice water. The precipitate was removed by centrifuging, evaporated twice to dryness with excess concentrated nitric acid, and the residue taken up in dilute nitric acid. The solution was treated with acetic anhydride in the usual manner, and the nickel titrated with perchloric acid in dioxane.

Cadmium and Magnesium

A solution of three milliequivalents of each metal was made up in the usual way, chilled, and saturated with dry hydrogen iodide gas. The precipitate was removed by centrifuging, washed, and the resulting solution of magnesium titrated.

Tin and Magnesium

A solution of three milliequivalents of each metal in acetic acid was prepared in the usual way, but kept at 100°C. A five-fold excess of oxalic acid solution in acetic acid was added, and the mixture chilled. The precipitate of magnesium oxalate was removed by centrifuging, evaporated to dryness twice with concentrated nitric acid, and the residue
taken up in dilute nitric acid. Acetic anhydride was added to react with the water and decompose the nitric acid, after which the magnesium was titrated in the usual way.

The results of all these determinations are summarized in Table IV in the next section.

D. Introduction of Metals Into Acetic Acid Solution

Acetic acid itself is effective in dissolving only the most electropositive of the metals. If, however, the acid strength could be increased, more metals could be introduced directly into the organic phase. A possible method of accomplishing this suggests itself from the following considerations:

If AB is a very weak organic base and HX a weak acid, then a mixture of AB and HX will remain a mixture (or solution) of one in the other with no chemical reaction occurring. On the other hand, if AB is a strong organic base and HX a strong acid, a salt will be produced on mixing:

\[ AB + HX \rightarrow AB^+ + X^- \]

With a fairly weak acid (say CH₃COOH) and a fairly strong base (piperidine for example) one would obtain a compound of the sort AB·...H⁺···X⁻ with a hydrogen bond, and a greater or lesser "activity" depending on the strength of the base and the temperature. If the activity is sufficiently great, the positive ion may be displaced by metals of high enough potential.

To test this theory, twenty five representative metals
were treated with ammonium acetate, piperidinium acetate, and dicyclohexylammonium acetate, the latter to give a higher boiling salt. Test tube experiments only were carried out, to cover the ground as rapidly as possible. No attempt was made to determine the extent of the reaction if the metal did not dissolve completely. The results of the tests are summarized in Table IV and Table V.

Preparation of Piperidinium Acetate

Piperidine (49.4 ml.) and acetic acid (28.6 ml.) were dissolved in separate portions of acetone. Mixing immediately produced a well-crystallized white precipitate. The compound was not stable toward heat; drying at 55°C. caused it to turn yellow. Therefore, after filtering and washing with ether, the salt was stored in vacuo until dry. The yield was 71.5 gm. (98%) of a solid melting at 101-104°C. with decomposition.

Preparation of Dicyclohexylammonium Acetate

Dicyclohexylamine (100.7 ml.) and acetic acid (28.6 ml.) were dissolved in separate portions of acetone. Mixing produced a powdery white precipitate in 98% yield, melting at 116-118°C.

A second method of increasing the activity of an acid is to introduce electro-negative atoms into the molecule, as in the chloroacetic acids. To determine the extent of this increase in activity a survey was made of the reactivity of the twenty-five metals mentioned toward pure monochloroacetic,
dichloroacetic, and trichloroacetic acids and equimolar solutions of each in acetic acid. Each test was carried out from room temperature to the boiling point of the acid considered. These results are also summarized in Table IV and Table V.

However, for reasons discussed in the next section, these acids were unsatisfactory for general use, and the following method was adopted. To introduce the metals into acetic acid solution, sufficient nitric acid was used to bring the metal(s) into aqueous solution, followed by sufficient acetic anhydride to react with all the water added and to decompose all the nitrate present. In certain cases, aqua regia was required, but in general this method was fast and efficient.

III. RESULTS AND DISCUSSION

A. Determination of the Potentiometric End-Point

The titration curves obtained are illustrated in plates II-XII. The first in each set is a plot of volume of titrant v. e.m.f. reading. The end point is, of course, the inflection point on the curve, but in titrations the potential break was not sharp enough to determine the end point accurately from the graph. A more precise method is to plot $\frac{\Delta E}{\Delta V}$, the change in potential per unit volume, v. V, the volume added near the end point, as was done in the second graph in each set. Since the point of inflection
in the titration curve has the condition $\frac{d^2E}{dV^2} = 0$, the corresponding point on the differential curve must be a maximum, i.e. $\frac{d}{dV} \left( \frac{dE}{dV} \right) = 0$. If the latter curve is not symmetrical, the end-point may be found by extrapolation (39), assuming that in a small region about the end-point $\frac{dE}{dV}$ varies linearly with $V$. For all but the most basic of the metal acetates, the sensitivity of the titration did not justify extrapolating the volume to fractions of a drop. The end points are indicated on all the graphs.

An attempt was made to calculate the error involved in the titrations on a theoretical basis, by adapting the method of Roller (54-56). This was found to be impossible, however, because of a lack of data on dissociation constants in acetic acid.

The sensitivity of the method may be increased by drilling a hole in the side of the beaker and inserting one electrode horizontally so that the tip is very close to that of the other electrode, which is in the usual vertical position. The increase in sensitivity is caused by a decrease in electrical resistance.

Since fluorosulphonic acid is too active to exist in water, it was thought it might be stronger in acetic acid than perchloric acid, and hence give better defined end-points with the weaker bases. However, this was not the case; the acidity, as measured by the potential, was less than that of perchloric acid. Moreover the end-point
obtained when the fluorosulphonic acid was used as titrant was very poorly defined.

B. Titration of Metal Salts

The results obtained from the titrations are summarized in Table I; the titration curves are illustrated in Plates II - XIV. The titration curves show the same changes as one proceeds from strong to weak bases as is found in water. Acetates of the first and second group metals show a pronounced potential "break" at the end-point, while those of metals usually considered "weak" in water show a less pronounced break. An exception was ammonium acetate, which in acetic acid is as strong as potassium acetate. In the case of nickel cobalt and cadmium, the accuracy of the titration was not always as great as the results in Table I might indicate, since the end-point was poorly defined.

Contrary to the results published by Pifer and Wollish (51) no end-point could be found for bismuth, antimony and tin, and a very low value was obtained for the percentages of iron. Inspection of Plates shows that the curves obtained for bismuth, antimony, copper, tin, and uranium are of the same form as that for the solvent alone i.e. their acetates are bases too weak to be titrated in acetic acid with perchloric acid.

The curves for chromium, iron and aluminum yielded end-points showing approximately 11-12% purity, while the gravimetric analysis gave results close to 100%. This in spite of the fact that the potential breaks are more
### TABLE I

**TITRATION OF METAL SALTS**

<table>
<thead>
<tr>
<th>Salt</th>
<th>% Purity Found</th>
<th>Gravimetric Determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOAc</td>
<td>99.59</td>
<td>99.58</td>
</tr>
<tr>
<td>KOAc</td>
<td>99.56</td>
<td>99.48</td>
</tr>
<tr>
<td>LiOAc</td>
<td>99.73</td>
<td>99.75</td>
</tr>
<tr>
<td>Ba(OAc)$_2$</td>
<td>99.40</td>
<td>99.41</td>
</tr>
<tr>
<td>Sr(OAc)$_2$</td>
<td>99.65</td>
<td>99.41</td>
</tr>
<tr>
<td>NH$_4$OAc</td>
<td>97.58</td>
<td>97.73</td>
</tr>
<tr>
<td>Mg(OAc)$_2$</td>
<td>99.82</td>
<td>99.85</td>
</tr>
<tr>
<td>Mn(OAc)$_2$</td>
<td>99.69</td>
<td>99.62</td>
</tr>
<tr>
<td>Ca(OAc)$_2$</td>
<td>98.95</td>
<td>98.96</td>
</tr>
<tr>
<td>Cd(OAc)$_2$</td>
<td>98.72</td>
<td>98.60</td>
</tr>
<tr>
<td>Co(OAc)$_2$</td>
<td>91.35</td>
<td>91.06</td>
</tr>
<tr>
<td>Ni(OAc)$_2$</td>
<td>93.61</td>
<td>93.29</td>
</tr>
<tr>
<td>Zn(OAc)$_2$</td>
<td>97.73</td>
<td>97.40</td>
</tr>
<tr>
<td>Pb(OAc)$_2$</td>
<td>98.36</td>
<td>98.30</td>
</tr>
<tr>
<td>Ag(OAc)$_2$</td>
<td>99.72</td>
<td>99.83</td>
</tr>
<tr>
<td>Fe(OAc)$_3$</td>
<td>11.36</td>
<td>98.96</td>
</tr>
<tr>
<td>Cr(OAc)$_3$</td>
<td>11.71</td>
<td>99.65</td>
</tr>
<tr>
<td>Al(OAc)$_3$</td>
<td>11.06</td>
<td>99.03</td>
</tr>
<tr>
<td>ClCH$_2$COONa</td>
<td>97.96</td>
<td>98.10</td>
</tr>
<tr>
<td>ClCH$_2$COOK</td>
<td>97.83</td>
<td>98.96</td>
</tr>
<tr>
<td>(ClCH$_2$COO)$_2$Ba</td>
<td>97.36</td>
<td>97.50</td>
</tr>
<tr>
<td>(ClCH$_2$COO)$_2$Mg</td>
<td>97.35</td>
<td>97.49</td>
</tr>
</tbody>
</table>

* First column in "% purity found" had concentration of three milliequivalents of sample per 45 ml. of solvent, the second six milliequivalents and the third nine milliequivalents per 45 ml. Each value in "% purity found" represents the mean of two determinations.
clearly defined than those for certain metals whose curves yield reasonable results. A possible explanation for these low results may be in the work of Weinland et al. (65-70), who found that solutions of chromic and ferric salts in acetic acid give rise to numerous complexes many of which were quite stable. One of these has the form $\left[Cr_3(OH)_2(\text{AcO})_6\right]\text{AcO}$. Titrating this with perchloric acid solution would result in the compound $\left[Cr_3(OH)_2(\text{AcO})_6\right]\text{ClO}_4$, that is, only one molecule of $\text{HClO}_4$ has been consumed for three atoms of chromium instead of the expected three molecules of $\text{HClO}_4$ for one atom of chromium. This would give rise to a result 11.11% of the theoretical, not far from the values obtained. Moreover, the values obtained remained essentially constant over a three-fold increase in concentration, which would indicate that a definite compound or set of compounds is involved, under the conditions at hand, and not an equilibrium mixture. Further work along this line would promise to yield very interesting results.

When the end-point is indistinct or poorly defined in acetic acid alone, it may be improved, as shown recently by Pifer et al., (53) by the addition of a miscible organic liquid of low dielectric constant. This was illustrated by the improvement of the end-point for cobalt, nickel, and cadmium acetates when a solution of perchloric acid in dioxane was used as a titrant. The reason for the increase in sensitivity is that perchloric acid is less ionized in
the solvent of lower dielectric constant, and hence, as shown in the introduction, the solution has a higher acidity.

C. Solubilities in Acetic Acid

Zinc acetate is the only one quantitatively insoluble in acetic acid; those of silver and thorium, aluminium and bismuth are only partly soluble. When an aqueous solution of arsenious acid is treated with acetic anhydride, a white precipitate forms, but it is doubtful if this is arsenic acetate. The results of the tests with possible precipitating reagents, as summarized in Table II, have several interesting features. In many cases the solubilities parallel those in the aqueous system, but there are some outstanding exceptions. For instance, strontium and barium nitrates are precipitated immediately and quantitatively upon the addition of concentrated nitric acid or a solution of sodium nitrate in acetic acid. Lead is also precipitated, but not quantitatively, and magnesium precipitates after standing overnight.

Although barium chloride was insoluble in acetic acid, strontium chloride was very soluble, in comparison with other chlorides. Cadmium chloride also precipitated readily, but tended to dissolve in excess HCl. Precipitation was not quantitative, but was when hydrogen iodide is used.

Hydrogen sulphide gave precipitates which were less colloidal than those obtained in water in certain cases, notably cadmium lead and silver. (In general, precipitates
## TABLE II

RESULTS OF ADDING THE REAGENTS LISTED TO A SOLUTION OF 1 MILLIEQUIVALENT OF THE METAL ACETATE IN ACETIC ACID

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Ca</th>
<th>Mg</th>
<th>Th</th>
<th>Al</th>
<th>U</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Cd</th>
<th>Co</th>
<th>Na</th>
<th>Sn</th>
<th>Pb</th>
<th>Sb</th>
<th>Bi</th>
<th>As</th>
<th>Se</th>
<th>Te</th>
<th>Ag</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrous $\text{H}_2\text{SO}_4$</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>$\text{H}_2\text{SO}_4 + 5% \text{H}_2\text{O}$</td>
<td>$\times$</td>
<td>$\times$</td>
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<td>$\times$</td>
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<tr>
<td>$15\text{N} \text{HNO}_3$</td>
<td>$\times$</td>
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<td>$\times$</td>
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<td>Dry HCl gas</td>
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<td>Dry HI gas</td>
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<td>Dry H$_2$S gas</td>
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<tr>
<td>$85% \text{H}_3\text{PO}_4$</td>
<td>$\times$</td>
<td>$\phi$</td>
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<tr>
<td>Salicylic acid</td>
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<tr>
<td>Benzoic Acid</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tartaric Acid</td>
<td>$\times$</td>
<td>$\times$</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Oxalic acid</td>
<td>$\times$</td>
<td>$\times$</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>$\times$</td>
<td></td>
</tr>
</tbody>
</table>

**LEGEND:**
- $x$ Quantitative precipitation.
- $\circ$ Non-quantitative precipitation
- $\star$ Quantitative precipitation on standing several hours.
- $\emptyset$ Non-quantitative precipitation on standing several hours.
- $-$ Not tested.
formed in acetic acid are not well crystallized). All the metals found in group II in the usual analytical scheme precipitated readily except tin, which remained in solution as long as no water was present. (Addition of 1% water caused formation of a brown precipitate.) Nickel and cobalt sulphides, which do not precipitate in acidic aqueous solutions, precipitated more slowly than the metals of group II, but precipitation was quantitative after fifteen minutes. There was also a reaction with chromium to produce a small amount of grey-green colloidal precipitate. This was somewhat surprising, as there was no such reaction with iron or aluminum, and prevented the separation of other metals from chromium using hydrogen sulphide.

Although no quantitative precipitations resulted from addition of salicylic acid, color changes in several cases showed complexes had been formed. Iron changed from red to dark brown, cobalt from red to rust brown, nickel from green to yellow, and the solutions of aluminum and antimony from colorless to yellow. The molybdenum sample became deep red violet, with the formation of a very fine brown precipitate. Other substituents on the benzene nucleus might result in the formation of insoluble complexes.

Benzoic acid produced no precipitate with any metals, but tartaric and oxalic acids were very effective, almost all the precipitations being quantitative. Although precipitation is best done in a hot solution with these
reagents and salicylic acid because of solubility considera-
tions, precipitates were better crystallized when brought
down in the cold in acetic acid. However, almost all were
colloidal in nature, and so a centrifuge was much preferred
to a filter for separation.

Perhaps the most unusual phenomena occurred with sul-
phuric acid and the sulphates. The results of the experi-
ments carried out are summarized in Table III. According to
Davidson (14) sulphates in general are insoluble in acetic
acid, and metals precipitate on the addition of anhydrous
sulphuric acid. Table III shows that four hours refluxing
failed to dissolve an appreciable amount of any of the sul-
phates tested, but on the other hand, Table II shows that
most metals failed to be precipitated upon the addition of
sulphuric acid. Moreover, when the sulphates were dissolved
in water and the solution treated with acetic anhydride,
two, chromium and iron, failed to precipitate at all, and
the precipitation of several others was far from complete.
These results show that one cannot rely on the behavior of
the sulphates, and that sulphuric acid is not a good precip-
itating agent for this reason.

D. Separations

As mentioned before, precipitates formed in hot acetic
acid solution are very finely divided, and often difficult
to separate from the filtrate, even in a high-speed centri-
fuge. Precipitates formed in the cold settle more readily,
### TABLE III
RESULTS OF SOLUBILITY TESTS WITH SULPHATES

<table>
<thead>
<tr>
<th>Sulphate</th>
<th>Result of Refluxing with Glacial Acetic Acid</th>
<th>Result of dissolving in water and adding acetic anhydride.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>Insoluble</td>
<td>Quantitative precipitation</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>Insoluble</td>
<td>Precipitation almost quantitative</td>
</tr>
<tr>
<td>Cr</td>
<td>Insoluble</td>
<td>No precipitation</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>Insoluble</td>
<td>Partial precipitation on addition of last 5% of acetic anhydride, but precipitate dissolves on boiling</td>
</tr>
<tr>
<td>Ca</td>
<td>Insoluble</td>
<td>Quantitative precipitation</td>
</tr>
<tr>
<td>Co</td>
<td>Insoluble</td>
<td>Partial precipitation</td>
</tr>
<tr>
<td>Ni</td>
<td>Insoluble</td>
<td>Partial precipitation</td>
</tr>
<tr>
<td>Sn</td>
<td>Insoluble</td>
<td>Precipitation almost quantitative.</td>
</tr>
</tbody>
</table>
but are not well crystallized and clog filter paper. Thus a centrifuge should be used whenever possible.

The results obtained are listed in Table IV. They show that good precision and accuracy are obtainable with this method, often with appreciable saving of time. The complete analysis of an alloy of cadmium and magnesium, for example, requires approximately forty-five minutes, if a standard perchloric acid solution is available. If a rough estimation of a binary alloy of copper or antimony with a titratable metal is required, it may be completed in fifteen minutes by titrating the metal in the presence of the copper or antimony.

E. Introduction of Metals Into Acetic Acid Solution

The results of the tests carried out with the amine acetates, acetic acid, and the chloroacetic acids are summarized in Tables V and VI. Ammonium acetate and piperidinium acetate were completely ineffective in attacking metals other than calcium and magnesium, and these reactions were very slow. For this reason they are not included in the table.

The results with chloroacetic acids show that even elements below hydrogen in the electromotive series (such as copper and mercury) are attacked vigorously by these acids. According to Doughty (18) the reaction between copper and trichloroacetic acid is not a simple one. A variety of compounds, depending on the temperature and concentration, are produced, such as copper chloroacetate, copper dichloroacetate, chloroform and other products.
### TABLE IV
RESULTS OF TITRATING METALLIC MIXTURES

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Theoretical % of Metal Determined</th>
<th>% Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-Mg</td>
<td>27.11</td>
<td>27.00</td>
</tr>
<tr>
<td>Mg determined</td>
<td></td>
<td>26.95</td>
</tr>
<tr>
<td>Zn-Cu</td>
<td>50.70</td>
<td>50.59</td>
</tr>
<tr>
<td>Zn determined</td>
<td></td>
<td>50.50</td>
</tr>
<tr>
<td>Ba-Ca</td>
<td>22.58</td>
<td>22.56</td>
</tr>
<tr>
<td>Ca determined</td>
<td></td>
<td>22.75</td>
</tr>
<tr>
<td>Ag-Al</td>
<td>79.99</td>
<td>79.86</td>
</tr>
<tr>
<td>Ag determined</td>
<td></td>
<td>79.91</td>
</tr>
<tr>
<td>Pb-Sn</td>
<td>63.58</td>
<td>63.42</td>
</tr>
<tr>
<td>Pb determined</td>
<td></td>
<td>63.49</td>
</tr>
<tr>
<td>Mg-Sb</td>
<td>16.65</td>
<td>16.48</td>
</tr>
<tr>
<td>Mg determined</td>
<td></td>
<td>16.53</td>
</tr>
<tr>
<td>Mg-Sb</td>
<td>16.65</td>
<td>17.53</td>
</tr>
<tr>
<td>Mg determined</td>
<td></td>
<td>17.67</td>
</tr>
<tr>
<td>Mg-Cu</td>
<td>27.67</td>
<td>27.38</td>
</tr>
<tr>
<td>Mg determined</td>
<td></td>
<td>27.46</td>
</tr>
<tr>
<td>Mg-Cu</td>
<td>27.67</td>
<td>29.58</td>
</tr>
<tr>
<td>Mg determined</td>
<td></td>
<td>29.65</td>
</tr>
<tr>
<td>Mg-Pb</td>
<td>10.50</td>
<td>10.57</td>
</tr>
<tr>
<td>Mg determined</td>
<td></td>
<td>10.40</td>
</tr>
<tr>
<td>Ni-Cr</td>
<td>53.03</td>
<td>52.85</td>
</tr>
<tr>
<td>Ni determined</td>
<td></td>
<td>52.89</td>
</tr>
<tr>
<td>Cd-Mg</td>
<td>17.79</td>
<td>17.60</td>
</tr>
<tr>
<td>Mg determined</td>
<td></td>
<td>17.69</td>
</tr>
<tr>
<td>Sn-Mg</td>
<td>17.00</td>
<td>16.87</td>
</tr>
<tr>
<td>Mg determined</td>
<td></td>
<td>16.91</td>
</tr>
<tr>
<td>Metal</td>
<td>Dicyclohexylammonium acetate</td>
<td>Pure equimolar soln. of chloroacetic acid</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>Ca</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>Mg</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>Th</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>+++</td>
</tr>
<tr>
<td>U</td>
<td>+</td>
<td>+++</td>
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<tr>
<td>Mn</td>
<td>+</td>
<td>+++</td>
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<tr>
<td>Zn</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>+</td>
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<tr>
<td>Mo</td>
<td>+</td>
<td>++</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Cd</td>
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</tr>
<tr>
<td>Co</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sn</td>
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<td>+</td>
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<tr>
<td>Pb</td>
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<tr>
<td>Sb</td>
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<tr>
<td>Bi</td>
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</tr>
<tr>
<td>As</td>
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</tr>
<tr>
<td>Cu</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Se</td>
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<td>Te</td>
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<tr>
<td>Hg</td>
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<td>W</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**LEGEND:**
+++ vigorous reaction  
++ moderate reaction  
+ slow reaction  
± slight reaction  
- no apparent reaction
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Metals which dissolve readily</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dicyclohexyl-ammonium acetate</td>
<td>None</td>
</tr>
<tr>
<td>Piperidinium acetate</td>
<td>None</td>
</tr>
<tr>
<td>Ammonium acetate</td>
<td>Ca</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>Ca, Mg, Mn, Fe</td>
</tr>
<tr>
<td>Equimolar chloroacetic in acetic</td>
<td>Ca, Mg, Al, Mn, Zn // Cr, Fe</td>
</tr>
<tr>
<td>Equimolar dichloroacetic in acetic</td>
<td>Ca, Mg, U, Mn, Zn, Cr, Fe, Cd, Sn, Pb // Co</td>
</tr>
<tr>
<td>Equimolar trichloroacetic in acetic</td>
<td>Ca, Mg, U, Mn, Zn, Cr, Fe, Sn, Pb // Mo, Co, Hg</td>
</tr>
<tr>
<td>Pure chloroacetic</td>
<td>Ca, Mg, Zn, Mn, Cr, Fe // U</td>
</tr>
<tr>
<td>Pure dichloroacetic</td>
<td>Ca, Mg, Mn, Zn // Cr, Fe, Cd, Sn, Pb, Sb</td>
</tr>
<tr>
<td>Pure trichloroacetic</td>
<td>Ca, Mg, Mn, Zn, Cr, Mo, Fe, Sn, Pb, Sb, Cu // Al, U, Co, Bi</td>
</tr>
</tbody>
</table>

Those elements after the double stroke in the table react much less rapidly than those before it.
Beside possible undesirable side reactions, another disadvantage of these acids from the point of view of titrations was the large quantity of acid often required to dissolve the metal completely. Because of the limited solubility of chloroacetic and trichloroacetic acids in acetic acid, the resulting mixture was often not completely soluble in acetic acid. Moreover, the table shows certain common alloys would not react readily with a single acid. For these reasons the method of introducing metals into acetic acid solution using nitric acid and acetic anhydride was preferred. Using this method, alloys corresponding to the metal acetate mixtures discussed previously may readily be analysed in a minimum of time and with good accuracy.

IV. CONCLUSIONS

Alloys, and mixtures of the less soluble metal compounds, may be conveniently introduced into acetic acid solution using nitric acid (or aqua regia) and acetic anhydride. Quantitative separations may often be effected in this medium using common reagents such as hydrogen sulphide and hydrogen iodide, nitric, oxalic and tartaric acids. The constituents may then be titrated rapidly and accurately with a standard solution of perchloric acid in acetic acid.

In spite of the interest shown in analytical methods such as the one described, comparatively little is known of the chemistry of acetic acid solutions. Much work needs
to be done on the determination of dissociation constants, on solubility relationships, and on the founding of a more rigorous theoretical approach to the question of acidity in non-aqueous solutions. With a clear insight into these questions, this type of analysis may prove to be of much wider applicability than is now imagined.
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    (c) Ber. 59: 793. 1926.  
    (d) Ber. 59: 1096. 1926.  
    (e) Ber. 60: 1933. 1927.  
    (f) Z. Electrochem. 29: 221. 1923.  
    (g) Z. Electrochem. 30: 194. 1924.  
    (h) Z. Electrochem. 31: 167. 1925.  


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65. Weinland, R. Ber. 41: 3236. 1908.
FIGURE II A

Potentiometric Titration of Ten Milliliters of Standard Sodium Acetate Solution, With Perchloric Acid In Acetic Acid

ML. TITRANT ADDED (0.09927N.)

END POINT
FIGURE II B
Precise Determination of the End Point for Figure II A

END POINT

VOLUME ADDED NEAR END POINT (1 DROP = 0.0148 ML.)
FIGURE III A
Titration (potentiometric) of Approximately Three Milliequivalents of Barium Acetate With Perchloric Acid in Acetic Acid

END POINT

ML. TITRANT ADDED (0.09927N.)
FIGURE III B

Precise Determination of the End Point for Figure III A

END POINT

VOLUME ADDED NEAR END POINT (1 DROP = 0.0148 ML.)
FIGURE IV A

Potentiometric Titration of Approximately Three Milliequivalents of Lithium and Strontium Acetates in Acetic Acid With Perchloric Acid.

Ammonium and Potassium Acetates Each Yield A Similar Curve.
FIGURE IV B
Precise Determination of the End Point for Figure IV A
FIGURE V A
Potentiometric Titration of Approximately Three Milliequivalents of Magnesium Acetate in Acetic Acid With Perchloric Acid

ML. TITRANT ADDED (0.09927N.)
FIGURE V B
Precise Determination of the
End Point for Figure V A

VOLUME ADDED NEAR END POINT (1 DROP = 0.0148 ML.)
FIGURE VI A

Potentiometric Titration of
Approximately Three Milliequivalents of Calcium Acetate
in Acetic Acid With Perchloric Acid

ML. TITRANT ADDED (0.09927N.)
FIGURE VI B
Precise Determination of the End Point for Figure VI A

END POINT

VOLUME ADDED NEAR END POINT (1 DROP = 0.0148 ML.)
FIGURE VII A
Potentiometric Titration of Approximately Three Milliequivalents Each of Cadmium and Manganese Acetate in ACETIC Acid with Perchloric Acid

END POINT

END POINT

24.00
25.00
26.00

ML. TITRANT ADDED (0.1008N.)
FIGURE VII B
Precise Determination of the End Points for Figure VII A

END POINT

VOLUME ADDED NEAR END POINT (1 DROP = 0.0109 ML.)
FIGURE VIII A

Potentiometric Determination of Approximately Three Milliequivalents of Cobalt Acetate in Acetic Acid With Perchloric Acid

Nickel Acetate Yields a Similar Curve.
FIGURE VIII B
Precise Determination of the End Point for Figure VIII A

VOLUME ADDED NEAR END POINT (1 DROP = 0.0138 ML.)
FIGURE IX A
Potentiometric Determination of
Approximately Three Milliequivalents of lead Acetate in
Acetic Acid With Perchloric Acid

ML. TITRANT ADDED (0.1116 N)
FIGURE IX B
Precise Determination of the End Point for Figure IX A

VOLUME ADDED NEAR END POINT (1 DROP = 0.0218 ML.)
FIGURE X A

Potentiometric Determination of Approximately Three Milliequivalents Each of Chromium, Iron (III), and Aluminum Acetates in Acetic Acid With Perchloric Acid

ML. TITRANT ADDED (0.09927 N.)
Precise Determination of the End Points for Figure X A
FIGURE XI
Curves Obtained from the Attempted Potentiometric Determination of Copper (II), Antimony (III), and Tin (II) Acetates in Acetic Acid With Perchloric Acid. The Curve Obtained Upon Adding Perchloric Acid to Acetic Acid Alone is Included for Reference.
FIGURE XII
Curves Obtained From the Attempted Potentiometric Determination of Bismuth (III) and Uranyl Acetates in Acetic Acid With Perchloric Acid. The Curve Obtained Upon Adding Perchloric Acid to Acetic Acid Alone is Included for Reference.
Potentiometric Determination of Approximately Three Milliequivalents of Barium Chloroacetate in Acetic Acid with Perchloric Acid. The Curves Obtained for the Other Chloroacetates Tested Were Similar to the Curves Obtained for the Corresponding Acetates.
FIGURE XIII B
Precise Determination of the End Point for Figure XIII A

VOLUME ADDED NEAR END POINT (0.0148 ML. = 1 DROP)