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March 9, 1950

BEHAVIOR OF PLUTONIUM (III) CHLORIDE IN TITRATIONS WITH BASE AND ACID

by

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ABSTRACT

The preliminary results of potentiometric titrations of solutions of plutonium (III) chloride, lanthanum chloride and aluminum chloride are presented. It is demonstrated that both plutonium and lanthanum form "basic salts" with the generalized empirical formula $M(OH)_{2.5}Cl_{0.5}$.

The effect of oxygen on the course of a titration involving plutonium is demonstrated and discussed.

Values for the ion conductance of plutonium (III) ion are presented.

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I. INTRODUCTION

This study of the behavior of the plutonium (III) ion as revealed by potentiometric titrations with base and acid has been undertaken to increase the general understanding of the chemistry of plutonium and to compare the behavior of the plutonium (III) ion with other similar ions. The study is in progress at the present time, and this report summarizes work already completed. Included in the report are preliminary studies of the potentiometric curves obtained in the precipitation of aluminum, lanthanum, and plutonium (III) ions with sodium hydroxide, together with related conductimetric data.

II. EXPERIMENTAL

A. Materials - All materials used in the preparation of 0.1 N solutions were either Mallinckrodt or Merck purified chemicals which meet the A.C.S. specifications for analytical grade reagents. Oxygen was excluded from these solutions by preparing them from water boiled and cooled under helium and storing them under a helium atmosphere that had had oxygen removed by alkaline pyrogallol. The 0.0347 M aluminum sulfate solution was prepared from potassium aluminum sulfate. A 0.0349 M lanthanum chloride solution was prepared from lanthanum chloride which contained no other rare earth detectable by spectroscopic analysis. Both of these solutions were 0.0488 M in hydrochloric acid, and 10.00 ml samples were diluted as described below for the titrations.

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Solutions of plutonium were prepared from the metal which was 99.9% pure as determined by spectrographic analysis. The oxide coating was removed from each plutonium lump with a wire brush just prior to dissolving in strong hydrochloric acid. The metal dissolved to give a clear blue solution of plutonium (III) chloride in which the absorption bands of the higher oxidation states could not be detected with the spectrophotometer.

Solid $PuCl_3 \cdot 6H_2O$ was prepared from solutions containing excess hydrochloric acid by vacuum distillation at 25°C in the evaporator shown in Figure 1. A sample of the solid compound prepared in this manner was weighed, the chloride determined gravimetrically, and from the original weight of the metal, the composition of the solid was found to be 52.1% plutonium, 23.1% chloride, and 24.9% water as compared with the respective calculated values of 52.70%, 23.46%, and 23.84%. After such evaporations the solid was found to contain no free acid detectable by titration with base (note the original steep rise in the curves of Figure 5).

A solution of plutonium (IV) as the chloride was prepared from an acid solution of plutonium (III) chloride. A green precipitate of plutonium (IV) hydrated oxide was obtained by slowly adding sodium hydroxide solution to an acid solution of plutonium (III) chloride through which oxygen was bubbled simultaneously. The precipitate was centrifuged from the solution, washed, and then dissolved in a small excess of boiling concentrated hydrochloric acid.

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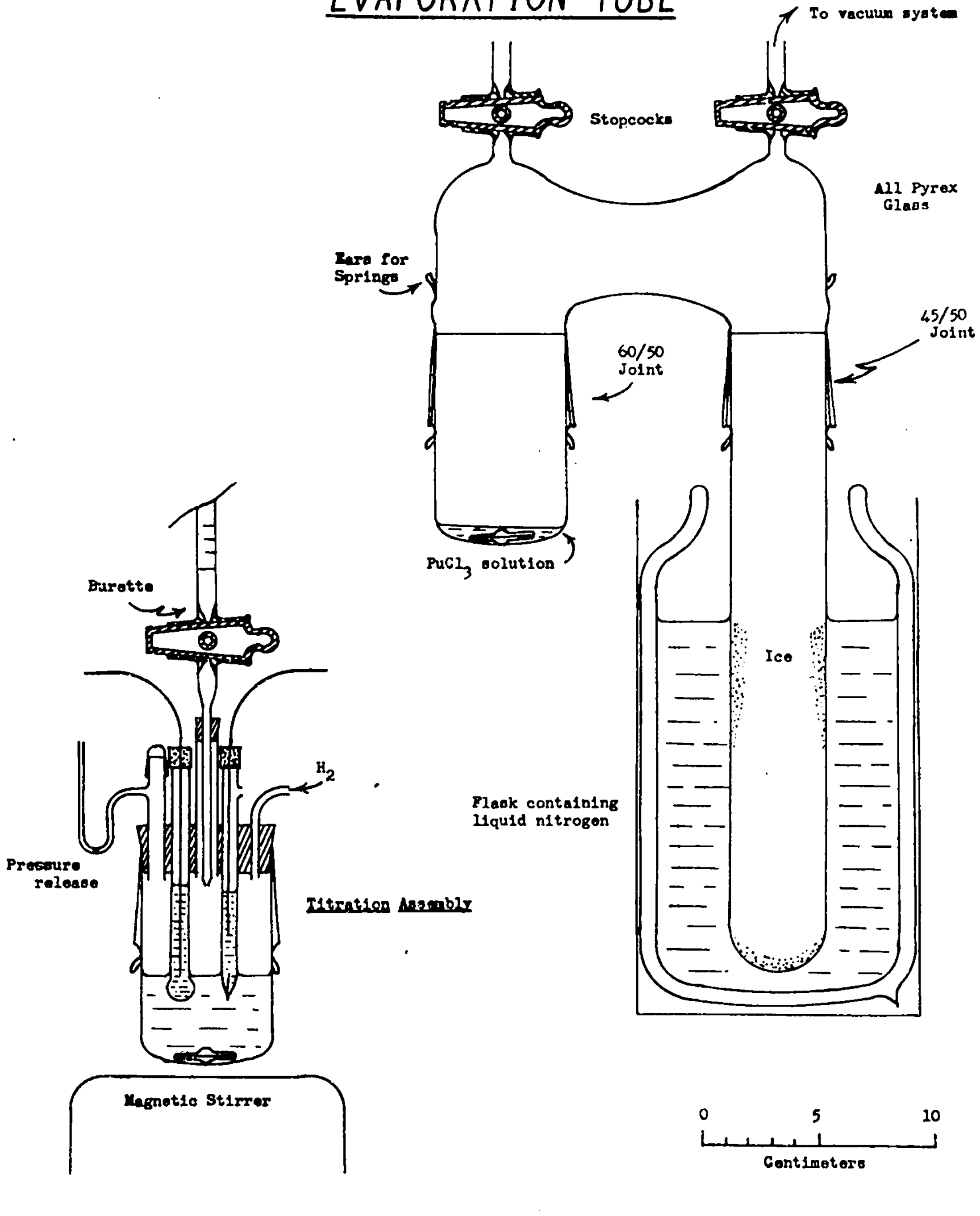
Figure 1

EVAPORATION TUBE



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B. Apparatus - Two titration vessels were used. One is shown in Figure 1 and consists of the closed standard taper joint used in conjunction with the evaporator together with a suitable cap which supports the electrodes. The solutions were stirred magnetically. After necessary electrodes were inserted, the solid samples of $PuCl_3.6H_2O$ prepared in this container were dissolved in 65.0 ml of water and titrated. In the case of the other salts, 10.00 ml samples of the standard solutions were pipetted into the vessel and diluted to 65 ml. Air was rigorously excluded from the titration vessel by a continuous flow of purified helium or hydrogen.

The second titration vessel was conical in shape and is shown in Figure 2. Solutions titrated in this vessel were diluted to 180 ml initially and were stirred by continuously bubbling hydrogen through the system as indicated. This vessel was fitted with three independent electrical circuits for measuring the pH, both by glass and hydrogen electrodes, as well as the electrical conductivity. The multiple switch shown in Figure 2 isolated all of the electrodes except the two used for a single measurement. The calomel electrodes with saturated potassium chloride were used for reference with both the hydrogen and glass electrodes.

Auxiliary apparatus for measuring potentials and conductivity was standard and incorporated no novel features.

C. Experimental Procedure - In a representative titration, the titration vessel was flushed well with purified hydrogen or helium,

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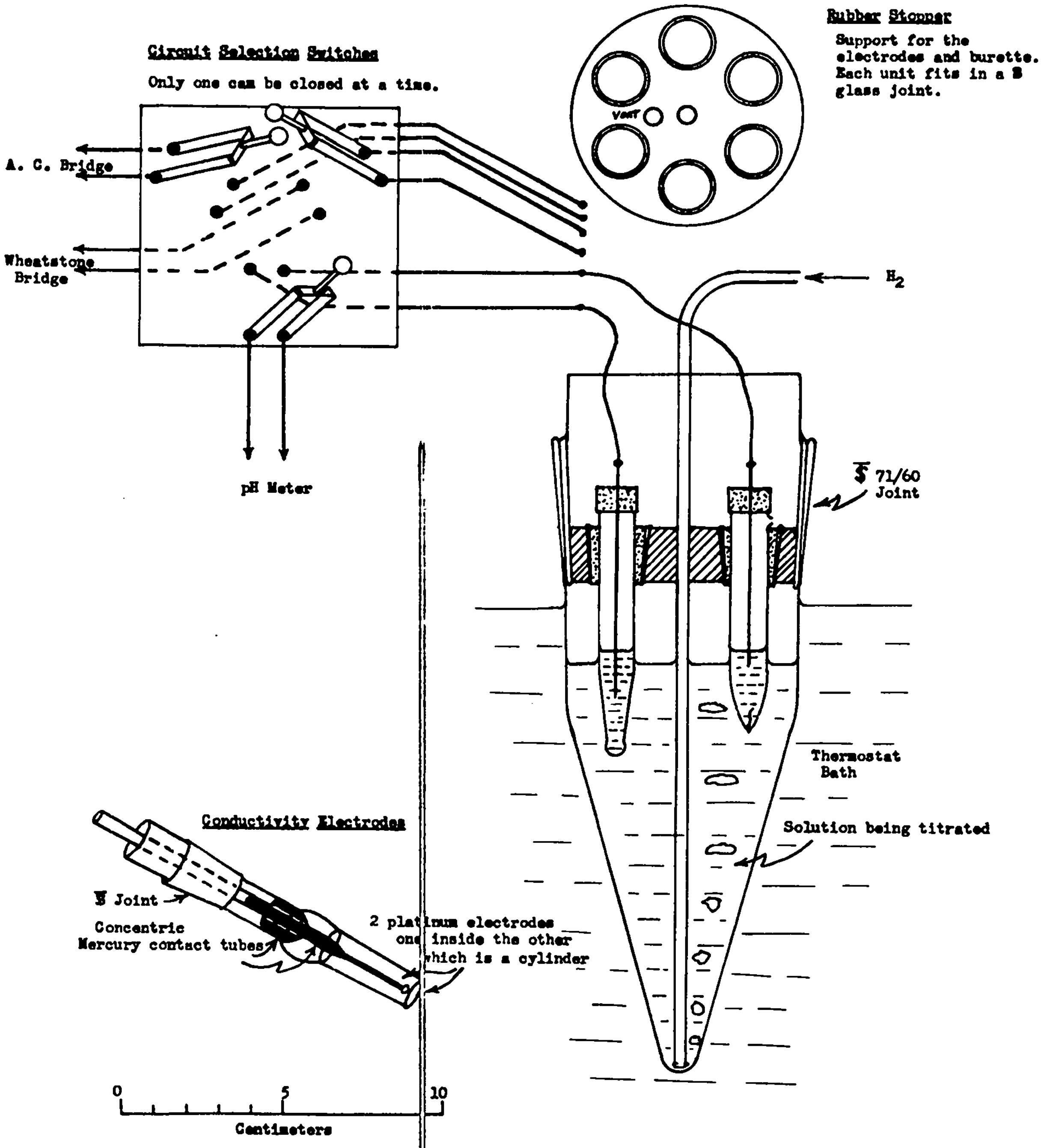
Figure 2

GAS STIRRED TITRATION VESSEL



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and air free water was added. Next, the sample to be titrated was added as a known volume of standard solution except in those cases involving plutonium. Standard solutions of plutonium (III) were found to be 10% oxidized in one week at a pH of 4 in an atmosphere as free from oxygen as could be produced. Because of this the plutonium chloride solutions were prepared from solid $PuCl_3 \cdot 6H_2O$ immediately before the titration. The plutonium metal samples used in the preparation of the individual samples of plutonium chloride weighed between 0.1 and 0.15 g each. While titrating, the base or acid was added dropwise and at least five minutes were allowed before the pH was read. The reaction did not reach equilibrium in this time as is indicated by the titration curves shown in Figure 5 and discussed later; therefore, longer periods were frequently used.

III. RESULTS AND DISCUSSION

A. Aluminum Titrations - The reliability of the equipment was tested by a series of titrations of 180 ml samples of 1.93×10^{-3} M potassium aluminum sulfate solution 2.71×10^{-3} M in hydrochloric acid. The solutions were titrated with 0.0986 M sodium hydroxide solutions. The graphs of the data obtained in such a titration are shown in Figure 3. The pH meter with the glass and saturated calomel electrodes was adjusted with a pH = 4.00 buffer solution for these titrations.

Values for the pH were calculated from E.M.F. measurements made with the hydrogen electrode, taking into account the partial pressure of hydrogen in the system at the time of the titration.

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The first break in the titration curve of aluminum (see Figure 3) is at the theoretical, free-acid end point. The pH at the mid-point of the precipitation plateau is 4.35. The second break, indicating the end of the precipiation, is not sharp, but precipiation does appear to have been completed before 3.0 equivalents of base per mole of aluminum had been added. The point of inflection appears to fall only slightly above the point at which 2.5 equivalents of base had been added. There follows a second plateau with a rather steep slope which has a mid-point at a pH of about 9.2 (as determined from the hydrogen electrode potential) where the precipitate is presumably dissolving to form the aluminate ion. A break in the curve occurs at approximately 3.8 equivalents. The precipitate was completely dissolved by the time 4.0 equivalents of base were added. Back titration with approximately 0.1 M hydrochloric acid shows breaks corresponding exactly to those just described; however, the plateaus were about 0.1 pH unit lower than in the previous instance, indicating that equilibrium had not been established.

The curve showing the specific conductivity of the solution during the titration shows a distinct break at the free acid end point in both the titration with base and with acid. The exact position of the breaks at about 2.5 equivalents of base per mole of aluminum is less well defined, and the break which might be expected at 4.0 equivalents possibly occurs somewhat before this point, the exact position being rather obscure.

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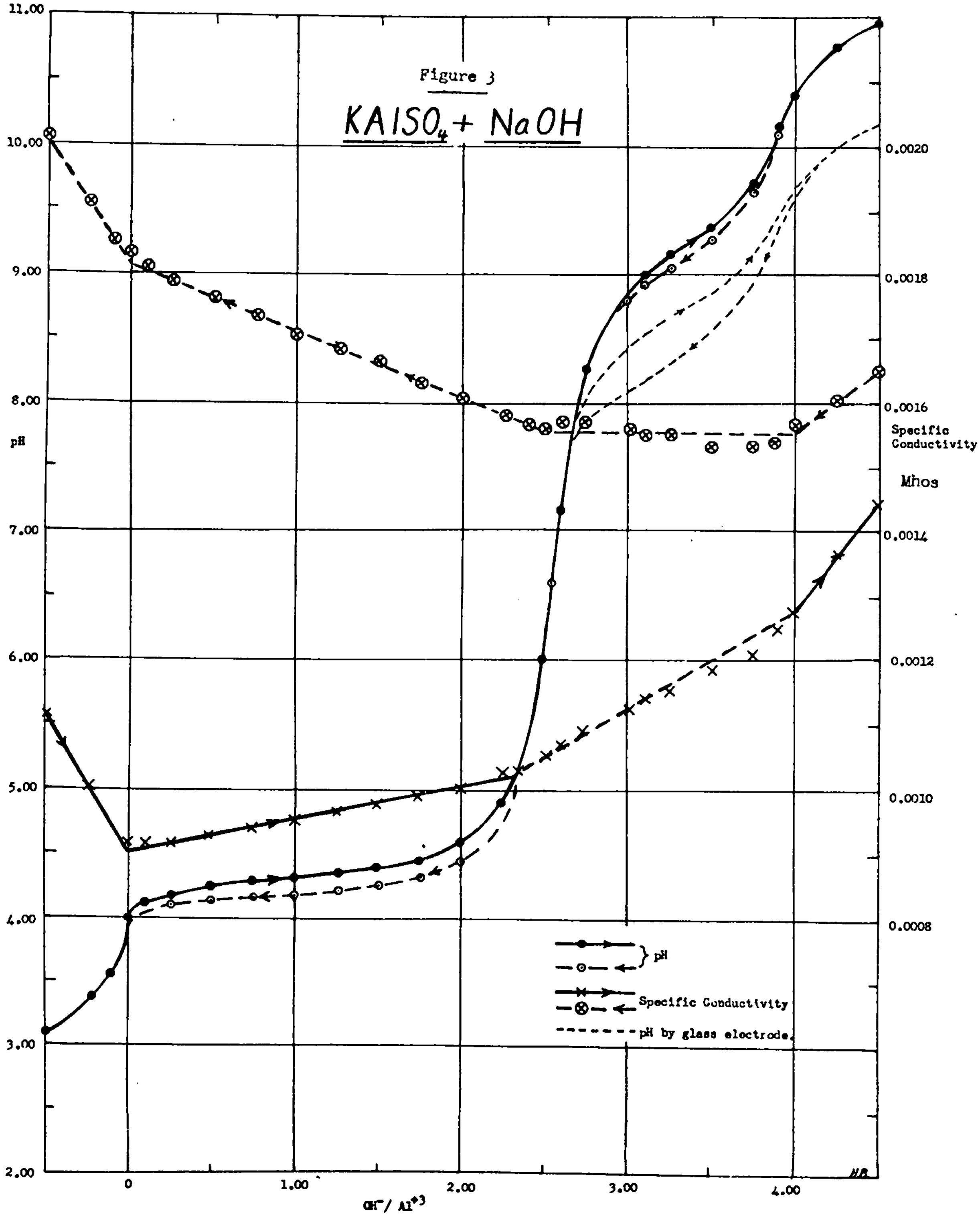

Figure 3

$KAlSO_4 + NaOH$

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A titration curve such as this is very difficult to interpret except in a very general way. There is a suggestion that a basic salt may have formed during the titration with base, but it would be difficult to assign a definite formula to such a compound from the data available. No attempt will be made to calculate a solubility product since both sulfate and chloride ions were present in the solution.

Electrometric titrations and precipitation studies of the aluminum ion (1-21) are extensively treated in the literature. The titration curves obtained by various investigators show wide variations in behavior, particularly in the "aluminate region" of the curve. There is no agreement as to whether the precipitated aluminum hydroxide dissolves to form an aluminate ion or is simply peptized (12), although there is good evidence for the latter. It has been recognized that the fact that less than three equivalents of base are required per mole of aluminum ion suggests basic salt formation (5, 7, 19), and it has been found that the number of equivalents required depends on the particular anion associated with the aluminum (7, 12, 19). Values found by various investigators for the number of equivalents of hydroxide ion required per mole of aluminum vary from about 2.3 to 3.0. Treadwell & Bonder (15) even found a second plateau between 2.5 and 3.0 presumably indicating the further hydrolysis of the primary precipitate. Näsänen and Tamminen (22) found a similar situation with the cupric ion. They found that $Cu(OH)_{1.5}Cl_{0.5}$ first formed and then the remaining chloride hydrolyzed before the final end point of their

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titration. Also they show that if the equations for the solubility product of $Cu(OH)_{1.5}Cl_{0.5}$ and $Cu(OH)_2$ are combined then

$$[OH] = (k_{OH}/k_{Cl})^2 \quad [Cl]$$

The symbols k_{Cl} and k_{OH} are respectively the solubility product constants for the basic salt and hydroxide. Thus the pH at which the final hydrolysis occurs is controlled by the anion concentration. A similar equation can be written for aluminum and other ions which produce a basic salt. It was found by Britton (11) that the solubility product calculated for different positions on the titration curve do not lead to a constant value but show a trend of increasing solubility product as precipitation progresses. Davis and Farnham (12) suggest that the precipitation end point is not sharp because of the adsorption of hydrogen ions from the precipitate such that in effect a buffer is formed. Davis & Farnham (12) found it necessary to remove their electrodes from the solution while the precipitate was forming in order to avoid spurious results; however, we experienced no such pronounced effect.

B. Lanthanum Titrations - Because of its similarity to the plutonium (III) ion, the acid-base titration of lanthanum ion has been studied. Lanthanum, however, has but one valance state; therefore, some of the complications which result with plutonium are eliminated. In Figure 4 are shown curves for the potentiometric and conductimetric titration of a solution 1.94×10^{-3} M in lanthanum chloride and 2.71×10^{-3} M in hydrochloric acid. The sodium hydroxide solution

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used in the titration was 0.0986 M; the potential was measured with both the hydrogen electrode and the glass electrode. The first break in the potentiometric curve appears at the theoretical free acid end point. In titrations where no excess acid was present, the pH of the initial lanthanum chloride solution was about 6.1. The mid-point of the precipitation plateau occurs at a pH of 8.45, and a second break which indicates the complete precipitation of lanthanum appears at approximately 2.5 equivalents of base per mole of lanthanum ion. It was found that this break could be induced somewhat earlier by increasing the total chloride ion concentration. For example, in 4.0 N sodium chloride solution only 2.2 equivalents of base were needed to precipitate each mole of lanthanum. A back titration of the hydroxide with 0.1 M acid shows the same equivalence points; however, the plateau which appears in the region where the hydroxide is dissolving is 0.6 pH unit lower than that found while the precipitate was forming. This indicates that the fifteen minutes allowed for equilibrium between reagent additions, while the precipitate was forming, was insufficient.

The conductivity measurements indicate a definite end point corresponding to the neutralization of the free acid, but the end point indicating complete precipitation of lanthanum ion seems to occur slightly before the point at which 2.5 equivalents of base have been added. The uncertainty in the values for the specific conductivity makes it impossible to determine whether a true discrepancy exists

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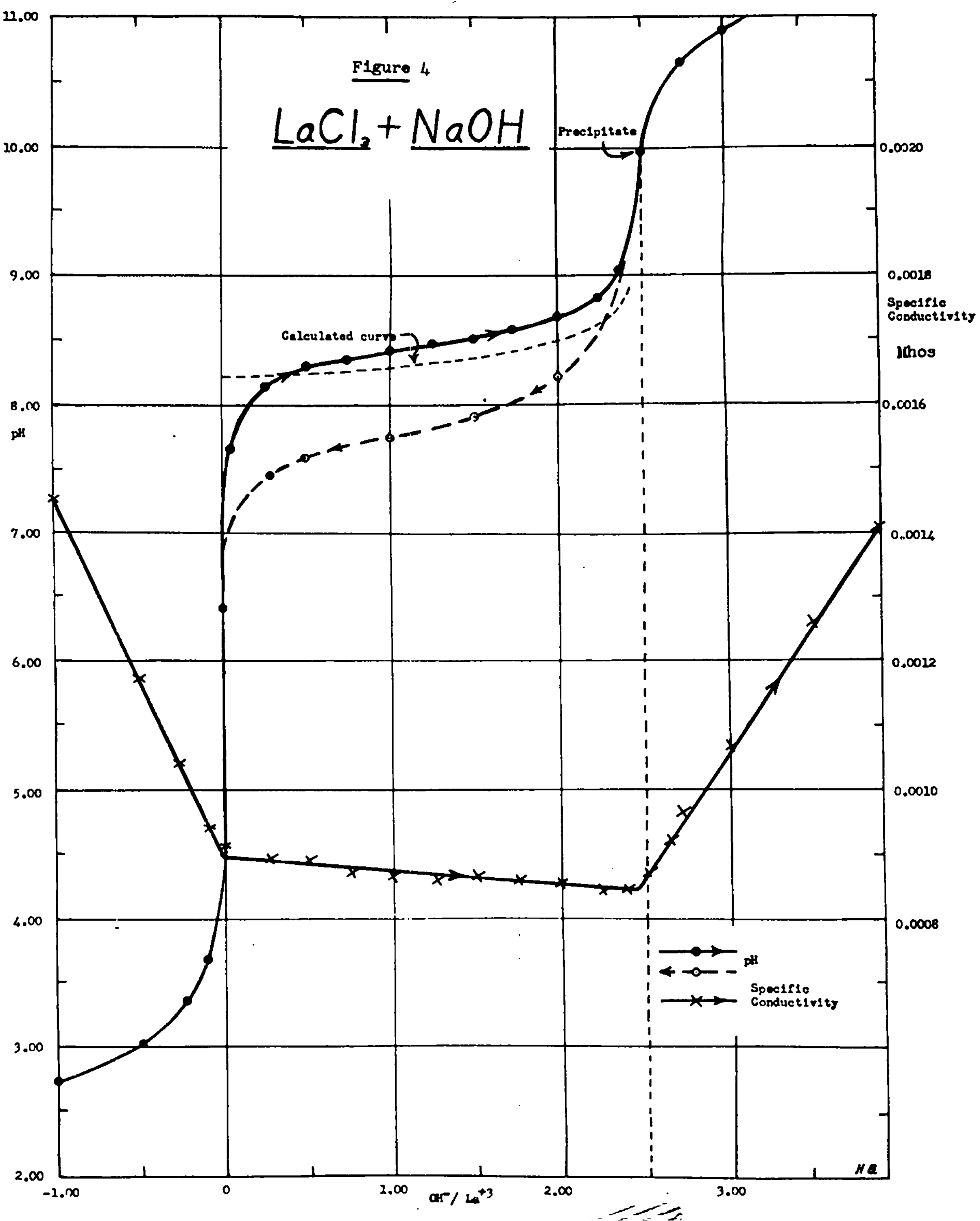

Figure 4

$LaCl_3 + NaOH$

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between the end points determined by the potentiometric and conductimetric methods.

Of special interest was an attempt to prepare lanthanum hydroxide free of chloride ion. Dilute lanthanum chloride solution was added dropwise to a very great excess of vigorously stirred 10N sodium hydroxide solution. The precipitate was centrifuged from this solution and the supernatant was replaced by fresh 10 N NaOH. This was repeated a number of times at the beginning and was continued at less frequent intervals for two weeks. At the end of this period the excess base was washed out by repeated leachings with distilled water. The precipitate dissolved with 2.4 equivalents of acid per mole of lanthanum and 2.5 equivalents of base were required to reprecipitate the same sample, there being no apparent reason for the discrepancy. This precipitate was analyzed for chloride and approximately the expected quantity of chloride ion was found.

The complete precipitation of lanthanum with less than the theoretical equivalents of base suggests the formation of a basic salt, and the titration curves indicate that the composition of the precipitate can be represented by the empirical formula, $La(OH)_{2.5}Cl_{0.5}$. Furthermore, since vigorous treatment with sodium hydroxide does not further hydrolyze the precipitate, it is evidently a rather stable species. Britton (7) titrated 0.0133 N lanthanum nitrate and found an equivalence point indicating a compound of the type $La(OH)_{2.6}(NO_3)_{0.4}$.

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It is impossible to make use of the slope of the specific conductivity curve as an aid in determining what chemical species are present in solution because of the great effect on the conductivity of the potassium chloride solution which may have leaked into the titration vessel from the saturated salt bridge leading to the calomel half-cell.

From the empirical formula for the precipitated basic salt, the solubility product expression can be written:

$$K_{sp} = [La^{+++}] \ [OH^-]^{2.5} \ [Cl^-]^{0.5}$$

From this expression and an arbitrary value for the pH, the calculated curve of Figure 4 was obtained. The pH of the solution does not rise as rapidly in the initial stage of the titration as the theoretical curve would predict. However, it is not unreasonable to assume that the shape of the curve in this region is controlled by the hydrolysis of the lanthanum ion according to one or more of the following equations:

$$La^{+++} + H_2O \rightarrow LaOH^{++} + H^+$$

$$LaOH^{++} + H_2O \rightarrow La(OH)_2^+ + H^+$$

That the curve rises somewhat more rapidly than is predicted in the final stage of the titration could be explained as buffering action (12) due to the adsorption of hydrogen ions by the precipitate.

If an intermediate value of 8.2 is assumed for the pH of the solution at the mid-point of the titration, the value of the solubility product constant for the basic salt, using the molar concentrations

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of the lanthanum and chloride ions and the activity of the hydroxyl ion, is 2.5×10^{-19}.

C. Plutonium Titrations - In Figure 5 are shown typical curves for the potentiometric and conductimetric titration with 0.0986 M sodium hydroxide of a 65 ml solution 7.34×10^{-3} molar in plutonium (III) chloride. Potentials for this particular curve were determined with the glass electrode. From this curve the end point of the titration is subject to no uncertainty. Both the conductimetric and potentiometric methods indicate a definite end point at 2.50 equivalents of base per mole of plutonium, corresponding to the formation of a basic salt having an empirical formula, $Pu(OH)_{2.5}Cl_{0.5}$. Analysis of both the precipitate and solution for chloride ion gives a material balance corresponding to this formula. As in the case of lanthanum and aluminum the back titration with hydrochloric acid confirms the end points but indicates a lack of equilibrium during the precipitation and dissolving of the basic salt. The drift toward an intermediate value of pH is indicated on the curve at an OH^-/Pu^{+3} ratio of 1.5 by successive points obtained at five minute intervals. The theoretical curve, shown in Figure 5, was calculated by means of the solubility product expression.

$$K_{sp} = [Pu]\ [OH]^{2.5}\ [Cl]^{0.5}$$

It was assumed that 7.32 represents the true equilibrium value of the pH at the mid-point of the titration. It may be noted that the shape of the actual curve is in much better agreement with the theoretical

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curve for plutonium than for lanthanum. Furthermore it seems probable that if sufficient time were allowed for equilibrium to be established, the experimental curve would parallel the theoretical curve over virtually its entire length. The solubility product for $Pu(OH)_{2.5}Cl_{0.5}$ corresponding to the theoretical curve is 9.1×10^{-21} in which the molar concentrations of plutonium and chloride ions and the activity of the hydroxyl ions are employed.

In order to obtain a titration curve such as is shown in Figure 5, it is necessary to rigorously exclude oxygen from the system. Oxygen readily oxidizes plutonium (III) to plutonium (IV) in basic solutions. In order to completely remove oxygen from the hydrogen used with the hydrogen electrode in the potentiometric titrations or from the helium or hydrogen used as an inert atmosphere over the solutions, it was necessary to bubble the gas through three consecutive solutions of chromous chloride and one solution of alkaline pyrogallol (followed by a sulfuric acid wash, a distilled water wash, and a liquid nitrogen trap to remove moisture) and finally to pass it over activated charcoal at liquid nitrogen temperature.

About three moles of gas are used with the hydrogen electrode during the course of a titration; consequently, in order that there be no detectable oxidation the oxygen content must be reduced to about 0.5 ppm. In Figure 6 are shown curves for successive titrations with base and acid in which the hydrogen electrode was employed, but the hydrogen was purified by passing it through the chromous

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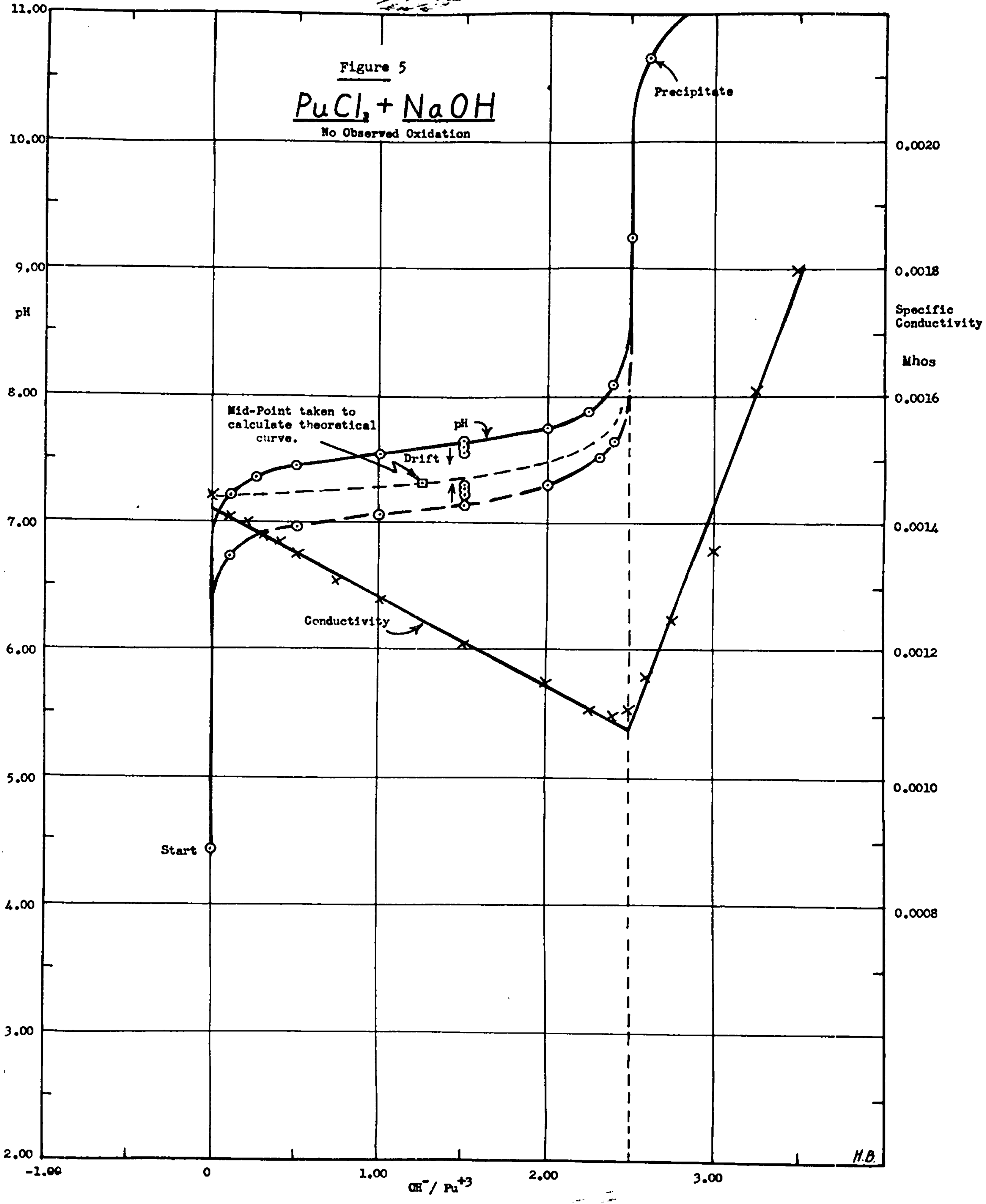

Figure 5

$PuCl_3 + NaOH$

No Observed Oxidation

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chloride and pyrogallol solutions only. The progressive oxidation can be noted with each successive cycle. In addition, the appearance of the green colloidal plutonium (IV) in the solution was quite apparent. It was also demonstrated that activated charcoal alone was insufficient to purify the hydrogen. It is interesting to note that 1) the precipitation end point has been unaffected by the progressive oxidation to plutonium (IV), indicating that the half mole of chloride ion per mole of plutonium combined in the precipitate with plutonium (III) is also retained by plutonium (IV) in basic solution and 2) the colloidal plutonium (IV) formed as a result of oxidation is not redissolved at a pH as low as approximately 3.5.

In Figure 7 is shown a titration curve for plutonium in the presence of "limited" oxygen, i.e., an effort was made to saturate the plutonium solution with oxygen previous to the titration, but additional oxygen was excluded. The glass electrode was used to measure the pH in this case. The oxidation of plutonium (III) by oxygen at a pH slightly above 4.0 is apparent. Figure 7 also shows a similar titration in which oxygen was bubbled through the solution continuously during the titration. The plateau with a mid-point at a pH of approximately 4.4 evidently corresponds to the minimum pH at which oxygen will readily oxidize plutonium (III) under the conditions of the experiment. The pH tended to drift with time toward lower values.

Also included in Figure 7 is a curve for the titration of a solution of plutonium (IV) chloride. The solution was prepared by

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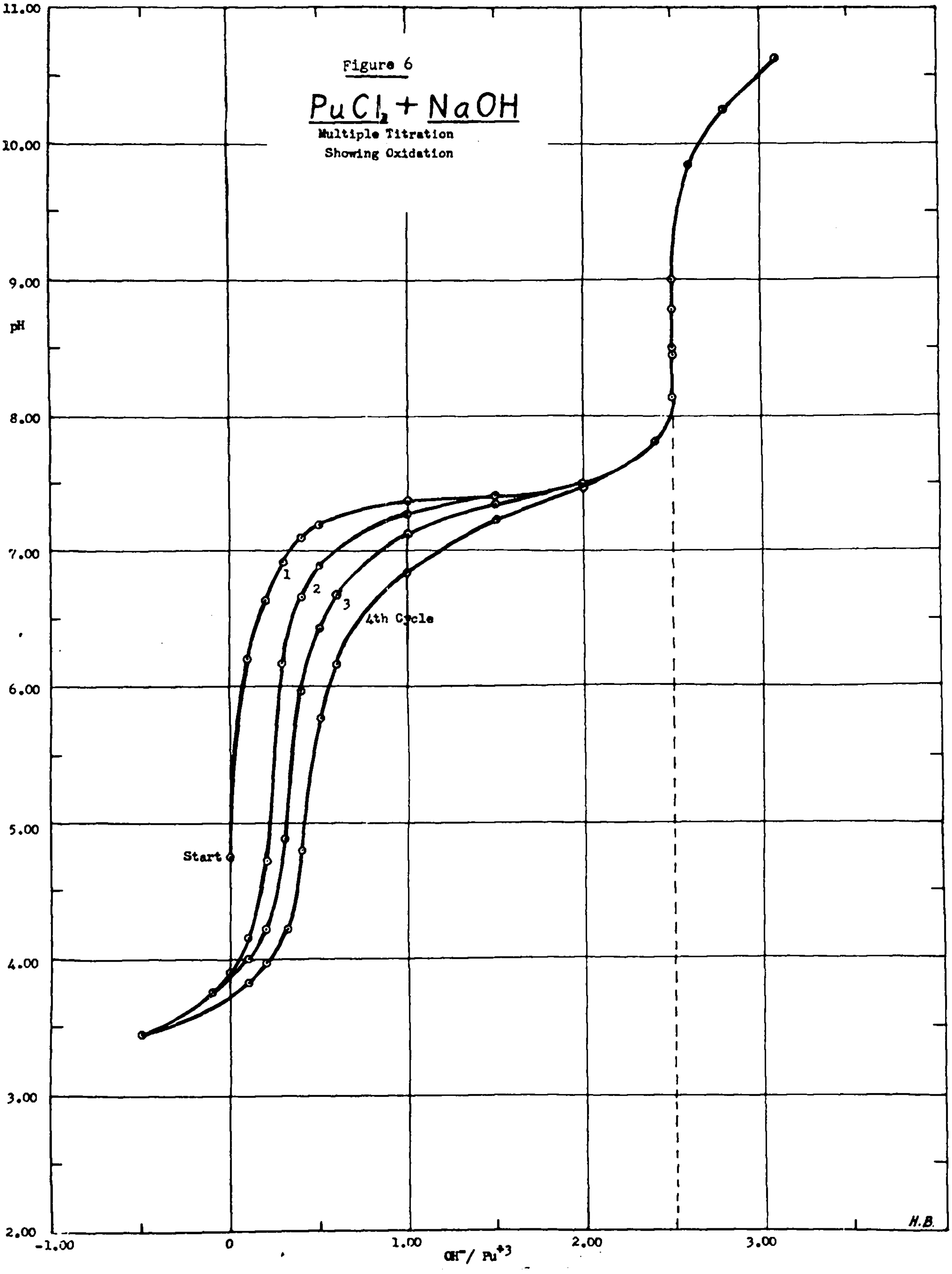

Figure 6

$PuCl_3 + NaOH$

Multiple Titration
Showing Oxidation

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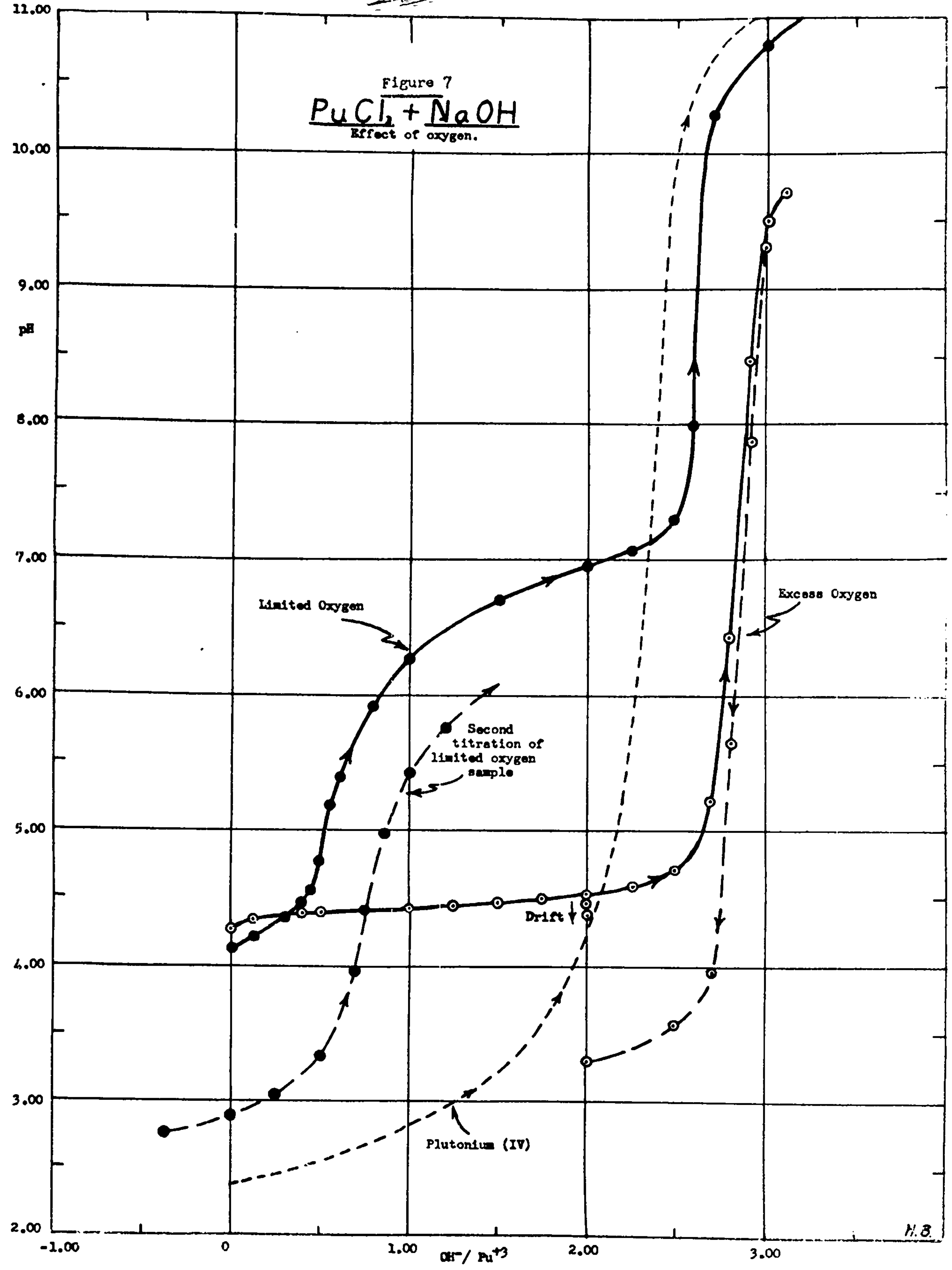

Figure 7

$PuCl_3 + NaOH$

Effect of oxygen.

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evaporating to dryness at 25°C a solution of the chloride in excess acid and dissolving the residue in water. The titration resulted, of course, in the formation of green polymer, but the equivalence point indicates that a relatively large amount of chloride ion is associated with the colloid.

The oxidation of plutonium (III) in a basic solution from which oxygen had been excluded was investigated. Tests were made in which samples of plutonium (III) chloride were dissolved in air free water in bulbs from which air was excluded. After boiling these solutions under vacuum at 25°C by pumping out the vapor for several minutes, enough air free sodium hydroxide was added to raise the pH to a definite value predetermined by titration of other samples. After one hundred hours about 15% of the plutonium had oxidized at a pH of either 7 or 10. This oxidation probably results from reaction with the water but is complicated by the oxidation due to the alpha activity.

Curves for the titration of solutions of plutonium (III) chloride and perchlorate given by Kraus and Dam (23) indicate that their results may have been complicated by excessive oxidation.

IV. SPECIFIC CONDUCTANCE OF $PuCl_3$

The cell constant for the cylindrical conductivity cell (See Figure 2) was found by using standard potassium chloride solutions. Plutonium (III) chloride was then prepared by dissolving the metal in hydrochloric acid and vacuum drying the compound formed at 25°C.

This solid was used to prepare solutions of known concentration. Table 1 shows the equivalent conductance of plutonium (III) chloride in reciprocal ohms as calculated from the observed electrical resistance and the cell constant. These values are probably accurate to about 4%.

Table 1

Equivalent Electrical Conductance of $PuCl_3$

(Mhos)

$PuCl_3$ Molarity

Temp.	0.0050 M	0.0080	0.0100	0.0200
5°C	72	69	70	66
10	83	80	80	75
15	95	91	91	85
18	103	97	98	91
20	107	102	102	96
25	120	113	114	106
30	132	127	126	117
40	160	153	152	141
50	191	181	180	167

A graph of the equivalent conductance versus the square root of the normality was extrapolated to infinite dilution using the same rate of change of slope as obtained from the literature (24) for lanthanum chloride. The ion conductance of the chloride ion was subtracted from the value so obtained to give the ion conductance of plutonium (III). This was repeated at several temperatures. The extrapolation cannot be considered to be highly accurate because of the lack of values at low concentrations. However, in Table 2 are

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tabulated the values obtained in reciprocal ohms compared to those of 1/3 La(III) (25).

Table 2

Ion Conductances of La(III) and Pu(III) Ions

(Mhos)

Temperature	1/3 La(III)	1/3 Pu(III)
18°C	61	40
25	72	67
50	119	146

V. BIBLIOGRAPHY

1. Blum, William, J.A.C.S. 35, 1499 (1913)
2. Hildebrand, Joel, J.A.C.S. 35, 863 (1913)
3. Mahin, Ingraham &, Steward, J.A.C.S. 35, 30 (1913)
4. Koltoff, I. M., Z. Anorg. allgem Chem. 112, 172-86 (1920)
5. Grobet, Ed., J. chim. phys. 19, 331 (1922)
6. Anderegg & Daubenspiel, Proc. Indiana Acad. Sci. 35, 141 (1925)
7. Britton, H. T. S., J. Chem. Soc. 127, 2110 (1925)
8. Miller, U. S. Public Health Reports, 40, 351 (1925)
9. Drossbach, Z. anorg. Allgem Chem., 166, 225 (1927)
10. Treadwell & Bernasconi, Helv. Chem. Acta 13, 500 (1930)
11. Britton, H. T. S., Trans. Far. Soc. 28, 531 (1932)
12. Davis & Farnham, J. Phys. Chem. 36, 1057-74 (1932)
13. Treadwell & Zurcher, Helv. Chim. Acta 15, 980 (1932)
14. Kanning & Kratli, Ind. Eng. Chem., Anal. Ed. 5, 381 (1933)
15. Treadwell & Boner, Helv. Chim. Acta 17, 774 (1934)
16. Jander & Jahr, Kolloid Beihefte 43, 295 (1936)
17. Marion & Thomas, J. Colloid Sci. I, 221 (1936)
18. Martin, A. E., J. Soc. Chem. Ind. 56, 179 T (1937)
19. Whitehead, T. H., J.A.C.S. 59, 1349 (1937)
20. Yoshio Oka, J. Chem. Soc. Japan 61, 311 (1940)
21. Zipper, Donald H., Chemist Analyst 37, 28 (1948)
22. Näsänen & Tamminen, J.A.C.S. 71, 1994 (1949)
23. Seaborg, Katz & Manning, "The Transuranic Elements," (Paper 4.14 by Kraus & Dam) McGraw-Hill, N. Y. (1949)
24. Glasstone, S., "Textbook of Physical Chemistry," Ind. ed., D. Van Nostrand Co., N. Y., (1946)
25. Johnston, J.A.C.S., 31, 1010 (1909)

[redacted]

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