THE RARE EARTH METALS AND THEIR COMPOUNDS.

THE NORMAL AND MODIFIED ACETYLACETONATES

By

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INTRODUCTION

The rare earths are a group of elements that are characterized by their difficulty of separation. It has been the underlying goal of rare earth chemists to effect a continuous separation of these metallic elements; however, due to their extreme similarity to one another, every method so far developed is one of fractionation.

Fractional crystallization, fractional precipitation, and fractional electrolytic methods have been employed, and although all of these processes are satisfactory to some degree, there is a time element that makes them prohibitive. Actually, each of these methods consists of a series of one-step operations. Liquid-liquid counter-current extractions have been suggested as a means of separation. Partial separation of lanthanum and neodymium by this method has been reported in the literature (1, 2). This scheme is likewise a fractionation and, as yet, has not been employed to obtain rare earth elements in a state of purity. More recently ion-exchange resins have been used as means of separating the rare earth ions (3, 4, 5). This process is also one of fractionation and has yet to be demonstrated as practical on more than a laboratory scale. The ion-exchange resins, however, are playing an ever increasingly important role in the separation of similar elements such as zirconium and hafnium (6), the actinides, and the lanthanides. The type of bonds that hold the metallic ions to the resins is of secondary nature and resembles the bonding encountered in chelated compounds. These bonds are broken

under conditions of controlled acidity, to yield a fractional separation of the ions introduced into the exchange column.

For this dissertation the primary purpose was to study some chelated compounds of the rare earths, first, to learn more of the nature of chelated compounds and the possible application of this study to the function of ion-exchange resins, and second, to observe the effect of various chelating agents on adjacent rare earths. It was constantly borne in mind that by a thorough study of these compounds a different or better mode of separation of the rare earths might be devised.

Chelate compounds formed by the interaction of metallic ions with acetylacetone, trifluoroacetylacetone, thenoyltrifluoroacetone, and ethyl trifluoroacetoacetate were prepared and investigated.

On page 3 is represented the structural formulas for the type compounds formed. The entire molecular formulas would be rather complicated so that "$\frac{R}{3}$" represents one-third of a rare earth ion.

To prepare these chelated compounds, it was first necessary to obtain the β-diketones. The normal acetylacetone was Eastman-Kodak Company grade, the thenoyltrifluoroacetone was a gift, the ethyltrifluoroacetoacetate was synthesized by Dr. R. A. Staniforth, and the trifluoroacetylacetone was synthesized in this laboratory by the method of Henne, Newman, Quill, and Staniforth (7).
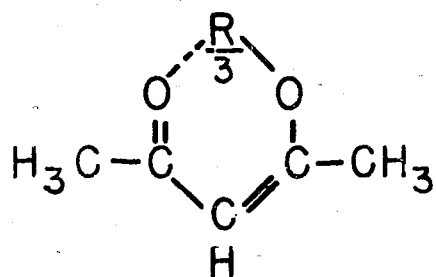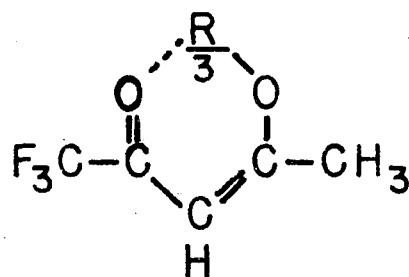
H_3C-C R_3 $C-CH_3$
O   O
C
H

ACETYLACETONATE

F_3C-C R_3 $C-CH_3$
O   O
C
H

TRIFLUORO—ACETYLACETONATE

HC—CH
HC   C—C R_3 C—CF$_3$
S   O   O
C
H

THENOYL—TRIFLUOROACETONATE

F_3C-C R_3 $C-O-C_2H_5$
O   O
C
H
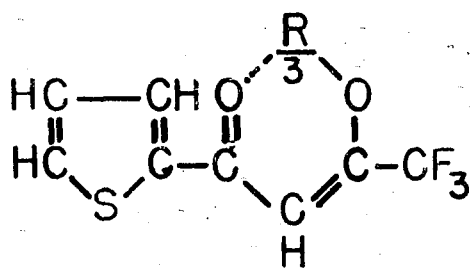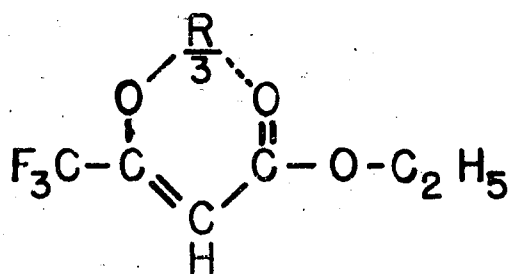
ETHYL TRIFLUORO—ACETOACETATE

PART A

I. Synthesis of Rare Earth Acetylacetonates

The problem of studying the rare earth chelates involved
a) the synthesis of the compounds, and b) the study of certain of
their properties.

The preparation of the rare earth acetylacetonates was first
described by Biltz (8) who synthesized the acetylacetonates of lantha-
num, cerium III, praseodymium, neodymium, aluminum, and thorium by the
addition of an ammoniacal solution of acetylacetone to an aqueous
metallic nitrate solution. Biltz did not report any percentage yields
but did describe the melting points of the products.

Jantsch and Meyer (9) prepared the acetylacetonates of
lanthanum, gadolinium, and yttrium by the method of Biltz and reported
yields of from 77 per cent to 92 per cent of theoretical.

Thorium acetylacetonate was first described by Urbain (10,
11), who synthesized the compound by the action of an alcoholic
solution of acetylacetone on freshly precipitated hydrous thorium
oxide and by a metathetical reaction between sodium acetylacetonate
and thorium nitrate. He reported a melting point of 170° C. for the
compound.

Young and Kovitz (12) prepared thorium acetylacetonate by
mixing ammoniacal solutions of acetylacetone and thorium nitrate.
After purification by sublimation in high vacuum, yields up to approxi-
mately 70 per cent of theoretical were reported. The melting point of
thorium acetylacetonate as reported by these authors is 171.5° C.

Staniforth, Quill, and McReynolds (13) prepared the acetylacetonates of lanthanum, cerium III, praseodymium, neodymium, samarium, europium, and yttrium by the addition of ammoniacal acetylacetone to a concentrated solution of rare earth nitrate. After recrystallization from alcohol solutions, yields up to 79 per cent of theoretical were reported.

From the examination of the literature one observes that there is a wide variance between yields of the acetylacetonates and that for the most part the yields are much lower than those expected from theoretical calculations. Since the enol-keto equilibrium of acetylacetone is pH dependent, and the relatively complete precipitation of many rare earth compounds is also pH dependent, it was reasoned that there must be a cause for this variance and that a synthesis in which the pH is controlled might lead to higher yields. For this research it was postulated that since acetylacetone is so easily oxidized, the chlorides of the rare earths might give more satisfactory results than the nitrates. Since the rare earth hydroxides are relatively insoluble, it was deemed advisable to run the reactions at a pH just below that of the precipitation of the hydroxides. The purpose of this procedure was twofold: 1) to prevent the precipitation of the hydroxides, and 2) to lessen the possibility of the formation of basic acetylacetonates.

Accordingly, the following general method for the preparation of the acetylacetonates of lanthanum, cerium III, praseodymium, neodymium, samarium, europium, yttrium, and thorium was developed.

A weighed quantity of rare earth oxide was dissolved in the minimum amount of dilute hydrochloric acid and the pH adjusted by the addition of dilute ammonium hydroxide to a value of approximately 5.0 as measured by the glass electrode (Beckman Model G pH meter). A solution of ammonium acetylacetonate was prepared by adding concentrated ammonium hydroxide, together with sufficient water for solution, to an amount of freshly distilled acetylacetone which was 50 per cent in excess of that required for complete reaction with the rare earth oxide. The solution of ammonium acetylacetonate was added slowly with stirring to the rare earth chloride solution. The pH of the reaction mixture was maintained at all times at a value just below the pH of precipitation of the hydroxide being studied (14) by the addition of either dilute ammonium hydroxide or hydrochloric acid as required. It was noted that if the solution were too acidic a precipitate did not form, and if too alkaline a gelatinous product was obtained. (The melting points of these gelatinous products were inconsistent, indicating the formation of a mixture of basic acetylacetonates.)

The reaction mixture was stirred for 12 hours to insure conversion of any basic acetylacetonate, which may have been formed due to localized excesses, and to allow for completeness of reaction. The crystalline precipitate which was obtained was filtered, washed with distilled water, air dried for 24 hours and then placed over magnesium perchlorate for 4 days. Yields approaching theoretical were obtained and the melting points checked favorably with those reported in the literature for the same compounds after purification.

As a specific example the preparation of lanthanum ace-
tylacetonate follows:

A sample of lanthanum oxide (5.3 grams), which was
obtained by the ignition of lanthanum oxalate for 12 hours at 800° C.,
was dissolved in dilute hydrochloric acid and the pH then adjusted to
5.5 with dilute ammonium hydroxide.

To 15 ml. of freshly distilled acetylacetone was added
9.9 ml. of concentrated ammonium hydroxide and sufficient water for
solution. The ammoniacal acetylacetone was added slowly with
stirring to the lanthanum chloride solution. The first precipita-
tion was noted at a pH of 6.0. The pH was maintained at 7.5 to
8.0 throughout the experiment. The mixture was stirred for 12 hours
after the last of the ammonium acetylacetonate was added to insure
conversion of any basic acetylacetonate to the normal compound.

The product was filtered, air dried for 24 hours, and
then placed in a desiccator over magnesium perchlorate for 4 days.
There was obtained 12.5 grams of white crystalline lanthanum ace-
tylacetonate. This is a yield of 87.5 per cent of theoretical.
The compound has a melting point of 142-3° C.

Acetylacetonates of cerium III, praseodymium, neodymium,
samarium, europium, yttrium, and thorium were prepared by analogous
methods. In the following only one synthesis is described for each
element. Actually, duplicate syntheses were made for each element
and the results were comparable to those presented.

Cerium Acetylacetonate

For the preparation of this compound 11.5 grams of cerium oxalate was dissolved in concentrated nitric acid and the resulting solution was boiled to decompose the oxalate. Then an excess of concentrated hydrochloric acid was added and again the solution was boiled to decompose the nitric acid. After the nitric acid was decomposed, as evidenced by the absence of brown fumes (N_2O_4), a small amount of hydrogen peroxide was added to reduce any cerium IV to cerium III. The solution was partially evaporated to about 50 ml. and then the standard procedure for preparation was employed while maintaining the pH at a value of 6.5. There was a yield of 11.75 grams (83 per cent of theoretical) of a yellow crystalline cerium acetylacetonate which melted at 147.5° C.

Praseodymium Acetylacetonate

For the preparation of this compound 5.47 grams of oxide was used. The pH of the solution was maintained at 6.5 and there was obtained a 12.58 gram yield (90 per cent) of a crystalline yellow-green precipitate. This precipitate of praseodymium acetylacetonate had a melting point of 143-4° C.

(Note – The praseodymium oxide used was not of spectroscopic purity but contained a small amount of lanthanum.)

Neodymium Acetylacetonate

For this synthesis 5.47 grams of freshly ignited neodymium oxide was dissolved in hydrochloric acid. By maintaining the solution at a pH of 6, and using the standard procedure, 14.42 grams (96 per cent theoretical) of neodymium acetylacetonate was obtained. The

violet crystalline precipitate melted at 144-5° C. after having been dried over magnesium perchlorate.

Samarium Acetylacetonate

Using 5.675 grams of samarium oxide which had been freshly ignited, the standard procedure was employed for the synthesis of the acetylacetonate while maintaining the solution at a pH of 6.1. A yield of 14.93 grams of cream-colored samarium acetylacetonate was obtained. After drying, this compound melted at 145° C. This yield is 100 per cent of theoretical.

Europium Acetylacetonate

Europium oxide (2.8486 grams) was dissolved in hydrochloric acid and the pH of this solution was adjusted to 5.5. Thence, the standard procedure was employed, except that only one-half the usual amount of acetylacetone was used. This smaller amount was necessitated because of the small amount of europium oxide available. The pH was maintained at 6.5 throughout the reaction. There was obtained 7.1075 grams (98 per cent of theoretical) of white europium acetylacetonate which had a melting point of 144-5° C.

Yttrium Acetylacetonate

This compound was prepared by the usual procedure using 3.673 grams of freshly ignited yttrium oxide and maintaining the pH of the reaction mixture at 6.4. There was obtained 11.7024 grams of a cream-colored yttrium acetylacetonate which had a melting point of 131-2° C. This represents a yield of 93.4 per cent of theoretical.

Thorium Acetylacetonate

A synthesis of this compound was included but not intensely studied. For the preparation of this compound 16.62 grams of thorium nitrate crystals $[Th(NO_3)_4 \cdot 12H_2O]$ was dissolved in concentrated hydrochloric acid and the solution was then boiled until visible fumes of nitrogen dioxide were no longer evolved. The solution was evaporated almost to dryness. The standard procedure was employed while maintaining the pH at 6.75. A more recent work (14) gives a pH of precipitation of the hydroxide at a lower value than that used in the synthesis. Further study is necessary on the compound; nevertheless, the melting point obtained (171-2° C.) agrees closely with the melting point reported in the literature (10). There was 14.1612 grams of thorium acetylacetonate obtained which represents a 94 per cent yield.

For comparative purposes the yields of the above rare earth acetylacetonates using the nitrates as starting materials were determined. Experiments analogous to those previously outlined were performed employing nitric acid rather than hydrochloric acid. In each case lower yields of the acetylacetonates were obtained from nitrate solutions except in the case of thorium.

A summary of the data including percentage yields is tabulated in Table I.

TABLE I

Rare Earth	Grams of Oxide	pH of Solution	pH of Pptn. of Hydroxide	Chloride		Nitrate		Color	m.p.	m. p. Literature	Reference
				Gms. of AcAc Obtained	% Yield	% Yield	Gms. of AcAc Obtained				
La	5.3	7.5	8.03	12.5	89	75	10.70	White	142-3	142-3	(13)
Ce	11.5	6.5	7.41	11.75	83	74	10.51	Yellow	144-5	145	(8)
Pr	5.47	6.5	7.05	12.58	90	65	9.07	Green	143-4	146	(8) (13)
Nd	5.47	6.0	7.02	14.42	95.6	67	9.1	Violet	144-5	144-6	(8) (13)
Sm	5.68	6.1	6.83	14.93	100	88	12.79	Cream	145	146-7	(8) (13)
Eu	2.85	6.5	6.8 ca	7.11	98	90	6.51	White	142-3	144-5	(13)
Y	3.67	6.4	6.78	11.70	93.4	89	11.11	Cream	131-2	131	(9)
Th	16.62	6.75	-	14.16	94	96	15.54	White	171-2	170	(10)

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II. Yield of Rare Earth Acetylacetonates with Changing pH

Another phase of the synthetic problem was the determination of the yield of the rare earth acetylacetonates as the pH was varied. For this purpose 5.3 grams of freshly ignited lanthanum oxide was dissolved in concentrated hydrochloric acid. The solution was then diluted to about 50 ml. and an ammoniacal solution of acetylacetone (15 ml. of freshly distilled acetylacetone dissolved in 9.9 ml. of concentrated ammonium hydroxide plus sufficient water for solution) was added. The pH did not rise above 5.0 and there was no visible precipitate. The resulting solution was stirred vigorously and small increments of dilute ammonium hydroxide were added slowly until the first visible precipitate appeared. This precipitate appeared at a pH of 5.5 and was filtered off. The filtrate was returned to the flask and more dilute ammonium hydroxide added until a pH of 6.0 was reached; again the mixture was filtered. The process of alternate precipitation and filtration was repeated at every 0.5 pH unit from 5.5 to 7.8. The yield of acetylacetonate obtained from solutions above a pH of 7.8 was not determined because a gelatinous product resulted from such solutions. The results are tabulated in Table II and represented graphically in Figure 1.

TABLE II

pH	Grams of Acetylacetonate	Per Cent of Theoretical
5.5	0.0023	1
6.0	8.0875	57.3
6.5	1.8076	70.0
7.0	1.5046	81.0
7.5	0.5978	85.1
7.8	0.5077	89.0
	12.5075	

III. Effect of Nitrate Solutions on Yields of Rare Earth Acetyl-
acetonates

Since yields of the acetylacetonates obtained from nitrate

solutions were lower than those obtained from chloride solutions, it

was thought that acetylacetone might be affected by the nitrate ion.

Accordingly, to prove this point a solution containing 15 ml. of

acetylacetone, 9.9 ml. of concentrated ammonium hydroxide, and suf-

ficient water and dilute nitric acid to make 100 ml. of solution was

determined in the visible region through a 5.0 cm. cell on a Cenco-

Sheard Spectrophotelometer. After standing for 24 hours the absorp-

tion spectrum of the solution was again determined. An interpretation

of the results obtained was that, since there was shift of approxi-

mately 20 mμ toward the ultraviolet in the absorption spectrum curve,

there had been a change in the acetylacetone. This shift is too

large to be attributed entirely to experimental error. Undoubtedly,

the shift in the absorption spectrum curve was due to a partial oxi-

dation of the acetylacetone by the nitric acid.

These results support the idea that higher yields of purer

acetylacetonates can be obtained when chloride solutions are used

rather than when nitrate solutions are used. Following are tabulated

the data obtained in this experiment (Table III). These data are

represented graphically in Figure 2.

TABLE III

Data for First Absorption Curve					Data for Absorption Curve Obtained 24 Hours After First One			
$m\mu$	Io	I	$\log \frac{Io}{I}$		$m\mu$	Io	I	$\log \frac{Io}{I}$
420	3	.5	0.7782		400	1.8	0.2	0.9543
425	3.5	1.8	0.2888		405	2	0.8	0.3979
430	4.2	3.0	0.1461		410	2	1.0	0.3010
435	5.0	3.9	0.1179		415	5.2	3.5	0.1719
440	6.2	4.8	0.1112		420	6	4.4	0.1347
445	7.2	6.0	0.0891		425	7	5.5	0.1047
450	8.5	7.0	0.0843		430	7.8	6.2	0.0997
455	9.8	8.0	0.0881		435	8.8	7.2	0.0872
460	11.0	9.5	0.0637		440	10.2	8.6	0.0741
465	12.2	11.0	0.0450		445	11.2	9.9	0.0536
470	14.0	12.6	0.0457		450	12.5	11.0	0.0555
475	15.5	14.0	0.0442		455	13.8	12.4	0.0465
480	17.4	16.0	0.0364		460	16.0	14.4	0.0458
485	19	17.8	0.0284		465	17.0	15.8	0.0318
490	21.2	20.0	0.0253		470	19.2	18.0	0.0280
495	23.2	22.0	0.0231		475	21.0	19.6	0.0278
500	25.2	24.0	0.0211		480	23.0	22.0	0.0193
505	27.8	26.4	0.0224		485	25.0	23.8	0.0204
510	29.0	28.0	0.0152		490	28.0	26.5	0.0239
515	32.5	31.0	0.0205		495	30.0	28.5	0.0223
520	34.0	33.0	0.0130		500	32.0	31.0	0.0148
525	37.0	35.5	0.0180		505	35.0	33.5	0.0190
530	39.8	38.5	0.0144		510	36.5	35.4	0.0133
535	41.5	40.1	0.0149		515	39.5	38.5	0.0111
540	45.0	44	0.0097		520	40.2	39.0	0.0132
					525	42.0	40.5	0.0158
					530	46.0	43.5	0.0243
					535	47.0	46.5	0.0047
					540	51.5	50.0	0.0128

LANTHANUM ACETYLACETONATE

FIGURE 1

YIELD IN GRAMS

pH OF PRECIPITATION
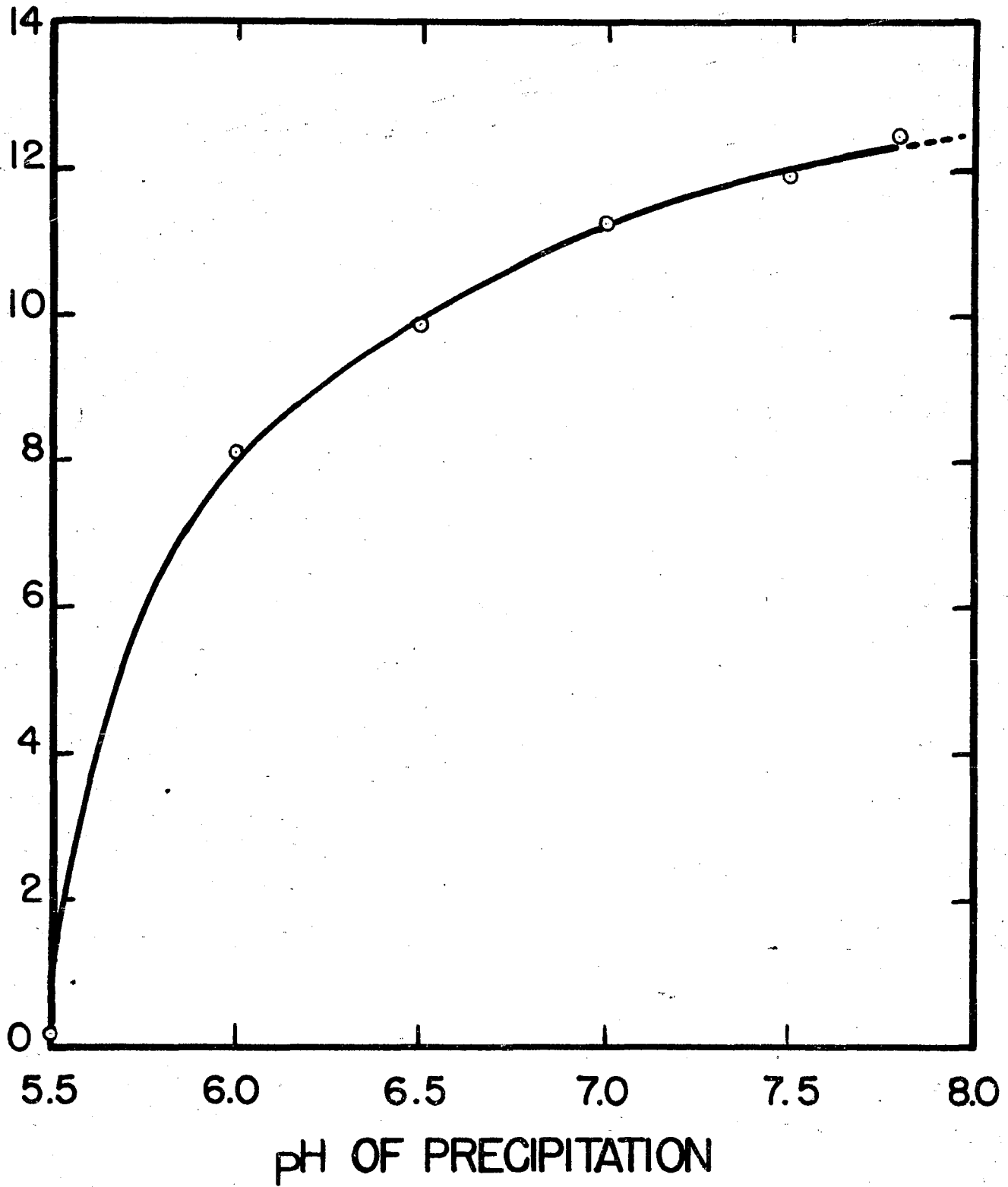
FIGURE 2
ABSORPTION SPECTRUM CURVES OF ACETYLACETONE

o = 1ST. ABSORPTION SPECTRUM CURVE

x = ABSORPTION SPECTRUM AFTER 24HRS.

LOG $\frac{I_0}{I}$

Mμ

17
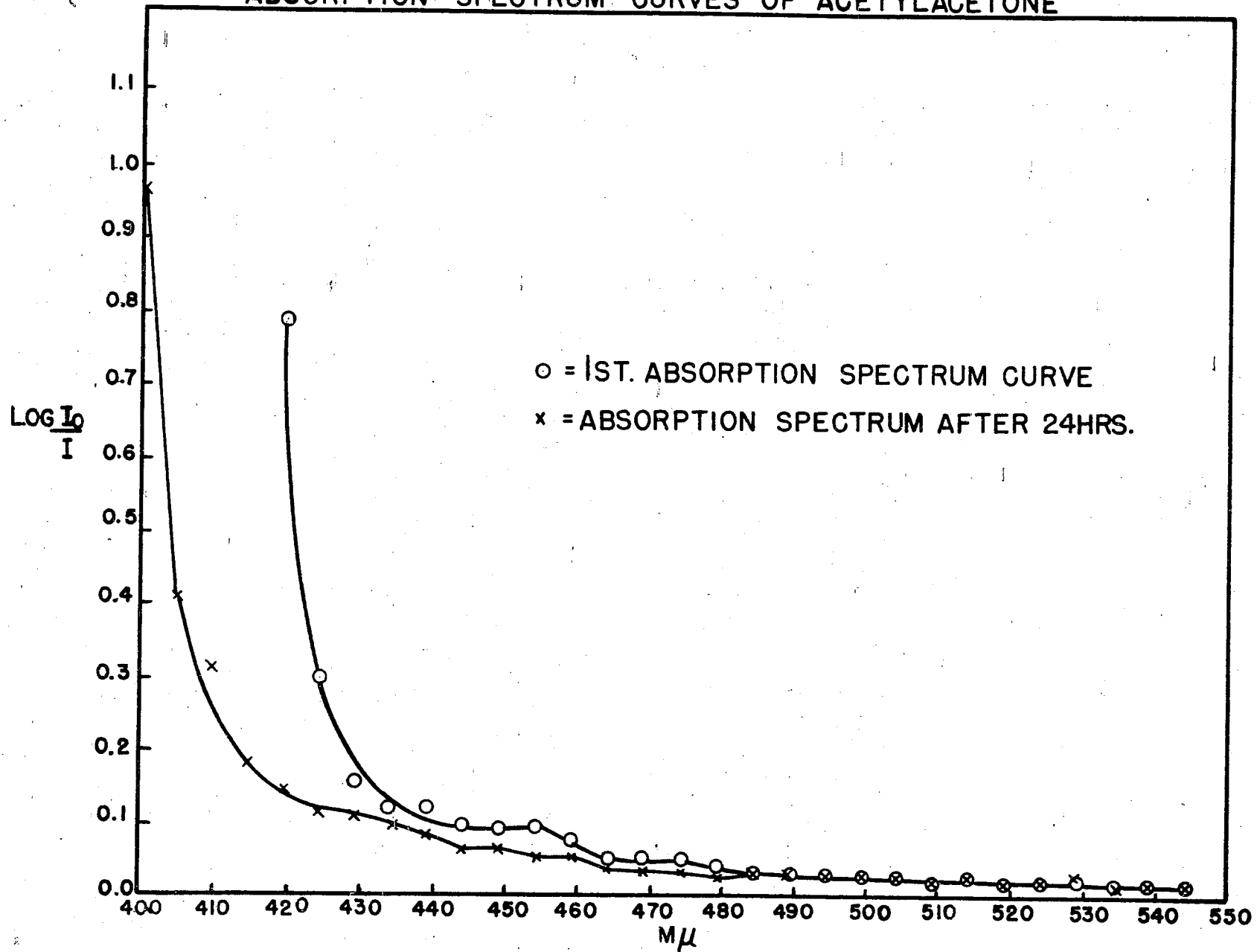
Since in the preceding experiment the determination had been in the visible region an attempt was made to determine the spectrum with a Beckman ultraviolet spectrophotometer. Solutions of the same concentration as employed in the preceding experiment were used. A very high value for $\log \frac{I_o}{I}$ was obtained (1.728) as a low reading. In order to obtain a lower reading the concentration of acetylacetone was halved, but instead of the expected lower reading there was complete absorption. This extinction was noticeable even in concentrations of one part per hundred of acetylacetone.

For the purposes of this problem the measurement of the ultraviolet absorption spectrum of ammonium acetylacetonate was abandoned, since apparently the behavior of the compound in dilute solutions is different from the behavior in concentrated solutions. The extinction upon dilution might be explained as being due to the hydrolysis of ammonium acetylacetonate with the subsequent formation of hydrogen bonds.

Solutions of different concentrations of acetylacetone alone show no shift of bonds (15). This phenomenon can be explained since the acetylacetone is an extremely weak acid; and, thus, there would be only a very slight effect on the dissociation by dilution.

According to Morton, et. al, (16), however, alkali will ionize even the weak acid, and the ionic form shows the shift in absorption. Later in this discussion this point will again be brought out.

IV. Conclusions

From the results on the synthetic work thus far obtained several conclusions can be drawn:

1. The agreement of melting points of the rare earth acetyl-acetonates obtained, as compared to those recorded in the literature, even after purification, indicates a product of high purity.

2. The formation and precipitation of rare earth acetylaceto-nates is a pH dependent phenomenon. If the solutions in which the compounds are prepared are too acidic no precipitate forms, and if too alkaline a gelatinous product is obtained. This latter fact indicates the formation of a basic acetylacetonate and, too, the melting points of different samples of the gelatinous type of material were not consistent.

3. Higher yields of the acetylacetonates of lanthanum, cerium III, praseodymium, neodymium, samarium, europium, and yttrium are obtained when appropriate chlorides instead of nitrates are used.

4. A higher yield of pure rare earth acetylacetonate is obtained by maintaining the pH of the solution just below that of the pH of precipitation of the rare earth hydroxide.

5. The melting points of the acetylacetonates of the various rare earths are very nearly the same value, indicating very close similarity in crystal structure. Apparently, the individual rare earth elements lose much of their identity when they are the central atom of a chelate compound.

PART B

I. Preparation of Trifluoroacetylacetone

The preparation of trifluoroacetylacetone was undertaken so that the physical properties of the normal and trifluoroacetyl-acetonates of the rare earths could be compared and contrasted. For this preparation the method of Henne, Newman, Quill, and Staniforth (7) was used, and entailed a Claissen condensation of acetone and ethyltrifluoroacetate. It was necessary to purify and dry the reactants and solvents, which was done as follows:

Xylene

Xylene (C. P. grade) was refluxed over sodium metal for six hours and distilled through a dry glass system into dried bottles. Sodium wire was added to maintain dryness.

Ether

Ethyl ether (C. P. anhydrous) was refluxed over sodium for eight hours and then distilled into dried bottles. Sodium wire was placed in the ether to maintain dryness; as the wire lost its luster it was replaced.

Ethanol

Approximately one-third mole of sodium (seven grams) was dissolved in small portions in one liter of commercial absolute alcohol, 27.5 grams of ethyl phthalate was added, and the solution was refluxed for an hour in a system protected from moisture. The anhydrous alcohol was then distilled carefully through a ten cm. column. Moist air was excluded throughout the distillation by the

use of drying tubes filled with indicating Drierite at all apertures.

Acetone

Acetone was dried over anhydrous potassium carbonate for two days with occasional shaking. The potassium carbonate was then removed by filtration and the acetone allowed to stand for several hours over P_2O_5 from which it was then distilled directly.

Ethyl Trifluoroacetate

Ethyl trifluoroacetate (Columbia Organic Chemicals Company) was dried over P_2O_5 for 24 hours and then distilled.

Synthesis

One mole (23 grams) of freshly cut sodium metal was placed in a 1-liter 3-necked flask equipped with an efficient reflux condenser (both a West and a Graham condenser were used, with the Graham condenser inserted directly above the West condenser), a 250 ml. dropping funnel, and a Hershberg stirrer. Both the condenser and dropping funnel were protected from moisture with drying tubes filled with indicating Drierite. The stirrer which was made carefully to fit the contours of the flask was powered with a Cenco cone-drive stirring motor operating at its highest speed. All glass apparatus was used throughout the synthesis. Three hundred milliliters of the anhydrous xylene was added and the system flushed out with nitrogen. The flask was gently heated with a Bunsen burner until the sodium melted. The motor was started at high speed and the sodium metal was reduced to a finely powdered form in about 60 seconds. The stirrer was removed and a filter stick inserted. The xylene was filtered off

and the sodium washed with two 100 ml. portions of anhydrous ether.

It was necessary to exercise great care in preventing any sodium and

ether from coming in contact with water. The stirrer was replaced

and provision was made to lead the hydrogen gas formed to a vent.

Three hundred milliliters of anhydrous ether was added to the sodium.

One mole (46 gm.; 58 ml.) of ethanol (anhydrous) was placed in the

dropping funnel. The stirrer was started and the ethanol was allowed

to drop slowly into the sodium-ether mixture. The rate of addition

was determined by the rate of reflux of the ether. The addition of

the ethanol was complete in about two hours, during which time the

mixture turned from gray to white. The mixture was refluxed for four

hours after the addition of the ethanol to insure complete reaction.

Then one mole (142 grams) of ethyl trifluoroacetate was slowly added.

Again a small amount of heat was generated, causing gentle reflux.

The mixture was stirred for an hour and allowed to stand for 48 hours.

The mixture was carefully transferred to a 3-liter 3-necked flask. One

mole (60 gm.; 63 ml.) of glacial acetic acid was added with stirring.

Hydrated copper acetate (120 gm.) was dissolved in 1.6 liters of hot

water and the solution filtered through Filtercell to remove basic

salts. This solution was slowly added to the acidified mixture in the

3-necked flask. A blue solid separated, which was largely soluble in

the ether layer. The ether was stripped; the copper salt remained as

a purplish blue waxy precipitate in the water solution. This mixture

was cooled in an ice bath and filtered. After air drying, 260 grams

of a blue crystalline solid was obtained. This solid was recrystallized

from anhydrous ethanol yielding a green crystalline mass which was filtered, washed once with cold ethyl alcohol, and air dried. On drying, the green crystals turned blue; indicating, perhaps, that the green crystalline solid might have been an alcoholate. After drying, the copper trifluoroacetylacetonate was dissolved in 750 ml. of anhydrous ether and dry H_2S gas was bubbled into the solution. Black copper sulfide was precipitated. The mixture was filtered through Superfilterol to remove the copper sulfide. The ether was then stripped by distilling through a column (15 mm. x 30 cm.) packed with glass helices. The remaining liquid was fractionated. The trifluoroacetylacetone obtained weighed 150 grams and boiled at 106° C. The trifluoroacetylacetone had a definite mercaptyl odor about it. Although this odor was not mentioned in the thesis of Staniforth (13), it was learned through a private communication from him that the odor has been observed. Perhaps the hydrogen sulfide step should be omitted and sulfuric acid added, forming cupric sulfate from which the β-diketone could be distilled.

The equations for the above reactions are:

(1) $\overset{\overset{\displaystyle O}{\|}}{CH_3-C-CH_3}$ + NaOEt ——— $\overset{\overset{\displaystyle O-Na}{|}}{CH_2=C-CH_3}$ + EtOH

(2) $\underset{\overset{\displaystyle \|}{O}}{F_3C-C-O-Et}$ $\overset{\overset{\displaystyle CH_2=\overset{\overset{\displaystyle O-Na}{|}}{C}-CH_3}{| \quad |}}{}$ ——— $F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle OEt}{|}}{C},ONa \, CH_3$

(3) $F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle OEt}{|}}{C},ONa \, CH_3$ ——— $F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH=\overset{\overset{\displaystyle ONa}{|}}{C}-CH_3$ + EtOH

(4) $F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH=\overset{\overset{\displaystyle ONa}{|}}{C}-CH_3$ + HOAc ——— $F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ + NaOAc

(5) $F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ + $Cu(OAc)_2$ ——— $Cu(F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH=\overset{\overset{\displaystyle O}{|}}{C}-CH_3)_2$ + 2HOAc

(6) $Cu(F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH-\overset{\overset{\displaystyle O}{|}}{C}-CH_3)_2$ + H_2S ——— CuS + $F_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$
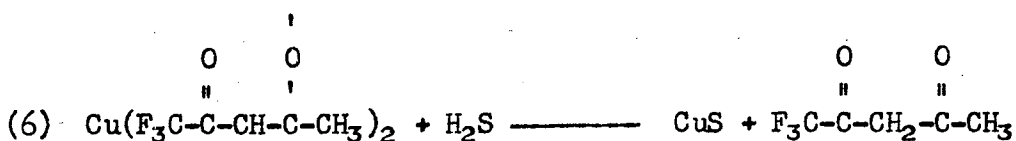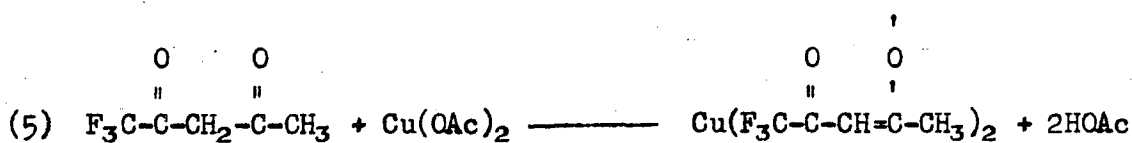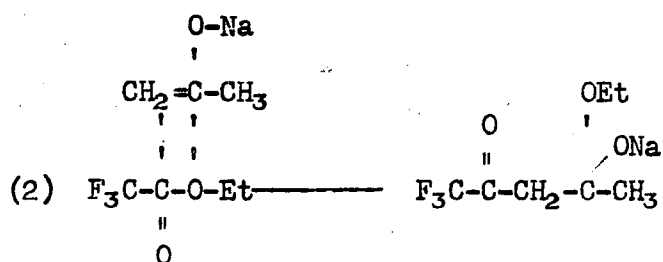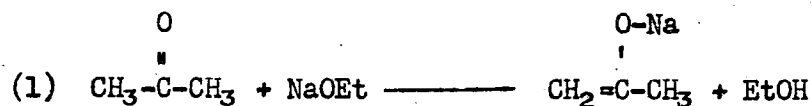
II. Preparation of the Trifluoroacetylacetonates of the Rare Earths

        After preparing trifluoroacetylacetone the next step was
the synthesis of the rare earth trifluoroacetylacetonates. Since a
detailed study of the preparation of the normal acetylacetonates had
been described, the synthesis of the fluorinated derivatives was per-
formed using analogous techniques.

Lanthanum Trifluoroacetylacetonate

        For this synthesis 3.53 grams of lanthanum oxide (La_2O_3)
was dissolved in the minimum quantity of dilute hydrochloric acid
and the pH adjusted to approximately the value of 5.0. Trifluoro-
acetylacetone (10 grams) was dissolved in ammonium hydroxide and
sufficient water for solution. The ammonium trifluoroacetylacetonate
solution was added slowly with vigorous stirring to the lanthanum
chloride solution. After the addition of the last ammonium trifluoro-
acetylacetonate solution the pH was adjusted to 7.9 and maintained at
this value throughout the remainder of the synthesis by the addition
of dilute ammonium hydroxide or hydrochloric acid as required. The
mixture was stirred for an hour, then allowed to stand for 24 hours,
after which time it was filtered, washed with water, and air dried for
48 hours. There is a 7.3345 gram yield of white crystalline lanthanum
trifluoroacetylacetonate which has a melting point of 164.5° C. This
yield represents only 58 per cent of theoretical, which indicates that
either the triflurooacetylacetone was not pure or that the pH of pre-
cipitation is not the same as for the normal compound.

Praseodymium Trifluoroacetylacetonate

To prepare praseodymium trifluoroacetylacetonate, 3.58 grams of praseodymium oxide (Pr_6O_{11}) was dissolved in a minimum quantity of diluted hydrochloric acid and the pH adjusted to approximately 5.0 with dilute ammonium hydroxide. Ten grams of trifluoroacetylacetone was dissolved in ammonium hydroxide and a sufficient amount of water for solution. (It is noted that ammonium trifluoroacetylacetonate is much more insoluble in water than the ammonium acetylacetonate.) The ammonium acetylacetonate solution was added slowly with vigorous stirring to the praseodymium chloride solution while the pH of the solution was maintained at 7.0. The mixture was stirred for one hour and allowed to stand for 24 hours. It was then filtered, washed with water and allowed to dry in air. There is a 9.8788 gram yield of green praseodymium trifluoroacetylacetonate which melted at 162.0° C. This yield is 72 per cent of theoretical.

Neodymium Trifluoroacetylacetonate

A sample of neodymium oxide (Nd_2O_3; 3.59 grams) was dissolved in dilute hydrochloric acid, and the same procedure as outlined for lanthanum and praseodymium trifluoroacetylacetonate was used while maintaining the pH at 6.0. There was obtained 6.2314 grams of purple crystalline neodymium trifluoroacetylacetonate which melted at 162.5-163° C. This represents a yield of 49 per cent of theoretical.

Samarium Trifluoroacetylacetonate

The same technique as for lanthanum, praseodymium, and neodymium acetylacetonates was employed, using 3.78 grams of samarium oxide. A pH of 6.0 was maintained throughout the reaction. After

drying there was obtained 10.8668 grams of cream-colored samarium tri-fluoroacetylacetonate which melts at 160-2° C. This yield is 83.5 per cent of theoretical.

Table IV shows the tabulated data described above.

TABLE IV

Metal	Grams of Oxide	pH of Reaction	Grams Yield	% Yield	m.p.	m.p. Literature
La	3.53	7.9	7.3345	58	164.5° C.	169° C. (13)
Pr	3.58	7.0	9.8788	72	162° C.	133-4° C. (13)
Nd	3.59	6.0	6.2314	49	162.5° C.	133-4° C. (13)
Sm	3.78	6.0	10.8668	83.5	160-2° C.	136-7° C. (13)

It is noted that there is some inconsistency in the melting points obtained as compared with those found in the literature. The tri-fluoroacetylacetonates, because of the unsymmetrical structure of the molecule, should be more polar and thus have a higher melting point. Likewise, from the examination of other references (17), the differences in properties between lanthanum and praseodymium seem insufficient to account for the differences in this case. It is noted that there are some inconsistencies in yields; the following are contributing factors:

1) Since these were the first preparations, nothing was known of optimum conditions.

2) The pH studies described in Part C of this thesis afford data which will permit improvement.

3) The acid dissociation constant of trifluoroacetylacetone is in the same pH range as the pH of precipitation of the rare earth trifluoroacetylacetonates which will necessitate very closely controlled conditions.

A more detailed study of both the synthesis of the trifluoroacetylacetone and the rare earth trifluoroacetylacetonates should be made.

PART C

Titration Studies

Introduction

This part of the discussion is on the determination of the solubilities of rare earth acetylacetonates in water and various other solvents. The only quantitative determinations were made on the solubilities in water and water-dioxane solutions. The rare earth acetylacetonates are not soluble to any noticeable degree in the water-dioxane solutions and less than 1 part per 1000 soluble in water. However, in water some inconsistencies were noted and apparently the solubility in water is a function of the pH.

To answer the question which arose concerning the variation of solubility with pH, experiments were performed in which rare earth acetylacetonates were suspended in water and titrated with standard acid. From these experiments it was noted that the acetylacetonates went into solution in the acid medium, but the pH at which solution occurred was not constant for a given rare earth. Also, the initial pHs for the mixtures of the various rare earth acetylacetonates were not consistent. It was also noted that all of the solid acetylacetonate did not enter into the reaction since it was not wetted by the water and clung to the sides of the reaction vessel.

Since the method outlined above of titrating the rare earth acetylacetonate against an acid to effect solution was not satisfactory, a different approach to the problem was made. It was thought that more consistent results might be obtained if a rare earth salt

were dissolved in water or water-dioxane solution containing the chelating agent, the pH of the solution adjusted to some arbitrarily determined value, and titrated with standard bases. In essence, this was the method employed by Calvin and Wilson (18) for the measurement of the strength of chelate bonds.

At the insistence of Dr. Quill it was decided from the outset to allow sufficient intervals of time between successive additions of reagent to permit the attainment of equilibrium. This idea was a carry over from experience gained in the titration of rare earth sulfates in the presence of an excess of sodium ions by Wilson and Quill (19).

Using the technique outlined above, preliminary titrations of the rare earth ions and acetylacetone produced unexpected results. The curves plotted from the data obtained were much more complex in nature and entirely different except in the very high pH range from those of copper, which was used as the standard metal ion in the work by Calvin and Wilson (18). Consequently, an attempt was made to reproduce the data and curves presented by those authors; but when a minimum of 3-5 minutes was allotted between successive additions of alkali, it was found impossible to duplicate the work. However, when as little time as possible was allotted between successive additions it was possible to reproduce Calvin's data exactly.

These discoveries presented a problem of interpretation, a discussion of which will constitute the major portion of the remainder of the dissertation.

The three groups of titration studies made were: 1) the chelating agents in the absence of a metal ion which tends to chelate, 2) the chelating agents in the presence of copper, zinc and nickel ions, and 3) the chelating agents in the presence of rare earth ions. The sequence of study in the laboratory is different from the sequence presented in the thesis.

All of the titration studies were made under conditions as identical as possible. For example, the chelating agent or the metallic chloride was dissolved in 100 ml. of a 50 per cent water - 50 per cent dioxane solution; the pH was adjusted to 1.80, a value which was determined arbitrarily. (The dioxane was secured from the Eastman Kodak Company and was purified by refluxing for eight hours with ten per cent by weight of 1 N. hydrochloric acid, and then drying over solid potassium hydroxide. The dried dioxane was then distilled quickly through a column 15 mm. x 30 cm. packed with glass helices.) The volume of solution was maintained as closely to 100 ml. as was possible throughout the entire titration. The reaction mixture was stirred vigorously and continuously by air-driven stirrers. The water-dioxane solutions were used, since the purpose was to compare and contrast the results obtained with those reported by Calvin, et al. (18), who used the mixed solvents in order to obtain a greater solubility of the chelated compounds. It was discovered, however, in later work that little difference in solubility is noted irrespective of solvents used. Water alone seems to be equally effective for the studies. The data, curves, and conclusions obtained from the experimental work are presented in the following pages.

I. Titration of Chelating Agents in Absence of Chelating Metal Ions
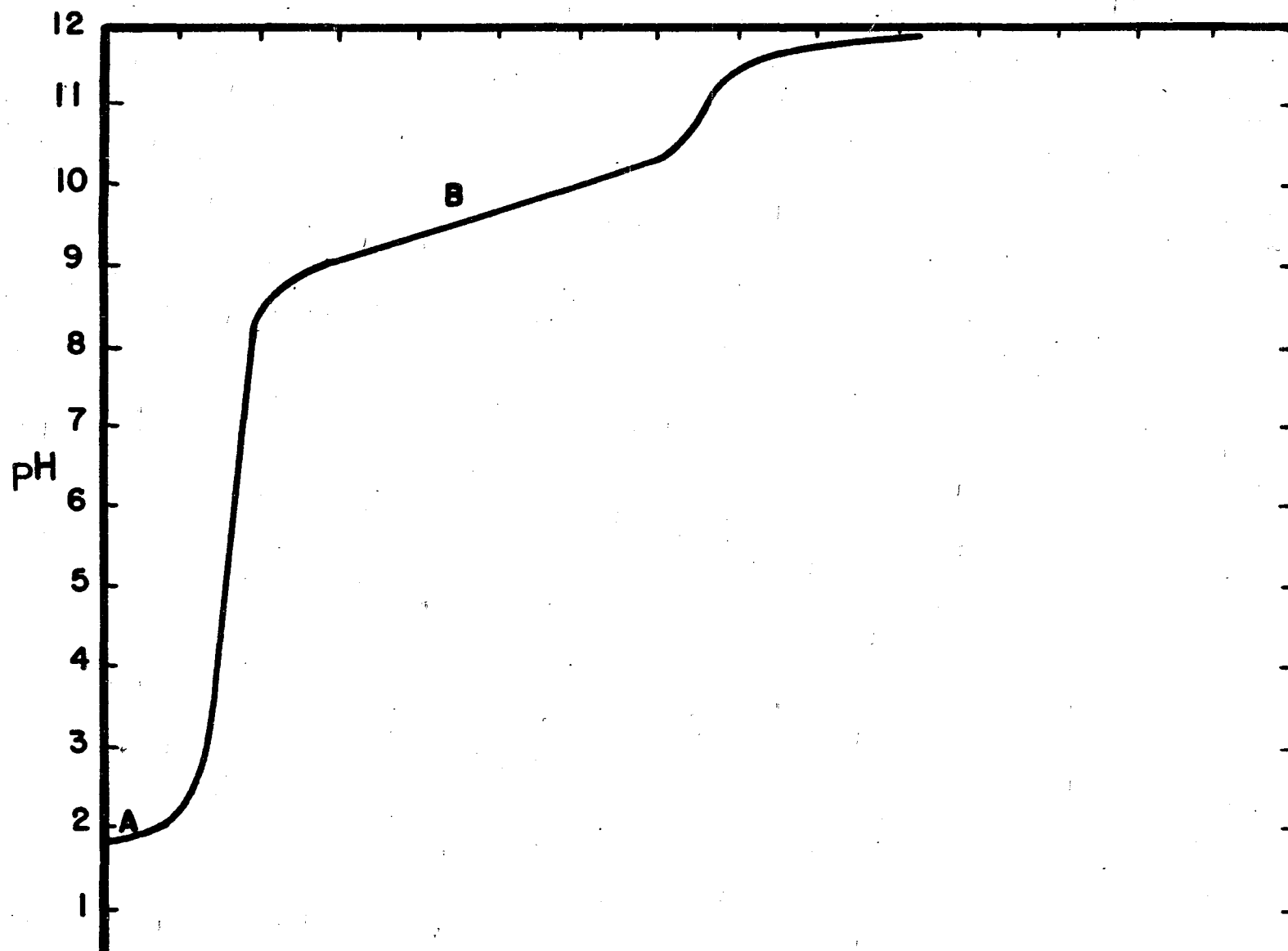
    a. Acetylacetone

        The method of Calvin and Wilson (18) was employed to measure the relative strengths of the chelate bonds as well as the behavior of the chelated rare earth compounds in solutions of varying acidity. It was desirous to know the behavior of the chelating agents with respect to the alkali and in the absence of a metal ion which tends to chelate.

        To obtain the data on acetylacetone, 0.60 grams of freshly distilled acetylacetone was dissolved in 100 ml. of 50 per cent water - 50 per cent dioxane and the pH adjusted with 1:1 hydrochloric acid to 1.80. Then with vigorous agitation 1.0672 N. sodium hydroxide was added in increments of 0.2 ml. At least three minutes were allowed between the successive additions of alkali. Since there were no phase changes, longer time intervals were not deemed necessary. The data obtained are tabulated in Table V in the Appendix and represented graphically in Figure 3.

        Plateau $\underline{A}$ in Figure 3 represents the neutralization of excess acid. Plateau $\underline{B}$ represents the reaction of acetylacetone with sodium hydroxide to form sodium acetylacetonate. The midpoint of this plateau was taken as the acid dissociation constant of the ketone and for acetylacetone is $10^{-9.67}$, which is in good agreement with the value ($10^{-9.7}$) reported in the literature (18). The small acid dissociation constant value verifies the fact that acetylacetone is an extremely weak acid and that the displacement of the proton should take place in acid solution only in the presence of a metal ion which has strong chelating tendencies.

FIGURE 3
ACETYLACETONE

b. Trifluoroacetylacetone

For the titration study of trifluoroacetylacetone, 0.924 grams of the β-diketone was dissolved in 100 ml. of a 50 per cent water – 50 per cent dioxane and the pH adjusted to approximately 1.8 with hydrochloric acid. As in the titration of normal acetylacetone, sodium hydroxide (1.0672 N.) was added with stirring in increments of 0.2 ml., allowing approximately three minutes between successive additions of alkali.

The results obtained are represented graphically on Figure 4, and the data are tabulated in Table VI in the Appendix.

Again, the first plateau A represents the neutralization of excess acid. Plateau B represents the reaction of the trifluoroacetylacetone with the alkali to form sodium trifluoroacetylacetonate. Since this compound is a salt of a strong base and an extremely weak acid, one would not expect the plateau to be flat. The midpoint of plateau B is calculated to be $10^{-6.5}$ which is taken to be the acid dissociation constant. This value is in close agreement with that reported in the literature ($10^{-6.7}$) (18).

It is noted that the acid dissociation constant, K_D, for trifluoroacetylacetone is much lower than the K_D for normal acetylacetone. This should more or less be expected since the three fluorine atoms cause a change in the polarity of the acetylacetone molecule and, undoubtedly, weaken the hydrogen bond of the enol form of the β-diketone. Thus, it follows that the trifluoroacetylacetonates should form at a lower pH than the normal compounds. This postulation will be verified later.

ML. OF 1.0672N NAOH

FIGURE 4
ETHYL TRIFLUOROACETOACETATE
TRIFLUOROACETYLACETONE

FIGURE 5
THENOYL TRIFLUOROACETONE

---ETFA
___TFA

ML. OF 1.0672 N NaOH
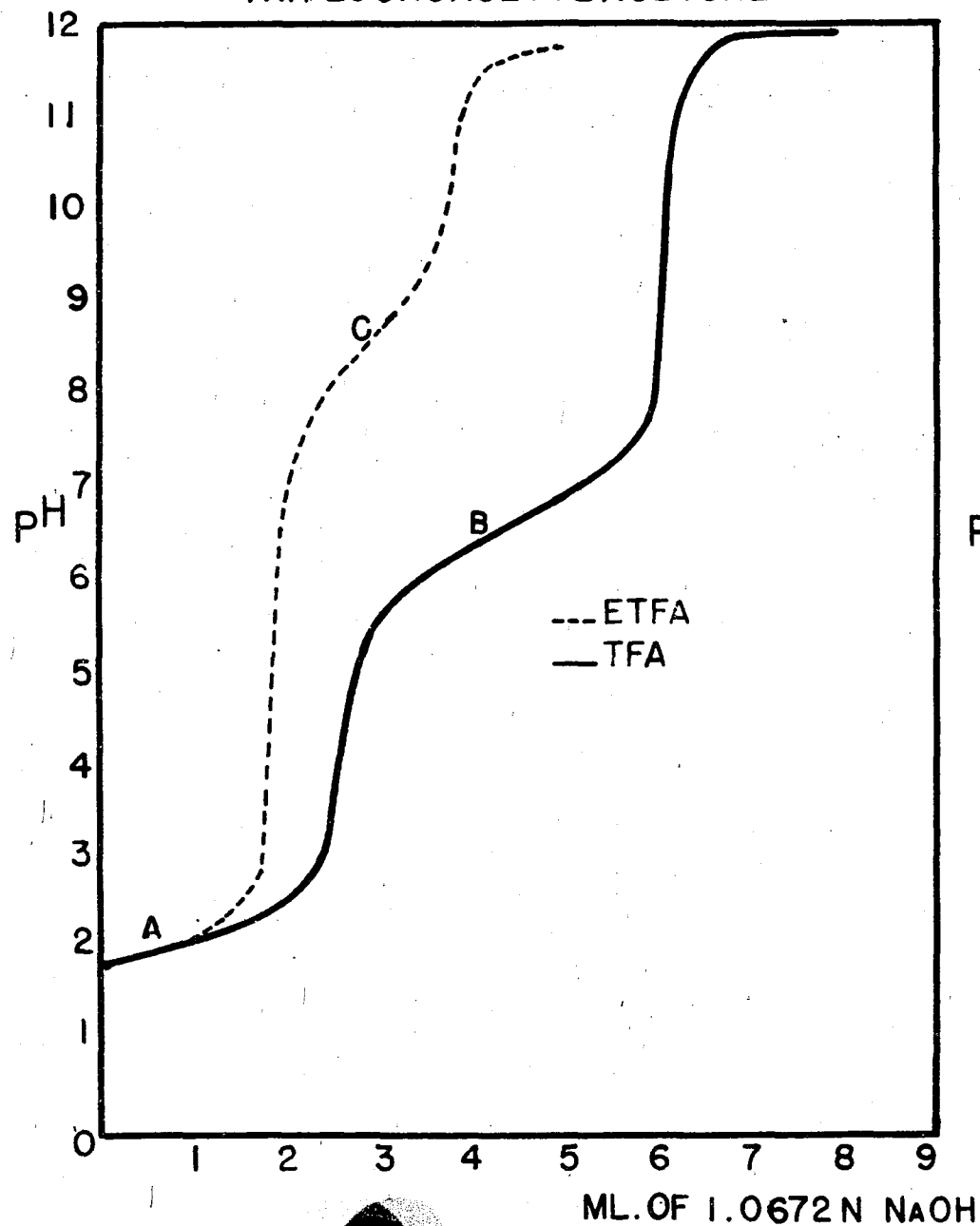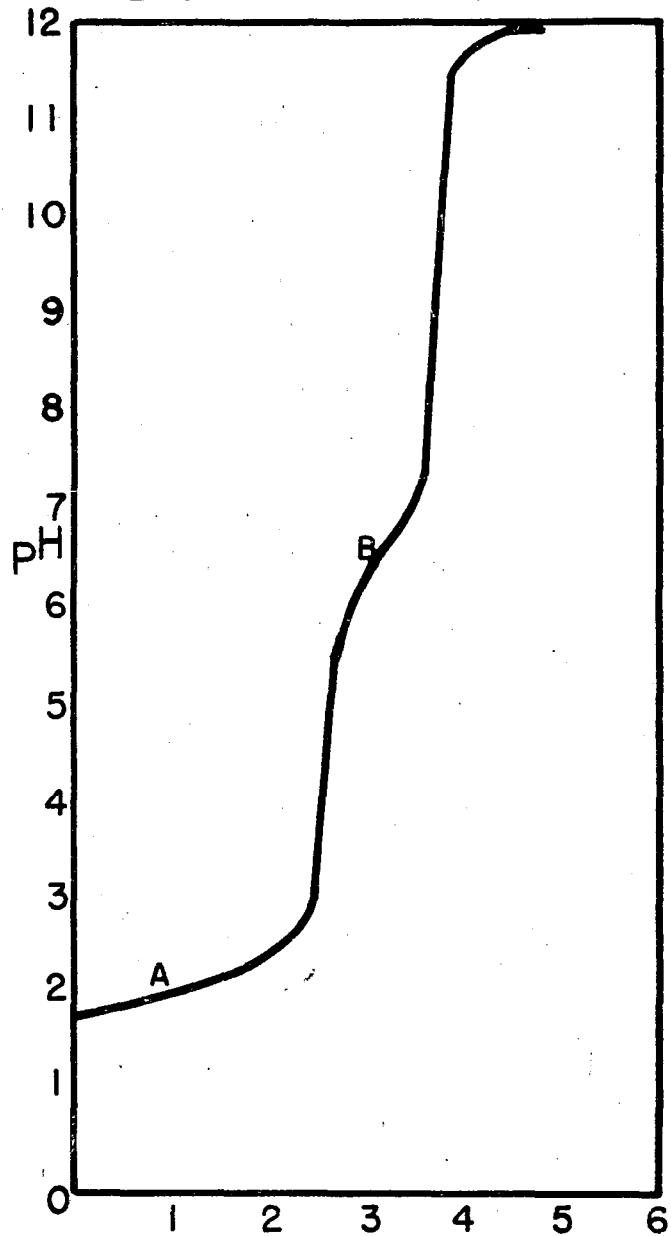
c. Thenoyltrifluoroacetone

This compound has been studied extensively as a chelating agent in the Manhattan District Project (20). However, to date, there has been only a small amount of data released on its properties.

For the titration of this compound, 0.444 grams of thenoyltrifluoroacetone was dissolved in 100 ml. of a 50 per cent water - 50 per cent dioxane solution and the pH adjusted to 1.90. The resulting solution was titrated with 1.0672 N. sodium hydroxide added with stirring in increments of 0.2 ml. Again, approximately three minutes were allowed between successive additions of reagent.

The data obtained for this titration are presented in Table VII (Appendix) and in Figure 5. The plateau A of Figure 5 represents the neutralization of excess acid. Plateau B is the reaction of the thenoyltrifluoroacetone with the alkali to form the non-chelated sodium thenoyltrifluoroacetonate. The midpoint of plateau B is calculated to be at pH 6.62 which represents a value of $10^{-6.62}$ for the acid dissociation constant. Since the acid dissociation constants are of approximately the same value, with all other factors constant, the chelating strength of thenoyltrifluoroacetone should be comparable to that of the trifluoroacetylacetone. However, it must be kept in mind that there is a possibility of a five-membered ring being formed involving the sulfur of the thenoyl group, which is available for chelation. It is known that five-membered chelate rings are more stable than either the four or six-membered rings.

d. Ethyl Trifluoroacetoacetate

A sample of ethyl trifluoroacetoacetate (0.388 grams) was
dissolved in 100 ml. of 50 per cent water - 50 per cent dioxane solu-
tion and the pH was adjusted to approximately 1.80 with 1:1 hydro-
chloric acid. The titration was then made by adding standard sodium
hydroxide (1.0672 N.) in increments of 0.2 ml. and observing the pH
after the solution had stirred for about three minutes after each
addition.

The results of this titration are tabulated in the Appendix
(Table VIII) and are represented graphically in Figure 6. From exami-
nation of the data the acid dissociation constant of ethyl trifluoro-
acetoacetate is calculated to be $10^{-8.4}$. This value is higher than
the K_D value for trifluoroacetylacetone and thenoyltrifluoroacetone
but lower than the K_D value for the normal acetylacetone. This
observation may be of significance in considering the strength of the
coordinate bonds formed when ethyl trifluoroacetoacetate reacts with
a metal ion to form a chelate compound.

II. Titrations of Chelating Agents in the Presence of Metallic Ions: Copper, Zinc, and Nickel

a. Copper Acetylacetonate

Since one of the objectives of this study was to determine the behavior of various chelating agents with respect to the rare earths, it was deemed advisable to use a well known metal ion as a reference in order to compare the chelating strengths of the various chelating agents. For this purpose the cupric ion was chosen since its properties are well known, and since it is a metal ion which forms stable compounds with many chelating agents.

Calvin and Wilson (18) had used the cupric ion as a standard in the measurement of the stability of chelate compounds and, thus, an attempt was made to duplicate their work in order to obtain a complete set of data. For this experiment 0.1592 grams (2×10^{-3}M) of cupric oxide (C.P.) was dissolved in a minimum amount of hydrochloric acid. The resulting solution was evaporated nearly to dryness and then cooled. A solution of the resulting cupric chloride was made by adding 100 ml. of a 50 per cent water - 50 per cent dioxane solution. Then 0.8 grams (8×10^{-3} moles) of acetylacetone was added. This amount is 100 per cent in excess of that necessary for complete reaction as will be the case in all titrations involving a chelating agent and a metal ion. When the acetylacetone was added to the copper solution there was a definite deepening in color which indicates a formation of a coordination complex. The pH was adjusted to 1.8. At this point the solution was quite blue and a precipitate was not visible. Sodium hydroxide (1.0672 N.) was then added in increments

of 0.2 ml., allowing 5-10 minutes between each successive addition.
(See Table IX, Appendix, and Figure 7.) The pH of solution rose
slowly and the intensity of the color increased as the excess acid
was neutralized. In Figure 7, A designates this portion of the curve.
As more alkali was added the pH rose until, at the value of 2.70,
additional alkali did not cause a change in pH (Point B). At this
pH a purplish blue solid precipitated and was identified as copper
acetylacetonate. After the copper acetylacetonate was precipitated
the pH increased with the addition of alkali to a value of 6.72, at
which point there was another break in the increasing pH as repre-
sented by the plateau at Point C. In the plateau regions it was
necessary to allow 8-12 hours between successive additions of sodium
hydroxide for the attainment of equilibrium. At the pH of 6.72 the
nature of the precipitate changed, becoming gelatinous in nature.
This gelatinous precipitate is apparently a basic acetylacetonate.
Above a pH of 6.72 the curve corresponds to the titration curve of
acetylacetone, which is to be expected since an excess of acetylace-
tone was added.

The titration curve obtained in the preceding experiment
was not a reproduction of the curves presented by Calvin and Wilson
(18), but was further complicated by the appearance of the two pla-
teaus. It was presumed that there was a difference in the respective
procedures. A number of different titrations were made while changing
certain variables such as concentration, cupric salts, and time
between successive additions of reagent. It was found, if a minimum

FIGURE 7
"SLOW" COPPER ACETYLACETONATE

ML. OF 1.0267 N NaOH
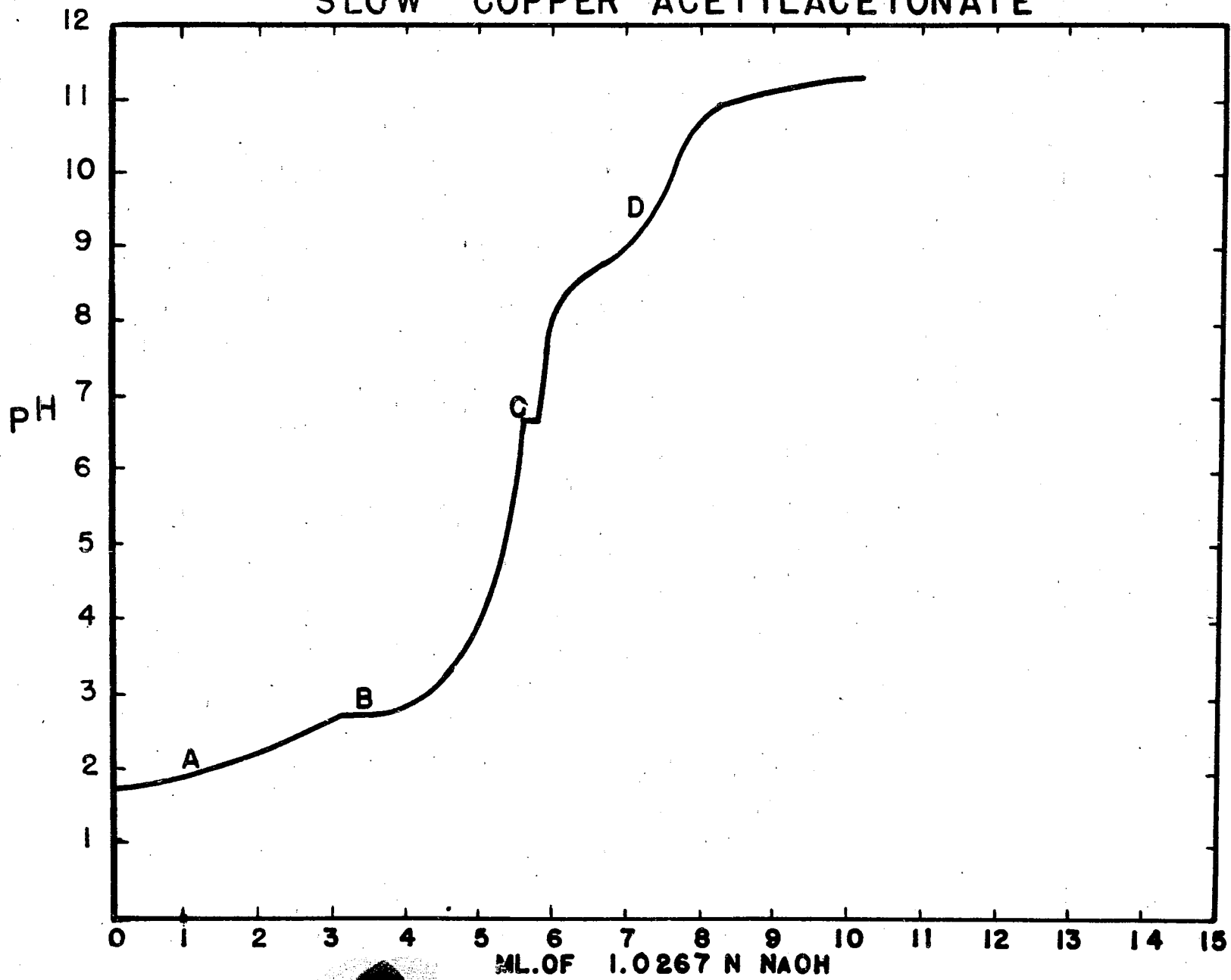
amount of time were allowed between successive additions of alkali,
that the data presented by Calvin (18) could be duplicated exactly.
(See Table X, Appendix, and Figure 8.) On the curve there is a com-
plete absence of plateaus at a pH of either 2.70 or 6.72, which indi-
cates that equilibrium was not established. It can also be deduced
from the Tables IX and X that a greater volume of sodium hydroxide is
necessary to attain the same value of pH when equilibrium is reached
than when equilibrium is not reached. Since a majority of the calcu-
lations presented by Calvin and Wilson involve the concentration of
alkali, the results seem to indicate that probably there will be some
other discrepancies in their data.

More explicitly, the calculations of Calvin and Wilson
involve the determination of the average number of bound ketone
molecules, $\bar{n}$. From this value are calculated K_1, which is
$(CuKe^-)/(Cu^{++})(Ke^-)$, K_2, which is $(CuKe_2)/(CuKe^+)(Ke^-)$, and K_{av},
which is $(K_1K_2)^{1/2}$, by the method of Bjerrum (21).

For the calculation of $\bar{n}$, which is the average number of
Ke^- bound to a Cu^{++}, the equation $\bar{n} = (Na^+ - A + H^+)/T_{Cu^{++}}$ is used.
In this equation, Na^+ is the sodium ion concentration, H^+ is the
hydrogen ion concentration, A is excess acid, and $T_{Cu^{++}}$ is total
copper ion present. Since conditions were duplicated as much as
possible in both the 'slow' and 'fast' titrations, A, H^+, and $T_{Cu^{++}}$
are constant. However, the sodium ion concentration for comparable
pHs is different, and since $\bar{n}$ varies directly as Na^+, the values of

FIGURE 8
FAST COPPER ACETYLACETONATE

42
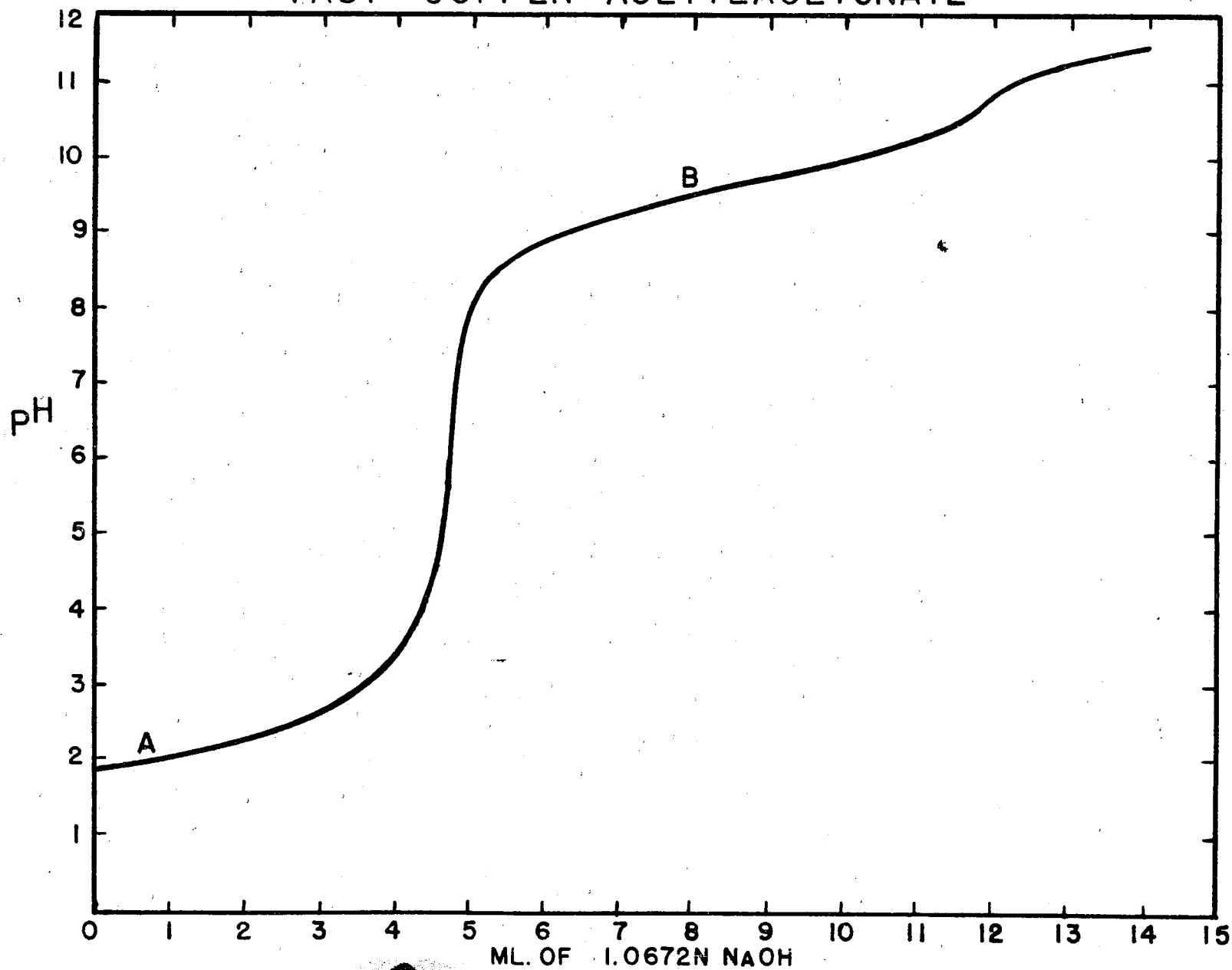
K_1, K_2, and K_{av} will be affected accordingly. More detailed calcu-

lations showing these differences were not made since Bjerrum's book

(21) was not available.

It is also to be noted that in his article (18) Calvin

mentions that the reason for using a water-dioxane solution was to

prevent precipitation of the chelated compounds. However, when a

'slow' titration is made there is a precipitate formed and at a

very definite pH. Also, Calvin explains the first portion of the

curve (Point A on Figures 7 and 8) as being the formation of the

chelated compound, but even in water solution there are no precipi-

tates formed at a pH of 1.8 which indicates that no chelate is

formed. This point will be discussed in more detail later.

The next several pages present a discussion of the effect

of other chelating agents on the cupric ion as well as the effect of

acetylacetone on the zinc and nickelous ions.

b. Zinc Acetylacetonate

For comparison it was deemed advisable to study the behavior

of some of the more common metallic ions which form coordination com-

plexes in the presence of acetylacetone. Zinc and nickelous ions were

chosen for this reason.

For the titration of zinc ions in the presence of acetylace-

tone, zinc oxide (0.1628 grams; 2×10^{-3} M) was dissolved in dilute hydro-

chloric acid and the resulting solution evaporated almost to dryness.

Then acetylacetone (0.80 grams; 8×10^{-3} M) was added along with 100 ml.

of a 50 per cent water - 50 per cent dioxane solution. The pH was then

FIGURE 9
ZINC   ACETYLACETONATE

pH (vertical axis, values 1–12)

ML. OF 1.0672N NaOH (horizontal axis, values 0–15)

A, B, C, D (labeled points on curve)
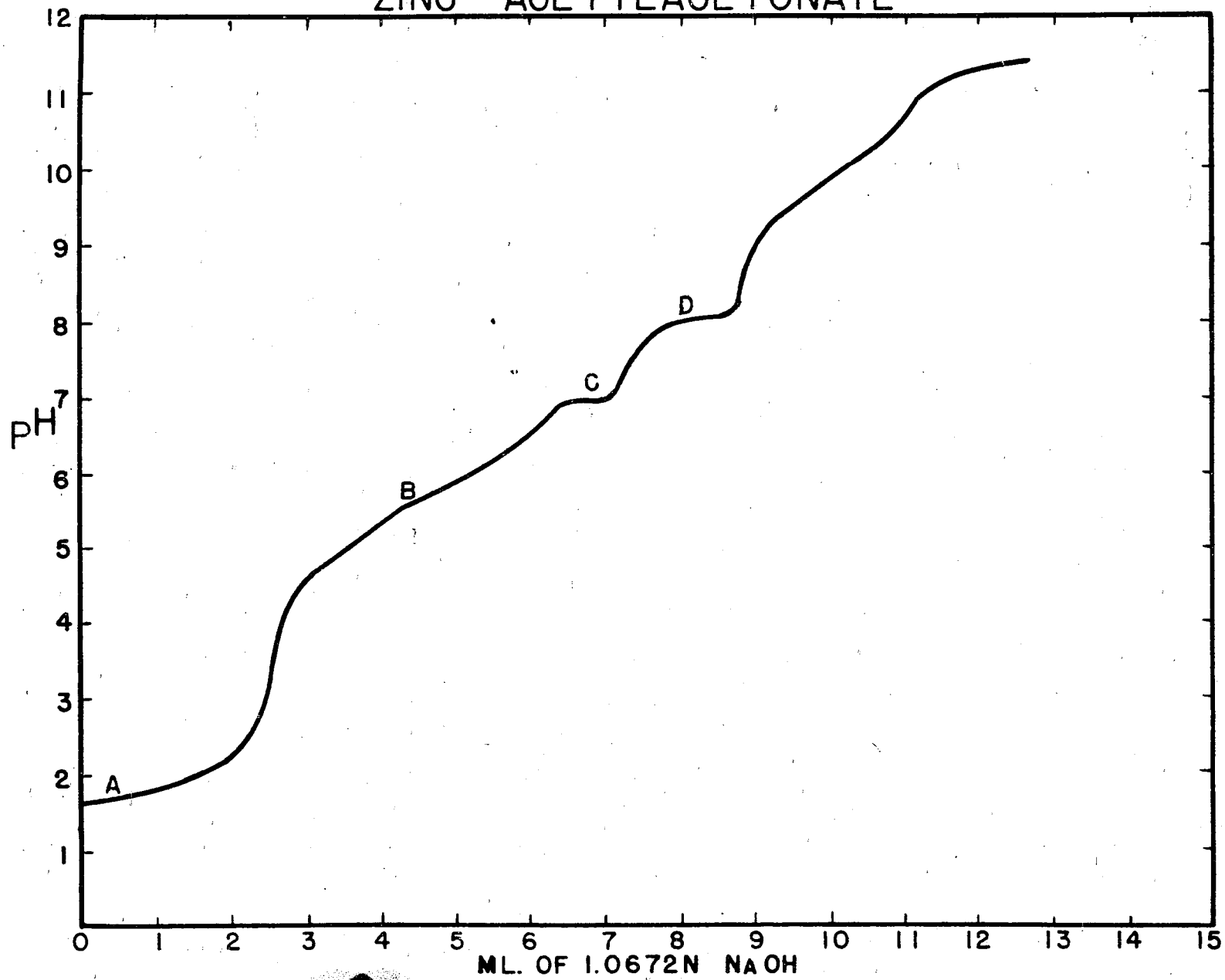
adjusted to a value of approximately 1.80. Sodium hydroxide (1.0672 N.) was added in increments of 0.20 ml. and the pH read after each addition. The data taken are in Table XI (Appendix) and Figure 9.

From an examination of the data several observations can be made. Point A (Figure 9) represents the neutralization of excess acid and B represents the displacement of protons from coordinated acetylacetones. Plateau C is the precipitation of zinc acetylacetonate at a pH of 7.0 and plateau D (pH = 8.08) represents the hydrolysis of the zinc acetylacetonate to form the basic compound. Before making other comparisons a discussion of the titration of nickelous ion in the presence of acetylacetone will be presented.

c. Nickel Acetylacetonate

The titration of nickel ion in the presence of acetylacetone was made by dissolving nickel chloride ($NiCl_2 \cdot 6H_2O$ C.P.; 0.4754 grams; 2×10^{-3}M) in 100 ml. of 50 per cent water – 50 per cent dioxane solution and adding acetylacetone (0.80 grams; 8×10^{-3}M) to the solution. There was an immediate intensifying of the color. The pH was adjusted to approximately 1.80 and sodium hydroxide (1.0672N.) then added in increments of 0.2 ml. while allowing 3-5 minutes between successive additions, before taking the pH readings. When a pH of 6.74 was reached a green precipitate of nickel acetylacetonate formed; this pH corresponds to plateau C (Figure 10). After this plateau was passed the pH again rose to a value of 7.20 where another plateau was observed (D, Figure 10). The data obtained for this titration are tabulated in Table XII (Appendix). In the plateau regions as long as 12

FIGURE 10

NICKEL ACETYLACETONATE

FIGURE 10
NICKEL ACETYLACETONATE

pH vs. ML. OF 1.0672 N NAOH
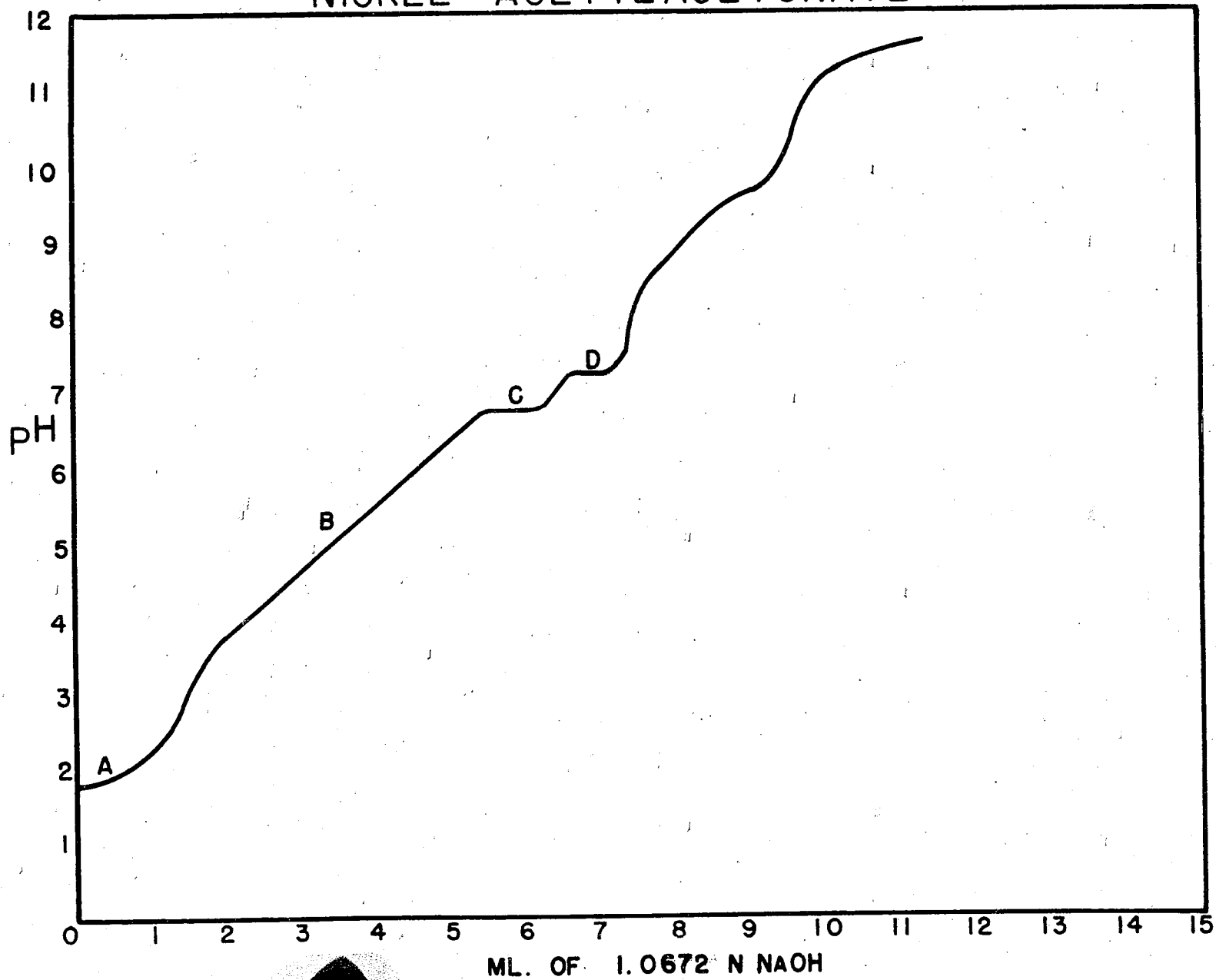
hours are necessary between successive additions of alkali for the attainment of equilibrium.

The observed pH of precipitation of copper acetylacetonate is 2.70, of zinc acetylacetonate is 7.00, and of nickel acetylacetonate is 6.74. The observed order of precipitation of the acetylacetonates is not in agreement with the order of increasing atomic number. It appears that the pH of precipitation of the copper acetylacetonate is out of line and such an observation requires an explanation.

An attempt was made to find some physical property of the three elements, nickel, copper, and zinc, which could account for this difference in the pHs of precipitation of the acetylacetonates. The pH of precipitation of copper hydroxide is 5.4, of zinc hydroxide is 5.2, and of nickel hydroxide is 6.78 (22). Thus, apparently, the difference in basicities cannot account for the difference in the pH of precipitation of the acetylacetonates. The ionic radius for zinc is 0.74 Å, for nickel is 0.70 Å (17), and for copper is 0.82 Å (23), so again, there seems to be too small a change in ionic radii to account for so large a change in pH of precipitation.

The thought also came to mind that the differences might be due to the structure of the coordination complexes. Pauling (17) points out that copper acetylacetonate is a planar structure and that the corresponding compounds of zinc and nickel are tetrahedral. This difference in structure can be explained on the basis of electronic configurations. The copper ion has nine 3d electrons. The odd electron can be displaced

leaving the $3\underline{d}$, $4\underline{s}$, and $4\underline{p}$ orbitals vacant for coordination. The $\underline{dsp}^2$ bonds are coplanar. The zinc ion has the $3\underline{d}$ shell completely filled so that only the $4\underline{s}$ and $4\underline{p}$ orbitals are available for coordination. The $\underline{sp}^3$ bonds are tetrahedral. The nickel ion has only eight $3\underline{d}$ electrons, six of which are paired. The remaining two are each in a $3\underline{d}$ orbital but the energy relationships are such that they are not displaced as in the case of the copper. Thus, as with zinc the nickel coordination complexes are tetrahedral since only the $4\underline{s}$ and $4\underline{p}$ orbitals are available. To prove this structure, Pauling (17) made magnetic measurements on nickel acetylacetonate which was found to be paramagnetic with values of u about 2.6, indicating two unpaired electrons. It is interesting to note that the $\underline{dsp}^2$ bonds are much stronger than the $\underline{sp}^3$ bonds. Thus, copper acetylacetonate, since it is planar, is more stable and should be precipitated in a more acid solution than either zinc or nickel acetylacetonate.

Mellor and Maley (24) in studying the titrations of some of the common metal ions by the method of Calvin and Wilson make the statement that there is no simple relation between the order of the chelating powers of metals and their electronegativity or their covalent radii.

It is postulated that the basicities (or electronegativities) of the elements may be in the same order as the chelating strengths when the same type of crystals are formed. This postulation

is borne out in the studies on the rare earth chelates, a discussion
of which follows in this dissertation.

    d.   Copper Trifluoroacetylacetonate

       Since trifluoroacetylacetone is very similar in properties
to the normal acetylacetone, it was desired to compare the chelating
tendencies of the two compounds. The titration study of the tri-
fluoroacetylacetone was made in the presence of the cupric ion, using
the same techniques as employed in the study on the normal acetylace-
tone. Cupric chloride (0.3410 grams; 2×10^{-3} M) was dissolved in
100 ml. of a 50 per cent water – 50 per cent dioxane solution, tri-
fluoroacetylacetone (1.232 grams; 8×10^{-3} M) was added and the pH
adjusted to a value of approximately 1.80 by the addition of hydro-
chloric acid. Sodium hydroxide (1.0672 N.) was then added in incre-
ments of 0.2 ml. and the pH recorded using a glass electrode. The
data for this experiment are tabulated in Table XIII (Appendix) and
represented graphically in Figure 11. From the examination of these
data, it can be seen that there are plateaus at a pH of 2.25 (Point B)
and at a pH of 6.48 (Point D). These plateaus represent, respectively,
the precipitation of copper trifluoroacetylacetonate and the trans-
formation of the copper trifluoroacetylacetonate to the basic compound.
The precipitate at D becomes definitely more gelatinous.

       Point A on this curve represents the neutralization of excess
acid and the displacement of protons from coordinated trifluoroacetyl-
acetone and C represents the completion of this reaction. At a pH of
5.18 there is no copper left in solution as is evidenced by the lack of
color when the solid is allowed to settle.

FIGURE 11
COPPER TRIFLUORO ACETYLACETONATE
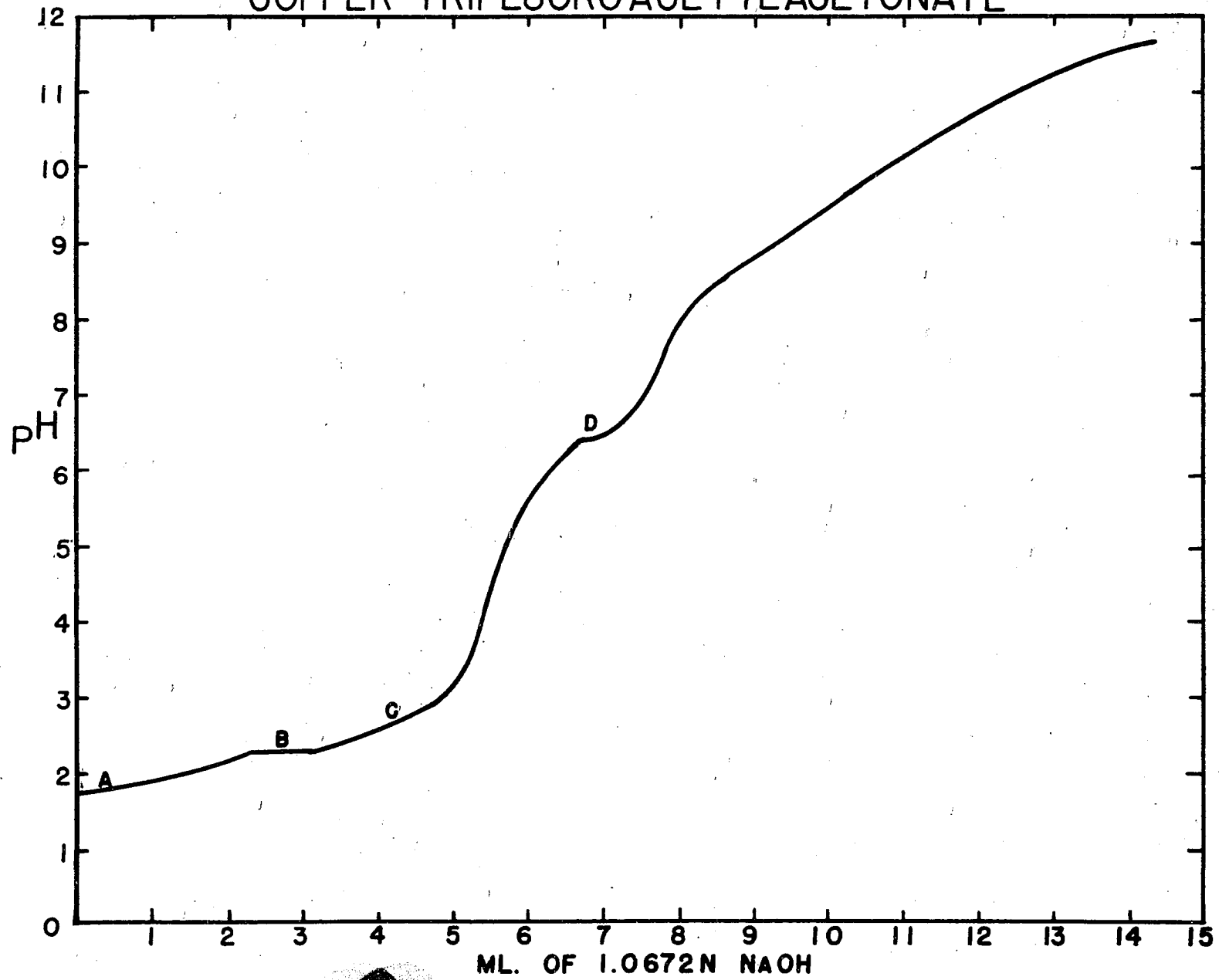
The pH of precipitation of copper acetylacetonate is 2.70 while the pH of precipitation of copper trifluoroacetylacetonate is 2.25. This difference in the pH indicates that trifluoroacetylacetone is the better chelating agent; that is, the trifluoroacetylacetonates are more stable in acid solutions. There may well be some correlation between this stability and the differences in acid dissociation constants of the respective chelating agents. Also, since there are the three fluorines on one carbon of trifluoroacetylacetone, this compound undoubtedly is more polar and, thus, the hydrogen bond of the enol form is more easily broken, which further explains the higher acid dissociation constant value. Since the trifluoroacetylacetone is more polar than the normal compound it follows that the trifluoroacetylacetonates will be more stable than the normal acetylacetonates.

e. Copper Thenoyltrifluoroacetonate

To study the behavior of copper thenoyltrifluoroacetonate in solutions of varying acidity, copper chloride (0.1705 grams; 1×10^{-3}M) was dissolved in 100 ml. of 50 per cent water – 50 per cent dioxane solution and thenoyltrifluoroacetone (0.444 grams; 2×10^{-3}M) was added. At a pH of 1.80 there was a heavy precipitate of copper thenoyltrifluoroacetonate, so that it was necessary to adjust the initial acidity to 1.55 in order to keep the precipitate from forming. As in the previous experiments, sodium hydroxide (1.0672 N.) was added in increments of 0.20 ml. and the pH was noted using a Beckman pH meter and glass electrode. It was necessary

FIGURE 12

COPPER THENOYL TRIFLUOROACETONATE

ML. OF 1.0672N NaOH
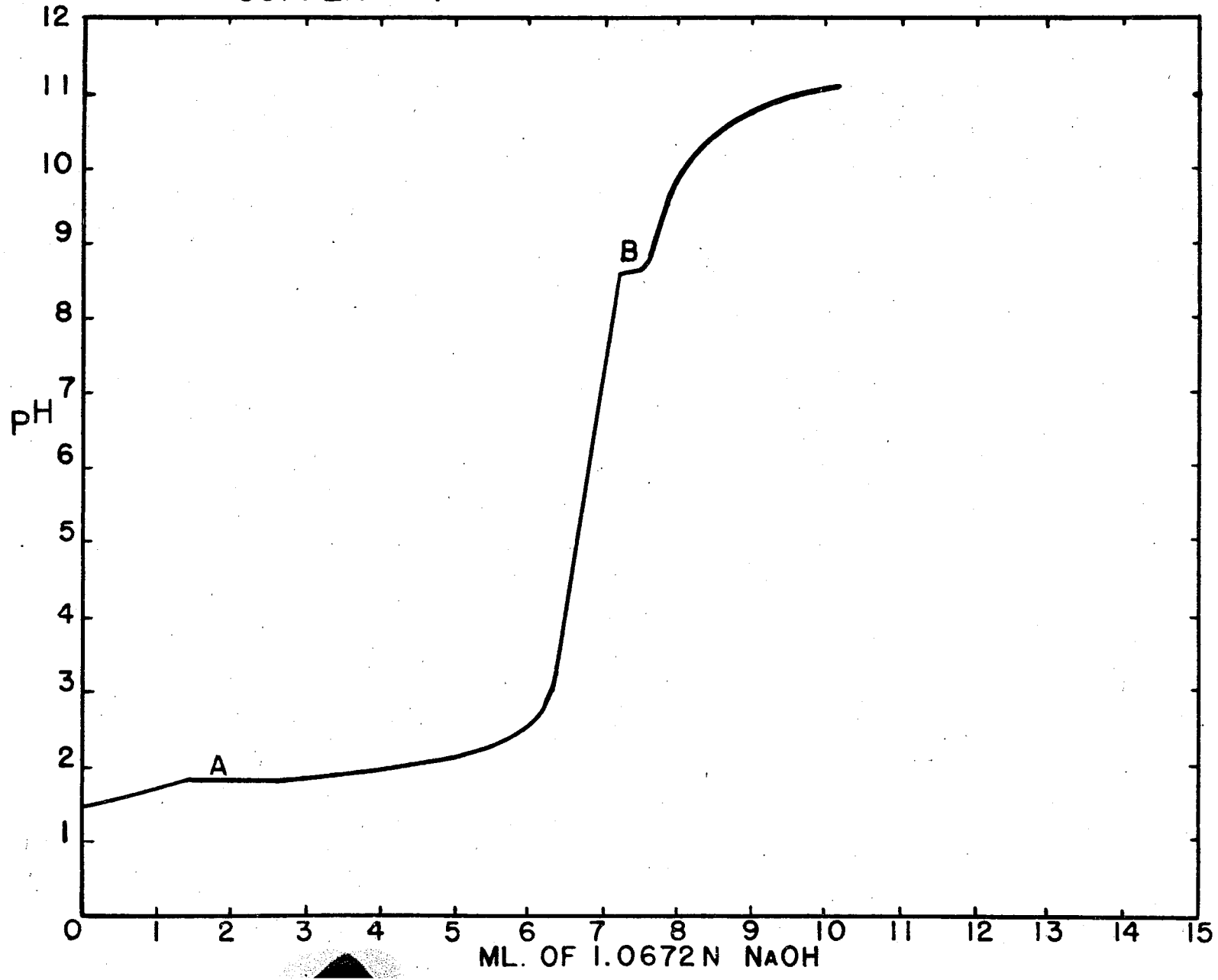
to allow 12 or more hours between additions, at times, in order to
attain equilibrium. This was especially true for pHs represented
by the plateau regions. The data for this titration are tabulated
in Table XIV (Appendix). At pH 1.72 copper thenoyltrifluoroaceto-
nate precipitates as blue crystals (A on Figure 12). At a pH of
8.56 there is a partial hydrolysis of the chelated compound to form
a basic thenoyltrifluoroacetonate. Since there was available only
a small amount of the thenoyltrifluoroacetone, an excess was not
used in this titration. This accounts for the relative simplicity
of the curve in the higher pH range.

It is to be noted that copper thenoyltrifluoroacetonate
precipitates at a pH of 1.72. This is a much lower pH than was
expected, but can be explained since thenoyltrifluoroacetone can be
a tridentate group. This strong chelating tendency is also demon-
strated and will be discussed in detail in the following sections.

f. Copper Ethyltrifluoroacetoacetate

The final titration study of copper was made using ethyl-
trifluoroacetoacetate as the chelating agent. For this experiment
cupric chloride (0.170 grams; $1 \times 10^{-3}M$) was dissolved in 100 ml.
of 50 per cent water - 50 per cent dioxane solution and ethyltri-
fluoroacetoacetate (0.736 grams; $4 \times 10^{-3}M$) was added. There was
no noticeable deepening of color in the cupric solution when the
chelating agent was added. The pH of the solution was adjusted
to approximately 1.80 and, employing the usual technique, sodium
hydroxide was added in small increments. After each addition 3-5

FIGURE 13
COPPER   ETHYLTRIFLUOROACETOACETATE
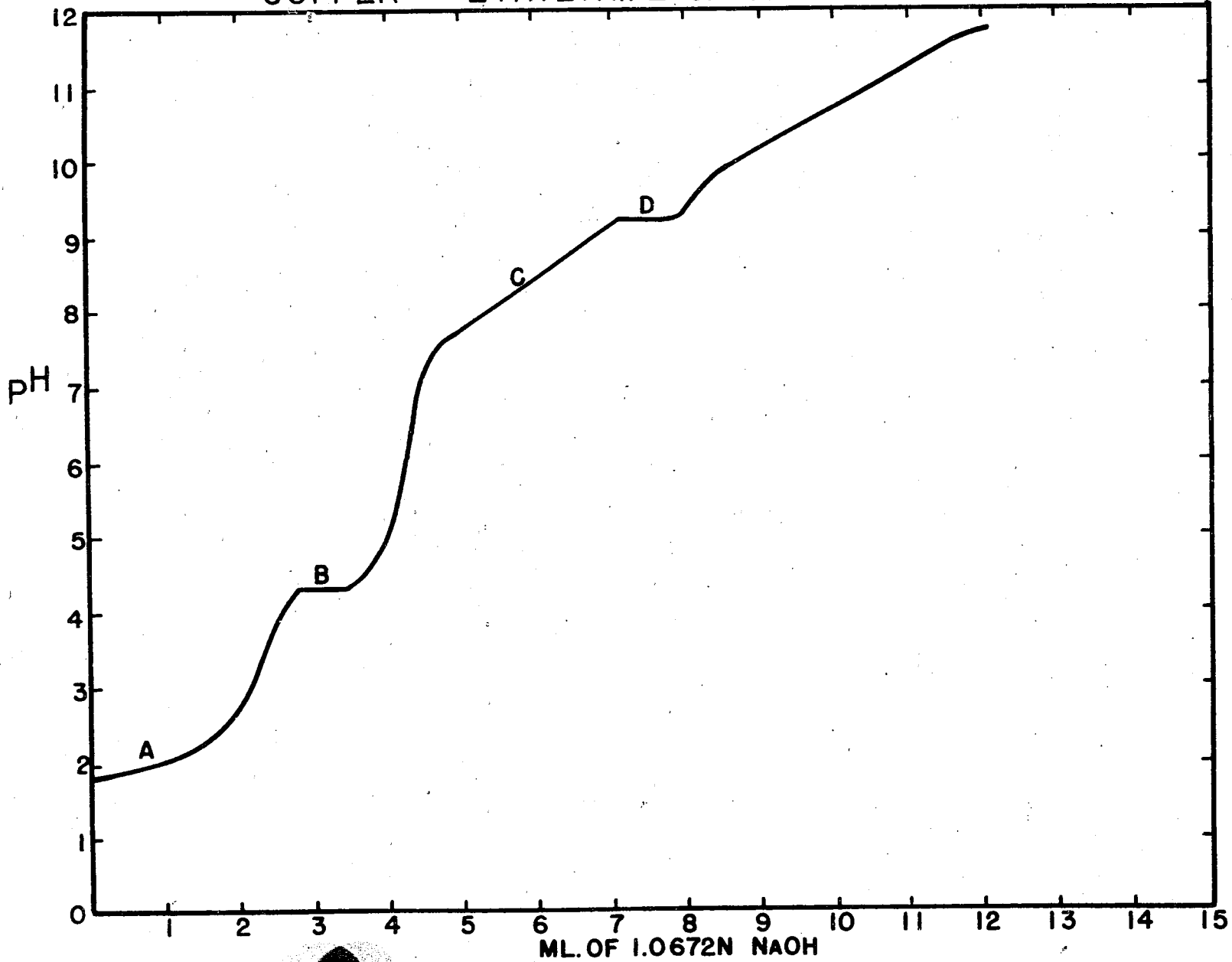
minutes were allowed, except in the plateau regions when as much

as 12 hours were necessary for the attainment of equilibrium, before

measuring the pH using a Beckman pH meter and glass electrode. The

data for this titration are found in Table XV and are represented

graphically in Figure 13. On the titration curve, A represents the

neutralization of excess acid, plateau B represents the precipitation

of copper ethyltrifluoroacetoacetate (pH = 4.27), C represents the

formation of the sodium enolate and D designates the partial hydroly-

sis of the copper chelate to a basic compound.

It is of interest to note that the precipitate which forms

at a pH of 4.27 is pale blue in color while the precipitate which is

noted at a pH of 9.20 is much deeper blue, but semigelatinous.

A more extensive study should be made of this reaction

since 1) the pH of precipitation of copper ethyltrifluoroacetoace-

tate (4.27) is much higher than would be expected from previous data,

2) the color of copper ethyltrifluoroacetoacetate is not the same color

as was noted for other copper complexes, and 3) little work of any type

has been done on metallic complexes of this particular chelating agent.

The following table lists the various data obtained from

the titration studies of the copper (zinc and nickel) and chelating

agents.

TABLE XVI

	Copper		
Chelating Agent	Acid Dissociation Constant	pH of Pptn. of Cu Chelate	pH of Hydrolysis
Acetylacetone	$10^{-9.67}$	2.70	6.72
Trifluoroacetyl-acetone	$10^{-6.50}$	2.25	6.48
Thenoyltrifluoro-acetone	$10^{-6.62}$	1.72	8.56
Ethyltrifluoro-acetoacetate	$10^{-8.40}$	4.27	9.20
	Zinc		
Acetylacetone	$10^{-9.67}$	7.00	8.08
	Nickel		
Acetylacetone	$10^{-9.67}$	6.74	7.20

III. Titrations of Chelating Agents in the Presence of Rare Earth
Metal Ions

The primary purpose of the titration studies was to

determine the behavior of rare earth acetylacetonates in solutions

of varying acidity. Thus, titrations, analogous to those in which

copper was used as the metal ion, were made with the rare earth ions

in the presence of chelating agents. The results and interpretations

of these titrations are presented in the following section.

a. Lanthanum Acetylacetonate

For this titration lanthanum oxide (0.326 grams; 2×10^{-3}M)

was dissolved in a minimum quantity of dilute hydrochloric acid. The

resulting solution was boiled almost to dryness. Then acetylacetone

(1.20 grams; 1.2×10^{-2}M) was added along with 100 ml. of 50 per cent

water - 50 per cent dioxane solution. The pH of the resulting solu-

tion was adjusted to a value of 1.80 and the titration made by adding

sodium hydroxide (1.0672 N.) in increments of 0.20 ml. The pH was

observed just before each addition, using a Beckman Model G pH meter

and a glass electrode. These titrations are very slow since ample

time must be allowed between successive additions to attain equi-

librium. As long as 8-12 hours were allotted between additions and

at all times the solution was agitated vigorously by means of an air

driven stirrer.

The data taken for this titration are tabulated in Table XVII

in the Appendix and are represented graphically in Figure 14.

In Figure 14, A represents the neutralization of excess acid,

B represents the removal of protons from coordinated acetylacetone

FIGURE 14
LANTHANUM ACETYLACETONATE
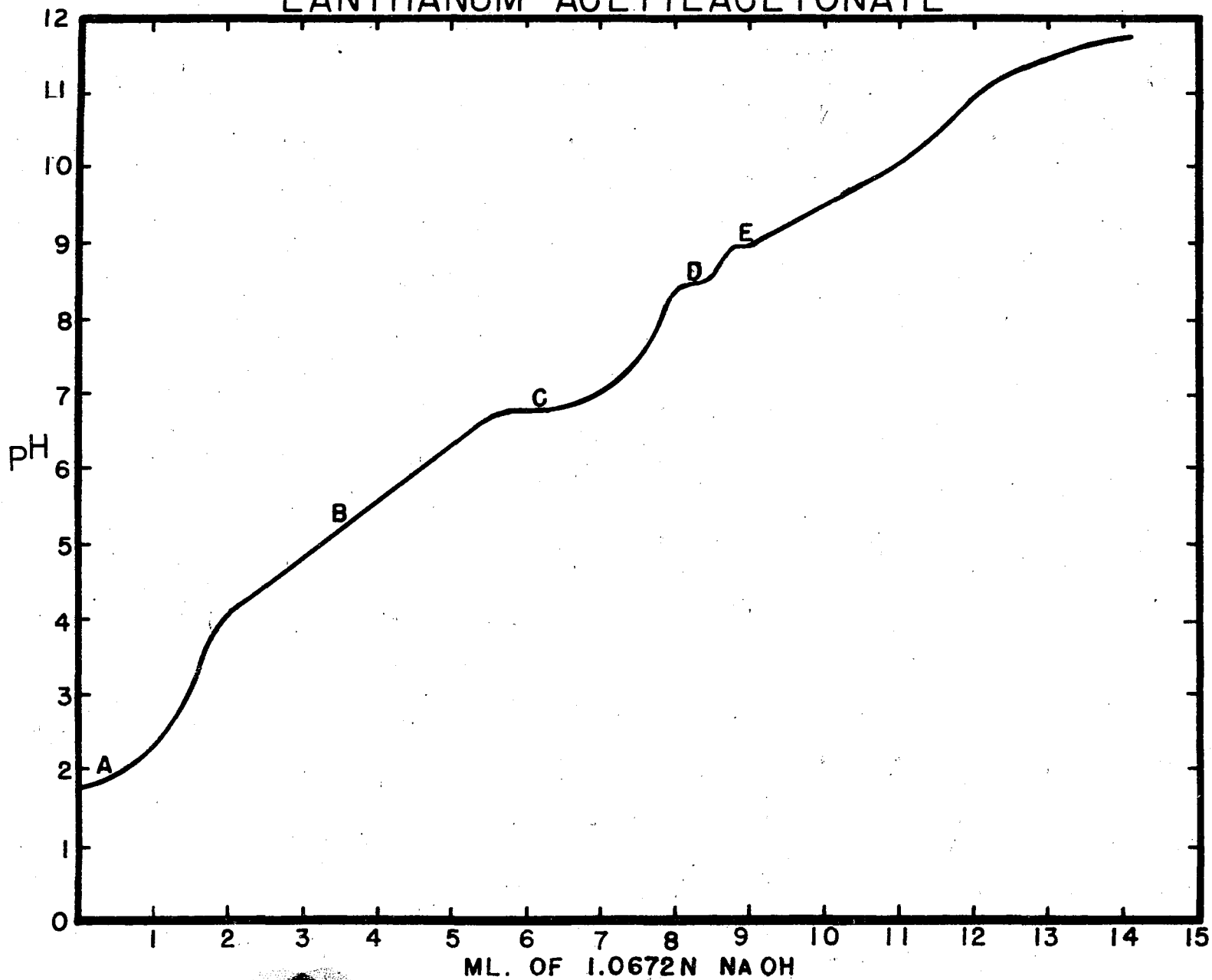
molecules, C represents the precipitation of lanthanum acetylaceton-
ate (pH = 6.74), D represents the first hydrolysis of the lanthanum
acetylacetonate (pH = 8.50) to form the monobasic derivative, and E
represents the second hydrolysis (pH = 9.00) to form the dibasic ace-
tylacetonate.

Since some discrepancies were noted in the titration studies
of copper acetylacetonate when the length of time between additions of
alkali was varied, it was deemed advisable to make a 'fast' rare earth
titration.

This study was made with initial conditions exactly as they
were for the 'slow' lanthanum acetylacetonate titrations. Sodium
hydroxide (1.0672 N.) was added to the acid solution (initial pH =
1.80) in increments of 0.2 ml. and pH readings taken as rapidly as
possible after each succeeding addition. The data for this titration
are presented in Table XVIII in the Appendix and in Figure 15. From
the examination of the data it can be seen that there is little simi-
larity between these results and those obtained in the preceding
titration. There is a complete lack of plateaus except at A (Figure 15)
and this plateau is very short. Even in the solutions of higher pH
there is little similarity noted.

These results serve to emphasize the importance of allowing
sufficient time for reaction to take place before continuing the
addition of alkali. In order to obtain reproducible results, the
reaction must be in a state of equilibrium before adding more alkali.

FIGURE 15
"FAST" LANTHANUM ACETYLACETONATE
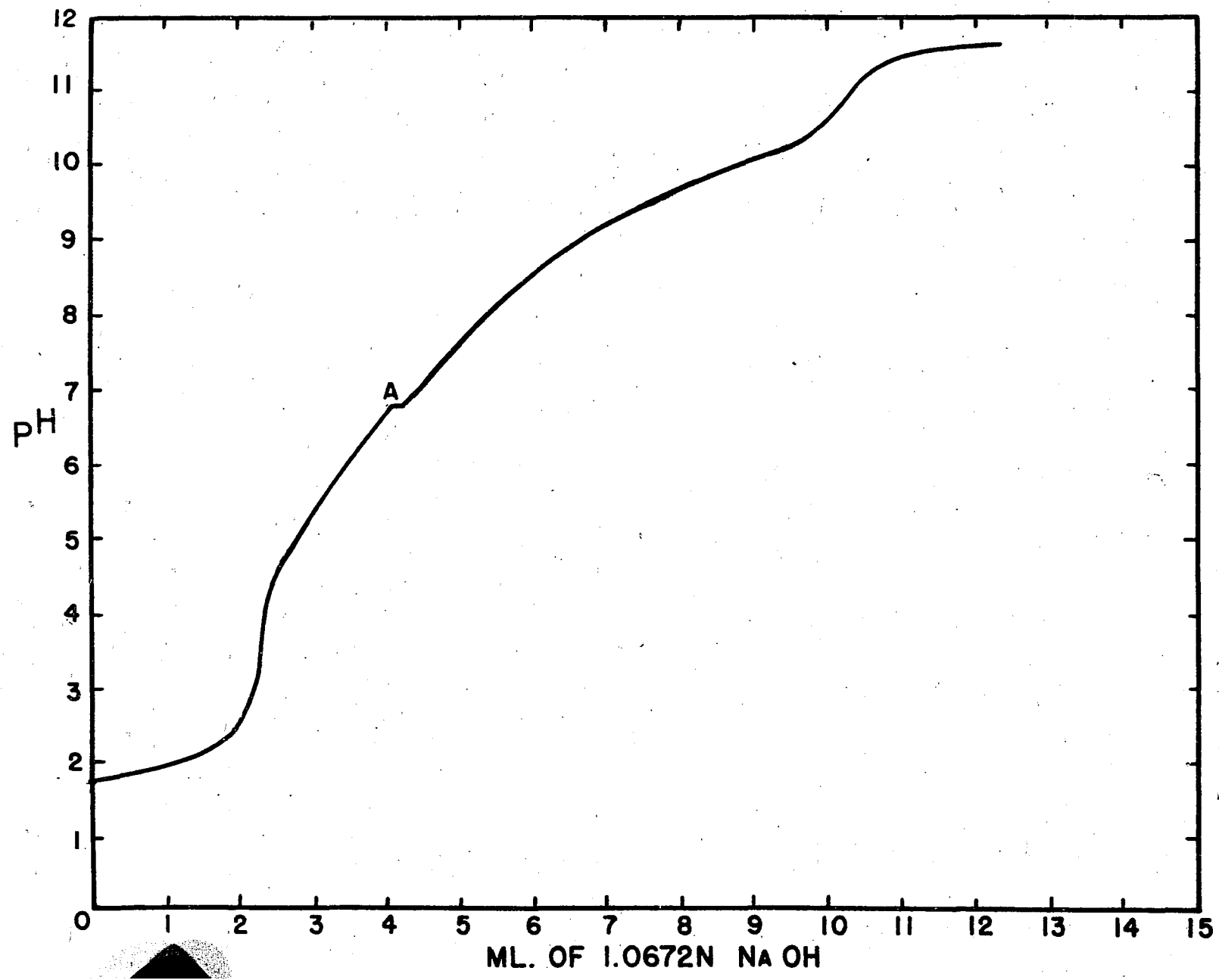
b. <u>Cerium III Acetylacetonate</u>

Cerous chloride was not available as starting material for this titration and, thus, had to be made from ceric oxide. For this purpose, ceric oxide (0.3443 grams; 2 x 10^{-3} M) was dissolved in concentrated sulfuric acid. This resulting yellow solution was diluted to 1.5 liters and oxalic acid added in order to precipitate cerous oxalate. The precipitated oxalate was washed several times by decantation and finally filtered. After several more washings with distilled water, 10 ml. of 1:1 nitric acid was poured over the precipitate on the filter paper in order to dissolve the oxalate. The nitric acid solution was then evaporated to approximately one milliliter and concentrated hydrochloric acid then added. The solution was again boiled and more hydrochloric acid added until the brown fumes of nitrogen dioxide were no longer formed. Then a small amount of hydrogen peroxide was added to the acid solution to reduce any ceric ion to cerous. The nearly colorless solution was diluted with 100 ml. of 50 per cent water - 50 per cent dioxane solution. Acetylacetone (1.20 grams; 1.2 x 10^{-3} M) was added to the salt solution and the pH then adjusted to approximately 1.80. The titration was made in the usual way by adding sodium hydroxide (1.0672 N.) in increments of 0.2 ml. After each addition sufficient time was allowed for the attainment of equilibrium before any pH readings were made.

The data for this titration are presented in Table XIX in the Appendix and in Figure 16. From an examination of the data, it is seen that the general shape of the titration curve is similar to

FIGURE 16
CERIUM ACETYLACETONATE "SLOW"

ML. OF 1.0672 N NaOH

62
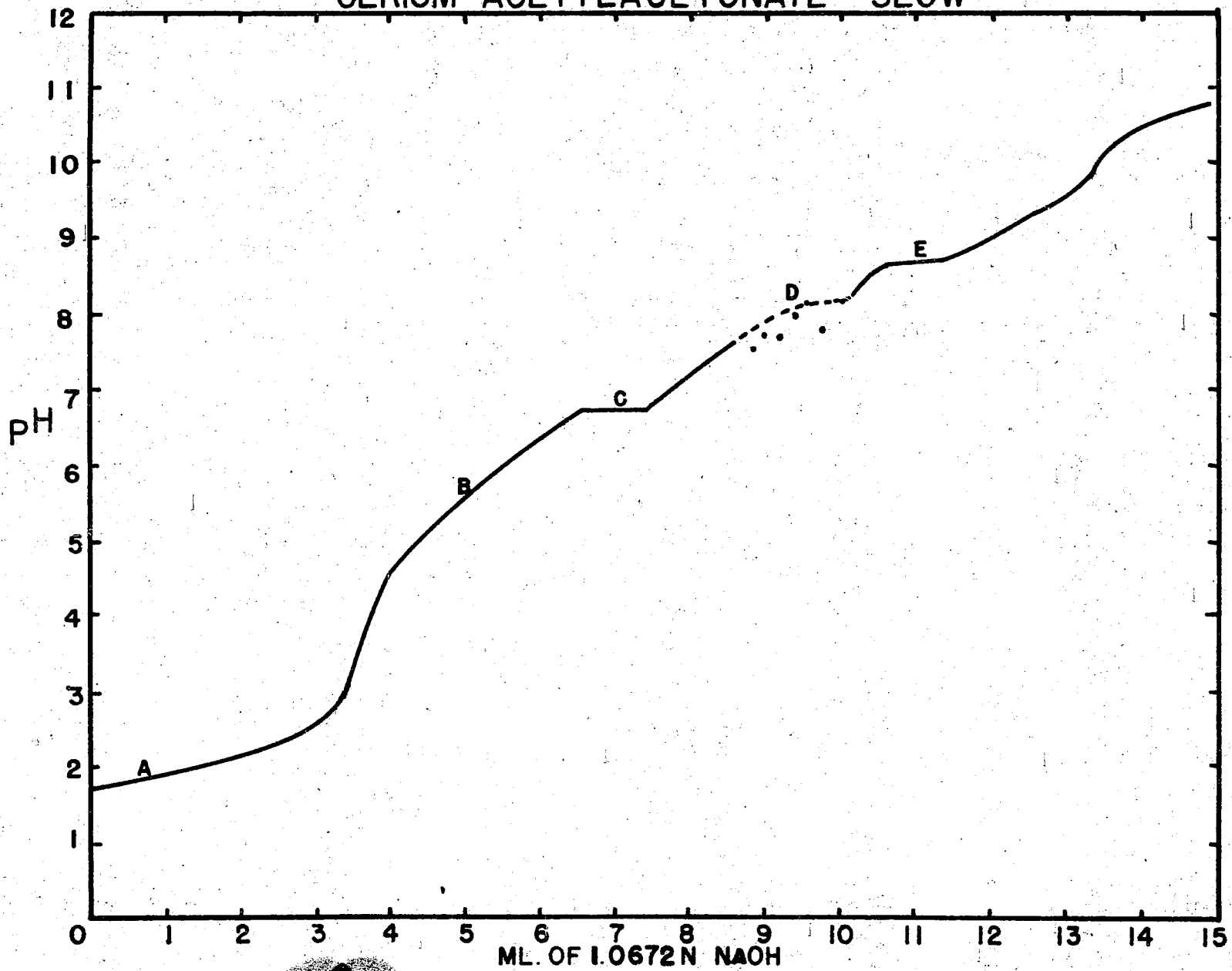
that of the lanthanum acetylacetonate. Plateau A, Figure 16, represents the neutralization of excess acid, B represents the replacement of the protons from the coordinated acetylacetone molecules, and plateau C is formed by the precipitation of cerous acetylacetonate (pH = 6.70).

The plateau at D, undoubtedly, represents the first hydrolysis of the acetylacetonate. However, the pH readings in this range were very erratic. Since this was in alkaline solution and since long periods of time were allowed between successive additions of alkali, there probably is a partial oxidation of the cerium. Since cerium IV is less basic than cerium III, this might account for the fluctuations in pH.

Plateau D, which represents the first hydrolysis, was drawn at a pH of 8.18. This may or may not be the correct value, but was chosen since it fits in the order of hydrolyses exhibited by the other rare earth acetylacetonates. Plateau E at a pH of 8.70 represents the second hydrolysis of cerium acetylacetonate to form the dibasic compound.

Above the plateau E the curve corresponds to the titration curve of acetylacetone as would be expected since there is an excess of this reagent present.

The results obtained in the experiment on cerium do not appear to be as dependable and reproducible as for the other rare earths. The change in color of the solutions as the pH is increased is a strong indication of the fact that some oxidation has occurred.

A more detailed study of cerium acetylacetonate should be made to learn of its behavior in alkaline solutions.

c. Praseodymium Acetylacetonate

The titration study of praseodymium acetylacetonate was made by dissolving praseodymium oxide (Pr_6O_{11}; 0.340 grams; 2×10^{-3}M of Pr) in dilute hydrochloric acid and evaporating almost to dryness. Then 100 ml. of 50 per cent water - 50 per cent dioxane was added along with acetylacetone (1.2 grams; 1.2×10^{-2}M) and the resulting solution adjusted to a pH of 1.80. Sodium hydroxide (1.0672 N.) was added in increments of 0.2 ml. and the solution was vigorously stirred after each addition. After equilibrium had been established as evidenced by no further change in pH, the pH was recorded and another 0.2 ml. of alkali was added. These additions and readings were continued until at a pH above 11.00 the addition of as much as one milliliter of alkali caused no appreciable change in the pH of the solution. The data which were recorded for this titration study are tabulated in Table XX in the Appendix and shown graphically in Figure 17.

From the data compiled it can be seen that the titration curve for praseodymium is very similar to that obtained for lanthanum (Figure 16). On the curve A again represents the neutralization of the excess acid, B represents the removal of protons from coordinated acetylacetone molecules, and the plateau at C represents the precipitation of praseodymium acetylacetonate (pH = 6.65). Plateau D (pH = 7.98) represents the first hydrolysis of the praseodymium acetylacetonate to the monobasic derivative and plateau E (pH = 8.38) represents the second hydrolysis.

FIGURE 17

PRASEODYMIUM ACETYLACETONATE

ML. OF 1.0672N NAOH

pH
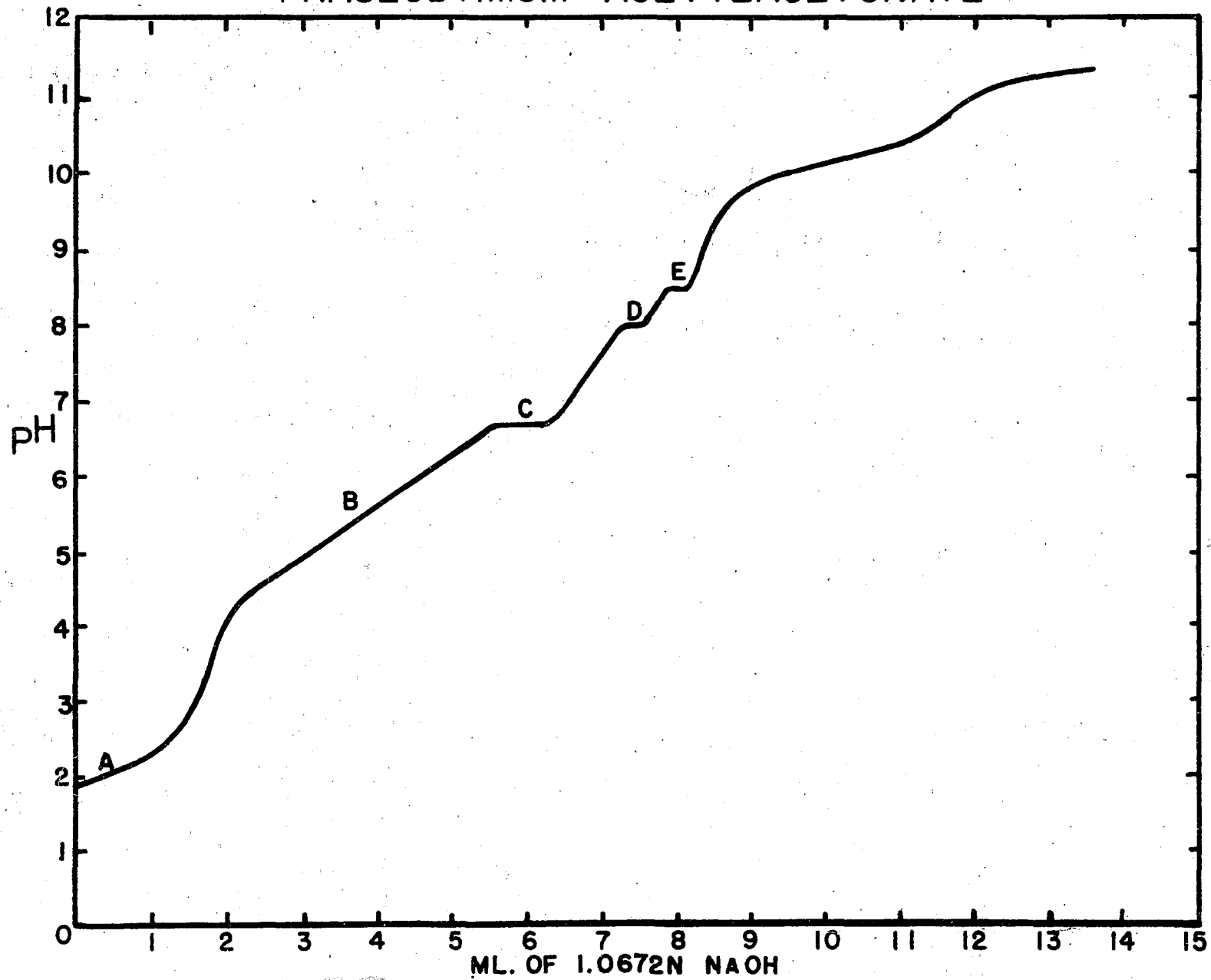
A more detailed discussion of the reactions which take place during the titrations will be found following this section.

d. Neodymium Acetylacetonate

For the titration study of neodymium acetylacetonate, neodymium oxide (0.3365 grams; 2×10^{-3}M of Nd) was dissolved in dilute hydrochloric acid and the resulting solution was evaporated almost to dryness. To this concentrated solution was added 100 ml. of a 50 per cent water - 50 per cent dioxane solution along with acetylacetone (1.20 grams; 1.2×10^{-2}M). The pH of the solution was then adjusted to 1.80 and the titration carried out in the usual manner. Again, sufficient time was allotted between successive additions of alkali to allow for the attainment of equilibrium.

The data obtained from this titration is presented in Table XXI and Figure 18.

Point $\underline{A}$ on Figure 18 represents the neutralization of excess acid and $\underline{B}$ represents the replacement of protons from coordinated acetylacetone molecules. Plateau $\underline{C}$ at a pH of 6.58 represents the precipitation of neodymium acetylacetonate and plateaus $\underline{D}$ (pH = 7.92) and $\underline{E}$ (pH = 8.33) represent the first and second hydrolyses respectively.

There is remarkable similarity between the data obtained for neodymium and praseodymium.

e. Samarium Acetylacetonate

Freshly ignited samarium oxide (0.3489 grams; 2×10^{-3}M) was dissolved in dilute hydrochloric acid, as the first step in this study. The resulting solution was evaporated almost to dryness and

FIGURE 18

NEODYMIUM ACETYLACETONATE

ML. OF 1.0672N NAOH
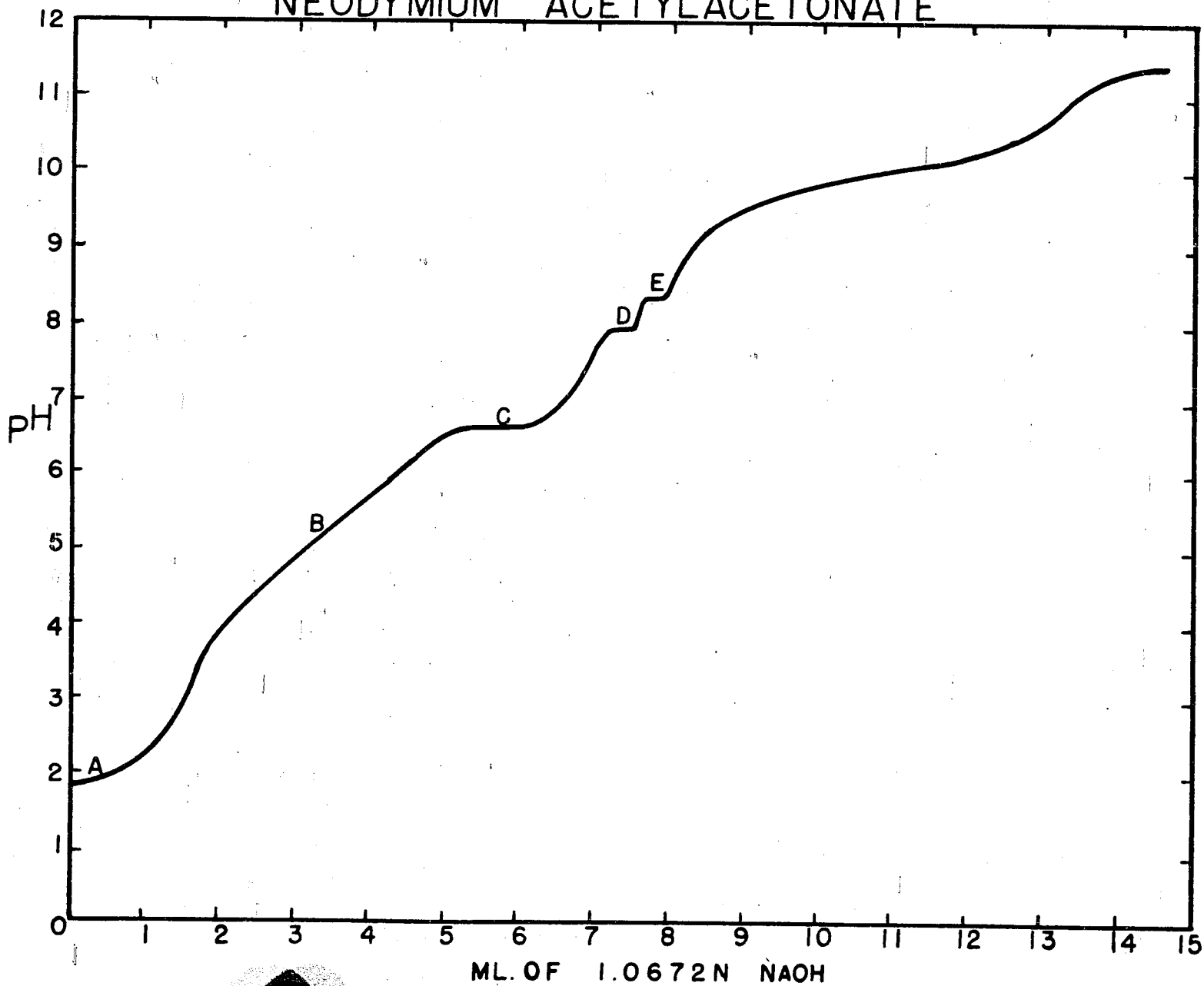
then diluted with 100 ml. of 50 per cent water - 50 per cent dioxane

solution. Acetylacetone (1.20 grams; 1.2×10^{-2}M) was then added and

the pH adjusted to 1.80. The titration was then made in the same

general way, as was outlined for the other rare earths, adding sodium

hydroxide (1.0672 N.) in 0.20 ml. increments. Sufficient time was

allowed between successive additions of alkali for the attainment of

equilibrium.

The data for this titration are tabulated in Table XXII in

the Appendix and are presented graphically in Figure 19.

Point A, Figure 19, represents the neutralization of excess

acid and B represents the removal of protons from coordinated acetyl-

acetone molecules. Plateau C (pH = 6.48) is at the pH of precipi-

tation of samarium acetylacetonate, and the plateaus D (pH = 7.50)

and E (pH = 7.82) represent the first and second hydrolyses of the

acetylacetonate to the basic compound.

Samarium is the least basic of the rare earths studied and

it is interesting to note that the pH of precipitation of the acetyl-

acetonate is lower than for any other of the rare earths studied.

Titration studies of the trifluoroacetylacetonates of some

of the rare earths are described in the following sections.

f. Lanthanum Trifluoroacetylacetonate

For the titration study of lanthanum trifluoroacetylace-

tonate, lanthanum oxide (0.3258 grams; 2×10^{-3}M) was dissolved in

dilute hydrochloric acid. The resulting solution was evaporated almost

to dryness and then trifluoroacetylacetone (1.848 grams; 1.2×10^{-2}M)

FIGURE 19
"SLOW" SAMARIUM ACETYLACETONATE
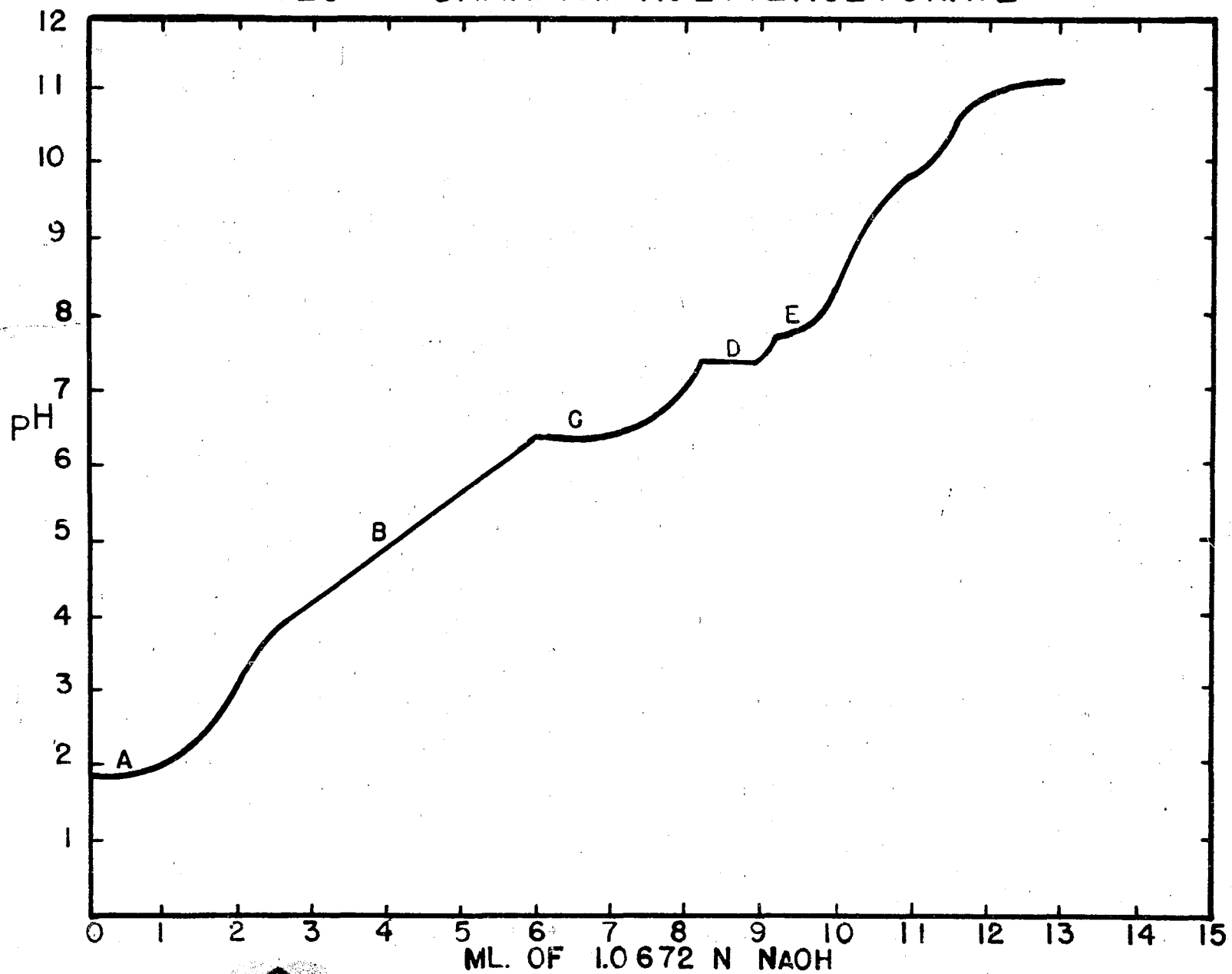
and 100 ml. of 50 per cent water - 50 per cent dioxane solution was added. The pH of this solution was then adjusted to 1.80 and the titration made by adding sodium hydroxide (1.0672 N.) in 0.2 ml. increments. As in the case of the titration studies of the normal acetylacetonates sufficient time was allowed between successive additions of alkali for the attainment of equilibrium. As long as 12 hours were necessary between additions in the plateau regions.

The data for this titration are tabulated in Table XXIII in the Appendix and are represented graphically in Figure 20. From an examination of this data it is apparent that at a pH of 5.30 the lanthanum trifluoroacetylacetonate was precipitated (B, Figure 20) and that the first (C) and second (D) hydrolyses were at pHs of 7.37 and 8.50 respectively.

The reaction between sodium ion and trifluoroacetylacetone takes place at a much lower pH than for the normal acetylacetone so that it might be expected that plateau B would be much shorter and at a lower pH than was noted for lanthanum acetylacetonate.

It also is to be noted that A (Figure 20) is much longer than was noted for the same portion of the curves obtained from the normal acetylacetonates. Again, this can be explained, since the acid dissociation is at a lower pH for the fluorinated derivative and since the replacement of protons will most likely take place also at a lower pH, these portions of the curve would be adjacent and, thus, result in a continuous slope.

FIGURE 20

LANTHANUM TRIFLUOROACETYLACETONATE

pH vs. ML. OF 1.0672N NAOH
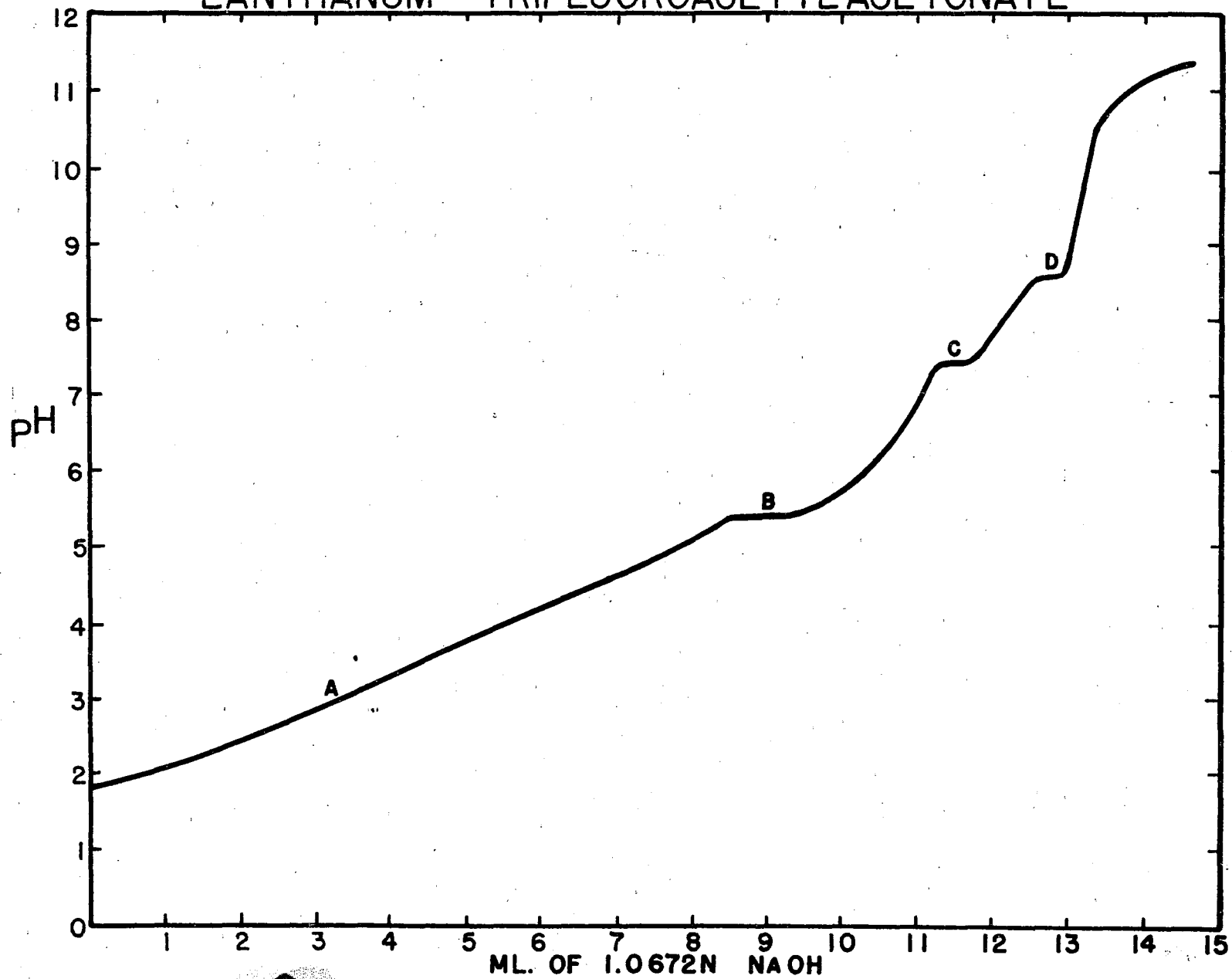
Further differences will be brought out in the following discussions on other trifluoroacetylacetonates.

g. Cerium Trifluoroacetylacetonate

For the titration study of cerium trifluoroacetylacetonate, ceric oxide (0.3884 grams; 2×10^{-3}M) was dissolved in concentrated sulfuric acid. The ceric sulfate solution was then diluted and the cerium precipitated as cerous oxalate. The oxalate precipitate was filtered and then dissolved in dilute nitric acid and boiled to decompose the oxalate. Then concentrated hydrochloric acid was added and the solution again boiled and evaporated almost to dryness. More concentrated hydrochloric acid was added and the boiling continued until the brown fumes of nitrogen dioxide were no longer visible. Hydrogen peroxide (three per cent) was added to the acid solution in order to reduce the cerium and, then, the solution was again evaporated almost to dryness. This concentrated cerous chloride solution was diluted by adding 100 ml. of a 50 per cent water - 50 per cent dioxane solution along with 1.884 grams of trifluoroacetylacetone. The pH of this solution was adjusted to 1.80 and the general procedure followed for the titration. Sodium hydroxide (1.0672 N.) was added in increments of 0.20 ml., and the pH determined after sufficient time was allowed for the attainment of equilibrium following each addition. The data for this titration study is recorded in Table XXIV in the Appendix and in Figure 21.

FIGURE 21
CERIUM TRIFLUOROACETYLACETONATE
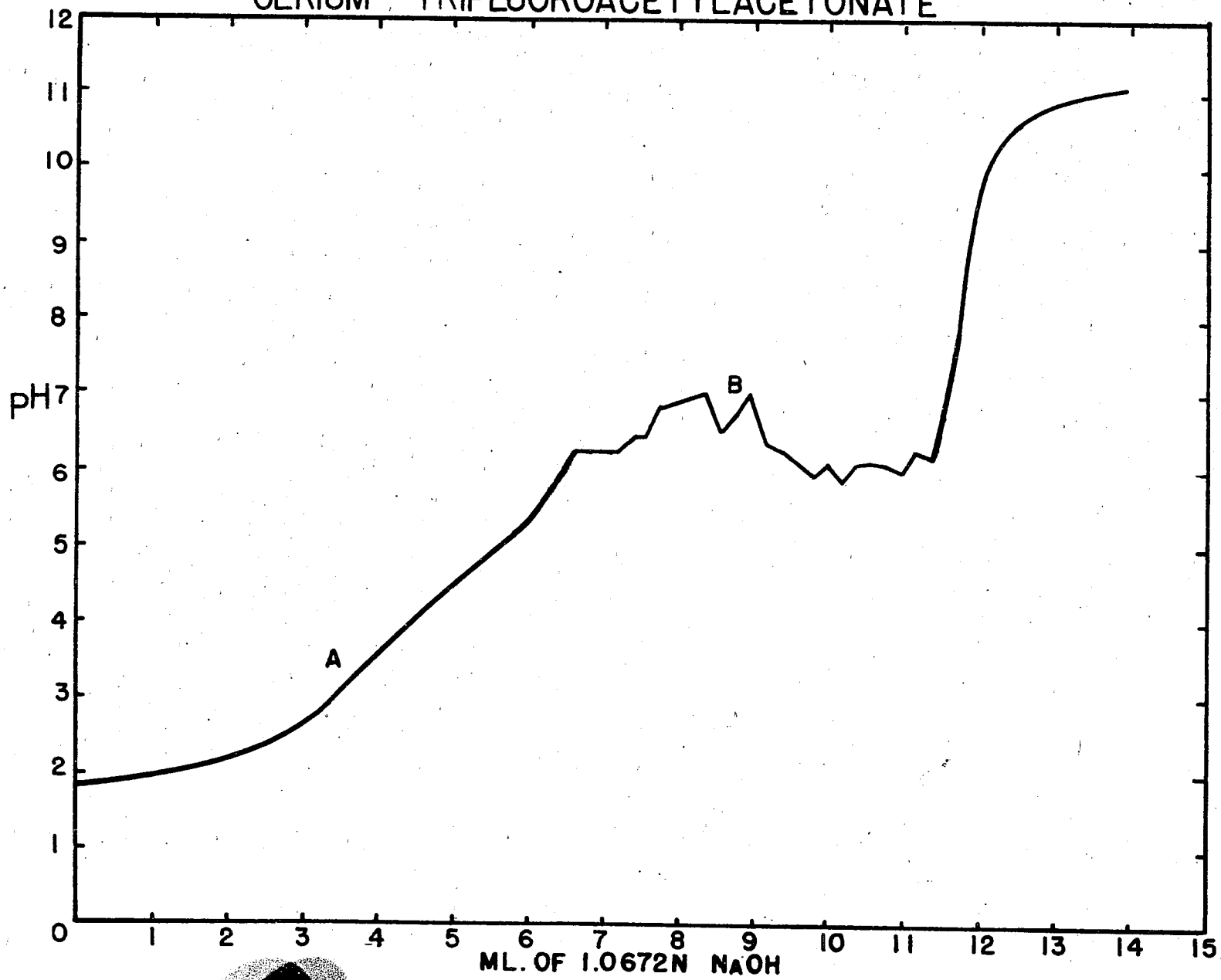
A precipitate began forming at a pH of 5.40. After 8.40 ml. of alkali had been added (pH = 7.00) the pH became erratic upon the addition of successive increments of the base. Apparently there is an oxidation of the cerium as evidenced by a definite deepening in color of the solution above a pH of 3.67. This oxidation may account for the erratic pH above 8.40 ml. Further work on this reaction should be done to determine the exact cause of the noted discrepancies. Perhaps by making the titration in an inert atmosphere some of the difficulties could be overcome. Further work should also be done on determining the behavior of tetravalent ions in the presence of chelating agents.

On Figure 21, the lower portion of the curve, $\underline{A}$, is analogous to the corresponding portion found for the lanthanum, praseodymium, and neodymium trifluoroacetylacetonates. Above this portion of the curve, however, there is little similarity.

h. Praseodymium Trifluoroacetylacetonate

For the titration study of praseodymium trifluoroacetylace-tonate, praseodymium oxide (Pr_6O_{11}; 0.340 grams; 2 x 10^{-3}M) was dissolved in dilute hydrochloric acid. The praseodymium chloride solution was evaporated almost to dryness and then trifluoroacetylacetone (1.848 grams; 1.2 x 10^{-2}M) and water-dioxane solution (100 ml.; 1:1) was added. The pH of the resulting solutions was adjusted to 1.80. The titration of this acidified mixture was made by adding sodium hydroxide (1.0672 N.) in increments of 0.2 ml. The pH was recorded after each successive addition of alkali, when the solution had reached

FIGURE 22

PRASEODYMIUM TRIFLUOROACETYLACETONATE
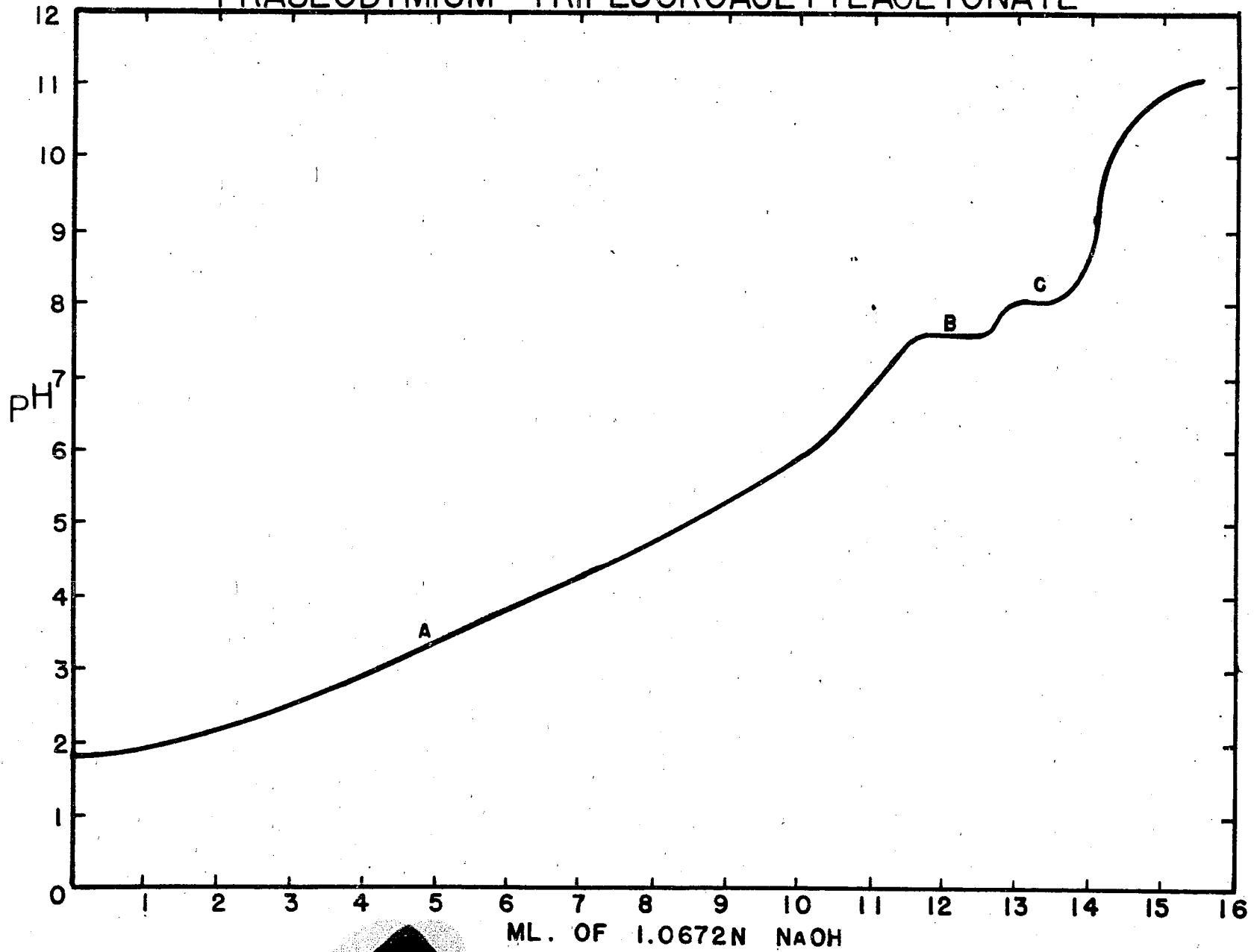
equilibrium. The data obtained from this titration are presented in Table XXV in the Appendix and in Figure 22.

It is to be noted from the data that there is no plateau formed for the pH of precipitation of praseodymium trifluoroacetyl-acetonate. It is postulated that this lack of plateau is due to the fact that there are several competing reactions going on at this parti-cular pH, namely the reaction between trifluoroacetylacetone and sodium hydroxide, the removal of protons from coordinated trifluoroacetylace-tone molecules, and the reaction between coordinated trifluoroacetyl-acetone molecules and rare earth ions.

This same lack of plateau for the precipitation of the tri-fluoroacetylacetonate is noted, also, in the case of neodymium. A short plateau was noted for the lanthanum precipitation (Figure 20) which might be expected since lanthanum is much more basic than either praseodymium or neodymium.

On Figure 22, B represents the first hydrolysis of praseo-dymium trifluoroacetylacetonate (pH = 7.58) and C represents the second hydrolysis (pH = 8.00).

A precipitate of praseodymium trifluoroacetylacetonate was first noted at a pH of 5.42 and precipitation was apparently complete at a pH of 5.90.

There is marked similarity between the results obtained in this study and those which follow for neodymium.

i. Neodymium Trifluoroacetylacetonate

The titration study on neodymium trifluoroacetylacetonate was analogous to that made for the praseodymium compound. Neodymium

oxide (0.3370 grams; 2 x 10^{-3}M) was dissolved in hydrochloric acid

and the resulting solution evaporated almost to dryness. Then 50 per

cent water - 50 per cent dioxane solution (100 ml.) and trifluoroace-

tylacetone (1.8480 grams; 1.2 x 10^{-2}M) was added to the neodymium

chloride. The solution was then adjusted to a pH of 1.80. The

titration was made by adding sodium hydroxide (1.0672 N.) in 0.20 ml.

increments and allowing sufficient time between successive additions

of alkali for the attainment of equilibrium.

The data for this experiment are recorded in Table XXVI

in the Appendix and in Figure 23.

As was also noted in the praseodymium trifluoroacetylaceto-

nate titration, there is no plateau for the pH of precipitation of

neodymium trifluoroacetylacetonate. The neodymium compound did pre-

cipitate between the pHs of 5.32 and 5.90.

Plateau B, Figure 23, at a pH of 7.00 represents the first

hydrolysis of neodymium trifluoroacetylacetonate. This is at a slightly

lower pH than was expected from the results obtained for praseodymium,

but still is in line from the standpoint of basicities.

Plateau C, (pH = 7.70) represents the second hydrolysis of

the neodymium trifluoroacetylacetonate.

The results obtained for all of the rare earth trifluoroace-

tylacetonate titrations do not correspond to what would be expected

from the results of studies of other rare earth chelates. However, it

is felt that a more detailed study of the rare earth trifluoroacetylace-

tonates should be made in order to explain these discrepancies.

FIGURE 23

NEODYMIUM TRIFLUOROACETYLACETONATE
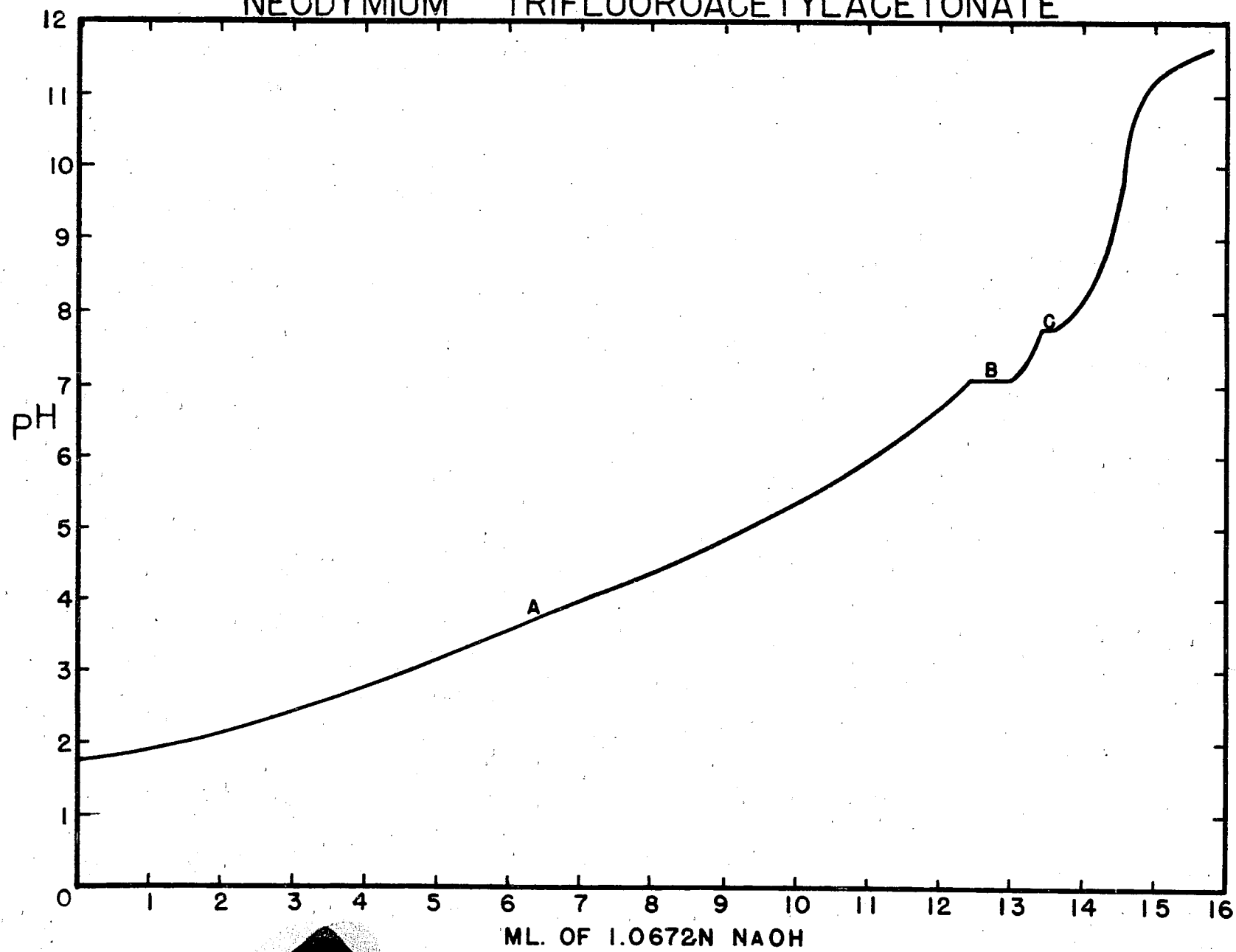
j. Lanthanum Thenoyltrifluoroacetonate

To determine the behavior of lanthanum ions in the presence of thenoyltrifluoroacetone in solutions of varying acidity, lanthanum oxide (0.1642 grams; 1 x 10^{-3}M) was dissolved in dilute hydrochloric acid and the resulting solution was evaporated almost to dryness. Thenoyltrifluoroacetone (1.332 grams; 6 x 10^{-3}M) was dissolved in 100 ml. of a 50 per cent water - 50 per cent dioxane solution and the resulting solution was added to the lanthanum chlordie. The pH of this mixture was then adjusted to a value of 1.72. The titration was made by adding sodium hydroxide (1.0672 N.) in increments of 0.20 ml. and allowing the solution to come to equilibrium before taking the pH reading and adding more alkali.

See Table XXVII in the Appendix and Figure 24 for the data obtained for this titration study.

From an examination of this data it is seen that the pH of precipitation of lanthanum thenoyltrifluoroacetonate (3.62) is much lower than that noted for any of the previously studied rare earth chelates. Also, it is noted that the pH of the first hydrolysis is at a higher value (9.34) than for any of the other chelates. These two facts are indicative of the greater stability of lanthanum thenoyltrifluoroacetonate.

The acid dissociation constant of thenoyltrifluoroacetone is $10^{-6.62}$ and for trifluoroacetylacetone is $10^{-6.50}$, so that it would be postulated that the chelating strengths might also be comparable. However, the thenoyltrifluoroacetone is much the stronger

FIGURE 24

LANTHANUM THENOYL TRIFLUOROACETONATE

ML. OF 1.0672N NaOH
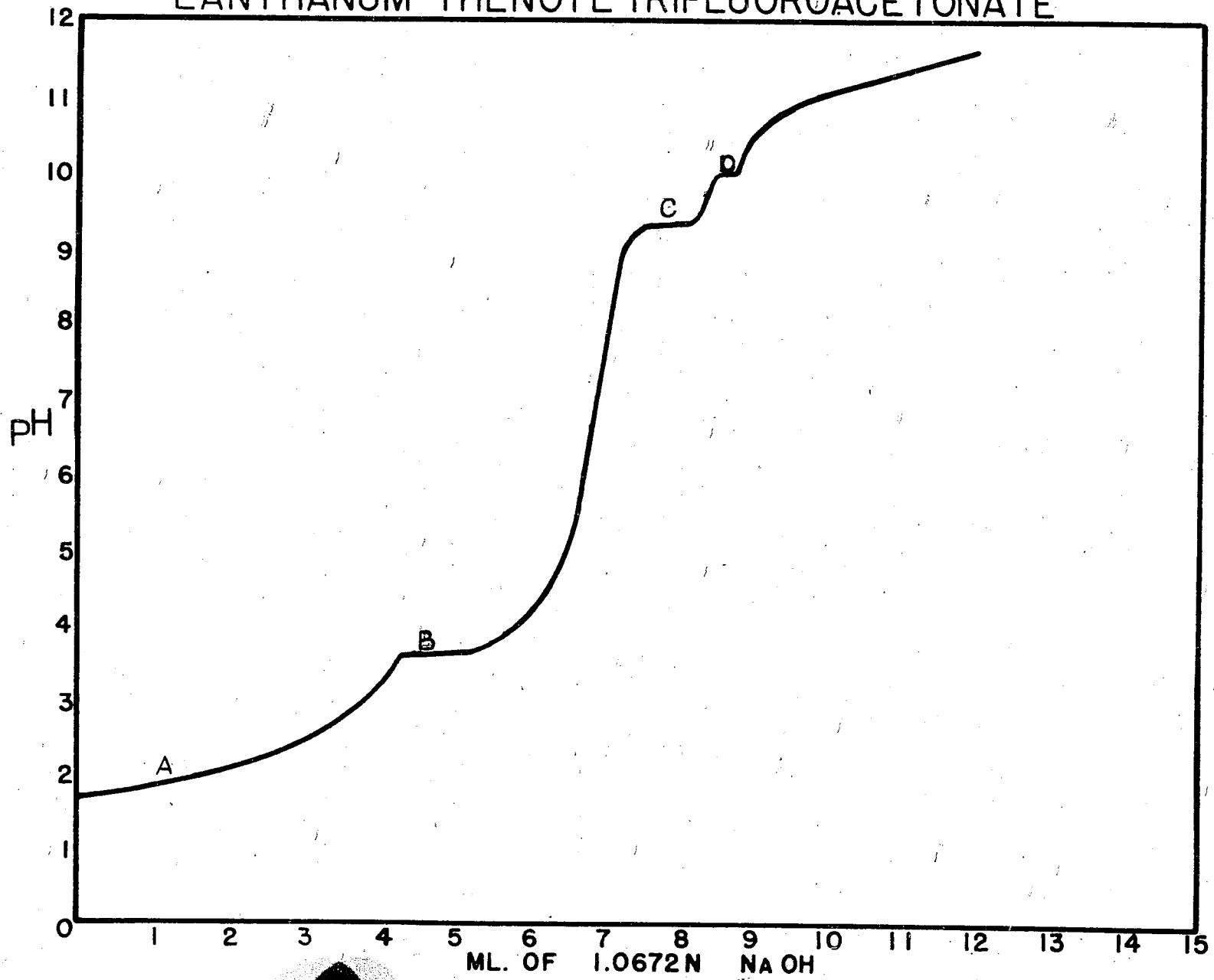
chelating agent, which indicates that there may be a third coordinate
bond formed between the rare earth ion and the sulfur of the thenoyl
group. The thenoyltrifluoroacetonates of the rare earths should be
studied more extensively, since they possess greater stability than
is noted for any of the other chelate compounds of the rare earths.

On Figure 24, $\underline{A}$ represents the replacement of protons from
coordinated thenoyltrifluoroacetone molecules, as well as the neutrali-
zation of excess acid, $\underline{B}$ (pH = 3.62) represents the pH of precipitation
of lanthanum thenoyltrifluoroacetonate, $\underline{C}$ (pH = 9.34) represents the
first hydrolysis of the chelate compound, and $\underline{D}$ (pH = 9.90) represents
the second hydrolysis.

The thenoyltrifluoroacetonates of the rare earths because
of their greater stability may possess some of the properties which
are desired for the separation of rare earth elements by diffusion
and sublimation methods.

k. Lanthanum Ethyltrifluoroacetoacetate

The titration study of lanthanum ethyltrifluoroaceto-
acetate was undertaken by dissolving lanthanum oxide (0.3258 grams;
2×10^{-3}M) in dilute hydrochloric acid and the resulting solution
evaporated almost to dryness. Then to the lanthanum chloride was
added 100 ml. of a 50 per cent water - 50 per cent dioxane solution
along with 2.209 grams (1.2×10^{-2}M) of ethyltrifluoroacetoacetate.
The pH of the resulting solution was adjusted to 1.80 as measured by
the glass electrode. The titration was then made as in all previous

FIGURE 25

LANTHANUM ETHYLTRIFLUOROACETOACETATE
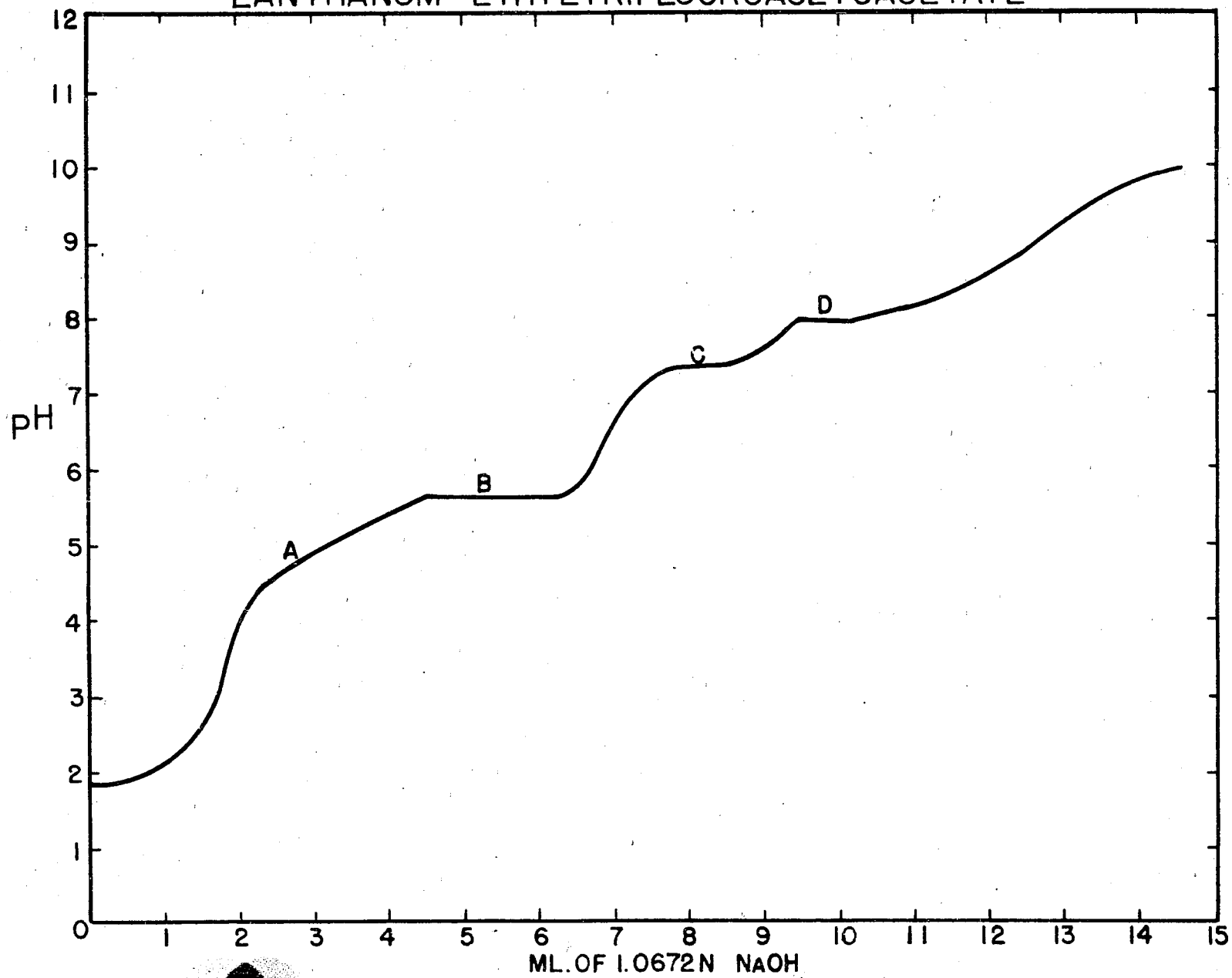
cases by adding standard sodium hydroxide solution (1.0672 N.) in increments of 0.20 ml. Sufficient time was allowed between successive additions for the attainment of equilibrium.

The data obtained from this experiment are presented in Table XXVIII in the Appendix and in Figure 25.

Upon examination of the results, it is noted that portion A of the titration curve (Figure 25) represents the removal of protons from coordinated ethyltrifluoroacetoacetate molecules; B represents the precipitation of lanthanum ethyltrifluoroacetoacetate at a pH of 5.65; C represents the first hydrolysis of the chelated compound (pH = 7.40); and D represents the second hydrolysis at pH = 7.95.

Lanthanum ethyltrifluoroacetoacetate is a crystalline white solid which apparently is more stable than the acetylacetonate but less stable than the thenoyltrifluoroacetonate.

In summary, Table XXIX shows some of the data obtained from these titration studies on the rare earths.

TABLE XXIX

| | Acetylacetonates | | |
Rare Earth	pH of Pptn. of Chelate	pH of First Hydrolysis	pH of Second Hydrolysis
La	6.74	8.50	9.00
Ce	6.70	8.18 (?)	8.70
Pr	6.65	7.98	8.38
Nd	6.58	7.92	8.33
Sm	6.48	7.50	7.82

	Trifluoroacetylacetonates		
La	5.30	7.37	8.50
Ce	5.40 (?)	-	-
Pr	5.42 (?)	7.58	8.00
Nd	5.32 (?)	7.00	7.70

	Thenoyltrifluoroacetonates		
La	3.62	9.34	9.90

	Ethyltrifluoroacetoacetates		
La	5.65	7.40	7.95

DISCUSSION

Considerable work has been done on the preparation of chelate compounds and upon their structures (25, 26) yet few attempts have been made to determine in a quantitative manner how the structural factors, other than the simple geometry of ring formation, influence the tendency of organic chelating agents to form chelate compounds with heavy metal ions. One such as attempt was made by Calvin and Wilson (18), who published the first of a series of articles by Calvin on the strength of the chelate bond.

An incomplete quantitative survey employing the method of Calvin and Wilson was made to determine the influence of certain structural factors upon the stability of chelate compounds of several rare earth metals. This survey is called incomplete since, because of lack of time, it was necessary to define only one phase of work in this thesis; namely, a study of the behavior in solutions of varying acidity of some rare earth ions in the presence of various chelating agents. Other factors which were not studied are: 1) solubilities, 2) effects of concentration upon behavior, 3) effects of temperature on such reactions, and 4) more complete studies of various metals and of other chelating agents.

As a result of the study which has been made, some discrepancies have been found in the theory presented by Calvin, et al., which are clarified by the observations on the rare earth chelates.

For example, Calvin and Wilson explain the first flat portion of their titration curve as representing the formation of the chelate and the sharp rise, indicating that chelate formation is complete. However, when a 'slow' titration is run the chelated compound precipitates at a very definite pH. This pH of precipitation is noted not only for the copper chelates, studied by Calvin and Wilson, but also for the rare earth chelates.

The interpretation which has been developed from the results obtained in the titration studies in this dissertation explains these discrepancies.

As a reference, Figure 14, representing the titration of lanthanum acetylacetonate, will be used. The first flat portion of the curve A, represents the neutralization of excess acid rather than the formation of the chelate as theorized by Calvin and Wilson. When a chelating agent such as acetylacetone, trifluoroacetylacetone, etc. is added even to a very acid solution of copper salt there is a deepening of the blue color which is assumed to be due to coordination. Acetylacetone is hydrogen bonded (1, Figure 26); however, with the metal ion such as copper, rare earth, etc. present this hydrogen bond is broken. Since complex compounds such as copper acetylacetonate are non-polar, the solubility in water is negligibly small. However, these compounds are soluble in the acid medium which indicates that the chelate ring is not closed (see 2, Figure 26), but rather is in a polar form. At higher pHs (B, Figure 14) the acid hydrogen from the three coordinated acetylacetone molecules is removed. Formula 3,
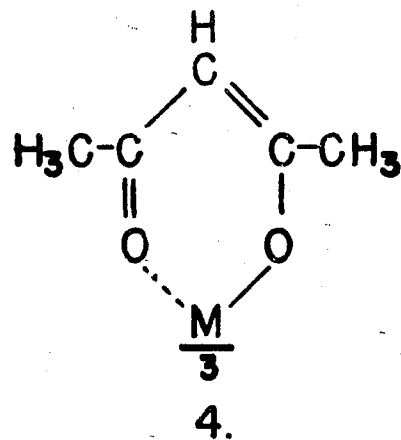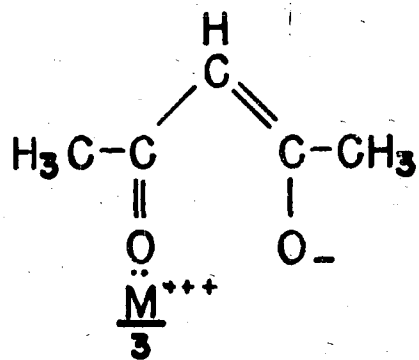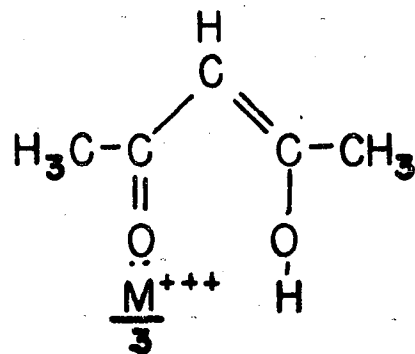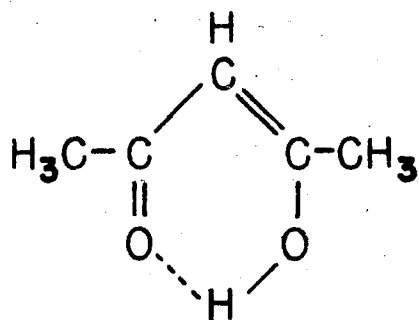
FIGURE 26

Figure 26, represents this transition state of the molecule.

After the proton is removed the chelate ring closes. The stoichi-ometrical data from these curves indicate that curve $\underline{B}$ is equivalent to four milliequivalents, meaning that two protons from the three coordinated acetylacetone molecules have been removed. At plateau $\underline{C}$ the proton from the third acetylacetone molecule is removed with the formation of the completely chelated compound. Plateau $\underline{C}$ for all titrations involving the rare earth acetylacetonates is equivalent to two milliequivalents which is to be expected since there were two millimoles of rare earth ion used in each titration study.

The equations representing the equilibria encountered in the titration studies are:

a) $M^{+++} + 3HKe \rightleftharpoons M(HKe)_3^{+++}$
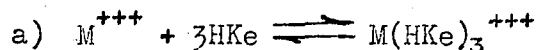
(This reaction is complete even in strongly acid solutions)

b) $M(HKe)_3^{+++} + OH^- \rightleftharpoons M(HKe)_2Ke^{++} + H_2O$

c) $M(HKe)_2Ke^{++} + OH^- \rightleftharpoons M(HKe)Ke_2^+ + H_2O$
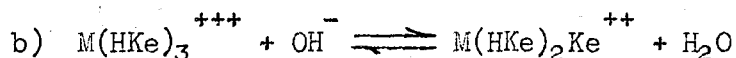
This reaction (c) is complete at the upper end of portion $\underline{B}$ of the titration curve. Upon the removal of the third proton from the coordi-nated acetylacetone molecule there is a closure of the third chelate ring; a non-polar molecule is formed and precipitates from the water solution.

d) $M(HKe)Ke_2^+ + OH^- \rightleftharpoons MKe_3 + H_2O$
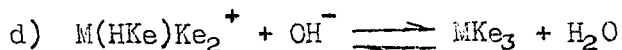
In solution of higher pH as represented by plateaus $\underline{D}$ and $\underline{E}$, Figure 14, two other equilibria are noted:

e) $MKe_3 + OH^- \rightleftharpoons MKe_2OH + Ke^-$

f) $M(Ke_2)OH + OH^- \rightleftharpoons MKe(OH)_2 + Ke^-$
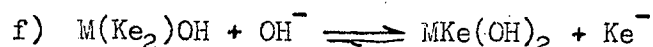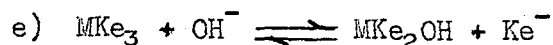
Equilibrium constants can be assigned for all of the above reactions. In order to prove the products of equations d, e, and f, samples of the precipitate were taken at each of the respective pHs and these samples were ignited to rare earth oxide. From the percentage of rare earth oxide in each sample it was proved that there is the step-wise hydrolysis of the acetylacetonate. From experimental data it has been determined that at the maximum pH of the titration there is not a complete hydrolysis to the rare earth hydroxide. This hydroly-sis was not expected to be complete since there are molecules of the acetylacetone present which still could coordinate. The behavior of acetylacetonates in concentrated and in dilute alkali solutions may be entirely different. In the concentrated alkaline solutions the course of the reactions would be much more difficult to follow.

When the data for the titration studies of the various rare earth acetylacetonates were tabulated (Table XXIX) it was noted that the pHs of precipitation of the various compounds are very nearly the same value. Apparently, the rare earth ions, when they are the central atom of a chelated complex, lose much of their individual identity. The pHs of precipitation of the acetylacetonates, although still in the same order as the relative basicities of the rare earth elements are much closer together than the pHs of precipitation of the rare earth hydroxide from ionic compounds.

Marsh (27) has measured the molecular volumes of several rare earth acetylacetonates and has found them to be very nearly the same value. This small difference in molecular volumes of the various rare earth acetylacetonates is also indicative of the fact that the rare earths lose most of their individual identity in chelated complexes. It is of interest to note that such ionic compounds as the ferricyanides, basic nitrates and acetates of the rare earths show a much greater decrease in molecular volume with increasing atomic weight, than do chelate complexes. If the pHs of formation of the chelated compounds of the rare earth elements are so much closer together, as compared to the pHs of formation of the hydroxides from ionic compounds, then this type of compound will be of little use in the separation of these elements.

Also, the data show that at higher pHs the acetylacetonates of the rare earth elements hydrolyze to give, first, the monobasic derivative and, second, the dibasic derivative. Greater differences in the pHs of formation of these basic acetylacetonates of successive rare earths were observed than in the pHs of precipitation of the normal chelates. These greater differences can be attributed to the fact that upon hydrolysis the rare earth ions once again assume their normal basic characteristics.

From the titration studies it may be concluded that it would be possible to allow the pH to rise to a higher value than was originally proposed in the syntheses of the acetylacetonates. Also by allowing the pH to rise to a higher value, more consistent

results should be obtained in the syntheses of the trifluoroacetyl-acetonates. More work is to be done in the near future on this particular problem. It should be possible to select, and particularly for more concentrated solutions, the pH of the midpoint of the vertical curve between the pH of precipitation and that of the first hydrolysis as the maximum pH of the reaction.

Numerous other problems and ramifications of this problem came to mind as the work progressed. The most important of these problems are:

1) A study of the molecular volumes of various chelated compounds,

2) Solubility studies of rare earth chelates in both aqueous and non-aqueous solvents,

3) A study of the preparation of other chelated rare earth compounds in solutions of controlled acidity,

4) A study of the effect of different methods of preparation of the unsymmetrical β-diketonates on isomerization,

5) Research on the synthesis of trifluoroacetylacetone omitting the hydrogen sulfide step, and

6) A study comparing and contrasting the citrate, tartrate, tannate, etc. complexes of the rare earths with the normal and modified acetylacetonates.

SUMMARY

1) Rare earth acetylacetonates have been prepared in high yields in solutions of controlled acidity.

2) Trifluoroacetylacetone has been prepared by the method of Staniforth with minor ramifications.

3) Trifluoroacetylacetonates of the rare earths have been prepared by the method employed for the synthesis of the normal acetylacetonates, but the yields were not as high as in the former case.

4) Titration studies of some of the rare earth elements and the following chelating agents have been made:

a) acetylacetone   c) thenoyltrifluoroacetone

b) trifluoroacetylacetone   d) ethyl trifluoroacetoacetate

5) Differences in the behavior of the metal ions in fast and in slow titrations have been observed.

6) The pHs of formation of the acetylacetonates of the rare earths have been observed to be different from the pHs of formation of the respective hydroxides.

7) The formation of the rare earth chelates proceeds in a stepwise manner from coordination in highly acid solutions through the removal of protons from coordinated chelating agent molecules to the precipitation of the chelated compound.

8) Thenoyltrifluoroacetone apparently forms the more stable chelated compound with the rare earths than any of the other chelating agents used.

9) There apparently is no complete hydrolysis of rare earth chelates to the hydroxide in highly alkaline solutions.

10) Copper, zinc, and nickel acetylacetonates were studied and the results obtained were analogous to those for the rare earth chelates.

11) Copper apparently forms planar molecules with acetylacetone while zinc and nickel form tetrahedral molecules.

12) Ethyl trifluoroacetoacetate does not behave in an analogous manner to acetylacetone, trifluoroacetylacetone and thenoyltrifluoroacetone in the presence of copper ion. Copper ethyl trifluoroacetoacetate does not have the characteristic deep blue color of most cupric complexes.

The research on the chelated compounds of metals which was described in this dissertation has led to several different problems, the study of which would clarify many of the questions concerning the nature of chelation.

APPENDIX

TABLE V

Acetylacetone Titration

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.30	4.40	9.48
0.20	1.80	4.60	9.53
0.40	1.85	4.80	9.58
0.60	1.93	5.00	9.63
0.80	2.03	5.20	9.70
1.00	2.21	5.40	9.76
1.20	2.43	5.60	9.82
1.40	3.19	5.80	9.88
1.60	5.28	6.00	9.95
1.80	6.78	6.20	10.01
2.00	8.31	6.40	10.10
2.20	8.60	6.60	10.20
2.40	8.76	6.80	10.29
2.60	8.86	7.00	10.41
2.80	8.95	7.20	10.55
3.00	9.03	7.40	10.73
3.20	9.10	7.60	11.00
3.40	9.16	8.00	11.40
3.60	9.22	8.50	11.55
3.80	9.30	9.00	11.60
4.00	9.36	9.50	11.65
4.20	9.43	10.00	11.70

TABLE VI

Trifluoroacetylacetone Titration

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.86	3.80	6.12
0.20	1.88	4.00	6.23
0.40	1.92	4.20	6.37
0.60	1.96	4.40	6.46
0.80	2.00	4.60	6.55
1.00	2.04	4.80	6.65
1.20	2.10	5.00	6.78
1.40	2.16	5.20	6.89
1.60	2.27	5.40	7.04
1.80	2.37	5.60	7.20
2.00	2.49	5.80	7.50
2.20	2.68	6.00	8.00
2.40	3.01	6.20	10.82
2.60	4.40	6.40	11.60
2.80	5.22	6.60	11.72
3.00	5.54	6.80	11.77
3.20	5.75	7.00	11.80
3.40	5.90	7.60	11.80
3.60	6.02		

TABLE VII

Thenoyltrifluoroacetone

Volume of Alkali	pH
0.00	1.90
0.20	1.92
0.40	1.94
0.60	1.97
0.80	2.00
1.00	2.06
1.20	2.10
1.40	2.15
1.60	2.23
1.80	2.31
2.00	2.42
2.20	2.60
2.40	2.85
2.60	3.68
2.80	5.73
3.00	6.23
3.20	6.62
3.40	6.93
3.60	7.38
3.80	10.92
4.00	11.72
4.20	11.82
4.40	11.87
5.00	11.90

TABLE VIII

Ethyl Trifluoroacetoacetate

Volume of Alkali	pH
0.00	1.82
0.20	1.84
0.40	1.89
0.60	1.94
0.80	2.00
1.00	2.07
1.20	2.14
1.40	2.28
1.60	2.48
1.80	2.87
2.00	6.48
2.20	7.48
2.40	7.89
2.60	8.10
2.80	8.30
3.00	8.50
3.20	8.68
3.40	8.90
3.60	9.22
3.80	9.82
4.00	11.13
4.20	11.40
4.40	11.52
5.00	11.63

TABLE IX

'Slow' Copper Acetylacetonate Titration

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.80	4.60	3.35
0.20	1.83	4.80	3.70
0.40	1.88	5.00	4.13
0.60	1.92	5.20	4.70
0.80	1.95	5.40	5.40
1.00	1.98	5.60	6.72
1.20	2.02	5.80	6.72
1.40	2.09	6.00	8.05
1.60	2.12	6.20	8.30
1.80	2.18	6.40	8.42
2.00	2.23	6.60	8.51
2.20	2.28	6.80	8.87
2.40	2.36	7.00	9.06
2.60	2.43	7.20	9.32
2.80	2.51	7.40	9.50
3.00	2.60	7.60	9.80
3.20	2.70	7.80	10.36
3.40	2.70	8.00	10.70
3.60	2.70	8.20	10.92
3.80	2.78	8.40	11.02
4.00	2.83	8.60	11.10
4.20	3.00	9.00	11.12
4.40	3.16	9.40	11.21
		10.00	11.26

TABLE X

'Fast' Copper Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.80	4.80	6.68
0.20	1.82	5.00	8.07
0.40	1.86	5.20	8.50
0.60	1.90	5.40	8.68
0.80	1.94	5.60	8.82
1.00	1.99	5.70	8.88
1.20	2.03	6.20	9.11
1.40	2.10	6.70	9.28
1.60	2.15	7.20	9.40
1.80	2.21	7.70	9.50
2.00	2.31	8.20	9.60
2.20	2.36	8.70	9.70
2.40	2.43	9.20	9.80
2.60	2.52	9.70	9.91
2.80	2.60	10.20	10.04
3.00	2.71	10.70	10.18
3.20	2.83	11.20	10.34
3.40	2.93	11.70	10.60
3.60	3.06	12.20	11.00
3.80	3.18	12.70	11.20
4.20	3.50	13.20	11.28
4.40	4.10	13.70	11.31
4.60	5.35	14.20	11.32

TABLE XI

Zinc Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.70	5.80	6.42
0.20	1.70	6.00	6.55
0.40	1.74	6.20	6.69
0.60	1.77	6.40	6.82
0.80	1.82	6.60	7.00
1.00	1.86	6.80	7.00
1.20	1.92	7.00	7.00
1.40	2.00	7.20	7.20
1.60	2.09	7.40	7.48
1.80	2.14	7.60	7.88
2.00	2.22	7.80	8.08
2.20	2.35	8.00	8.08
2.40	2.78	8.20	8.08
2.60	3.72	8.40	8.08
2.80	4.23	8.60	8.08
3.00	4.58	8.80	8.08
3.20	4.79	9.00	8.95
3.40	4.98	9.20	9.30
3.60	5.15	9.40	9.50
3.80	5.30	9.60	9.70
4.00	5.42	9.80	9.85
4.20	5.52	10.00	9.98
4.40	5.62	10.20	10.15
4.60	5.72	10.40	10.32
4.80	5.84	10.60	10.42
5.00	5.98	11.00	10.75
5.20	6.07	11.50	11.20
5.40	6.18	12.00	11.40
5.60	6.32		

TABLE XII

Nickel Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.78	5.80	6.74
0.20	1.85	6.00	6.74
0.40	1.92	6.20	6.74
0.60	2.02	6.40	7.00
0.80	2.16	6.60	7.20
1.00	2.30	6.80	7.20
1.20	2.59	7.00	7.20
1.40	2.91	7.20	7.20
1.60	3.28	7.40	7.61
1.80	3.51	7.60	8.27
2.00	3.76	7.80	8.38
2.20	3.96	8.00	8.85
2.40	4.12	8.20	8.97
2.60	4.32	8.40	9.13
2.80	4.49	8.60	9.30
3.00	4.68	8.80	9.48
3.20	4.83	9.00	9.59
3.40	5.01	9.20	9.71
3.60	5.18	9.40	9.89
3.80	5.38	9.60	10.40
4.00	5.52	9.80	10.92
4.20	5.68	10.00	11.11
4.40	5.80	10.20	11.22
4.60	5.98	10.40	11.33
4.80	6.12	10.60	11.40
5.00	6.29	10.80	11.48
5.20	6.50	11.00	11.51
5.40	6.72	11.50	11.58
5.60	6.74		

TABLE XIII

Copper Trifluoroacetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.76	7.00	6.48
0.50	1.82	7.20	6.73
1.00	1.91	7.40	7.10
1.50	2.01	7.60	7.78
2.00	2.18	7.80	8.05
2.50	2.25	8.00	8.10
2.60	2.25	8.20	8.38
2.80	2.25	8.60	8.52
3.00	2.25	8.80	8.55
3.20	2.29	9.00	8.70
3.40	2.32	9.20	8.89
3.60	2.40	9.40	9.05
3.80	2.48	9.60	9.22
4.00	2.52	10.00	9.45
4.20	2.62	10.20	9.62
4.40	2.70	10.40	9.76
4.60	2.78	10.60	9.90
4.80	2.82	10.80	10.05
5.00	2.99	11.20	10.20
5.20	3.36	11.40	10.38
5.40	4.00	11.60	10.40
5.60	4.62	11.80	10.45
5.80	5.18	12.00	10.50
6.00	5.59	12.50	10.90
6.20	5.83	13.00	11.20
6.40	6.11	13.50	11.40
6.60	6.25	14.00	11.60
6.80	6.48	14.50	11.65

TABLE XIV

Copper Thenoyltrifluoroacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.55	5.20	2.10
0.50	1.59	5.40	2.17
1.00	1.65	5.60	2.22
1.50	1.71	5.80	2.33
1.70	1.72	6.00	2.50
1.90	1.72	6.20	2.80
2.00	1.72	6.40	3.82
2.20	1.72	6.60	5.17
2.40	1.78	6.80	5.58
2.60	1.79	7.20	8.56
2.80	1.80	7.40	8.55
3.00	1.81	7.60	8.60
3.20	1.78	7.80	9.34
3.40	1.78	8.00	9.70
3.60	1.80	8.20	10.11
3.80	1.82	8.60	10.48
4.00	1.86	9.00	10.68
4.20	1.91	9.20	10.76
4.40	1.93	9.40	10.79
4.60	1.98	9.60	10.90
4.80	2.02	9.80	10.95
5.00	2.08	10.00	11.00

TABLE XV

Copper Ethyltrifluoroacetoacetate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.74	5.40	7.93
0.20	1.79	5.60	8.08
0.40	1.86	5.80	8.20
0.60	1.90	6.00	8.31
0.80	1.92	6.20	8.49
1.00	1.98	6.40	8.62
1.20	2.00	6.60	8.80
1.40	2.18	6.80	8.95
1.60	2.25	7.00	9.20
1.80	2.48	7.20	9.20
2.00	2.70	7.40	9.20
2.20	3.22	7.60	9.20
2.40	3.80	7.80	9.22
2.60	4.16	8.00	9.39
2.80	4.27	8.20	9.65
3.00	4.27	8.40	9.80
3.20	4.27	8.60	9.90
3.40	4.27	8.80	10.00
3.60	4.32	9.00	10.12
3.80	4.52	9.50	10.41
4.00	4.83	10.00	10.70
4.20	5.79	10.50	11.00
4.40	7.22	11.00	11.30
4.60	7.44	11.50	11.58
4.80	7.68	12.00	11.72
5.00	7.80	12.50	11.85
5.20	7.90		

TABLE XVII

Lanthanum Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.80	6.80	6.80
0.20	1.81	7.00	6.91
0.40	1.89	7.20	7.15
0.60	2.01	7.40	7.46
0.80	2.18	7.60	7.82
1.00	2.36	7.80	8.18
1.20	2.61	8.00	8.43
1.40	3.05	8.20	8.50
1.60	3.50	8.40	8.50
1.80	3.82	8.60	8.70
2.00	4.04	8.80	9.00
2.20	4.22	9.00	9.00
2.40	4.40	9.20	9.02
2.60	4.59	9.40	9.10
2.80	4.75	9.60	9.38
3.00	4.87	9.80	9.48
3.20	5.00	10.00	9.55
3.40	5.17	10.20	9.65
3.60	5.31	10.40	9.72
3.80	5.45	10.60	9.80
4.00	5.60	10.80	9.87
4.20	5.73	11.00	9.92
4.40	5.90	11.20	10.02
4.60	6.03	11.40	10.12
4.80	6.19	11.60	10.30
5.00	6.32	11.80	10.49
5.20	6.45	12.00	10.70
5.40	6.58	12.20	10.90
5.60	6.71	12.40	11.08
5.80	6.74	12.60	11.21
6.00	6.74	12.80	11.38
6.20	6.74	13.00	11.42
6.40	6.74	13.60	11.62
6.60	6.75		

TABLE XVIII

'Fast' Lanthanum Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.78	5.30	7.80
0.20	1.80	5.50	8.00
0.40	1.85	5.70	8.20
0.60	1.90	6.00	8.50
0.80	1.92	6.20	8.70
1.00	2.00	6.40	8.84
1.20	2.04	6.60	8.95
1.40	2.11	7.00	9.12
1.60	2.12	7.20	9.22
1.80	2.28	7.40	9.32
2.00	2.62	7.60	9.45
2.20	2.95	7.80	9.52
2.40	3.95	8.00	9.61
2.60	4.52	8.20	9.73
2.80	4.88	8.40	9.82
3.00	5.26	8.60	9.93
3.20	5.56	8.80	10.00
3.40	5.86	9.00	10.12
3.60	6.15	9.20	10.18
3.80	6.42	9.40	10.25
4.00	6.62	9.60	10.35
4.20	6.84	9.80	10.50
4.30	6.78	10.00	10.72
4.40	6.88	10.50	11.21
4.50	7.02	11.00	11.55
4.70	7.22	11.50	11.61
4.90	7.46	12.00	11.59
5.10	7.72	12.50	11.62

TABLE XIX

Cerium Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.74	7.00	6.70
0.20	1.75	7.40	6.72
0.40	1.78	7.60	6.95
0.60	1.81	8.00	7.28
0.80	1.84	8.20	7.40
1.00	1.87	8.40	7.49
1.20	1.90	8.60	7.72
1.40	1.95	8.80	7.55
1.60	2.00	9.20	7.73
1.80	2.03	9.40	7.98
2.00	2.10	9.60	8.18
2.20	2.15	9.80	7.78
2.40	2.22	10.00	8.18
2.60	2.30	10.20	8.38
2.80	2.40	10.40	8.55
3.00	2.56	10.60	8.70
3.20	2.61	10.80	8.62
3.40	3.01	11.00	8.77
3.60	3.60	11.20	8.67
3.80	4.22	11.40	8.72
4.00	4.58	11.60	8.82
4.20	4.81	11.80	8.82
4.40	5.02	12.00	9.02
4.60	5.25	12.20	9.11
4.80	5.42	12.40	9.28
5.00	5.60	12.60	9.42
5.20	5.74	12.80	9.48
5.40	5.89	13.00	9.50
5.60	6.02	13.20	9.74
5.80	6.20	13.40	10.00
6.00	6.32	13.60	10.22
6.20	6.45	13.80	10.38
6.40	6.62	14.00	10.50
6.60	6.70	14.50	10.70
6.80	6.70	15.00	10.80

TABLE XX

Praseodymium Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.81	6.60	6.88
0.20	1.83	6.80	7.06
0.40	1.91	7.00	7.25
0.60	1.98	7.20	7.40
0.80	2.08	7.40	7.98
1.00	2.21	7.60	7.98
1.20	2.38	7.80	8.14
1.40	2.55	8.00	8.38
1.60	3.00	8.20	8.38
1.80	3.55	8.40	8.84
2.00	3.90	8.60	9.30
2.20	4.15	8.80	9.68
2.40	4.31	9.00	9.76
2.60	4.55	9.20	9.80
2.80	4.70	9.40	9.96
3.00	4.84	9.60	10.00
3.20	4.98	10.00	10.02
3.40	5.12	10.20	10.12
3.60	5.20	10.40	10.20
3.80	5.32	10.60	10.28
4.00	5.50	10.80	10.33
4.20	5.62	11.00	10.38
4.40	5.75	11.20	10.45
4.60	5.90	11.40	10.56
4.80	6.00	11.60	10.65
5.00	6.11	11.80	10.78
5.20	6.30	12.00	10.90
5.40	6.42	12.20	11.05
5.60	6.58	12.40	11.20
5.80	6.65	12.60	11.25
6.00	6.65	12.80	11.30
6.20	6.65	13.00	11.35
6.40	6.75	13.50	11.40

TABLE XXI

Neodymium Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.80	7.00	7.45
0.20	1.85	7.20	7.92
0.40	1.92	7.40	7.92
0.60	2.01	7.60	8.33
0.80	2.10	7.80	8.33
1.00	2.20	8.00	9.74
1.20	2.39	8.20	9.01
1.40	2.88	8.40	9.21
1.60	3.21	8.60	9.32
1.80	3.65	8.80	9.43
2.00	3.92	9.00	9.51
2.20	4.18	9.20	9.58
2.40	4.30	9.40	9.63
2.60	4.50	9.60	9.67
2.80	4.68	9.80	9.70
3.00	4.82	10.00	9.75
3.20	5.00	10.20	9.80
3.40	5.13	10.40	9.85
3.60	5.31	10.60	9.91
3.80	5.49	10.80	9.96
4.00	5.50	11.00	10.00
4.20	5.61	11.20	10.03
4.40	5.75	11.40	10.07
4.60	6.00	11.60	10.15
4.80	6.16	11.80	10.20
5.00	6.29	12.00	10.25
5.20	6.40	12.20	10.31
5.40	6.58	12.40	10.34
5.60	6.58	12.60	10.42
5.80	6.58	12.80	10.51
6.00	6.58	13.00	10.65
6.20	6.58	13.50	11.06
6.40	6.72	14.00	11.30
6.60	6.95	14.50	11.35
6.80	7.12		

TABLE XXII

Samarium Acetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.80	6.60	6.48
0.20	1.80	6.80	6.48
0.40	1.92	7.00	6.48
0.60	1.98	7.20	6.58
0.80	2.07	7.40	6.70
1.00	2.10	7.60	6.83
1.20	2.15	7.80	7.00
1.40	2.27	8.00	7.36
1.60	2.42	8.20	7.50
1.80	2.63	8.40	7.50
2.00	2.92	8.60	7.50
2.20	3.42	8.80	7.50
2.40	3.68	9.00	7.60
2.60	4.00	9.20	7.82
2.80	4.18	9.40	7.82
3.00	4.33	9.60	7.88
3.20	4.50	9.80	8.12
3.40	4.67	10.00	8.55
3.60	4.80	10.20	8.95
3.80	4.97	10.40	9.36
4.00	5.10	10.60	9.75
4.40	5.25	10.80	10.00
4.60	5.38	11.00	10.18
4.80	5.50	11.20	10.30
5.00	5.60	11.40	10.42
5.20	5.71	11.60	10.55
5.40	5.83	11.80	10.70
5.60	5.98	12.00	10.90
5.80	6.12	12.20	11.00
6.00	6.29	12.40	11.10
6.20	6.42	12.60	11.18
6.40	6.48		

TABLE XXIII

Lanthanum Trifluoroacetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.80	7.20	4.62
0.20	1.82	7.40	4.70
0.40	1.90	7.60	4.79
0.60	1.95	7.80	4.90
0.80	1.98	8.00	4.98
1.00	2.01	8.20	5.10
1.20	2.08	8.40	5.20
1.40	2.12	8.60	5.30
1.60	2.19	8.80	5.30
1.80	2.24	9.00	5.32
2.00	2.32	9.20	5.40
2.20	2.41	9.40	5.48
2.40	2.50	9.60	5.60
2.60	2.60	9.80	5.62
2.80	2.70	10.00	5.73
3.00	2.80	10.20	5.90
3.20	2.91	10.40	6.05
3.40	3.01	10.60	6.22
3.60	3.11	10.80	6.55
3.80	3.20	11.00	6.95
4.00	3.29	11.20	7.30
4.20	3.38	11.40	7.37
4.40	3.47	11.60	7.37
4.60	3.52	11.80	7.45
4.80	3.60	12.00	7.75
5.00	3.69	12.20	8.00
5.20	3.73	12.40	8.28
5.40	3.82	12.60	8.50
5.60	3.91	12.80	8.50
5.80	4.02	13.00	8.50
6.00	4.11	13.20	9.68
6.20	4.20	13.40	10.70
6.40	4.30	13.60	10.92
6.60	4.39	13.80	11.10
6.80	4.48	14.00	11.18
7.00	4.55	14.50	11.30

TABLE XXIV

Cerium Trifluoroacetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.78	6.80	6.30
0.20	1.80	7.00	6.30
0.40	1.82	7.20	6.30
0.60	1.86	7.40	6.48
0.80	1.89	7.60	6.45
1.00	1.92	7.80	6.82
1.20	1.97	8.00	6.88
1.40	2.00	8.20	6.98
1.60	2.05	8.40	7.03
2.00	2.15	8.60	6.52
2.20	2.22	8.80	6.77
2.40	2.30	9.00	6.95
2.60	2.38	9.20	6.37
2.80	2.48	9.40	6.29
3.00	2.60	9.60	6.13
3.20	2.78	9.80	5.98
3.40	2.95	10.00	6.14
3.60	3.21	10.20	5.88
3.80	3.45	10.40	6.09
4.00	3.67	10.60	6.12
4.20	3.83	10.80	6.08
4.40	4.02	11.00	6.00
4.60	4.18	11.20	6.25
4.80	4.34	11.40	6.15
5.00	4.50	11.60	6.70
5.20	4.62	11.80	8.32
5.40	4.80	12.00	9.65
5.60	4.93	12.20	10.10
5.80	5.10	12.40	10.34
6.00	5.40	12.60	10.58
6.20	5.62	13.00	10.80
6.40	6.05	13.50	10.92
6.60	6.30	14.00	11.00

TABLE XXV

Praseodymium Trifluoroacetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.78	8.20	4.78
0.20	1.80	8.40	4.89
0.40	1.81	8.60	4.99
0.60	1.83	8.80	5.09
0.80	1.87	9.00	5.20
1.00	1.89	9.20	5.31
1.20	1.92	9.40	5.47
1.40	1.95	9.60	5.58
1.60	1.98	9.80	5.72
1.80	2.02	10.00	5.90
2.00	2.07	10.20	6.10
2.20	2.11	10.40	6.30
2.40	2.16	10.60	6.51
2.60	2.20	10.80	6.87
2.80	2.28	11.00	6.97
3.00	2.34	11.20	7.13
3.20	2.42	11.40	7.27
3.40	2.50	11.60	7.60
3.60	2.62	11.80	7.58
3.80	2.73	12.00	7.60
4.00	2.82	12.20	7.58
4.20	2.94	12.40	7.58
4.40	3.05	12.60	7.58
4.60	3.15	12.80	7.93
4.80	3.25	13.00	7.95
5.00	3.37	13.20	7.98
5.20	3.45	13.40	8.00
5.40	3.52	13.60	7.98
5.60	3.62	13.80	8.05
5.80	3.69	14.00	9.22
6.00	3.78	14.20	10.38
6.20	3.85	14.40	10.42
6.40	3.95	14.60	10.50
6.60	4.05	14.80	10.52
6.80	4.16	15.00	10.85
7.00	4.21	15.20	10.90
7.20	4.30	15.40	11.00
7.40	4.39	15.60	11.10
7.60	4.49	15.80	11.12
7.80	4.58	16.00	11.30
8.00	4.67		

TABLE XXVI

Neodymium Trifluoroacetylacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.80	8.00	4.45
0.20	1.80	8.20	4.50
0.40	1.80	8.40	4.60
0.60	1.80	8.60	4.70
0.80	1.82	8.80	4.80
1.00	1.88	9.00	4.89
1.20	1.91	9.20	5.00
1.40	1.96	9.40	5.10
1.60	2.00	9.60	5.20
1.80	2.05	9.80	5.32
2.00	2.10	10.00	5.42
2.20	2.17	10.20	5.52
2.40	2.22	10.40	5.65
2.60	2.27	10.60	5.77
2.80	2.33	10.80	5.90
3.00	2.43	11.00	6.00
3.20	2.49	11.20	6.12
3.40	2.57	11.40	6.22
3.60	2.63	11.60	6.37
3.80	2.70	11.80	6.56
4.00	2.80	12.00	6.58
4.20	2.88	12.20	6.70
4.40	3.00	12.40	7.00
4.60	3.09	12.60	7.00
4.80	3.18	12.80	7.00
5.00	3.26	13.00	7.00
5.20	3.33	13.20	7.00
5.40	3.40	13.40	7.70
5.60	3.48	13.60	7.70
5.80	3.56	13.80	7.78
6.00	3.62	14.00	8.01
6.20	3.70	14.20	8.45
6.40	3.77	14.40	8.75
6.60	3.84	14.60	10.12
6.80	3.92	14.80	10.83
7.00	4.00	15.00	11.12
7.20	4.10	15.20	11.30
7.40	4.18	15.40	11.40
7.60	4.27	15.60	11.50
7.80	4.35		

TABLE XXVII

Lanthanum Thenoyltrifluoroacetonate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.72	5.40	3.64
0.20	1.75	5.60	3.70
0.40	1.78	5.80	3.86
0.60	1.82	6.00	4.07
0.80	1.90	6.20	4.43
1.00	1.92	6.40	4.67
1.20	1.98	6.60	5.31
1.40	2.00	6.80	6.20
1.60	2.02	7.00	7.20
1.80	2.10	7.20	8.85
2.00	2.17	7.40	9.34
2.20	2.22	7.60	9.34
2.40	2.30	7.80	9.34
2.60	2.39	8.00	9.34
2.80	2.49	8.20	9.34
3.00	2.60	8.40	9.35
3.20	2.72	8.60	9.91
3.40	2.89	8.80	9.90
3.60	3.08	9.00	10.45
3.80	3.25	9.20	10.61
4.00	3.40	9.40	10.68
4.20	3.62	9.60	10.73
4.40	3.62	9.80	10.89
4.60	3.62	10.00	11.00
4.80	3.62	10.20	11.08
5.00	3.62	10.40	11.10
5.20	3.62		

TABLE XXVIII

Lanthanum Ethyltrifluoroacetoacetate

Volume of Alkali	pH	Volume of Alkali	pH
0.00	1.80	7.40	7.10
0.20	1.83	7.60	7.22
0.40	1.89	7.80	7.34
0.60	1.97	8.00	7.40
0.80	2.02	8.20	7.42
1.00	2.10	8.40	7.40
1.20	2.22	8.60	7.45
1.40	2.40	8.80	7.52
1.60	2.63	9.00	7.62
1.80	3.18	9.20	7.76
2.00	3.98	9.40	7.89
2.20	4.34	9.60	7.95
2.40	4.53	9.80	7.95
2.60	4.68	10.00	7.95
2.80	4.80	10.20	8.07
3.00	4.92	10.40	8.09
3.20	5.02	10.60	8.18
3.40	5.11	10.80	8.18
3.60	5.19	11.00	8.20
3.80	5.28	11.20	8.25
4.00	5.35	11.40	8.28
4.20	5.42	11.60	8.38
4.40	5.58	11.80	8.45
4.60	5.65	12.00	8.62
4.80	5.65	12.20	8.68
5.00	5.65	12.40	8.82
5.20	5.65	12.60	9.08
5.40	5.65	12.80	9.20
5.60	5.65	13.00	9.32
5.80	5.65	13.20	9.42
6.00	5.65	13.40	9.51
6.20	5.65	13.60	9.60
6.40	5.65	14.00	9.78
6.60	5.78	14.50	9.94
6.80	6.18	15.00	10.11
7.00	6.68	15.50	10.22
7.20	6.95	16.00	10.36

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