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The Chelation of Praseodymium as a Function of pH Using Thenolytrifluoroacetone

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Keenan — The Chelation of Praseodymium

THE CHELATION OF PRASEODYMIUM AS A FUNCTION OF pH USING THENOYLTRIFLUOROACETONE

By

Thomas K. Keenan

A Thesis
In partial fulfillment of the
Requirements for the Degree of
Master of Science in Chemistry

The University of New Mexico
1950

This thesis, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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May 17, 1950

DATE

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Thesis committee

John F. Suttle

CHAIRMAN

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Guido H. Daub

J. L. Riebsomer

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The author wishes to express his thanks for the advice and guidance given to him by Dr. John F. Suttle under whom this work was carried out.

He is also indebted to the personnel of the Los Alamos Scientific Laboratory who were helpful in arranging for irradiations of the praseodymium used.

Dr. R. P. Hammond of the Los Alamos Scientific Laboratory obtained a sample of extremely pure praseodymium for use as tracer. This sample greatly expedited the progress of this entire project.

TABLE OF CONTENTS

I. INTRODUCTION

The rare earth elements, including elements 57 through 71, provide many diverse series of studies through their chemical reactions. Inasmuch as these elements are all in Group III of the periodic table, they are markedly similar in their properties. The separation, isolation and purification of the various rare earths from one another has long been a problem of great interest to the chemist. All of these elements show a principal valence of plus three. Cerium has a well-defined plus four state, stable in aqueous solution and europium forms a stable, insoluble divalent sulfate.[1] These two exceptions, however, are the only cases of valence states other than plus three which are stable under normal conditions. Consequently, procedures taking advantage of oxidation state differences cannot generally be used to effect a separation.

The similarity of these elements in their common chemical reactions is most readily grasped from an understanding of their electronic structure. Table I[2] shows the best available data for these structures.

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1. Yost, Russell and Garner, <u>The Rare Earth Elements and Their Compounds</u>, John Wiley & Sons, New York, 1947, pp. 62-67.
2. Yost, Russell and Garner, <u>op</u>. <u>cit</u>., p. 3.

TABLE I

ELECTRONIC CONFIGURATION OF THE RARE EARTHS

Element	At. No.	Configuration*				
		4f	5s	5p	5d	6s
Lanthanum	57	0	2	6	1	2
Cerium	58	2	2	6	0	2
Praseodymium	59	3	2	6	0	2
Neodymium	60	4	2	6	0	2
Promethium	61	5	2	6	0	2
Samarium	62	6	2	6	0	2
Europium	63	7	2	6	0	2
Gadolinium	64	7	2	6	1	2
Terbium	65	8	2	6	1	2
Dysprosium	66	10	2	6	0	2
Holmium	67	11	2	6	0	2
Erbium	68	12	2	6	0	2
Thulium	69	13	2	6	0	2
Ytterbium	70	14	2	6	0	2
Lutecium	71	14	2	6	1	2

*The inner shells are completely filled and are not shown.

As can be seen from a study of this table, electrons are being added to the inner 4f shell as the atomic number increases, whereas the outer valence shells remain relatively unchanged. This building up of an inner shell results in a shrinkage of the entire electron cloud and it is this shrinkage, increasing from element to element, that determines to a great degree the slight differences in the extent of the reactions that the rare earths undergo.

The 4f electrons are not involved in the formation of chemical bonds. However, certain 4f states, i.e. $4f^0$, $4f^7$ and $4f^{14}$, are semi-stable structures and indicate the

[illegible]

[illegible]	[illegible]	[illegible]
Lanthanum	[illegible]	[illegible]
Cerium	[illegible]	[illegible]
Praseodymium	[illegible]	[illegible]
Neodymium	[illegible]	[illegible]
Promethium	[illegible]	[illegible]
Samarium	[illegible]	[illegible]
Europium	[illegible]	[illegible]
Gadolinium	[illegible]	[illegible]
Terbium	[illegible]	[illegible]
Dysprosium	[illegible]	[illegible]
Holmium	[illegible]	[illegible]
Erbium	[illegible]	[illegible]
Thulium	[illegible]	[illegible]
Ytterbium	[illegible]	[illegible]
Lutetium	[illegible]	[illegible]

[illegible]

[illegible] unchanged. [illegible] the possibility that the [illegible].

[illegible] of chemical bonds [illegible] and Cr [illegible] existence of plus two states for europium and ytterbium, plus four states for cerium, praseodymium and terbium and a plus five state for praseodymium. With the exception of the two specific examples previously mentioned, none of these odd-valence states are stable under normal conditions and are attainable only with some difficulty.

With the increase in atomic number, and the attending increasing positive charge on the nucleus, the overall result of the electron cloud shrinkage is to make the outer electrons less available to any one anion. This tends to make the coordinate type of linkage more pronounced toward the elements of higher atomic number. Another way of stating this situation is that the basicity, or tendency to assume the ionic state, decreases with increasing atomic number.

Von Hevesy[3,4] made a very complete study of this shrinkage by measuring the change in ionic radii of these elements. Since the building up of the rare earths involves the addition of electrons to an inner level, the corresponding attractive forces between the increasingly positive nucleus

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[3] Von Hevesy, Z. anorg. allgem. Chem., 147, 217 (1925).

[4] Von Hevesy, Z. anorg. allgem. Chem., 150, 68 (1925).

existence of [illegible] and [illegible]
plus four states [illegible]
a plus five state, or [illegible]
of the two possible [illegible]
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With the [illegible]
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toward the [illegible]
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atomic number.

Van Vleck[3] [illegible]
a maximum by computing the [illegible]
elements. Since the [illegible]
the addition [illegible]
attraction [illegible]

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3. Van Vleck, [illegible] (1930).
4. Van Vleck and [illegible] (1929).

and the outer electrons are not nullified and hence these electrons are more and more tightly held to the atom. Near holmium, (element 67) this balancing of size and charge result in an atom approximately the size of yttrium (element 29) and this accounts for the difficulty of separating yttrium from mixtures of rare earths. From these considerations, von Hevesy concluded that the basicities of the rare earths should decrease exactly as atomic number increased, with yttrium falling between dysprosium and holmium.

Thus, a series of reactions which take advantage of these slight differences in basicity could have application in separations procedures for the rare earths. First, however, is the problem of finding such a procedure that lends itself to relatively simple operations in the laboratory.

Moeller and Kremers[5] have published an excellent review of the basicities of the rare earths. These authors completely summarize the existing information dealing with this topic at the date of publication.

For an estimation of the relative value of the basicity of any element, two methods are available. The

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5. Moeller and Kremers, Chem. Rev., 37, 97 (1945).

and the colour change [illegible]
electrons [illegible]
four bonds, [illegible]
charge results [illegible]
[illegible]
separation [illegible]
these conditions, [illegible]
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simple [illegible]
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review of the [illegible]
completely [illegible]
this topic at the [illegible]

For [illegible]
basicity of [illegible]

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5. [illegible]

first, as outlined by Cartledge,[6] depends on the magnitude of the ratio: cation charge/cation radius (in Å units). This value, "ϕ", was designated as the ionic potential and the hydroxide of any element was said to be basic, amphoteric or acidic if the value of the square root of the ionic potential was less than 2.2; between 2.2 and 3.2; or greater than 3.2, respectively. It follows immediately that the smaller the value of the square root of the ionic potential, the more basic is the element concerned.

A second relative estimation of basicity has been developed by Sun and Li.[7] This depends on the ratio: AV/n^5 where A is the atomic number, V is the valence and n is the principal quantum number of the highest level in the ground state of the atom. A hydroxide is basic, amphoteric or acidic when the value of this ratio is less than 1.44; around 1.44; or greater than 1.44, respectively. The same relative considerations among basicities of elements apply here as in the above case. Table II lists the values of these two ratios as given by Moeller and Kremers.[8] The values of the ionic radii used by these

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[6] Cartledge, J. Am. Chem. Soc., 50, 2855 (1928).

[7] Sun and Li, J. Chinese Chem. Soc., 7, 69 (1940), as quoted by Moeller and Kremers, *loc. cit.*, p. 106.

[8] Moeller and Kremers, *loc. cit.*, p. 105.

authors are also given in column 3 of the table. These values of ionic radii were determined by Grimm and Wolff.[9]

The obvious weakness of the first of these methods is the limitation of experimental techniques for the determination of the cation radius. Nevertheless, it is a valuable tool for the calculation of relative basicity values.

Many experimental approaches have been followed for the determination of the relative basicities among the rare earths. A brief outline of these is listed in the section following.

TABLE II

RELATIVE BASICITY VALUES

Element	ø	AV/r^3	Radii (Å)
Lanthanum	1.73	0.792	1.00
Cerium	1.79	0.806	0.93
Praseodymium	1.82	0.819	0.91
Neodymium	1.83	0.833	0.90
Samarium	1.85	0.861	0.87
Europium	1.86	0.875	0.87
Gadolinium	1.87	0.889	0.86
Terbium	1.88	0.903	0.84
Dysprosium	1.89	0.917	0.83
Holmium	1.90	0.931	0.82
Erbium	1.91	0.944	0.81
Thulium	1.92	0.958	0.81
Ytterbium	1.95	0.972	0.79
Lutecium	1.95	0.986	0.79

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[9] Grimm and Wolff, Z. physik. Chem., <u>119</u>, 254 (1926).

systems are [illegible] given in Table [illegible] of the [illegible]. The values of [illegible]

The studies [illegible] in the field of [illegible] of the [illegible] valuable tool for the [illegible] values.

Many [illegible] have been used for the determination of the [illegible] along the [illegible] the following:

Method	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible] (19[illegible]).

II. EXPERIMENTAL METHODS OF DETERMINING BASICITY

A. Order of Precipitation of Hydroxides

One of the simplest methods that suggests itself is a determination of the order of precipitation of rare earth hydroxides from a solution of rare earth ions by the gradual addition of some soluble alkali hydroxide. Since such precipitation involves the consumption of hydroxyl ions, the least basic material will precipitate first, followed in order by the more basic elements. Levy,[10] in reporting results of experiments carried out in this fashion, lists the rare earths, in order of decreasing basicity as follows: lanthanum, cerium, praseodymium, neodymium, yttrium, europium, gadolinium, samarium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and luteoium. Within limits, this order follows the predicted order of atomic number rather closely.

However, in the general picture of precipitation by addition of alkali hydroxide, the method is open to criticism on the grounds that one must necessarily assume that the soluble portion of the hydroxides are all dissociated to the same extent in solution; and, furthermore, that these soluble portions are completely dissociated

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[10] Levy, The Rare Earths, Edward Arnold, London (1924), pp. 114-15.

IV. [illegible]

A. [illegible]

Use of [illegible] in a determination of [illegible] the practical [illegible] Since such [illegible] hydroxyl [illegible] [10] [illegible] in this [illegible] the practical [illegible]

However [illegible] by addition of [illegible] that the [illegible]

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10. [illegible]

in solution. Thus, by assuming the decreasing basicity of the rare earths, it does not seem unreasonable to predict that the actual ionic species present in solution will vary slightly in each case, every successive rare earth element following lanthanum bearing a slightly smaller charge than the limiting La^{+++}. Also, initial concentration differences of the various rare earth ions may give erroneous results. Localized excesses of alkali may cause one specific ion to be precipitated out of its true place and the process of this hydroxide going back into solution and reprecipitating at the proper time is then a function of the time of digestion, temperature and the particular concentrations present.

B. Solubility Product

Perhaps a better method of determining the order of precipitation is a rigorous determination of the equilibrium constant (i.e., solubility product constant) of the equation:

$$R_2O_3 \cdot xH_2O \rightleftharpoons 2\,R^{+++} + 6\,OH^- + (x - 3)\,H_2O.$$

In this case, assuming a pure starting material (the oxide), it could be allowed to come to complete equilibrium in aqueous solution over a period of time, this time period

being long enough to insure no errors due to digestion. Kolthoff and Elmquist[11] made a very thorough study of this constant in the case of lanthanum by digesting with water for ten days at 25°, filtering and carefully determining the amount of material remaining in solution. Their data yielded a solubility product constant for lanthanum hydroxide of 9.1×10^{-22}. However, these authors did not continue this work for the other elements in the lanthanide series.

Simple calculations will show (again making the necessary assumption that the rare earths all exist in solution as the same ionic species) that the ratio of solubility product constants will be the same as the ratio of the solubilities of the metal ions. These ratios will be a measure of the attractive force of the ion concerned for hydroxyl groups and thus a measure of basicity. Such determinations, of course, must be made in solutions of the same pH to give proper correlations.

C. Solubility Product in Buffered Solutions

Endres[12] determined the solubility product constants

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[11] Kolthoff and Elmquist, J. Am. Chem. Soc., 53, 1217 (1931).

[12] Endres, Z. anorg. allgem. Chem., 205, 321 (1932).

of lanthanum, praseodymium, neodymium, samarium, gadolinium, yttrium and dysprosium in ammonium hydroxide-ammonium nitrate-cadmium nitrate buffer solutions to maintain constant pH. From the data which he obtained, he established a relative scale of basicities, this scale being frequently quoted by other authors.[13,14,15] These relative values are given in Table III along with a second series of values determined by Moeller and Kremers[16] in later work on studies of the precipitation pH of the rare earths. With the exception of praseodymium, the two are in reasonable agreement.

TABLE III

RELATIVE BASICITY VALUES

Ratio of element referred to yttrium	Endres	Moeller and Kremers
Lanthanum	1300	1235
Cerium (III)		185
Praseodymium	80	335
Neodymium	47	23.5
Samarium	8	8.4
Europium		4.2
Gadolinium	3.4	2.6
Terbium		
Dysprosium	0.5	
Yttrium	1.0	1.0

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[13] Hopkins, J. Chem. Ed., 13, 363 (1936).
[14] Sherwood and Hopkins, J. Am. Chem. Soc., 55, 3117 (1933).
[15] Yost, Russell and Garner, *op. cit.*, p. 57.
[16] Moeller and Kremers, J. Phys. Chem., 48, 395 (1944).

However, in any such scale of basicities, it seems logical that the values of the ratios of any two elements will be a function of the particular ionic environment in which the determinations are made. The order of basicities should not be changed, but the magnitude of one compared to another might well be distorted in different solutions, as these solutions vary as to temperature, pH or oxidising power.

D. pH at Precipitation Incidence

Another method for measuring relative basicities is a determination of the exact pH at which a distinguishable precipitate of each specific rare earth formed and remained. While such determinations are closely related to the solubility product constant determinations mentioned before, they represent another technique of evaluating the extent of dissolution of any one ion and hence are a measure of the basicity of the various elements concerned.

Britton,[17] using a hydrogen electrode in solutions approximately 0.01 N in rare earth ions, added sodium hydroxide and observed a noticeable decrease of the pH at precipitation incidence in the series: lanthanum, cerium, praseodymium, neodymium, samarium and yttrium and thus was

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[17] Britton, J. Chem. Soc., 127, 2142 (1925).

However, [illegible] England that the [illegible] still be a [illegible] which the [illegible] point.

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Another method for [illegible]

[illegible][11] [illegible]

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11. [illegible]

able to state that the basicities decreased in this order.

Moeller and Kremers[18] made a rather thorough investigation of this method of establishing basicities by adding sodium hydroxide to solutions of rare earth nitrates, sulfates and acetates in approximately 0.1 M concentrations. While an observable decrease in precipitation pH was noted in every case, there were unique differences in the ratios of the precipitation pH's for any two elements. This would seem to further bear out the hypothesis that the ratios of basicities are largely dependent on the type of ionic environment utilized for the particular determination. Table IV lists the various values that these authors obtained.

TABLE IV

pH PRECIPITATION INCIDENCE

Element	At $OH^-/R = 0.4$		
	NO_3^-	$C_2H_3O_2^-$	$SO_4^=$
Lanthanum	8.23	8.13	7.78
Cerium	7.76	7.99	7.56
Praseodymium	7.67	7.96	7.50
Neodymium	7.40	7.65	7.23
Samarium	7.06	7.48	6.93
Europium	6.90	7.37	6.82
Gadolinium	6.94	7.31	6.95
Yttrium	6.90	7.15	6.90
Erbium	6.84	6.93	6.58
Thalium	6.70	6.77	6.38
Ytterbium	6.65	6.73	6.32
Lutecium	6.63	6.73	6.32

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[18] Moeller and Kremers, J. Phys. Chem., <u>48</u>, 395 (1944).

These authors found in all instances that precipitation was complete before the calculated amount of three moles hydroxide ion per mole of rare earth ion had been added. Such data are an excellent indication of the formation of basic salts which precipitate before the $R(OH)_3$. Whether or not there is an equilibrium between these basic salts and the hydroxide was not investigated. An empirical formula for the basic salt was not determined.

Once knowing these precipitation pH's, it is then possible to calculate the solubility product constant for all of the rare earths. These data are shown in Table V. The ratios of these solubility product constants are the ratios given earlier in Table III.

TABLE V

SOLUBILITY PRODUCT CONSTANTS

Element	$K_{sp.}$
Lanthanum	1.0×10^{-19}
Cerium	1.5×10^{-20}
Praseodymium	2.7×10^{-20}
Neodymium	1.0×10^{-21}
Samarium	6.8×10^{-22}
Europium	3.4×10^{-22}
Gadolinium	2.1×10^{-22}
Yttrium	8.1×10^{-23}
Erbium	1.3×10^{-23}
Thulium	3.3×10^{-24}
Ytterbium	2.9×10^{-24}
Lutecium	2.5×10^{-24}

Generally speaking, it can be seen that solubility

Three exceptions found in all tests were that precipitation was complete before the calculated amount of three moles [illegible] per mole of [illegible] had been added. [illegible] data are an excellent indication of the [illegible] of [illegible] when [illegible] precipitation [illegible]. Whether or not there is an equilibrium between these [illegible] salts and the [illegible] was not determined. An empirical formula for the black salt was not determined.

Generally speaking, where precipitation occurs, it is then possible to calculate the solubility product constants for all of the salts formed. These data are shown in Table V. The ratios of these solubility product constants are the ratios given earlier in Table III.

TABLE V

SOLUBILITY PRODUCT CONSTANTS

Element	Ksp
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

Generally speaking, it can be seen that solubility product constant measurements are a valuable indication of the relative positions of the basicities of the different rare earths; but, any finite ratios between these basicities will vary from solution to solution, depending on the particular situation encountered.

E. Degree of Hydrolysis

A fifth method of establishing relative basicities is to determine, by various means, the degree of hydrolysis of the different rare earths. Katz and James[19] have investigated the equation:

(R = any rare earth)

$$R_2(SO_4)_3 + 5\ KI + KIO_3 + 3\ H_2O \rightarrow 2\ R(OH)_3 + 3\ K_2SO_4 + 3\ I_2.$$

In this work, they allowed solutions of the various rare earth sulfates to approach equilibrium with the proper amounts of potassium iodide and potassium iodate and then titrated the liberated iodine with standard sodium thiosulfate. As predicted, they obtained increasing amounts of iodine in the series: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, erbium and ytterbium, thus indicating that these elements hydrolyzed

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[19] Katz and James, J. Am. Chem. Soc., <u>36</u>, 779 (1914).

product compared [illegible] give a valuable indication of the relative [illegible] of the [illegible] of the different rare earths [illegible] these [illegible] will [illegible] depending on the [illegible].

E. [illegible]

A fifth method of [illegible] is to [illegible] of the different rare earths. [illegible] have investigated the reaction:

(M = rare earth)

$$M_2(SO_4)_3 + 5\ KI + KIO_3 + 3\ H_2O \longrightarrow 2\ M(OH)_3 + 3\ K_2SO_4 + 3\ I_2$$

In this work, they allowed solutions of the rare earth sulfates to [illegible] amounts of potassium iodide and potassium iodate and [illegible] sulfates. As would be [illegible] of [illegible] in the [illegible] lanthanum, cerium, praseodymium, neodymium, samarium, [illegible] and [illegible] the [illegible].

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18. [illegible]

to an increasing degree with atomic number.

Brauner and coworkers[20,21,22] measured the effects of rare earth sulfate solutions upon the hydrolysis of methyl acetate and the inversion of sucrose, both reactions being acid-catalyzed. The results of these experiments showed that the rare earths group themselves into two rather well-defined series of basicities; namely, lanthanum, cerium, praseodymium, neodymium, samarium and gadolinium, terbium, erbium and ytterbium. From the hydrolysis of methyl acetate, the percentage hydrolysis of these rare earths were calculated to be: lanthanum, 0.48; cerium, 0.59; praseodymium, 1.59; neodymium, 1.80; samarium, 6.14; gadolinium, 0.90; and ytterbium, 2.57.

Sherwood[23] studied the hydrolysis of the rare earth nitrites in boiling solution. He used physical methods of analysis, i.e., adsorption spectra and magnetic susceptibilities and determined a general decrease in basicity with atomic number.

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[20] Brauner and Svagr, Collection Czechoslov. Chem. Commun., <u>4</u>, 49 (1932), as quoted by Moeller and Kremers, Chem. Rev., <u>37</u>, 97 (1945).

[21] Brauner and Svagr, Collection Czechoslov. Chem. Commun., <u>4</u>, 239 (1932), as quoted by Moeller and Kremers, <u>Ibid</u>.

[22] Brauner and Pavlicek, J. Chem. Soc., <u>81</u>, 1243 (1902).

[23] Sherwood and Hopkins, J. Am. Chem. Soc., <u>55</u>, 3117 (1933).

Hughes and Hopkins[24] extended this work utilizing arc spectra and magnetoöptic measurements. Through these latter, they postulated the position of promethium (then called illinium) and set up a scale of decreasing basicities as follows: lanthanum, praseodymium, neodymium, (illinium), yttrium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium.

Vesterberg[25,26] made a series of relative hydrolysis studies on scandium, yttrium and lanthanum. He measured the extent of hydrolysis of acetate solutions through the extraction of the liberated acetic acid with ether and titration, taking into account the partition coefficient of acetic acid between water and ether. Lanthanum acetate was found to be 0.315 per cent hydrolyzed in N/5 solution and 0.286 per cent hydrolyzed in N/10. Scandium and yttrium showed a degree of hydrolysis of 11.40 per cent and 0.71 per cent, respectively, in N/10 solutions of the acetate.

More rigorous determinations were made of the degree

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24. Hughes and Hopkins, J. Am. Chem. Soc., <u>55</u>, 3121 (1933).
25. Vesterberg, Z. anorg. allgem. Chem., <u>94</u>, 371 (1916).
26. Vesterberg, Z. anorg. allgem. Chem. <u>99</u>, 11 (1917).

of hydrolysis through conductivity measurements. If pure reagents are available, conductivity measurements are capable of yielding results of high accuracy.

Jones and coworkers[27,28] found that lanthanum chloride solutions were hydrolyzed to a very small degree as no hydrolysis corrections were necessary in their studies. Klotz[29] showed that europic chloride and nitrate solutions had the same conductivity as the lanthanum salt solutions (at equivalent concentrations) and if hydrolysis is ruled out in the one case, it must logically (from these data) be ruled out in the second.

One additional method of determining the extent of hydrolysis in aqueous media is a measurement of the hydrogen-ion concentration in aqueous solution. Meyer[30] reports the work of Bodländer who carried out a thorough series of studies in this respect. Neish and Burns[31] employed a

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[27] Jones and Bickford, J. Am. Chem. Soc., 56, 602 (1934).

[28] Jones and Pendergast, J. Am. Chem. Soc., 58 1476 (1936).

[29] Klotz, J. Chem. Phys., 6, 907 (1938).

[30] Meyer, Naturwissenschaften, 2, 781 (1914), as quoted by Moeller and Kremers, Chem. Rev., 37, 97 (1945).

[31] Neish and Burns, Can. Chem. Met., 5, 69 (1921), as quoted by Moeller and Kremers, Chem. Rev., 37, 97 (1945).

of hydrolysis through intramolecular mechanisms. [illegible] enzymes are available, consequently compounds which are capable of yielding reactive activated esters.

[illegible] and [illegible][57,58] have found that [illegible] molecule [illegible] from hydrolysis to a very small degree as an [illegible] [illegible] were [illegible] in their studies. [illegible][59] [illegible] that [illegible] [illegible] and [illegible] solutions and the same conductivity as the [illegible] solutions [illegible] and if hydrolysis is carried out in the [illegible], [illegible] [illegible] [illegible] and in the [illegible].

One additional method of activating the [illegible] hydrolysis in [illegible] is a [illegible] of the [illegible] [illegible] [illegible] [illegible][60] [illegible] the work of [illegible] and [illegible] studies in [illegible] and [illegible][61] [illegible] a

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57. [illegible], J. Am. Chem. Soc., [illegible] (1958).
58. [illegible], J. Am. Chem. Soc., [illegible] (1958).
59. [illegible], J. Am. Chem. Soc., [illegible] (1957).
60. [illegible] [illegible] (1958); see also [illegible] and [illegible], Chem. Ind., [illegible] (1958).
61. [illegible] and [illegible], J. Am. Chem. Soc., [illegible] (1958); [illegible] (1958).

hydrogen electrode to measure the same effect and their results, together with those of Meyer and Kleinheksel and Kremers[32] are given in Table VI. The data of Kleinheksel and Kremers are not in agreement with the other; however, these authors stated that they used anhydrous chlorides in preparing their solutions which may have had a contributing effect.

TABLE VI

pH VALUES IN AQUEOUS SOLUTION

Element	Chlorides[33]	Nitrates[34]	Chlorides[35]	
	N/10	N/100	N/10	N/100
	pH	pH	pH	pH
Scandium	3.05			
Yttrium	4.98		1.0	1.3
Lanthanum	5.49		3.7	5.0
Cerium	5.28	6.61	1.8	2.5
Praseodymium	5.37	5.68	3.1	4.5
Neodymium	5.31	4.24	2.5	3.2
Samarium	5.12	4.53	1.4	2.1
Gadolinium	5.21			
Dysprosium	4.91		5.8	6.8
Holmium				1.0
Erbium	4.81		1.1	1.7

It can be seen from a consideration of this table that such measurements are not too reliable for the determination of the degree of hydrolysis. In these experiments,

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[32] Kleinheksel and Kremers, J. Am. Chem. Soc., 50, 959 (1928).

[33] Meyer, *loc. cit.*

[34] Neish and Burns, *loc. cit.*, as quoted by Moeller and Kremers, Chem. Rev., 37, 97 (1945).

[35] Kleinheksel and Kremers, *loc. cit.*

especially those which give anomalous results from the predicted decrease of pH with atomic number, the purity of the rare earth compound must be questioned.

F. Ion-Exchange Methods

Perhaps the most reliable means of determining the relative basicities of the different rare earths is the known manner in which these ions are eluted from ion-exchange columns.[36] Furthermore, the radiochemical analyses of these elutants provide the most rigorous and most exact of any method developed for the rare earths. Long columns were filled with a synthetic organic resin, containing free sulfonic acid groups which exert a complexing action on the rare earth cations. A small volume of solution, containing a mixture of rare earths is added to the top of the column and elution is then begun with a solution of a second complexing agent, usually citric acid buffered with ammonium hydroxide. As this eluting solution flows through the column, a series of competing reactions is established among the various rare earth ions for the sulfonic acid groups on the resin and the citric acid molecules in the eluting solution.

Thus the least basic of the ions will exist largely

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[36] Tompkins, et. al., J. Am. Chem. Soc., <u>69</u>, 2769 (1947).

especially H-ag which gave anomalous results. For the predicted decrease of pH with chain length, the purity of the rare earth compound must be ascertained.

Ion-Exchange Methods

Perhaps the most reliable means of determining the relative basicities of the different rare earths is the displacement of rare earth ions from an organic cation-exchange column.[30] Furthermore, the radiochemical analyses of these elements [illegible] and most exact of any method developed for the rare earths. Long columns are filled with a cation-exchange resin, containing long molecule acid groups [illegible] A small volume of solution, containing a mixture of rare earths is added to the top of the column and adsorbed. In this region a solution of a complexing agent, usually of citric acid buffered with ammonium hydroxide, is allowed to flow through the column, a number of competitive reactions is established among the various rare earth ions for the sulfonic acid groups on the resin and the citrate ions dissolved in the eluting solution.

Thus the least basic of the ions will exist longer

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30. Tompkins, et. al., J. Am. Chem. Soc., 69, 2769 (1947).

as the citrate complex and will proceed rather rapidly through the column. The more basic elements have a slower reaction rate in the process of adsorption and desorption on the resin and so the various cations will spread themselves into bands, each proceeding through the column at a different rate.

By using tracer amounts of rare earth elements and analysing these various bands as they are eluted in turn from the column, very excellent separations have been obtained. The rare earths were taken from the columns in the reverse order of atomic number. Even samples of rare earth compounds previously stated to be spectroscopically pure proved resolvable into three or more components. Such experimental conditions as column length, flow rate, pH of complexing solution, resin size and concentration of citric acid solution were varied and the kinetics and equilibria of the various reactions were studied. In general, it was found desirable to have a reasonably small column diameter per fixed column length, slow flow rate, pH's of approximately 2.5-4.0, as small a resin size as possible without attaining the colloidal state and a citric acid concentration of about 5 per cent.

as the nitrate complex and will proceed rather rapidly through the column. The more basic elements have a stronger retention rate in the presence of [illegible] and thus on the resin, and as the [illegible] solution [illegible] moves into [illegible], gradually proceeding through the column at a different rate.

By taking repeated amounts of very small volume (1 ml.) and analyzing these various bands as they are eluted or come from the column, very complicated procedures have been obviated. The more basic ones are taken from the column in the reverse order of atomic numbers. When samples of rare earth compounds previously stated to be spectroscopically pure were passed separately into a resin column, [illegible] experimental conditions as column length, flow rate, pH of complexing solution, resin size and concentrations of nitric acid solution were varied and the kinetics and equilibria of the various reactions were studied. In general, it was found desirable to have a reasonably small column diameter per fixed column length, slow flow rate, pH's of approximately 0.5-1.0, as small a resin size as possible without shrinking the cellular flow and a nitric acid concentration of about 6 per cent.

G. Extent of Chelation

A method that seems to give reasonable correlations of basicities among the rare earths is the varying degree of chelation of the rare earth ions as a function of pH. This topic is discussed at length in the following section.

III. CHELATION, GENERAL DISCUSSION

The dependence of chelation of metal ions upon pH has been reported by a number of workers,[37,38,39,40,41,42] using diketones as the chelating agent. The use of a two-liquid phase system for the extraction of the metal chelate compound is common practice. Selection of the appropriate chelating agent is dependent upon a number of factors. Calvin[43] has summarized some of the desirable properties necessary for a good chelating agent. These properties include: (1) formation of un-ionized chelate compounds with high solubility in a water-immiscible organic phase and small solubility in water, (2) appreciable ionization and solubility of the chelating agent in the water phase.

Derivatives of acetylacetone in which one of the $-CH_3$ groups has been replaced by a $-CF_3$ group have been widely used as chelating agents. The $-CF_3$ group increases the acidity of the enol form. One of the most successful

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37. McBride, ORNL-303.
38. Broido, AECD-2616.
39. Bolomey and Wish, AECD-2665.
40. Huffman and Beaufait, AECD-2367.
41. Suttle, LADC-749.
42. Suttle, LADC-776.
43. Calvin, AECD-2710.

chelating agents is thenoyltrifluoroacetone[44] (referred to as TTA).

The overall equilibrium involved in the distribution of the metal ion between the aqueous phase and the organic phase (benzene) may be represented by the following equation:

$$M^{n}_{aq} + m\,HT_{bz} \rightleftharpoons MT_{m\,bz} + n\,H^{+}_{aq}$$

M^{n} = metal ion of valence "n"
HT = enol form of TTA
MT_{m} = metal chelate
aq = aqueous
bz = benzene

This equation is only an approximation and represents the resultant of several independent equilibria. It can be applied to praseodymium in the following manner:

$$Pr(OH)^{n}_{3-n} + m\,HT \longrightarrow PrT_{m} + n\,H^{+} + (3 - n)\,H_2O$$

The equilibrium expression for this reaction is:

$$K_{eq.} = \frac{\left[PrT_{m}\right]_{bz} \times \left[H^{+}\right]^{n}_{aq}}{\left[Pr(OH)^{n}_{3-n}\right]_{aq} \times \left[HT\right]^{m}_{bz}}$$

The distribution ratio, D. R., is equal to:

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[44] King and Reas, BC-69.

chelating agents is thenoyltrifluoroacetone[44] (referred to as TTA).

The overall equilibrium involved in the distribution of the metal ion between the aqueous phase and the organic phase (benzene) may be represented by the following equation:

$$M^{n+}_{aq} + n\,HT_{bz} \rightleftharpoons MT_{n\,bz} + n\,H^{+}_{aq}$$

M^{n+} = metal ion of valence n+
HT = enol form of TTA
MT_n = metal chelate
aq = aqueous
bz = benzene

This equation is only an approximation and represents the resultant of several independent equilibria. It can be applied to praseodymium in the following manner:

$$Pr(H_2O)^{n+}_{x\,aq} + n\,HT_{bz} \longrightarrow PrT_{n\,bz} + n\,H^{+}_{aq} + (x-n)\,H_2O$$

The equilibrium expression for this reaction is:

$$\frac{{}_{aq}\left[H^{+}\right]^{n} \times {}_{bz}\left[PrT_n\right]}{{}_{bz}\left[HT\right]^{n} \times {}_{aq}\left[Pr(H_2O)^{n+}_{x}\right]} = K_{eq}.$$

The distribution ratio, D, is equal to:

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[44] King and Reas, 51-60.

$$\frac{\left[PrT_n\right]_{bz}}{\left[Pr(OH)_{3-n}^{n}\right]_{aq}}$$

The distribution ratio can be evaluated by the use of Pr^{142} as a tracer and counting equal aliquots of each phase. King and Reas[45] have reported the thermodynamic acitivity coefficients for TTA. The activity coefficient for the metallic chelate in benzene is assumed to be equal to the known coefficient for the unchelated TTA. Kielland[46] lists the activity coefficients for praseodymium. Hydrogen-ion activity was determined directly as pH using a Model G Beckman pH Meter. The equilibrium concentration of the unchelated TTA was taken as the original concentration since a large excess was always present.

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[45] King and Reas, loc. cit.
[46] Kielland, J. Am. Chem. Soc., 59, 1675 (1937).

IV. EXPERIMENTAL OPERATIONS

The aqueous phase was prepared to contain 1 mg./ml. of praseodymium ion and ammonium chloride was added to give an ionic strength of 0.1. The benzene phase was either 0.2 molar or 0.5 molar in TTA, depending upon the series of runs being made. Praseodymium trichloride, supplied by the Fairmount Chemical Co., was used to make up the aqueous stock solutions. Neutron irradiation of this praseodymium indicated the presence of impurities, thus making this sample unsuitable for the tracer solution. Mandeville[47] states that only one 1.9 Mev gamma was emitted per 25 betas from this isotope. Consequently, traces of strong gamma-emitters (such as La^{140}) completely blocked out the Pr^{142} gamma and made it necessary to count betas. The author is indebted to R. P. Hammond of the Los Alamos Scientific Laboratory for a sample of very pure praseodymium oxide, containing less than 0.1 per cent of neodymium, lanthanum and cerium oxides. This pure compound was converted to the chloride and used only for tracer. The TTA was obtained from the Dow Chemical Company.

Samples of approximately 0.2 gram were irradiated. Because of the short half-life (19.3 hours), fresh samples were irradiated about twice a week. After irradiation,

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[47] Mandeville, Phys. Rev., 75, 1017 (1949).

the active sample was dissolved in 50 ml. water and one-half ml. of this solution was added to 100 ml. of 0.1 μ ionic strength stock solution. This gave a stock solution containing around 30,000-50,000 counts per 10 ml. sample used. The variation in counts was due to changes in the time of bombardment. It was assumed that the small amount of praseodymium added in the form of Pr^{142} would not affect the ionic strength.

The reaction vessel was made from 45 mm. glass tubing. A section about 20 mm. long was sealed at one end and the open end fused to a 24/40 condenser joint. A stirrer, fitted with a 24/40 bearing, was lowered into the vessel to provide constant agitation. The entire apparatus was placed in a constant temperature bath at a temperature of 25.1°. Photographs of these pieces of apparatus are shown in the appendix.

Fifty ml. of the TTA-benzene solution and 10 ml. of the 0.1 praseodymium trichloride solution were used in each run. Since, for the purposes of this experiment, it was desired to measure the amount of chelation as a function of pH, either dilute ammonium hydroxide or hydrochloric acid was added to vary the hydrogen-ion concentration. Very little acid or base was needed. One drop of 1N ammonium hydroxide was sufficient to vary the pH of the

the amino acids was [illegible] one-half ml. of this solution was added to [illegible] basic strength [illegible] containing about [illegible] used. The solution [illegible] tion of [illegible] of [illegible] the basic strength.

The reaction [illegible] A section about [illegible] open and [illegible] filled with [illegible] to provide [illegible] placed in a constant temperature bath [illegible] 25.1°. Photographs of [illegible] in the appendix.

Fifty ml. of [illegible] The 0.1 [illegible] each run. Since, for the [illegible] it was desired to [illegible] of pH, [illegible] acid was added to [illegible] very [illegible] ammonium hydroxide was [illegible] resulting solution by one unit or more.

After completion of a run, the contents of the reaction vessel were poured into a separatory funnel and aliquots of each phase were taken. The pH of the aqueous phase was taken immediately to minimize losses due to evaporation. After the pH determination, the praseodymium in the aqueous phase was precipitated by oxalic acid (at high pH values, praseodymium carrier was added). The precipitate was washed with water, then with acetone, these washings being discarded. Radiochemical analyses by Suttle[48] indicate that rare earth oxalates are insoluble in acetone. More acetone was added and the praseodymium oxalate was taken up as a slurry with micro-pipets made from 8 mm. glass tubing. This slurry was pipetted onto a 20 mm. filter paper held by a glass chimney-and-spring arrangement on a flat, fritted glass disc. The precipitate was allowed to settle before any suction was applied. Suction was continued for five or ten minutes after all the acetone had been removed in order to dry and shrink the precipitate. The sides of the chimney were washed with acetone to remove any traces of oxalate. The dry precipitate was mounted on a counting card with scotch tape. Counting rates were

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48. Suttle, Unpublished work (1950).

resulting solution by the acid or base.

After completion of a run, the contents of the reaction vessel were poured into a separatory funnel and aliquots of each phase were taken. The pH of the aqueous phase was taken immediately to minimize changes due to evaporation. After the pH determination, the protactinium in the aqueous phase was precipitated by oxalic acid (at high pH values, praseodymium carrier was added). The precipitate was washed with acetone, then with alcohol, the washings being discarded. Earlier work reported by [illegible][46] indicate that rare earth oxalates are insoluble in acetone. Then acetone was added and the precipitated oxalate was taken up as a slurry with a [illegible] pipet made from 8 mm. glass tubing. This slurry was pipetted onto a 20 cm. filter paper held by a glass chimney-and-spring arrangement on a flat, fritted glass disc. The precipitate was allowed to settle before any suction was applied. Suction was continued for five or ten minutes after all the acetone had been removed in order to dry and stabilize the precipitate. The sides of the chimney were washed with acetone to remove any traces of oxalate. The dry precipitate was mounted on a counting card with Scotch tape. Counting rates were

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[46] [illegible], Unpublished work (1950).

held within one per cent error.

The activity was removed from the benzene phase as follows: 5 ml. of the benzene phase was added to 20 ml. of saturated oxalic acid solution in a 50 ml. centrifuge tube. Inactive praseodymium carrier was added, until a slight precipitate formed. A high-speed stirrer was lowered into this mixture and it was stirred constantly for one hour. No attempt was made to fit the centrifuge tube with an airtight bearing as the benzene aliquot was discarded after extraction. This procedure was carried out directly in the centrifuge tube to reduce handling errors. After stirring for one hour, the benzene phase sample and the oxalic acid solution were centrifuged. Special care was taken to remove all oxalate from the interface of the two phases. After separation, the benzene was discarded and the precipitate was washed with water and acetone and treated in the same manner as the aqueous phase.

Several runs were made to determine the accountability of this method of extraction. In every case, a complete recovery of activity was obtained. No attempt was made to determine whether the extraction from the benzene phase was complete in less than one hour.

The two samples from any one run were always counted within a few minutes of one another to minimize the error due to decay. No adsorption corrections were made, since the beta associated with Pr^{142} has a maximum energy of 2.2 Mev.

V. DISCUSSION OF RESULTS

From an examination of the equilibrium equation for this reaction, it would seem that the hydrogen-ion concentration is "nth" power dependent. Rewriting the equilibrium expression in logarithmic form gives:

$$\log K_{eq.} = \log D.R. + n \log H^{+} - 3 \log HT$$

or:

$$\log D.\ R. = -n \log H + 3 \log HT + \log K_{eq.}$$

Therefore, a plot of log D. R. vs. -log H (or pH) should give a straight line whose slope, "n", represents both the average charge on the aqueous praseodymium species and the proper power for evaluating H in the equilibrium expression. Once the data were assembled, the value of "n" was calculated by the method of least squares, yielding values of 2.96 for the 0.5 M and 2.93 for the 0.2 M TTA. Since these were within experimental error of the limiting value of "3", $K_{eq.}$ was calculated, assuming that n = 3. These results are given in Table VII. The values marked with asterisks (*) indicate that this value was approached from the benzene phase. In these runs, all the activity was initially extracted into the benzene phase at a high pH, approximately 4.4-4.6. Following this, the phases were separated and the aqueous phase discarded. A solution

[illegible]

Without consideration of the mechanism of reaction for this reaction, it would appear that the hydrogen ion concentration is the [illegible] determining factor. [illegible] the equilibrium expression in logarithmic form gives

$$\log K_{eq.} = \log [illegible] + n \log H^+ - [illegible] \log M$$

or

$$\log [illegible] = [illegible] + [illegible] + \log K_{eq.}$$

Therefore, a plot of log [illegible] vs. log H for pH should give a straight line whose slope, [illegible] with the exponent of the hydrogen ion [illegible], [illegible] the proper power for [illegible] in the equilibrium expression. From the data here plotted, the value of "n" was calculated by the method of least squares, giving values of 0.98 for the [illegible] and [illegible] for the [illegible]. Since these were within experimental error of the limiting value of [illegible], [illegible] was calculated, assuming n = 1. These results are given in Table [illegible]. The values [illegible] with calculated [illegible] indicate that this value was approached from the reverse [illegible]. In these [illegible], [illegible] the solution was initially saturated [illegible] at a pH = [illegible], approximately [illegible]. [illegible], the phases were separated and the [illegible] phase [illegible].

containing only the proper amount of ammonium chloride was added to the reaction vessel and the contents were again allowed to approach equilibrium.

TABLE VII

EQUILIBRIUM CONSTANTS IN 0.2 M AND 0.5 M TTA

0.2 M TTA			0.5 M TTA		
pH	D.R.	K x 10^9	pH	D.R.	K x 10^9
3.00	0.0183	3.26	2.85	0.0934	3.82
3.10	0.0406	3.77	2.90	0.139	4.02
3.20	0.0771	3.43	3.00	0.266	3.86
3.25	0.100	3.15	3.10	0.464	3.37
3.30	0.204	4.55	3.18	0.720	3.03
3.34	0.235	3.98	3.20	0.856	3.12
3.36	0.259	3.82	3.30	1.34	2.45
3.46	0.436	3.22	3.38	2.79	2.94
3.50	0.529	2.96	3.41	3.11	2.66
3.60	1.01	2.84	3.46*	5.71	3.46
3.68*	2.04	3.30	3.55	11.5	3.74
3.71	2.48	3.26	3.59*	19.8	4.89
3.80	5.37	3.79	3.68	25.3	3.08
3.86	6.46	3.01	3.89	96.1	2.99
3.90	6.70	2.37	3.92	134.	3.38
3.96*	13.2	3.09			
4.09*	36.6	3.49			
4.18	61.1	3.13			
4.21	72.9	3.03			
Average = 3.34 ± 0.23			Average = 3.39 ± 0.37		

The results of these runs agree well with those obtained by introduction of the activity in the aqueous phase.

The data are shown in graphical form on the sheets in the appendix. The straight lines through the points are the calculated slopes of 2.93 and 2.96. A second graph

shows, in addition to the 0.2 M TTA and praseodymium, the data obtained by Suttle[49,50] for lanthanum and cerium in 0.2 M TTA. From a consideration of this second plot, it should be possible to separate lanthanum (or cerium) from praseodymium by this method. Preliminary investigations[51] have shown that this separation does proceed and the method will be developed in the near future. A lack of sufficient lanthanum activity prevented extensive examination of this separation at the present time.

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[49] Suttle, LADC-749.
[50] Suttle, LADC-776.
[51] Suttle and Keenan, Unpublished work (1950).

atoms, in addition to the [illegible] and ground states, the data obtained by [illegible] for [illegible] and [illegible]. [illegible] should be possible to [illegible] [illegible] been [illegible] method will be [illegible] [illegible] of [illegible] of the [illegible].

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49. [illegible]
50. [illegible]
51. [illegible] and [illegible], [illegible]

VI. SUMMARY

The slopes obtained by Suttle[52,53] (2.85 for lanthanum and 2.35 for cerium) do not agree with the slope calculated for praseodymium. The increasing basicity of the rare earths indicate that this slope, "n", should decrease with increasing atomic number. Possible complicating effects arising from the hydrolytic reactions of TTA may explain this. Certain contradictory evidence has been reported in the literature[54,55,56,57,58,59] regarding the hydrolysis of rare earth ions in aqueous solution. Such results indicate the need of extensive examination of this degree of hydrolysis from the standpoint of the particular anion and ionic environment involved.

The values of $K_{eq.}$ obtained for lanthanum and praseodymium do bear out this increasing basicity. Suttle[60]

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[52] Suttle, LADC-749.
[53] Suttle, LADC-776.
[54] Brauner and Svagr, Collection Czechoslov. Chem. Commun. 4, 49 (1932), as quoted by Moeller and Kremers, Chem. Rev. 37, 97 (1945).
[55] Brauner and Svagr, Collection Czechoslov. Chem. Commun. 4, 239 (1932), as quoted by Moeller and Kremers, *ibid.*
[56] Brauner and Pavlicek, *loc. cit.*
[57] Jones and Bickford, *loc. cit.*
[58] Jones and Pendergast, *loc. cit.*
[59] Klotz, *loc. cit.*
[60] Suttle, LADC-749.

DISCUSSION

The [illegible] obtained [illegible] lactone [illegible] oriented [illegible] the race so the [illegible] indicate [illegible] compound [illegible] has any [illegible] been reported in the literature [illegible] the individual [illegible] been [illegible] of this [illegible] particular [illegible]

The results of [illegible] obtained [illegible] procedure [illegible]

[illegible]

obtained a value of 1.6 x 10^{-10} for lanthanum in 0.2 M TTA. Thus the ratio of $K_{eq.}$'s for praseodymium/lanthanum is 20.8. This is in reasonable agreement with the value obtained by Endres[61] for the ratios of basicities of these elements.

A second graph indicates the percentage chelation as a function of pH. This shows clearly that the amount of chelation rises rapidly through a relatively narrow pH range.

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[61] Endres, loc. cit.

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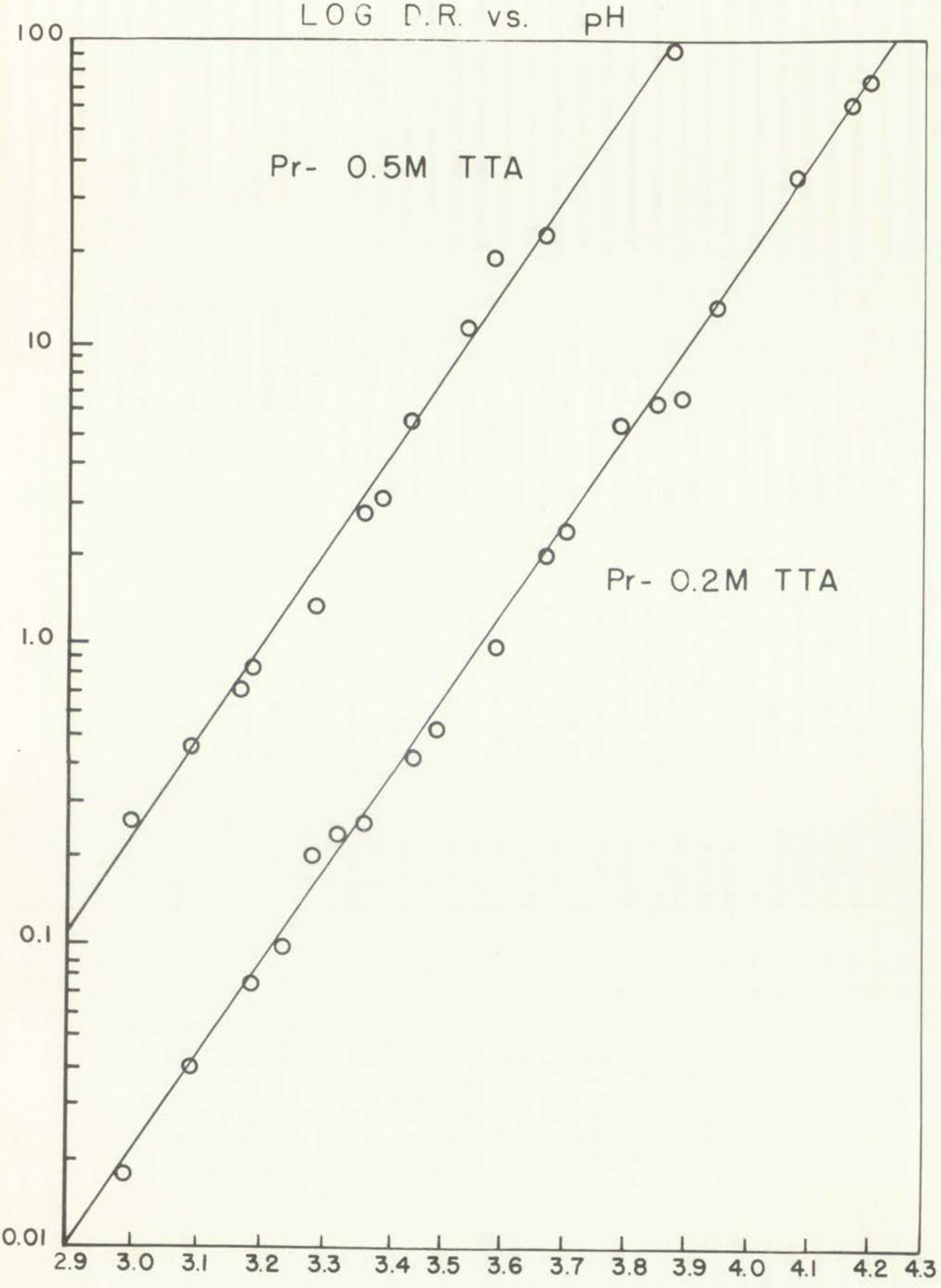
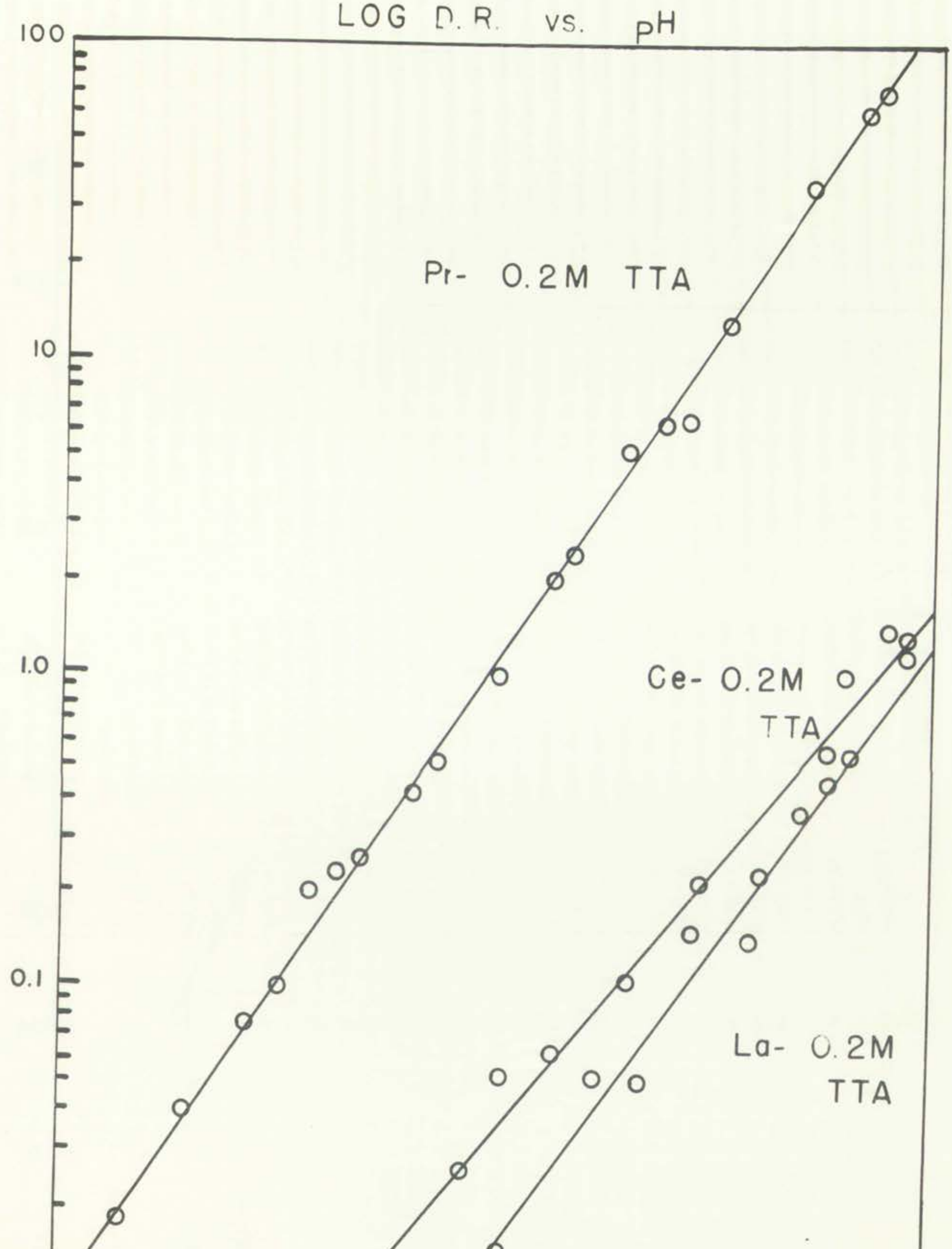
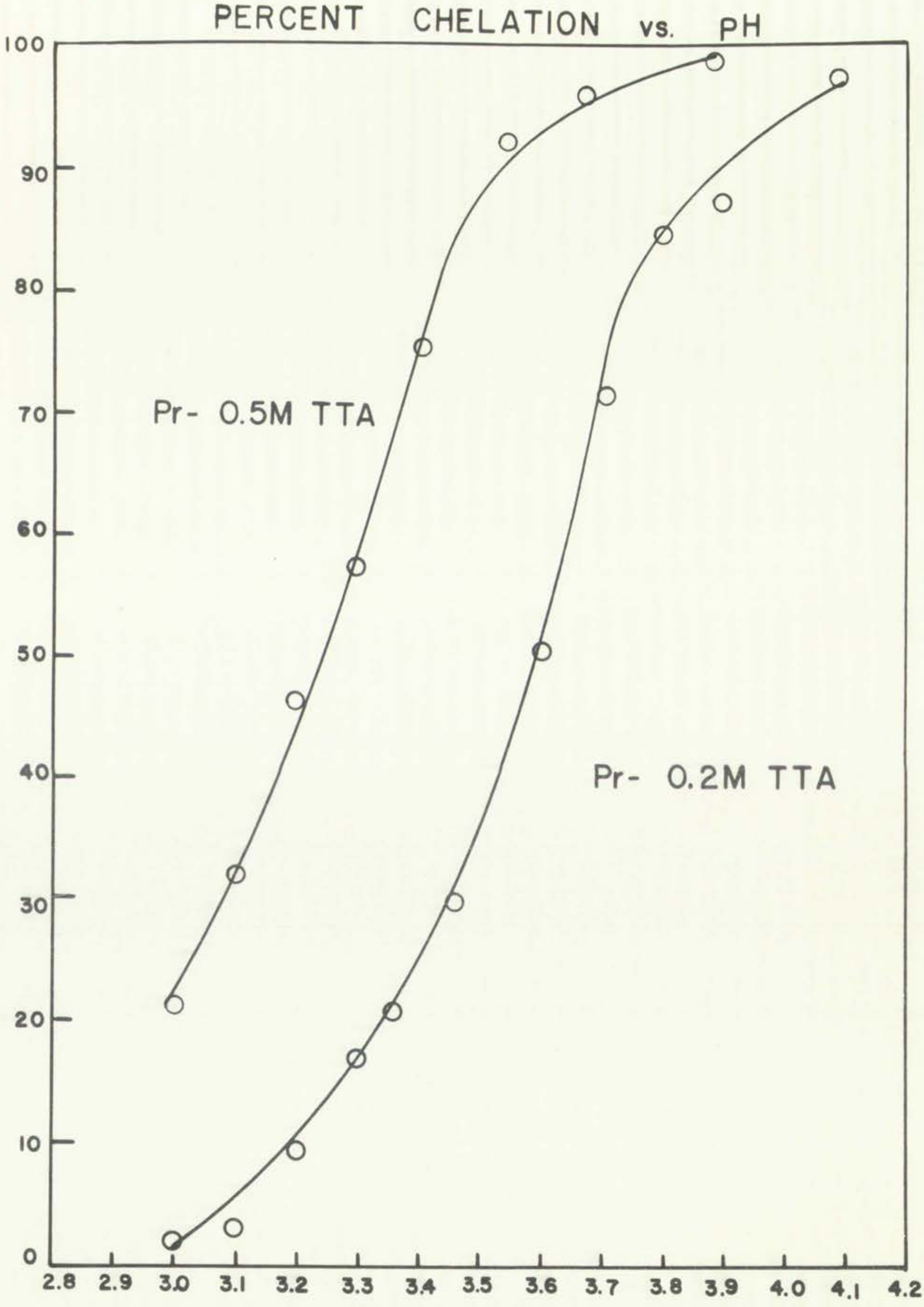
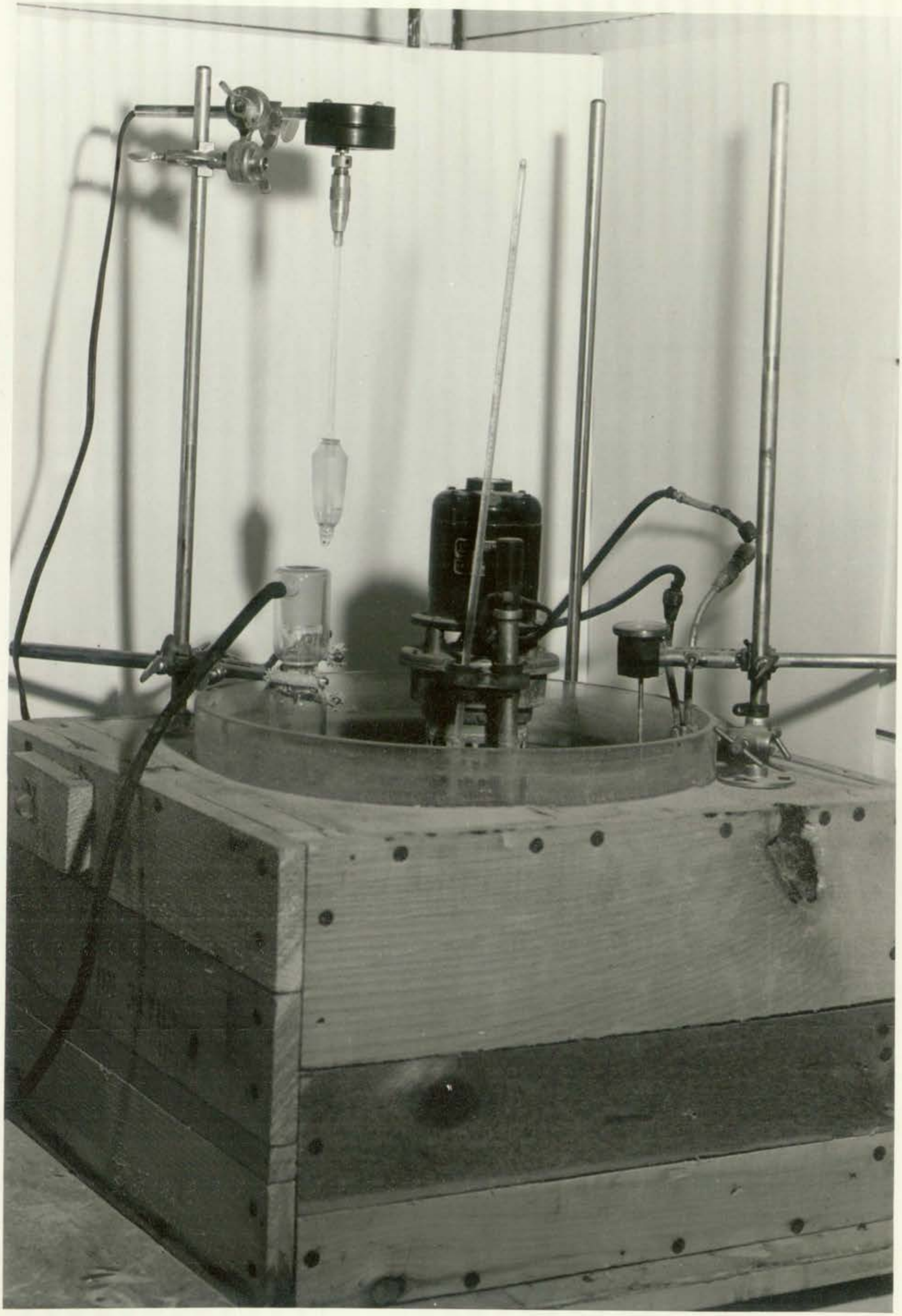
VIII. APPENDIX

LOG D.R. vs. pH
Pr- 0.5M TTA
Pr- 0.2M TTA
100
10
1.0
0.1
0.01
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3


LOG D.R. vs. pH
Pr- 0.2M TTA
Ce- 0.2M TTA
La- 0.2M TTA
100
10
1.0
0.1
0.01
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3


PERCENT CHELATION vs. PH
100
90
80
70
60
50
40
30
20
10
0
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
Pr- 0.5M TTA
Pr- 0.2M TTA



D.1.