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Chelation of the Rare Earth Elements as a Function of pH Using Thenoyltrifluoroacetone

Hugh James Bronaugh

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CHELATION OF THE RARE EARTH ELEMENTS
AS A FUNCTION OF pH USING
THENOYLTRIFLUOROACETONE

By
Hugh James Bronaugh

A Dissertation
In partial fulfillment of the
Requirements for the Degree of
Doctor of Philosophy in Chemistry

The University of New Mexico
1953

This dissertation, 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

DOCTOR OF PHILOSOPHY

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I. INTRODUCTION

The rare earth elements, or lanthanides, having atomic numbers 57 through 71 occupy only one space in the periodic chart of the elements. These fifteen elements, which have extraordinarily similar chemical and physical properties, are placed in group three of the periodic table, between barium of group two and hafnium of group four. This series of elements has been the subject of extensive study in the past. The development of atomic energy has significantly increased the interest in the rare earths in the past ten years.

The similarity in the properties of the lanthanides is due to the entry of electrons into the 4f shell, instead of the outer layers being built up as the atomic number increases. The addition of electrons at this depth has little effect on the chemical properties of the atom. As a consequence of the filling of the 4f shell as the atomic number increases from number 57 to number 71, the valence electrons remain in the same electron level and thus the force exerted on them by the nucleus becomes steadily larger. This increasing force exerted by the nucleus results in a steady decrease in the atomic volume of the rare earth elements as the atomic number increases. So great is the decrease in atomic volume that between dysprosium and holmium the value for the atomic volume of yttrium is attained, and the value for scandium lies beyond lutecium. Von Hevesy¹ studied this contraction extensively and from theoretical considerations predicted that the basicities of the rare earth elements

should decrease exactly as the atomic number increases, with yttrium falling close to holmium.

The term "basicity" has been used to describe a variety of phenomena concerning the chemistry of metallic elements and their compounds. Therefore a definition of the word as it applies to the chelation reaction follows. Any property that measures the tendency of an element to lose or gain electrons, in turn measures the basicity of that element. Thus the greater the tendency for an element to lose electrons the more basic is that element. However, in the experimental work to be presented the converse of the preceding statement is used. That is, once the electrons have been lost from an element, the less the tendency for the resulting cation to attract electrons or anions the more highly basic the material.

A review of all the existing work done on the basicity of the rare earths, up to the year 1945, has been published by Moeller and Kremers². Their survey reveals the following methods which were used to determine basicities:

1. Order of precipitation of the hydroxides.
2. Determination of solubility product constant.
3. Determination of precipitation pH.
4. Degree of hydrolysis.

Some of the methods used to study the basicities of the rare earths published after 1945 include; (1) ion-exchange methods and (2) extent-of-chelation. The ion-exchange methods³ have verified the older methods of determining basicities and the best order of decreasing basicity

determined so far for the rare earths is as follows: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu. Yttrium has been placed among the rare earth elements because it is always found as an impurity and because its atomic volume indicates this position. Basicity differences in the region of samarium to gadolinium and thulium to lutecium are comparatively small².

Since the experimental work to be presented is based upon the measurement of the basicities of the rare earth elements by the extent-of-chelation method, it seems advisable to discuss briefly some of the aspects of complex formation.

A. COMPLEX COMPOUNDS

Many compounds are known which are formed by the union, in stoichiometric ratio, of otherwise saturated molecules which are themselves capable of independent existence. As an illustration of the formation of such compounds, one molecule of ferrous cyanide can combine with four molecules of potassium cyanide to form stable potassium ferrocyanide, $K_4Fe(CN)_6$, which has properties that are entirely different from those of the constituent compounds and which in solution dissociates into potassium ions and ferrocyanide ions. Such compounds have been named coordination compounds. Attempts to write formulas for coordination compounds on the basis of the classical theory of valency fail completely if the usual valences of atoms are considered. Since two apparently saturated compounds can combine to form a third and completely different compound, it must be assumed that the reacting compounds must still possess additional combining capacity. In an attempt to explain this fact Werner⁴ introduced the concept of auxiliary or secondary valence. According to this theory, neutral molecules or oppositely charged ions are grouped or coordinated about a central ion in what is termed the first sphere of attraction or coordination sphere. The number of such groups which may be arranged about the central ion is equal to the coordination number of the central ion. This number is a function of the size of the central ion and the size of the attached groups. As a general rule the coordination number for the majority of the metals is six and in the case of the smaller non-metals such as

carbon, boron and nitrogen the number is four. Some complexes are known in which the central ion has a coordination number of two and eight. For example, $K_4 Mo(CN)_8$ and $K HF_2$. Neutral water molecules, chloride, bromide, cyanide, hydroxyl ions and ammonia molecules occupy only one coordination position each. On the other hand bivalent radicals such as oxalate, sulfate and carbonate may occupy one or two positions. The following structures are examples of two complexes of cobalt.

Compound (A), hexammine cobaltic chloride, has six molecules of ammonia around the central ion, which can be thought of as being in the first sphere of attraction, while the chlorine is held ionically. Compound (B), oxalato-tetrammine cobaltic chloride, shows an oxalate radical taking the positions which were formerly occupied by two ammonia molecules. Other bifunctional groups, such as ethylenediamine also tend to form cyclic structures, as in (B), through the coordination of each of the two amine groups about a central atom, thus:

(c)

Cyclic compounds, like that depicted in (C) have been named chelation compounds by Morgan and Drew⁵. The term chelation has been used to describe these types of ring systems, and since many organic molecules can be linked to a central atom through more than two groups, Morgan suggested that the words bidentate, tridentate and quadridentate be used to further describe the ring systems.

To summarize the above discussion the following may be stated. A complex, or coordination compound is formed when a metal ion combines with an electron donor. If a metal ion combines with a molecule that contains two or more donor groups so that one or more rings are formed utilizing a covalent link and a coordinate-covalent link the resulting compound is called a chelation compound or a metal chelate. A molecule containing two or more donor groups, capable of combining with a metal ion, is called a chelating agent. The only difference between a chelation compound and a complex compound lies in the formation of heterocyclic rings⁶.

Many compounds, such as trinitrato-triammine-cobalt, which contain equal numbers of coordinating groups and monovalent anions coordinated about a metal atom are non-electrolytes. If the coordinating group and

acidic radical are combined as parts of the same molecule, such as in an organic molecule, the resulting chelation compound formed is very stable, very slightly soluble in water and very soluble in organic solvents. Non-electrolytes of this type are called inner-complex salts. The terms inner-complex and chelation compounds are sometimes used interchangeably. This usage, however is erroneous since all chelation compounds do not possess the properties associated with inner-complex salts. Typical of the compounds containing groups capable of forming inner-complex salts and a chelate ring is glycine. An example of this type compound is shown in (D).

(D)

It would be advantageous to list some of the more important groups capable of salt formation. Groups which may unite with metals by the replacement of an hydrogen atom and thus using a primary valence are as follows according to decreasing activity: $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{OH}$, $-\text{N} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}$, and $\text{N} \begin{smallmatrix} \text{R} \\ \text{H} \end{smallmatrix}$. As secondary valence groups which combine with metals by simple coordination, the following groups are listed according to decreasing activity: $-\text{NH}_2$, $-\text{NH}$, $-\text{N}-$, $-\text{N}=\text{}$, $=\text{NOH}$, $=\text{O}$, and $-\text{S}-$.⁷

In addition to the character of the groups present in the chelating agent, chelation also depends to a large extent upon the positions these groups occupy in the molecule. In general, groups must be so located with respect to one another that the chelate ring which is formed will contain not less than three nor more than eight members. Most of the known rings usually contain four, five or six members. Some of the conditions necessary for the formation of a stable chelate are: (1) the ring that is formed must not be an excessively strained structure and (2) the ring formed must be planar or nearly so. The most stable ring structure will usually be one that is capable of resonance.

In summarizing some of the desirable properties necessary for a good chelating agent, Calvin⁸ has included the following: (1) formation of an un-ionized chelate compound with high solubility in a water immiscible organic phase and very low solubility in water, (2) appreciable ionization and solubility of the chelating agent in the water phase. Thus an inner-complex makes the best type of chelating agent.

II. THE CHELATION OF THE RARE EARTH ELEMENTS AS A FUNCTION OF pH USING THENOYLTRIFLUOROACETONE.

Thenoyltrifluoroacetone has been synthesized by Calvin and Reid⁹ by condensing ethyl trifluoroacetate with acetothienone. The behavior and properties of this chelating agent have been studied extensively by a number of workers^{10,11,12,13}. Thenoyltrifluoroacetone has the following structural formula and will be referred to as TTA.

This compound is a weak acid and has the following structure in the enol form:

The effect of the trifluoromethyl group is to increase the acidity of the enol form⁹. The use of TTA as a chelating agent to complex various cations has been reported by several workers.¹⁴⁻²² All of these researchers used a two-phase system, benzene-water, for the collection of data.

A study of the TTA molecule indicates that it possesses many of the characteristics that have been discussed as criteria for a good chelating agent. The active groups present in the enol form of TTA, and the position of these groups should result in the formation of a stable metal chelate. The replacement of the hydrogen atom of the hydroxyl group of the enol form of TTA by a metal ion and the combining of the carbonyl oxygen atom by a coordinate-covalent link with the metal ion, would result in a stable ring structure of six members with two double bonds. Thus:

The above metal chelate would possess the properties of an inner-complex salt, namely (1) very stable, (2) very slightly soluble in water, (3) very soluble in organic solvents, (4) a non-electrolyte.

Previous work has been reported on the chelation of the rare earth series of elements using TTA by Broido¹⁵, Suttle^{18,19}, Keenan²⁰ and Cornish²². The aim of the following experimental work has been to complete the chelation data of the rare earths and to utilize the complete data in an attempt to work out separation procedures for some of the rare earths.

The overall equilibrium involved in the distribution of a rare earth metal ion between the aqueous phase and the benzene solution of TTA can be represented by the following equation:

where:

M^{+3} = rare earth metal ion
 HT = the enol form of TTA
 MT_3 = The metal chelate
 Aq and Bz refer to the aqueous phase and benzene phase, respectively.

The above equilibrium equation is only an approximation which represents the sum of the following equilibria:

If equation (1) is to represent the chelation reaction of a rare earth metal ion with TTA then the following assumptions must be made: (1) formation of a water soluble metal chelate is negligible, (2) that MT_3 is the only important species in the benzene phase, and (3) that no side reactions take place that will decrease the +3 charge of the rare earth ion, such as: complexing by chloride ion or hydrolysis.¹⁷

With the above assumptions in mind an equilibrium constant (K_{eq}) can be written for equation (1).

$$K_{eq} = \frac{[MT_3]_{Bz} [H^+]_{Aq}^3}{[M^{+3}]_{Aq} [HT]_{Bz}^3} \quad (2)$$

Where the brackets indicate thermodynamic activities. Equation (2) can be rearranged to give:

$$\frac{[MT_3]_{Bz}}{[M^{+3}]_{Aq}} = K_{eq} \frac{[HT]_{Bz}^3}{[H^+]_{Aq}^3} \quad (3)$$

If

$$\frac{[MT_3]_{Bz}}{[M^{+3}]_{Aq}} = \text{D. R. (distribution ratio)}$$

then

$$\text{D. R.} = K_{eq} \frac{[HT]_{Bz}^3}{[H^+]_{Aq}^3} \quad (4)$$

Equation (4) shows that the distribution ratio at a given pH increases as the third power of the TTA concentration, and that with constant TTA concentration the D. R. decreases as the third power of the hydrogen ion concentration in the water phase. Therefore, the chelation of a rare earth metal ion will increase as the pH and the concentration of TTA increases.

From the previous discussion of the basicities of the rare earth elements it can be said that the tendency for the rare earths to form a metal chelate with TTA will increase as the atomic number increases, at a constant pH.

Equation (4) can be rearranged as follows:

$$\log D. R. = \log K_{eq} - 3 \log [H^+] + 3 \log [HT] \quad (5)$$

From equation (5) it can be seen that if the concentration of TTA is held constant then a plot of $\log D. R.$ versus pH will give a straight line with a positive slope of three, with the y-intercept equal to $\log K_{eq} + 3 \log HT$. The experimental data will be represented by such a graph.

A. EXPERIMENTAL

The distribution ratio, $\frac{(MT_3)_{Bz}}{(M^{+3})_{Aq}}$, was evaluated by using a

radioactive tracer of the element under investigation, and counting the activity found in equal aliquots from each phase at the end of the reaction.

PREPARATION OF ACTIVE SAMPLES AND COUNTING TECHNIQUES

A weighed amount (about 0.2 g.) of the rare earth compound was placed in a quartz tube for neutron irradiation. After irradiation the sample was dissolved in a calculated amount of hydrochloric acid and enough potassium chloride solution added to give an ionic strength of 0.1 at the final dilution, which contained 1 milligram of M^{+3} per ml.

One ml. of this stock solution was then pipetted into the reaction vessel, 5 ml. of benzene-TTA solution added and the reaction vessel shaken until equilibrium was reached. The reaction mixture was then centrifuged to separate the two phases. The water phase was removed using a disposable pipette made by pulling down 8 mm. tubing. A sample of the water phase, usually 5 or 10 λ (0.005 or 0.010 ml.), was then transferred to the center of a tantalum disc (31 mm. dia.), the pipette rinsed with 1N nitric acid, and this rinse solution added to the tantalum disc. To keep this solution from spreading across the disc, a circle of Zapon (*) varnish was painted on the disc having a diameter of about 7 mm. After the sample and rinse acid had been added to the tantalum disc within the Zapon circle, a drop of 10% insulin-water solution was added to spread the sample completely over the area inclosed by the Zapon circle. The sample was evaporated to dryness under a heat lamp and then fired in an induction furnace until the edge of the tantalum disc turned red. The sample of the water phase was then ready for counting. It was found that the above mounting procedure gave reproducible counting results. A sample of the benzene phase could not be mounted directly in the above manner, because the benzene would spread past the Zapon ring. In order to get a count of the benzene phase, 1 ml. of this phase was extracted with 1 ml. of 6N hydrochloric acid then an aliquot of the 6N hydrochloric acid phase, equal in volume to that taken from the aqueous phase of the reaction mixture, was removed and mounted in the same manner as described above. This method of sampling and mounting

(*) Made by Zapon Division of Atlas Powder Company, Stamford, Conn.

the benzene phase gave reproducible counting results. For counting the mounted samples, a constant-flow methane proportional counter, operating at one atmosphere of pressure and 4,000 volts, (window thickness, ca. 2 mg./cm.²), was employed. Whenever possible, the volume of the samples taken from each phase was so adjusted as to give a counting rate in the vicinity of 5,000 c/m at a distribution ratio of about one.

PREPARATION OF TTA SOLUTIONS

Weighed amounts of TTA, (Dow Chemical Company), were dissolved in thiophene-free benzene (Mallinckrodt) to make the necessary concentrations. No further purification of the TTA or the benzene was made.

pH MEASUREMENTS

A standard Model-G Beckman pH meter was used to determine the hydrogen ion concentration of the aqueous phase. The pH meter was standardized, using a Beckman buffer solution, at a pH of four.

APPARATUS AND PROCEDURE

The reaction vessels were made of 18 mm. pyrex tubing, 10 cm. long, with a test tube end at the bottom and a 12/18 ground glass joint fused to the top. One ml. of the aqueous phase, containing 1 milligram of the rare earth ion under investigation together with its radioactive tracer was transferred to the reaction vessel. Then 5 ml. of the

benzene-TTA solution was added. In order to increase the pH of the successive runs, 5 λ (0.005 ml.) of potassium hydroxide of the appropriate molarity was spotted on the inside of the vessels above the two phases. The potassium hydroxide was added in this way in order to minimize the local precipitation of rare earth hydroxide. The reaction vessel was then closed with a ground glass stopper and agitated for fifteen minutes in a mechanical shaker, which was inclosed in a constant temperature air bath ($25^{\circ} \pm 0.3^{\circ} \text{C.}$). This mechanical shaker could accommodate five reaction vessels at one time. Preliminary experiments showed that equilibrium was reached in less than five minutes. After the shaking was completed, the reaction vessels were removed from the constant temperature bath, samples of each phase taken for counting and the pH of the aqueous phase determined as described previously.

Table I gives data concerning the rare earths used in this work, together with the radioactive isotopes used as tracers. Table II shows the experimental data obtained and the K_{eq} values calculated from these data according to equation (2). The thermodynamic activity coefficients for TTA have been reported by King and Reas¹⁰. The activity coefficient for the metal chelate in the benzene phase has been assumed to be equal to the known coefficient for the unchelated TTA. Kielland²³ lists the activity coefficient for lanthanum, cerium, praseodymium, neodymium, samarium and yttrium. It is assumed that the activity coefficient of the rest of the rare earths is the same value as that listed for the above named ones. The equilibrium concentration of the unchelated TTA was assumed to be the same as the original concentration since a large excess was always present.

TABLE I

Compound Irradiated	Source	Tracer	Determined Half life	Reported Half life	Spectrographic Data
La_2O_3	Lindsay-Light & Chem., Spec pure	La^{140}	41 h	40 h	
CeCl_3 (anhy.)	G. F. Smith	Ce^{141}	26 d	30 d	
Pr_6O_{11}	Iowa State College	Pr^{142}	19.4 h	19.3 h	$< 0.1\% \text{ Nd}_2\text{O}_3$ $< 0.1\% \text{ La}_2\text{O}_3$ $< 0.1\% \text{ Ce}_2\text{O}_3$
Nd_2O_3	Los Alamos Scient. Lab.	Nd^{147}	10.25 d	11.0 d	$\text{Pr} = 0.2\%$ $\text{Sm} = 0.1\%$
Pm (*) See end of table.		Pm^{149}	52 h	47 h	
Sm_2O_3	Research Chemicals Inc., Burbank Calif.	Sm^{153}	47 h	47 h	No other rare earths detected
Eu_2O_3	Johnson & Matthey Co.	Eu^{152}	10 h	9.2 h

TABLE I (CONTINUED - 2)

Compound Irradiated	Source	Tracer	Determined Half life	Reported Half life	Spectrographic Data
Gd_2O_3	Adam Hilger Ltd. Spectroscopically Standardized No. 11817	Gd^{159}	19 h	18 h	
Tb_4O_7	Johnson & Matthey Co., Lab No. 3755	Tb^{160}	66 d	77 d	Gd - all Sen Lines Yb - $\begin{bmatrix} 3987.994 \\ 3694.203 \\ 3289.37 \end{bmatrix}$ - F. Vis
Dy_2O_3	Johnson & Matthey Co., Lab. No. 3355	Dy^{165}	2.5 h	2.4 h	Dy - All Sen Lines V.F. Vis. Tb - all Sen Lines Ho - $\begin{bmatrix} 3891.02 \\ 3456.00 \end{bmatrix}$ - F. Vis. 3398.98 V. F. Vis
Y_2O_3	Johnson & Matthey Co.	Y^{90}	64 h	65 h	
Ho_2O_3	Johnson & Matthey Co., Lab. No. 2339	Ho^{166}	27 h	27.5 h	Dy - all prin. Lines Y - all prin. Lines

TABLE I (CONTINUED - 3)

Compound Irradiated	Source	Tracer	Determined Half life	Reported Half life	Spectrographic Data
Tm_2O_3	Johnson & Matthey Co., Lab. No. 2607	Tm^{170}	126 d	127 d	Yb - 3987.994 3694.203 - Strong 3289.37
					Lu - 2911.39 V. F. Vis.
					3397.07 3359.56 - B. Vis. 3077.60
Yb_2O_3	Johnson & Matthey Co., Lab No. 3754	Yb^{175}	99 h	99 h	Y - 4374.935 3710.290 - V. F. Vis
Lu_2O_3	Johnson & Matthey Co., Lab.No. 4055	Lu^{176}	7 h	3.7 h	Tm - All Sen. Lines Y - Sen. Lines F. Vis. Er - 3372.750 V. F. Vis.
					3906.316 - B. Vis. 3692.652
					Yb - 3987.994 3694.203 - V. F. Vis. 3289.37

TABLE I (CONTINUED - 4)

Compound Irradiated	Source	Tracer	Determined Half life	Reported Half life	Spectrographic Data
Sc_2O_3	Johnson & Matthey Co., Lab. No. 8941 Spec. Pure	Sc^{46}	85 d	85 d	

(*) Pm^{149} was obtained in the following manner:

Spec. Data: F = Faintly, V = Very, Vis. = visible, B = barely, S = strong

TABLE II

Chelation Data Using 0.20 M and 0.50 M TTA

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.20 M

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.50 M

Lanthanum

pH	D. R.	K_{eq}
3.80	0.0409	1.06×10^{-10}
3.88	0.0883	1.31
3.92	0.146	1.63
3.93	0.121	1.27
4.00	0.233	1.50
4.14	0.406	1.01
4.20	0.651	1.06
4.51	6.68	1.28

Average K_{eq} = $1.27 \pm 0.17 \times 10^{-10}$

Slope of Least Sq. plot = 2.95

pH	D. R.	K_{eq}
3.11	0.0111	2.55×10^{-10}
3.30	0.0503	3.09
3.40	0.0991	3.04
3.41	0.113	3.27
3.52	0.214	2.88
3.65	0.565	3.11
3.65	0.622	3.41
3.84	2.13	3.13

Average K_{eq} = $3.06 \pm 0.25 \times 10^{-10}$

Slope of Least Sq. plot = 3.09

Cerium

3.43	0.0597	1.98×10^{-9}
3.50	0.0741	1.53
3.55	0.0916	1.32
3.60	0.146	1.50
3.65	0.213	1.55
3.70	0.257	1.33
3.71	0.363	1.74
3.86	0.854	1.45
3.88	1.06	1.57

Average K_{eq} = $1.53 \pm 0.22 \times 10^{-9}$

Slope of Least Sq. plot = 2.83

2.99	0.0376	1.98×10^{-9}
3.04	0.0673	2.51
3.10	0.0744	1.83
3.19	0.122	1.60
3.20	0.188	2.32
3.30	0.274	1.68
3.40	0.643	1.98
3.60	2.46	1.91

Average K_{eq} = $1.98 \pm 0.26 \times 10^{-9}$

Slope of Least Sq. plot = 2.91

TABLE II (CONTINUED - 2)

Chelation Data Using 0.20 M and 0.50 M TTA

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.20 M

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.50 M

Praseodymium

pH	D. R.	K_{eq}
3.14	0.0297	7.30×10^{-9}
3.20	0.0332	5.40
3.30	0.0748	6.08
3.31	0.0742	5.63
3.34	0.107	6.56
3.41	0.148	5.70
3.49	0.271	5.97
3.60	0.452	4.64

Average K_{eq} = $5.91 \pm 0.75 \times 10^{-9}$

Slope of Least Sq. plot = 2.83

pH	D. R.	K_{eq}
2.65	0.0176	9.62×10^{-9}
2.83	0.0749	11.80
2.90	0.102	9.89
2.91	0.136	12.30
3.04	0.218	8.13
3.08	0.357	10.00
3.13	0.487	9.69

Average K_{eq} = $10.2 \pm 1.34 \times 10^{-9}$

Slope of Least Sq. plot = 2.85

Neodymium

3.11	0.0352	1.06×10^{-8}
3.21	0.0679	1.03
3.22	0.105	1.49
3.23	0.0865	1.14
3.31	0.145	1.10
3.36	0.208	1.12
3.50	0.476	0.967
3.66	1.36	0.922

Average K_{eq} = $1.10 \pm 0.17 \times 10^{-8}$

Slope of Least Sq. plot = 2.81

2.71	0.0557	2.01×10^{-8}
2.80	0.0876	1.70
2.82	0.113	1.90
2.86	0.142	1.82
2.90	0.195	1.90
2.96	0.264	1.70
3.10	0.686	1.68
3.21	1.41	1.61
3.22	1.46	1.56

Average K_{eq} = $1.76 \pm 0.17 \times 10^{-8}$

Slope of Least Sq. plot = 2.83

TABLE II (CONTINUED - 3)

Chelation Data Using 0.20 M and 0.50 M TTA

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.20 M

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.50 M

Promethium (* see end of table)

pH	D. R.	K_{eq}	pH	D. R.	K_{eq}
3.02	0.0815	4.58×10^{-8}	2.67	0.139	6.62×10^{-8}
3.09	0.132	4.59	2.72	0.180	6.09
3.18	0.214	3.98	2.77	0.230	5.50
3.19	0.168	2.92	2.80	0.295	5.70
3.21	0.249	3.77	2.84	0.377	5.58
3.30	0.402	3.27	2.91	0.545	4.92
3.33	0.481	3.17	3.02	0.991	4.21
3.48	1.05	2.48	3.09	1.353	3.56

Average K_{eq} = $3.60 \pm 0.69 \times 10^{-8}$

Slope of Least Sq. plot = 2.45

Average K_{eq} = $5.27 \pm 0.95 \times 10^{-8}$

Slope of Least Sq. plot = 2.39

Samarium

2.76	0.0271	9.21×10^{-8}	2.46	0.0593	12.1×10^{-8}
2.88	0.0552	8.19	2.52	0.0885	11.9
2.90	0.0732	9.44	2.53	0.102	12.9
3.00	0.150	9.67	2.56	0.114	11.7
3.18	0.399	7.44	2.60	0.171	13.2
3.20	0.655	10.20	2.63	0.201	12.5
3.24	0.605	7.46	2.76	0.547	14.0
			2.86	0.801	10.3

Average K_{eq} = $8.80 \pm 1.06 \times 10^{-8}$

Slope of Least Sq. plot = 2.93

Average K_{eq} = $12.2 \pm 1.0 \times 10^{-8}$

Slope of Least Sq. plot = 2.90

TABLE II (CONTINUED - 4)

Chelation Data Using 0.20 M and 0.50 M TTA

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.20 M

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.50 M

Europium

pH	D. R.	K_{eq}
2.73	0.0229	9.53×10^{-8}
2.87	0.0589	9.35
2.91	0.0878	10.5
2.95	0.113	10.3
3.01	0.170	10.3
3.15	0.386	8.89
3.32	1.04	7.39
3.37	1.44	7.24

Average K_{eq} = $9.19 \pm 1.18 \times 10^{-8}$

Slope of Least Sq. plot = 2.76

pH	D. R.	K_{eq}
2.45	0.0551	12.0×10^{-8}
2.50	0.0850	13.1
2.53	0.105	13.1
2.55	0.126	13.8
2.60	0.169	13.0
2.63	0.215	13.5
2.77	0.493	11.8
2.87	1.02	12.2
2.98	1.87	10.5

Average K_{eq} = 12.6×10^{-8}

Slope of Least Sq. plot = 2.85

Gadolinium

2.73	0.0259	1.08×10^{-7}
2.80	0.0423	1.08
2.86	0.0686	1.16
2.88	0.0886	1.32
2.98	0.135	1.01
3.00	0.197	1.27
3.15	0.491	1.14
3.30	1.38	1.13
3.38	1.78	0.826

Average K_{eq} = $1.11 \pm 0.17 \times 10^{-7}$

Slope of Least Sq. plot = 2.88

2.43	0.0583	1.46×10^{-7}
2.50	0.0918	1.41
2.51	0.107	1.54
2.55	0.141	1.54
2.60	0.192	1.49
2.66	0.282	1.44
2.79	0.667	1.38
2.93	1.74	1.37
3.00	2.70	1.31

Average K_{eq} = $1.42 \pm 0.22 \times 10^{-7}$

Slope of Least Sq. plot = 2.90

TABLE II (CONTINUED - 5)

Chelation Data Using 0.20 M and 0.50 M TTA

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.20 M

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.50 M

Terbium

pH	D. R.	K_{eq}
2.85	0.0744	1.35×10^{-7}
2.99	0.177	1.22

Average K_{eq} = 1.29×10^{-7}

Slope of Least Sq. plot = 2.57

pH	D. R.	K_{eq}
----	-------	----------

Dysprosium

2.59	0.0310	3.40×10^{-7}
2.68	0.0574	3.70
2.70	0.0798	4.09
2.74	0.0981	3.82
2.78	0.148	4.37
2.86	0.232	3.93
3.00	0.594	3.83
3.18	1.71	3.19

Average K_{eq} = $3.79 \pm 0.37 \times 10^{-7}$

Slope of Least Sq. plot = 2.94

2.34	0.0726	4.47×10^{-7}
2.40	0.105	4.28
2.41	0.129	4.91
2.45	0.163	4.70
2.50	0.234	4.77
2.54	0.329	5.10
2.70	0.908	4.66
2.98	4.85	3.63
3.00	5.995	3.87

Average K_{eq} = $4.50 \pm 0.44 \times 10^{-7}$

Slope of Least Sq. plot = 2.85

TABLE II (CONTINUED - 6)

Chelation Data Using 0.20 M and 0.50 M TTA

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.20 M

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.50 M

Yttrium

pH	D. R.	K_{eq}
2.60	0.0172	1.77×10^{-7}
2.70	0.0374	1.93
2.76	0.0458	1.55
2.80	0.0714	1.84
2.83	0.0943	1.97
2.83	0.0936	1.95
2.92	0.149	1.65
2.97	0.172	1.37
2.99	0.202	1.40

Average K_{eq} = $1.68 \pm 0.40 \times 10^{-7}$

Slope of Least Sq. plot = 2.69

pH	D. R.	K_{eq}
2.33	0.0420	2.11×10^{-7}
2.40	0.0674	2.09
2.48	0.112	2.00
2.50	0.137	2.11
2.56	0.258	2.65
2.59	0.231	1.93
2.61	0.328	2.38
2.70	0.631	2.46

Average K_{eq} = $2.22 \pm 0.19 \times 10^{-7}$

Slope of Least Sq. plot = 3.21

Holmium

2.63	0.0327	2.72×10^{-7}
2.79	0.0807	2.21
2.90	0.188	2.46
2.99	0.274	1.90
3.13	0.794	2.10

Average K_{eq} = $2.28 \pm 0.26 \times 10^{-7}$

Slope of Least Sq. plot = 2.75

TABLE II (CONTINUED - 7)

Chelation Data Using 0.20 M and 0.50 M TTA

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.20 M

Thulium

pH	D. R.	K_{eq}
2.51	0.0230	4.39×10^{-7}
2.66	0.0734	4.97
2.67	0.0655	4.14
2.79	0.154	4.22
2.80	0.205	5.27
3.10	1.38	4.49

Average K_{eq} = $4.58 \pm 0.40 \times 10^{-7}$

Slope of Least Sq. plot = 3.01

Ytterbium

2.49	0.0299	6.58×10^{-7}
2.61	0.0766	7.35
2.72	0.190	8.51
2.80	0.338	8.64
2.99	1.08	7.48

Average K_{eq} = $7.71 \pm 0.79 \times 10^{-7}$

Slope of Least Sq. plot = 3.13

TABLE II (CONTINUED - 8)

Chelation Data Using 0.20 M and 0.50 M TTA

Conc. of M^{+3} = 1.0 mg./ml.Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.20 M

Conc. of TTA = 0.50 M

Lutecium

pH	D. R.	K_{eq}	pH	D. R.	K_{eq}
2.32	0.0092	6.53×10^{-7}			
2.72	0.159	7.10			

Average K_{eq} = $6.82 \pm 0.14 \times 10^{-7}$

Slope of Least Sq. plot = 3.13

Scandium

0.97	0.844	0.664	0.92	7.79	0.657
1.00	1.02	0.658	0.97	10.2	0.609
1.02	1.34	0.755	1.00	11.5	0.560
1.10	1.96	0.637	1.02	14.4	0.609
1.11	2.30	0.697	1.05	17.1	0.648
1.14	2.97	0.729	1.09	20.4	0.536
1.15	2.69	0.619	1.13	25.0	0.497
1.19	3.99	0.697	1.19	28.3	0.372
1.21	4.80	0.729	1.20	34.6	0.429

Average K_{eq} = 0.687 ± 0.045 Average K_{eq} = 0.546 ± 0.095

Slope of Least Sq. plot = 3.02

Slope of Least Sq. plot = 2.24

(*) The data for promethium was obtained using tracer amounts of Pm^{149} and milligram amounts of neodymium carrier.

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DISCUSSION OF RESULTS

Figures 1 and 2 are plots of the D. R. versus pH at a TTA concentration of 0.20 M and 0.50 M, respectively. Both graphs indicate that the extent of chelation of the rare earth metal ions at a given pH tends to increase as the atomic number increases. The predicted order of decreasing basicity is proved by this data with the exception of the anomalous results of holmium. It will be noticed that the curve for holmium falls before dysprosium in Figure 1. The calculated half-life of the holmium isotope used as a tracer agrees very well with the reported half-life, however, the spectroscopic data for this element indicates the presence of yttrium. This apparent reversal of the order of basicity of holmium and dysprosium cannot be explained on the basis of the data presented here.

If the assumptions that have been made with regard to equation (1) are valid, then the slope of each curve in Figures 1 and 2 should be equal to three. The least squares method has been used to determine the best straight line through the data. Most of the calculated slopes fall considerably below the value of three. This difference is greater than the calculated error of the slope and is apparently not due to systematic errors. The low slope for promethium can be explained on the basis of the method used to obtain the active isotope (see footnote at end of Table I). In this instance, the contaminating activity of Nd^{147} must be assumed to be present. There could be several reasons suggested to explain the fact that the slopes of the curves

are smaller than expected, such as: hydrolysis of the M^{+3} at the higher values of pH and the complexing of M^{+3} with the chloride ion. These would have the effect of lowering the charge on the rare earth metal ion and thus decreasing the slope of the curve.

The differences in the basicities of the lighter rare earths, from lanthanum to samarium are quite large as shown in Figures 1 and 2. However, in the heavier elements the differences are much less pronounced. In the region, samarium to terbium, the differences in basicities are quite small, and in Figure 1, it will be noticed that the curves for thulium and lutecium coincide, which suggests that the basicities of these elements are equal.

A careful examination of Figures 1 and 2 reveals that the gap between any two curves in Figure 1 is greater than for the same two curves in Figure 2. The gap between the curves can be represented by

the ratio, $\frac{(D. R.)_{N+1}}{(D. R.)_N}$ (where N = atomic number of the rare earth

and the pH is held constant), which may be called the separation factor.

Thus the value of the separation factor between cerium and lanthanum,

$\frac{(D. R.)_{Ce}}{(D. R.)_{La}}$, is about 11 when using 0.20 M TTA and about 6.3 when

using 0.50 M TTA. On the basis of these results, the separation factor appeared to increase as the concentration of TTA decreased. In order to check this effect, chelation data for some of the rare earths were obtained using 0.50 M TTA and 0.10 M TTA. These data are recorded in Table III and plotted in Figures 3 and 4.

TABLE III

Chelation Data Using 0.050 M and 0.10 M TTA

Conc. of TTA = 0.050 M

Conc. of M^{+3} = 1.0 mg./ml.

Conc. of TTA = 0.10 M

Conc. of M^{+3} = 1.0 mg./ml.Lanthanum

pH	D. R.	K_{eq}
4.25	0.0238	1.51×10^{-10}
4.37	0.0476	1.31
4.42	0.0735	1.44
4.45	0.0975	1.55
4.53	0.171	1.56
4.60	0.268	1.51
4.61	0.265	1.40
4.70	0.474	1.34

Average K_{eq} = $1.45 \pm 0.14 \times 10^{-10}$

Slope of Least Sq. plot = 2.96

pH	D. R.	K_{eq}
4.02	0.0374	1.54×10^{-10}
4.14	0.125	2.26
4.23	0.199	1.94
4.30	0.348	1.04
4.42	0.655	1.72
4.52	1.10	1.43

Average K_{eq} = $1.66 \pm 0.36 \times 10^{-10}$

Slope of Least Sq. plot = 2.87

Cerium

3.78	0.00637	10.3×10^{-10}
4.10	0.0770	13.7
4.11	0.0598	9.96
4.25	0.141	8.93
4.30	0.178	7.97
4.30	0.188	8.43
4.39	0.302	7.26
4.41	0.395	8.26
4.45	0.371	5.88

Average K_{eq} = $0.897 \pm 0.207 \times 10^{-9}$

Slope of Least Sq. plot = 2.69

3.47	0.00568	1.06×10^{-9}
3.74	0.0613	1.75
3.79	0.0610	1.23
3.90	0.125	1.18
3.96	0.163	1.02
3.99	0.172	0.873
4.06	0.258	0.812
4.09	0.317	0.807

Average K_{eq} = $1.09 \pm 0.28 \times 10^{-9}$

Slope of Least Sq. plot = 2.75

TABLE III (CONTINUED - 2)

Chelation Data Using 0.050 M and 0.10 M TTA

Conc. of TTA = 0.050 M

Conc. of M^{+3} = 1.0 mg./ml.Praseodymium

pH	D. R.	K_{eq}
3.75	0.0135	2.70×10^{-9}
3.96	0.0558	2.61
3.97	0.0433	1.89
4.02	0.0733	2.26
4.10	0.134	2.39
4.13	0.194	2.81
4.15	0.205	2.58
4.24	0.327	2.21
4.30	0.508	2.27
4.51	1.71	1.79

Average K_{eq} = $2.45 \pm 0.30 \times 10^{-9}$

Slope of Least Sq. plot = 2.84

Samarium

3.31	0.00559	2.34×10^{-8}
3.60	0.0391	2.21
3.68	0.0694	2.46
3.75	0.105	2.10
3.80	0.138	1.95
3.90	0.266	1.88
3.97	0.378	1.65
4.00	0.598	2.12

Average K_{eq} = $2.09 \pm 0.22 \times 10^{-8}$

Slope of Least Sq. plot = 2.84

TABLE III (CONTINUED - 3)

Chelation Data Using 0.050 M and 0.10 M TTA

Conc. of TTA = 0.050 M

Conc. of M^{+3} = 1.0 mg./ml.Gadolinium

pH	D. R.	K_{eq}
3.22	0.00608	4.85×10^{-8}
3.50	0.0487	5.53
3.58	0.0638	4.15
3.68	0.124	4.00
3.74	0.204	4.36
3.76	0.197	3.68
3.87	0.292	2.54
3.91	0.512	3.38

Average K_{eq} = $4.06 \pm 0.60 \times 10^{-8}$

Slope of Least Sq. plot = 2.57

Chelation of Rare Earths with 0.05MTTA

Log. D. R. vrs pH

0

1

Fig. 3

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Table IV summarizes the effect of TTA concentration on the separation factor between four pairs of rare earths.

TABLE IV

Effect of TTA Concentration on the Separation Factor

Rare Earth pair	Separation factor, 0.5 M TTA	Separation factor, 0.2 M TTA	Separation factor, 0.1 M TTA	Separation factor, 0.05 M TTA
Ce-La	6.3	11	4.7	5.3
Gd-Sm	1.19	1.26		1.72
Sm-Pr	10.4	14.2		7.5
Y-Ce	110	67		

The above data do not indicate any specific trend with respect to the separation factor as the concentration of TTA is changed. It would appear that the optimum concentration of TTA for the separation of cerium from lanthanum would be 0.2 M. However, for separating gadolinium from samarium and yttrium from cerium and the optimum concentration of TTA appears to be, 0.050 M and 0.50 M, respectively.

All of the average K_{eq} values as calculated from equation (2), using various concentrations of TTA have been assembled in Table V. This table is arranged according to the decreasing basicities of the rare earths as found from the preceding data. Yttrium has been placed immediately following terbium as indicated by the K_{eq} values and Figures 1 and 2. The scarcity of data for the heavier rare earth elements is a result of the limited availability of pure samples. Only a few milligrams of the pure oxides of lutecium, thulium and terbium were obtainable. No data has been collected for erbium because a pure sample of this rare earth was not available.

TABLE V

Average K_{eq} Values As Calculated From Equation (2).

Element	0.5 M TTA	0.2 M TTA	0.1 M TTA	0.05 M TTA
La	$3.06 \pm 0.25 \times 10^{-10}$	$1.27 \pm 0.17 \times 10^{-10}$	$1.66 \pm 0.36 \times 10^{-10}$	$1.45 \pm 0.14 \times 10^{-10}$
Ce	$1.98 \pm 0.26 \times 10^{-9}$	$1.53 \pm 0.22 \times 10^{-9}$	$1.09 \pm 0.28 \times 10^{-9}$	$0.897 \pm 0.207 \times 10^{-9}$
Pr	$10.2 \pm 1.34 \times 10^{-9}$	$5.91 \pm 0.75 \times 10^{-9}$		$2.45 \pm 0.30 \times 10^{-9}$
Nd	$1.76 \pm 0.17 \times 10^{-8}$	$1.10 \pm 0.17 \times 10^{-8}$		
Pm	$5.27 \pm 0.95 \times 10^{-8}$	$3.60 \pm 0.69 \times 10^{-8}$		
Sm	$12.2 \pm 1.0 \times 10^{-8}$	$8.80 \pm 1.06 \times 10^{-8}$		$2.09 \pm 0.22 \times 10^{-8}$
Eu	12.6×10^{-8}	$9.19 \pm 1.18 \times 10^{-8}$		
Gd	$1.42 \pm 0.22 \times 10^{-7}$	$1.11 \pm 0.17 \times 10^{-7}$		$0.406 \pm 0.06 \times 10^{-7}$
Tb		1.29×10^{-7}		
Y	$2.22 \pm 0.19 \times 10^{-7}$	$1.68 \pm 0.40 \times 10^{-7}$		
Ho		$2.28 \pm 0.26 \times 10^{-7}$		
Dy	$4.50 \pm 0.44 \times 10^{-7}$	$3.79 \pm 0.37 \times 10^{-7}$		
Tm		$4.58 \pm 0.40 \times 10^{-7}$		
Yb		$7.71 \pm 0.79 \times 10^{-7}$		
Lu		$6.82 \pm 0.14 \times 10^{-7}$		
Sc	0.546 ± 0.095	0.687 ± 0.045

III. SEPARATION OF SOME OF THE RARE EARTHS USING A CHELATION METHOD

The over-all equilibrium involved in the distribution of a rare earth metal ion between the aqueous phase and a benzene solution of TTA has been shown in equation (1). From this equation, it can be seen that the distribution of the rare earth metal ion between the benzene phase and the water phase is dependent on the basicity of the metal ion and the pH of the aqueous solution. A study of the lanthanum and cerium curves in Figures 1, 2, 3, and 4 shows that at a constant pH the distribution ratio of cerium, $\frac{(CeT_3)_{Bz}}{(Ce^{+3})_{Aq}}$, is much greater than

that for lanthanum. Thus the concentration of cerium in the benzene phase is enriched and a separation of cerium from lanthanum can be effected.

Several types of continuous extraction apparatus were investigated, and a diagram of the design which proved to be the most satisfactory is shown in Figure 5.

The water phase containing the mixture of rare earths to be separated is put in the chelator, and the TTA-benzene solution is allowed to run into the chelator through the fritted glass disc at C, from the reservoir A. A turbo-stirrer assures intimate mixing of the two phases. At B, pH electrodes are inserted in the chelator. A phase separation is obtained in the right side of the chelator and the TTA-benzene solution containing the chelate complex passes out of the chelator through the upper stopcock and flows by gravity into Extractor #1 through the

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fritted glass disc at D. Extractors #1 and #2 contain 6N hydrochloric acid which is intimately mixed with the flowing benzene phase by vigorous stirring. The vessel labeled "wash" contains distilled water to wash the benzene phase free of any acid carried over from the extractors. After the benzene is washed it is returned to the reservoir, A, through the pump E.

As the reaction takes place in the chelator the pH of the water phase will decrease. Thus a method for keeping the pH of the water phase at some predetermined value must be employed. During the first attempt to separate cerium from lanthanum with the apparatus depicted in Figure 5, ammonia, diluted with nitrogen, was passed into the solution contained in the chelator in order to keep the pH constant. This method of pH control proved to be unsatisfactory. Therefore, it was decided to use a acetic acid-sodium acetate buffer as the water phase. Chelation data using the buffer as the water phase for cerium, lanthanum and yttrium is shown in Figure 6. These data are only qualitative since no attempt was made to keep the ionic strength of the water phase at a constant value. The total amount of cerium or lanthanum in the water phase was maintained at one milligram, however, the concentration of the water phase for the yttrium data varied from 0.5 to 1.5 milligrams of yttrium per ml. of the buffer solution. This probably accounts for the radically different slope of the yttrium curve. Even though this data is only qualitative, it makes possible an estimation of pH to be used to effect a separation of these rare earths.

Log. D.R. vrs. pH

Water Phase Buffered With HAc-NaAc

Y-0.2M TTA

Ce-0.2M TTA

La-0.2M TTA

Fig. 6

01 2.0 2.4 2.8 3.2 3.6 4.0 4.4 4.8

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END

A. SEPARATION OF CERIUM FROM LANTHANUM

Acetic acid-sodium acetate buffered solutions were prepared containing various amounts of cerium and lanthanum. A measured amount from these solutions was transferred to the chelator of the continuous extraction apparatus shown in Figure 5. The benzene solution of TTA was then allowed to flow into the chelator and the apparatus was put into operation. The data for the separations carried out are summarized in Table VI. The first column of Table VI shows the data for a cerium from lanthanum separation using ammonia gas diluted with nitrogen as a method of pH control.

TABLE VI

Results Of The Cerium-Lanthanum Separation

Unit of Apparatus (water phase analysis)	Run I, pH control by NH ₃ + N ₂		Run II, Buffered		Run III, Buffered		Run IV, Buffered	
	Ce	La	Ce	La	Ce	La	Ce	La
Present in chelator at start (mgs.)	14.5	12.43	11.1	12.33	11.6	6.38	10.6	21.3
Found in chelator at end of Run (mgs.)	1.1	3.43	2.4	7.25	5.2	5.32	5.8	16.5
Found in Extractor #1 at end of Run (mgs.)	10.2	6.63	7.4	4.00	4.7	0.75	2.6	3.13
Found in Extractor #2 at end of Run (mgs.)	2.2	1.30	0.7	0.40	1.3	0.23	1.4	1.03
Found in wash at end of Run (mgs.)	0.0	0.00	0.0	0.00	0.2	0.00	0.2	0.13
Found in final benzene phase	00	00	00	00	00	00	00	00
Total amount extracted (mgs.)	12.4	7.93	8.1	4.40	6.2	0.98	4.2	4.29
Percent extracted	85.5%	63.7%	73%	35.7%	53.5%	15.4%	39.6%	20.1%
Material Balance (percent error)	7.1%	8.6%	5.4%	5.5%	1.7%	1.3%	5.66%	2.4%

TABLE VI (CONTINUED - 2)

Results Of The Cerium-Lanthanum Separation

Unit of Apparatus (water phase analysis)	Run I, pH control by $\text{NH}_3 + \text{N}_2$		Run II, Buffered		Run III, Buffered		Run IV, Buffered	
	Ce	La	Ce	La	Ce	La	Ce	La
Volume of 0.20 M TTA- benzene solution used	300 ml.		300 ml.		400 ml.		400 ml.	
Length of Run	60 min		60 min.		40 min.		30 min.	
pH range	begin end		begin end		begin end		begin end	
	3.20 4.00		3.30 3.20		3.25 3.10		3.12 3.05

B. SEPARATION OF YTTRIUM FROM CERIUM

Table VII summarizes the data collected when using the continuous extraction apparatus to effect a separation of yttrium from cerium. In this separation the cerium was retained in the water phase of the chelator while the benzene phase was enriched with yttrium.

TABLE VII

Results Of The Yttrium-Cerium Separation

Unit of Apparatus (water phase analysis)	Run I, Buffered		Run II, Buffered	
	Y	Ce	Y	Ce
Present in chelator at start of Run (mgs.)	14.00	11.4	28.04	11.4
Found in chelator at end of Run (mgs.)	4.94	8.2*	8.23	8.9
Found in Extractor #1 at end of Run (mgs.)	7.60	2.4	16.58	3.2
Found in Extractor #2 at end of Run (mgs.)	1.78	0.8	3.09	0.8
Found in wash at end of Run (mgs.)	0.23	0.0	0.43	0.2
Found in final benzene phase	00	00	00	00
Total amount extracted (mgs.)	9.61	3.2	20.10	4.2
Percent extracted	68.6%	28.1%	71.7%	36.8%
Material Balance (percent error)	3.9%		1.0%	15%

TABLE VII (CONTINUED - 2)

Results Of The Yttrium-Cerium Separation

Unit of Apparatus
(water phase analysis)Volume of 0.20 M TTA-
benzene solution used

Length of Run

pH range

Run I,
Buffered

Y	Ce
---	----

400 ml.

30 min.

begin end

2.18 2.25

Run II,
Buffered

Y	Ce
---	----

400 ml.

30 min.

begin end

2.15 2.20

* Calculated by difference.

C. DISCUSSION OF RESULTS

The analytical data presented in Tables VI and VII were obtained in the following manner. Aliquots were removed from the water phase of each unit of the continuous extraction apparatus. The cerium present was determined by oxidizing the Ce^{+3} to Ce^{+4} with potassium persulfate, using a small amount of silver ion to act as a catalyst and then making a potentiometric titration with a microburet using ferrous sulfate. The analysis of the yttrium and lanthanum was obtained by using radioactive tracers. Aliquots from each unit of the apparatus were counted using a scintillation counter and these counts were then compared with a standard containing a known amount of yttrium or lanthanum carrier together with the proper isotopic radioactive tracer.

The data for Run I of the cerium-lanthanum separation (Table VI) show that an appreciable amount of lanthanum was extracted with the cerium. This is obviously the result of faulty pH control as it will be noticed that at the end of the Run the pH had reached a value of 4.00, due to the addition of an excess of ammonia. In Runs II, III and IV of the cerium-lanthanum separation the pH decreased slightly during the separation. This could be expected to happen if the amount of the buffer was not sufficient to hold the pH constant. However, in the two Runs of the yttrium-cerium separation the pH increased. Since the yttrium from cerium separation had to be carried out at a relatively low pH the ratio of acid to acetate was of necessity quite high. Apparently some of the acetic acid of the buffered solution was extracted into the benzene phase, thus decreasing the acid to acetate ratio and resulting in an increase in pH.

IV. SUMMARY AND CONCLUSIONS

Equilibrium constants for the chelation reaction of the rare earth metal ions with TTA, employing a two-phase system, have been determined. The equilibrium constants for scandium, yttrium and all the rare earths except erbium have been tabulated in Table V. These data verify the decreasing basicity of the elements of the rare earth series with the exception of anomolous results for holmium. The data collected show the extent of chelation of the rare earth metal ions, at a given pH, tends to increase as the atomic number increases. It has also been shown that the chelation increases as the concentration of TTA increases at a constant pH.

A method for the separation of the lighter rare earths from each other has been devised by utilizing the chelation reaction. A liquid-liquid continuous extraction apparatus was designed and used to make fractional separations of cerium from lanthanum and yttrium from cerium. The data in Tables VI and VII show that this method of separation is feasible. It is believed the efficiency of this apparatus can be increased by the following methods: (1) modification of Extractors #1 and #2 to increase the efficiency of stripping the rare earths from the benzene phase and (2) use of a buffered water phase in Extractors #1 and #2 in order to selectively strip out one rare earth from the benzene phase in greater quantities than the other which might be present. The apparatus was designed as a single-stage, batch-wise extractor. It is reasonable to assume that a better separation of the rare earths would

be possible if the apparatus were redesigned to include multi-stage, counter-current features. However with this type of equipment problems involving a concentration effect would undoubtedly be encountered. For instance, the data for the cerium-lanthanum separation (Table VI) indicates that the separation factor possibly changes when the concentration of cerium and lanthanum differ greatly. This effect would probably be more pronounced if the water phase contained micro amounts of cerium and macro amounts of lanthanum and should certainly be investigated further. Another factor, which might have an effect on the separation of any two rare earth ions, is the use of different solvents for the organic phase such as: toluene, chloroform or carbon tetrachloride.

The use of a buffered water phase as a method of pH control is certainly not limited to the acetic acid-sodium acetate system. A different buffer possibly would give a better separation. The data presented here show that the curves for the chelation reaction (Figures 1, 2, and 6) are shifted along the X-axis toward a lower pH as the anion is changed from chloride to acetate. Thus by using other buffer systems for the water phase, optimum conditions for a more efficient separation might be obtained.

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