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Some properties of rare earth-nitrilotriacetate complexes

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SOME PROPERTIES OF RARE EARTH-

NITRILOTRIACETATE COMPLEXES

by

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A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

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Iowa State University
Of Science and Technology
Ames, Iowa

1962

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INTRODUCTION

Strictly speaking, the rare-earth or lanthanide series is comprised of the group of inner-transition elements with atomic numbers 58 to 71, in which the shielded 4f orbitals are being filled. Elements 57, lanthanum ($5d^1 6s^2$), and 39, yttrium ($4d^1 5s^2$), although having no 4f electrons, are commonly considered to be rare earths because of their chemical similarity to the lanthanides. These elements occur in nature associated with the lanthanides, since they have essentially the same external electronic configuration and similar ionic radii. The similarities in chemical behavior are most marked in aqueous systems of their simple salts.

The rare earths, although relatively abundant in nautre, usually occur in low concentrations in ore bodies and are always associated with each other in their minerals. Due to the similarity of their chemical properties, isolation of individual rare earths by conventional wet methods is generally slow and difficult. Not until the discovery of the ion-exchange technique of separating the rare earths, have large quantities of individual rare earths (except lanthanum and cerium) been available for study.

In the ion-exchange method of separating macro-amounts of pure rare earths, separation is effected by passing a dilute solution of a chelating agent over a band of mixed rare-earth ions, sorbed on a cation-exchange column (1, 2).

The separation depends for the most part upon differences in the stability of complexes formed between individual rare-earth ions and the chelating anion used. Therefore, in any theoretical treatment of this method of separation, the stability constants of the metal-chelate complexes are an important factor. In the study of chelation, in general, thermodynamic data are necessary for a complete understanding of the processes involved. Measurements on a series of rare-earth complexes is also a good way of evaluating differences in properties of the individual rare-earth elements which are a reflection of the effect of underlying electronic levels (4f in the rare-earth case) on physical and chemical properties of the elements.

One of the many organic ligands that can be used for the above-mentioned separation is nitrilotriacetate (NTA). It was one of the first chelating agents used for the separation of rare earths by the ion-exchange method (3, 4, 5). However, this was not the first use for the reagent in rare-earth separations. Beck (6, 7, 8) worked out a procedure for separating some of the rare earths which involved fractional precipitation with NTA. A solution of the mixed rare earth-NTA complexes in the presence of an oxalate salt was made slightly alkaline and Ce(IV) was separated from the other rare earths by addition of hydrogen peroxide to the weakly alkaline solution. This resulted in the precipitation of the orange ceric peroxide hydrate. The solution was then carefully acidified

with acetic acid; whereupon, precipitation of the individual rare-earth oxalates occurred at the following pH values: La 6.0, Pr and Nd 5.5, Sm 5.0, Gd 4.5 and Er 4.0.

The first use of NTA as an eluant in the ion-exchange separation of the rare earths was made by Fitch and Russell (3). Although NTA does not readily promote complete separation throughout the entire rare-earth series, as will be shown later in this thesis in the section dealing with stability constants, this work led to the investigation of other amino-polycarboxylic acids as possible chelating agents for use in the ion-exchange process of separating rare earths. Partly as a result of these investigations, the current Ames Laboratory processes which employ ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) and N'-(hydroxyethyl)-ethylenediamine-N,N,N'-triacetic acid (HEDTA) were developed.

It is the object of this thesis to determine the stability constants and some thermodynamic data for the rare earth-NTA chelates. It is hoped that such information will lead to a better understanding of chelation and of the chemistry of the individual rare-earth elements.

A survey of the literature shows a conspicuous lack of information and data regarding solid metal-chelate compounds, especially those of the rare-earth metals. Therefore, some data on the solid rare earth-NTA chelates is included in this thesis. The research done on the solid compounds was intended

to be mainly a preliminary survey, and it is hoped that these preliminary investigations will stir up sufficient interest in the area to promote other investigations which will lead eventually to a complete understanding of these complex compounds.

STABILITY CONSTANTS AND THERMODYNAMIC DATA

Review

Various methods have been employed in the measurement of the stability constants of metal chelates. Several adequate summaries of these methods have appeared in the recent literature (9, 10, 11, 12), so only brief mention will be made of methods other than the polarographic determination used in this thesis.

Methods used in determining stability constants

Potentiometric (pH)

Method A   The stability constants of the alkaline earth-EDTA complexes were measured by Schwarzenbach et al. (13, 14) using a titration of EDTA with standard KOH in the presence of a 15-fold excess of the alkaline earth, the pH being measured with hydrogen and silver-silver chloride electrodes. The constants were calculated from the total EDTA concentration, the concentration of alkaline earth, the amount of base added and pH of the solution. This method is applicable to complexes of low to intermediate stability.

Method B   Schwarzenbach and co-workers (15, 16, 17) modified the above method so that the stability constants of very stable complexes could be measured. Two chelating agents were used which competed with each other in complexing one heavy metal ion. Then a second metal was introduced

which formed a very stable complex with one of the ligands, but no complex with the other. Wheelwright (10) used this method to measure the rare earth-EDTA and rare earth-HEDTA constants, using copper as the competing metal ion and β ,β' ,β'',-triaminotriethylamine (tren) as the second chelating agent.

Potentiometric (Redox)

<u>Method A</u>   The stability constants of iron(II)- and iron(III)-EDTA were measured by Schwarzenbach and Heller (18), using a gold electrode to follow the titration of iron(II) sulfate with iodine in the presence of excess EDTA. They also calculated constants for the various hydroxy complexes formed by the metal chelates.

<u>Method B</u>   Carini and Martell (19, 20, 21) devised a method for measuring the true thermodynamic equilibrium constants for the reaction of alkaline earth ions with EDTA. This was done by measuring the emf of the cell

$$Pt-H_2, \; K^{+(m_1)}, \; M^{+2}(m_2), \; Cl^{-(m_3)}, \; H_nY^{n-4}(m_4), \; AgCl-Ag,$$

at various temperatures and concentrations, with n varying from 0 to 2, Y being the EDTA anion.

<u>Spectrophotometric</u>   Kolthoff and Auerbach (22) measured the iron(III)-EDTA stability constants using spectrophotometric means. Due to the great stability of this complex, the measurements were made in 0.6 to 1.0 molar perchloric acid

to suppress the ionization of the protonated EDTA species, thus preventing all of the iron from being complexed. The concentration of the iron chelate was determined spectrophoto-metrically and the concentration of uncomplexed iron by dif-ference. The concentration of Ch^{-4} was calculated from the known total EDTA concentration, its four acid dissociation constants and the pH. The stability constant was finally cal-culated from the equation

$$K_{FeCh^-} = \frac{[FeCH^-]}{[Fe^{+3}][Ch^{-4}]} \quad .$$

Radiochemical   The Ni-EDTA stability constant was measured by the use of radioactive tracers by Cook and Long (23). Nickel(II) ions were added to a solution of radioactive Ni^{63}-EDTA, whereupon a slow exchange took place between the free Ni^{+2} ions and the complexed Ni^{63}. At timed intervals, aliquots were removed and the uncomplexed nickel was pre-cipitated as the hydroxide. The stability constant was cal-culated from the measured activity of the precipitate and the pH of the solution.

Ion exchange   The theory of the ion-exchange method of measuring stability constants was developed by Fronaeus (24, 25, 26). The method depends upon the fact that, in a system comprised of the metal ion to be measured, the chelat-ing agent and a cation-exchange resin, the quantity of the

metal ion bound to a definite amount of resin is proportional to the concentration of free metal ion in solution over a wide range. To calculate the constant, it is necessary to measure the exchange constant in the presence and in the absence of the chelating agent. This method works best for complexes of low stability.

Mercury electrode   Reilley and Schmid (27) applied the mercury-electrode method to measure some metal-EDTA stability constants. Schwarzenbach (28) then extended the theory to cover any chelating agent and showed that the formation constants of protonated and hydroxy substituted complexes could be determined, as well as the usual stability constant, by simultaneous measurement of the pH and the mercuric-ion concentration. In this method the concentration of mercuric-ion in equilibrium (a) is measured potentiometrically with the mercury electrode.

$$Hg^{+2} + H_n Ch^{n-a} \rightleftharpoons HgCh^{2-a} + nH^+ \ . \tag{a}$$
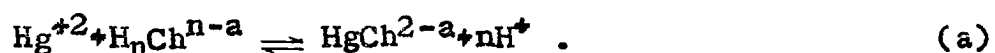
The mercury chelate stability constant is calculated from the measured mercuric-ion concentration and the acid dissociation constants of the ligand acid. Then, the concentration of mercuric ion in equilibrium (b) is measured with the mercury electrode,

$$M^{+m} + HgCh^{2-a} \rightleftharpoons MCh^{m-a} + Hg^{+2} \ . \tag{b}$$
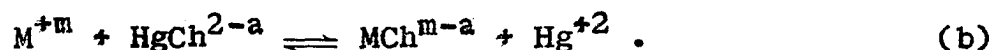
From the equilibrium constant for this reaction, K_b, and the mercury chelate stability constant, the constant of the metal chelate can be calculated.

Conductivity   Stability constants of uncharged complexes can be measured by conductance methods (29).

Distribution methods   Measuring the distribution of a metal ion between two immiscible solvents is, in effect, measuring the concentration of an uncharged complex in one solvent, thus allowing the calculation of the stability constant of the neutral complex (30, 31, 32, 33).

Polarographic

Method A   The half-wave potential of a metal ion is shifted when the ion is complexed by a chelating agent. The magnitude of the shift depends upon the logarithm of the stability constant of the chelated metal ion. Therefore, by measuring the half-wave potentials of the free metal ion and the complexed species, the stability constant can be calculated (10, 34). This method is applicable only if the electrode process is reversible.

Method B   In the case of non-reversible electrode processes, if the rate of formation and dissociation of the complex is sufficiently low that restoration of the disturbed equilibrium in the vicinity of the electrode does not proceed

at a sufficient rate to contribute to the wave height, the polarograph can be used to measure stability constants. In a solution containing free and complexed metal ions, each species is reduced at the dropping mercury electrode at a different potential. If the half-wave potentials for the individual reductions differ by 0.2 volts or more, the polarographic waves do not overlap and individual waves may be measured. The height of each wave, which is a measure of the diffusion current, is a direct measure of the concentration of the species in solution which is being reduced. Thus, the polarograph may be used as an analytical tool for the measurement of one or more species involved in the equilibrium

$$M^{+m} + NCh^{n-a} \rightleftharpoons MCh^{m-a} + N^{+n} \; .$$

This method has been used quite frequently in the past to measure stability constants (10, 11, 35, 36, 37, 38, 39, 40, 41, 42, 43), and is used in this thesis to measure the rare earth-NTA stability constants. A slight modification of the method was used to measure the second stability constants of the rare earth-NTA's, that is, the constants for the equilibrium

$$RNTA + NTA^{-3} \rightleftharpoons F(NTA)_2^{-3} \; .$$
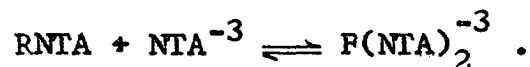
This will be described in the next section.

Experimental

Derivation of the experimental methods used to measure the stability constants

Acid dissociation constants of H₃NTA   From the reported pK values of H_3NTA (42), it can be seen that in solutions of pH greater than five the first two constants can be ignored. Therefore, only pK_3 was measured in the 10° to $40^\circ C$ range. For the equilibrium

$$HNTA^{-2} \rightleftharpoons NTA^{-3} + H^+ , \qquad\qquad 1$$

material balance equations can be written for the total amount of NTA and for the total amount of hydroxide added. These in turn are

$$[NTA]_T = [HNTA^{-2}] + [NTA^{-3}] \qquad\qquad 2$$

$$[NTA]_T = (\frac{[H^+]}{k_3} + 1) \, [NTA^{-3}] \qquad\qquad 2a$$

and

$$[OH]_T = [NTA^{-3}] + [OH^-] \qquad\qquad 3$$

$$(a-2)[NTA]_T - [OH^-] = [NTA^{-3}] \qquad\qquad 3a$$

where a is the number of moles of base added per mole of NTA present. Substituting 3a in 2a we find that

$$[NTA]_T = (\frac{[H^+]}{k_3} + 1) \, \left\{ (a-2)[NTA]_T - [OH^-] \right\} \qquad\qquad 4$$

from which

$$\frac{[H^+]}{k_3} = \frac{[NTA]_T}{(a-2)[NTA]_T - [OH^-]} - 1 \qquad\qquad 5$$

Therefore,

$$k_3 = \frac{\dfrac{[H^+]}{[NTA]_T}}{\dfrac{}{(a-2)[NTA]_T - [OH^-]} - 1} \qquad\qquad 6$$

By calling

$$\frac{[NTA]_T}{(a-2)[NTA]_T - [OH^-]} = \psi , \qquad\qquad 7$$

the final expression for k_3 can be written

$$k_3 = \frac{[H^+]}{\psi - 1} \qquad\qquad 8$$

The cadmium-NTA stability constant   Values reported in the literature for the $CdNTA^-$ stability constant at $20^\circ C$ (43) indicate that it is of the same order of magnitude as the first acid formation constant of NTA ($K_H = 1/k_3$). Therefore, when hydrogen ion competes with cadmium ion for the NTA anion, the $CdNTA^-$ constant can be calculated from a knowledge of the third acid dissociation constant of the ligand acid, the pH, and the concentration of Cd^{+2} determined polarographically. For the equilibrium

$$HNTA^{-2} + Cd^{+2} \rightleftharpoons CdNTA^- + H^+ \qquad\qquad 9$$

the exchange constant is defined as

$$K_{ex} = \frac{K_{CdNTA^-}}{K_H} = \frac{[CdNTA^-][H^+]}{[HNTA^{-2}][Cd^{+2}]} \qquad\qquad 10$$

Under proper conditions material balance equations for NTA and cadmium can be written as follows,

$$[NTA]_T = [CdNTA^-] + [HNTA^{-2}] \qquad\qquad 11$$

and

$$[Cd]_T = [CdNTA^-] + [Cd^{+2}] \ . \qquad\qquad 12$$

Combining 11 and 12 and solving for $[HNTA^{-2}]$ yields

$$[HNTA^{-2}] = [NTA]_T - [Cd]_T + [Cd^{+2}]. \qquad\qquad 13$$

If the original solutions are equimolar in NTA and $Cd(NO_3)_2$, then

$$[HNTA^{-2}] = [Cd^{+2}],$$

and the exchange constant is simply

$$K_{ex} = \frac{K_{CdNTA^-}}{K_H} = \frac{([Cd]_T - [Cd^{+2}])[H^+]}{[Cd^{+2}]^2} \qquad\qquad 14$$

from which

$$K_{CdNTA^-} = \frac{K_H([Cd]_T - [Cd^{+2}])[H^+]}{[Cd^{+2}]^2} \ . \qquad\qquad 15$$

The second rare earth-NTA stability constant, (i.e., K
for $RNTA + NTA^{-3} \rightleftharpoons R(NTA)_2^{-3}$ As was mentioned earlier, a
slight modification of the polarographic method was used to
evaluate the second formation constants. Instead of proceed-
ing as usual by allowing two metals to compete for a chelating
anion, this time the 1:1 chelate species was allowed to com-
pete against Cd for additional anion. The success of this
method depends upon the facts that the first rare earth-NTA
formation constant in each case is much stronger than the
second and that the CdNTA⁻ constant is similar in magnitude
to the second constant being measured.

In solutions, which are equimolar in R^{+3} and Cd^{+2} and having twice this concentration of NTA, the following equilibria take place with the respective constants:

$$R^{+3} + NTA^{-3} \rightleftharpoons RNTA \; ; \; K_1 = \frac{[RNTA]}{[R^{+3}][NTA^{-3}]} \qquad (I)$$

$$RNTA + NTA^{-3} \rightleftharpoons R(NTA)_2^{-3} \; ; \; K_2 = \frac{[R(NTA)_2^{-3}]}{[RNTA][NTA^{-3}]} \qquad (II)$$

$$Cd^{+2} + NTA^{-3} \rightleftharpoons CdNTA^- \; ; \; K_{Cd} = \frac{[CdNTA^-]}{[Cd^{+2}][NTA^{-3}]} \qquad (III) \qquad 16$$

$$H^+ + NTA^{-3} \rightleftharpoons HNTA^{-2} \; ; \; K_H = \frac{[HNTA^{-2}]}{[H^+][NTA^{-3}]} \qquad (IV)$$
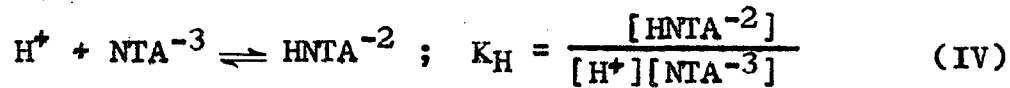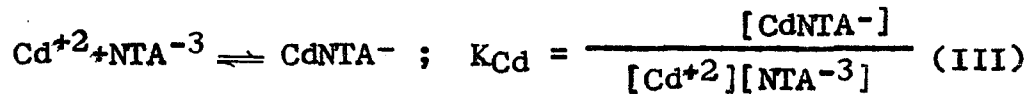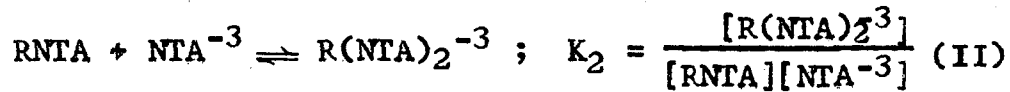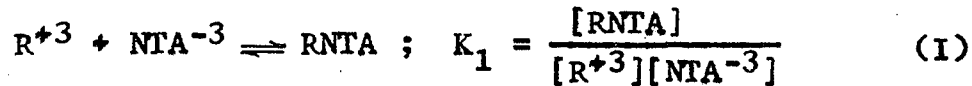
The first two acid dissociation constants have again been neglected. Material balance equations for total NTA, rare earth and cadmium may be written as follows:

$$[NTA]_T = [HNTA^{-2}] + [RNTA] + 2[R(NTA)_2^{-3}] + [CdNTA^-] \qquad 17$$

Substituting from equations 16 and factoring out $[NTA^{-3}]$ yields

$$[NTA]_T = \left\{ K_H[H^+] + K_1[R^{+3}] + 2K_1K_2[R^{+3}][NTA^{-3}] + K_{Cd}[Cd^{+2}] \right\}$$

$$[NTA^{-3}] \, . \qquad 17a$$

$$[R]_T = [RNTA] + [R(NTA)_2^{-3}], \qquad 18$$

assuming all the rare earth is complexed, which is quite reasonable considering the amount of NTA added and the strength of the 1:1 complex. Again substituting from equations 16

$$[R]_T = \left\{ 1 + K_2[NTA^{-3}] \right\} K_1[R^{+3}][NTA^{-3}] \qquad \text{18a}$$

and

$$[Cd]_T = [Cd^{+2}] + [CdNTA^{-}], \qquad \text{19}$$

the only cadmium complex formed being the 1:1 species (44).
Substitution from equations 16 leads to

$$[Cd]_T = \left\{ 1 + K_{Cd}[NTA^{-3}] \right\} [Cd^{+2}] . \qquad \text{19a}$$

Rearrangement of equation 19a yields

$$[NTA^{-3}] = \frac{[Cd]_T - [Cd^{+2}]}{K_{Cd}[Cd^{+2}]} . \qquad \text{20}$$

Solving equation 18a for $[R^{+3}]$ we obtain

$$[R^{+3}] = \frac{[R]_T}{K_1[NTA^{-3}] + K_1 K_2[NTA^{-3}]^2} . \qquad \text{18b}$$

Rearrangement of equation 17a, with subsequent substitution
of equation 18b yields

$$\frac{[NTA]_T}{[NTA^{-3}]} - K_H[H^+] - K_{Cd}[Cd^{+2}] = \frac{[R]_T\left\{ K_1 + 2K_1 K_2[NTA^{-3}] \right\}}{K_1[NTA^{-3}] + K_1 K_2[NTA^{-3}]^2} \qquad \text{21}$$

which can be simplified by calling

$$\frac{[NTA]_T}{[NTA^{-3}]} - K_H[H^+] - K_{Cd}[Cd^{+2}] = \emptyset . \qquad \text{22}$$

Substitution of equation 22 into equation 21, cross multi-
plying and collecting terms yields the expression

$$\left\{ \emptyset[NTA^{-3}] - [R]_T \right\} K_1 + \left\{ \emptyset[NTA^{-3}]^2 - 2[R]_T[NTA^{-3}] \right\} K_1 K_2 = 0. \qquad \text{23}$$

Since $K_1 \neq 0$,

$$\emptyset[NTA^{-3}] - [R]_T + \left\{ \emptyset[NTA^{-3}]^2 - 2[R]_T[NTA^{-3}] \right\} K_2 = 0 \qquad 24$$

and

$$K_2 = \frac{[R]_T - \emptyset[NTA^{-3}]}{\emptyset[NTA^{-3}]^2 - 2[R]_T[NTA^{-3}]} \qquad 25$$

Thus, by measuring the $[Cd^{+2}]$ polarographically and the pH, and substituting into and solving equations 20 and 22, the second stability constants of the rare earth-NTA's are obtained from equation 25.

The first rare earth-NTA stability constants (i.e., K for $R^{+3}+NTA^{-3} \rightleftharpoons RNTA$)   The first stability constant for the rare earth-NTA species was originally measured by a competition between the rare earth and cadmium for the NTA anion. However, the results were not as good as expected. This was due to the fact that the rare-earth complexes, on the average, are about one hundred times as stable as the cadmium complex, resulting in very little of the cadmium being complexed. This yielded polarograms representing seventy-five to ninety-five per cent free cadmium. This condition leads to relatively large errors in K_1, due to an absolute error of about $\pm 2\%$ in reading the polarogram (10, 11). It can be seen that a 2 per cent error in $[Cd^{+2}]$ would introduce a substantial error in $([Cd]_T - [Cd^{+2}])$ when $[Cd^{+2}]$ is 95 per cent of $[Cd]_T$. Such errors in computation are minimized when the Cd^{+2} con-

centration is from thirty to seventy per cent of $[Cd]_T$.
Therefore, europium was chosen as the standard. Since it is
a rare earth, situated at approximately the center of the
series, and is reducible in aqueous media, the resulting polar-
ograms center around the fifty per cent region.

The solutions for measuring the 1:1 rare earth-NTA
stability constants contained equimolar amounts of rare-earth
ion, europium ion and NTA. All of the equilibria in equation
(16) pertain, with the exception of (III), and the equilibria

$$Eu^{+3} + NTA^{-3} \rightleftharpoons EuNTA \; ; \quad K_{Eu} = \frac{[EuNTA]}{[Eu^{+3}][NTA^{-3}]} \qquad (V)$$

$$16a$$

$$EuNTA + NTA^{-3} \rightleftharpoons Eu(NTA)_2^{-3}; \quad K_{2Eu} = \frac{[Eu(NTA)_2^{-3}]}{[EuNTA][NTA^{-3}]} \quad (VI)$$
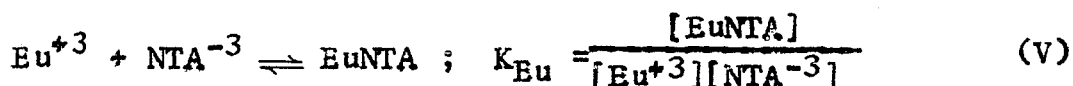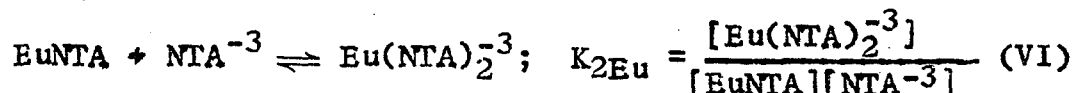
must be considered. The following material balance equations
can be written

$$[NTA]_T = [HNTA^{-2}] + [RNTA] + 2[R(NTA)_2^{-3}] + [EuNTA] + 2[Eu(NTA)_2^{-3}] \quad 26$$

Substitution from equations 16 and 16a yields

$$[NTA]_T = \left\{ K_H[H^+] + K_1[R^{+3}] + 2K_1K_2[R^{+3}][NTA^{-3}] + K_{Eu}[Eu^{+3}] \right.$$

$$\left. + 2K_{Eu} K_{2Eu}[Eu^{+3}][NTA^{-3}] \right\} [NTA^{-3}] , \qquad 26a$$

$$[R]_T = [R^{+3}] + [RNTA] + [R(NTA)_2^{-3}] \qquad 27$$

$$[R]_T = \left\{ 1 + K_1[NTA^{-3}] + K_1K_2[NTA^{-3}]^2 \right\} [R^{+3}] \qquad 27a$$

and

$$[Eu]_T = [Eu^{+3}] + [EuNTA] + [Eu(NTA)_2^{-3}] . \qquad 28$$

Substituting from equation 16a and grouping terms give the quadratic expression

$$K_{Eu}K_{2Eu}[NTA^{-3}]^2 + K_{Eu}[NTA^{-3}] + \left\{1 - \frac{[Eu]_T}{[Eu^{+3}]}\right\} = 0 \qquad 28a$$

from which

$$[NTA^{-3}] = \frac{-K_{Eu} \pm \sqrt{K_{Eu}^2 - 4K_{Eu}K_{2Eu}\{1 - [Eu]_T/[Eu^{+3}]\}}}{2K_{Eu}K_{2Eu}} . \qquad 28b$$

Rewriting equation 26a and substituting for $[R^{+3}]$ from equation 27a yields

$$\emptyset = \frac{[R]_T\{K_1 + 2K_1K_2[NTA^{-3}]\}}{1 + K_1[NTA^{-3}] + K_1K_2[NTA^{-3}]^2} , \qquad 29$$

where

$$\emptyset \equiv \frac{[NTA]_T}{[NTA^{-3}]} - K_H[H^+] - K_{Eu}[Eu^{+3}] - 2K_{Eu}K_{2Eu}[Eu^{+3}][NTA^{-3}]. \qquad 30$$

Cross multiplication and collection of terms in equation 29 yields

$$K_1\left\{[NTA^{-3}]\emptyset + K_2[NTA^{-3}]^2\emptyset - [R]_T - 2[R]_TK_2[NTA^{-3}]\right\} + \emptyset = 0 \qquad 31$$

therefore,

$$K_1 = \frac{\emptyset}{[R]_T - [NTA^{-3}]\left\{\emptyset + K_2[NTA^{-3}]\emptyset - 2[R]_TK_2\right\}} . \qquad 32$$

The first stability constant is now known as a function of free $[Eu^{+3}]$, pH and the K_2 calculated from equation 25. This method works well for the light members of the series, but as the K_1 increases, the amount of the species $Eu(NTA)_2^{-3}$

becomes negligible. This is evident from the values of $[NTA^{-3}]$ calculated in equation 28b, which remain constant for the rare earths above europium. Therefore, from gadolinium on up, an expression similar to equation 20 was used. All this amounts to is neglecting the $Eu(NTA)_2^{-3}$ species.

Materials and equipment

Preparation of stock solutions

Rare earth nitrate solutions
The rare-earth oxides of greater than 99.9% purity were supplied by the rare-earth separation group of the Ames Laboratory of the Atomic Energy Commission under the direction of Dr. J. E. Powell. These were dissolved in a slight excess of reagent grade nitric acid and the resulting solutions were filtered. The excess acid was removed by evaporating to incipient dryness and the residues were dissolved in distilled water. An aliquot of each was titrated potentiometrically to find the pH of the neutral equivalence point. All solutions were then adjusted to the neutral point. The solutions were standardized by complexometric titration with EDTA using a mercury electrode to indicate the end-point (27, 45, 46, 47, 48). Hundredth molar solutions were prepared from these stock solutions.

Tri-potassium NTA
The NTA was obtained from Geigy Industrial Chemicals, and was purified further by re-crystallization from hot water. One-hundredth molar K_3NTA

was prepared by adding 0.06 moles of carbonate-free KOH to 0.02 moles of dried, thrice recrystallized H_3NTA and diluting to 2000 ml.

Carbonate-free potassium hydroxide   Standard solutions of carbonate-free potassium hydroxide were prepared by the method of Powell and Hiller (49) and standardized by the method of Powell, Fritz and James (50), using cadmium acid HEDTA as a primary standard.

Potassium nitrate   Two liters of a 1.0 M solution of potassium nitrate was prepared by dissolving 202.21 grams of dried reagent grade KNO_3 in distilled water and diluting to 2000 ml.

Cadmium nitrate   Reagent grade cadmium nitrate was dissolved in distilled water and standardized by complexometric titration with EDTA using a mercury indicator electrode. The stock solution was then diluted to hundredth molar.

Description of equipment

pH meter   pH measurements were made with a Beckman Model G pH meter. A fiber type saturated calomel electrode and a "General Purpose" glass electrode were used.

Polarograph   A Sargent model XXI polarograph was used. The cell was constructed from a 100-milliliter beaker.

A saturated calomel electrode was used as a reference. This was prepared in the usual manner (51) and was connected to the cell by a saturated potassium chloride-agar bridge.

Mercury electrode   A Beckman Model G pH meter set to read "plus millivolts" was used as the potentiometer. The mercury electrode consisted of a J-shaped tube with a platinum wire sealed into the end connecting the drop of mercury in the cup-shaped end to the potentiometer. A fiber type saturated calomel electrode was used as a reference.

Constant temperature baths   The constant temperature baths were controlled by microset mercury thermoregulators coupled with electronic relays manufactured by Precision Scientific Company, Chicago, Illinois. The relays operated 500-watt immersion heaters. The 20° and $30^\circ C$ baths had tap water flowing through a copper cooling coil immersed in the bath. The $40^\circ C$ bath required no cooling facilities. The $10^\circ C$ bath had $5^\circ C$ water pumped through the cooling coil. The $5^\circ C$ water was supplied by a refrigeration unit. The bath temperatures were checked by a narrow-range thermometer calibrated by the National Bureau of Standards and were held to within $\pm\ 0.02^\circ C$.

Procedure

Acid dissociation constants of H3NTA   As was mentioned earlier, only the third acid dissociation constant is needed

for the stability constant measurements. A saturated solution of H_3NTA was prepared and standardized with carbonate-free KOH. 200 milliliters of the $0.00712\underline{M}$ H_3NTA solution were added to each of five 250-milliliter volumetric flasks. To each flask was added a different amount of $0.1533\underline{N}$ KOH varying between 22.50 and 23.30 milliliters. 18.00 milliliters of $1.0\underline{M}$ KNO_3 was then added to each flask, and the solutions were then diluted to the mark in a 20°C bath. A correction factor was calculated to convert pH readings to hydrogen-ion concentration from activity coefficient data for the different temperatures involved (52). This correction is in agreement with the one experimentally determined by Mackey (48) and is given in Table 1. Hydroxide-ion concentrations were calculated from the corrected hydrogen-ion concentrations and the auto-ionization constants for water at the different temperatures (52). The pH of each solution was then measured at each of the temperatures involved, and the acid dissociation constant calculated from equation (8).

Cadmium-NTA stability constant   A cadmium standard was prepared for the polarograph which consisted of a $0.0010\underline{M}$ $Cd(NO_3)_2$ solution adjusted to an ionic strength of 0.10 with $1\underline{M}$ KNO_3. Six solutions were prepared for the stability constant measurements. These consisted of mixtures containing $0.0010\underline{M}$ $Cd(NO_3)_2$, $0.0010\underline{M}$ K_3NTA, and different amounts of

Table 1. pH meter corrections at ionic strength = 0.10 (KNO$_3$)

Temperature, °C.	Correction
10	-0.10
20	-0.10
30	-0.10
40	-0.11

HNO$_3$ to keep the pH between 5.5 and 6.5, and each was adjusted to an ionic strength of 0.10 with the 1$\underline{M}$ KNO$_3$ solution. The free cadmium-ion concentration of each solution was measured polarographically and the pH was measured at each of the four temperatures involved. The samples were equilibrated in a constant temperature bath for twenty-four hours before measuring on the polarograph. Pure argon, saturated with 0.10$\underline{M}$ KNO$_3$ at the appropriate temperature, was bubbled through each solution for approximately 15 to 20 minutes before the polarogram was taken. This was done to remove any oxygen present. The cadmium-NTA stability constant was then calculated by use of equation 15.

Second rare earth-NTA stability constant   A set of solutions was prepared consisting of 0.0010$\underline{M}$ Cd(NO$_3$)$_2$, 0.0010$\underline{M}$ rare earth nitrate, 0.0020$\underline{M}$ K$_3$NTA and adjusted to an ionic strength of 0.10 with KNO$_3$. The free cadmium-ion concentration and the pH of each was measured at the four tem-

peratures and the second stability constant was calculated
by use of equations 20, 22 and 25.

First rare earth-NTA stability constant   A europium
standard for the polarograph was prepared by adjusting the
ionic strength of a $0.0010\underline{M}$ $Eu(NO_3)_3$ solution to 0.10 with $1\underline{M}$
KNO_3. A set of solutions for the determination of the con-
stants was prepared consisting of $0.0010\underline{M}$ rare earth nitrate,
$0.0010\underline{M}$ europium nitrate, $0.0010\underline{M}$ K_3NTA and adjusted to an
ionic strength of 0.10 with $1\underline{M}$ KNO_3. The pH of each solution
was adjusted to approximately 5.5 with nitric acid, in order
to prevent any hydrolysis of the free europium or rare-earth
ions. The free europium-ion concentration was measured
polarographically and the hydrogen-ion concentration was
measured with the pH meter at each of the four temperatures.
To each of these solutions, one drop of a 0.2 per cent basic
fuchsine solution was added to suppress the maximum. The
rare earth-NTA stability constants were then calculated from
equation 32.

Results and discussion

The results of the acid dissociation constant measure-
ments are given in Table 2. At $20^{\circ}C$, the value pK_3 = 9.73
reported by Schwarzenbach (43) is used.

A plot of pK_3 versus the reciprocal of the temperature

results in a straight line. Thus, the reported values agree with the theory, in that the enthalpy change over a small temperature range is constant.

Table 2. pK_3 of H_3NTA at ionic strength = 0.10 (KNO_3)

Number	10°C	20°C	30°C	40°C
1	9.90		9.60	9.48
2	9.90		9.59	9.45
3	9.89		9.57	9.44
4	9.87		9.57	9.44
5	9.89		9.56	9.46
Average	9.89	9.73	9.58	9.45

The values of the cadmium-NTA stability constant are shown in Table 3. Again, if the values of log K are plotted versus the reciprocal of the temperature, a straight line results. This agreement with the theory gives an added degree of confidence to the measured values.

Values for the second stability constant of the rare earth-NTA species are listed in Table 4, and are also represented in Figure 1. These values are in excellent agreement with the values reported by Anderegg (53) for a portion of the rare-earth series. Raw data for this determination can be found in Table 8 in the Appendix. Values of the first

Table 3. Log K_{CdNTA^-} at ionic strength = 0.10 (KNO$_3$)

Number	10°C	20°C	30°C	40°C
1	9.77	9.63	9.44	9.31
2	9.88	9.65	9.39	9.17
3	9.85	9.61	9.53	9.17
4	9.80	9.54	9.43	9.26
5	9.76	9.54	9.46	9.22
6	9.71	9.64	9.46	9.25
Average	9.80	9.60	9.45	9.23

Table 4. Log $K_{R(NTA)_2^{-3}}$ at ionic strength = 0.10 (KNO$_3$)

$R(NTA)_2^{-3}$	10°C	20°C	30°C	40°C
La	7.68	7.39	7.73	7.67
Ce	8.17	7.75	8.10	8.11
Pr	8.38	8.31	8.34	8.26
Nd	8.60	8.52	8.52	8.42
Sm	9.07	8.96	8.95	8.81
Eu	9.34	9.17	9.12	9.03
Gd	9.33	9.21	9.17	9.00
Tb	9.45	9.34	9.28	9.13
Dy	9.43	9.27	9.24	9.03
Ho	9.34	9.23	9.15	8.97
Er	9.14	9.11	9.05	8.97
Tm	9.03	9.05	9.02	8.93
Yb	9.04	9.07	9.05	8.95
Lu	9.18	9.16	9.12	8.99
Y	8.93	8.99	8.95	8.80

rare earth-NTA stability constants are listed in Table 5 and shown in Figure 2. The raw data are listed in Table 9 in the Appendix.

Only one source of error is apparent in this method, namely, the error made in the determination of the per cent

Table 5. Log K_{RNTA} at ionic strength = 0.10 (KNO_3)

RNTA	10°C	20°C	30°C	40°C
La	9.86	9.87	10.45	10.41
Ce	10.18	10.43	10.55	10.61
Pr	10.67	10.93	10.89	10.98
Nd	10.94	11.13	11.07	11.32
Sm	11.05	11.38	11.34	11.67
Eu	11.20	11.35	11.48	11.62
Gd	11.03	11.17	11.37	11.61
Tb	11.03	11.31	11.52	11.70
Dy	11.22	11.38	11.65	11.83
Ho	11.33	11.53	11.68	11.87
Er	11.44	11.66	11.88	12.03
Tm	11.67	11.79	12.02	12.25
Yb	11.82	11.98	12.18	12.29
Lu	11.86	12.10	12.23	12.43
Y	10.89	11.23	11.49	11.71

uncomplexed metal ion. This error amounts to about ± 2 per cent (10, 11) and should be constant for all determinations. This error results in an uncertainty range of approximately ± 0.10 log units in the rare-earth chelate stability constants.

Since these constants depend upon the value of the CdNTA⁻ constant, and in the case of K_1 upon the EuNTA constant also,

Figure 1. Logarithm of the second stability constant of the
           rare earth-NTA chelates
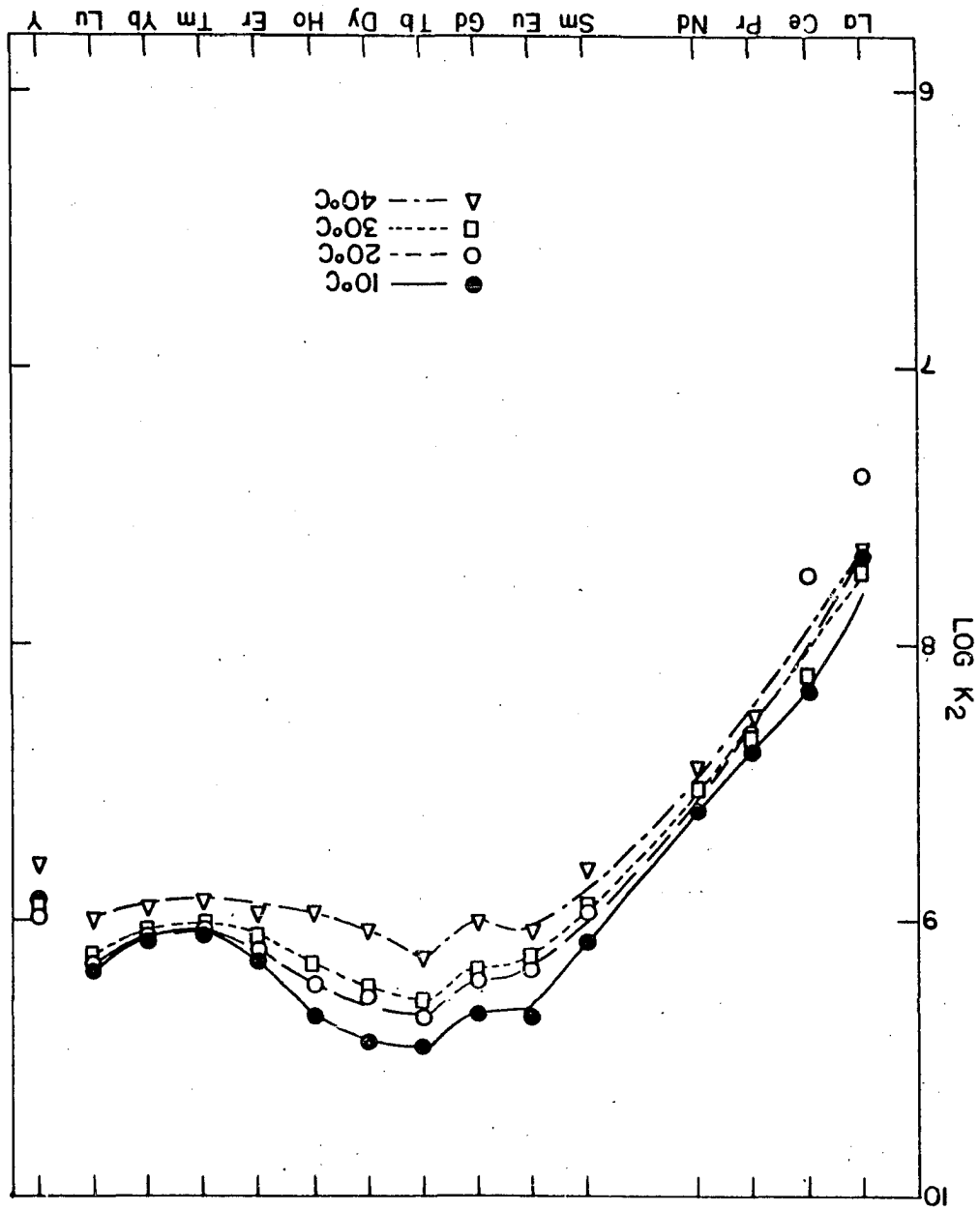
Figure 2.   Logarithm of the first stability constant of the
rare earth-NTA chelates

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y

$LOG\ K_1$

9

10

11

12

13

- ● 10°C
- ○ 20°C
- □ 30°C
- ▽ 40°C
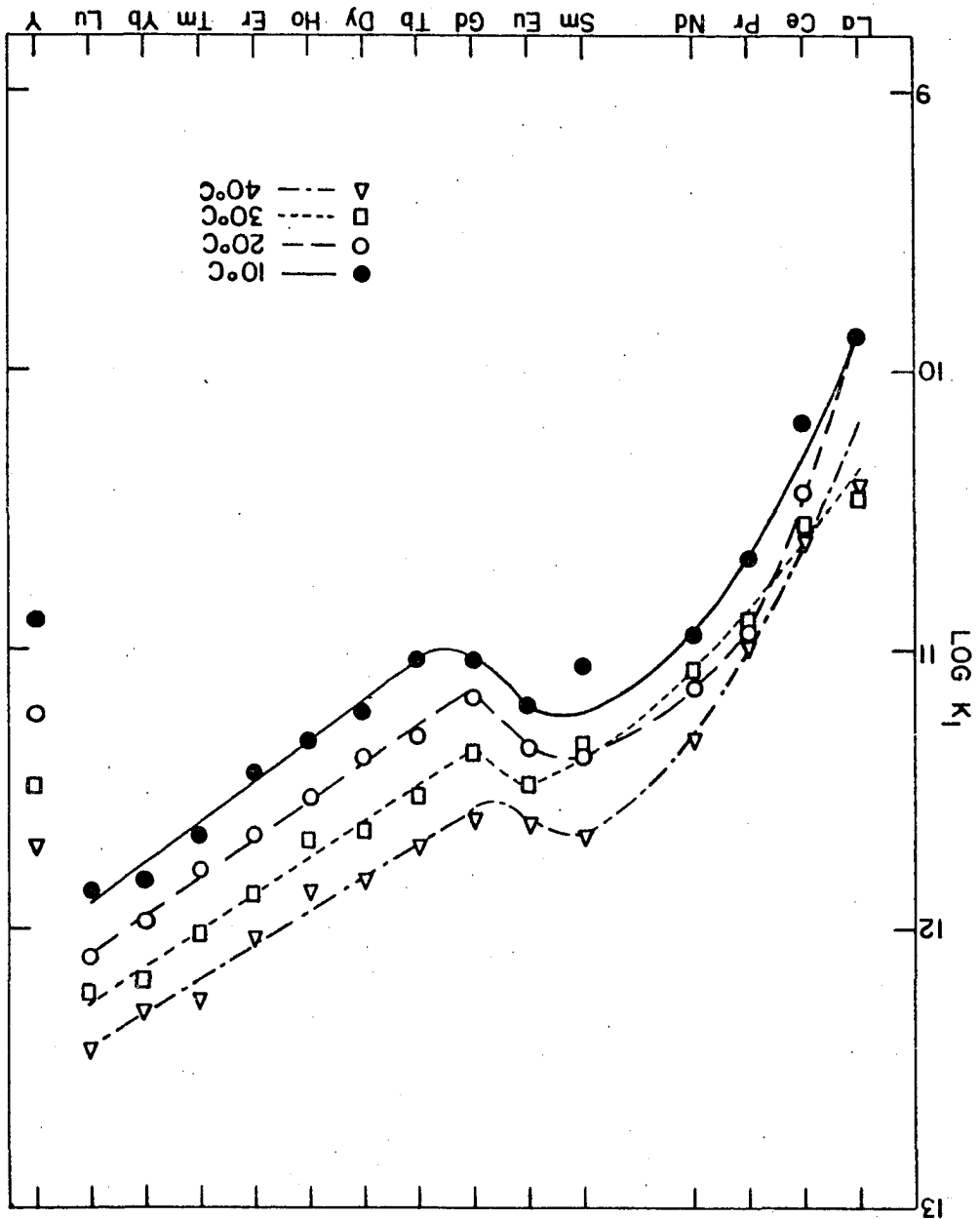
the absolute value will be affected by any error in these constants. However, the relative values are virtually independent of any "outside" errors.

The 1:1 rare earth-NTA stability constants, with the exception of that of europium, were originally measured versus cadmium. The half-wave potential of europium lies so close to that of cadmium that the polarographic waves overlap, making measurement of the Cd^{+2} diffusion current impossible. The values of the constants at 10° and $20^\circ C$ appeared reasonable and were within the experimental error of the values reported in Table 5. In the $30^\circ C$ run the constants for the light members of the series agreed substantially with the values in Table 5, but the constants of the heavy members appeared to be too low. At $40^\circ C$, all of the values appeared to be too low. An interesting trend was noted in each of the last two determinations. A plot of log K_1 versus atomic number, as in Figure 2, resulted in a staggered effect in which a line drawn through the odd-atomic-numbered rare earths formed a smooth curve, parallel to and approximately 0.2 log units above a similar curve drawn through the even-atomic numbered rare earths. An attempt to determine whether or not this effect was real led to the use of europium as a standard for the measurement of the first stability constants. The value of the EuNTA stability constant was evaluated from the runs versus cadmium. As previously mentioned, the rare earth constants at 10° and $20^\circ C$ were good, so the europium constant

was interpolated from these values. At 30° and $40^{\circ}C$ a europium constant was calculated from the per cent free europium ion, measured in the run versus europium, and the rare-earth constants, measured in the runs versus cadmium, by rearranging equation 32 and solving for K_{Eu}. In the $30^{\circ}C$ calculations, a constant value for K_{Eu} was apparent only with the light members of the rare-earth series through terbium. Therefore, the EuNTA stability constant at $30^{\circ}C$ was taken as the average value of those calculated from lanthanum through terbium. In the $40^{\circ}C$ calculations, none of the values calculated for K_{Eu} remained constant, so a least squares line was drawn through the 10°, 20° and $30^{\circ}C$ values and extrapolated to $40^{\circ}C$. This value was used in the $40^{\circ}C$ runs versus europium. The europium values are given in Table 6.

Table 6. Log K_{EuNTA} at ionic strength = 0.10 (KNO_3)

Temperature, $^{\circ}C$	log K_{EuNTA}
10	11.20
20	11.35
30	11.48
40	11.62

The reason for the inaccuracy of the 1:1 rare earth-NTA stability constants measured versus cadmium lies in the fact that the rare-earth chelate stability constants are from over 10 to better than 1000 times larger than the CdNTA constant. This results in the measurement of free cadmium-ion concentrations from near 80 per cent to over 95 per cent of the standard concentration. The most accurate range for computation centers around the figure of 50 per cent free Cd^{+2}. The 80-95 per cent readings introduced uncertainties of appreciable magnitude. The higher the temperature, the greater the effect, since the RNTA stability constants increase with increasing temperature and the CdNTA constant decreases. This is why europium, whose constant lies within the extremes of the other constants, was chosen as the optimum reference material.

As was mentioned earlier, the absolute value of the stability constants depends upon the value chosen for K_{Eu} which in turn, depends upon the value of K_{Cd}, while the relative values are independent of the reference value. Nevertheless, the absolute values obtained in this research agree fairly well with previously reported values (43). It should be pointed out, however, that in none of the previous determinations was a correction made for the formation of 1:2 rare-earth chelate species. Also, most of the previous polaro-

graphic work was done in the presence of acetate buffer, approximately ten-fold as concentrated as the rare-earth ion, with no correction made for complexing of the rare earths by acetate. Sonesson (54, 55) has shown that the rare earths do form complexes with acetate, the stability constants of which were measured by Kolat (56). An acetate correction for the polarographically determined stability constants of the rare earth-EDTA chelates was worked out by Hiller (11) and this correction was applied to his values by Kolat. The correction amounted to a change as large as 0.4 log units in some constants.

Examination of Figures 1 and 2 indicates that the values reported for the heavy members of the rare-earth series appear to be more reliable than those reported for the lighter members. This was discussed by Wheelwright (10) in the polarographic determination of the rare earth-EDTA stability constants. In both sets of curves an irregularity known as the "gadolinium break", occurs in the center of the series. The position of yttrium is of interest, since it does not fall on the stability constant curve in the position where it might be expected to from a consideration of its ionic radius. K_1 for yttrium is closest to that of terbium, while K_2 for yttrium is near that of samarium. It has been suggested (57, 58) that the ligand-field stabilization effect on the 4f electrons should be considered in correlating the stability constants

of rare-earth chelate species. Such a consideration might explain the gadolinium break, which occurs for nearly all chelates studied, and the low values observed for yttrium. Yttrium which has no 4f electrons and gadolinium with a half-filled shell would possibly not be stabilized in their complexes by the ligand field. More work needs to be done in this field before an exact correlation can be made.

The values of log β_2 are listed in Table 7. Values of β_2 are the products of the first and second stability constants, and it is the change in log β_2, as one proceeds across the rare-earth series, that determines what separations will occur when NTA is used as the eluant in ion-exchange elution processes.

The separation factor of any two rare earths is defined as

$$\alpha = \frac{\overline{X}_R / \overline{X}_{R'}}{[R]_T / [R']_T} , \qquad 33$$

where $\overline{X}_R$ and $\overline{X}_{R'}$ are the mole fractions of R and R' in the resin phase and $[R]_T$ and $[R']_T$ are the total concentrations of R and R' in the aqueous phase. If α is unity, no separation can occur. The absolute magnitude of the difference of α from unity is a measure of the ease with which the separation can be effected. The magnitude of α is primarily determined by the ratio of β_2 values or by the difference in

Table 7. Log β_2 of rare earth-NTA species at ionic
strength = 0.10 (KNO_3)

Rare earth	$10^{\circ}C$	$20^{\circ}C$	$30^{\circ}C$	$40^{\circ}C$
La	17.54	17.26	18.18	18.08
Ce	18.35	18.18	18.65	18.72
Pr	19.05	19.24	19.23	19.24
Nd	19.54	19.65	19.57	19.74
Sm	20.12	20.34	20.29	20.48
Eu	20.54	20.52	20.60	20.65
Gd	20.36	20.38	20.54	20.61
Tb	20.48	20.65	20.80	20.83
Dy	20.65	20.65	20.89	20.86
Ho	20.67	20.76	20.83	20.84
Er	20.58	20.77	20.93	21.00
Tm	20.70	20.84	21.04	21.18
Yb	20.86	21.05	21.23	21.24
Lu	21.04	21.26	21.35	21.42
Y	19.82	20.22	20.44	20.51

log β_2 values (59). It turns out that the greater the difference between two values of log β_2, the greater the separation factor.

Examination of Table 7 indicates that the light rare earths, lanthanum through samarium, should be separated quite well by elution with NTA. The middle rare earths, samarium

through erbium, should separate poorly and the heavy rare earths should separate moderately well. In the 10° and 20°C runs, yttrium should elute between samarium and neodymium, while at 30° and 40°C, it should elute between europium and samarium.

In some recent work at the Ames Laboratory (60) the elution sequence of the rare earths with NTA was investigated. The elutions were performed at room temperature (approximately 27°C) with an eluant consisting of $0.0183\underline{M}$ NTA at a pH of 8.8. The eluate pH varied between 3 and 3.5. The results of this investigation showed fairly good separation between the light rare earths, lanthanum through samarium, with fair, but not as sharp, separations between the heavier members of the series. Yttrium eluted between europium and samarium. The poorest separations occurred in the middle of the rare-earth series, especially in the yttrium-europium-gadolinium region where there was a very large overlap.

This experimental work is a verification of the constants measured at 30°C, showing that the position of yttrium in the elution sequence and the extent of separation indicated by the constants, are correctly predicted. In future investigations it would be interesting to perform a controlled-temperature elution with NTA somewhere between 10° and 20°C, to ascertain whether the position of yttrium shifts behind samarium as indicated by the data in Table 7.

The thermodynamic properties $\triangle F^O$, $\triangle H^O$ and $\triangle S^O$ for the rare earth-NTA complexes are given in Tables 10 through 14 in the Appendix. The values for $\triangle H^O$ and $\triangle S^O$ are summarized in Figures 3, 4, 5 and 6. These quantities were calculated from the expressions

$$\triangle F^O = -RT \log_e K$$

$$\triangle H^O = -R \frac{d(\log_e K)}{d(1/T)}$$

$$\triangle S^O = \frac{\triangle H^O - \triangle F^O}{T} \, .$$

The values for $\triangle H^O$ were evaluated by a least squares treatment with $1/T$ as the abscissa and $\log_e K$ as the ordinate.

These quantities are not true thermodynamic quantities, since they were measured at an ionic strength of 0.10. However, due to the inherent errors in the temperature dependence method of determining these quantities and the fact that the solutions were fairly dilute, the values reported are a good approximation to the true thermodynamic quantities as measured by this method.

An examination of these data shows that the significant effect in the formation of the rare earth-NTA complexes is the entropy change. This is in agreement with the theory explained by Martell and Calvin (9). In measuring the thermodynamic properties of the alkaline earth-NTA complexes,

Figure 3. Enthalpy change for the formation of the 1:1
rare-earth nitrilotriacetate species from their
ions in aqueous solution at ionic strength =
0.10 (KNO_3)
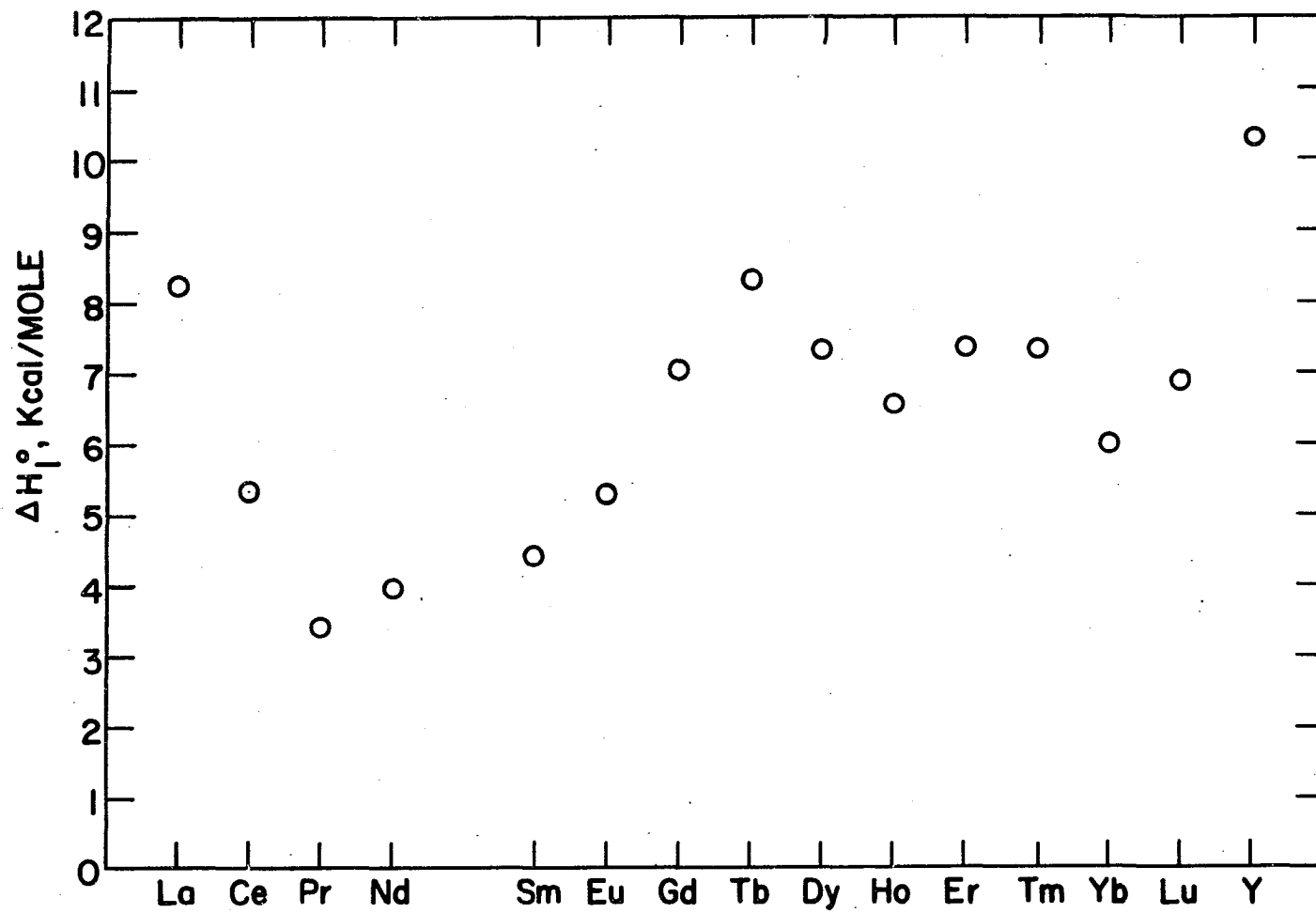
Figure 4. Enthalpy change for the formation of the 1:2
          rare-earth nitrilotriacetate species from their
          ions in aqueous solution at ionic strength =
          0.10 (KNO_3)
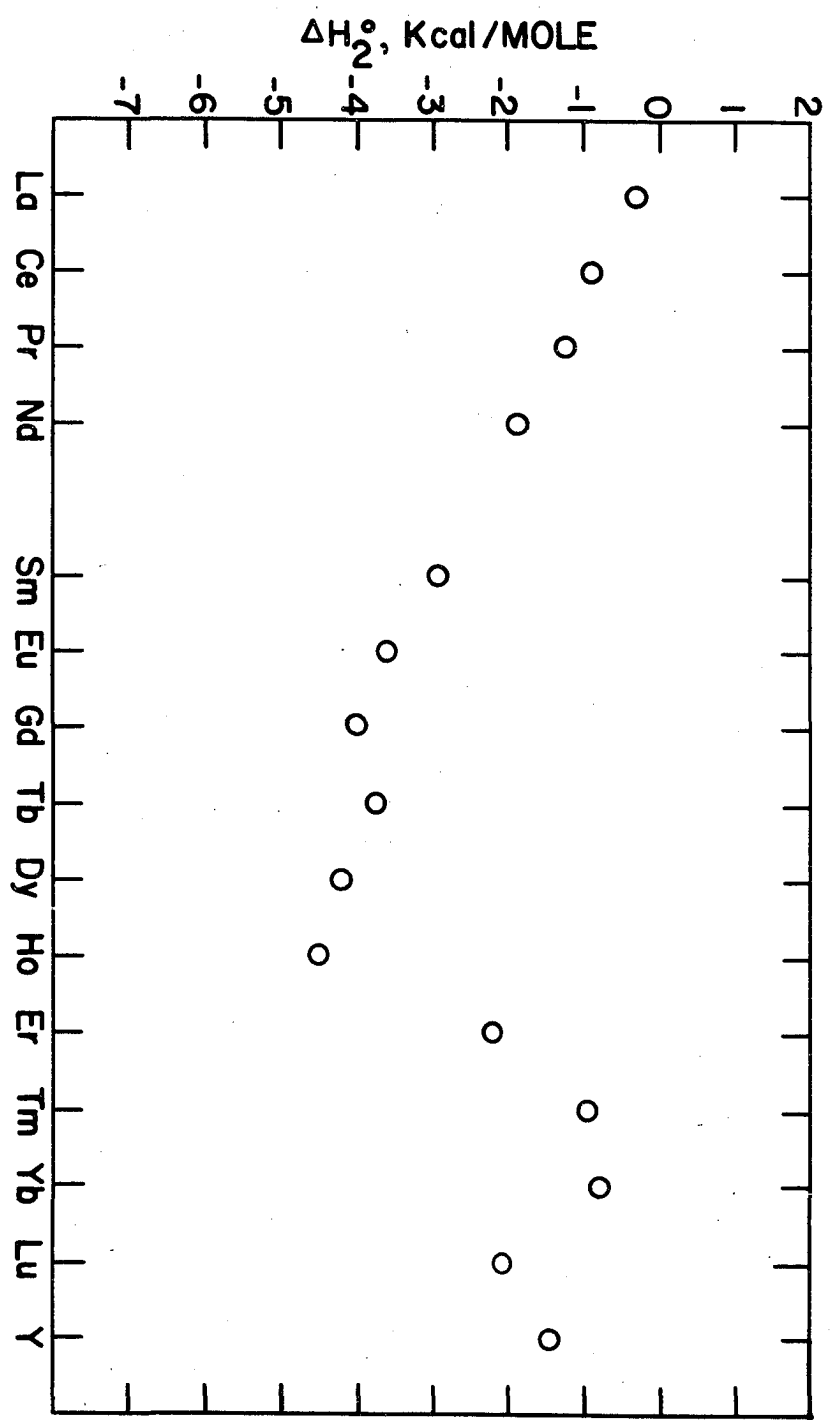
Figure 5. Entropy change for the formation of the 1:1 rare-
earth nitrilotriacetate species from their ions
in aqueous solution at ionic strength = 0.10 (KNO_3)
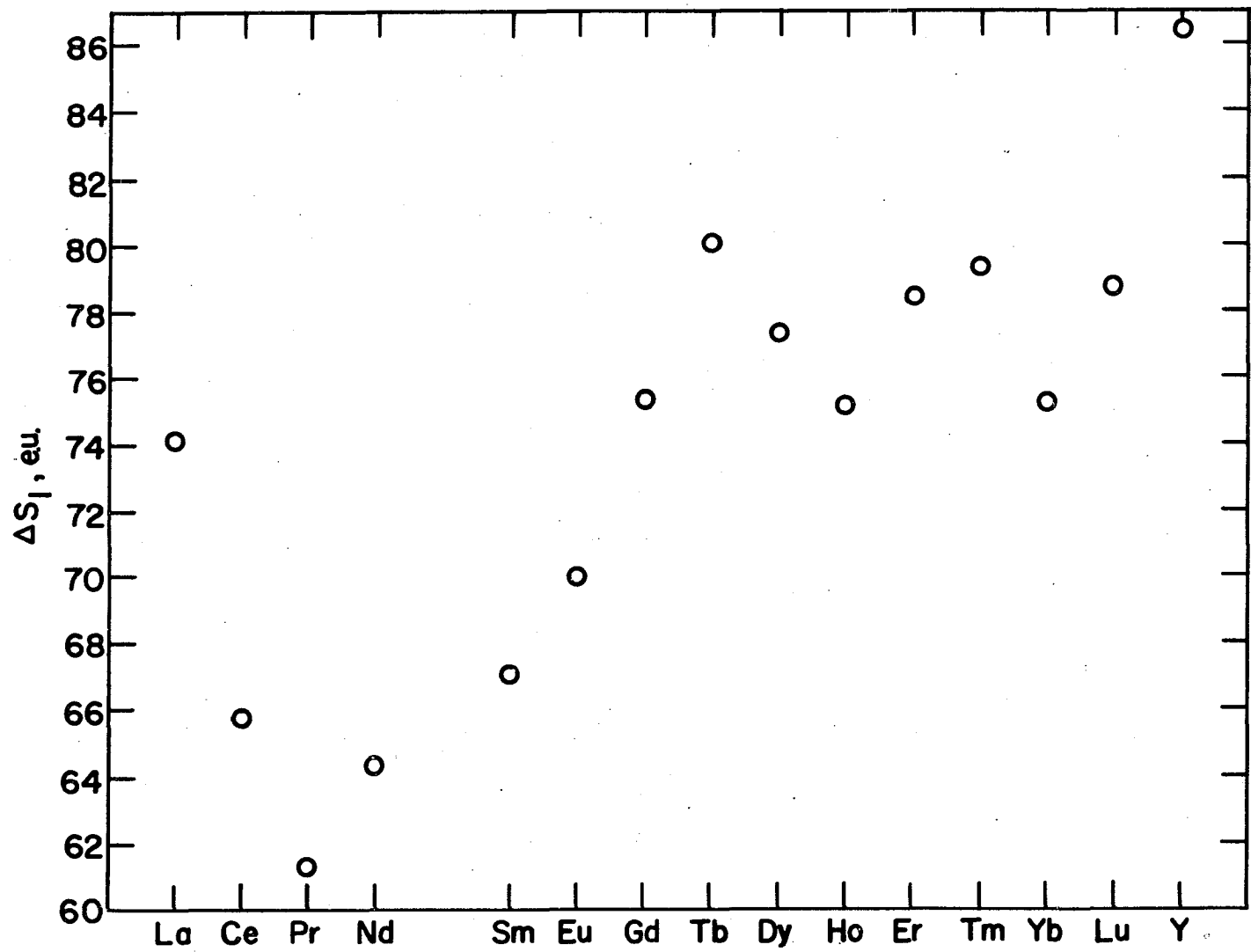
Figure 6. Entropy change for the formation of the 1:2 rare-
          earth nitrilotriacetate species from their ions
          in aqueous solution at ionic strength = 0.10 (KNO_3)
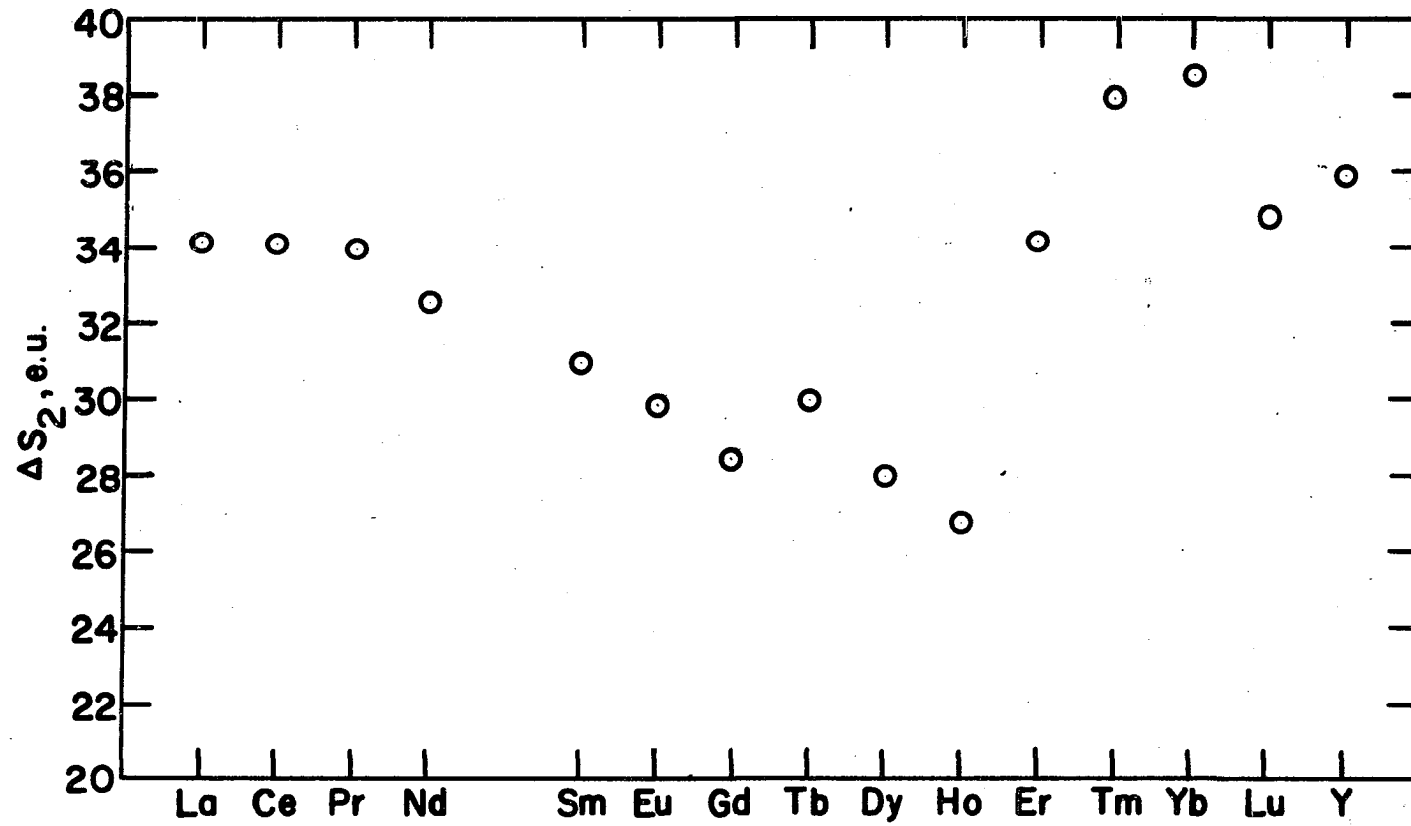
Martell (61) and Hughes and Martell (62) found that the stabilities of these compounds were due almost entirely to the favorable entropy increase, and that enthalpy changes are relatively unimportant.

The large entropy effect may be explained in the following manner. If one assumes that the tri-positive rare-earth ions are coordinated to six water molecules in aqueous solution, the formation of a rare-earth complex is illustrated by the following reaction

$$R^{+3}(H_2O)_6 + NTA^{-3} \longrightarrow RNTA(H_2O)_2 + 4H_2O , \qquad (I)$$
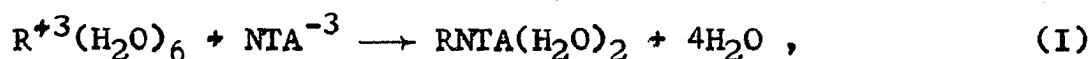
assuming that the tetradentate ligand NTA displaces four of the coordinated water molecules from the hydration sphere of the rare-earth ion. Similarly, the formation of a 1:2 rare earth-NTA complex can be written

$$RNTA(H_2O)_2 + NTA^{-3} \longrightarrow R(NTA)_2^{-3} + 2H_2O . \qquad (II)$$
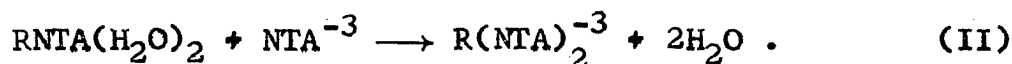
In reaction (I) two species on the left side of the arrow react to form five species on the right side. This "increase in the disorder" of the system is reflected by a large increase in entropy. In reaction (II), a similar increase in the number of species from two to three is noted. This smaller increase in disorder results in a smaller, but still very significant, increase in entropy.

It should also be noted that the entropy changes remain constant over the temperature range studied. This too, seems reasonable, since the products in reactions (I) and (II) will all be isolated by the solvent. They might be thought of as occupying a hole or cavity in the liquid, which is completely surrounded by water molecules. A small change in temperature, while changing the thermal energy of the system and causing some expansion, does not in any way affect the disorder of the system. Thermal expansion, over the narrow temperature range studied, is probably negligible compared to the disorder caused by the reactions (I) and (II).

Martell found that the temperature-coefficient method of determining enthalpy changes may easily lead to an error of $\pm$ 1 Kcal in $\triangle H$, which would correspond to an uncertainty of $\pm$ 3 entropy units in the $\triangle S$ values (61). It should be pointed out at this time that any errors affecting the absolute values of the stability constants does not affect these enthalpy calculations. It is the change in the relative values of these constants at the different temperatures from which the heats are calculated.

SOLUBILITIES OF THE VARIOUS HYDRATED SPECIES

Introduction

In practical applications of ion-exchange techniques to
the separation of individual rare earths, stability constant
data alone does not give enough information to predict whether
or not the separation will be successful. Another important
factor which must be taken into consideration is the solu-
bility of each species present during the elution. Obviously,
if the solubility of one of the chelate species present during
the process is exceeded, that species will precipitate on the
resin and hinder the flow of eluant. Therefore, in this sec-
tion of the thesis, the solid rare earth-NTA chelate species
were prepared and the solubility of each measured. The va-
riation in hydration was also studied.

Experimental

Materials

Rare earth chloride solutions   Solutions of the rare
earth chlorides were prepared by dissolving a weighed amount
of each individual rare-earth oxide, with the exception of
cerium, in a slight excess of hot, reagent-grade, hydrochloric
acid. The solutions were filtered and diluted to the desired
concentration. Cerium(IV) oxide was dissolved by adding hy-
drogen peroxide to the hydrochloric acid while heating.

Procedure

The solid rare earth-NTA chelates were prepared by adding an equivalent amount of each rare-earth chloride solution to a solution of $(NH_4)_3NTA$ in a Pyrex beaker. The excess acid was then neutralized by adding ammonia until a pH of 5.0 was reached, the beakers were placed on a hot plate for approximately twelve hours, and the precipitates were collected by filtration. In all cases three crops of crystals were removed and thoroughly washed to insure against contamination from NH_4Cl. Subsequent tests showed no trace of NH_4Cl in any sample. A second set of crystals was prepared, this time at room temperature rather than on the hot plate. Gravimetric analyses were done on both sets of crystals after grinding them thoroughly with a mortar and pestle and allowing the powder to dry in the air. A portion of each prepared sample was weighed into a weighed crucible and ignited to the oxide in an 800°C muffle. Then the crucibles and contents were cooled in a desiccator and weighed. The molecular weights of the complex compounds were calculated from the original weights and the weights of the oxide residues. In some cases there was a discrepancy in the degree of hydration observed, so more solid chelates were prepared at 60°, 80°, 90° and 100°C and analyzed.

Thermal decomposition studies were made on the set of chelates which were prepared on the hot plate. The samples

were ground with a mortar and pestle and then dried in a constant temperature drying oven at 106°, 129° and $150^{\circ}C$ for 12 to 18 hours.

The solubilities of the rare earth-NTA complexes were measured at 25° and $60^{\circ}C$. The constant temperature baths were controlled to within $\pm$ $0.1^{\circ}C$ by microset mercury thermo-regulators coupled with electronic relays. The samples were placed in serum bottles supplied by Fisher Scientific Company. The bottles were filled with boiling distilled water, sealed and immersed in boiling water for one to two hours to insure sterility. This precautionary measure was taken to avoid action by micro-organisms on the organic part of the compounds. The serum bottles were then fastened to a holder which was connected to a motorized shaker and immersed in the baths. The samples were left on the shaker in the baths for five to six months. The solubilities were measured gravimetrically. A portion of the solution was weighed in a constant weight crucible, then evaporated carefully to dryness under heat lamps. The residue was finally ignited to the oxide in an $800^{\circ}C$ muffle. Samples of the solid chelates in equilibrium with the saturated solutions were also analyzed. This served two purposes: first, it showed for which hydrate the solubility was being measured; and second, since samples of every hydrate found for each rare earth-NTA compound were studied, it established which hydrate was most stable at each temperature.

Results and discussion

The results of the gravimetric analyses are given in Table 15 in the Appendix, and are summarized in Figure 7. The small deviations from whole-number hydrates is probably due to occluded water and/or experimental errors in the analyses. Large deviations from integral numbers of water, on the other hand, were thought to be due to mixtures of two different hydrates. This was proven in the case of TbNTA prepared at 100°C which showed an apparent hydration of 1.62 moles of water per mole. Examination of the sample revealed two types of crystals, flat plates and needles. Subsequent separation and analyses of the two types of crystals showed that the plates were monohydrated and the needles were tetrahydrated. The dihydrates formed by the heavy RNTA compounds prepared on the hot plate were not formed at any of the other temperatures up to 100°C. This indicates that there may have been some degree of superheating taking place at the glass surface in contact with the hot plate. TmNTA.2H$_2$O and LuNTA.2H$_2$O were the most stable compounds formed. Upon heating to 150°C for 18.5 hours, they still retained both waters. LuNTA.2H$_2$O was heated to 186°C before it lost water and formed the anhydrous compound. However, the ErNTA.2H$_2$O and YbNTA.2H$_2$O species dehydrated after heating at 106°C for 12 hours. Results of thermal decomposition for the complete series of

compounds are given in Table 16 in the Appendix. Figures 8, 9 and 10 show the results of heating, with the numbers rounded off to the nearest half-integer. The results were rather irregular. Similar determinations carried out with the tetrahydrates of the heavy members showed a loss of three waters in all cases between 110° and $120^\circ C$. This indicates a different structure for the tetrahydrates than for the dihydrates of these compounds.

The solubilities of the various rare earth-NTA hydrates at 25° and $60^\circ C$ are summarized in Table 17 in the Appendix. Examination of this data reveals that the complexes are not very soluble. Due to the low values, care must be taken that the solubilities of these species are not exceeded in the ion-exchange separation of the rare earths with NTA. Advantage is taken of the fact that the 1:2 rare earth-NTA species are quite soluble. This was shown when an attempt to prepare them in a manner similar to the preparation of the 1:1 chelate species resulted in no precipitation. The solutions had to be evaporated nearly to dryness before any precipitate was evident. Due to the concentration of other species, such as NH_4Cl, the resultant di-chelate compounds were contaminated by this procedure, and further work with them was discontinued.

When using NTA in separating the rare earths by the ion-exchange process, very dilute solutions are employed (see

Figure 7.   Hydrates of the solid 1:1 rare earth-NTA species
            prepared at various temperatures
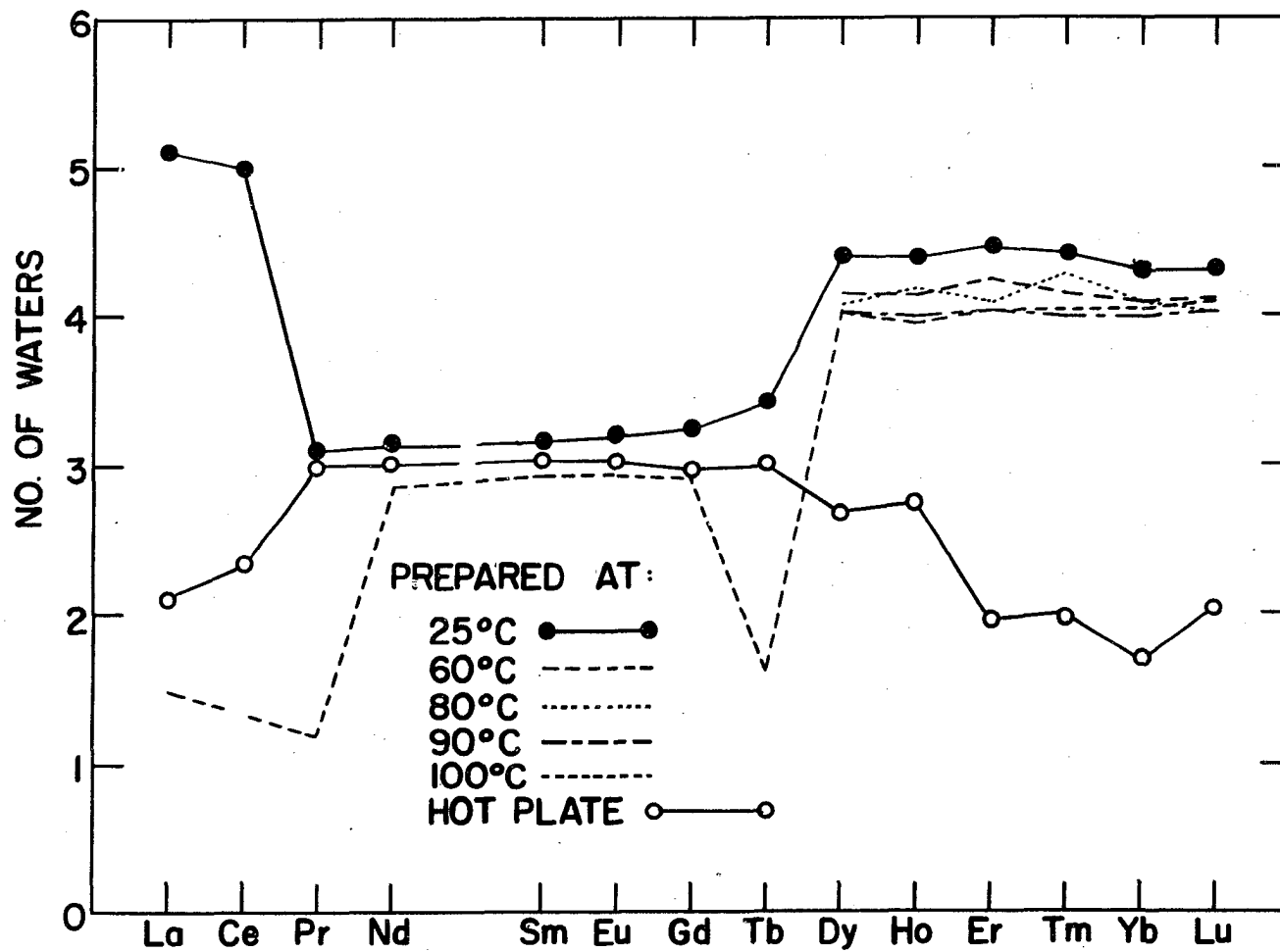
Figure 8.   Hydrates of the 1:1 rare earth-NTA species, air
            dried at room temperature and dried in an oven
            at 106°C
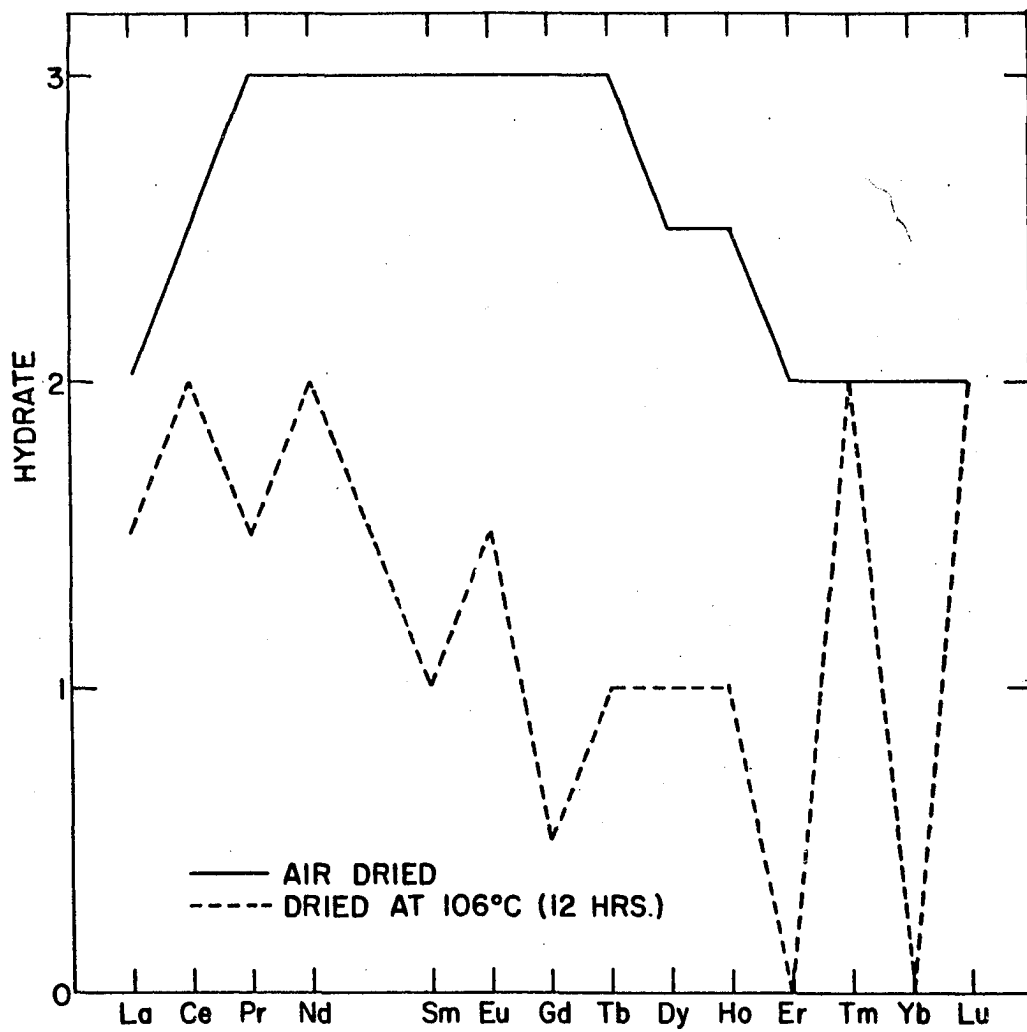
Figure 9. Hydrates of the 1:1 rare earth-NTA species, air
dried at room temperature and dried in an oven
at 129°C
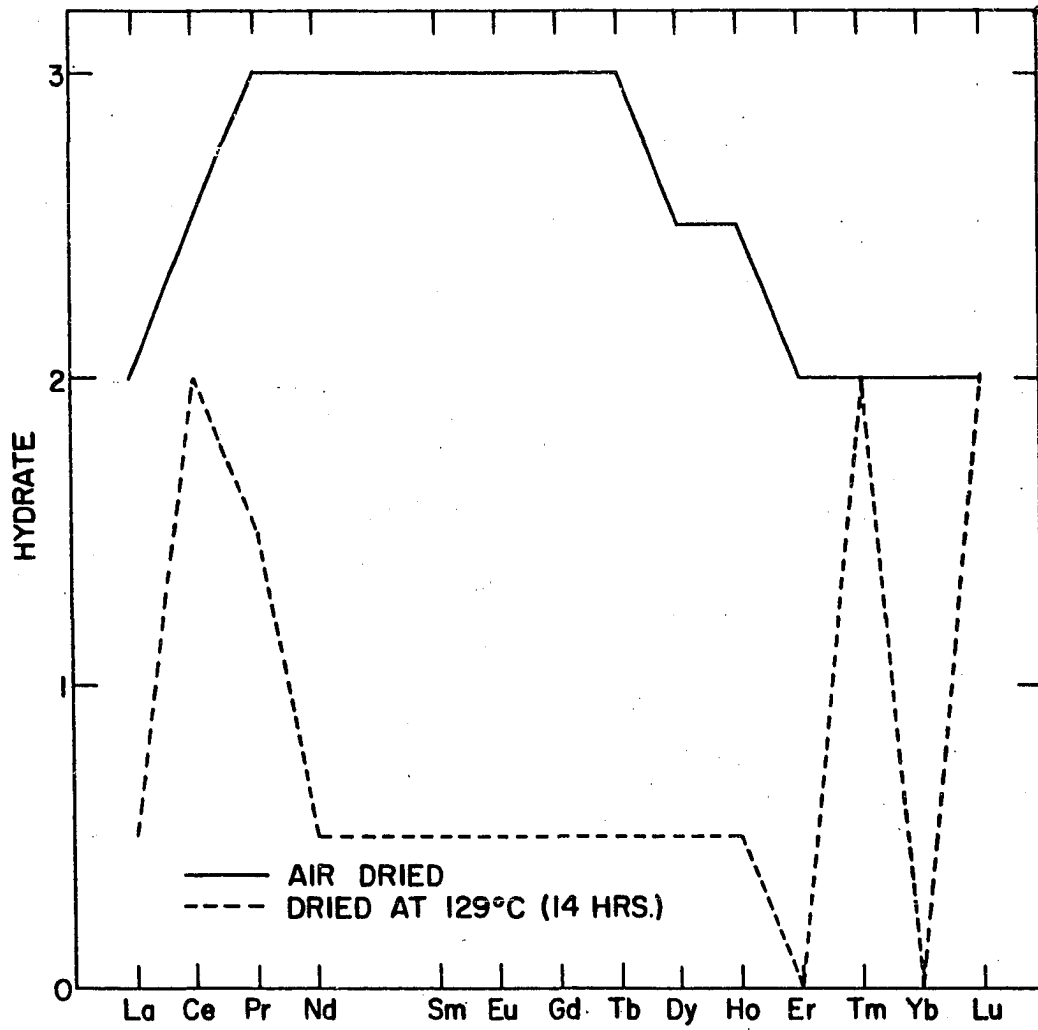
Figure 10.   Hydrates of the 1:1 rare earth-NTA species, air
dried at room temperature and dried in an oven
at 150°C
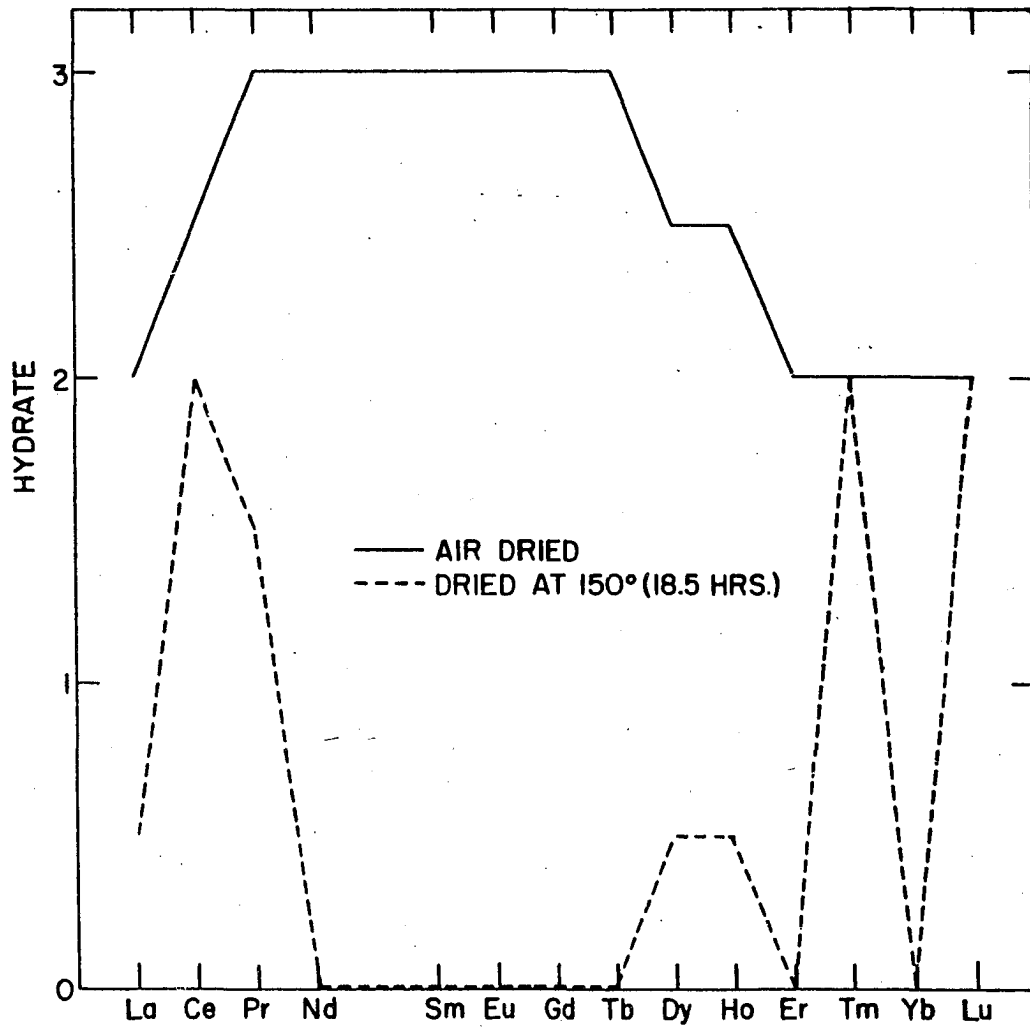
page 38), and the concentration of NTA is at least twice the concentration of the rare-earth ions. Because of the excess NTA, one is sure that at least part of the rare-earth ions present are associated with two NTA anions, thereby reducing the concentration of the insoluble 1:1 rare-earth chelate species.

Gravimetric analyses on the solids in equilibrium with the saturated solutions used in the solubility determinations resulted in some unusual and puzzling results. The lightest members of the series, lanthanum, cerium and praseodymium, proved to be the most anomalous. Both the $LaNTA.2H_2O$ and $LaNTA.5H_2O$ species appeared to be approaching a composition of $LaNTA.2.5H_2O$ at 25° and $60^{\circ}C$. The dihydrated and pentahydrated cerium chelates appeared to be approaching a composition closer to two waters at these temperatures. The $PrNTA.H_2O$ and $PrNTA.3H_2O$ were converted to $PrNTA.5H_2O$ at $25^{\circ}C$, but seemed to be going to $PrNTA.2H_2O$ at $60^{\circ}C$. The trihydrates of the 1:1 chelate species of the middle rare earths, neodymium through terbium, were stable at both temperatures. For the heavier members of the series, the tetrahydrated NTA complex appeared to be the stable form. The exceptions occurred with the dysprosium and holmium chelates, which in addition to a tetrahydrated species, appeared to form mixtures of different hydrates, resulting in non-integral hydration numbers.

There appears to be no simple explanation for the ir-
regular behavior of these compounds and, since this was just
a cursory investigation, no attempt was made to generalize
the data. However, it is hoped that this strange behavior
will arouse further interest and that a thorough investiga-
tion into these and similar compounds will be made, which will
throw more light upon their interesting and anomalous behavior.

SUMMARY

1. The stability constants of the 1:1 and 1:2 rare earth-NTA complexes were measured at 10°, 20°, 30° and 40^OC at an ionic strength of 0.10.

2. The thermodynamic functions $\triangle F^O$, $\triangle H^O$ and $\triangle S^O$ were calculated for the 1:1 and 1:2 rare earth-NTA complexes from the temperature dependence of the stability constants. It was found that the main driving force for chelation was a favorable entropy change.

3. The solid 1:1 rare earth-NTA chelates were prepared at temperatures ranging from room temperature to 100^OC. Analyses were done on all the chelates to determine their composition (waters of hydration), and thermal decompositions were done on the various hydrates found.

4. The solubility of each hydrate of the rare earth-NTA chelates were measured at 25° and 60^OC. Analysis of the solids in equilibrium with the saturated solutions indicated the most stable hydrate at each of these temperatures.

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ACKNOWLEDGMENTS

APPENDIX

Table 8. Raw data for the calculation of the stability constant of the 1:2 rare earth-NTA complexes at ionic strength = 0.10 (KNO$_3$)

R.E. sample	Cd standard height	Cd height	% Cd	$[Cd^{+2}]$ x10^4	pH	$[H^+]$ x10^7 corrected	$[NTA^{-3}]$	ϕ	K2
					A. 10°C				
La	22.60	1.80	7.96	0.80	6.70	2.51	1.83×10^{-9}	5.90×10^5	4.76×10^7
Ce	22.60	3.07	13.58	1.36	6.36	5.50	1.01×10^{-9}	1.12×10^6	1.49×10^8
Pr	22.08	3.60	16.30	1.63	6.58	3.31	8.13×10^{-10}	1.43×10^6	2.39×10^8
Nd	22.08	4.42	20.02	2.00	6.39	5.13	6.35×10^{-10}	1.89×10^6	3.94×10^8
Sm	21.98	6.60	30.03	3.00	6.58	3.31	3.70×10^{-10}	3.52×10^6	1.17×10^9
Eu	20.40	7.60	37.25	3.72	6.50	3.98	2.68×10^{-10}	5.12×10^6	2.21×10^9
Gd	22.10	8.11	36.70	3.67	6.40	5.01	2.74×10^{-10}	4.99×10^6	2.12×10^9
Tb	22.10	8.91	40.32	4.03	6.52	3.80	2.36×10^{-10}	5.94×10^6	2.85×10^9
Dy	22.03	8.70	39.49	3.95	6.40	5.01	2.44×10^{-10}	5.72×10^6	2.69×10^9
Ho	22.03	8.18	37.13	3.71	6.40	5.01	2.70×10^{-10}	5.08×10^6	2.19×10^9
Er	22.55	7.20	31.93	3.19	6.40	5.01	3.39×10^{-10}	3.89×10^6	1.38×10^9
Tm	22.55	6.60	29.27	2.93	6.25	7.08	3.84×10^{-10}	3.36×10^6	1.06×10^9
Yb	21.79	6.40	29.37	2.94	6.25	7.08	3.81×10^{-10}	3.39×10^6	1.10×10^9
Lu	21.79	7.20	33.04	3.30	6.32	6.03	3.22×10^{-10}	4.13×10^6	1.53×10^9
Y	21.79	5.93	27.21	2.72	6.10	10.00	4.26×10^{-10}	2.97×10^6	8.47×10^8

Table 8. (Continued)

R.E. sample	Cd standard height	Cd height	% Cd	$[Cd^{+2}]$ $\times 10^4$	pH	$[H^+]$ $\times 10^7$ corrected	$[NTA^{-3}]$	$\emptyset$	K_2
					B. 20°C				
La	26.01	2.68	10.30	1.03	6.60	3.16	2.17×10^{-9}	5.07×10^5	2.44×10^7
Ce	26.45	3.91	14.78	1.48	6.75	2.24	1.44×10^{-9}	8.00×10^5	5.61×10^7
Pr	26.45	4.80	18.15	1.82	6.49	4.07	1.12×10^{-9}	1.06×10^6	2.05×10^8
Nd	25.58	5.70	22.28	2.23	6.46	4.37	8.69×10^{-10}	1.41×10^6	3.31×10^8
Sm	25.58	8.32	32.53	3.25	6.31	6.17	5.19×10^{-10}	2.55×10^6	9.20×10^8
Eu	26.15	9.90	37.86	3.79	6.40	5.01	4.09×10^{-10}	3.37×10^6	1.49×10^9
Gd	25.95	10.07	38.80	3.88	6.20	7.94	3.92×10^{-10}	3.54×10^6	1.62×10^9
Tb	25.95	11.00	42.39	4.24	6.30	6.31	3.39×10^{-10}	4.20×10^6	2.17×10^9
Dy	25.81	10.50	40.68	4.07	6.28	6.61	3.64×10^{-10}	3.86×10^6	1.87×10^9
Ho	25.81	10.20	39.52	3.95	6.29	6.46	3.83×10^{-10}	3.64×10^6	1.70×10^9
Er	26.05	9.40	36.08	3.61	6.30	6.31	4.41×10^{-10}	3.09×10^6	1.29×10^9
Tm	26.05	9.08	34.86	3.49	6.12	9.55	4.65×10^{-10}	2.89×10^6	1.13×10^9
Yb	25.99	9.11	35.05	3.51	6.27	6.76	4.60×10^{-10}	2.94×10^6	1.18×10^9
Lu	25.99	9.74	37.48	3.75	6.22	7.59	4.17×10^{-10}	3.30×10^6	1.45×10^9
Y	25.95	8.60	33.14	3.31	6.10	10.00	5.03×10^{-10}	2.64×10^6	9.70×10^8

Table 8. (Continued)

R.E. sample	Cd standard height	Cd height	% Cd	$[CD^{+2}]$ $x10^4$	pH	$[H^+]$ $x10^7$ corrected	$[NTA^{-3}]$	$\emptyset$	K_2
				C. 300C					
La	22.66	2.77	12.22	1.22	6.77	2.14	$2.54x10^{-9}$	$4.41x10^5$	$5.38x10^7$
Ce	22.66	3.98	17.56	1.76	6.77	2.14	$1.65x10^{-9}$	$7.10x10^5$	$1.26x10^8$
Pr	23.03	5.09	22.10	2.21	6.48	4.17	$1.25x10^{-9}$	$9.70x10^5$	$2.17x10^8$
Nd	23.03	5.99	26.01	2.60	6.32	6.03	$1.01x10^{-9}$	$1.24x10^6$	$3.32x10^8$
Sm	22.80	8.24	36.14	3.61	6.41	4.90	$6.26x10^{-10}$	$2.17x10^6$	$8.91x10^8$
Eu	22.72	9.19	40.45	4.05	6.43	4.68	$5.17x10^{-10}$	$2.72x10^6$	$1.32x10^9$
Gd	22.80	9.53	41.80	4.18	6.41	4.90	$4.93x10^{-10}$	$2.88x10^6$	$1.47x10^9$
Tb	23.10	10.41	45.06	4.51	6.31	6.17	$4.29x10^{-10}$	$3.38x10^6$	$1.91x10^9$
Dy	23.10	10.10	43.72	4.37	6.36	5.50	$4.54x10^{-10}$	$3.17x10^6$	$1.72x10^9$
Ho	22.72	9.40	41.37	4.14	6.30	6.31	$5.01x10^{-10}$	$2.82x10^6$	$1.40x10^9$
Er	23.00	8.88	38.61	3.86	6.40	5.01	$5.63x10^{-10}$	$2.46x10^6$	$1.11x10^9$
Tm	23.00	8.70	37.83	3.78	6.32	6.03	$5.81x10^{-10}$	$2.37x10^6$	$1.04x10^9$
Yb	23.08	8.93	38.69	3.87	6.41	4.90	$5.57x10^{-10}$	$2.49x10^6$	$1.13x10^9$
Lu	22.48	9.18	40.84	4.08	6.30	6.31	$5.15x10^{-10}$	$2.73x10^6$	$1.33x10^9$
Y	22.48	8.08	35.94	3.59	6.33	5.89	$6.28x10^{-10}$	$2.16x10^6$	$8.81x10^8$

Table 8. (Continued)

R.E. sample	Cd standard height	Cd height	% Cd	$[CD^{+2}]$ $\times 10^4$	pH	$[H^+]$ $\times 10^7$ corrected	$[NTA^{-3}]$	ϕ	K_2
					D. 40°C				
La	24.61	3.55	14.43	1.44	6.68	2.69	3.48×10^{-9}	3.28×10^5	4.72×10^7
Ce	24.61	5.30	21.54	2.15	6.88	1.70	2.13×10^{-9}	5.71×10^5	1.29×10^8
Pr	25.80	6.37	24.69	2.47	6.54	3.72	1.78×10^{-9}	7.00×10^5	1.84×10^8
Nd	25.80	7.26	28.14	2.81	6.59	3.31	1.49×10^{-9}	8.60×10^5	2.63×10^8
Sm	25.59	9.81	38.34	3.83	6.40	5.13	9.42×10^{-10}	1.46×10^6	6.47×10^8
Eu	25.97	11.53	44.40	4.44	6.43	4.79	7.33×10^{-10}	1.97×10^6	1.08×10^9
Gd	25.59	11.19	43.73	4.37	6.22	7.76	7.54×10^{-10}	1.90×10^6	1.01×10^9
Tb	25.33	11.90	46.98	4.70	6.40	5.13	6.59×10^{-10}	2.23×10^6	1.34×10^9
Dy	25.33	11.23	44.33	4.43	6.36	5.62	7.35×10^{-10}	1.96×10^6	1.08×10^9
Ho	25.88	11.00	42.50	4.25	6.40	5.13	7.91×10^{-10}	1.80×10^6	9.42×10^8
Er	25.88	10.96	42.35	4.23	6.46	4.47	7.98×10^{-10}	1.79×10^6	9.30×10^8
Tm	25.63	10.53	41.08	4.11	6.28	6.76	8.38×10^{-10}	1.69×10^6	8.49×10^8
Yb	25.63	10.75	41.94	4.19	6.28	6.76	8.11×10^{-10}	1.75×10^6	8.91×10^8
Lu	26.10	11.28	43.22	4.32	6.20	8.13	7.69×10^{-10}	1.86×10^6	9.77×10^8
Y	26.10	9.90	37.93	3.79	6.10	10.20	9.58×10^{-10}	1.44×10^6	6.33×10^8

Table 9. Raw data for the calculation of the stability constant of the 1:1 rare earth-NTA complexes at ionic strength = 0.10 (KNO_3)

R.E. sample	Eu standard height	Eu height	% Eu	$[Eu^{+3}]$ x10^4	pH	$[H^+]$ x10^7 corrected	$[NTA^{-3}]$	$\emptyset$	K_1
A. 10°C									
La	20.92	3.90	18.64	1.86	6.40	5.01	2.56×10^{-11}	6.10×10^6	7.21×10^9
Ce	20.92	5.70	27.24	2.72	6.35	5.62	1.71×10^{-11}	1.20×10^7	1.50×10^{10}
Pr	20.92	7.15	34.18	3.42	6.50	3.98	1.14×10^{-11}	3.06×10^7	4.66×10^{10}
Nd	20.92	8.56	40.92	4.09	6.38	5.25	8.53×10^{-12}	5.00×10^7	8.64×10^{10}
Sm	20.78	9.88	47.55	4.76	6.40	5.01	7.11×10^{-12}	6.30×10^7	1.12×10^{11}
Eu	This value interpolated from 10°C curve versus cadmium								1.59×10^{11}
Gd	20.78	9.41	45.28	4.53	6.45	4.47	7.60×10^{-12}	6.00×10^7	1.06×10^{11}
Tb	20.78	9.50	45.72	4.57	6.40	5.01	7.47×10^{-12}	6.10×10^7	1.06×10^{11}
Dy	20.78	10.60	51.01	5.10	6.30	6.31	6.04×10^{-12}	8.50×10^7	1.66×10^{11}
Ho	21.33	11.52	54.01	5.40	6.40	5.01	5.36×10^{-12}	1.01×10^8	2.12×10^{11}
Er	21.33	12.15	56.96	5.70	6.38	5.25	4.75×10^{-12}	1.20×10^8	2.73×10^{11}
Tm	20.80	13.17	63.32	6.33	6.53	3.72	3.63×10^{-12}	1.74×10^8	4.68×10^{11}
Yb	20.80	13.93	66.97	6.70	6.48	4.17	3.08×10^{-12}	2.18×10^8	6.57×10^{11}
Lu	21.75	14.85	68.28	6.83	6.50	3.98	2.91×10^{-12}	2.35×10^8	7.30×10^{11}
Y	21.75	9.20	42.30	4.23	6.50	3.98	8.54×10^{-12}	4.70×10^7	7.69×10^{10}

Table 9. (Continued)

R.E. sample	Eu standard height	Eu height	% Eu	$[Eu^{+3}]$ $\times 10^4$	pH	$[H^+]$ $\times 10^6$ corrected	$[NTA^{-3}]$	ϕ	K_1
					B. $20^{\circ}C$				
La	18.78	3.55	18.90	1.89	5.52	3.80	1.95×10^{-11}	6.50×10^6	7.44×10^9
Ce	18.78	5.08	27.05	2.71	5.50	3.98	1.20×10^{-11}	2.04×10^7	2.70×10^{10}
Pr	18.78	6.75	35.94	3.59	5.42	4.79	7.49×10^{-12}	5.20×10^7	8.48×10^{10}
Nd	18.78	7.55	40.20	4.02	5.43	4.68	5.99×10^{-12}	7.50×10^7	1.35×10^{11}
Sm	18.63	8.78	47.13	4.71	5.32	6.03	4.49×10^{-12}	1.16×10^8	2.38×10^{11}
Eu	This value interpolated from $20^{\circ}C$ curve versus cadmium								2.24×10^{11}
Gd	18.63	8.42	45.20	4.52	5.32	6.03	5.43×10^{-12}	8.30×10^7	1.47×10^{11}
Tb	18.63	9.17	49.22	4.92	5.32	6.03	4.62×10^{-12}	1.06×10^8	2.02×10^{11}
Dy	18.63	9.53	51.15	5.12	5.31	6.17	4.24×10^{-12}	1.21×10^8	2.42×10^{11}
Ho	18.30	10.10	55.19	5.52	5.45	4.47	3.61×10^{-12}	1.53×10^8	3.36×10^{11}
Er	18.30	10.80	59.02	5.90	5.41	4.90	3.11×10^{-12}	1.90×10^8	4.58×10^{11}
Tm	18.30	11.42	62.40	6.24	5.45	4.47	2.69×10^{-12}	2.32×10^8	6.12×10^{11}
Yb	18.30	12.34	67.43	6.74	5.49	4.07	2.16×10^{-12}	3.12×10^8	9.51×10^{11}
Lu	18.05	12.70	70.36	7.04	5.32	6.03	1.87×10^{-12}	3.77×10^8	1.26×10^{12}
Y	18.05	8.42	46.64	4.66	5.23	7.41	5.13×10^{-12}	9.10×10^7	1.69×10^{11}

Table 9. (Continued)

R.E. sample	Eu standard height	Eu height	% Eu	$[Eu^{+3}]$ x10^4	pH	$[H^+]$ x10^6 corrected	$[NTA^{-3}]$	$\emptyset$	K_1

C. 30°C

R.E. sample	Eu standard height	Eu height	% Eu	$[Eu^{+3}]$ x10^4	pH	$[H^+]$ x10^6 corrected	$[NTA^{-3}]$	$\emptyset$	K_1
La	21.05	4.55	21.62	2.16	5.53	3.72	1.12×10^{-11}	2.14×10^7	2.81×10^{10}
Ce	21.05	5.93	28.17	2.82	5.49	4.07	8.70×10^{-12}	2.70×10^7	3.52×10^{10}
Pr	21.05	7.37	35.01	3.50	5.49	4.07	6.21×10^{-12}	5.22×10^7	7.70×10^{10}
Nd	21.05	8.60	40.86	4.09	5.41	4.90	4.97×10^{-12}	7.44×10^7	1.18×10^{11}
Sm	21.19	10.08	47.57	4.76	5.37	5.37	3.73×10^{-12}	1.22×10^8	2.21×10^{11}
Eu	This value calculated from the La-Tb values measured vs cadmium								3.05×10^{11}
Gd	21.19	9.90	46.72	4.67	5.43	4.68	3.75×10^{-12}	1.25×10^8	2.32×10^{11}
Tb	21.19	10.88	51.34	5.13	5.41	4.90	3.12×10^{-12}	1.65×10^8	3.33×10^{11}
Dy	20.90	11.48	54.93	5.49	5.70	2.51	2.70×10^{-12}	2.03×10^8	4.44×10^{11}
Ho	21.19	11.85	55.92	5.59	5.46	4.37	2.59×10^{-12}	2.16×10^8	4.84×10^{11}
Er	20.81	12.75	61.27	6.13	5.40	5.01	2.07×10^{-12}	2.96×10^8	7.61×10^{11}
Tm	20.81	13.50	64.87	6.49	5.40	5.01	1.77×10^{-12}	3.67×10^8	1.04×10^{12}
Yb	20.81	14.40	69.20	6.92	5.42	4.79	1.46×10^{-12}	4.74×10^8	1.53×10^{12}
Lu	20.81	14.60	70.16	7.02	5.30	6.31	1.39×10^{-12}	5.05×10^8	1.68×10^{12}
Y	20.90	10.50	50.24	5.02	5.22	7.59	3.25×10^{-12}	1.55×10^8	3.08×10^{11}

Table 9. (Continued)

R.E. sample	Eu standard height	Eu height	% Eu	$[Eu^{+3}]$ x10^4	pH	$[H^+]$ x10^6 corrected	$[NTA^{-3}]$	ϕ	K_1

D. 40°C

R.E. sample	Eu standard height	Eu height	% Eu	$[Eu^{+3}]$ x10^4	pH	$[H^+]$ x10^6 corrected	$[NTA^{-3}]$	ϕ	K_1
La	16.42	3.53	21.50	2.15	5.67	2.75	8.88×10^{-12}	2.10×10^7	2.58×10^{10}
Ce	16.42	4.56	27.77	2.78	5.68	2.69	6.66×10^{-12}	3.20×10^7	4.06×10^{10}
Pr	16.42	6.15	37.45	3.75	5.55	3.63	4.44×10^{-12}	6.70×10^7	9.52×10^{10}
Nd	16.42	6.88	41.90	4.19	5.57	3.47	3.33×10^{-12}	1.24×10^8	2.10×10^{11}
Sm	15.69	8.20	52.26	5.23	5.48	4.27	2.22×10^{-12}	2.31×10^8	4.72×10^{11}
Eu	This value extrapolated from 10°, 20° and 30°C values								4.17×10^{11}
Gd	15.69	7.81	49.78	4.98	5.41	5.01	2.41×10^{-12}	2.07×10^8	4.11×10^{11}
Tb	16.31	8.55	52.42	5.24	5.40	5.13	2.17×10^{-12}	2.42×10^8	5.05×10^{11}
Dy	16.31	9.13	55.98	5.60	5.62	3.09	1.88×10^{-12}	2.98×10^8	6.74×10^{11}
Ho	16.31	9.33	57.20	5.72	5.46	4.47	1.79×10^{-12}	3.20×10^8	7.46×10^{11}
Er	16.31	10.05	61.62	6.16	5.40	5.13	1.49×10^{-12}	4.14×10^8	1.08×10^{12}
Tm	16.20	10.90	67.28	6.73	5.40	5.13	1.16×10^{-12}	5.81×10^8	1.78×10^{12}
Yb	16.20	11.10	68.52	6.85	5.42	4.90	1.10×10^{-12}	6.23×10^8	1.97×10^{12}
Lu	16.20	11.63	71.79	7.18	5.28	6.76	9.43×10^{-13}	7.61×10^8	2.69×10^{12}
Y	16.20	8.51	52.53	5.25	5.23	7.59	2.17×10^{-12}	2.42×10^8	5.07×10^{11}

Table 10. $\triangle F_1^0$ Kcal/mol, for formation of RNTA at ionic strength = 0.10 (KNO_3)

Rare earth	10°C	20°C	30°C	40°C
La	-12.78	-13.24	-14.50	-14.91
Ce	-13.19	-13.99	-14.64	-15.20
Pr	-13.82	-14.66	-15.11	-15.74
Nd	-14.17	-14.93	-15.36	-16.22
Sm	-14.32	-15.27	-15.73	-16.72
Eu	-14.51	-15.23	-15.93	-16.65
Gd	-14.29	-14.98	-15.78	-16.64
Tb	-14.29	-15.17	-15.98	-16.77
Dy	-14.54	-15.27	-16.16	-16.95
Ho	-14.68	-15.47	-16.20	-17.01
Er	-14.82	-15.64	-16.48	-17.24
Tm	-15.12	-15.81	-16.67	-17.55
Yb	-15.31	-16.07	-16.90	-17.61
Lu	-15.36	-16.23	-16.97	-17.81
Y	-14.11	-15.06	-15.94	-16.78

Table 11. $\triangle F_2^0$ Kcal/mol, for formation of $R(NTA)_2^{-3}$ at ionic strength = 0.10 (KNO_3)

Rare earth	10°C	20°C	30°C	40°C
La	-9.95	-9.91	-10.72	-10.99
Ce	-10.59	-10.40	-11.23	-11.62
Pr	-10.86	-11.15	-11.57	-11.83
Nd	-11.15	-11.43	-11.82	-12.06
Sm	-11.75	-12.02	-12.42	-12.62
Eu	-12.10	-12.30	-12.65	-12.94
Gd	-12.09	-12.35	-12.72	-12.90
Tb	-12.24	-12.53	-12.87	-13.08
Dy	-12.22	-12.44	-12.82	-12.94
Ho	-12.10	-12.38	-12.69	-12.85
Er	-11.84	-12.22	-12.55	-12.85
Tm	-11.70	-12.14	-12.51	-12.80
Yb	-11.71	-12.17	-12.55	-12.82
Lu	-11.89	-12.29	-12.65	-12.88
Y	-11.57	-12.06	-12.42	-12.61

Table 12. Enthalpy changes for formation of rare earth-NTA complexes at ionic strength = 0.10 (KNO_3)

Rare earth	ΔH_1^o, $\frac{Kcal}{mol}$	ΔH_2^o, $\frac{Kcal}{mol}$
La	8.23	-0.32[a]
Ce	5.33	-0.93[a]
Pr	3.40	-1.25[a]
Nd	3.97	-1.91
Sm	4.41[b]	-2.98
Eu	5.25	-3.62
Gd	7.03	-4.05
Tb	8.31	-3.76
Dy	7.31	-4.25
Ho	6.54	-4.55
Er	7.31	-2.21
Tm	7.31	-0.99
Yb	5.96	-0.85
Lu	6.88	-2.07
Y	10.29	-1.49

[a]Omitted 20°C value in calculation

[b]Omitted 10°C value in calculation

Table 13. ΔS_1^o entropy units, for formation of RNTA at ionic strength = 0.10 (KNO_3)

Rare earth	10°C	20°C	30°C	40°C
La	74.2	73.2	75.0	73.9
Ce	65.4	65.9	65.9	65.6
Pr	60.8	61.6	61.1	61.1
Nd	64.1	64.5	63.8	64.5
Sm	66.9	67.1	66.4	67.5
Eu	69.8	69.9	69.9	69.9
Gd	75.3	75.1	75.2	75.6
Tb	79.8	80.1	80.1	80.1
Dy	77.2	77.0	77.4	77.5
Ho	74.9	75.1	75.0	75.2
Er	78.2	78.3	78.5	78.4
Tm	79.2	78.9	79.1	79.4
Yb	75.1	75.1	75.4	75.3
Lu	78.5	78.8	78.7	78.8
Y	86.2	86.5	86.5	86.4

Table 14. ΔS_2^0 entropy units, for formation of $R(NTA)_2^{-3}$ at ionic strength = 0.10 (KNO_3)

Rare earth	$10^{\circ}C$	$20^{\circ}C$	$30^{\circ}C$	$40^{\circ}C$
La	34.0	32.7	34.3	34.1
Ce	34.1	32.3	34.0	34.1
Pr	33.9	33.8	34.0	33.8
Nd	32.6	32.5	32.7	32.4
Sm	31.0	30.8	31.1	30.8
Eu	29.9	29.6	29.8	29.8
Gd	28.4	28.3	28.6	28.3
Tb	29.9	29.9	30.1	29.8
Dy	28.1	27.9	28.3	27.7
Ho	26.7	26.7	26.9	26.5
Er	34.0	34.1	34.1	34.0
Tm	37.8	38.0	38.0	37.7
Yb	38.4	38.6	38.6	38.2
Lu	34.7	34.9	34.9	34.5
Y	35.6	36.1	36.1	35.5

Table 15. Hydrates of the solid rare earth-NTA species formed at various temperatures

RNTA	$25^{\circ}C$	$60^{\circ}C$	$80^{\circ}C$	$90^{\circ}C$	$100^{\circ}C$	Hot plate
La	5.11				1.49	2.12
Ce	5.00					2.34
Pr	3.13				1.18	2.99
Nd	3.14				2.85	3.00
Sm	3.17				2.93	3.03
Eu	3.18				2.93	3.02
Gd	3.23				2.91	2.96
Tb	3.41				1.62	2.99
Dy	4.40	4.14	4.06	4.01	4.01	2.68
Ho	4.39	4.13	4.17	3.98	3.97	2.74
Er	4.47	4.23	4.08	4.03	4.03	1.96
Tm	4.42	4.13	4.27	3.99	4.01	1.97
Yb	4.29	4.07	4.07	3.99	4.03	1.68
Lu	4.29	4.11	4.03	4.01	4.09	2.03

Table 16. Thermal decomposition of the rare earth-NTA
hydrates

RNTA	Hydrate, after drying at:			
	Room temp.	106°C	129°C	150°C
La	2.12	1.48	0.68	0.57
Ce	2.34	1.94	1.75	1.89
Pr	2.99	1.67	1.33	1.41
Nd	3.00	1.84	0.46	0.19
Sm	3.03	1.14	0.46	0.19
Eu	3.02	1.59	0.24	0.07
Gd	2.96	0.63	0.56	0.16
Tb	2.99	0.81	0.62	0.19
Dy	2.68	0.92	0.66	0.28
Ho	2.74	0.97	0.71	0.67
Er	1.96	0.14	0.32	0.18
Tm	1.97	2.02	2.06	1.73
Yb	1.68	0.16	0.26	0.16
Lu	2.03	2.29	1.97	2.02

Table 17. Solubilities of rare earth-NTA hydrates,
$$\frac{\text{grams RNTA}}{100 \text{ grams H}_2\text{O}}$$

RNTA	Original hydrate	6 months at 25°C		6 months at 60°C	
		Hydrate	Solubility	Hydrate	Solubility
La	2.12	2.46	0.0105	2.41	0.0280
La	5.11	2.41	0.0130	2.39	0.0322
Ce	2.34	2.39	0.0270	2.21	0.0463
Ce	5.00	2.23	0.0237	2.15	0.0524
Pr	2.99	5.10	0.0959	2.16	0.1178
Pr	1.18	5.07	0.0653	1.42	0.2140
Nd	3.00	3.09	0.1402	2.96	0.1756
Sm	3.03	3.07	0.0800	3.05	0.1183
Eu	3.02	2.99	0.0724	3.12	0.1078
Gd	2.96	3.04	0.0845	2.96	0.1187
Tb	2.99	3.04	0.0929	3.09	0.1459
Dy	2.68	2.93	0.1545	2.74	0.1928
Dy	4.01	4.00	0.0644	3.95	0.1506
Ho	2.74	3.64	0.3355	1.64	0.1902
Ho	3.97	4.01	0.0580	3.97	0.1274
Er	1.96	2.76	0.2320	2.06	0.1940
Er	4.03			3.99	0.1188
Tm	1.97	4.02	0.0518	4.02	0.1024
Yb	1.68	4.12	0.0575	4.14	0.1006
Lu	2.03	4.04	0.0578	4.02	0.1026
Y	3.98	3.90	0.0536	3.87	0.1315