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Complex Ions of Lanthanum in Aqueous Solutions

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DISSERTATION

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of the

UNIVERSITY OF CALIFORNIA

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ABSTRACT

The complexing of lanthanum by various anions and weak acids was investigated by observing the light absorption of the complex formed with thenoyltrifluoroacetone (TTA). This species showed the properties needed for a satisfactory spectrophotometric method of analysis.

In order to determine the equilibrium constants for the complexing reactions, the aqueous spectra of TTA and its enolate ion were checked and the acid dissociation constant for TTA redetermined. The experimental value, $K_{298}^{\circ} = 2.96 \times 10^{-7}$, was found to disagree with the constant reported previously: $K_{298}^{\circ} = 6.7 \times 10^{-7}$.

The molar extinction coefficient for the lanthanum-TTA complex ion was measured and then used to determine the concentration of the complex in the various solutions. The complexing constant was studied as a function of temperature at an ionic strength of unity.

Acetate-acetic acid buffers were used to fix the hydrogen ion concentration in most experiments. Acetate ion was found to complex lanthanum ion partially under the conditions used and the equilibrium constant for the reaction was investigated as a function of temperature.

The complexing of lanthanum by a large number of anions was studied by observing the decrease in the concentration of the TTA complex as the lanthanum concentration was diminished by the added complexing agent. In this way values of complexing constants for Cl^- , NO_3^- , SO_4^{2-} , ClO_3^- , acetate, succinate, tartrate, phthalate, lactate, and citrate were determined. Some of these were studied as a function of temperature and values of the heat and entropy were calculated for

the reactions.

Lithium ion was found to form a weak complex with TTA. Its stability was measured as a function of temperature and ionic strength.

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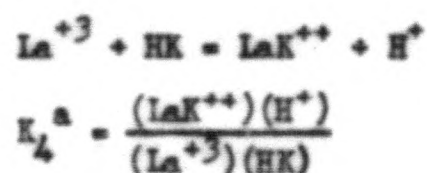
INTRODUCTION

The study of lanthanum complex-ion formation was undertaken as an exemplary aid in the treatment of the chemistry of other tripositive ions. The chemistry of the plus-three lanthanum ion should be typical of the chemistry of the tri-positive ions of both the rare-earth and actinide elements as well as the other metals in the same column as lanthanum, in the periodic table. To a lesser extent, ionic complex formation by various other plus-three metallic ions should be similar.

The spectrophotometric method of analysis was used as a convenient measure of complex-ion formation. The choice of a complexing substance was limited by the requirements of the method of analysis: the complex-ion must have an absorption spectrum within the limits of the equipment used; the complexing substance should have no absorption spectrum, or one sufficiently different from that of the complex-ion to permit the analysis for one in the presence of the other; the complexing substance must be stable in aqueous solution and inert toward chemical action, other than complex-formation, with the other ionic species involved in making up the solution; and the equilibrium constant for the lanthanum complex-ion formation should be large enough to permit the use of sufficiently dilute solutions that the lanthanum complex-ion formation will not materially change the reaction medium. Several organic complexing agents were considered before TTA, thenoyltrifluoroacetone^(1,2), was selected. The availability of previously determined absorption spectra data^(3,4,5) for the various species of TTA and of the acid dissociation constant⁽³⁾ for HK (designation for the weak acid form of the diketone, TTA), plus the previous, successful use of this chelating

agent with the extraction technique^(5,6,7), for complex-ion and salt formation of other metallic ions, made this choice seem the most promising.

The spectrophotometric analysis of the buffered experimental solutions gave the concentration of the lanthanum-chelate complex-ion directly. Knowing this and the hydrogen-ion concentration, an equilibrium constant was calculated for the reaction:



Two solutions were then prepared, which were identical except that one contained a complexing substance A. If A complexed the plus-three lanthanum ion to a detectable extent, the free-lanthanum ion concentration dropped and a corresponding decrease in the lanthanum-chelate complex-ion absorption was observed. The difference between the absorption of the blank and the sample was then a measure of the amount of complexing by A. In making the calculation, it was necessary to apply corrections to the blank to allow for the amount of lanthanum used up in complexing by A and to correct for any change in acidity between the two solutions.

Various inorganic and organic anions were investigated in this manner and the equilibrium constants for the individual lanthanum complex-ion formations were calculated. Spectrophotometric observations of all solutions were made at 25°C and one or more solutions of some of the complexes studied, were measured at 40°C and at a convenient temperature near 20°C.

The appreciable temperature effect on the acid dissociation constants of HK⁽³⁾, acetic acid^(8,9) used in buffering the experimental

^a(concentration) equilibrium constants are used throughout this paper.

solutions, and the lanthanum complex ions studied, required careful thermostating of the quartz absorption cells used in obtaining the spectrophotometric data required for the calculation of the acid dissociation and complexing constants.

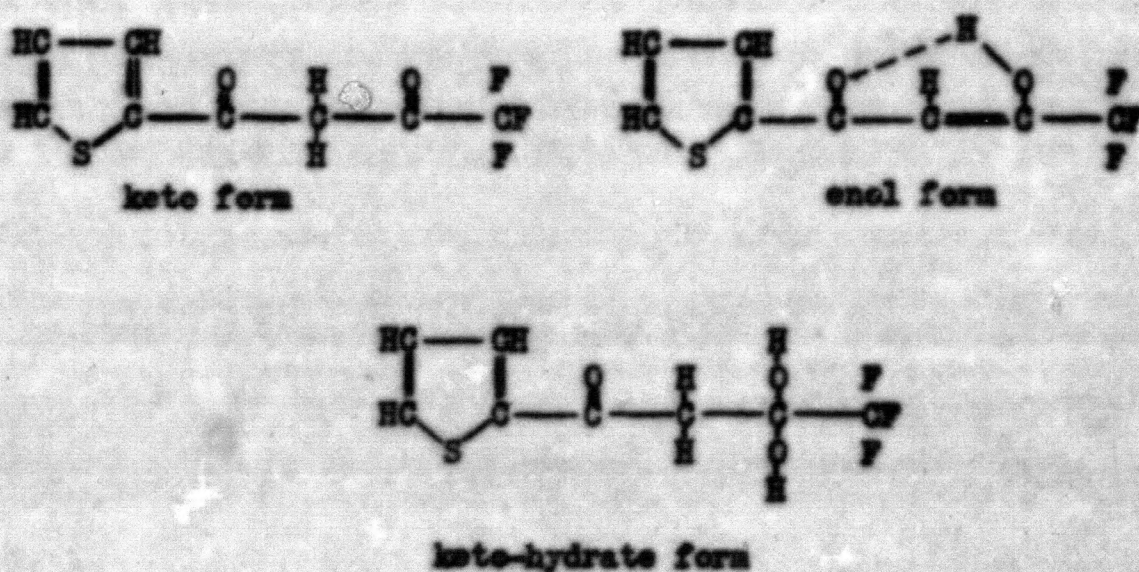
The initial survey observations on the spectra of the chelating agent, the chelate-ion, and the lanthanum-chelate complex-ion were made using the Cary Recording Spectrophotometer. More precise measurements, including all data used in calculating the various constants reported in this work, were then made using the Beckman Model DU Spectrophotometer.

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THE OPTICAL AND THERMODYNAMIC PROPERTIES OF TTA.

The choice of TTA, as the complexing agent to be used in this spectrophotometric study, required a knowledge of: the stability of its species in solution; its absorption spectrum, or spectra if more than one species is present in appreciable concentrations; and the absorption spectrum of the dissociated chelate-ion. The variance of these characteristics with ionic strength, acidity, and media must also be known.

The species of TTA, in solvents used in this work, have been reported^(2,3,4) as: approximately ninety-eight percent keto-hydrate form and two percent enol form in aqueous solution, at least ninety-seven percent enol form and possibly three percent keto form in "dry" benzene, and approximately ten percent keto-hydrate form with ninety percent enol form in benzene solutions which have been previously equilibrated with an aqueous phase.

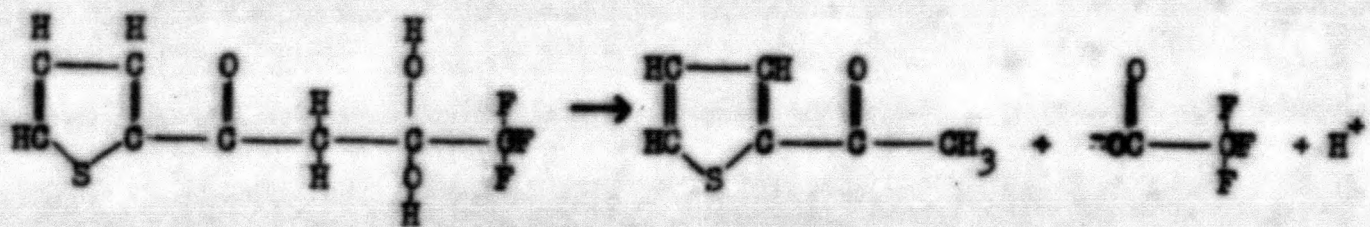


Throughout this paper, thionyltrifluoroacetone will be designated as TTA or HK depending on the interpretation desired. "TTA" will always

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refer to the total of all species present, i.e. $(TTA) = (HK) + (K^-) + (LaK^{++})$, while "HK" is used to designate only the portion of the total TTA present as a weak acid, i.e. $(HK) = (TTA) - (K^-) - (LaK^{++})$.

Hydrolysis of TTA-Hydrate.— Previous work on TTA ⁽³⁾ has shown a slow, nearly linear with respect to time, decomposition of aqueous solutions:



(This is not to be confused with the photochemical decomposition reported by King and Reas ⁽⁴⁾ on the basis of a large change in the spectrum of benzene solutions following prolonged exposure to light. The precaution was taken of keeping aqueous TTA stock solutions in opaque containers). Of the two decomposition or hydrolysis products, trifluoroacetic acid and 2-acetyl-thiophene, significant light absorption interference is due only to the latter. As may be seen from Figure 1, the absorption spectrum of aqueous solutions of 2-acetyl-thiophene (hereafter referred to as AT) is very similar, in shape and intensity of absorption, to that of aqueous TTA solutions. The two TTA maxima are displaced about fifty angstroms toward longer wavelengths from the equivalent AT maxima and the TTA molar extinction coefficients at these peaks are slightly larger than those in the aqueous AT absorption spectrum. This similarity precludes the spectrophotometric analysis of aqueous TTA stock solutions that have stood long enough for an appreciable amount of hydrolysis to have taken place. A reliable analysis for TTA concentration required the extraction of TTA into benzene, from an acidified aqueous solution, and the subsequent

analysis of the benzene solution. In this solvent, the acetyl-thiophene absorption does not interfere with the TTA absorption, since the maxima of the latter have been moved to longer wavelengths, as seen in Figure 6. The spectrophotometrically obtained TTA concentration in the benzene solution was then corrected for the non-extracted TTA, remaining in the aqueous phase at equilibrium with the organic phase, by the proper use of the distribution coefficient⁽⁴⁾ for the TTA concentration involved. This method of analysis gave agreement to better than one percent with the weight concentrations and the aqueous spectrophotometric analysis of freshly prepared aqueous TTA stock solutions.

Zebreski⁽³⁾ studied the rate of decomposition of aqueous solutions by observing the change in pH of unbuffered stock solutions upon standing over a period of five months. His analysis is based on the complete dissociation of the decomposition product, tri-fluoroacetic acid, to liberate hydrogen ion. Assuming a first order rate law,

$$\frac{d(H^+)}{dt} = - \frac{d(TTA)}{dt} = k(TTA)$$

with the appearance of one H⁺ accompanying the disappearance of one TTA, the observed Δ(H⁺) is very nearly equal to the -Δ(TTA). A first order rate constant of 5.0 x 10⁻⁷ min.⁻¹ was calculated, which was apparently independent of hydrogen ion. Recalculation of his data, taking into consideration the decreased dissociation of HF with decreasing pH, gave a value for the rate constant of (4.5 to 6.5) x 10⁻⁷ min.⁻¹. Using data obtained from benzene extraction measurements, made on aqueous TTA stock solutions used in this current research, a first order rate constant of (8.4 to 9.2) x 10⁻⁷ min.⁻¹ was obtained. Why there should be a discrepancy between the two methods is not understood,

although a small difference in the temperature at which the stock solutions were kept could cause an appreciable variation in the rate of hydrolysis. The benzene extraction analyses, made at irregular intervals, were plotted for each of the various TTA stock solutions and the daily stock concentration was read off the graph.

Absorption Spectrum of HK.—Discrepancies in spectral data, reported by several authors^(3,4,5), required that the molar extinction coefficients of the chelating agent and of the enolate ion be checked at the absorption spectra peaks most suitable for quantitative measurement. The experimentally determined molar extinction coefficient values, for the two maxima characteristic of the predominant keto-hydrate species of TTA in aqueous solution, were in good agreement with Orr's data but did not agree as well with the values reported by Zebroski⁽³⁾ and by King and Reas⁽⁴⁾. These molar extinction coefficients at the given wavelengths, were obtained from the observed optical densities, at the individual wavelengths, of acidified, aqueous TTA solutions (made up by dissolving a known weight of vacuum distilled TTA in conductivity water and diluting to a known volume with the required amount of acid). The optical density (D_{λ}) is equal to the product of the cell length (l) in centimeters, the molar extinction coefficient (ϵ_{λ}), and the molar concentration (c) of the absorbing species. By definition, the optical density equals the logarithm, to the base ten, of the quotient of the incident light intensity divided by the transmitted light intensity.

$$D_{\lambda}^{cm.} = (l_{(cm.)})(\epsilon_{\lambda})(c) = \log I_0/I$$

Slight differences in the experimental media used by the aforementioned authors are shown in Table 1, which lists the molar extinction coeffi-

TABLE 1

Calculated Molar Extinction Coefficients of HK.

Expt.	$M \times 10^4$	$M \text{ HClO}_4$	$D^2 \text{ cm. } 3470\text{\AA} \epsilon_{\text{HK}}$	$D^2 \text{ cm. } 3380\text{\AA} \epsilon_{\text{HK}}$	$D^2 \text{ cm. } 2920\text{\AA} \epsilon_{\text{HK}}$	$D^2 \text{ cm. } 2665\text{\AA} \epsilon_{\text{HK}}$				
1	0.437	0.04	—	—	.0260	298	.6850	7840	.8780	10030
2	0.437	1.0	—	—	—	—	.6880	7870	.8810	10080
3	8.506	0.011	.1805	106	.5095	299	—	—	—	—
4	8.506	0.155 ^a	.1805	106	.5095	299	—	—	—	—
5	0.44	0.02	.0265	108	.0095	301	.6850	7880	—	—
6	0.3646	0.10	—	—	—	—	.5695	7810	—	—
7	0.4455	0.02	—	—	—	—	.7000	7850	.9050	10150
8	0.4027	0.238	—	—	.0241	300	.6304	7830	.7995	9920
Mean calculated values:				106	299	7850	10040			
Zebroski, BC-63 (in 0.001 $M \text{ HClO}_4$)				—	—	7950	10080			
King and Reas, AECG 2573 (in 0.133 $M \text{ HCl}$)				—	—	7940±60	10080±70			
Orr, UCRL 196 (in 0.01 $M \text{ HCl}$)				100	287	7840	10000			
Molar Extinction Coefficients ^b for 2-Acetyl-Thiophene at tabulated wavelengths.				45(53)	120(121)	6790	9460			

All optical densities tabulated above are corrected values ($D_{\text{obs.}} - D_{\text{blank}}$).^aUsed HCl in place of HClO_4 .^bValues calculated from Figure 3A in BC-63. The values at 3470 \AA and 3380 \AA were checked by rough calculations of data taken from experiments using old, partially hydrolyzed, aqueous TTA stock solution and showed satisfactory agreement (calculated values in parentheses).

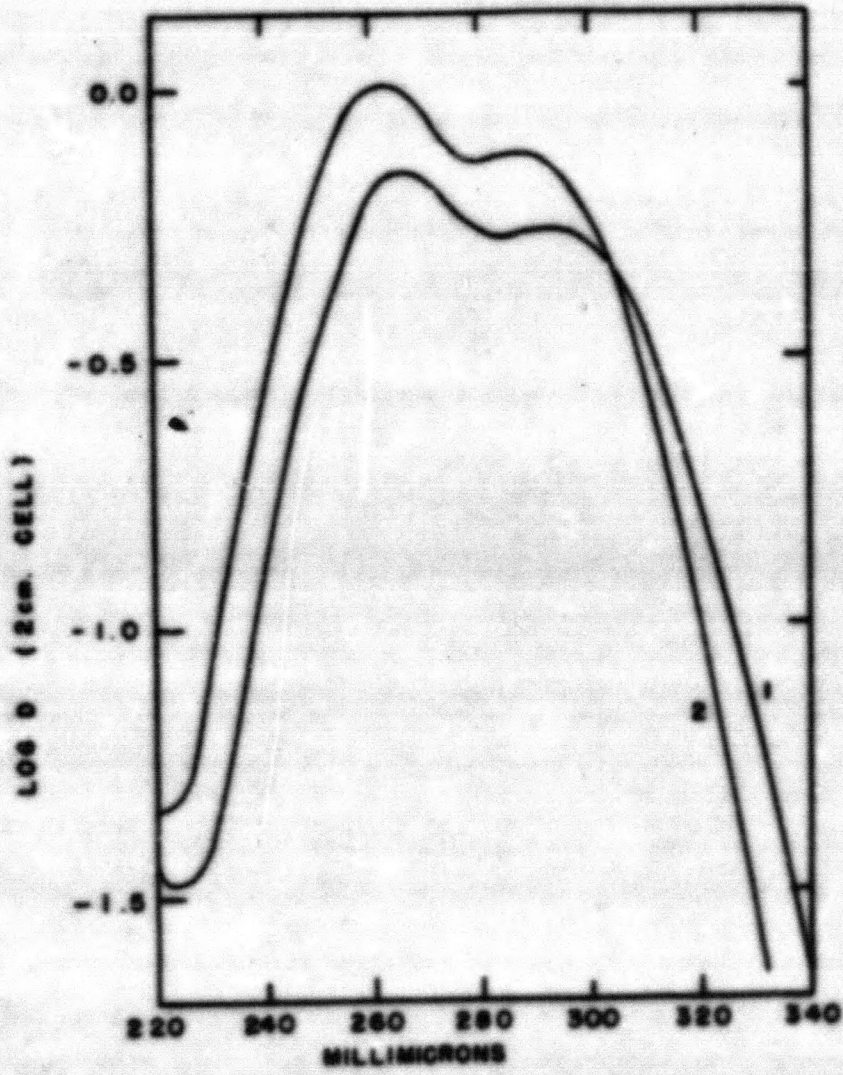
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coefficients for HK at the enolate ion maximum and at the lanthanum-chelate complex-ion maximum as well as the two HK maxima. The aqueous spectra of HK and its similarly absorbing product, acetyl-thiophene, are presented in Figure 1, to give a better over-all picture of their absorption characteristics. The mutual absorption interference of HK and enolate ion, in the wavelength region of the HK maxima, are shown in Figure 2. The data from figures 1 and 2 were taken from reference 3.

In order to investigate the observed discrepancies in the molar extinction coefficients, at varying acidities, a series of aqueous TTA solutions was prepared, with the acidity ranging from 0.01 M to 2.38 M (the ionic strength was approximately equal to the H^+ concentration in these solutions), and spectrophotometric observations were made at 3380Å and 3470Å. An increase in absorption with increasing acidities was noted at these wavelengths as seen in Figures 3 and 4. The more rapid increase in absorption of the solutions acidified by perchloric acid with respect to those acidified with hydrochloric acid may be due to the larger activity effect of perchlorates over chlorides. Orr⁽⁵⁾ reported similar observations and Zebroski⁽³⁾ reported an increase in the absorption with increasing acidity at the two HK maxima, as well. This phenomenon explains the variation in the molar extinction coefficients of HK, tabulated in Table 1, reported by authors mentioned and the values calculated in this paper. Zebroski offered the possibility of the formation of an oxonium-ion form of the keto-hydrate, as an explanation of this effect.

A further deviation in calculated molar extinction coefficients of HK was noted when acidified TTA blanks containing various amounts of sodium perchlorate were observed to give greater absorption than

FIG. 1



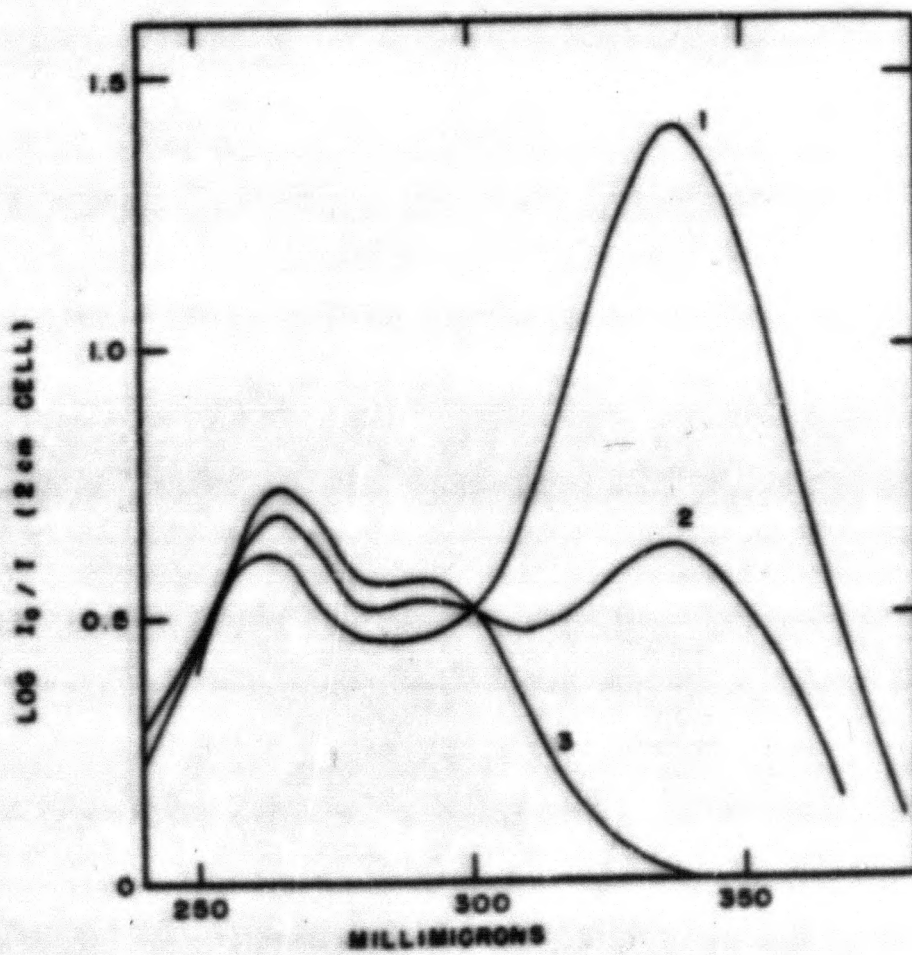
1. 3.52×10^{-5} M TTA IN 0.001 M HClO₄
2. 5.11×10^{-5} M 2-ACETYL THIOPHENE IN WATER

THE AQUEOUS SPECTRUM OF TTA AND 2-ACETYL THIOPHENE SOLUTIONS.

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FIG. 2

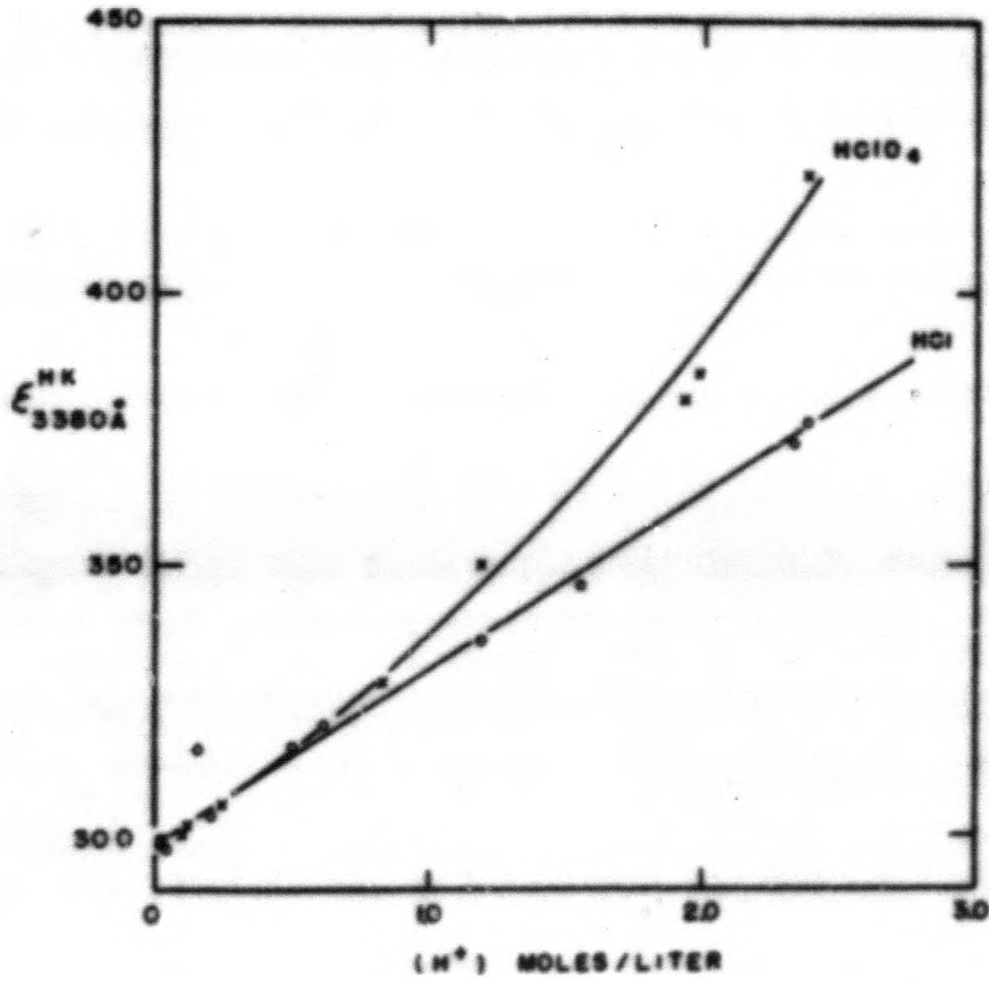


4.40×10^{-3} M TTA 1. AT pH 9.08
2. AT pH 6.81
3. AT pH 1.58

PARTIALLY NEUTRALIZED AQUEOUS SOLUTIONS OF TTA.

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FIG. 3

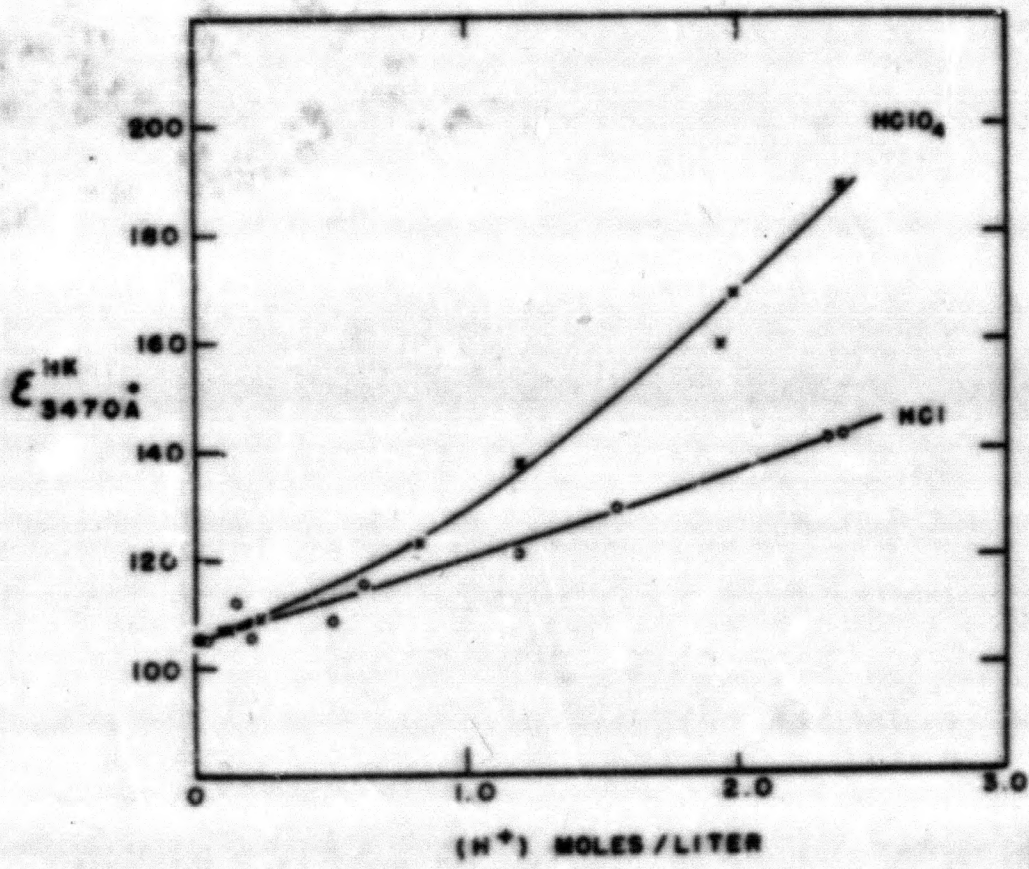


MOLAR EXTINCTION COEFFICIENT OF HK AT 3380 Å
AS A FUNCTION OF ACIDITY.

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FIG. 4

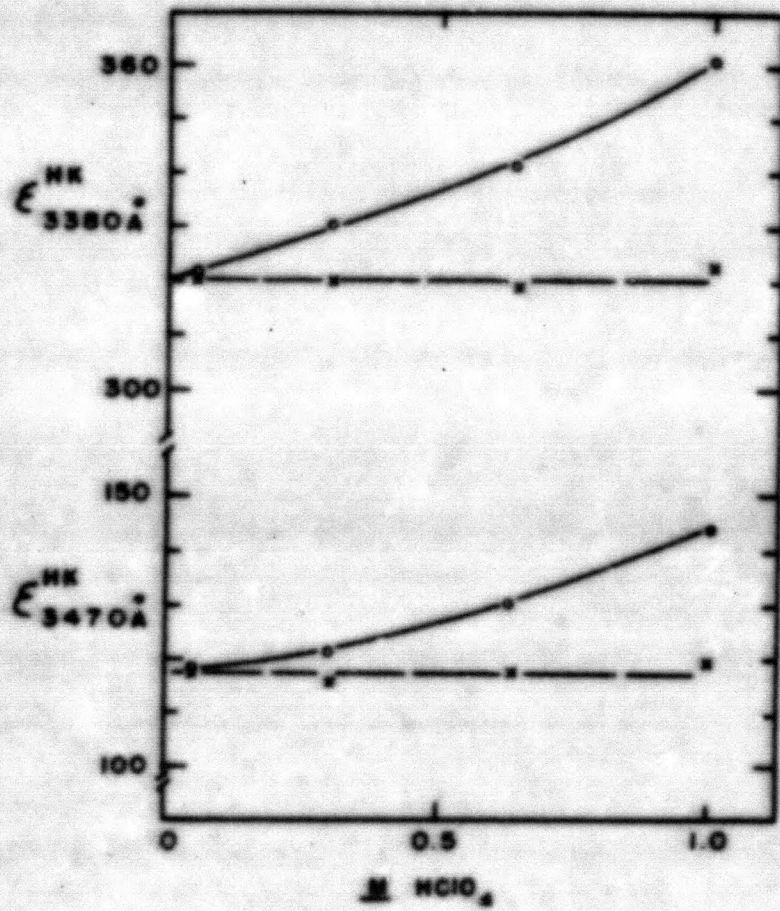


MOLAR EXTINCTION COEFFICIENT OF HK AT 3470 Å
AS A FUNCTION OF ACIDITY

MU 1155

similarly acidified, salt-free, aqueous TTA stock solutions. Another series of aqueous TTA stock solutions was made one molar in sodium perchlorate and acidified to varying degrees with perchloric acid. The molar extinction coefficients for HK, calculated from the observed optical densities and weight concentration of TTA, appear as the upper curves in Figure 5. Once more, the absorption increased with increasing acidity. The data taken from the series of solutions used to investigate the perchloric acid effect on the molar extinction coefficients of HK (Figure 4) were used to correct each of the currently determined values to zero molar perchloric acid concentration. The difference between the values, at the acid concentration in question and at zero molar perchloric acid, determined from the perchloric acid effect series, was subtracted from the molar extinction coefficient determined for the solution containing both acid and salt. The corrected molar extinction coefficients were found to be roughly invariant over the ionic strength range, but were approximately seven percent greater at 3470\AA and over eleven percent greater at 3380\AA than the values shown in Table 1, calculated from 0.04 M perchloric acid solutions of TTA, indicating that the salt effect and the effect of acidity were additive. These corrected values appear as the plotted points connected by horizontal broken lines in Figure 5.

FIG. 5



SOLID LINES CONNECT EXPMTL. POINTS.
BROKEN LINES CONNECT EXPMTL. POINTS AFTER
CORRECTING TO 0.0M $HClO_4$ FROM DATA
PRESENTED IN FIG. 3 AND 4.

SALT EFFECT AND EFFECT OF ACIDITY ON THE
MOLAR EXTINCTION COEFFICIENTS OF HK.

MU156

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THE ABSORPTION DUE TO ENOLATE ION.

A brief study of Figures 1 and 2 will show that the spectrophotometric analysis for HK in the presence of enolate-ion is not feasible; hence, the measurement of the enolate-ion absorption was used for the calculation of the acid dissociation constant of HK. For this measurement it is necessary to know the molar extinction coefficient of enolate-ion at its absorption maximum at 3470\AA . At this wavelength, the absorption by HK will be negligible for a pH = 8.2. There will be only one percent or less of the TTA present as HK at this pH. The total absorption at 3470\AA is due to enolate-ion under these conditions, for there is a factor of 200 fold between the molar extinction coefficients of the two species.

The required hydrogen ion concentration, for this direct measurement of the enolate-ion molar extinction coefficient, causes a much more rapid decomposition⁽³⁾ of the TTA in the solution than was observed for the acidified or neutral aqueous TTA stock solutions. In order to calculate a rate of decomposition for the alkaline hydrolysis, which would permit one to determine the TTA concentration at the time of observation, one must first find some means of exactly reproducing the method of preparation of the experimental solutions. Attempts to reproduce absorption spectrum readings between solutions, showed that an appreciable amount of the hydrolysis takes place during the initial mixing process and rather elaborate apparatus would be required to reproduce this step exactly.

Zebroski⁽³⁾ investigated the alkaline hydrolysis of TTA solutions

by observing the decrease in light absorption at the enolate-ion maximum, over a period of twelve hours. His rate expression for these observations was:

$$-\frac{d(K^-)}{dt} = k(K^-) \cdot f(\text{OH}^-)$$

where,

$$k \cdot f(\text{OH}^-) = 3.5 \times 10^{-5} \text{ moles/liter/min. at pH-6.99}$$

$$k \cdot f(\text{OH}^-) = 2.3 \times 10^{-4} \text{ moles/liter/min. at pH-9.44}$$

A mechanism explaining these rate data would require the introduction of some hydrolysable species, other than HK, which would increase in concentration with decreasing hydrogen ion concentration. The most obvious one would be enolate ion; however, when solid TTA is dissolved directly into 1 M NaOH, the observed rate of decrease in absorption at the enolate ion maximum is smaller than when an acidic, aqueous solution of TTA is made alkaline and taken to the same pH. The explanation given⁽³⁾ is that in the latter case the change of the hydrate to enolate ion is slow and the hydrate hydrolyzes more rapidly at these high pH's than does enolate ion.

In lieu of an accurate, empirical method of correcting the initial TTA concentration to the actual concentration at the time of the spectrophotometric observation, some direct measurement of the enolate-ion concentration, or of the TTA concentration, must be made.

Enolate Ion Molar Extinction Coefficient.—The simultaneous determination of the enolate ion concentration and the light absorption at the enolate-ion maximum was required for the determination of the molar extinction coefficient of enolate-ion. By working at a pH = 8.2, essentially all of the TTA was present as enolate ion. The acidification of an aliquot

of the experimental solution halted the hydrolysis process and converted all TTA present to the acid form, HK. The determination of the concentration of HK in this acidified aliquot gave the total TTA concentration in the experimental solution at the time of acidification. The absorption of one of the hydrolysis products, 2-acetyl-thiophene^a, which is present at appreciable concentration because of the large amount of hydrolysis, prevented the spectrophotometric determination of HK in this aqueous solution; however, the aqueous aliquot was extracted with benzene and the TTA concentration^b in the benzene phase was determined spectrophotometrically. The distribution coefficient^c data⁽⁴⁾, for TTA between benzene and dilute acid, were used to correct the TTA concentration in the benzene phase to the actual concentration of TTA in the aqueous phase

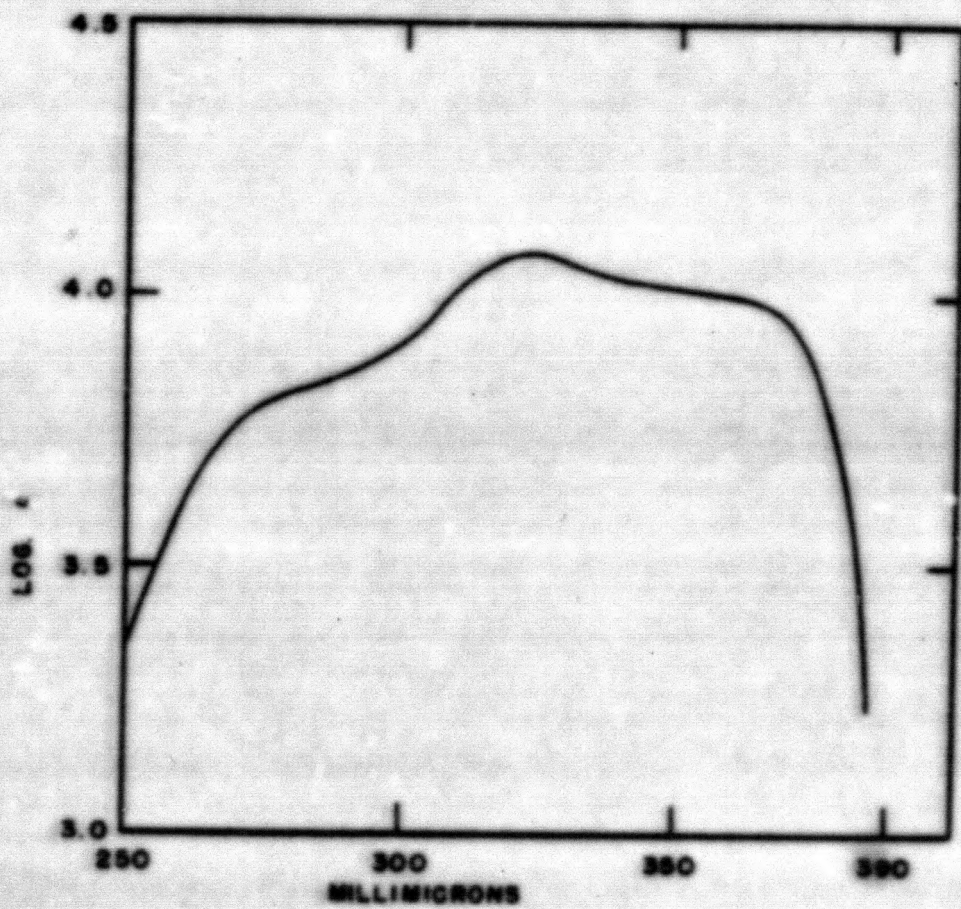
^aSince the molar extinction coefficient for acetyl-thiophene in aqueous solution is less than one percent of that for enolate-ion and the respective concentration ratio is about one to twenty, the error introduced by considering all light absorption at the enolate-ion maximum to be due to enolate-ion will be well within the limits of experimental accuracy.

^bThe absorption spectrum data for TTA in "wet" benzene, as reported by King and Reas⁽⁴⁾, were used for the determination of the TTA concentration in the benzene phase. The optical density of the benzene solution, observed at the absorption maximum of 3250 μ , was used for the analysis. ($\epsilon_{3250\mu}^{TTA \text{ benzene}} = 11,345$). The absorption spectrum of TTA in benzene is reproduced in Figure 6.

^cA TTA distribution coefficient ($TTA_{\text{benzene}}/TTA_{\text{aqueous}} = 40$) was used to correct the TTA concentration in the benzene phase for non-extracted TTA. This corrected TTA concentration is then equal to the concentration of enolate-ion at the time of acidification.

U-117-27

FIG. 6



ABSORPTION SPECTRUM OF TTA IN BENZENE SOLUTION.
MU 1157

U-117-28

at the time of acidification.

A typical experiment proceeded in the following manner: A solution (B) was prepared at a sufficiently high pH to neutralize essentially 100% of the acid form of HK, leaving only enolate ion as a significantly absorbing species. The neutralization of HK was approached in two ways: first, the dissolution of solid TTA in 0.1 N NaOH, and secondly, the dissociation of HK in pH = 8.4 (H_2BO_3 , NaCl, NaOH) buffer. An aliquot of (B) was acidified with perchloric acid just before, and another just after the recording of the optical density of the enolate-ion solution. The two acidified aliquots were then extracted with benzene and the total TTA concentrations of solution (B) determined, as described above, at the times corresponding to the times of acidification. An interpolation between these concentrations gave the concentration of K^- in the solution at the time of recording the optical density. The quotient of the optical density, corrected for blank absorption of solution (B) divided by the product of the absorption cell length and the calculated K^- concentration is the desired molar extinction coefficient for enolate-ion. The values obtained from several solutions, in this manner, showed good agreement with one another and were considerably higher than the approximate value of 16,000 reported by Zebroski⁽³⁾. The experimental data and calculated values are tabulated in Table 2. The complete method of calculation for one of the "dissolution of solid TTA" experiments is presented in Appendix I, and one of the "dissociation of aqueous TTA solution" experiments is presented in Appendix II.

Acid Dissociation Constant for HK.—Sufficient information is now available to permit the determination of the acid dissociation constant for

TABLE 2

MOLAR EXTINCTION COEFFICIENT OF ENOLATE ION

Expt.	$(K^-)^a$ $M \times 10^6$	pH	2 cm. $D_{3380\text{Å}}$	$\epsilon_{3380\text{Å}}$ (K^-)	Deviation from Mean
1	9.33	10.75	0.402	21,550	-10
2	17.9	11.05	0.7705	21,500	+50
3	9.355	10.45	0.401	21,440	-110
4 ^b	38.60	8.25	1.669	21,600	+50
5 ^b	38.50	8.70	1.669	21,650	+100

Mean Value = 2.15×10^4

^aTTA concentration was determined by acidification of the enolate-ion solution and extraction of the HK into benzene, immediately before and after the optical density of the enolate ion solution was recorded. This TTA concentration was corrected for undissociated HK in determining the (K^-) concentration.

^bAqueous TTA stock was buffered to desired pH with (H_2BO_3 , NaCl, NaOH) buffer. Other experiments had solid TTA dissolved in approximately 0.05 M NaOH and were then diluted to suitable concentrations, using 0.1 M NaOH to maintain the proper pH.

the reaction:



A series of buffered aqueous solutions of constant HK concentration, constant ionic strength, and varying hydrogen ion concentrations was prepared and spectrum measurements taken. The hydrogen ion concentrations were controlled with sodium acetate-acetic acid buffers; ionic strength was controlled with sodium perchlorate (solutions were also run using lithium perchlorate, sodium chloride, or lithium chloride). The optical densities at 3380 μ , of the buffered solutions, were obtained and corrected for background absorption due to HK, buffers, and ionic strength media. From the corrected optical densities at 3380 μ , the concentrations of enolate-ion were determined for the various solutions. The HK concentrations were obtained by differences between the TTA^a and the K⁻ concentrations.

In calculating the enolate ion concentration it was assumed that its molar extinction coefficient was independent of ionic strength and temperature. These assumptions seem quite probable; however, it is possible that there may be a temperature effect on the enolate ion absorption. For example, elevated temperatures might increase the freedom of rotation in the ion and thereby decrease the planarity in structure which is necessary for maximum resonance energy of the absorbing species.

The H⁺ concentrations presented in Table 3 were calculated from known acetic acid constant data⁽⁸⁾ and the ratio of the buffer consti-

^aThe rate of hydrolysis of aqueous TTA solutions is small at pH's of less than five or six, hence no detectable loss of TTA occurred during the experiment.

tuents added to each solution.^a Using these data, the acid dissociation equilibrium constant for HK was determined at an ionic strength of unity. The method of calculation is presented in detail in Appendix III. The resulting K_1 values for the solutions made up to ionic strength with lithium perchlorate and lithium chloride, were considerably larger than the values for the sodium perchlorate and sodium chloride solutions.^b The acid dissociation constant, obtained for HK in a sodium perchlorate solution of unit ionic strength, was nearly fifteen percent lower than the previously reported value⁽³⁾ for HK at zero ionic strength ($K_1^0 = 6.7 \times 10^{-7}$). Correction of K_1 from $\mu = 1$ to $\mu = 0$ should decrease its value and make the discrepancy considerably greater. The acid dissociation constant data and calculated values are presented in Table 4.

The ionic strength effect upon the acid dissociation constant for HK was investigated in an attempt to determine the validity of the previously reported K_1^0 mentioned above, and to check the ionic strength

^aIn lieu of information on the acid dissociation constant of acetic acid in lithium perchlorate and sodium perchlorate media, the data⁽⁸⁾ reported for lithium chloride and sodium chloride solutions were used to determine the hydrogen ion concentrations of the experimental solutions. The assumption of equal dissociation of the buffer acid in chloride and perchlorate solutions may introduce an appreciable error in all the concentration equilibrium constants, however it was considered to be a far better approximation than to use the hydrogen ion concentrations obtained from the observed pH readings.

^bA literature search, in an attempt to uncover sufficient activity data on the Na^+ and Li^+ ions, disclosed no information which would permit the explanation of this phenomenon on an activity basis alone. This absorption increase will be discussed later in this paper.

TABLE 3

The Acid Dissociation Constant for Acetic Acid for Various Ionic Strengths and Temperatures.

μ (M)	$K_a \times 10^5$ for Acetic Acid										
	16.2°	16.4°	16.6°	16.7°	17.6°	19°	20°	20.5°	25°	40°	—Temp. (°C)
.036	2.37			2.375					2.395	2.34	
.133				2.90					2.94	2.88	
.236				3.08					3.14	3.10	
.285	3.12			3.14					3.20	3.16	
.339				3.18					3.24	3.22	
.540		3.22		3.22					3.30	3.30	
.545				3.22					3.28	3.28	
.751				3.16					3.25	3.26	
.794			3.12	3.12					3.16	3.23	
1.00	2.98	2.98	2.98	2.98	3.01	3.02	3.03	3.04	3.08	3.12	

K_a is based on concentrations in moles/liter at approximately 25°C, rather than at the temperature of the experiment. Corrections were applied to the values calculated from the data of Harned and Hickey, for molal concentrations, in arriving at the above values.

TABLE 4

Acid Dissociation Constant Data^a for HK at Various Ionic Strengths. (25°C)

Expt.	Ionic Strength	$D_{3380}^{2\% \text{ HK}}$ Expt. ^b	$D_{3380}^{2\% \text{ HK}}$ Blank	(K ⁻) $\text{M} \times 10^6$	(HK) $\text{M} \times 10^4$	(H ⁺) $\text{M} \times 10^5$	K_1 $\times 10^7$
1	0.030	0.561	0.255	7.21	4.17	2.40	4.15
1'	0.030	0.551	0.255	6.97	4.17	2.40	4.01
2	0.236	0.560	0.260	7.07	4.17	3.14	5.45
3	0.545	0.573	0.267	7.21	4.17	3.28	5.66
4	0.751	0.590	0.272	7.50	4.17	3.25	5.84
5	1.00	0.599	0.277	7.60	4.17	3.08	5.63
6	0.030	0.540	0.255	6.62	4.14	2.40	3.90
7	0.133	0.546	0.257	6.81	4.14	2.94	4.84
8	0.339	0.552	0.261	6.86	4.14	3.24	5.37
9	0.030	0.550	0.253	7.00	4.09	2.40	4.11
10	0.236	0.556	0.257	7.05	4.09	3.14	5.40
11	0.545	0.580	0.264	7.45	4.09	3.28	5.99
12	0.751	0.589	0.269	7.55	4.08	3.25	6.01
13	1.00	0.605	0.274	7.80	4.08	3.08	5.87

^a0.03M HAc and 0.03M HAc buffer used; ionic strength adjusted with NaClO₄.^bTabulated optical densities have been corrected for cell blank.

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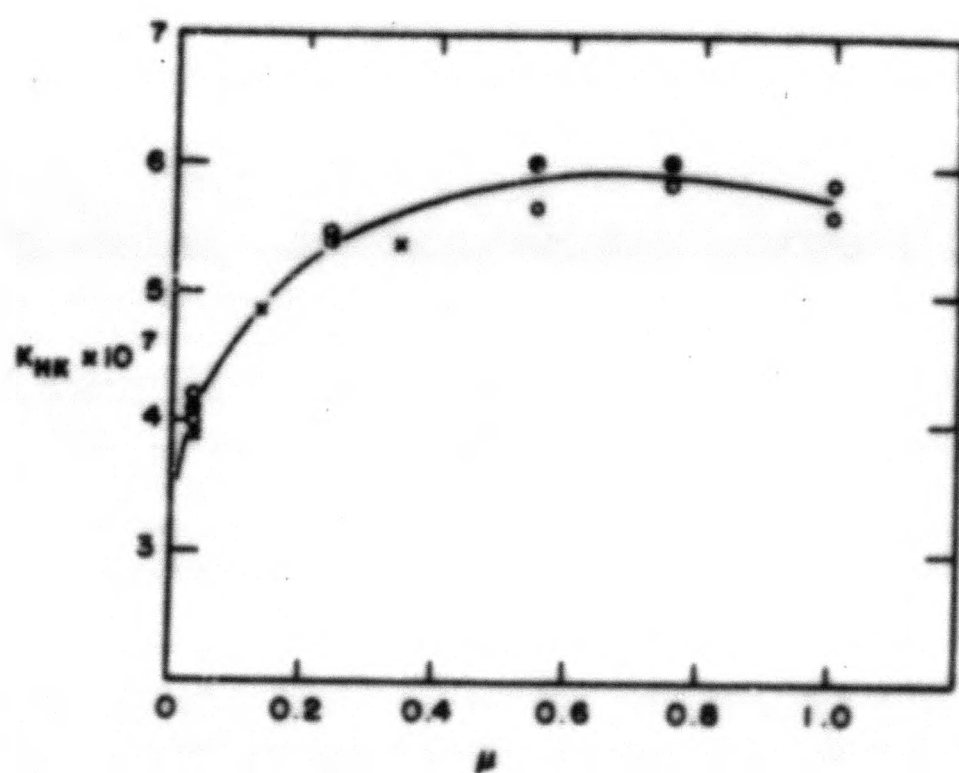
effect. It was considered probable that the variation of K_1 with ionic strength was roughly similar to that of acetic acid.

A series of aqueous solutions of constant HK concentrations, constant buffer composition, and variable ionic strength was prepared and the optical density was observed at the enolate-ion maximum. From the optical density corrected for background absorption, the K^- concentrations were determined. The H^+ and HK concentrations were evaluated in the manner previously mentioned. The acid dissociation constants were then calculated and are presented in Table 4 for the various ionic strengths investigated. A plot of the acid dissociation equilibrium constant versus ionic strength is presented in Figure 7. The curve is very similar in shape and position of its maximum to a similar plot for acetic acid.

Graphical extrapolation to zero ionic strength from the data of Figure 7 is not possible. However, if it is assumed that at low ionic strengths the dissociation constant varies the same as that of acetic acid, the zero ionic strength value can be calculated. The data at $\mu = 0.030$ were averaged and multiplied by the factor observed for acetic acid to give a value of $K_1^0 = 2.96 \times 10^{-7}$ at zero ionic strength. This is less than half the value previously reported⁽³⁾.

Thermo-Chemical Heats for the Dissociation of HK.—If the previously reported K_1^0 is incorrect, then the heat of ionization⁽³⁾ derived from its temperature variation is probably incorrect. It seemed worthwhile to re-evaluate the ΔH and ΔS values for the dissociation reaction, in view of the current interest in TTA as a complexing agent and as an extraction tool for metal separations. The solutions at an ionic

FIG. 7



- EXPMTS 1 THRU 5
- × EXPMTS 6 THRU 8
- EXPMTS 9 THRU 13

THE ACID DISSOCIATION CONSTANT OF HK AS
A FUNCTION OF IONIC STRENGTH.

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strength of unity, which were used in the ionic strength study of the HK acid dissociation constant, were observed at 40°C and 16.7°C, as well as at 25°C. The K⁻ and HK concentrations were determined as before. The H⁺ concentrations were calculated using the data of Harned and Hickey⁽⁹⁾, corrected from molal to molar concentrations. The experimental data and the calculated values are tabulated in Table 5. A plot of the temperature effect on K₁ is shown in Figure 8. From the slope^a of the experimental curve at 25°C, ΔH²⁹⁸ = 8.5 kcal./mol. was obtained for the reaction:



A value of K₁²⁹⁸ = 5.75 x 10⁻⁷ corresponds to ΔF²⁹⁸ = 8.5 kcal./mol.. Consequently, ΔS²⁹⁸ is approximately zero.

Zebroski⁽³⁾ measured the temperature dependence of the pH of half-neutralized aqueous TTA solutions and reported ΔH²⁹⁸ = 10.4 ± 0.5 kcal./mol. and ΔS²⁹⁸ = +6.7 ± 1.6 e.u. for the ionization reaction. Zebroski's measurements for the acid dissociation constant of TTA were made on solutions whose ionic strength was approximately .01 molar. Although there would be a measurable dilution effect on the value of the heat of dissociation, it does not seem probable that it could be nearly so large as the difference between his value and the value reported in this paper. Zebroski prepared his solutions by mixing sodium hydroxide and TTA solutions together and measuring the pH. It is possible that there was appreciable decomposition of the TTA during the mixing and that this accounts for the discrepancy between the two sets of results.

^a $\frac{Rd(\ln K)}{d(1/T)} = -\Delta H$ Plotting (-4.578 log K) versus (1/T) gives a quick graphical analysis of the observed data for ΔH, which is equal to the slope of a tangent to the curve at the temperature of interest.

TABLE 5

Acid Dissociation Constant Data^a for HK at Various Temperatures. ($\mu = 1.00$).

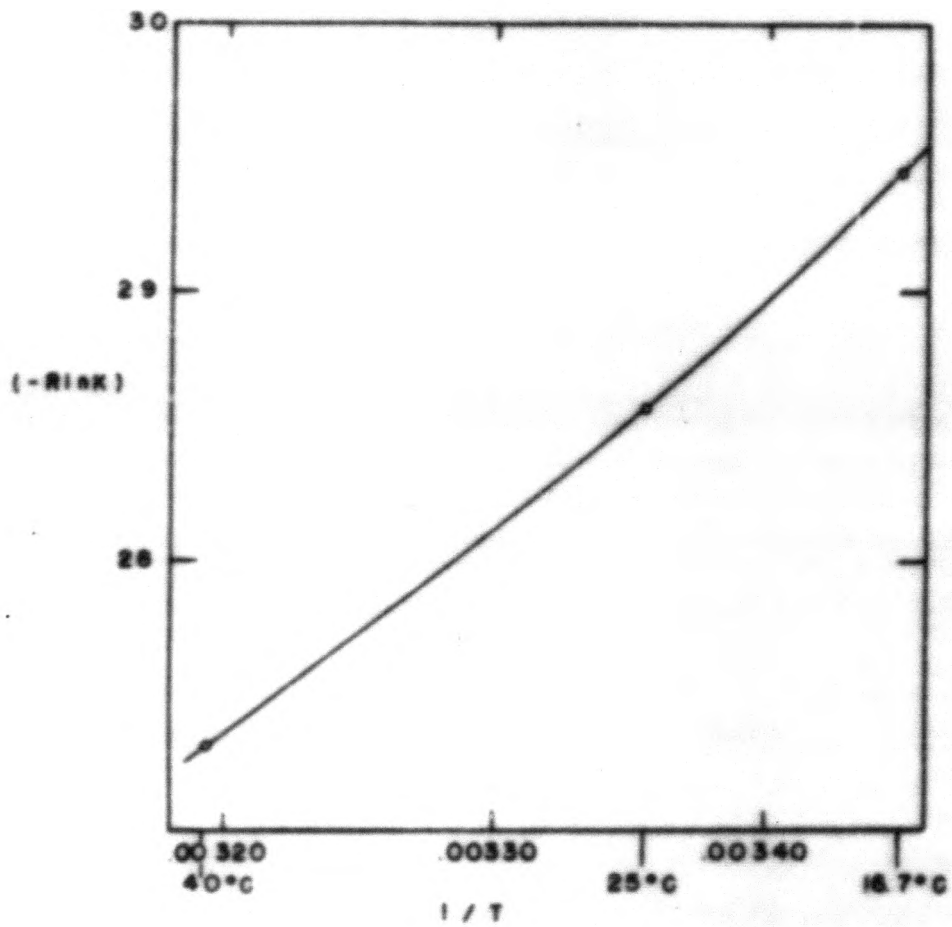
Expt.	T°C	$D_{3380}^{2 \text{ cm.}} \text{ \AA}$ Expt. ^b	$D_{3380}^{2 \text{ cm.}} \text{ \AA}$ Blank	(K ⁻) $\text{M} \times 10^6$	(HK) $\text{M} \times 10^4$	(H ⁺) $\text{M} \times 10^5$	K_1 $\times 10^7$
1	16.7	.469	.253	5.17	4.193	2.98	3.68
1	25.0	.599	.277	7.60	4.17	3.08	5.63
1	40.0	.917	.313	14.47	4.10	3.12	11.0
2	16.7	.466	.252	5.12	4.11	2.98	3.71
2	25.0	.605	.274	7.80	4.08	3.08	5.87
2	40.0	.880	.312	13.62	4.02	3.12	10.6

^a0.03 M NaAc and 0.03 M HAc buffer used; ionic strength adjusted with NaClO₄.^bTabulated optical densities have been corrected for cell blank.

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FIG. 8



THE ACID DISSOCIATION CONSTANT OF HX AS A
FUNCTION OF TEMPERATURE.

MU 1159

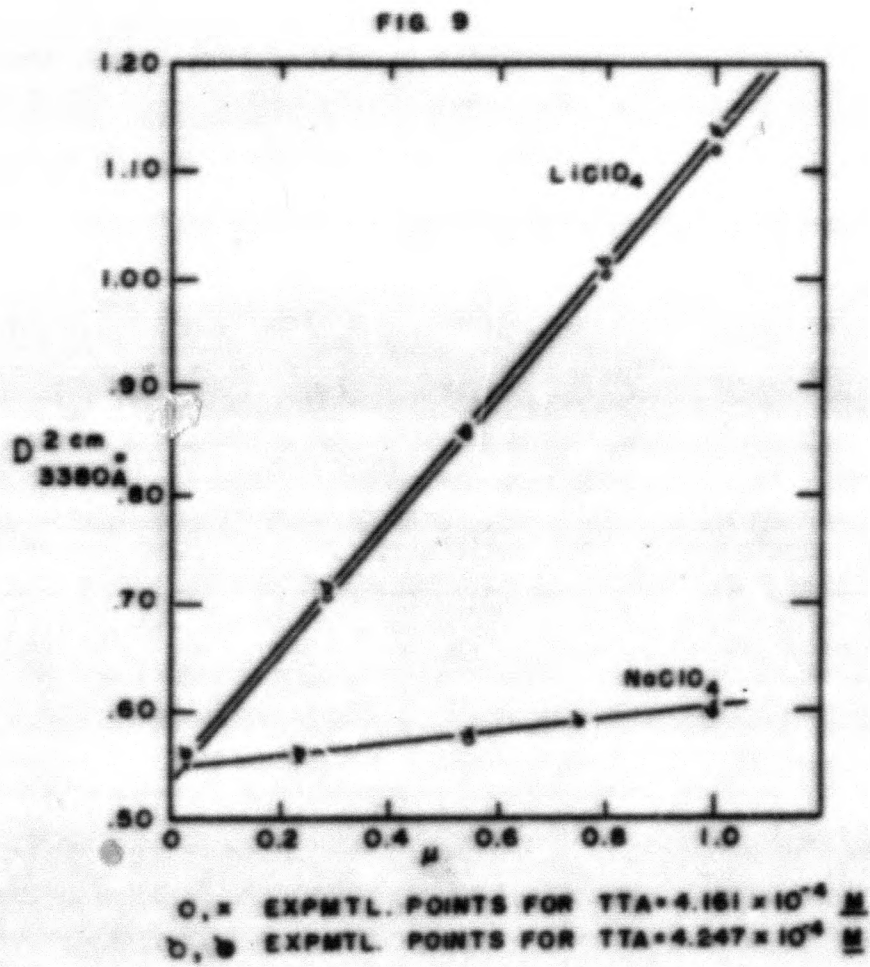
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The ΔS^{298} of most weak acids has been shown to be -20 ± 5 e.u. (8,12).

This value is not necessarily expected for TTA, since the dissociation reaction involves the loss of a molecule of water from the keto-hydrate form as well as the ionization of the weak acid. However the loss of a molecule of water of hydration would be expected to contribute only about +5 e.u. to the ionization reaction. Therefore the entropy change appears to be roughly 15 entropy units more positive than predicted. It is to be noted that Zebroski's value is even more positive than that found here. No plausible explanation for this disagreement can be offered at this time.

Lithium Chelate Complex Formation.—When lithium perchlorate was used in place of sodium perchlorate for adjusting the ionic strength, in the experiments for determining the dissociation constant of HK, the optical absorption was considerably increased at 3380\AA . The experimental data are plotted in Figure 9. The increase seemed much too large to be accounted for by specific activity differences caused by replacing sodium ion by lithium ion. At first it was suspected that the lithium perchlorate contained metal ion impurities which were being complexed by TTA and thus giving rise to the enhanced absorption. Repetition of the experiments with different sources of lithium perchlorate and also lithium chloride proved the effect was due to lithium ion itself.

The most plausible explanation of the phenomenon was that lithium ion was being complexed by enolate ion. An attempt to isolate the lithium chelate species by benzene extraction failed. Any attempt to maintain a large enough aqueous TTA concentration to give appreciable



THE ABSORPTION OF AQUEOUS TTA SOLUTIONS, USING
LiClO₄ vs NaClO₄ FOR IONIC STRENGTH CONTROL.

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complexing required such a high concentration of TTA in the benzene that any absorption due to LiK would be very difficult to detect. It was evident that any attempt to determine a molar extinction coefficient for the aqueous LiK species would have an extremely large inherent error, since only a small part of the TTA was chelated in 1 M lithium ion solution. There was no evidence for a change in the wavelength of the absorption spectrum maximum in the region of the enolate ion peak when lithium chelate was present, therefore the molar extinction coefficient for LiK was assumed to be equal to that for enolate-ion^a.

Using the data obtained from the series of experiments reported above, complexing constants for the formation of LiK in lithium perchlorate media were determined. The detailed method of calculation is presented in Appendix IV and the equilibrium constant data for the formation of lithium chelate complex, at various ionic strengths and 25°C, is tabulated in Table 6.

The calculation of the lithium chelate concentration, as with the enolate ion concentration, was based on the assumption that its molar extinction coefficient has no ionic strength or temperature dependence.

Once more, the unit ionic strength solutions were observed at three temperatures. The pertinent data and calculated lithium chelate complexing constants are presented in Table 7 for 40°C, 25°C, and 17.6°C. A plot of the temperature effect on the complexing constant appears in Figure 10. The slope of the experimental curve, at an ionic

^aThis assumption will be supported later when it is shown that the molar extinction coefficients for enolate ion and lanthanum-chelate complexion differ by less than seven percent.

TABLE 6

Equilibrium Constant Data for Lithium Chelate Formation at Various Ionic Strengths. (25°C)

Expt.	μ (M) ^a	(Li ⁺) M	(H ⁺) M x 10 ⁵	K ₁ at μ .	D _{3380 Å} ² cm. (LiClO ₄)	D _{3380 Å} ² cm. (NaClO ₄)	D _{3380 Å} ² cm. ^b (LiK)	(LiK) M x 10 ⁶	(HK) ^c M x 10 ⁴	K ₃ ^d x 10 ⁶
1	0.236	0.206	3.185	5.35	0.677	0.556	0.126	2.93	4.06	1.11
2	0.545	0.515	3.515	5.90	0.863	0.580	0.293	6.81	4.03	1.15
3	0.751	0.721	3.56	5.95	0.9825	0.589	0.4075	9.475	4.00	1.17
4	1.00	0.97	3.59	5.75	1.120	0.605	0.535	12.45	3.97	1.16
5	0.236	0.206	3.185	5.35	0.682	0.561	0.124	2.882	4.15	1.07
6	0.545	0.515	3.515	5.90	0.867	0.573	0.304	7.06	4.11	1.17
7	0.751	0.721	3.56	5.95	0.990	0.590	0.414	9.62	4.09	1.16
8	1.00	0.97	3.59	5.75	1.138	0.599	0.5575	12.98	4.06	1.18

^a0.03 M NaAc, 0.03 M Hac buffer used throughout.

$$D_{LiK}^b = \left[D_{LiClO_4} - \frac{(HK) + (K^-)}{(TTA)} \times D_{NaClO_4} \right]$$

^c(HK) concentration corrected for enolate ion that would be in equilibrium with it at the given (H⁺).^dK₃ is for the reaction: Li⁺ + HK = LiK + H⁺. This type reaction should be nearly invariant with respect to ionic strength, in agreement with the tabulated values.

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TABLE 7

Equilibrium Constant Data for Lithium Chelate Formation at Various Temperatures. ($\mu = 1.00$)^a

Expt.	T(°C)	(Li ⁺) M	(H ⁺) M x 10 ⁵	K ₁ x 10 ⁷	D ₃₃₈₀ ² cm. (LiClO ₄)	D ₃₃₈₀ ² cm. (NaClO ₄)	D ₃₃₈₀ ² cm. (LiK)	(LiK) M x 10 ⁶	(HK) ^c M x 10 ⁴	K ₃ ^d x 10 ⁶
4	40	0.97	3.12	10.8	1.809	0.880	0.977	22.7	3.80	1.92
4	25	0.97	3.59	5.75	1.120	0.605	0.535	12.45	3.97	1.16
4	16.7	0.97	2.98	3.70	0.812	0.466	0.3555	8.28	4.03	0.632
8	40	0.97	3.12	10.8	1.741	0.917	0.868	20.2	3.91	1.66
8	25	0.97	3.59	5.75	1.138	0.599	0.5575	12.98	4.06	1.18
8	16.8	0.97	2.98	3.70	0.815	0.469	0.355	8.25	4.11	0.616

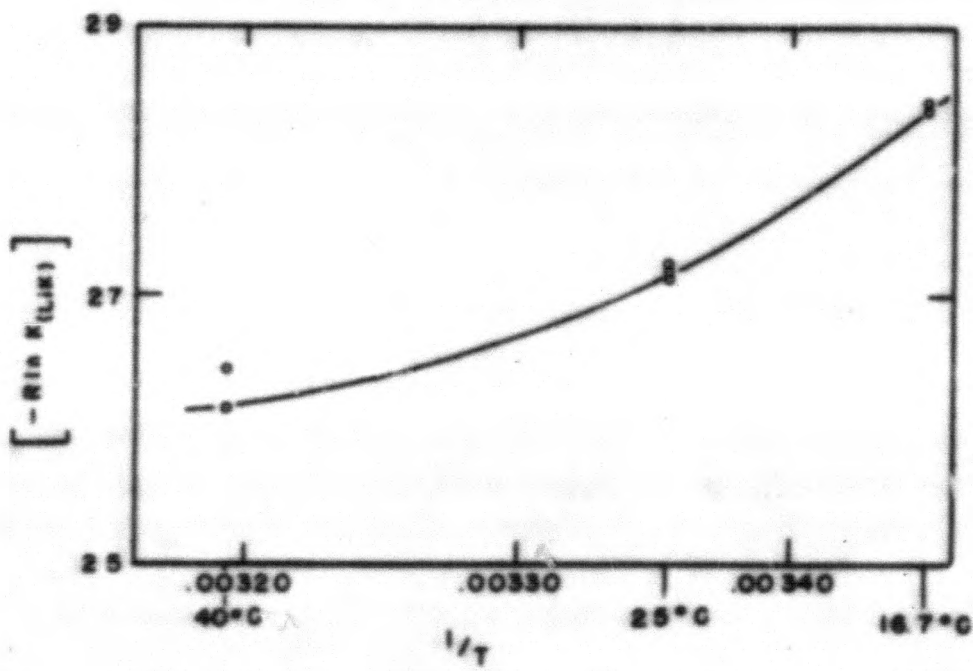
^a0.03 M NaAc, 0.03 M HAc buffer used throughout.

$$D_{LiK}^{2} = \left[D_{LiClO_4} - \frac{(HK) + (K^-)}{(TTA)} \times D_{NaClO_4} \right]$$

^c(HK) concentration corrected for enolate ion that would be in equilibrium with it at the given (H⁺).^dK₃ is for the reaction: Li⁺ + HK = LiK + H⁺.

44-611-2

FIG. 10



THE EQUILIBRIUM CONSTANT FOR LITHIUM CHELATE FORMATION AS A FUNCTION OF TEMPERATURE. MU 1161

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strength of unity gave, for the reaction $\text{Li}^+ + \text{HK} = \text{LiK} + \text{H}^+$:

$$\Delta H^{298} = 9.8 \text{ kcal./mol.}$$

$$\Delta F^{298} = 8.1 \text{ kcal./mol. } (K_3^{25^\circ\text{C}} = 1.17 \times 10^{-6})$$

$$\Delta S^{298} = 6 \text{ e.u.}$$

The observed ΔS for this reaction is small as is to be expected. The number and charge of the species is the same on each side of the equation. The reaction consists only in the substitution of a lithium ion for an H_3O^+ . It is to be noted that a molecule of water is actually liberated with the H^+ because the TTA is in the form of the hydrate. The small increase in entropy may be due to the smaller size of Li^+ compared to H_3O^+ .

LANTHANUM-CHELATE COMPLEX-ION FORMATION.

In order to make a spectrophotometric study of the formation of lanthanum complex-ions, the light absorption of the complexed species, LaK^{++} , was investigated. The concentration of the lanthanum-chelate complex ion was obtained from its absorption spectrum, after first determining its molar extinction coefficient.

A preliminary investigation of the singly-chelated lanthanum complex-ion, using the Cary Recording Spectrophotometer, showed that the enolate ion maximum was shifted approximately ninety angstroms toward longer wave lengths by its interaction with the tri-positive lanthanum cation.

Molar Extinction Coefficient for the LaK^{++} Complex-Ion.—The similarity in absorption spectra of enolate ion and lanthanum chelate required that conditions be created such that the chelate complex-ion became the predominant species present in solution. An approximate value for the complexing constant was calculated, assuming a molar extinction coefficient for lanthanum-chelate complex-ion equal to that for enolate ion, from which the necessary conditions were determined. Solutions were prepared at a pH of approximately six by adjusting the hydrogen ion concentration with the addition of 0.1 M NaOH. The first few solutions observed showed that the amount of decomposition of the TTA was greatly affected by the order of addition of the reagents. By carefully adjusting the hydrogen ion concentration of a solution, containing all the constituents except TTA and then adding the TTA, the decomposition loss of TTA, during the five to fifteen minute experimental life of the solution, should be negligible under these condi-

tions⁽³⁾. The stability of the resulting solutions was verified by observing the absorption of the solutions as a function of time. No significant change in absorption was noted during the half hour following the first observation, taken within approximately three minutes of mixing. Any decomposition of TTA would have been accompanied by an appreciable decrease in absorption at this wavelength. The careful standardization of the glass electrode with a buffered solution of similar concentrations, plus checking the instrument with a standard buffer immediately before and after measuring the pH of the experimental solution gave sufficient credence to the calculated hydrogen ion concentration to permit a valid calculation of the ratio of $(LaK^{++})/(HK)$. The LaK concentration was calculated by correcting the TTA concentration for the uncomplexed HK^a . The molar extinction coefficient values for the lanthanum-chelate complex-ion, determined in this way, were in remarkably good agreement with one another and showed good agreement with the more roughly determined, and slightly smaller, values calculated from data obtained from buffered solutions with less complete complexing. The experimental procedure and method of calculation of the LaK^{++} molar extinction coefficient may be followed through in Appendix V. The experimental data and calculated values appear in Table 8.

One might expect to find a cumulative effect in the molar extinction coefficients for singly-, doubly-, and triply-chelated complexes,

^aNo correction for enolate ion concentration was made, since it cancelled itself by having a molar extinction coefficient of the same order of magnitude as that for the absorbing species. If a correction were made it would have to be applied to the observed optical density, as well as in the determination of the LaK^{++} concentration.

TABLE 8

Calculated Molar Extinction Coefficients of the LaK^{++} Complex-Ion.(25°C; $\mu = 1.0$)

Expt.	(TTA) $M \times 10^5$	(XLa) $M \times 10^2$	(NaClO_4) M	(H^+) ^a $M \times 10^7$	(LaK^{++}) $M \times 10^5$	$D_{2 \text{ cm.}}^{25470 \text{ Å}}$	$\epsilon_{(\text{LaK}^{++})}$
1	1.699	5.44	0.672	8.3	1.649	0.763	23,150
2	1.699	5.44	0.672	8.7	1.638	0.755	23,090
3	1.699	5.44	0.672	14.5	1.64	0.757	23,100
Mean Molar Extinction Coefficient							23,100

^aThe hydrogen ion concentration was determined with the Model G Beckman pH Meter. The meter was calibrated with a buffered solution of similar concentration, and the calculated correction applied to the observed pH's. (See Appendix V). Varying amounts of 0.1 M NaOH were added to the solution to give the desired pH.

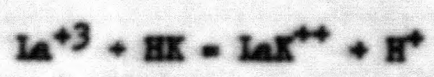
^bOptical density corrected for cell blank.

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i.e., that the molar extinction coefficient at the maximum would be proportional to the number of chelate groups. Zebroski⁽³⁾ reported a molar extinction coefficient of 46,500 at approximately 3450Å for LaK₃ in benzene. He stated that analysis of his dry, benzene soluble, LaK₃ showed a considerable amount of basic substances present. This was, presumably, a La(OH)K₂ or LaOK species, hence, his value would be predicted to lie between 43,000 and 69,300 on the basis of the ε of LaK⁺⁺. His reported value either indicates that there was nearly as much singly-chelated complex as there was triply-chelated complex, or refutes the suggested cumulative effect.

Complexing Constant for Lanthanum-Chelate Complex-Ion Formation.—The determination of the complexing constant for the formation of the lanthanum-chelate complex-ion, according to the reaction:



$$K_4 = \frac{(LaK^{++})(H^+)}{(La^{+3})(HK)}$$

required the simultaneous knowledge of the LaK⁺⁺, La⁺³, H⁺ and HK concentrations. The optical density at 3470Å gave the LaK⁺⁺ concentration and permitted, with the aid of the previously determined acid dissociation constant for HK, the determination of the HK concentration by difference. The attempt to measure the hydrogen ion concentrations with the Beckman pH meter showed too much irreproducibility to be reliable. With sufficient care, readings on the instrument could be reproduced to approximately 0.05 pH units, however the precautions^a

^aIrreproducible pH readings, at high perchlorate concentrations, were believed to be due to the precipitation of potassium perchlorate in the vicinity of the diffusion reed in the calomel electrode assembly. A large diameter potassium chloride bridge was found effective in decreasing this effect. The KOH bridge was inconvenient and required frequent refilling to insure reproducible results.

required were too time consuming to be practicable. Instead, acetic acid-sodium acetate buffer solutions were used and the acidity calculated from the composition and the known ionization constant. The lanthanum ion concentration was simply the difference between the total lanthanum ion and the lanthanum-chelate complex-ion concentrations, provided no further complexing of the tri-positive ion was taking place.

It soon became apparent that the concentration of one of the four substances involved in the complexing constant was not being calculated properly. When the individual equilibrium constant values, calculated in the belief that only one complex-ion was being formed, were compared, a definite trend toward decreasing values at lower acidities was observed. There was no increased discrepancy between the observed and calculated pH's, as the acidity was decreased, which seemed to rule out any buffer deficiency. Since the chelates of any metal-ion impurities would be expected to absorb light, any change in the HK concentration from this source would be reflected in the spectrum measurements in such a way as to cause an increase in the complexing constant. The source of trouble was, therefore, believed to be confined to the lanthanum ion concentration. Only the formation of a non-absorbing lanthanum complex-ion, with its subsequent lowering of the La^{+3} concentration, could cause the observed decrease in the value of the complexing constant. A ten-fold buffer concentration increase showed an even greater lowering of the calculated lanthanum-chelate complexing constant and made evident the formation of a lanthanum-acetate complex ion.

The presence of a second complex-ion in the lanthanum-chelate complex-ion solutions required the simultaneous determination of the two complexing constants and the correction of the free lanthanum ion concentration, for the amount of lanthanum-acetate complex-ion present.

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Experiments run at high-acetate concentration to give pronounced lanthanum acetate complexing, were used to evaluate the acetate complexing constant (see next section). This constant was then used to correct the lanthanum ion, acetate ion, and hydrogen ion concentrations, and the complexing constant for the formation of lanthanum-chelate complex-ion was calculated.

Two series of experiments with constant ionic strength ($\mu = 1.0$, maintained by sodium perchlorate in one series and lithium perchlorate in the other series) were observed at 25°C. The H^+ , La^{+3} , and TTA concentrations were varied in both series of experiments. The experimental data and calculated equilibrium constants at 25°C are presented in Tables 9 and 10, respectively, for the sodium perchlorate solutions, and in Tables 11 and 12, respectively, for the lithium perchlorate solutions. A sample calculation, showing the method used to determine the complexing constant, appears in Appendix VI.

Thermochemical Heats for the Formation of Lanthanum-Chelate Complex-Ion.

Several of the experimental solutions whose ionic strengths were maintained at unity with sodium perchlorate, were observed at various temperatures. The LaK^{++} , HK , and La^{+3} concentrations were obtained from the observed optical density, using the values of K_5 and K_1 appropriate to the temperature and ionic strength.

In calculating the concentration of lanthanum-chelate complex-ion, the assumption was made that its molar extinction coefficient was independent of ionic strength and temperature. The molar extinction coefficient was also assumed not to be affected by the changing media in the following study of lanthanum complexing by other anions.

The hydrogen ion concentrations were calculated from the data of

TABLE 9

Experimental Data for the Formation of Lanthanum-Chelate Complex-Ion.

 $\mu = 1.00$ (NaClO_4); 25°C

Expt.	(ΣLa) $\text{M} \times 10^3$	(TTA) $\text{M} \times 10^5$	(ΣAc^-) $\text{M} \times 10^2$	(ΣHAc) $\text{M} \times 10^2$	$D_{3470\text{\AA}}^2$ cm. sample	$D_{3470\text{\AA}}^2$ cm. blank
1	2.34	324.0	$[4.76 \times 10^{-3} \text{M}(\text{H}^+)]$		0.944	0.750
2	2.34	81.6	$[1.904 \times 10^{-3} \text{M}(\text{H}^+)]$		0.316	0.204
3	0.780	81.6	$[1.904 \times 10^{-3} \text{M}(\text{H}^+)]$		0.593	0.499
4	2.117	32.10	0.1909	4.81	0.220	0.090
5	2.117	32.16	0.341	4.66	0.297	0.098
6	2.34	33.05	0.833	4.17	0.644	0.134
7	2.34	33.62	0.833	4.17	0.666	0.132
7	2.34	33.62	0.833	4.17	0.666	0.134
8	2.34	33.10	0.833	4.17	0.642	0.1305
9	2.34	32.68	0.833	4.17	0.640	0.126
10	1.560	33.84	0.833	4.17	0.498	0.134
11	2.117	32.15	0.964	4.04	0.694	0.140
12	2.34	32.46	0.800	3.200	0.750	0.135
13	2.34	32.46	0.878	3.122	0.813	0.145
14	2.117	32.36	1.432	3.567	0.9585	0.1755
15	2.117	32.31	1.167	2.833	0.998	0.172
16	2.117	17.60	2.500	2.500	1.027	0.162
17	2.117	34.75	3.333	1.667	3.17	0.522
18	2.34	3.246	3.333	1.667	0.331	0.048
19	2.117	17.31	3.333	1.667	1.5945	0.2695
20	2.117	34.75	33.33	16.67	1.43	0.552
21	0.234	33.00	2.667	1.333	0.937	0.538

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TABLE 10

Equilibrium Constant Data for the Formation of Lanthanum-Chelate
Complex-Ion. $\mu = 1.00$ (NaClO_4); 25°C .

Expt.	(La ³⁺) M x 10 ³	(LaAc ⁺⁺) M x 10 ⁴	(HK) M x 10 ⁵	(H ⁺) M x 10 ⁵	(LaK ⁺⁺) M x 10 ⁵	K ₄ x 10 ³
1	2.336	—	324.	476.	0.424	2.67
2	2.338	—	81.3	190.4	0.243	2.44
3	0.779	—	81.5	190.4	0.0823	2.47
4	2.053	0.61	31.82	59.5	0.283	2.58
5	2.023	0.90	31.64	38.4	0.434	2.60
6	2.122	2.07	31.80	15.48	1.113	2.55
7	2.121	2.07	32.34	15.47	1.169	2.63
7	2.121	2.07	32.35	15.47	1.162	2.62
8	2.122	2.07	31.82	15.47	1.118	2.56
9	2.122	2.07	31.40	15.46	1.121	2.60
10	1.412	1.39	32.9	15.34	0.794	2.62
11	1.890	2.16	30.90	13.00	1.210	2.09
12	2.125	2.02	30.96	12.40	1.344	2.53
13	2.139	2.17	30.83	11.06	1.460	2.48
14	1.800	3.04	30.50	7.79	1.715	2.43
15	1.847	2.52	30.27	7.60	1.810	2.46
16	1.622	4.76	15.40	3.135	1.910	2.40
17	1.48	5.78	27.8	1.575	5.92	2.26
18	1.680	6.56	2.518	1.570	0.633	2.35
19	1.498	5.89	13.83	1.570	2.966	2.25
20	0.422	16.74	31.57	1.550	1.77	2.29
21	0.1706	0.545	30.9	1.540	0.896	2.62

Mean Value: $K_4 = 2.52 \times 10^{-3}$

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TABLE 11

Experimental Data for the Formation of Lanthanum-Chelate Complex-Ion,
in the Presence of Lithium Chelate Complex. ($\mu = 1.0$; 25°C).

Expt.	(LiCl) M	(LiCl) M $\times 10^3$	(TTA) M $\times 10^5$	(LiAc) M $\times 10^2$	(LiAc) M $\times 10^3$	$D_{3470}^{2\text{ cm.}}$ sample	$D_{3470}^{2\text{ cm.}}$ blank
22	0.946	3.96	42.8	0.360	40.0	0.602	0.188
23	0.946	3.96	42.8	0.360	10.00	1.854	0.418
24	0.90	9.48	6.29	2.88	19.2	1.277	0.234
25	0.90	9.48	4.72	3.20	16.0	1.113	0.190
26	0.90	9.48	6.18	3.60	12.0	0.836	0.164
27	0.90	9.48	4.63	3.84	9.60	0.707	0.148
28	0.89	9.48	3.93	4.00	8.00	1.330	0.327
29	0.90	9.48	3.09	4.11	6.86	0.534	0.132
30	0.90	9.48	3.09	4.11	6.857	0.496	0.1345
31	0.90	9.48	3.09	4.40	4.00	0.5865	0.1955

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TABLE 12

Equilibrium Constant Data for the Formation of Lanthanum-Chelate
Complex-Ion, in the Presence of Lithium-Chelate
Complex. ($\mu = 1.0, 25^\circ\text{C}$).

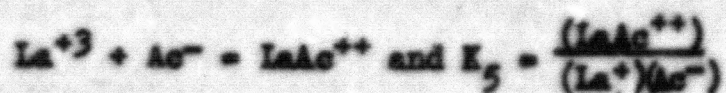
Expt.	(Li ⁺) M	(La ⁺³) M x 10 ³	(LaAc ⁺⁺) M x 10 ³	(HK) ₅ M x 10 ⁵	(H ⁺) ^a M x 10 ⁵	(LaK ⁺²) ₅ M x 10 ⁵	K ₄ x 10 ³
22	0.946	3.79	0.173	41.7	37.30	0.904	2.13
23	0.946	3.77	0.156	39.0	10.18	3.17	2.19
24	0.90	7.18	2.28	3.61	2.60	2.455	2.46
25	0.90	6.99	2.47	2.34	1.946	2.186	2.61
26	0.90	6.75	2.70	2.57	1.297	3.29	2.46
27	0.90	6.63	2.83	1.56	0.970	2.808	2.63
28	0.89	6.54	2.91	1.065	0.776	2.647	2.95
29	0.90	6.49	2.97	0.759	0.646	2.138	2.81
30	0.90	6.50	2.96	0.927	0.645	1.928	2.06
31	0.90	6.34	3.12	0.510	0.353	2.34	2.56

Mean value: $K_4 = 2.57 \times 10^{-3}$

^aK₂ = 3.58×10^{-5} at 25°C and $\mu = 1.0, \text{LiClO}_4$.

Harned and Hickey⁽⁹⁾ and the ratio of concentrations of the buffer constituents. The experimental data and calculated constants for the formation of the lanthanum-chelate complex-ion appear in Tables 13 and 14, respectively. A plot of the calculated values for the complexing constant as a function of temperature is presented in Figure 11. The slope of the experimental line, at 25°C gave $\Delta H^{298} = -7.2$ kcal./mol. for the chelation reaction. A $K_4^{298} = 2.52 \times 10^{-3}$ corresponds to $\Delta F^{298} = 3.55$ kcal./mol. and $\Delta S^{298} = 12$ entropy units.

Lanthanum-Acetate Complex-Ion Formation.—The presence of a lanthanum-acetate complex-ion became evident during the study of the formation of the lanthanum-chelate complex-ion. Highly acetate-complexed solutions at unit ionic strength, having a ten-fold acetate concentration range, were observed at various temperatures. The experimental observations and calculated data, presented in Tables 15 and 16 respectively, were used to determine the equilibrium constant for the reaction:



The calculated constants for the formation of LaAc^{++} appear in Table 17 and are plotted as a function of temperature in Figure 12. The method of calculation of the complexing constant for the formation of the lanthanum-acetate complex-ion, in the presence of LaK^{++} is shown in Appendix VII. From Figure 12, a $\Delta H^{298} = 2.4$ kcal./mol. was calculated for the complexing reaction expressed above. From the $K_5^{25^\circ\text{C}} = 12$, a value of $\Delta F_{298} = -1.47$ kcal/mol. was determined, and therefore $\Delta S^{298} = 13$ e.u..

TABLE 13

Experimental Data for the Formation of Lanthanum-Chelate Complex-Ion
at Various Temperatures.

($\mu = 1.0, \text{NaClO}_4$)

Expt.	(ΣLa) $M \times 10^3$	(TTA) $M \times 10^4$	(ΣAc^-) $M \times 10^3$	(ΣHAc) $M \times 10^2$	$D_{\text{sample}}^{2 \text{ cm. } 3470\text{\AA}}$	$D_{\text{blank}}^{2 \text{ cm.}}$	T °C
5	2.117	3.216	3.41	4.66	0.4895	0.143	40°
5	"	"	"	"	0.297	0.098	25°
10	1.560	3.384	8.33	4.17	0.822	0.2135	40°
10	"	"	"	"	0.498	0.134	25°
10	"	"	"	"	0.406	0.120	19°
13	2.34	3.246	8.78	3.122	1.336	0.231	40°
13	"	"	"	"	0.813	0.145	25°
13	"	"	"	"	0.6915	0.1305	20°

All experiments prepared at approximately 25°C and solutions observed at the three temperatures reported.

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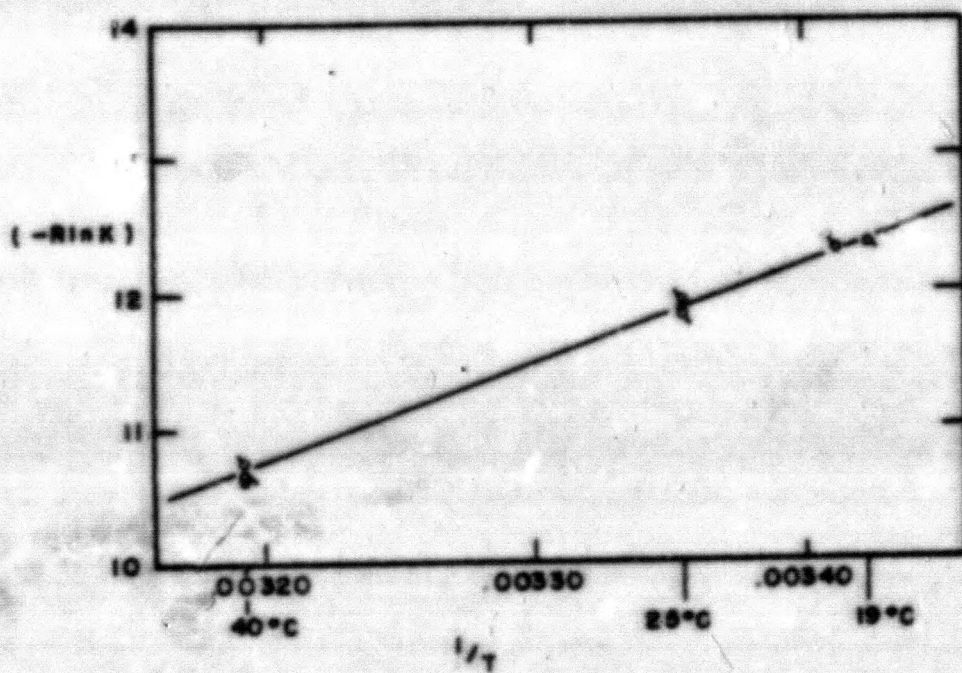
TABLE 14

Equilibrium Constant Data for the Formation of Lanthanum-Chelate
Complex-Ion at Various Temperatures. ($\mu = 1.0, \text{NaClO}_4$).

Expt.	(La ⁺³) M x 10 ³	(LaAc ⁺⁺) M x 10 ⁴	(HK) M x 10 ⁴	(H ⁺) M x 10 ⁴	(LaK ⁺⁺) M x 10 ⁵	K ₄ x 10 ³	T°C
5	2.001	1.08	3.13	3.92	0.756	4.73	40°
5	2.023	0.90	3.164	3.84	0.434	2.60	25°
10	1.382	1.651	3.23	1.56	1.337	4.66	40°
10	1.412	1.39	3.29	1.534	0.794	2.62	25°
10	1.422	1.31	3.31	1.503	0.624	1.99	19°
13	2.057	2.58	2.98	1.127	2.43	4.47	40°
13	2.120	2.08	3.10	1.088	1.227	2.03	20°
13	2.109	2.17	3.08	1.106	1.46	2.48	25°

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FIG. II



THE EQUILIBRIUM CONSTANT FOR LANTHANUM-CHELATE
COMPLEX-ION FORMATION AS A FUNCTION OF
TEMPERATURE. MU 1162

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TABLE 15

Experimental Data for the Formation of Lanthanum-Acetate Complex-Ion
at Various Temperatures. ($\mu^{\text{H}} 1.0 \text{ } \text{NaClO}_4$).

Expt.	(La) M x 10 ³	(TTA) M x 10 ⁴	(Ac ⁻) M	(HAc) M	$\frac{3470\lambda}{D_{\text{sample}}^2 \text{ cm.}}$	$\frac{3470\lambda}{D_{\text{blank}}^2 \text{ cm.}}$	T°C
1	2.117	3.48	0.0333	0.01667	3.17	0.522	25°
2	2.117	1.732	0.0333	0.01667	2.30	0.469	40°
2	"	"	"	"	1.595	0.270	25°
2	"	"	"	"	1.404	0.244	20.5°
3	2.117	1.732	0.1667	0.0833	1.404	0.480	40°
3	"	"	"	"	0.958	0.276	25°
3	"	"	"	"	0.843	0.2415	20.5°
4	2.117	3.48	0.333	0.1667	1.43	0.552	25°
5	2.117	1.732	0.333	0.1667	1.067	0.487	40°
5	"	"	"	"	0.715	0.2815	25°
5	"	"	"	"	0.6215	0.2415	20.5°

^aAn error made in calculating the concentration of the buffer in preparing these solutions, resulted in ionic strengths slightly larger than unity. For experiments 4 and 5, μ is 1.07; for 3, μ is 1.03; for 1 and 2, μ is 1.00.

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TABLE 16

Equilibrium Constant Data for the Formation of Lanthanum-Acetate Complex-Ion at Various Temperatures. ($\mu \approx 1.0$, NaClO_4).

Expt.	$(\text{La}^{+3}) + (\text{LaAc}^{++})$ $M \times 10^3$	(Ac^-)	HK $M \times 10^4$	(H^+) $M \times 10^5$	D_{3470}^2 of LaK^{++}	T°C
1	2.058	0.0327	2.784	1.578	2.74	25°
2	2.075	0.0326	1.230	1.592	1.95	40°
2	2.087	0.0327	1.384	1.576	1.372	25°
2	2.091	0.0328	1.430	1.550	1.197	20.5°
3	2.096	0.1652	1.421	1.572	0.986	40°
3	2.102	0.1653	1.521	1.552	0.707	25°
3	2.104	0.1653	1.550	1.535	0.621	20.5°
4	2.097	0.3316	3.265	1.550	0.910	25°
5	2.104	0.3316	1.495	1.570	0.619	40°
5	2.107	0.3316	1.577	1.550	0.449	25°
5	2.109	0.3317	1.597	1.531	0.392	20.5°

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TABLE 17

Calculated Equilibrium Constants^a for Lanthanum-Acetate Complex-Ion
Formation at Various Temperatures. ($\mu \approx 1.0$, NaClO_4).

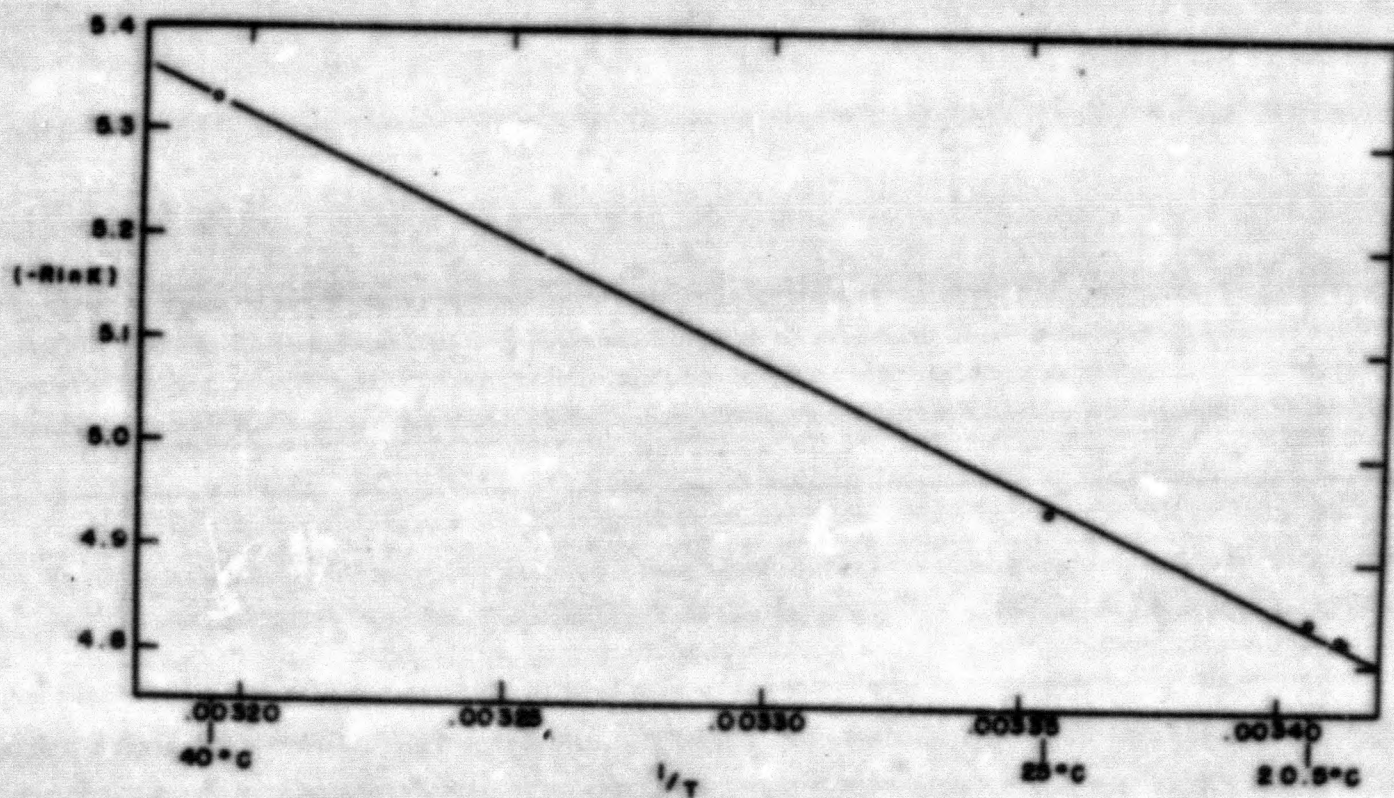
Expts. Equated	(Ac ⁻) Range	$K_5^{20.5^\circ\text{C}}$	$K_5^{25^\circ\text{C}}$	$K_5^{40^\circ\text{C}}$
1 and 4	0.03 - 0.3		11.9	
2 and 3	0.03 - 0.17	11.7	12.6	15.1
5 and 3	0.17 - 0.3	11.0	10.7	13.3
2 and 5	0.03 - 0.3	11.4	12.0	14.6
	Values chosen ^b	11.4	12.0	14.6

^aSee Appendix VII for method used to determine K_5 .

^bThe widest range of acetate concentration should give greater accuracy than smaller concentration differences.

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FIG. 12



THE EQUILIBRIUM CONSTANT FOR LANTHANUM-ACETATE COMPLEX-ION FORMATION AS A FUNCTION OF TEMPERATURE.

MUI163

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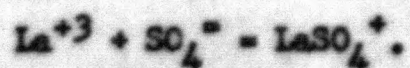
Lanthanum-Sulfate Complex-Ion Formation.—To unit ionic strength solutions, similar to those used in the study of lanthanum-chelate complex-ion formation, a measured amount of di-sodium sulfate (Merck-reagent grade) solution was added. The decreased absorption of such a solution, with respect to a similar, sulfate-free solution, was used to determine the LaSO_4^+ complex-ion concentration. Using the data of Bray and Liebhafer⁽¹⁰⁾, for the dissociation of bi-sulfate ion, an extrapolated value for the acid dissociation constant was determined for an ionic strength of unity, at 25°C. Assuming that this ionic strength effect will continue to hold over the temperature range 40°C to 20°C, Hamer's⁽¹¹⁾ data for the temperature effect on the bi-sulfate dissociation was treated in the same manner and values for the constant were approximated at the other temperatures.

$$K_a^{25} = \frac{(\text{H}^+)(\text{SO}_4^{2-})}{(\text{HSO}_4^-)} = 0.09, \mu = 1.0$$

$$K_a^{313} = 0.073, \mu = 1.0$$

$$K_a^{292} = 0.097, \mu = 1.0$$

Formation of the weak acid HSO_4^- and of the lanthanum-acetate complex-ion required that a correction be applied to the $(\text{HAc})/(\text{Ac}^-)$ buffer ratio in order to calculate the hydrogen ion concentration. A thirty-fold total sulfate ion concentration range was investigated. Using the observed data and applying all the required concentration corrections, the complexing constant was calculated for the reaction:



$$K_6 = \frac{(\text{LaSO}_4^+)}{(\text{La}^{+3})(\text{SO}_4^{2-})}$$

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The experimental data and the calculated complexing constants are presented in Tables 18 and 19 respectively. The method and equations used are shown in Appendix VIII. The accuracy of some of the calculated constants is not great because of the relatively small degree of complex formation. A fair indication of the inaccuracy is given by the ratio of lanthanum ion to complex-ion concentrations. A small error in the experimental data will be enhanced by a factor roughly equal to this ratio.

The temperature dependence of the equilibrium constant for the formation of the lanthanum-sulfate complex-ion was also investigated. The experimental data and calculated constants appear in Tables 18, and 19 also. A value of $K_4^{298} = 25$, represents a $\Delta F^{298} = -1.9$ kcal./mol.. A $\Delta H^{298} = 2.5 \pm 0.7$ kcal./mol. was determined, hence ΔS^{298} is 15 ± 3 e.u..

The value of 25 for the equilibrium constant at 25°C is to be compared with a value of 60 found by Connick and Mayer⁽¹³⁾ for the cerous sulfate complex at the same temperature and an ionic strength of 0.5 (NaClO_4). The constant for cerous ion would be expected to be somewhat larger because of the smaller size of the +3 ion. The ionic strength effect is difficult to predict at these ionic strengths but is probably in the direction necessary to account for the difference between the two values.

It is interesting to note that the value of K_6 for experiment 1 of Table 19 is significantly higher than that of experiment 2 at 25°. At least part of the difference may arise from the presence of some of the second complex, i.e., $\text{La}(\text{SO}_4)_2^-$. If such is the case, the value of K_6 for experiment 2 should be decreased a few percent.

TABLE 18

Experimental Data for the Formation of the Lanthanum-Sulfate Complex-
Ion at Various Temperatures. $\mu = 1.0$, NaClO_4

Each experiment contains:

$1.560 \times 10^{-3} \text{ M La}$

$8.33 \times 10^{-3} \text{ M La}^+$

$3.384 \times 10^{-4} \text{ M TTA}$

$4.17 \times 10^{-2} \text{ M HAc}$

Expt.	(SO_4^{2-}) M	D^2 cm. sample	3470\AA D^2 cm. blank	T°C
LaK ⁺⁺ Blank	—	0.822	0.214	40°
"	—	0.498	0.134	25°
"	—	0.406	0.120	19°
1	0.1000	0.2387	0.135	25°
2	0.0300	0.550	0.206	40°
"	"	0.361	0.135	25°
"	"	0.298	0.120	19°
3	0.01000	0.433	0.135	25°
4	0.00300	0.480	0.135	25°

2-117-67

TABLE 19

Equilibrium Constant Data for the Formation of the Lanthanum-Sulfate
Complex-Ion at Various Temperatures. $\mu = 1.0$, NaClO_4

Expt.	(La^{+3}) $M \times 10^3$	(H^+) $M \times 10^4$	(LaSO_4^+) $M \times 10^4$	(SO_4^-) $M \times 10^3$	K_6	$T^\circ\text{C}$
LaK ⁺⁺ Blank	1.382	1.56	—	—	—	40°
"	1.412	1.53	—	—	—	25°
"	1.422	1.50	—	—	—	19°
1	0.390	1.49	11.23	98.7	29.	25°
2	0.774	1.53	6.84	29.25	30.2	40°
"	0.868	1.52	5.99	29.4	23.5	25°
"	0.876	1.49	5.98	29.35	23.3	19°
3	1.15	1.53	2.86	9.69	26.	25°
4	1.34	1.53	0.83	2.91	~21	25°

21-117-68

Complexing of Lanthanum by Cl^- , NO_3^- , ClO_3^- —The solutions to be investigated were prepared in the same manner as those used in the determination of the lanthanum-sulfate complexing constant. Mallinkrodt, analytical reagent NaCl and NaNO_3 and Baker and Adamson, C.P. NaClO_3 were used as sources of anions to be studied. Since these complexing agents are the anions of strong acids, the small corrections, arising from the different degrees of acetate complexing, between the sample and the blank, gave negligible changes in acidity. The method given in Appendix VIII was used for the calculations.

The complexing constants were determined from the experimental data, according to the equations:



$$K_7 = \frac{(\text{LaCl}^{++})}{(\text{La}^{+3})(\text{Cl}^-)} \quad K_8 = \frac{(\text{LaNO}_3^{++})}{(\text{La}^{+3})(\text{NO}_3^-)} \quad K_9 = \frac{(\text{LaClO}_3^{++})}{(\text{La}^{+3})(\text{ClO}_3^-)}$$

The chloride and nitrate complexing constants were also studied as a function of temperature. The experimental data and calculated constants for all temperatures appear in Tables 20 and 21, respectively. The accuracy is not great because of the small degree of complexing.

From the data the following values of ΔF , ΔH and ΔS are calculated for the formation of the chloride and nitrate complexes (at $\mu = 1$):

	chloride	nitrate
ΔF^{298}	-0.2 ± 0.1 kcal.	$+0.3 \pm 0.1$ kcal.
ΔH^{298}	$+1.4 \pm 1.0$ kcal.	$+1.7 \pm 1.5$ kcal.
ΔS^{298}	$+4 \pm 4$ e.u.	$+5 \pm 5$ e.u.

The effect of temperature on the complexing was small.

By means of ion-exchange studies, Connick and Mayer⁽¹³⁾ evaluated

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TABLE 20

Experimental Data for the Complexing of Lanthanum by Cl^- , NO_3^- , and ClO_3^- at Various Temperatures. $\mu = 1.0$, NaClO_4 .

Expt.	(ΣLa) $\text{M} \times 10^3$	(TTA) $\text{M} \times 10^4$	(ΣAc^-) $\text{M} \times 10^3$	(ΣHAc) $\text{M} \times 10^{-2}$	(ΣX^-) ^a M	D^2 cm. sample	D^2 cm. blank	$\frac{3470\lambda^2}{\text{cm.}}$	$T^\circ\text{C}$
Lanthanum-Chloride complex-ion formation									
LaK^{++} Blank	2.34	3.31	8.33	4.17	—	0.642	0.131		25°
1	"	"	"	"	0.352	0.546	0.130		25°
2	"	"	"	"	0.1408	0.598	0.130		25°
3	"	"	"	"	0.0422	0.627	0.130		25°
(LaK^{++}) Blank	"	"	"	"	—	1.066 ^b	0.208 ^b		40°
2	"	"	"	"	0.1408	0.993	0.217		40°
(LaK^{++}) Blank	"	"	"	"	—	0.5255 ^b	0.116 ^b		19°
2	"	"	"	"	0.1408	0.494	0.121		19°
Lanthanum-nitrate complex-ion formation									
LaK^{++} Blank	2.34	3.305	8.33	4.17	—	0.644	0.134		25°
4	"	"	"	"	0.50	0.542	0.134		25°
5	"	"	"	"	0.20	0.600	0.134		25°
LaK^{++} Blank	"	"	"	"	"	1.066 ^b	0.208 ^b		40°
5	"	"	"	"	"	1.001	0.217		40°
LaK^{++} Blank	"	"	"	"	"	0.5255 ^b	0.116 ^b		19°
5	"	"	"	"	"	0.502	0.125		19°

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TABLE 20 (continued)

Expt.	(ΣLa) $\text{M} \times 10^3$	(TTA) $\text{M} \times 10^4$	(ΣAc^-) $\text{M} \times 10^3$	(ΣHAc) $\text{M} \times 10^2$	(ΣX^-) ^a M	D^2 cm. sample	D^2 cm. blank	$T^\circ\text{C}$
Lanthanum-chlorate complex-ion formation								
LaK^{++}								
Blank	2.34	3.27	8.33	4.17	—	0.640	0.126	25°
6	"	"	"	"	0.20	0.599	0.126	25°
7	"	"	"	"	0.08	0.621	0.126	25°
8	"	"	"	"	0.04	0.627	0.126	25°

^aX⁻ is Cl⁻, NO₃⁻ or ClO₃⁻.

^bThese blanks were calculated from the 25°C blanks, using the experimental temperature coefficient of the LaK⁺⁺ blanks of Table 18.

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TABLE 21

Equilibrium Constant Data for the Complexing of Lanthanum by Cl^- , NO_3^- ,
and ClO_3^- at Various Temperatures. $\mu = 1.0$, NaClO_4 .

Expt.	(La^{+3}) $M \times 10^3$	(H^+) $M \times 10^4$	$(\text{LaX}^{++})^a$ $M \times 10^4$	$(\text{X}^-)^a$ M	K_n	$T^\circ\text{C}$
Lanthanum-chloride complex-ion formation					K_7	
LaK ⁺⁺ Blank	2.122	1.55	—	—	—	25°
1	1.72	1.54	4.4	0.352	0.73	25°
2	1.94	1.54	2.00	0.141	0.73	25°
3	2.06	1.545	0.69	0.0422	0.8	25°
LaK ⁺⁺ Blank	2.07	1.58	—	—	—	40°
2	1.86	1.57	2.36	0.141	0.90	40°
LaK ⁺⁺ Blank	2.13	1.52	—	—	—	19°
2	1.94	1.51	2.12	0.141	0.78	19°
Lanthanum-nitrate complex-ion formation					K_8	
LaK ⁺⁺ Blank	2.122	1.55	—	—	—	25°
4	1.69	1.54	4.7	0.500	0.56	25°
5	1.93	1.54	2.1	0.200	0.54	25°
LaK ⁺⁺ Blank	2.07	1.58	—	—	—	40°
5	1.87	1.57	2.2	0.200	0.59	40°
LaK ⁺⁺ Blank	2.13	1.52	—	—	—	19°
5	1.96	1.51	1.9	0.200	0.48	19°

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TABLE 21 (Continued)

Expt.	(La ³⁺) M x 10 ³	(H ⁺) M x 10 ⁴	(LaX ⁺⁺) ^a M x 10 ⁴	(X ⁻) ^a M	E _m	T ^o C
Lanthanum-chlorate complex-ion formation					E ₉	
LaX ⁺⁺ Blank	2.122	1.55	—	—	—	25°
6	1.95	1.54	1.9	0.200	0.49	25°
7	2.04	1.55	0.86	0.0800	0.53	25°
8	2.07	1.55	0.56	0.0399	~0.7	25°

^aX⁻ is Cl⁻, NO₃⁻ or ClO₃⁻.

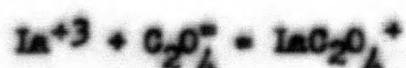
equilibrium constants for the formation of cerous chloride and nitrate complexes of approximately 1.5 and 2 in 1 M hydrochloric and 1 M nitric acid, respectively. Apart from the size difference of the +3 ions, it is not unreasonable that the values would be appreciably different in the pure acids than in sodium perchlorate solutions.

Complexing of Lanthanum by Anions of Organic Acids.—The anions of a number of weak organic acids showed the ability to complex lanthanum ion in varying degrees. The complexing was studied in the manner previously described. Rather large uncertainties appear in the constants calculated from the experimental data taken from these solutions.

The inaccuracy, in some cases, arose from the small degree of complexing which could be obtained without precipitation of lanthanum compounds. Further, the hydrogen ion concentration could not be calculated from acid dissociation constants of the weak acids because the latter are not known accurately in 1 M sodium perchlorate solution. Therefore, it was necessary to measure the acidity with a pH meter. The LaK^{++} blank was then calculated by interpolation to this same acidity. The pH meter was calibrated to give concentrations of hydrogen ion by measuring the pH of acetic acid-sodium acetate buffer solutions of known acidity at $\mu = 1.00$ (NaClO_4).

Oxalate Complexing.—The complex-ion formation proceeded to such an extent that attempted evaluation of the data indicated that, within the experimental accuracy of the method, complete complexing of all the oxalate in solution had taken place. The order of magnitude

of the complexing constant was determined from a solution initially three ten-thousandths molar in total oxalate concentration and a hydrogen ion concentration of $1.5 \times 10^{-4} \text{ M}$ to be greater than one thousand for the reaction



$$K_{10} = \frac{(\text{LaC}_2\text{O}_4^{+})}{(\text{La}^{+3})(\text{C}_2\text{O}_4^{2-})} \quad 10^3 .$$

From the data of Grouthamel and Martin⁽¹⁶⁾, on the formation of oxalate complexes of cerous ion, a concentration constant was calculated for the above reaction at $\mu = 0.42$ of 6×10^4 at 25°C . If the lanthanum-oxalate complexing constant is this large, the uncomplexed oxalate species would not be detectable in the calculation of the data obtained here.

Succinate Complexing.—These experiments showed considerable complex formation. Merck, reagent grade succinic acid was used as the source of the complexing agent. The experimental conditions and results are given in Tables 22 and 23. The data are presented in terms of a gross complexing constant defined by the equations:



$$K_{11} = \frac{(\text{LaX})}{(\text{La}^{+3})(\text{X})}$$

where (LaX) is the sum of the concentration of lanthanum complexes with all succinate species. Presumably only succinate ion and bisuccinate ion are involved. The interpretation of the experimental data is

TABLE 22

Experimental Data for Lanthanum Complexing by Other Anions at 25°C.

 $\mu = 1.0$ (NaClO₄)

Expt.	(La) $M \times 10^3$	(TA) $M \times 10^4$	(X ⁻) ^c $M \times 10^3$	$D_{\text{Sample}}^{2 \text{ cm}}$	$D_{\text{Blank}}^{2 \text{ cm}}$
Lanthanum-succinate complex-ion formation					
1	2.12	3.22	83.3	0.508	0.140
2	2.34	3.25	83.3	0.530	0.148
3	0.706	3.22	83.3	0.560	0.319
4	0.705	3.24	83.3	0.721	0.416
Lanthanum-tartrate complex-ion formation					
5	2.12	3.21	5.00	0.229	0.097
6	2.12	3.21	1.00	0.445	0.127
Lanthanum-phthalate complex-ion formation					
7	2.12	3.21	53.3	0.213	0.101
8	2.12	3.21	16.00	0.261	0.105
Lanthanum-lactate complex-ion formation					
9	2.12	3.215	100	.189	0.115
10	2.12	3.215	20.0	.298	0.114
Lanthanum-citrate complex-ion formation					
11	2.12	3.24	4.0	.251	0.143
12	2.12	3.24	0.6	.780	0.156

^aX⁻ is succinate, tartrate, phthalate, lactate, or citrate. The symbol (X⁻)^c represents the stoichiometric concentration.

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Table 23

Equilibrium Constant Data for Lanthanum Complexing by Other Anions
at 25°C. $\mu = 1.0$ (NaClO_4)

Expt.	(La^{+3}) $M \times 10^3$	(H^+) $M \times 10^4$	$(\text{LaX})^a$ $M \times 10^4$	$(\text{X})^b$ $M \times 10^2$	K_n^c
Lanthanum-succinate complex-ion formation					K_{11}
1	1.14	1.41	9.7	8.24	10.3
2	1.26	1.29	10.6	8.22	10.2
3	0.218	0.380	4.82	8.29	26.7
4	0.183	0.237	5.17	8.28	34.2
Lanthanum-tartrate complex-ion formation					K_{12}
5	1.39	5.0	7.2	.429	1.2×10^2
6	1.67	2.45	4.4	.0560	ca. 5×10^2
Lanthanum-phthalate complex-ion formation					K_{13}
7	1.17	5.3	9.3	5.24	15.2
8	1.51	4.8	6.0	1.54	26.
Lanthanum-lactate complex-ion formation					K_{14}
9	0.514	3.24	16.0	9.8	32.
10	1.32	3.31	7.9	1.92	31.
Lanthanum-citrate complex-ion formation					K_{15}
11	0.30	1.23	17.8	0.222	2.7×10^3
12	1.57	1.06	3.9	0.021	1.2×10^3

^a(LaX) is the total concentration of lanthanum complexed by species of X.

^b(X) = (X⁻) - (LaX) X⁻ has same significance as in Table

$$^c K_n = \frac{(\text{LaX})}{(\text{La}^{+3})(\text{X})}$$

dependent upon the knowledge of the acid dissociation constants for succinic acid, neither of which is known at an ionic strength of unity. The values for zero ionic strength were roughly corrected to the desired ionic strength by multiplying the first constant by the ratio of the acetic acid dissociation constant at unit ionic strength to the value for zero ionic strength, and the second constant by the ratio of the bi-sulfate dissociation constant at unit ionic strength to that at zero ionic strength.

$$K_I = \frac{(H^+)(H \text{ Succ}^-)}{(H_2 \text{ Succ})} = 1.14 \times 10^{-4}, \mu = 1.0; K_{II} = \frac{(H^+)(\text{Succ}^-)}{(H \text{ Succ}^-)} = 2.11 \times 10^{-5}, \mu = 1.0$$

Referring to the values of K_{II} in Table 23 it is apparent that within the accuracy of the data the gross equilibrium constant is a decreasing function of the hydrogen ion concentration, but less than first power. In this region $HSucc^-$ is the principal species. It must be concluded that complexes of the formula $LaHSucc^{++}$ exist as well as $LaSucc^+$. A quantitative analysis of the data in terms of these two complexes and using previously listed, rough values for the succinic equilibrium constants, indicated that the data could be satisfactorily interpreted in terms of these two species. Since the values of the acid ionisation constants are so uncertain, the calculated complexing constants will not be reported.

An experiment not reported, with all conditions the same as number 3 of Tables 22 and 23 except for a 3.3 fold lower $ESucc$ concentration, gave a value of approximately 7 for K_{II} . If there is not a gross error in the experiment, this would be evidence for appreciable amounts of complexes containing more than one succinate or bisuccinate

group. Then the interpretation in terms of LaHSucc^{++} and LaSucc^+ would have to be modified.

Tartrate Complexing.—The tartrate solutions were prepared by partial neutralization of Merck Reagent tartaric acid, with sodium hydroxide.

The data are presented in Tables 22 and 23. It is apparent that appreciable complexing took place under the conditions of the experiment. The gross equilibrium constant K_{12} is defined by the equation:

$$K_{12} = \frac{(\text{La Tart})}{(\text{La}^{+3})(\text{Tart})}$$

The value of K_{12} for experiment 6 is not very accurate because a rather small fraction of the lanthanum is complexed and the error in the LaTart concentration is magnified two fold in obtaining the value of (Tart) . Thus 0.02 pH units error causes approximately a 40% error in K_{12} .

Values for the acid ionization constants were estimated for $\mu = 1$ and 25°C by the method used for succinic^(14,15,8) acid:

$$K_I = \frac{(\text{H}^+)(\text{C}_4\text{O}_6\text{H}_5^-)}{(\text{C}_4\text{O}_6\text{H}_6)} = 1.7 \times 10^{-3} \quad K_{II} = \frac{(\text{H}^+)(\text{C}_4\text{O}_6\text{H}_4^{--})}{(\text{C}_4\text{O}_6\text{H}_5^-)} = 2.3 \times 10^{-4}$$

The principal species under the conditions of the experiments should be tartrate and bitartrate ions. If $\text{La}(\text{C}_4\text{O}_6\text{H}_4)^+$ is the only important complex, the acid dependence of K_{12} should be between zero and first order, and nearer the latter. The experimental data appear to give a second order dependence, but it probably could be first order within the accuracy of the data. If $\text{La}(\text{C}_4\text{O}_6\text{H}_5)^{++}$ were also present the order should be even less than with $\text{La}(\text{C}_4\text{O}_6\text{H}_4)^+$ which is in disagreement with

the experiments.

Phthalate Complexing.— A stock solution of Kahlbaum Chemische Fabric analytical phthalic acid, partially neutralized with sodium hydroxide, was used in the preparation of the experiments. The experimental data are presented in Table 22. Sufficient complexing took place under the conditions of the experiments to permit the calculation of a gross complexing constant, K_{13} .

$$K_{13} = \frac{(\text{LaPhth})}{(\text{La}^{+3})(\text{Phth})}$$

The values of the constant given in Table 23 are not consistent within their limits of accuracy. The acidity differs only ten percent between the two experiments and therefore cannot explain 1.7 fold factor in the values of K_{13} . The discrepancy is in the opposite direction to be expected for the formation of complex containing one lanthanum and two phthalate groups.

The acid dissociation constants were estimated for phthalic^(8, 15) acid at $\mu = 1$, and 25°C by the method discussed previously.

$$K_I = \frac{(\text{H}^+)(\text{PC}_2\text{O}_4\text{H}^-)}{(\text{PC}_2\text{O}_4\text{H}_2)} = 2.28 \times 10^{-3} \quad K_{II} = \frac{(\text{H}^+)(\text{PC}_2\text{O}_4^{--})}{(\text{PC}_2\text{O}_4\text{H}^-)} = 3.1 \times 10^{-5}$$

The experimental conditions require that $\text{PC}_2\text{O}_4\text{H}^-$ be the predominant species.^a Since the acidity was not varied significantly, it is not possible to decide whether the complex contains phthalate or acid phthalate ion or is a mixture of the two types. If it is assumed that all the complex is $\text{La}(\text{PC}_2\text{O}_4\text{H})^{++}$, the complexing constant for the

^a ϕ represents the phenyl radical.

reaction: $\text{La}^{+3} + \phi\text{C}_2\text{O}_4\text{H}^- = \text{La}(\phi\text{C}_2\text{O}_4\text{H})^{++}$ is ca. 25. If all the complex is assumed to be $\text{La}(\phi\text{C}_2\text{O}_4)^{++}$, the complexing constant for the reaction: $\text{La}^{+3} + \phi\text{C}_2\text{O}_4^- = \text{La}(\phi\text{C}_2\text{O}_4)^+$ is ca. 4×10^3 .

Lactate Complexing.— The lactate experiments were prepared using Merck Reagent lactic acid which had been partially neutralized with sodium hydroxide.

The experimental data appear in Table 22. The gross complexing constant showed good agreement between the separate experimental values when calculated for the reaction:

$$K_{14} = \frac{(\text{LaLact}^{++})}{(\text{La}^{+3})(\text{Lact})}$$

The values are listed in Table 23.

A value for the lactic acid ionization constant was estimated for $\mu = 1$ at 25°C in the manner previously described, using the value at zero ionic strength⁽⁸⁾:

$$K_a = \frac{(\text{H}^+)(\text{C}_3\text{O}_3\text{H}_5^-)}{(\text{C}_3\text{O}_3\text{H}_6)} = 2.42 \times 10^{-4}$$

Since the two experiments were at nearly the same acidity it is not possible to check the hydrogen ion dependence of the equilibrium. However, it is almost certain that only lactate ion would be involved in complex formation. Making this assumption and using the above dissociation constant for lactic acid, the following equilibrium constant is calculated:

$$K_{14} = \frac{(\text{LaC}_3\text{O}_3\text{H}_5^{++})}{(\text{La}^{+3})(\text{C}_3\text{O}_3\text{H}_5^-)} = 56$$

Citrate Complexing.—The citrate experiments were prepared using Merck Reagent tri-sodium citrate, dihydrate acidified to pH 4.0 with perchloric acid, and buffering the solution with sodium acetate, acetic acid buffer.

The experimental observations are presented in Table 22 and indicate considerable complexing of the lanthanum ion. A gross citrate complexing constant was determined and its calculated values are presented in Table 23:



$$K_{15} = \frac{(\text{LaCit})}{(\text{La}^{+3})(\text{Cit})}$$

where $\text{Cit} = \text{Cit}^{\ominus} + \text{HCit}^{\ominus} + \text{H}_2\text{Cit}^{\ominus} + \text{H}_3\text{Cit}$.

Values for the three acid dissociation constants were estimated for $\mu = 1$, at 25°C from the equations given by Bjerrum and Unmack: ^(17a)

$$K_I = \frac{(\text{H}^+)(\text{C}_6\text{O}_7\text{H}_7^{\ominus})}{(\text{C}_6\text{O}_7\text{H}_8)} = 1.1 \times 10^{-3} \quad K_{II} = \frac{(\text{H}^+)(\text{C}_6\text{O}_7\text{H}_6^{\ominus})}{(\text{C}_6\text{O}_7\text{H}_7^{\ominus})} = 3.2 \times 10^{-4}$$

$$K_{III} = \frac{(\text{H}^+)(\text{C}_6\text{O}_7\text{H}_5^{\ominus})}{(\text{C}_6\text{O}_7\text{H}_6^{\ominus})} = 8 \times 10^{-7}$$

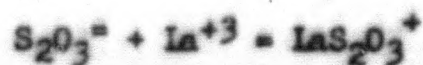
These values are at best rough approximations for the high ionic strength used. The principal species should be $\text{C}_6\text{O}_7\text{H}_6^{\ominus}$, and $\text{C}_6\text{O}_7\text{H}_7^{\ominus}$ at somewhat smaller concentration. The acidity variation in the experiments was too small to check the acid dependence and cannot account for the change in K_{15} . The principal difference between the two experiments was a ten fold change in the gross citrate concentration. The K_{15} values could

be explained if there is somewhat more than one citrate per lanthanum complex on the average. In this connection it is interesting to note that ion-exchange studies^(18,19) of citrate complexing, under other conditions, have been interpreted in terms of the formation of $\text{La}(\text{C}_6\text{O}_7\text{H}_7)_3$ directly, without the presence of significant amounts of the intermediate complexes. Such a formulation would not fit the present experimental results.

Phosphate Complexing.--An attempt was made to obtain the equilibrium constant for lanthanum-phosphate complexing. The limited solubility of lanthanum phosphate species made such a determination very unreliable because of the small difference between the absorption by the blank and that by the phosphate complex solution. Attempts to attain a larger differential in optical densities resulted in precipitation.

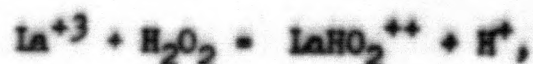
An approximate value for the ratio of lanthanum to phosphate in the precipitate was found to be 0.95. This would indicate that the precipitate was $\text{LaPO}_4 \cdot x\text{H}_2\text{O}$. The calculated pH change for such a reaction agreed fairly well with the difference in the pH of the solution just before adding the final lanthanum perchlorate, and the pH of the solution after precipitation had taken place.

Thiosulfate Complexing.--Attempts to measure thiosulfate complexing of lanthanum were greatly hindered by the decomposition of the former substance. Thus only solutions of low thiosulfate concentration could be measured. A complexing constant for the reaction:



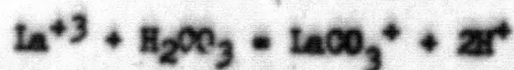
was determined to be ca. 6, but the experimental accuracy was poor. The value can be safely assumed to be less than 10.

Peroxide Complexing.—The experimental data indicated insufficient complexing to permit the determination of the complexing constant. An upper limit for the equilibrium constant for the reaction:



at $\mu = 1$ and 25°C was calculated to be 6×10^{-6} .

Carbonate Complexing.—The addition of powdered "dry ice" to a buffered lanthanum chelate solution produced no decrease in the optical density. Within the experimental accuracy, no carbonate complexing occurred. Any attempt to raise the pH of the solution and increase the carbonate ion concentration resulted in the precipitation of some basic lanthanum species. An upper limit for the formation of a lanthanum-carbonate complex-ion was estimated for the reaction, assuming that the solution was at least half-saturated with CO_2 .



$$K_{18} = \frac{(\text{LaCO}_3^+)(\text{H}^+)^2}{(\text{La}^{+3})(\text{H}_2\text{CO}_3)} \ll 10^{-9}$$

Iodide Complexing.—No significant complexing of lanthanum by iodide was detected. The complexing constant must be less than 0.5.

Correlation of Complexing Constants.—It is of interest to see what correlations can be found in the complexing constants obtained in this work. The complexes of lanthanum with singly charged negative ions will be discussed first.

One obvious correlation is to compare the relative tendency of two different positive ions to be coordinated to the same series of anions. The most convenient (but not the most comparable) ion to use is hydrogen ion. It is found that the complexing constants appear to follow roughly the same order as the acid constants. The anions of the strong acids, i.e. I^- , Cl^- , NO_3^- and ClO_3^- are all very weakly bound to lanthanum ion. The organic acids, lactic and acetic, are more strongly complexed, and the considerably weaker acid, TTA, gives a complexing constant of 4.5×10^2 when calculated for enolate ion.

This systematization shows some irregularities and is probably fortuitously good. Thus the constant for lactate ion is 56 while that for acetate ion is 12, even though acetic acid is an eight fold weaker acid. Undoubtedly the complexing by lactate ion is aided by the presence of the OH group adjacent to the carboxylate group.

The acid constant for the TTA hydrate is not a fair basis for comparison, but rather that for the enol form should be used. If it is assumed that roughly two percent of aqueous TTA is present in the enol form, the acid constant becomes ca. 3×10^{-5} which is nearly the same as for acetic acid. The complexing constants for lanthanum differ nearly 40 fold. Again the structure must play an important role. One factor is the decrease in resonance in the conjugated system (involving three carbons and two oxygens) of

enolate ion when a proton is added. The corresponding decrease for the conjugated system (involving only two oxygens and one carbon) in acetate ion should be considerably less. Therefore the addition of a proton to enolate ion is inhibited relative to acetate ion.

It is found from models that the two coordinating oxygens in enolate ion can get closer together for chelate formation with a metal ion than is possible with acetate ion; this is probably another important factor in their relative complexing tendencies.

A comparison of the complexing of the doubly charged anions is not possible because of the lack of data.

The entropies of lanthanum complex formation, which were measured for a number of reactions, in general are positive but not greatly so. If the complex ions behaved like monatomic ions of the same net charge, the entropy changes would be considerably more positive than is observed. Therefore it must be concluded that such a model is incorrect and that the water molecules are more rigidly held around the complex ions than the net charge would indicate. A similar behavior is shown by uranyl ion, UO_2^{++} .

APPENDIX I

The Calculation of the Molar Extinction Coefficient of Enolate-Ion; Dissolution of TTA(s) in 0.1 M NaOH(aq.):

No.	Solution	D_{λ}^2 cm.	Time
1-53	2 millimols TTA(s) 4 millimols NaOH(aq.) diluted to 200 ml.		01:02
2-53	Dilute aliquot of (1-53) 1000 fold, to give approximately: $10^{-5}M (K^-)$ $5 \times 10^{-4}M (OH^-)$	Obs. pH=10.58 μ corr. = $\frac{.17}{10.75}$	01:25
		$D_{3380\lambda}^b = .450$ $D_{blank} = .402$	
3-53	50 ml. (2-53) 5 ml. 11.9 M HClO ₄		01:14
4-53	5 ml. (3-53) 15 ml. H ₂ O 20 ml. benzene shaken to equilibrium.	$D_{3250\lambda}^b = .552$ $D_{blank} = .0805$.4715	
5-53	Repeat (3-53)		01:30
6-53	Repeat (4-53), using 5 ml. (5-53) A distribution coefficient, (TTA _{benzene} /TTA _{aqueous}), (4) equal to 40, was used to correct the (TTA) benzene concentration for the non-extracted portion (i.e. 41/40 = correction factor).	$D_{3250\lambda}^b = .549$ $D_{blank} = .0805$.4685	

$$\frac{.4715}{2 \times 11345} \times \frac{41}{40} \times \frac{20}{5} \times \frac{55}{50} = 9.38 \times 10^{-6} M (K^-) \text{ at } 01:14$$

$$9.31 \times 10^{-6} M (K^-) \text{ at } 01:30$$

hence, $9.332 \times 10^{-6} M (K^-) \text{ at } 01:25$

$$\frac{.402}{2 \times 9.332 \times 10^{-6}} = 21,550 = \epsilon_{3380\lambda}^{(K^-)}$$

b designates benzene solution.

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APPENDIX II

The Calculation of the Molar Extinction Coefficient of Enolate-Ion; Dissociation of TTA(aq) in Alkaline Buffer:

No.	Solution	D_{λ}^2 cm.	Time
1-55	$4.33 \times 10^{-5} M$ TTA. (H ₂ BO ₃) 0.1568M Buffer, pH=8.4 (NaCl) 0.9207M NaClO ₄ (NaOH) (Obs. pH of Solution is 8.08 μ corr. $\frac{.17}{}$ pH = 8.25)	$D_{3380\text{\AA}}^b = 1.710$ $D_{\text{blank}}^b = \frac{.041}{1.669}$	21:32 21:40
2-55	40 ml. (1-55) 10 ml. 2.38M HClO ₄		21:36
3-55	20 ml. (2-55) 20 ml. Benzene Shaken to equilibrium.	$D_{3250\text{\AA}}^b = .759$ $D_{\text{blank}}^b = \frac{.067}{.692}$	
4-55	20 ml. (1-55) 2 ml. 11.9 M HClO ₄ diluted to 100 ml.		22:12
5-55	20 ml. (4-55) 20 ml. Benzene Shaken to equilibrium.	$D_{3250\text{\AA}}^b = .235$ $D_{\text{blank}}^b = \frac{.067}{.168}$	

$$\frac{.692 \times 41 \times 5}{2 \times 11345 \times 40 \times 4} = 3.91 \times 10^{-5} M \text{ (HK) at 21:36}$$

$$= 3.80 \times 10^{-5} M \text{ (HK) at 22:12}$$

hence, $= 3.90 \times 10^{-5} M \text{ (HK) at 21:40}$

$$\text{at pH} = (8.08 + .17), \frac{(K^-)}{(HK)} = \frac{5.75 \times 10^{-7}}{5.6 \times 10^{-4}} = 102.7$$

$$\frac{102.7}{103.7} \times 3.90 \times 10^{-5} = 3.86 \times 10^{-5} M \text{ (K}^-) \text{ at 21:40}$$

$$\frac{1.669}{2 \times 3.86 \times 10^{-5}} = 21,600 = \epsilon_{3380\text{\AA}}^{(K^-)}$$

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APPENDIX III

Method Used in the Calculation of the Acid Dissociation Constant
for HK at any Ionic Strength.

a) It was necessary to obtain the absorption of an HK blank which contained no enolate ion. This was done by acidifying TTA samples and measuring the spectrum. In Figures 4 and 5, data were presented to show that the spectrum of such a solution varies with the acid and salt concentrations. The following data were used to take account of this dependence. (Also included are the data of experiment 13 which is to be used as the example).

Expt.	TTA M x 10 ⁴	M HClO ₄	M NaClO ₄	M H ⁺	μ	D ² cm. 3380 Å
B-1	4.10	0.238	0.000	0.238	0.238	0.257
B-2	4.10	0.228	0.770	0.228	0.998	0.2735
13	4.16	0.000	0.721	3.08x10 ⁻⁵	1.000	0.605

b) Correction of HK blanks of B-1 and B-2 to 0.0 M HClO₄, using the data of Table 4:

$$\frac{298}{306.5} \times .257 = .2495$$

$$\frac{298}{306} \times .2735 = .266$$

On the addition of perchloric acid the molar extinction coefficient of HK was observed to increase, on a percentage basis, to an equivalent degree whether there was added sodium perchlorate or not, as can be verified from Figure 5. Therefore a percentage correction was applied to the optical density.

c) Correction of blanks to TTA concentration of experiment 13:

$$\frac{4.16}{4.10} \times .2495 = .2535$$

$$\frac{4.16}{4.10} \times .266 = .270$$

- d) Calculated blank to be used at a given ionic strength:

$$D_{3380}^{2 \text{ cm.}}(\text{blank}) = \frac{(0.270 - 0.2535)}{(0.770)} (\mu) + 0.2535 = 0.0214 \mu + 0.2535$$

The assumption was made that the effect of sodium perchlorate on the absorption is linear with respect to the sodium perchlorate concentration.

- e) Blank for Experiment 13 = $0.0214 \times 1.00 + 0.2535 = 0.2749$
- f) Determination of the (K^-) concentration in Experiment 13 and, using this value, calculation of K_1 ($\mu = 1.0$):

$$0.605 - \frac{(HK)}{TTA} (0.275) = 0.335 \quad \frac{0.335}{2 \times 2.5 \times 10^4} = 7.78 \times 10^{-6} M (K^-)$$

$$(4.16 - .0778)10^{-4} = 4.08 \times 10^{-4} M (HK)$$

$$K_1 (\mu = 1.0) = \frac{(7.78 \times 10^{-6})(3.08 \times 10^{-5})}{(4.08 \times 10^{-4})} = 5.87 \times 10^{-7}$$

APPENDIX IV

Method Used in Calculating the Equilibrium Constant for the
Formation of Lithium Chelate.

Experiment 8: 25°C, $\mu = 1.0$

$$3.59 \times 10^{-5} \text{M (H}^+) \text{}$$

$$4.247 \times 10^{-4} \text{M (TTA)} \text{}$$

$$0.97 \text{M (Li}^+) \text{}$$

$$D_{3470}^{2 \text{ cm}^{-1}}$$

$$\frac{\text{LiClO}_4}{1.138}$$

$$\frac{\text{NaClO}_4}{0.599}$$

$$(a) \quad \frac{1.138 - \frac{(\text{TTA} - \text{LiK})}{(\text{TTA})} \approx 0.999}{2 \times 2.15 \times 10^4} = \frac{0.5575}{4.3 \times 10^4} = 1.298 \times 10^{-5} \text{M (LiK)}$$

$$(b) \quad \frac{4.247 \times 10^{-4} (\text{TTA}) - 0.130 (\text{LiK})}{4.117 \times 10^{-4} (\text{HK} + \text{K}^-)}$$

$$(c) \quad K_1 \text{ at } 25^\circ\text{C } (\mu = 1.0) = 5.75 \times 10^{-7}$$

$$\frac{5.75 \times 10^{-7}}{3.59 \times 10^{-5}} = \frac{(\text{K}^-)}{(\text{HK})} = 0.0160$$

$$(\text{HK}) = \frac{4.117 \times 10^{-4}}{1.016} = 4.055 \times 10^{-4} \text{M}$$

$$(d) \quad K_3 = \frac{(\text{LiK})(\text{H}^+)}{(\text{Li}^+)(\text{HK})} = \frac{(1.298 \times 10^{-5})(3.59 \times 10^{-5})}{(0.97)(4.055 \times 10^{-4})}$$

$$= 1.184 \times 10^{-6} \text{ (at } 25^\circ\text{C and } \mu = 1.0)$$

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APPENDIX V

Detailed Explanation of the Method Used to Determine the Molar Extinction Coefficient of the (LaK^{++}) Complex-ion.

30.0 ml. 0.0704 M $La(ClO_4)_3$)	Obs. pH = 5.80	
5.21 ml. 5.0 M $Na(ClO_4)_3$)	pH corr. + .08 ^a	$D_{3470}^{2\%} = 0.043$
0.02 ml. 0.10 M NaOH)	corr'd. pH = 5.88	

To 20.0 ml. of the above solution were added 2.0 ml. of an aqueous TTA stock solution, whose concentration was 1.823×10^{-5} M. The resulting solution had the following composition:

1.659×10^{-5} M TTA = (HK, K^- , LaK^{++})	Obs. pH = 5.76	
0.0544 M $\Sigma La = (La^{+3}, LaK^{++})$	pH corr. + .08 ^a	$D_{3470}^{2\%} = 0.800$
0.672 M $Na(ClO_4)_3$	corr'd. pH = 5.84	

$$\text{hence, } (H^+) = 1.45 \times 10^{-6} \text{ M}$$

Assuming an equilibrium constant for the formation of (LaK^{++}) complex-ion equal to 2.5×10^{-3} , one can correct the total TTA concentration for the equilibrium ratio of $(HK)/(LaK^{++})$ and thereby determine the (LaK^{++}) concentration.

$$\frac{(K_{LaK^{++}})(La^{+3})}{(H^+)} = \frac{(2.5 \times 10^{-3})(0.0544)}{(1.45 \times 10^{-6})} = \frac{(LaK^{++})}{(HK)} = 94$$

$$\text{hence, } \frac{94 \times 1.659 \times 10^{-5}}{95} = 1.64 \times 10^{-5} \text{ M } (LaK^{++})$$

$$\frac{0.800 - 0.043}{2 \times 1.64 \times 10^{-5}} = 2.31 \times 10^4 = \epsilon \left(\frac{LaK^{++}}{3470 \text{ \AA}} \right)$$

^aThe pH meter was calibrated with a known buffered solution of similar concentrations. A sodium acetate-acetic acid buffer was used to give the following solution a calculated pH = 4.28.

0.0546 M $La(ClO_4)_3$)	
0.74 M $Na(ClO_4)_3$)	Calc. pH = 4.28
0.0060 M (Ac^-))	Obs. pH = 4.20
0.01 M (HAc))	Add to Obs. pH + .08

APPENDIX VI

Method of Calculation of the Equilibrium Constant for the Formation of Lanthanum-Chelate Complex Ion.

Experiment 1 (Table 14 — 25°C and $\mu = 1.0$):

Initial concentrations:

$(\Sigma \text{La}^{+3}) = 1.56 \times 10^{-3} \text{ M La}(\text{ClO}_4)_3$	Experimental solution. (La ⁺³) free blank	$\frac{D^2 \text{ cm.}}{3670 \text{ Å}}$
$(\text{TTA}) = 3.384 \times 10^{-4} \text{ M}$		0.498
$(\Sigma \text{Ac}^-) = 8.33 \times 10^{-3} \text{ M NaAc}$		0.134
$(\Sigma \text{HAc}) = 4.17 \times 10^{-2} \text{ M HAc}$		

$$(\text{LaK}^{++}) = \frac{D_{\text{exp.}} - \frac{(\text{TTA}) - (\text{LaK}^{++})}{(\text{TTA})} \times D_{\text{blank}}}{1 \epsilon_{\text{LaK}^{++}}}$$

Solving for (LaK⁺⁺):

$$(\text{LaK}^{++}) = \frac{D_{\text{exp.}} - D_{\text{blank}}}{1 \epsilon_{\text{LaK}^{++}} - \frac{D_{\text{blank}}}{(\text{TTA})}}$$

$$(\text{LaK}^{++}) = \frac{0.498 - 0.134}{2 \times 2.31 \times 10^4 - \frac{0.134}{3.384 \times 10^{-4}}} = 7.94 \times 10^{-6} \text{ M}$$

$$\begin{aligned} (\text{La}^{+3}) &= (\Sigma \text{La}^{+3}) - (\text{LaK}^{++}) - (\text{LaAc}^{++}) \\ &= (\Sigma \text{La}^{+3}) - (\text{LaK}^{++}) - K_5 (\text{Ac}^-)(\text{La}^{+3}) \end{aligned}$$

Solving for (La⁺³):

$$(\text{La}^{+3}) = \frac{(\Sigma \text{La}^{+3}) - (\text{LaK}^{++})}{1 + K_5 (\text{Ac}^-)}$$

$$= \frac{1.56 \times 10^{-3} - 7.94 \times 10^{-6}}{1 + 12 \times 0.00833} = 1.411 \times 10^{-3} \text{ M}$$

APPENDIX VI (Continued)

$$(\text{LaAc}^{++}) = K_5 (\text{Ac}^-)(\text{La}^{+3})$$

$$= 12 \times 0.00833 \times 1.411 \times 10^{-3} = 1.41 \times 10^{-4} \text{ M}$$

$$(\text{Ac}^-) = (\Sigma \text{Ac}^-) - (\text{LaAc}^{++}) + (\text{H}^+) - (\text{LaK}^{++})$$

$$= 0.00833 - 1.41 \times 10^{-4} + 1.53 \times 10^{-4} - 7.94 \times 10^{-6} = 0.00833 \text{ M}$$

$$(\text{HAc}) = (\Sigma \text{HAc}) - (\text{H}^+) + (\text{LaK}^{++})$$

$$= 0.04167 - 1.53 \times 10^{-4} + 7.94 \times 10^{-6} = 0.04153 \text{ M}$$

$$(\text{H}^+) = \frac{K_2 (\text{HAc})}{(\text{Ac}^-)}$$

$$= \frac{3.08 \times 10^{-5} \times 0.04153}{0.00833} = 1.534 \times 10^{-4} \text{ M}$$

$$(\text{HK}) = (\text{TTA}) - (\text{LaK}^{++}) - (\text{K}^-) = (\text{TTA}) - (\text{LaK}^{++}) - \frac{K_1 (\text{HK})}{(\text{H}^+)}$$

Solving for (HK):

$$(\text{HK}) = \frac{(\text{TTA}) - (\text{LaK})}{1 + \frac{K_1}{(\text{H}^+)}}$$

$$= \frac{3.384 \times 10^{-4} - 7.94 \times 10^{-6}}{1 + \frac{5.75 \times 10^{-7}}{1.534 \times 10^{-4}}} = 3.29 \times 10^{-4} \text{ M}$$

$$K_4 = \frac{(\text{LaK}^{++})(\text{K}^-)}{(\text{La}^{+3})(\text{HK})}$$

$$= \frac{7.94 \times 10^{-6} \times 1.534 \times 10^{-4}}{1.411 \times 10^{-3} \times 3.29 \times 10^{-4}} = 2.62 \times 10^{-3}$$

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APPENDIX VII

Method of Calculation of the Equilibrium Constant for
the Formation of Lanthanum-Acetate Complex-Ion.

$$K_4 = \frac{(\text{LaK}^{++})(\text{H}^+)}{(\text{La}^{+3})(\text{HK})} = \frac{\frac{D}{\epsilon l} (\text{H}^+)}{(\text{La}^{+3})(\text{HK})}$$

where ϵ is the molar extinction coefficient of LaK^{++} and D is the optical density of the sample minus that of the blank corrected to the same TTA concentration as the sample. The formation of LaK^{++} causes the TTA concentration to be less in the sample.

$$\text{Let } k = \frac{1}{K_4 \epsilon l} = \frac{(\text{La}^{+3})(\text{HK})}{D (\text{H}^+)}$$

$$K_5 = \frac{(\text{LaAc}^{++})}{(\text{La}^{+3})(\text{Ac}^-)}$$

$$(\text{La}^{+3}) = \frac{(\text{La}^{+3}) + (\text{LaAc}^{++})}{1 + K_5 (\text{Ac}^-)}$$

$$\text{Therefore, } k = \frac{(\text{La}^{+3}) + (\text{LaAc}^{++})}{1 + K_5 (\text{Ac}^-)} \cdot \frac{(\text{HK})}{D(\text{H}^+)}$$

By equating the data for k of two separate experiments, the constant K_5 can be calculated. See Tables 16 and 17 for experimental data and values of K_5 .

APPENDIX VII

The Method of Calculating Complexing Constants.

The following method was found to be convenient for calculating complexing constants.

Let there be two solutions of identical stoichiometric composition with respect to TTA and having equal hydrogen ion concentration. Let one, the sample, contain lanthanum; the other is the blank.

Let D = optical density of sample solution

D° = optical density of blank

Then $D = D_{LaK^{++}} + D_{HK} + D_{K^{-}}$

$$D = (LaK^{++})\epsilon_{LaK^{++}} l + \left\{ (TTA) - (LaK^{++}) \right\} \epsilon_{HK + K^{-}} l \quad (1)$$

where $\epsilon_{HK+K^{-}}$ is a combined molar extinction coefficient for HK and K^{-} at the given acidity.

$$D^{\circ} = (TTA)\epsilon_{HK+K^{-}} l \quad (2)$$

Substituting (2) into (1):

$$D = (LaK^{++})\epsilon_{LaK^{++}} l + D^{\circ} \left(1 - \frac{(LaK^{++})}{(TTA)} \right)$$

Solving for (LaK^{++}) :

$$(LaK^{++}) = \frac{D - D^{\circ}}{\epsilon_{LaK^{++}} l - \frac{D^{\circ}}{(TTA)}}$$

When two sets of experiments with identical blanks (and same hydrogen ion concentration) are combined, the result is:

$$(LaK^{++})_1 = (LaK^{++})_2 \frac{(D_1 - D^{\circ})}{D_2 - D^{\circ}}$$

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APPENDIX VIII (continued)

$$\text{Since } \frac{(La^{+3})_1}{(La^{+3})_2} = \frac{(LaK^{++})_1 (HK)_2}{(LaK^{++})_2 (HK)_1} \quad (3)$$

$$\text{then } (La^{+3})_1 = \frac{(La^{+3})_2 (D_1 - D_0) (HK)_2}{(D_2 - D_0) (HK)_1}$$

In the complexing experiments, set 1 would be the "LaK⁺⁺ Blank" which contained no complexing agent and set 2 would have the same composition except for the presence of the complexing agent.

If acetate is used as a buffer, lanthanum is partially complexed by it. Then for the same acetate concentrations in sets 1 and 2 one can write:

$$(La^{+3})_1 + (LaAc^{++})_1 = \frac{(La^{+3})_2 + (LaAc^{++})_2 (D_1 - D_0) (HK)_2}{(D_2 - D_0) (HK)_1}$$

Assuming the complex to be LaX⁺⁺ one can write:

$$(LaX^{++}) = (2La^{+3}) - (LaK^{++})_1 - (La^{+3})_1 - (LaAc^{++})_1 \quad (4)$$

$$(X^-) = (2X^-) - (LaX^{++})$$

$$(La^{+3})_1 = \frac{(La^{+3})_1 + (LaAc^{++})_1}{1 + K_5 (Ac^-)}$$

$$K = \frac{(LaX^{++})}{(La^{+3})_1 (X^-)}$$

Complexing by weak acids is treated similarly through equation (4).

In the derivation, it was assumed that set 1 and set 2 were at the same acidity. This was not always the case because of changes of acidity caused by the complexing agents and it was then necessary to correct the LaK⁺⁺ blank to the proper hydrogen ion concentration.

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APPENDIX IX

The Preparation of Lanthanum, Lithium and Sodium Perchlorate and TTA Stock Solutions.

A sample of lanthanum oxide, procured from the Maywood Chemical Company, was heated to approximately one thousand degrees centigrade and maintained at that temperature for at least six hours. The sample was cooled in a desiccator over anhydrous calcium sulfate, Drierite, weighed as La_2O_3 and dissolved in a stoichiometric amount of G. F. Smith, double distilled perchloric acid. An arc-spectrographic analysis was made on the resulting solution and no detectable impurities of other rare earth or heavy metals were found. A gravimetric analysis of the stock solution was made by fuming with concentrated sulfuric acid and igniting to constant weight, at 1000°C . The gravimetric analysis was used as the experimental concentration.

Two different samples of TTA were used to prepare the stock solutions of the chelating agent. One sample was vacuum-distilled TTA. The other sample was doubly-recrystallized from hexane and dried in a vacuum desiccator. The TTA was weighed as the non-hydrated species, molecular weight 222.2 gms./mole, and dissolved in conductivity water. The dissolution is very slow, even for concentrations of less than one-thousandth molar. Warming the solution to the TTA melting point speeded up the process without any evidence of decomposition. Acidified aliquots of the aqueous solution were analyzed spectrophotometrically and showed good agreement with the weight concentrations. The presence of the decomposition product, 2-acetylthiophene, in solutions which had stood for an appreciable

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length of time, required that the later analyses be made by measuring the concentration of TTA extracted into benzene from acidified aqueous solutions.

G. F. Smith, Reagent lithium perchlorate was triply-recrystallized from conductivity water as $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. Only the well formed crystals in the center of the crystallizing dish were used; the portion adhering to the walls of the vessel was recycled prior to use. A gravimetric analysis of the solution was run in the same manner described for the $\text{La}(\text{ClO}_4)_3$. The samples were ignited in a muffle furnace at temperatures in excess of 500°C and weighed as Li_2SO_4 .

Sodium perchlorate was prepared by carefully neutralizing G. F. Smith, double distilled perchloric acid in conductivity water with Merck Reagent sodium carbonate. One of the stock solutions was prepared using Baker and Adamson Reagent sodium bicarbonate. The acidity of each solution was measured to make sure the pH was less than 6.5, to insure the absence of buffering due to incomplete neutralization of the bicarbonate ion. The solution was heated to drive off carbon dioxide before each pH measurement. The gravimetric analysis of the resulting solution was made in the manner described above.

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