1955

The formation of thallium chloride complexes and their extraction into ether

Donald Leonard Horrocks
Iowa State College

Recommended Citation

Horrocks, Donald Leonard, "The formation of thallium chloride complexes and their extraction into ether " (1955). *Retrospective Theses and Dissertations*. 13973.
https://lib.dr.iastate.edu/rtd/13973

UNCLASSIFIED

134

Title: The Formation of Thallium Chloride Complexes and their Extraction into Ether.

Author: Donald L. Horrocks

(Official certification of the classification shown is filed in the Ames Laboratory Document Library)

Signature was redacted for privacy.

W. E. Dreeszen

Secretary to Declassification Committee

UNCLASSIFIED

THE FORMATION OF THALLIUM CHLORIDE COMPLEXES AND THEIR EXTRACTION INTO ETHER

by

Donald Leonard Horrocks

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1955

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

TABLE OF CONTENTS

I. INTRODUCTION

Thallium is one of a large group of elements which are extracted into ether from halogen acid solutions. The general lack of knowledge of the extraction of these salts has given strong impetus to the study of all aspects of the extraction process.

As is the case with the trivalent cations of Group III B and many other trivalent cations, thallium, in its +3 oxidation state, forms a series of halogen complexes in an aqueous solution of the corresponding halogen acid. The partition of the metal between an acid solution of the metal-halogen complexes and ether has been studied under many conditions, but virtually no investigations have been carried out at constant ionic strength on the fundamental dependence of the equilibrium between the aqueous and ether solutions upon the hydrogen and chloride ion concentration.

It is the purpose of this work to study, by means of radiochemical methods, the partition of thallium(III) chloride complexes between $HClO_4$ - LiCl - $LiClO_4$ solutions and iso-propyl ether. The investigation has as its immediate objective the determination of the empirical formula of the thallium compound in the ether solution and the equilibrium constant for the extraction process. In this manner, it is hoped that our knowledge of the extraction process of trivalent metal-halogen complexes, and the more general topic of liquid-liquid partition, will be increased by another small amount.

II. REVIEW OF LITERATURE

A. Thallium Chemistry in General

The chemistry and literature of thallium, prior to 1950, have been reviewed by Waggaman, Heffner and Gee (1) and Howe and Smith (2). These reviews which include a long list of references are exceedingly useful in reviewing the chemistry of thallium. Waggaman, Heffner and Gee (1) review the properties, sources, recovery and uses of the element and its compounds and report on the methods of analysis of thallium. Howe and Smith (2) discuss the history, chemistry and properties of thallium with special emphasis on its metallurgy.

The discovery of thallium is generally credited to W. Crookes (3) who noted a new element while making a spectroscopic examination of seleniferous deposits in the lead chambers of a sulfuric acid factory. He named the new element thallium, derived from the Latin word thallus, meaning a budding twig, because of the characteristic green line it imparted to the spectrum.

In an independent investigation, A. Lamy (4) reported in 1862 that he had observed the characteristic green line while examining the sediment from the chambers of a sulfuric acid plant. He made valuable contributions in determining the physical and chemical properties of the new element.

Because of the comparative scarcity of thallium, it had continued to be a laboratory curiosity for many years. In 1919 the use of thallium in photosensitive cells was patented. Several new uses for thallium were developed in 1925, particularly as a poison for rodents and later as an insecticide. Thallium has now become a very important element.

Thallium sources are of two broad groups, natural occurrences and industrial wastes. The natural sources include deposits of thallium minerals in rocks or dissolved in brine. Thallium can be derived from industrial wastes and residues where the thallium from the original raw materials has been concentrated.

Hopkins (5) discussed the properties of thallium metal and its compounds quite thoroughly. He discussed at length many compounds of the two oxidation states of thallium; thallous and thallic, Tl(I) and TL(III) respectively. Thallous resembles the analogous compounds of the alkali metals in the soluble compounds and those of lead in the more difficulty soluble ones, while thallic resembles the compounds of iron and aluminum. Thallic compounds are considerably hydrolyzed and are stable only in the presence of an excess of acid. Thallous compounds are oxidized to thallic by $KMnO_4$, Cl_2, Br_2 and aqua regia but not by HNO_3 alone. The reduction of thallic to thallous is easily accomplished by $SnCl_2$, H_2SO_3, metallic thallium and $FeSO_4$. Thallous and thallic salts readily form complex salts with each other, such as $TlCl_3 \cdot 3TlCl$.

Hillebrand, Lundell, Bright and Hoffman (6) discussed methods of separation and determination of thallium. Thallium is not precipitated by H_2S in strong acid solutions, however, separations based on this fact are as a rule worthless, since thallium forms compounds with members of the H_2S group, such as arsenic, antimony, tin or copper. Thallium is completely precipitated as Tl_2S in acetic acid solutions by H_2S or by $(NH_4)_2S$. Hillebrand, et al. (6) discuss the separation of thallium from lead, silver, cadmium, iron, aluminum, chromium, cobalt, nickel, zinc, manganese, alkaline earths, magnesium, gallium and alkalies. They also mention the separation of thallium from a number of elements based upon the repeated extraction of thallic chloride from 6N HCl solution by means of ether (7). They discussed several methods of determination of thallium, of which the most important are weighing as Tl_2CrO_4 (8), Tl_2O_3 (9), and TlI (10).

Noyes and Bray (11) discuss the qualitative behavior of thallium (I) and thallium (III). They review the methods of separation and detection of the various compounds of thallium.

B. Extraction from Acid Solutions by Ether

Rothe (12) was the first to study the method of extraction of salts from acid solutions by means of ether. He studied the extraction of $FeCl_3$ into ether from HCl solutions. Other early workers on the extraction of $FeCl_3$ into ether included Langmuir (13), who applied it to the separation of iron and nickel, and Kern (14), who applied it to the separation of iron and uranium. The latter studies included work on the dependence of the extraction upon the concentration of the HCl. Speller (15) used the extraction method to separate iron from copper, manganese, aluminum, chrominum, cobalt and nickel.

In 1908 Noyes, Bray and Spear (7) reported the extraction of $TlCl_3$ into ether from HCl solution. They noted that 15 mg. of thallium as

$TlCl_3$ in HCl (sp. gr., 1.12) was completely removed from the aqueous solution after two extractions with ether. They reported that 90-95 percent of the original thallium as $TlCl_3$ was extracted when a 6 N HCl solution was shaken with ether.

Swift (16) reported that gallium, along with iron and thallium, was extracted by ether from a HCl solution. Experiments, carried out with small amounts of gallium in HCl solutions of various concentrations indicated that the extraction of gallium by ether was more nearly complete when the initial concentrations of the HCl was 5.5 N. Swift (16) showed that by treating a 4.9-5.9 N solution of HCl containing gallium with an equal amount of ether, previously saturated with a solution of HCl of the same concentration, about 97 percent of the gallium was extracted.

Wada and Ishii (17) reported that $TlBr_3$ can be separated from all other salts of metals except gold by shaking the HBr solution with ether. They showed that extraction of $TlCl_3$ and $TlBr_3$ could be carried out at much lower concentrations of acids than had been assumed earlier. They stated that 99 percent of the original thallium, present as $TlBr_3$ in HBr, was extracted into diethyl ether when the initial HBr concentration was 0.1N. At this HBr concentration no Fe(III), Ga(III) or In(III) was extracted, however, 99 percent of the original Au(III) was extracted.

"Solvent Extraction and Its Applications to Inorganic Analysis" is the title of a paper written by Irving (18) in which he attempts to present a comprehensive survey of liquid-liquid partition of inorganic substances. He discusses partition isotherms, extraction for removal and fractionation, factors favoring solvent extraction and the extraction of nitrates, chlorides, bromides, fluorides and other inorganic compounds. He also presents information about the extraction of organo-metallic complexes; dithizonates, oxinates, cupferrates and other metal complexes.

Irving (18) pointed out the curious and analytically important alterations in extractability in passing down Group III B, in the extraction from 6 N HCl by ether the extractabilities were approximately Al (0 percent), gallium (40-60 percent), indium (trace) and thallium (90-95 percent). The extraction of the metal bromides from 6 N HBr was approximately gallium (57 percent), indium (99 percent) and thallium (92 percent). Indium, which was extracted with difficulty from HCl solution, was removed completely from 4 to 6 N HBr solutions. The extraction of thallium(III) was complete over a large range of HBr concentrations, at least 99 percent extraction from 0.1 N to 5.0 N HBr. Using 0.5 N HBr thallium(III) was separated from all metals except gold, which was 99 percent extracted as $HAuBr_4$. The efficiency of extraction of iron was reduced by replacing HCl by HBr and the acidity for maximum extraction was also lowered.

Oxidation produces great changes in the extractability of metals. Edwards and Voigt (19) found that the distribution coefficient of Sb(V) between iso-propyl ether and 6.5-8.5 N HCl was greater than 200, whereas that of Sb(III) was only 0.016. Irving and Rossotti (20) report that Tl(III) can be extracted from dilute HCl so that very little iron or gallium are extracted. However, Tl(I) had a maximum extraction of 7.66 percent in 6.19 N HCl. When Tl(III) ether extracts are shaken with a reducing solution Tl(I) is transferred to the aqueous phase, thus giving a very good separation method for thallium. Irving (18) reports the following percentages of metal chloride oxidized-reduced pairs extracted by ether from 6 N HCl; Fe(II) (0 percent) and Fe(III) (99 percent), As(III) (68 percent) and As(V) (2-4 percent), Tl(I) (0 percent) and Tl(III) (90-95 percent), Sn(II) (15-30 percent) and Sn(IV) (17 percent) and Sb(III) (66 percent) and Sb(V) (81 percent).

Irving, Rossotti and Drysdale (21) investigated the extraction of indium by diethyl ether from halogen acids of various concentrations. They showed that the percentage of indium halide extracted by diethyl ether from the corresponding halogen acid increased in the order $Cl < Br < I$ and the maximum extraction occurs at decreasing acid concentrations in the same order. Indium iodide was extracted quantitatively from HI of normalities between 0.5 and 2.5, the distribution coefficient being greatest at 1.5 N.

The partition of minute tracer amounts of $GaCl_3$ between ether and HCl was studied by Grahame and Seaborg (22). They observed that the distribution ratio for $GaCl_3$ between ether and 6 N HCl was fairly constant for initial quantities of 10^{-12} g. and 7 mg., the distribution ratio being 17.5-19.0 and 16.9 respectively. Grahame and Seaborg (22) also reported the distribution ratios of several metallic halides between ether and HCl at low concentrations by the use of radioactive isotopes. They studied the distribution of $MnCl_2$, $CoCl_2$ and $FeCl_3$ between ether and HCl at various HCl concentrations. They observed that the maximum extraction of $GaCl_3$ occurred in about 5.5 N HCl, the same as reported by Swift (16). Grahame and Seaborg (22) reported that the activity coefficient of the $GaCl_3$ in the ether phase, at very low concentrations, was proportional to the concentration because of the relatively large amount of HCl dissolved in the ether.

Irving and Rossotti (20), with the aid of radio-nuclides, studied the extraction by ether of $GaBr_3$ and GaI_3, $InCl_3$ and InI_3, TlI_3 and TlCl, TlBr and TlI from the corresponding halogen acids over a range of acid normalities. They reported changes in the volume after equilibrium of ether and aqueous phases increased with the strength of the halogen acid in the order $HCl < HBr < HI$. They report only a small change in the volume of the phases for HCl strength of up to 5.0 N, while the volume change of the phases is very large for HBr strengths above 3.0 N and for HI strengths above 1.0 N.

Irving and Rossotti (20) showed that InI_3 was extracted quantitatively, over the range 0.5 - 2.5 N HI, while GaI_3 was not extracted under similar conditions. They showed that TlI_3, like $TlBr_3$ and $TlCl_3$, was quantitatively extracted from HI solutions of strength 0.05 to 2.0 N. Small amounts of TlI and TlBr, but not TlCl, were extracted quantitatively from 0.5 - 2.5 N HI and from 1.0 - 3.2 N HBr respectively. For all of the systems studies by Irving and Rossotti (20) the percentage extraction increased with acid normality and passed through a maximum; and the order of the halides for which the maximum extraction occurs at lower acid concentrations was $I < Br < Cl$.

The distribution of $GaCl_3$ between aqueous HCl and isopropyl ether was studied by Nachtrieb and Fryxell (23). They determined the empirical formula of the gallium complex in the ether phase by performing analyses of a number of ether phases for gallium, chloride and ionizable hydrogen. They reported that essentially equimolecular amounts of HCl and $GaCl_3$ are co-extracted from aqueous solutions initially less than 7 M.HCl. Extractions from 8 M HCl gave HCl : $GaCl_3$ ratios significantly greater than unity which corresponded to conditions favoring the formation of complex molecules containing more than one molecule of HCl. They stated that the empirical formula for the gallium complex was quite analogous to that determined for iron by Nachtrieb and Conway (24).

Nachtrieb and Fryxell (23) studied the variation of the distribution coefficient with $GaCl_3$ concentrations. They stated that on the assumption of a polymerized gallium complex in the ether phase, the extraction at sufficiently low gallium concentrations corresponded to the "ideal" behavior predicted by the simple Nernst distribution equation (25). However, at higher gallium concentrations the change is quite marked, possibly due to a decrease in the aqueous HCl concentration due to its extraction and the saturation of the gallium complex in the ether phase.

The distribution coefficients were determined as a function of the acidity for several initial gallium concentrations by Nachtrieb and Fryxell (23). They reported the optimum acidity for efficient extraction was about 7.2 M. They also reported the appearance of a three phase system for extractions made from 8.0 and 9.0 M HCl. Near the lower gallium concentration limit of the three-phase region the volume of the intermediate ("heavy ether") phase was comparatively small but became larger at higher concentration of $GaCl_3$, and at very high $GaCl_3$ concentrations the system again became two phases.

In an investigation of thallium, for the purpose of comparison it is of interest to discuss in some detail the extraction from HCl solutions into ether of its well-known homolog, iron. Since the early workers (7, 12-15), very little work was reported on the extraction of $FeCl_3$ from HCl solutions by ether until the paper by Dodson, Forney and Swift (26) in 1936. They studied the effects of varying the iron and acid concentrations, and of peroxide and alcohol upon the extraction of $FeCl_3$ by isopropyl ether. The optimum HCl concentration for efficient extraction with isopropyl ether ranged from 6.5 to 8.5 M. as compared to a range of 5.5 to 6.5 M. for extraction with diethyl ether. At acid concentrations between 7.5 and 9.0 M. three phases were observed, two ether layers and an aqueous layer. The "heavy" ether layer of intermediate density contained most of the extracted iron. They reported that at acid concentrations of 8.6 and 9.3 M the separate ether phase was metastable and dissolved in the other phases on continued shaking. The percentage of iron extracted was found to vary with the total amount of iron. Isopropyl ether was found to be superior to diethyl ether for the extraction of both small and large quantities of iron.

Axelrod and Swift (27) studied the extraction of Fe(III) from HCl solutions by dichloroethyl ether and reported the formula of the iron compound in the ether phase. They stated that for their studies dichlorethyl ether had a practical advantage over either ether or isopropyl ether in that it separates as the lower phase. They reported no evidence of a decrease in the distribution ratio at HCl concentrations as high as 11.5 M which is contrary the results of Dodson, Forney and

Swift (26) with diethyl and isopropyl ether. This indicated a continuous increase with increasing acid concentration of the concentration of the extracted compound. Axelrod and Swift (27) reported the empirical formula of the iron compound in the ether phase as $HFeCl_4 \cdot$ 4-5 H_2O, neglecting polymerzistion, and possible presence of ether in the molecule. This formula compared with the formula of $2(FeCl_3 \cdot HCl) \cdot 9H_2O \cdot 15\ (C_2H_5)_2O$ reported by Kato and Isii (28).

Nachtrieb and Conway (24) and Nachtrieb and Fryxell (29, 30) made a very thorough study of the extraction of $FeCl_3$ by isopropyl ether. Nachtrieb and Conway (24) showed that the empirical formula of the iron compound extracted from aqueous $FeCl_3$ which does not exceed 8 M. in HCl was $HFeCl_4$. However, for aqueous HCl concentrations exceeding 8 M. the mole ratio of $FeCl_3$ to HCl exceeds 1:1. They reported ratios for $FeCl_3$ to HCl of 1:1.94 at 8.0 M.HCl, 1:1.96 at 9.0 M.HCl, 1:3.04 at 10.0 M.HCl and 1:4.04 at 11.0 M.HCl. The absorption spectrum of the ether phase did not alter noticeably when the ratio of $FeCl_3$ to HCl exceeds 1:1, therefore it did not seem to indicate the formation of mixtures of higher complexes of the type H_2FeCl_5, H_3FeCl_6, etc. They studied the extraction of $FeCl_3$ as a function of temperature. Using the van't Hoff equation a heat of extraction of -1970 calories per mole was found for 0.9595 M.$FeCl_3$ in 3.50 M.HCl.

Nachtrieb and Fryxell (29) made a series of experiments in which the concentrations of aqueous hydrogen and chloride ions was kept constant and the concentration of the total trivalent cations was kept constant by making the combined concentrations of $AlCl_3$ and $FeCl_3$ equal to 0.500 M.

They reported that the effect of $AlCl_3$ was to increase the efficiency of extraction of low concentrations of iron, but it did not make the distribution coefficient independent of the total iron concentration. Since a non-extractable salt was capable of increasing the efficiency of extraction, they believed that a polymerization with rising concentrations of iron does not explain this increase in the partition coefficient. A self-salting out effect of $FeCl_3$ was postulated. They studied the distribution of $FeCl_3$ between aqueous HCl and isopropyl ether at a series of constant HCl concentrations. They observed a constant partition coefficient for a particular HCl concentration for sufficiently dilute $FeCl_3$ solutions.

Stoichiometric activity coefficients as determined by an e.m.f. cell method for $FeCl_3$ in 5 $\underline{F}$ HCl saturated with $FeCl_2 \cdot H_2O$ were reported by Nachtrieb and Fryxell (30). They stated that the increase in the partition coefficient of $FeCl_3$ between isopropyl ether and aqueous HCl with the increase in iron concentration was due to the remarkable decrease in the activity coefficient of that component with increasing concentration.

Myers, Metzler and Swift (31) studied the distribution of Fe(III) between HCl and isopropyl ether solutions to determine the compound extracted. At low acidities, 3 M. in HCl, the ratio of chloride to iron and hydrogen to iron are approximately 4:1 and 1:1 respectively. At higher acid concentrations two ether phases appeared and the ratios were somewhat higher in both phases. The amount of water coordinated with the ethereal iron was determined at number of acid concentrations. The ratio of moles of water to moles of iron in the ether phase varied from

5.5 to 4.8. They also studied the extraction of $FeCl_3$ by isopropyl ether at a constant acid concentration, 5.6 WF.HCl. At low iron concentrations the distribution ratio was approximately constant, but as the iron concentration increased the distribution ratio increased quite sharply. At quite high concentrations of iron the distribution ratio not only ceased to increase but actually decreased.

Myers and Metzler (32) calculated the effective polymerization of the ethereal iron. They studied the effect of the variation of the distribution constant with acid concentration and the effect of acid upon the apparent polymerization of the ethereal iron. They observed the formation of two ether phases at high acid concentrations and investigated the effect of acid concentration upon the composition of the two phases.

The visible and ultraviolet absorption spectrums of the isopropyl ether layers were examined by Metzler and Myers (33). They also studied the isopiestic and magnetic susceptibility of the iron in the ether layer.

III. MATERIAL

A. Thallium - 204

In any investigation employing radiochemical methods it is necessary to select the isotope which will facilitate analysis. The isotope selected for this investigation was Tl^{204}, which decays by emission of 0.76 Mev. beta (34) with a 4.1 ± 0.1 years half-life (35). The thallium was received as active $TlNO_3$ which was supplied by the Isotopes Branch, United States Atomic Energy Commission, Oak Ridge, Tennessee.

The active $TlNO_3$ had to be purified, the main impurities, all being stable, were iron and lead. The $TlNO_3$ was dissolved in aqua regia oxidizing the Tl (I) to Tl (III) which was extracted into isopropyl ether from a 6 M. HCl solution. The Tl (III) was re-extracted into water and reduced to Tl (I) with excess H_2SO_3. After removing the excess H_2SO_3 by boiling, the thallium was precipitated as TlI. The TlI was dissolved in aqua regia and the extraction was repeated three times with precipitation of $Tl(OH)_3$ between extraction steps. The $Tl(OH)_3$ from the final precipitation was dried at 110° C. for approximately two hours converting it to Tl_2O_3. The dark reddish-brown powder was stored in a weighing bottle for use in preparation of stock thallium solutions.

B. Thallium (III) Perchlorate

The Tl needed to make up solutions to the required concentrations was prepared as the perchlorate in order to be in a non-complexed state.

A solution of $Tl(ClO_4)_3$ was satisfactorily prepared from Tl_2O_3 by reaction with $HClO_4$. The Tl_2O_3 was obtained from thallium metal which was oxidized and purified in the same manner as the active thallium. The desired amounts of purified inactive and active Tl_2O_3 were dissolved in excess $HClO_4$. The resulting solution was diluted to 2 liters volume and used as the stock solution in the subsequent experiments.

A procedure for standardization of thallium solutions was reported by Kleinberg (36). This procedure involved reduction with sulfite and precipitation of Tl_2CrO_4 from a basic solution. The results of the standardization of the $Tl(ClO_4)_3$ solution are shown in Table 1. The stock solution was found to contain 2.81 mg. of Tl_2CrO_4 per ml. of solution, which equaled 0.0106 M.

To determine the exact concentration of $HClO_4$ in the stock solution, aliquots were titrated against standard NaOH to the phenolphthalem end-point. Both the free acid and the $Tl(ClO_4)_3$ were titrated. Just before the end-point the thallium precipitated as $Tl(OH)_3$, leaving a clear solution, so that the end-point was easily detected. By calculation, correcting for the $Tl(ClO_4)_3$, the concentration of $HClO_4$ in the stock solution was 4.05 M.

The stock solution of $Tl(ClO_4)_3$, 0.0106 M. in 4.05 M. $HClO_4$, has been very stable and has shown virtually no evidence of decomposition after several months at room temperature. The solution which initially gave no test for chloride ion, still gave no test after one year. Aliquots of the stock solution were titrated potentiometrically with $Ce(SO_4)_2$ in a Beckman Model G pH Meter to test for the presence of any

Table 1

Standardization of the Stock Solution of $Tl(ClO_4)_3$

	Determination	d	d^2
#1	0.0283 g.	0.0002	0.00000004
#2	0.0283 g.	0.0002	0.00000004
#3	0.0278 g.	0.0003	0.00000009
	$3\overline{)0.0844\text{ g.}}$		$3\overline{)0.00000017}$
	0.0281 g.		0.00000006
Average:	0.0281 ± 0.0002 g. / 10 ml.		0.0002
			$\sqrt[2]{0.00000006}$

thallium(I). There was no apparent break in the potential readings upon varying the amount of added $Ce(SO_4)_2$ from 3×10^{-8} moles to 10^{-4} moles for an aliquot of stock solution containing 10^{-3} moles of $Tl(ClO_4)_3$. The amount of thallium(I) which was present in the stock solution was less than 3×10^{-3} percent of the total thallium, a negligible amount for this investigation.

C. Lithium Chloride

The LiCl used in this investigation was Merck reagent grade LiCl which was dissolved and filtered through sintered glass to remove any insoluble matter. Several solutions of various concentrations were prepared, ranging from 0.496 M. to 6.70 M.

Standardization of the LiCl solutions was by a gravimetric method, as AgCl. These AgCl standardizations were checked by two alternate methods, an ion-exchange and a volumetric method using an adsorption indicator. In the ion-exchange method the LiCl sample was eluted through a Dowex - 50 cationic resin column in the acidic cycle. The effulent was titrated with standard NaOH to the phenolphthalien end-point. In the volumetric method the LiCl samples were titrated with standard $AgNO_3$ solutions using di-chlorofluorescein as the indicator. In order to obtain consistent and correct results by this method the sample has to be neutral during the titration. Both of the check methods gave results which agreed with those of the AgCl method.

D. Lithium Perchlorate

Solutions of $LiClO_4$ were prepared from G. Frederick Smith's reagent grade $LiClO_4$ for investigation of the extraction at constant ionic strength.

The $LiClO_4$ solution was filtered through a fine sintered glass funnel and recrystallized from water. A stock solution was prepared from the recrystallized $LiClO_4$. Two methods were used to determine the concentration of the $LiClO_4$ solutions, ion-exchange and a gravimetric method. In the ion-exchange method the $LiClO_4$ sample was eluted through a column of Dowex-50 cationic resin in the acidic cycle. The effulent was titrated with standard NaOH to the phenolphthalien end-point. In the gravimetric procedure the perchlorate was precipitated as tetraphenylarsonium perchlorate by the addition of tetraphenylarsonium chloride (37). The precipitate was congulated by the addition of HCl, filtered onto sintered glass crucibles, washed with dilute HCl solution, dried at 110° C. for one-half hour and weighed as tetraphenylarsonium perchlorate. The results of these two methods were in agreement.

E. Miscellaneous

Throughout the investigation G. Frederick Smith's doubly vacuum distilled $HClO_4$ was used. Standard solutions of NaOH were prepared from Baker and Adamson's reagent grade NaOH. Baker's "Baker Analyzed" reagent grade $AgNO_3$ was used to prepare $AgNO_3$ solutions. The pipetts and volumetric flasks used in the preparation of solutions were Kimble's Exax and Pyrex. All solutions were prepared with double distilled water.

IV. METHOD OF INTERPRETATION OF DATA

From the data for counting of samples of the aqueous and ether phases a distribution ratio was calculated,

$$K_T = \frac{[Tl]_e}{[Tl]_w} \qquad (1)$$

where:

$[Tl]_e$ = concentration of total thallium in the ether phase

$[Tl]_w$ = concentration of total thallium in the aqueous phase.

Since the measurements of K_T were made at equilibrium conditions, the concentration of thallium in the ether phase must be proportional to the activity of one or more of the thallium-chloride complexes in the aqueous phase, depending upon whether one or more of the chloride complexes are extracted.

It was of importance to consider the various complexes present in the system. Benoit (38) reported the dissociation constants for the mono-, di-, tri- and tetra-chloro complexes of thallium:

$$k_1 = \frac{(Tl^{+3})\,(Cl^-)}{(TlCl^{+2})} = 10^{-8.1} \quad ,$$

$$k_2 = \frac{(TlCl^{+2})\,(Cl^-)}{(TlCl_2^+)} = 10^{-5.5} \quad ,$$

$$k_3 = \frac{(TlCl_2^+)\,(Cl^-)}{(TlCl_3)} = 10^{-2.2} \quad ,$$

$$k_4 = \frac{(TlCl_3)\,(Cl^-)}{(TlCl_4^-)} = 10^{-2.2} \quad ,$$

and the dissociation constant for the first hydrolyzed thallium species:

$$k_{OH} = \frac{(Tl^{+3})\,(OH^-)}{(TlOH^{+2})} = 10^{-13.2} \quad .$$

In the above equations the symbol ( ) designates the activities of the various species present in the aqueous phase. By combining these equations a new set of constants was defined:

$$K_1 = \frac{(TlCl^{+2})}{(Tl^{+3})\,(Cl^-)} = 10^{8.1} \quad ,$$

$$K_2 = \frac{(TlCl_2^+)}{(Tl^{+3})\,(Cl^-)^2} = 10^{13.6} \quad ,$$

$$K_3 = \frac{(TlCl_3)}{(Tl^{+3})\,(Cl^-)^3} = 10^{15.8} \quad ,$$

$$K_4 = \frac{(TlCl_4^-)}{(Tl^{+3})\,(Cl^-)^4} = 10^{18} \quad ,$$

$$K_5 = \frac{(TlCl_5^{-2})}{(Tl^{+3})\,(Cl^-)^5} \quad ,$$

and

$$k_H = \frac{(TlOH^{+2})\ \ (H^+)}{(Tl^{+3})} = 0.159.$$

A value of K_5 was obtained from the experimental data and its determination will be shown in Section E of Chapter V.

It will be shown in Section D of Chapter V that the thallium species present in the ether phase was $HTlCl_4$. Knowing this the extraction equilibrium constant may be written as:

$$K = \frac{(HTlCl_4)_e}{(H^+)\ (TlCl_4^-)} = \frac{(HTlCl_4)_e}{(H^+)\ (Tl^{+3})\ (Cl^-)^4\ K_4} \qquad (2)$$

where $(X)_e$ designates the activity of X in the ether phase and (X) designates the activity of X in the aqueous phase.

Since the only thallium in the ether phase was present as $HTlCl_4$, the activity of $HTlCl_4$ in the ether phase may be written:

$$(HTlCl_4)_e = [Tl]_e\ \gamma^e_{HTlCl_4} \qquad (3)$$

where $\gamma^e_{HTlCl_4}$ represents the activity coefficient of $HTlCl_4$ in the ether phase and $[Tl]_e$ equals the concentration of $HTlCl_4$ in the ether phase. The total concentration of thallium in the aqueous phase was equal to the sum of the concentrations of the various thallium species in the aqueous phase:

$$\begin{aligned}[Tl]_w = [Tl^{+3}] + [TlCl^{+2}] + [TlCl_2^+] + [TlCl_3] + \\ [TlCl_4^-] + [TlCl_5^{-2}] + [TlOH^{+2}] \qquad (4)\end{aligned}$$

Using the relationship that the concentration is equal to the activity divided by the activity coefficient and the new set of constants obtained from the data of Benoit (38), namely K_1, K_2, K_3, K_4 and K_5, equation (4) can be rewritten:

$$\begin{aligned}
[\mathrm{Tl}]_w = {} & (\mathrm{Tl}^{+3}) / \gamma_{\mathrm{Tl}^{+3}} + (\mathrm{TlCl}^{+2}) / \gamma_{\mathrm{TlCl}^{+2}} + \\
& (\mathrm{TlCl}_2^{+}) / \gamma_{\mathrm{TlCl}_2^{+}} + (\mathrm{TlCl}_3) / \gamma_{\mathrm{TlCl}_3} + \\
& (\mathrm{TlCl}_4^{-}) / \gamma_{\mathrm{TlCl}_4^{-}} + (\mathrm{TlCl}_5^{-2}) / \gamma_{\mathrm{TlCl}_5^{-2}} + \\
& (\mathrm{TlOH}^{+2}) / (\mathrm{H}^+)\ \gamma_{\mathrm{TlOH}^{+2}} \\
= {} & (\mathrm{Tl}^{+3}) / \gamma_{\mathrm{Tl}^{+3}} + K_1\ (\mathrm{Tl}^{+3})\ (\mathrm{Cl}^-) / \gamma_{\mathrm{TlCl}^{+2}} + \\
& K_2\ (\mathrm{Tl}^{+3})\ (\mathrm{Cl}^-)^2 / \gamma_{\mathrm{TlCl}_2^{+}} + K_3\ (\mathrm{Tl}^{+3})\ (\mathrm{Cl}^-)^3 / \\
& \gamma_{\mathrm{TlCl}_3} + K_4\ (\mathrm{Tl}^{+3})\ (\mathrm{Cl}^-)^4 / \gamma_{\mathrm{TlCl}_4^{-}} + K_5\ (\mathrm{Tl}^{+3}) \\
& (\mathrm{Cl}^-)^5 / \gamma_{\mathrm{TlCl}_5^{-2}} + k_H\ (\mathrm{Tl}^{+3}) / (\mathrm{H}^+) \\
& \gamma_{\mathrm{TlOH}^{+2}} \qquad (5)
\end{aligned}$$

Solving equation (5) for the activity of Tl^{+3} and substituting this quantity and equation (3) into equation (2) yields:

$$\begin{aligned}
K = {} & \frac{[\mathrm{Tl}]_e\ \gamma^e_{\mathrm{HTlCl}_4}}{[\mathrm{Tl}]_w\ (\mathrm{H}^+)\ (\mathrm{Cl}^-)^4\ K_4} \Bigl(1 / \gamma_{\mathrm{Tl}^{+3}} + K_1\ (\mathrm{Cl}^-) / \\
& \qquad \gamma_{\mathrm{TlCl}^{+2}} + \ldots \\
& + \ldots\ K_5\ (\mathrm{Cl}^-)^5 / \gamma_{\mathrm{TlCl}_5^{-2}} + k_H / (\mathrm{H}^+)\ \gamma_{\mathrm{TlOH}^{+2}} \Bigr) \\
= {} & K_T\ \frac{\gamma^e_{\mathrm{HTlCl}_4}}{K_4\ (\mathrm{H}^+)\ [\mathrm{Cl}^-]^4\ \gamma^4_{\mathrm{Cl}^-}} \Bigl(\sum_{n=0}^{5} K_n\ \gamma^n_{\mathrm{Cl}^-}\ [\mathrm{Cl}^-]^n / \\
& \gamma_{\mathrm{TlCl}_n^{3-n}} + k_H / \gamma_{\mathrm{H}^+}\ [\mathrm{H}^+]\ \gamma_{\mathrm{TlOH}^{+2}} \Bigr) \qquad (6)
\end{aligned}$$

where

$K_0 = 1$ and $K_T = [\mathrm{Tl}]_e / [\mathrm{Tl}]_w$.

It was assumed that the activity coefficient of $HTlCl_4$ in ether was constant, since the concentration of $HTlCl_4$ in the ether phase was small and the species is not charged. It was also assumed that the activity of the hydrogen ion was constant for a given investigation since the extractions were studied at constant acid concentration and constant ionic strength. In all of the extractions studied the acid concentration was always sufficiently high that no hydrolyzed thallium was present and the term involving the concentration of $TlOH^2$ was therefore eliminated. When these conditions are incorporated into the extraction equilibrium constant of equation (6) a new extraction equilibrium constant can be calculated:

$$K' = \frac{K\,(H^+)}{\gamma^e_{HTlCl_4}} = \frac{K_T \sum_{n=o}^{5} K_n\, \gamma^n_{Cl^-}\, [Cl^-]^n / \gamma_{TlCl_n^{3-n}}}{K_4\, [Cl^-]^4\, \gamma^4_{Cl^-}} \qquad (7)$$

The value of K' should be fairly constant at the different LiCl concentrations, assuming that the activity coefficients of the thallium-chloride complexes and free chloride ion can be calculated.

Since the concentrations of the thallium-chloride complexes in the aqueous phase were kept small, it was assumed that their activity coefficients could be calculated by the extension of the Debye-Huckel expression:

$$-\log \gamma_i = \frac{A\, z_i^2 \sqrt{\mu}}{1 + B\, a_i \sqrt{\mu}} \qquad (8)$$

where:

A = 0.513 at 30° C.,

z_i = charge of thallium-chloride complex,

B = 0.3290×10^8 for water at 30° C.,

μ = ionic strength of the solution and

a_i = "effective diameter" of the ion in the solution. In most cases of large ions in aqueous solutions the product of Ba_i is assumed to be 3.0. Since all of the thallium-chloride complexes are large ions, equation (8) may be rewritten:

$$- \log \gamma_i = \frac{A z_i^2 \sqrt{\mu}}{1 + 3\sqrt{\mu}} . \qquad (9)$$

The activity coefficient of the chloride ion was estimated by two methods. For the first, the chloride activity coefficient was assumed to be constant as chloride and perchlorate concentrations were changed at a given ionic strength. Successive approximation for values of chloride activity coefficient were substituted into equation (7) until the values of K' were fairly constant over the range of LiCl concentrations used.

The second method was more difficult. A constant value of chloride activity coefficient at a given ionic strength was not assumed but the values of the activity coefficients of HCl and LiCl reported by Harned and Owen (39) and by Stokes and Robinson (40) were used. In the cases in which the concentration of acid was greater than the concentration of the free chloride the activity coefficient of the chloride ion was taken as equal to the mean activity coefficient of HCl at the concentration of the free chloride. In those cases in which the concentration of free chloride was greater than the concentration of acid the activity coefficient of the chloride ion was taken as equal to the weighted average of the activity coefficients of HCl and LiCl at the concentration of the free chloride.

Before K' could be calculated the free chloride ion concentration had to be determined. At high LiCl concentrations the free chloride ion concentration was assumed to be equal to the initial concentration of the LiCl. At intermediate LiCl concentration essentially all of the aqueous thallium was present at $TlCl_4^-$. Since the thallium present in the ether phase as $HTlCl_4$ also had four moles of chloride per mole of thallium, the free chloride ion concentration was taken as the initial LiCl concentration minus four times the initial concentration of $Tl(ClO_4)_3$.

At very low LiCl concentrations the calculation of the free chloride ion concentration became rather difficult. The total concentration of the aqueous chloride was equal to the initial concentration of the LiCl minus four times the concentration of the etheral thallium. Also the total aqueous chloride concentration was equal to:

$$[Cl^-]_w = [Cl^-] + [TlCl^{+2}] + 2[TlCl_2^+] + 3[TlCl_3] + 4[TlCl_4^-] + 5[TlCl_5^{-2}] \qquad (10),$$

where $[Cl^-]_w$ is the total aqueous concentration of chloride ion and $[Cl^-]$ is the free chloride ion concentration. To facilitate the calculation of the free chloride ion concentration the activity coefficients were neglected and K_1, K_2, K_3, K_4 and K_5 were assumed to be a ratio of the concentrations of the various species. Applying this assumption to equations (4) and (10) yields:

$$[Tl]_w = [Tl^{+3}] + [Tl^{+3}] (K_1 [Cl^-] + K_2 [Cl^-]^2 + K_3 [Cl^-]^3 + K_4 [Cl^-]^4 + K_5 [Cl^-]^5)$$

and

$$[Cl^-]_w = [Cl^-] + [Tl^{+3}](5K_5 [Cl^-]^5 + 4K_4 [Cl^-]^4 + 3K_3 [Cl^-]^3 + 2K_2 [Cl^-]^2 + K_1 [Cl^-]).$$

Solving these two equations for $[Tl^{+3}]$, equating and separating terms yields:

$$[Cl^-]^6 (K_5) + [Cl^-]^5 (5K_5 [Tl]_w - K_5 [Cl^-]_w + K_4) + [Cl^-]^4 (4K_4 [Tl]_w - K_4 [Cl^-]_w + K_3) + [Cl^-]^3 (3K_3 [Tl]_w - K_3 [Cl^-]_w + K_2) + [Cl^-]^2 (2K_2 [Tl]_w - K_2 [Cl^-]_w + K_1) + [Cl^-] (K_1 [Tl]_w - K_1 [Cl^-]_w + 1) = [Cl^-]_w \qquad (11).$$

From equation (11) the concentration of free chloride ion can be determined by successive approximations.

It should be pointed out that this method gives a very good determination of the equilibrium constant, K', since it is evaluated at a number of different chloride concentrations. The accuracy of the constant is dependent not only upon the accuracy of the physical measurements, but also upon the accuracy of the assumption that the values of K_1, K_2, K_3 and K_4 as calculated from data reported by Benoit (38) and the value of K_5 as calculated from the extraction data can be applied to all of the conditions employed in this investigation.

It also is very much dependent upon the assumptions made about the activity coefficients of the many species present in this complicated system.

V. EXPERIMENTAL INVESTIGATION

A. General Procedure

Preliminary investigations showed that Tl(III) chloride complexes extracted very rapidly into isopropyl ether. A more complete investigation revealed that complete equilibrium was reached between the aqueous and ether phases in approximately ten minutes. However, in most of the investigations the samples were shaken in a constant temperature bath, for about 40 minutes and allowed to settle for about 30 minutes. This longer contact time was used to ensure complete thermal equilibrium as well as the extraction equilibrium.

A simple extraction apparatus was assembled to study the distribution of Tl(III) chloride complexes between the ether and aqueous phases. An E. H. Sargent and Company constant temperature bath with a thermo-regulator mercury relay switch was used to regulate the temperature of the experiments. A Burrell Wrist-Action Shaker with automatic timer was used to shake the reaction tubes. Two types of reaction flasks were used in this investigation, 50 ml. pyrex volumethric flasks and 35 mm. pyrex tubes with 34/45 ground glass female joints and accompaning 34/45 ground glass male caps.

In the ensuing investigations the aqueous layer was prepared by placing the desired concentration of reactants in the reaction tubes and adding an equal volume of isopropyl ether. In all of the experiments, the initial aqueous and ether phases were each 10 ml.

After the reaction tubes were shaken in the constant temperature bath and allowed to settle, the samples were withdrawn with pyrex volumetric pipettes. During the early investigations, after the ether samples were withdrawn, the remaining ether phase and a small amount of the aqueous phase were removed with a pipette before the aqueous samples were withdrawn. In the later experiments the remaining portion of the ether phase was not removed before the aqueous samples were withdrawn. The pipette was passed through the remaining ether phase into the aqueous phase, a small amount of air was blown through the pipette to discharge any of the ether phase which might have been trapped in the pipette and the aqueous sample was withdrawn. The results obtained by these two sampling methods agreed within the limits of error of the experimental methods.

Approximately 2 to 3 ml. of water were added to the ether samples and the ether evaporated by allowing the samples to stand at room temperature for between 6 to 12 hours. Analyses were made for acid, chloride and thallium. The acid and chloride analyses were done volumetrically, the thallium analysis radiochemically. Since the amount of thallium present was not sufficient for precipitation and filtration, carrier $Tl(NO_3)_3$ in HNO_3 was added in a known amount.

Three methods of mounting the thallium samples were investigated with only one of them proving suitable. The two unacceptable methods were simple evaporation of an aliquot of each phase, and precipitation of the thallium as $Tl(OH)_3$. The evaporation method gave unreproducible and very flaky samples with considerable self-absorption of the Tl^{204} beta particles by the salts which remained upon evaporation. Since $Tl(OH)_3$ is a very fine precipitate which adheres to glass, it was difficult to filter and mount.

The procedure for the thallium analysis which was used in all further investigations was that used also for the standardization of the $Tl(ClO_4)_3$ solution, (see page 14), with a few changes. The Tl_2CrO_4 precipitates were allowed to digest at room temperature for from 2 hours to 12 hours in various investigations. The time of digestion was not too critical.

The Tl_2CrO_4 samples were filtered onto 23 mm. discs of Schleicher and Schuell, No. 589, filter paper with the use of chimney and sintered glass filter apparatus. The precipitates were washed with water and absolute alchol and dried at 110° C. for approximately 5 minutes. The samples were cooled to room temperature before mounting.

During the early investigations a chemical yield determination was made by weighing the Tl_2CrO_4 precipitate. The counting data was corrected to 100 percent chemical yield. However, in every case the chemical yield was between 93 and 104 percent, with the greatest majority of the yields being between 98 and 101 percent. It was believed that these yields were well within the limits of error of the radiochemical methods employed. The determination of the chemical yield was discontinued after the early investigations and the yields were assumed to be 100 percent in all the later investigations.

The cooled samples were covered with 3.3 mg./cm.^{2} celophane discs of 26 mm. diameter. The samples were mounted on cardboard backing and counted.

B. Preliminary Investigation

A series of preliminary investigations were performed in order to observe the optimum conditions for the study of the extraction.

1. Time and rate of shaking

The extraction was studied at two rates of shaking for varying times of contact for the two phases. At the lower rate of shaking, approximately 350 vibrations per minute and 3/4 inch stroke, the equilibrium was not obtained with a contact time of less than 30 minutes. However, after a contact time of only 10 minutes at the higher shaking rate, approximately 350 vibrations per minute and 1 inch stroke, equilibrium was observed. In this investigation it is also necessary to obtain a thermal equilibrium between the two phases. Complete separation of the two phase is an important condition. To satisfy these requirements, all subsequent investigation will be performed with the higher shaking rate, a contact time of 30 minutes and a stationary period of 30 minutes for separation.

2. Varying Lithium Chloride concentrations

The extraction was observed at various LiCl concentrations and constant acid concentration. The results of several runs are shown in Figure 1. However, since the ionic strength was not kept constant, the effect of the concentration of LiCl upon the extraction could not be determined from these data.

3. Varying Hydrochloric Acid concentration

In previous investigations (17, 18, 20) the extraction was studied

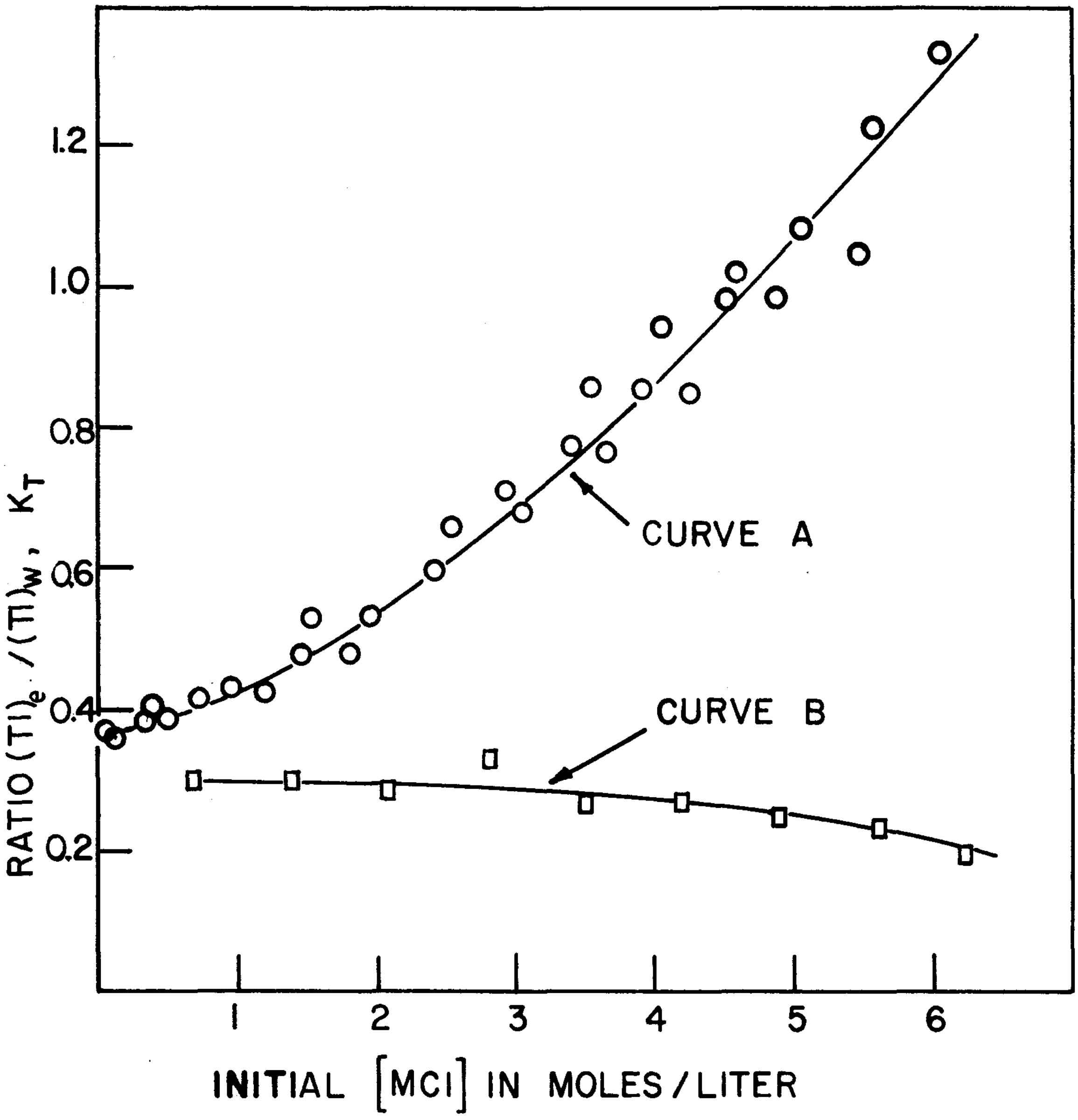


Figure 1. Extraction at varying MCl concentration, $[HClO_4] = 0.4$ M. $[Tl(ClO_4)_3] = 1.06 \times 10^{-3}$ M.

Curve A. MCl was LiCl. Curve B. MCl was NaCl.

at varying HCl concentrations, the concentration of thallium kept constant. The work of the previous investigators was repeated and the results shown in Figure 2. However, since the ionic strength was not maintained constant, the true effect of the concentration of HCl could not be determined.

The optimum extraction of about 92 percent occurred at approximately 6.5 M. HCl. However, the earlier investigators (17, 18, 20) reported that Tl(III) was extracted quantitatively from solutions of HCl concentrations as low as 2 M. by diethyl ether. Little comparison was made between the results of the present and the earlier investigations because of the different extraction solvent and concentration of thallium used.

4. Varying Sodium Chloride concentrations

The extraction was studied at constant acid concentration using NaCl to vary the chloride ion concentration and the results are compared to the experiments using LiCl in Figure 1. Once again no results were concluded from these data because the ionic strength was not kept constant.

5. Varying ionic strength

The extraction was investigated at constant $HClO_4$, $Tl(ClO_4)_3$ and LiCl concentrations while varying the ionic strength with $LiClO_4$. The results of one of the runs are shown in Figure 3. The very marked effect of the ionic strength is shown by the approximately 5.3 fold increase in the extraction coefficient for an increase in the concentration of $LiClO_4$ from 0.0 M. to 2.4 M. These data indicated a very strong salting-out effect.

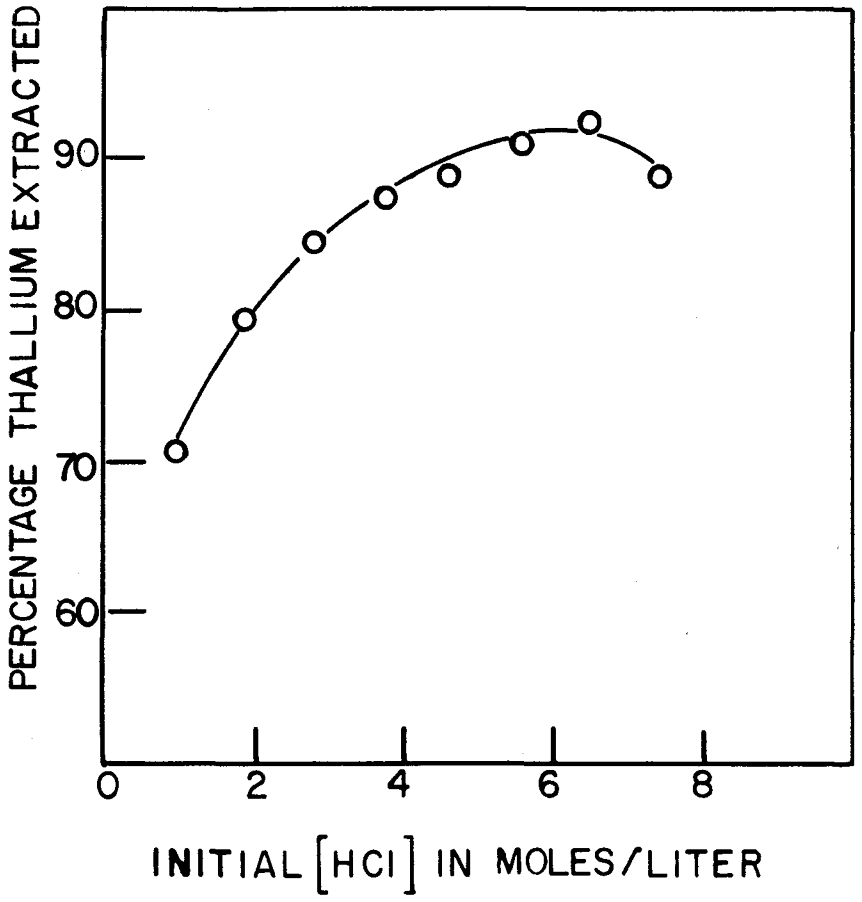


Figure 2. Extraction at varying HCl concentrations 1.06×10^{-3} M. $Tl(ClO_4)_3$.

Temperature = 20° C.

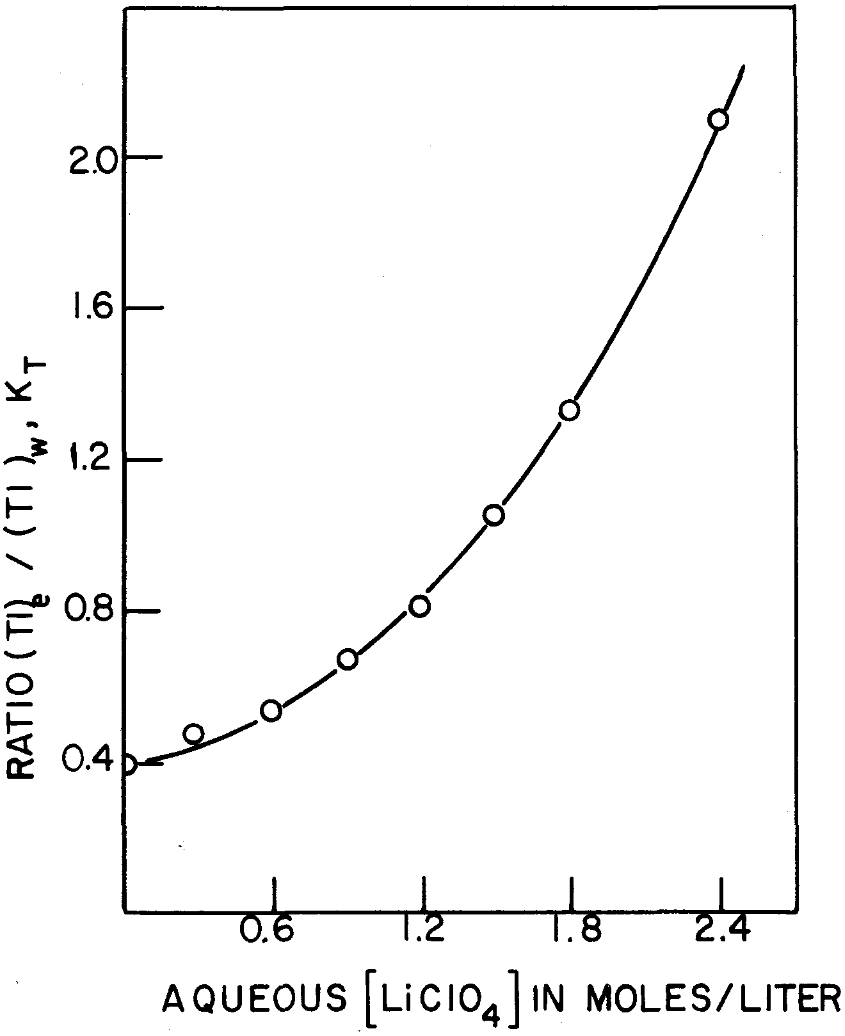


Figure 3. Extraction as function of increasing $LiClO_4$ concentration.

0.4 M. $HClO_4$, 0.67 M. LiCl, 1.06×10^{-3} M. $Tl(ClO_4)_3$.

6. Purity of Iso-propyl Ether

The need to purify the iso-propyl ether obtained from the stock room, Matheson, Coleman and Bell iso-propyl ether, was studied. The iso-propyl ether was purified by shaking with alkaline - $KMnO_4$ solution, drying over $CaCl_2$ and distilling. The middle fraction boiling in the range 68.5 to 69.0° C. at atmospheric pressure was collected. Several extractions were run at identical conditions using the normal and purified iso-propyl ether and the results are shown in Figure 4. Within the limit of error of the methods used no difference in the extraction was observed and in all further studies the stock room iso-propyl ether was used.

7. Varying ionic strength with Sodium Perchlorate

Since $NaClO_4$ is more soluble than $LiClO_4$, the extraction could be studied at higher salt concentrations. However, when $NaClO_4$ was added to the reaction mixtures, the chloride was oxidized to chlorine because $NaClO_4$ is such a strong oxidizing agent. Thus in all further investigations $LiClO_4$ was used to maintain the ionic strength constant.

C. Temperature Dependence of the Partition Coefficient

Two series of extraction of 0.00106 M. $Tl(ClO_4)_3$, in 0.4 M. $HClO_4$ and 0.6 M. $HClO_4$, at varying concentrations of LiCl were carried out at three different temperatures. The ionic strength was kept constant by adding the required amount of $LiClO_4$. The results of these runs are shown in Figure 5, Figure 6, and Table 2.

The plot of the R $\log_e [Tl]_e / [Tl]_w$ against 1/T is shown in

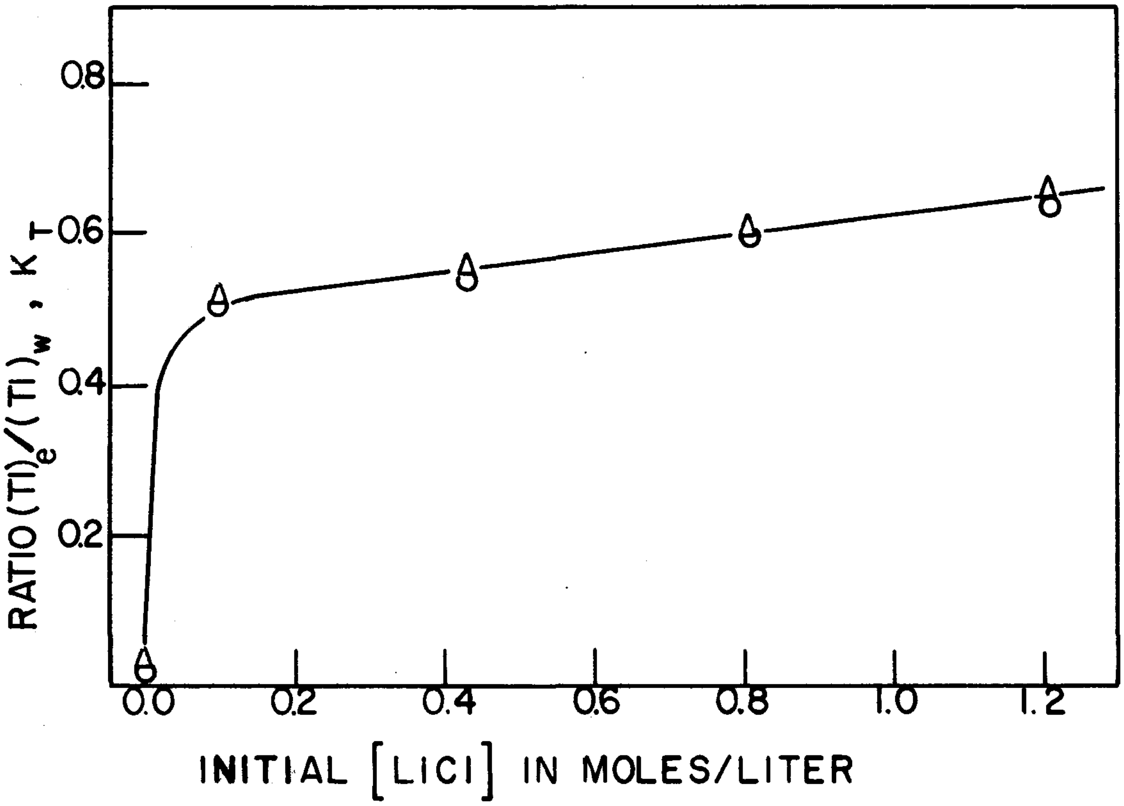


Figure 4. Extraction as function of ether purity.

0.4 M. $HClO_4$, 1.06×10^{-3} M. $Tl(ClO_4)_3$.

○ - Extraction using untreated ether.
△ - Extraction using purified ether.

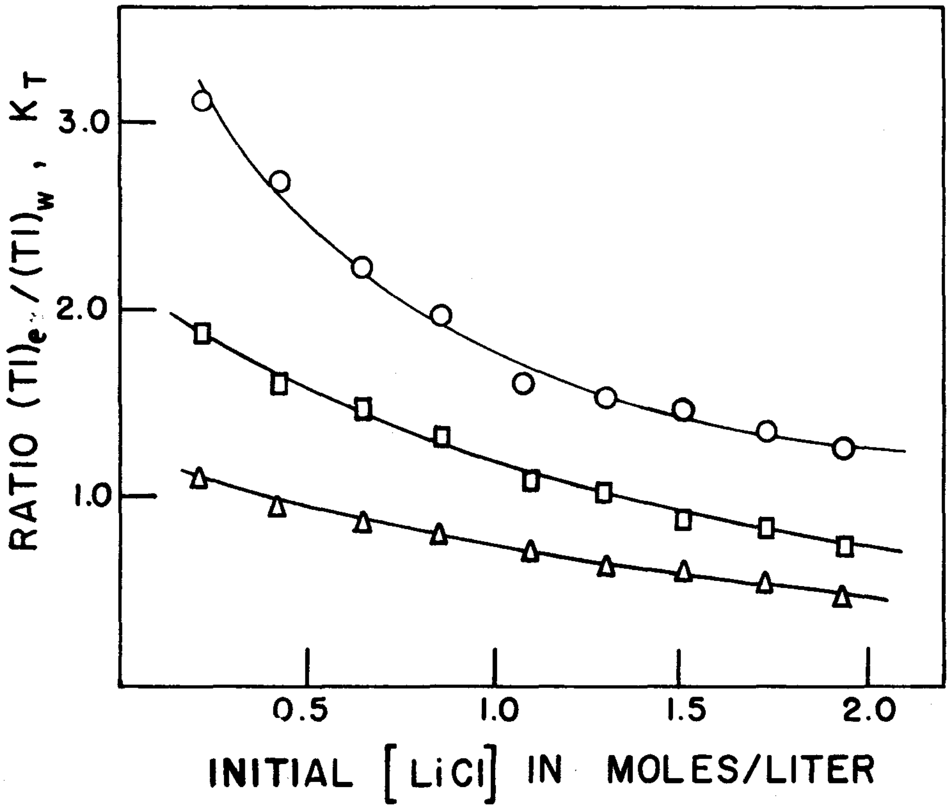


Figure 5. Extraction as function of temperature at $HClO_4$ concentration equal to 0.4 M.

○ - Temperature = 20° C.
□ - Temperature = 25° C.
△ - Temperature = 30° C.

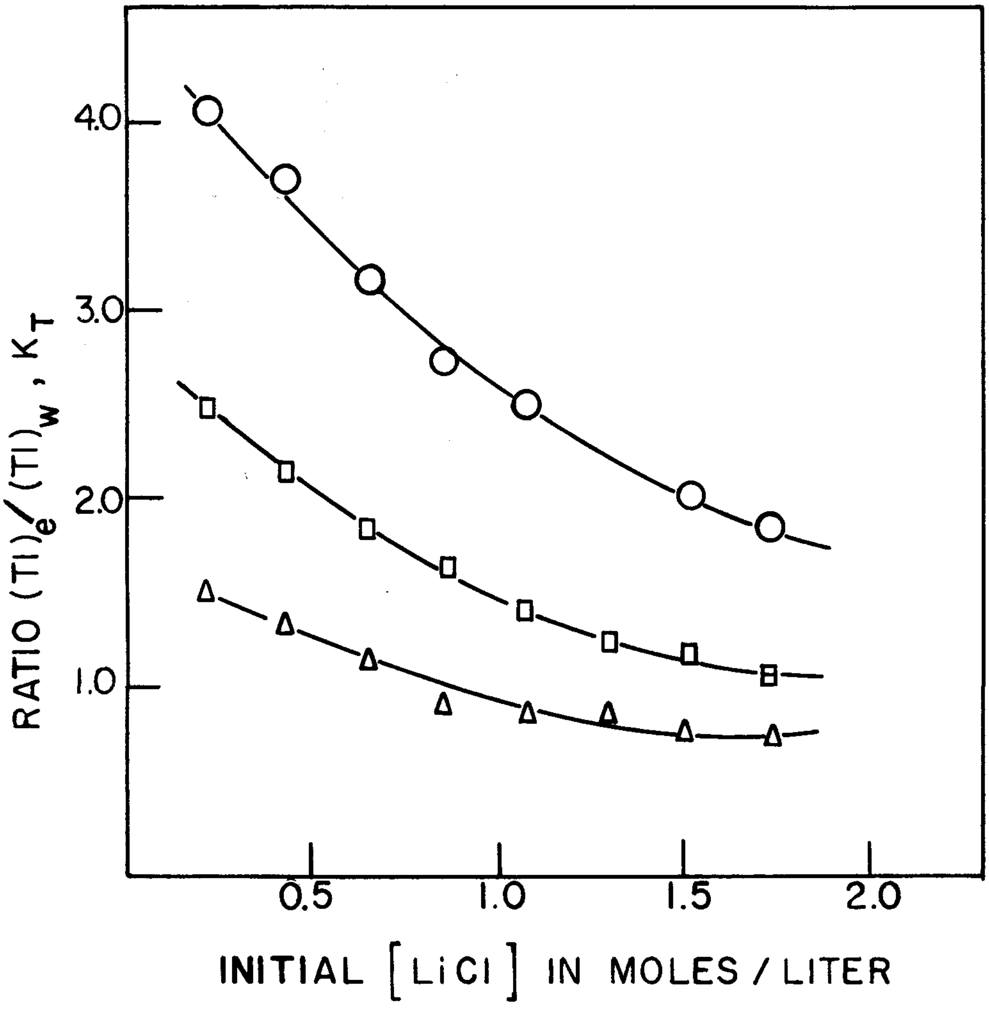


Figure 6. Extraction as function of temperature at $HClO_4$ concentration equal to 0.6 M.

○ - Temperature = 20° C.
□ - Temperature = 25° C.
△ - Temperature = 30° C.

Table 2

Temperature Dependence of the Partition Coefficient

Initial	$[HClO_4]$ = 0.4 M.			$[HClO_4]$ = 0.6 M.		
Aqueous $[LiCl]$	K_T at 30° C.	K_T at 25° C.	K_T at 20° C.[a]	K_T at 30° C.	K_T at 25° C.	K_T at 20° C.
0.22	1.112	1.690	3.113	1.500	2.470	4.040
0.43	0.958	1.601	2.680	1.310	2.138	3.690
0.65	0.877	1.495	2.218	1.140	1.854	3.165
0.86	0.785	1.308	1.946	0.908	1.653	2.735
1.08	0.703	1.112	1.602	0.858	1.430	2.495
1.30	0.632	1.033	1.530	0.864	1.240	-
1.51	0.585	0.897	1.465	0.782	1.176	2.010
1.73	0.636	0.844	1.336	0.744	1.066	1.842
1.94	0.476	0.764	1.249	-	-	-

[a] Average of two runs.

Figures 7 and 8. Applying the van't Hoff equation, a partial molar heat of extraction, ΔH, was calculated. Since the distribution ratio is proportional to the over-all thermodynamic equilibrium constant for the extraction, this application of the van't Hoff equation is valid and the slope of the curve is the negative of the partial molar heat of extraction. The calculations of the ΔH are shown in Table 3. The average ΔH's are -9500 cal./mole and -9900 cal./mole for the extraction from 0.4 M. and 0.6 M. $HClO_4$ solutions, respectively.

More exactly, the van't Hoff equation is written:

$$\frac{d\ln K}{dT} + \sum \frac{d\ln \gamma_e / \gamma_a}{dT} = \frac{\Delta H}{RT^2}$$

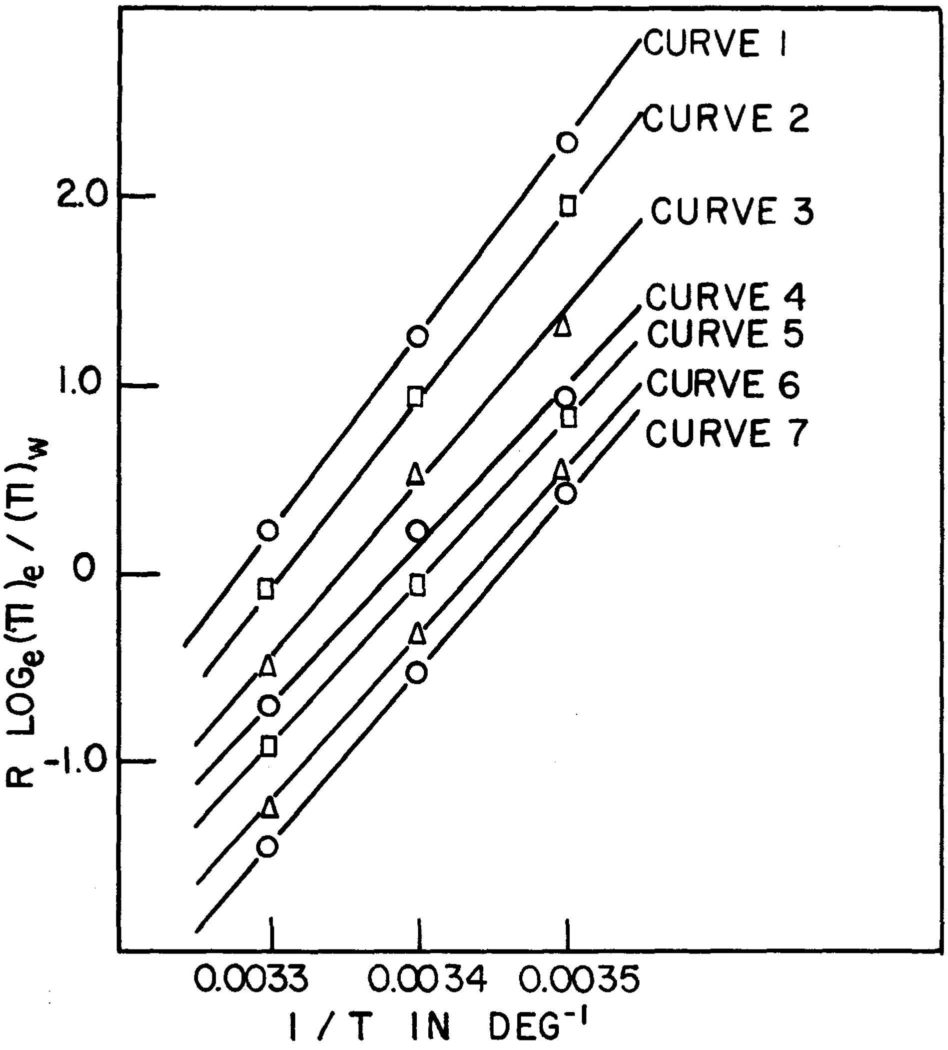


Figure 7. Van't Hoff Plot for partial molar heat of extraction from 0.4 M. $HClO_4$.

Curve 1 - 0.22 M. LiCl
Curve 2 - 0.43 M. LiCl
Curve 3 - 0.86 M. LiCl
Curve 4 - 1.08 M. LiCl
Curve 5 - 1.30 M. LiCl
Curve 6 - 1.73 M. LiCl
Curve 7 - 1.94 M. LiCl

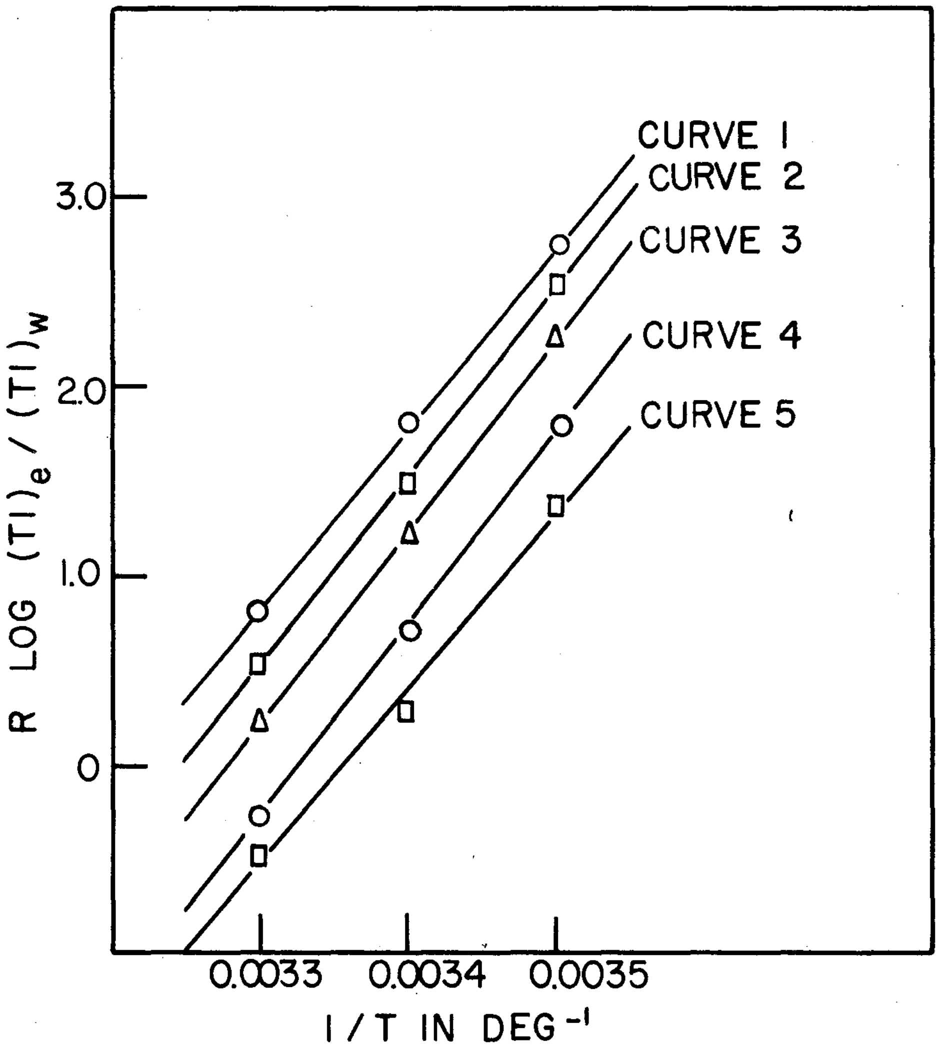


Figure 8. Van't Hoff Plot for partial molar heat at extraction from 0.6 M. $HClO_4$.

Curve 1 - 0.22 M. LiCl
Curve 2 - 0.43 M. LiCl
Curve 3 - 0.65 M. LiCl

Curve 4 - 1.08 M. LiCl
Curve 5 - 1.51 M. LiCl

Table 3

Partial Molar Heat of Extraction, ΔH

Curve No.	Initial LiCl	Slope (per .001 deg^{-1})	ΔH (kcal./mole)
	Initial Aqueous $[HClO_4]$ = 0.4 M.		
1	0.22	1.04	-10.4
2	0.43	1.04	-10.4
3	0.86	0.93	- 9.3
4	1.08	0.88	- 8.8
5	1.30	0.87	- 8.7
6	1.73	0.90	- 9.0
7	1.94	0.96	- 9.6
		Average ΔH =	-9.5 ± 0.66 kcal./mole
	Initial Aqueous $[HClO_4]$ = 0.6 M.		
1	0.22	0.98	- 9.8
2	0.43	1.00	-10.0
3	0.65	1.02	-10.2
4	1.08	1.02	-10.2
5	1.51	0.94	- 9.4
		Average ΔH =	-9.9 ± 0.30 kcal./mole

where K is the equilibrium constant measured in terms of concentration and γ_i are the activity coefficients for the various compounds in the two phases. These activity coefficient terms are included in the ΔH determined from Figures 7 and 8, and hence the temperature dependence of the concentration equilibrium constant does not determine the heat of extraction unless the various activity coefficient terms cancel.

D. Empirical Formula of Compound in Ether Phase

In the determination of the formula of the thallium compound in the ether phase the analytical procedure was essentially as follows, although minor refinements and modifications were made as the experiments progressed. Equal volumes of 10 ml. of the ether and the $Tl(ClO_4)_3$ - $HClO_4$ - LiCl - $LiClO_4$ solutions were shaken together, allowed to separate and the ether layer was analyzed for chloride, ionizable hydrogen and thallium content. The chloride content was determined by adding water to the ether sample and titrating with standard $AgNO_3$ to the dichlorofluorescein end-point. A second portion of the ether phase was analyzed for acid and thallium(III) by adding water and titrating it with standard NaOH to a phenolphthalein end-point. The amount of thallium in the ether phase was determined radiochemically by counting the Tl_2CrO_4 precipitate. The results are presented in Tables 4, 5 and 6 for three typical extraction experiments.

The amounts of hydrogen and chloride ions passing into the ether layer from solutions of the same composition of $HClO_4$, LiCl and $LiClO_4$ with no $Tl(ClO_4)_3$ present were determined. The results are shown in Tables 4, 5 and 6, compared with the data of the extraction experiment with $Tl(ClO_4)_3$ present.

The ratios of associated chloride and of associated hydrogen to thallium were calculated and are shown in Tables 7, 8 and 9. The corrected chloride ion concentration was equal to the amount extracted minus the amount of chloride ion soluble in ether at the given ionic strength and acid concentration. Since the amount of chloride soluble in the ether was below the limits of detection of the method of analysis

Table 4

I. Solubility of Hydrogen, Chloride and Thallium in Ether

Total Salt and Acid Concentration = 3.0 M.
Initial Aqueous $HClO_4$ Concentration = 0.4 M.

Initial Aqueous [LiCl]	With no $Tl(ClO_4)_3$		Initial $[Tl(ClO_4)_3] = 1.06 \times 10^{-3}$ M.		
	$[H^+] \times 10^3$	$[Cl^-]$	$[Acid] \times 10^3$	$[Cl^-] \times 10^3$	$[Tl] \times 10^4$
0.05	1.13	0.00	4.00	2.85	6.33
0.10	1.13	0.00	3.70	2.75	6.66
0.50	0.94	0.00	3.44	2.65	6.20
1.00	0.78	0.00	3.06	2.50	5.60
1.20	0.78	0.00	2.82	2.40	5.50
1.50	0.78	0.00	2.76	2.30	5.20
1.70	0.86	0.00	2.44	2.10	4.86
2.00	0.71	0.00	2.26	2.10	4.70
2.20	0.47	0.00	2.09	2.00	4.40
2.50	0.47	0.00	2.07	1.90	4.10

[ ] = Concentration in moles/liter in the ether phase.

Table 5

II. Solubility of Hydrogen, Chloride and Thallium in Ether

Total Salt and Acid Concentration = 2.0 M.
Initial Aqueous $HClO_4$ Concentration = 1.0 M.

Initial Aqueous [LiCl]	With no $Tl(ClO_4)$		Initial $[Tl(ClO_4)_3] = 1.06 \times 10^{-3}$ M.		
	$[H^+] \times 10^3$	$[Cl^-]$	$[Acid] \times 10^3$	$[Cl^-] \times 10^3$	$[Tl] \times 10^4$
0.005	1.11	0.00	2.51	1.55	3.95
.01	1.15	0.00	3.06	2.13	5.35
.05	1.11	0.00	3.68	2.95	6.34
.10	1.10	0.00	3.84	2.85	6.55
.20	1.00	0.00	3.65	2.85	6.61
.30	0.98	0.00	3.60	2.93	6.31
.50	0.90	0.00	3.36	2.95	6.15
.70	0.82	0.00	3.36	2.95	5.96
.90	0.72	0.00	3.06	2.85	5.81
1.00	0.66	0.00	2.98	2.70	5.75

[ ] = Concentration in moles/liter in the other phase.

Table 6

III. Solubility of Hydrogen, Chloride and Thallium in Ether

Total Salt and Acid Concentration = 3.0 M.
Initial Aqueous $HClO_4$ Concentration = 1.6 M.

Initial Aqueous [LiCl]	With no $Tl(ClO_4)_3$		Initial $[Tl(ClO_4)_3] = 1.06 \times 10^{-3}$ M.		
	$[H^+] \times 10^3$	$[Cl^-]$	$[Acid] \times 10^3$	$[Cl^-] \times 10^3$	$[Tl] \times 10^4$
0.005	3.84	0.00	6.51	2.8	6.95
0.01	3.76	0.00	7.02	3.5	8.12
0.05	3.60	0.00	7.34	3.9	8.80
0.20	3.45	0.00	7.08	3.9	8.70
0.40	3.13	0.00	6.58	3.8	8.63
0.60	2.82	0.00	6.40	3.7	8.20
0.80	2.66	0.00	5.96	3.6	8.12
1.00	2.35	0.00	5.52	3.5	7.92
1.20	2.19	0.00	5.33	3.4	7.61
1.40	1.96	1.00	4.96	3.3	7.49

[ ] = Concentration in moles/liter in the ether phase.

Table 7

I. Ratio of Associated Chloride and Hydrogen Ions to Thallium in the Ether

Total Salt and Acid Concentration = 3.0 M.
Initial Aqueous $HClO_4$ Concentration = 0.4 M.

Initial Aqueous [LiCl]	[Tl] x 10^4	Corrected [Cl^-] x 10^3	Corrected [H^+] x 10^4	Ratios Cl^- / Tl	Ratios H^+ / Tl
0.05	6.33	2.85	9.7	4.50	1.53
0.10	6.66	2.75	5.7	4.13	0.86
0.50	6.20	2.65	6.8	4.26	1.10
1.00	5.60	2.50	6.0	4.46	1.07
1.20	5.50	2.40	4.4	4.36	0.84
1.50	5.20	2.30	4.2	4.42	0.81
1.70	4.86	2.10	3.4	4.32	0.70
2.00	4.50	2.10	2.2	4.66	0.49
2.20	4.40	2.00	3.0	4.54	0.69
2.50	4.10	1.90	3.7	4.62	0.91
			Average	4.42	0.90

Table 8

II. Ratio of Associated Chloride and Hydrogen Ions to Thallium in the Ether

Total Salt and Acid Concentration = 2.0 M.
Initial Aqueous $HClO_4$ Concentration = 1.0 M.

Initial Aqueous [LiCl]	$[Tl] \times 10^4$	Corrected $[Cl^-] \times 10^3$	Corrected $[H^+] \times 10^4$	Ratios Cl^- / Tl	 H^+ / Tl
0.005	3.95	1.55	2.2	3.93	0.56
0.01	5.35	2.13	3.1	3.98	0.58
0.05	6.34	2.95	6.7	4.64	1.05
0.10	6.55	2.85	7.7	4.35	1.17
0.20	6.61	2.85	6.7	4.31	1.01
0.30	6.31	2.93	7.3	4.64	1.15
0.50	6.15	2.95	6.1	4.80	0.99
0.70	5.96	2.95	7.4	4.95	1.24
0.90	5.61	2.85	6.0	4.90	1.03
1.00	5.75	2.70	5.9	4.69	1.02
			Average	4.72	0.98

Table 9

III. Ratio of Associated Chloride and Hydrogen Ions to Thallium in the Ether

Total Salt and Acid Concentration = 3.0 M.
Initial Aqueous $HClO_4$ Concentration = 1.6 M.

Initial Aqueous [LiCl]	[Tl] x 10^4	Corrected [Cl^-] x 10^3	Corrected [H^+] x 10^4	Ratios Cl^- / Tl	Ratios H^+ / Tl
0.005	6.95	2.8	6.0	4.02	0.87
0.01	8.12	3.5	8.2	4.30	1.01
0.05	8.80	3.9	11.0	4.42	1.25
0.20	8.70	3.9	10.2	4.48	1.16
0.40	8.63	3.8	8.6	4.39	1.00
0.60	8.20	3.7	11.0	4.50	1.34
0.80	8.12	3.6	8.7	4.43	1.07
1.00	7.92	3.5	7.9	4.41	1.00
1.20	7.61	3.4	8.6	4.46	1.13
1.40	7.49	3.3	7.5	4.39	1.00
			Average	4.38	1.08

in every experiment, it was considered that the associated chloride was equal to the extracted chloride. The average ratios of associated chloride to thallium in the ether phase were 4.72, 4.42 and 4.38. The amounts of chloride titrated in the ether samples were between 4×10^{-5} and 1×10^{-4} moles and any small error in titration would produce a large error in the ratios. The calculated ratios are consistently higher than the predicted ratio of 4.0. This difference could be due to two factors, the titration of the indicator or the solubility of amounts of chloride in the ether which are relatively important but undetectible by the method of titration. The high chloride ratios might also be due to the extraction of thallium polymers of the type Li_2TlCl_5 or H_2TlCl_5. The ratio of associated chloride to thallium in the ether phase was accepted as 4.0 in all further investigations.

The corrected hydrogen ion concentration was equal to the equivalents of base used minus three times the thallium concentration in the ether phase and minus the amount of acid which is soluble in ether at the given ionic strength and acid concentration. The average ratios of associated hydrogen to thallium were 0.98, 0.90, and 1.08. Since the amount of associated hydrogen was obtained as a small difference between three larger numbers, a small error in the titration would produce a large error in the ratios. The calculated ratios are fairly close to 1.0. In all further investigations the ratio of associated hydrogen to thallium in the ether phase will be 1.0.

From this data it is assumed that there is only one thallium compound in the ether phase. The empirical formula of this compound is $HTlCl_4$.

E. Determination of K_5

Using the values for the formation constants of the thallium-chloride complexes as reported by Benoit (38) to calculate the values of K_1, K_2, K_3 and K_4 and the long equation (7) in Chapter IV values of K_5 were determined by successive approximations. The approximate values of K_5 were determined at high LiCl concentrations where the assumption was made that the initial aqueous chloride concentration was nearly equal to the final aqueous free chloride concentration. The value of K_5 which gave consistently the best evaluation of K' was 3.6×10^{17}.

F. Low Lithium Chloride Concentrations

The extraction of 0.00106 M. $Tl(ClO_4)_3$ from acid solutions was studied at very low LiCl concentrations, not exceeding 0.009 M. Since the total salt and acid concentration was 1.0 M., the ionic strength was essentially constant in these experiments.

The extraction was studied at 25° C. for two acid concentrations, 0.4 M. and 1.0 M. $HClO_4$. In the extraction study at 0.4 M. $HClO_4$ the solution was 0.6 M. in $LiClO_4$ to maintain the total salt and acid concentration at 1.0 M. The plot of the ratio of thallium in the ether phase to thallium in the aqueous phase, K_T, against the initial concentration of LiCl is shown in Figure 9. The results are tabulated in Tables 10 and 11.

Using the method outlined in Chapter IV the value of K' was determined for both $HClO_4$ concentrations over the range of LiCl concentrations employed. In this investigation the activity coefficient of the free

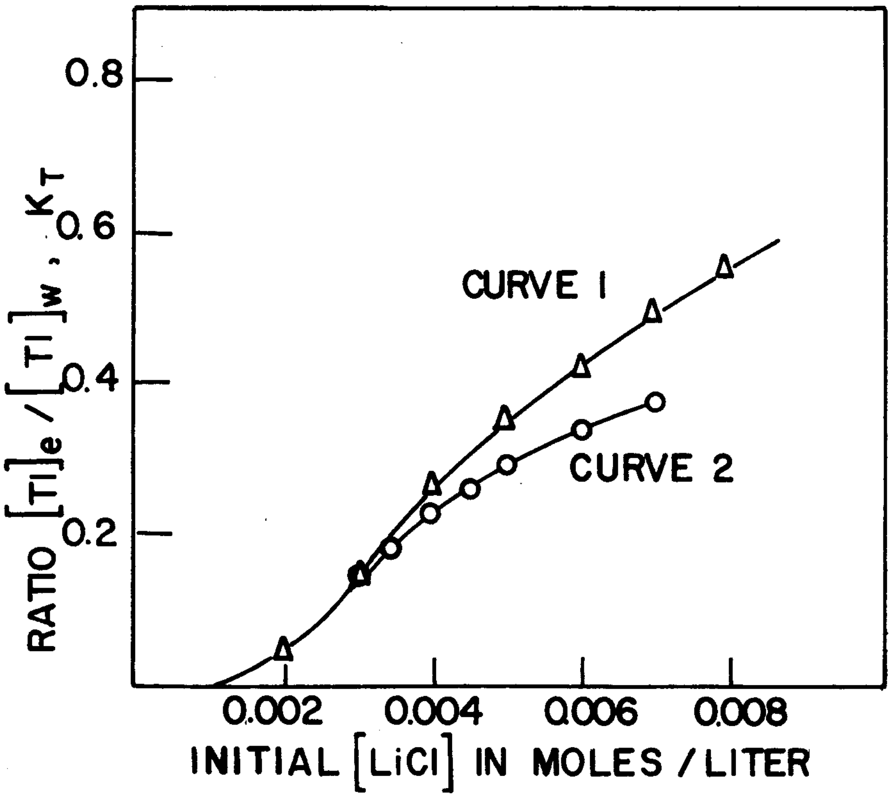


Figure 9. Extraction at very low LiCl concentrations.

Temperature = 25° C.

Curve 1 - 1.0 M. $HClO_4$
Curve 2 - 0.4 M. $HClO_4$

Table 10

Extraction of Thallium (III) Chloride from 0.4 M. $HClO_4$ and 0.6 M. $LiClO_4$ at Low LiCl Concentrations

Aqueous [LiCl] x 10^3 m./l. Initial	Residual	K_T	$[Tl]_e$ x 10^4 m./l.
1.00	1.00	0.002	0.00
2.00	1.83	0.042	0.43
3.00	2.47	0.142	1.32
3.50	2.85	0.181	1.63
4.00	3.22	0.227	1.96
4.50	3.62	0.260	2.18
5.00	4.05	0.290	2.38
6.00	4.92	0.337	2.67
7.00	5.85	0.374	2.88

$$K_T = \frac{[Tl]_e}{[Tl]_w}$$

Temperature = 25° C.

Table 11

Extraction of Thallium (III) Chloride from 1.0 M. $HClO_4$ at Low LiCl Concentrations

Aqueous [LiCl] x 10^3 m./l. Initial	Aqueous [LiCl] x 10^3 m./l. Residual	K_T	$[Tl]_e$ x 10^4 m./l.
1.00	1.00	0.001	0.00
2.00	1.80	0.043	0.44
3.00	2.46	0.147	1.36
4.00	3.11	0.266	2.23
5.00	3.89	0.357	2.79
6.00	4.74	0.424	3.16
7.00	5.60	0.495	3.51
8.00	6.49	0.555	3.78

$$K_T = \frac{[Tl]_e}{[Tl]_w}$$

Temperature = 25° C.

chloride was assumed to be the mean activity coefficient of HCl at the same concentration, since the concentration of $HClO_4$ was in excess of the LiCl concentration at all times.

The activity coefficients of the thallium-chloride complexes were calculated from the extension of the Debye-Huckel theory:

$$-\log \gamma_i = \frac{Az_i^2\sqrt{\mu}}{1 + 3\sqrt{\mu}}$$

The ionic strength, μ, was 1.0, neglecting the concentrations of $Tl(ClO_4)_3$ and LiCl since they were too small to effect the calculation. The constant A is 0.5085 at 25° C. The values of the activity coefficients of the thallium-chloride complexes which were calculated in this manner are shown in Table 12. It was not necessary to know the activity coefficients for $TlCl_5^{-2}$ and Tl^{+3} since the concentration of these species at any given LiCl concentration was too small to effect the calculation of K'.

The values of K' obtained by using the data of the extraction and the calculated activity coefficients are shown in Table 13 and Figure 10.

The values of K' tended toward a constant value at the higher LiCl concentrations employed for both acid concentrations, while the value of K' increased quite markedly at the lower LiCl concentrations. This variation in the value of K' indicated a different mode of extraction was occuring than was originally assumed. However, since the actual thallium species present in the ether phase at these low LiCl concentrations was not determined, it might well be that a thallium-chloride species other than $HTlCl_4$ was extracted, namely $TlCl_3$.

Dr. Paul Schonken of the Université de Louvain, Belgium, in a private communication, stated that in the extraction of auric gold-chloride complexes the determining factor in the extraction process at low etheral concentrations of Au(III) was the ionization of $HAuCl_4$ in the ether phase. Since the extraction of Au(III) and Tl(III)-chloride complexes are quite similar, it might also be assumed that at low values

Table 12

Activity Coefficients for Thallium-Chloride Complexes at Ionic Strength of 1.0

Complex	Charge	$-\log \gamma_i$	γ_i
$TlCl_5^{-2}$	2	0.509	0.310
$TlCl_4^-$	1	0.127	0.747
$TlCl_3$	0	0.000	1.000
$TlCl_2^+$	1	0.127	0.747
$TlCl^{+2}$	2	0.509	0.310
Tl^{+3}	3	1.144	0.072

Table 13

Evaluation of K' at Very Low LiCl Concentrations

Total Salt and Acid Concentration = 1.0 M.
Temperature = 25° C.

Initial Aqueous [LiCl]	$[HClO_4]$ = 0.4 M.		$[HClO_4]$ = 1.0 M.	
	γ_{Cl^-}	K'	γ_{Cl^-}	K'
0.003	0.975	29.4	0.975	30.3
0.004	0.958	7.62	0.960	11.7
0.005	0.952	5.65	0.951	6.68
0.006	0.940	3.47	0.940	4.37
0.007	0.935	2.72	0.935	3.79
0.008	-	-	0.925	3.62

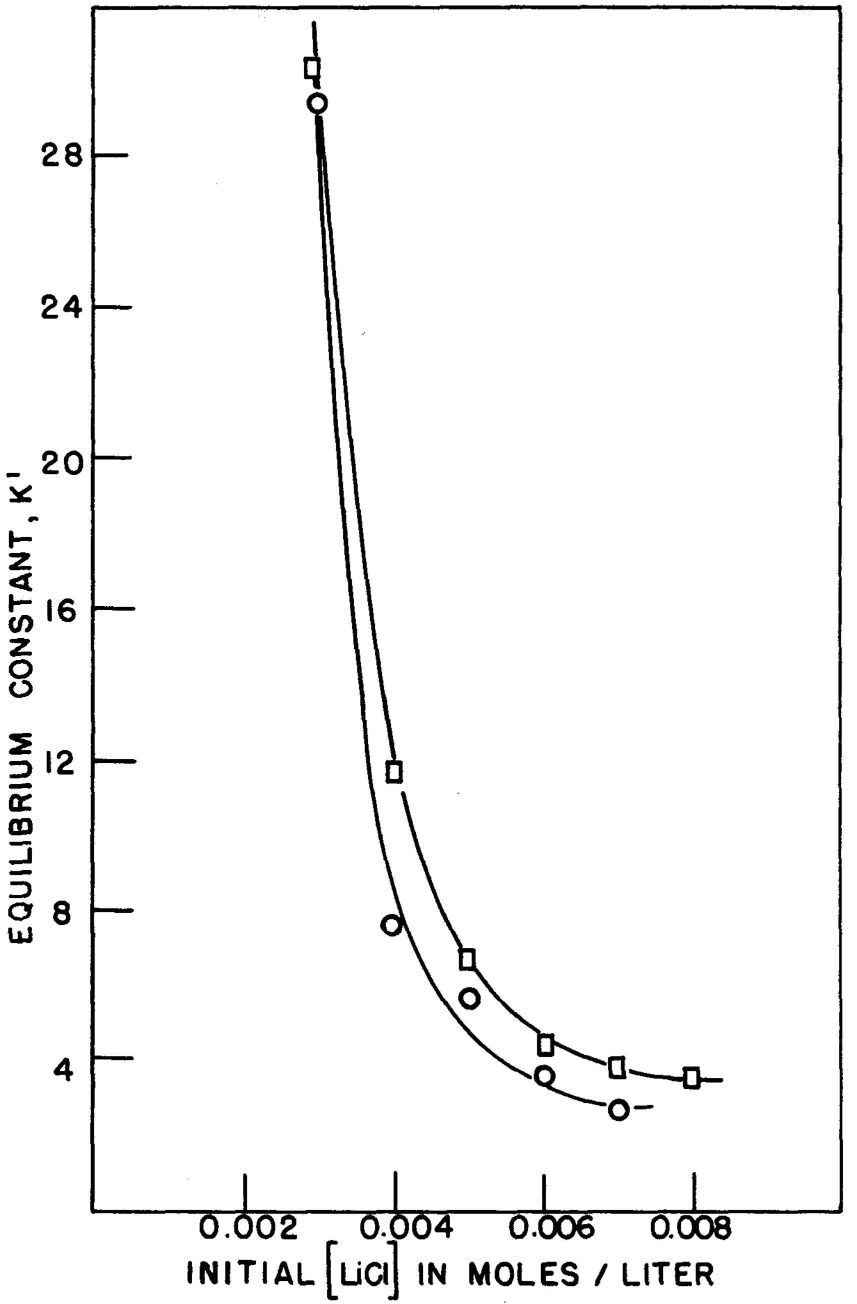


Figure 10. Dependence of K' upon [LiCl] for very low LiCl concentrations.

○ - 0.4 M. $HClO_4$.
□ - 1.0 M. $HClO_4$.

of the distribution coefficient, and hence low concentrations of thallium in the ether phase, the amount of thallium extracted might be partially controlled by the ionization of $HTlCl_4$ in the ether phase. At low etheral concentrations of $HTlCl_4$ the ionization will be quite complete, thus decreasing the activity of $HTlCl_4$ in the ether phase, and the amount of $HTlCl_4$ extracted would increase until both the ionization equilibrium constant of $HTlCl_4$ in ether and the extraction equilibrium constant were satisfied. This process would give rise to large values of K' at very low values of K_T, but the values of K' would decrease quite markedly as K_T increased.

Since both of these criteria are satisfied by the data, it may be assumed that both $TlCl_3$ and $HTlCl_4$ could be extracted at these low LiCl concentrations. With the data reported here the difference between these two processes of extraction can not be determined.

G. Extraction Studies at Constant Ionic Strength and High LiCl Concentrations

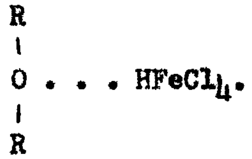
In order to determine the actual values of K' and to study the effects of LiCl and $HClO_4$ concentrations the extraction was studied at constant ionic strength. The total salt and acid concentrations employed were 2.0 M., 3.0 M. and 5.0 M. The results of these investigations are presented in the following sections.

1. Total salt and acid concentration equal to 5.0 M.

In this investigation the $HClO_4$ concentration was 4.0 M. and the sum of the concentrations of LiCl and $LiClO_4$ was 1.0 M. The initial aqueous concentration of $Tl(ClO_4)_3$ was 1.06×10^{-3} M. The results of this investigation are shown in Table 14.

Three phases were observed after the extraction equilibrium was obtained; a "light" ether, a "heavy" ether and an aqueous phase. The volume of each phase changed as the concentration of LiCl varied. It was also noted that at every LiCl concentration the total final volume obtained was 0.5 - 1.0 ml. less than the initial total volume. The heavy ether phase contained nearly all of the thallium, from 90 - 96 percent of the original thallium.

The three phase region has been observed by Dodson, Forney and Swift (26), Myers and Metzler (32) and Nachtrieb and Fryxell (30) in the investigation of the extraction of $FeCl_3$ into ether. Nachtrieb and Fryxell (23) observed a three phase region in the extraction of $GaCl_3$ into isopropyl ether. Nachtrieb and Fryxell (30) suggested the explanation for the distribution anomaly of the three phase system was not provided by thermodynamics, but would require structural evidence. They stated that in the case of Fe(III) extraction it was not unreasonable to suppose that the normal extraction was a kind of generalized acid-base reaction in which hydrogen bonding links the $HFeCl_4$ to the ether to form an "onium" salt:



$$\begin{matrix} R \\ | \\ O \cdots HFeCl_4. \\ | \\ R \end{matrix}$$

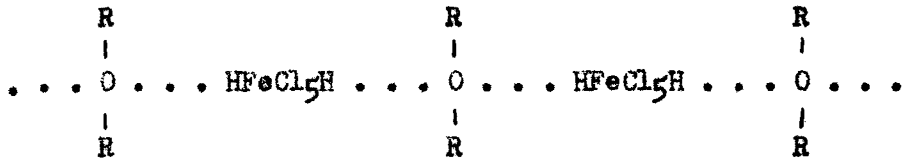
Deviation from the normal extraction may be due to polymers. Conceivably, chains might be formed by multiple hydrogen bonding.

Table 14

Extraction Data for Total Salt and Acid Concentration of 5.0 M.

Initial Aqueous $HClO_4$ Concentration = 4.0 M.
Initial Aqueous $Tl(ClO_4)_3$ = 1.06×10^{-3} M.
Temperature = 30° C.

Initial Aqueous [LiCl]	Volume of Each Phase			Percent Thallium in Each Phase		
	Light ether	Heavy ether	Aqueous	Light ether	Heavy ether	Aqueous
1.0	7.0 ml.	3.0 ml.	9.5 ml.	8.6	89.0	2.4
0.9	7.0	3.5	9.5	7.6	91.7	0.7
0.8	6.0	4.0	9.5	5.7	91.8	2.5
0.7	5.5	4.5	9.0	5.0	92.3	2.7
0.6	5.0	5.0	9.0	3.2	94.5	2.3
0.5	4.5	6.0	9.0	3.3	93.9	2.8
0.4	4.0	7.0	9.0	2.2	94.8	3.0
0.3	3.5	7.5	9.0	1.2	95.9	2.9
0.2	2.5	8.5	8.5	0.9	95.2	3.9
0.1	2.0	9.0	8.5	0.9	94.1	5.0



$$\ldots \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{O}} \ldots HFeCl_5H \ldots \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{O}} \ldots HFeCl_5H \ldots \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{O}} \ldots$$

In this investigation although empirical formulas have not been determined for the thallium species extracted some approximate ratios of

Cl^-/Tl and H^+/Tl in the ether phases have been calculated. The solubility of LiCl and $HClO_4$ in isopropyl ether was determined for the same salt and acid concentrations with no $Tl(ClO_4)_3$ present. The same three phases were present, but the volumes of like phases were not the same as when $Tl(ClO_4)_3$ was present. For this reason the actual correction of the etheral chloride and hydrogen ion concentrations for their solubility in ether could not be determined. Some of the approximate ratios were calculated and in the heavy ether phase it was noted that the ratios of Cl^-/Tl and H^+/Tl were greater than 4.0 and 1.0 respectively, which would indicate the possible formation of polymers in the heavy ether phase of the type H_xTlCl_y, where $x > 1.0$ and $y > 4.0$.

However, it is believed that at these very low etheral concentrations of thallium, from 0.001 to 0.01 M. in the "heavy" ether phase, the formation of polymers which include thallium seemed very unlikely. These same three phases were observed with no thallium present, keeping the concentrations of LiCl, $LiClO_4$ and $HClO_4$ the same. It seems that the formation of this third phase was most likely due to the solubilities of HCl, $HClO_4$ and their lithium salts in the iso-propyl ether.

Upon allowing the extraction mixture to stand for long periods of time, one of the ether layers disappeared indicating that it is a meta-stable phase. However, the reason for this is unknown.

2. Total salt and acid concentrations equal to 2.0 M.

Since the system was so complicated at the higher acid and salt concentrations the investigation was shifted to a study at a lower total salt and acid concentration equal to 2.0 M. The extraction equilibrium was studied at three different $HClO_4$ concentrations; 0.4 M., 1.0 M. and 1.6 M. For each $HClO_4$ concentration the LiCl concentration was varied keeping the total salt and acid concentration equal to 2.0 M. by the addition of required amounts of $LiClO_4$ solutions. At these lower concentrations of acid there was no noticeable difference in the volume of the ether and aqueous phase before and after the extraction equilibrium. The results of this investigation are shown in Figure 11 and Tables 15, 16 and 17.

The general shape of the plot of K_T against the initial LiCl concentration was similar for the extraction at the three acid concentrations. At LiCl concentrations below 0.1 - 0.2 M. K_T increased very rapidly as the LiCl concentration increased. There was a maximum in the plot at LiCl concentration of 0.1 - 0.2 M. For LiCl concentrations greater than 0.2 M. the K_T values decreased as the concentration of LiCl increased.

Since the concentrations of the thallium-chloride complexes were very small in every case, their activity coefficients were calculated from the extension of the Debye-Huckel theory:

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{\mu}}{1 + 3\sqrt{\mu}}$$

The ionic strength was essentially 2.0 since the concentrations of the thallium-chloride complexes were too small to effect the ionic strength. The constant A is 0.5130 at 30° C. The values of the activity coefficients of the thallium-chloride complexes which were calculated in this manner are shown in Table 18.

The varying activity coefficients of chloride were determined by the

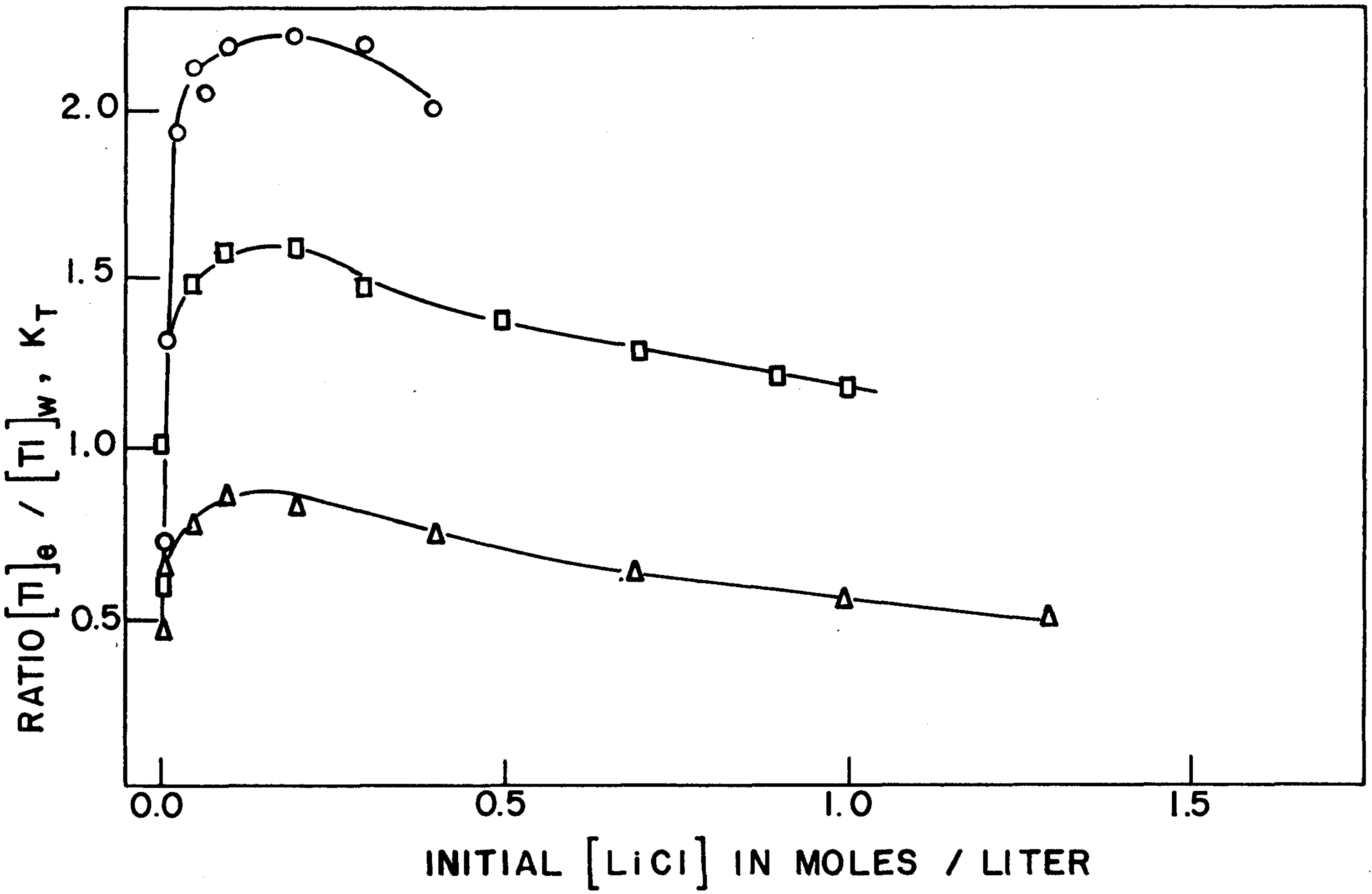


Figure 11. Extraction at total salt and acid concentration of 2.0 M.
○ - 1.6 M. $HClO_4$, □ - 1.0 M. $HClO_4$, △ - 0.4 M. $HClO_4$.

Table 15

I. Extraction Data for 2.0 M. Total Salt and Acid Concentration

Initial Aqueous $HClO_4$ Concentration = 1.6 M.
Initial Aqueous $Tl(ClO_4)_3$ Concentration = 1.06×10^{-3} M.
Temperature = 30° C.

Initial Aqueous [LiCl]	K_T	Varying γ_{Cl^-}	K' values for γ_{Cl^-} equal to		
			Varying γ_{Cl^-}	0.650	0.790
0.005	0.73	0.952	-	-	-
0.007	1.01	0.925	14.0	18.0	25.2
0.01	1.31	0.920	5.38	6.40	8.14
0.03	1.93	0.860	3.46	3.55	3.76
0.05	2.12	0.830	3.46	3.46	3.56
0.07	2.05	0.814	3.24	3.26	3.30
0.10	2.19	0.794	3.40	3.40	3.40
0.20	2.21	0.763	3.56	3.58	3.52
0.30	2.19	0.760	3.72	3.74	3.79
0.40	2.00	0.755	3.58	3.58	3.70

Table 16

II. Extraction Data for 2.0 M. Total Salt and Acid Concentration

Initial Aqueous $HClO_4$ Concentration = 1.0 M.
Initial Aqueous $Tl(ClO_4)_3$ Concentration = 1.06×10^{-3} M.
Temperature = 30° C.

Initial Aqueous [LiCl]	K_T	Varying γ_{Cl^-}	K' values for γ_{Cl^-} equal to Varying γ_{Cl^-}	0.650	0.790
0.005	0.593	0.951	12.8	25.0	17.2
0.01	1.02	0.920	4.44	6.72	5.30
0.05	1.49	0.828	2.43	2.51	2.45
0.10	1.58	0.794	2.45	2.45	2.45
0.20	1.60	0.763	2.56	2.54	2.61
0.30	1.47	0.760	2.50	2.44	2.52
0.50	1.38	0.753	2.61	2.50	2.82
0.70	1.29	0.770	2.80	2.56	2.82
0.90	1.21	0.790	2.80	2.59	2.80
1.00	1.19	0.786	2.87	2.65	2.87

Table 17

III. Extraction Data for 2.0 M. Total Salt and Acid Concentration

Initial Aqueous $HClO_4$ Concentration = 0.4 M.
Initial Aqueous $Tl(ClO_4)_3$ Concentration - 1.06×10^{-3} M.
Temperature = 30° C.

Initial Aqueous [LiCl]	K_T	Varying γ_{Cl^-}	K' values for γ_{Cl^-} equal to Varying γ_{Cl^-}	0.650	0.790
0.005	0.466	0.952	11.8	23.5	16.4
0.01	0.652	0.925	3.55	5.79	4.38
0.05	0.794	0.829	1.26	1.29	1.26
0.10	0.860	0.794	1.33	1.33	1.33
0.20	0.815	0.763	1.30	1.29	1.34
0.40	0.744	0.760	1.33	1.29	1.34
0.70	0.631	0.758	1.31	1.24	1.32
1.00	0.555	0.785	1.34	1.24	1.34
1.30	0.493	0.828	1.38	1.22	1.34

Table 18

Activity Coefficients of Thallium-Chloride Complexes of Ionic Strength = 2.0

Complex	Charge	$- \log \gamma_i$	γ_i
$TlCl_5^{-2}$	2	0.553	0.280
$TlCl_4^-$	1	0.138	0.730
$TlCl_3$	0	0.000	1.000
$TlCl_2^+$	1	0.138	0.730
$TlCl^{+2}$	2	0.553	0.280
Tl^{+3}	3	1.240	0.058

method outlined in Chapter IV. The two constant values of the activity coefficients of chloride were chosen as 0.650 and 0.790. Once again it should be pointed out that this constant chloride activity coefficient was selected only because it gave a constant value of K'.

The values of K' calculated from the extraction data and the assumed values of the chloride activity coefficients are tabulated in Tables 15, 16 and 17. It will be noted that there was very little difference in the K' values calculated from the three different chloride activity coefficients. Therefore to represent the data graphically the values of K' calculated from chloride activity coefficient equal to 0.650 were plotted against the initial LiCl concentration for the three different $HClO_4$ concentrations in Figure 12.

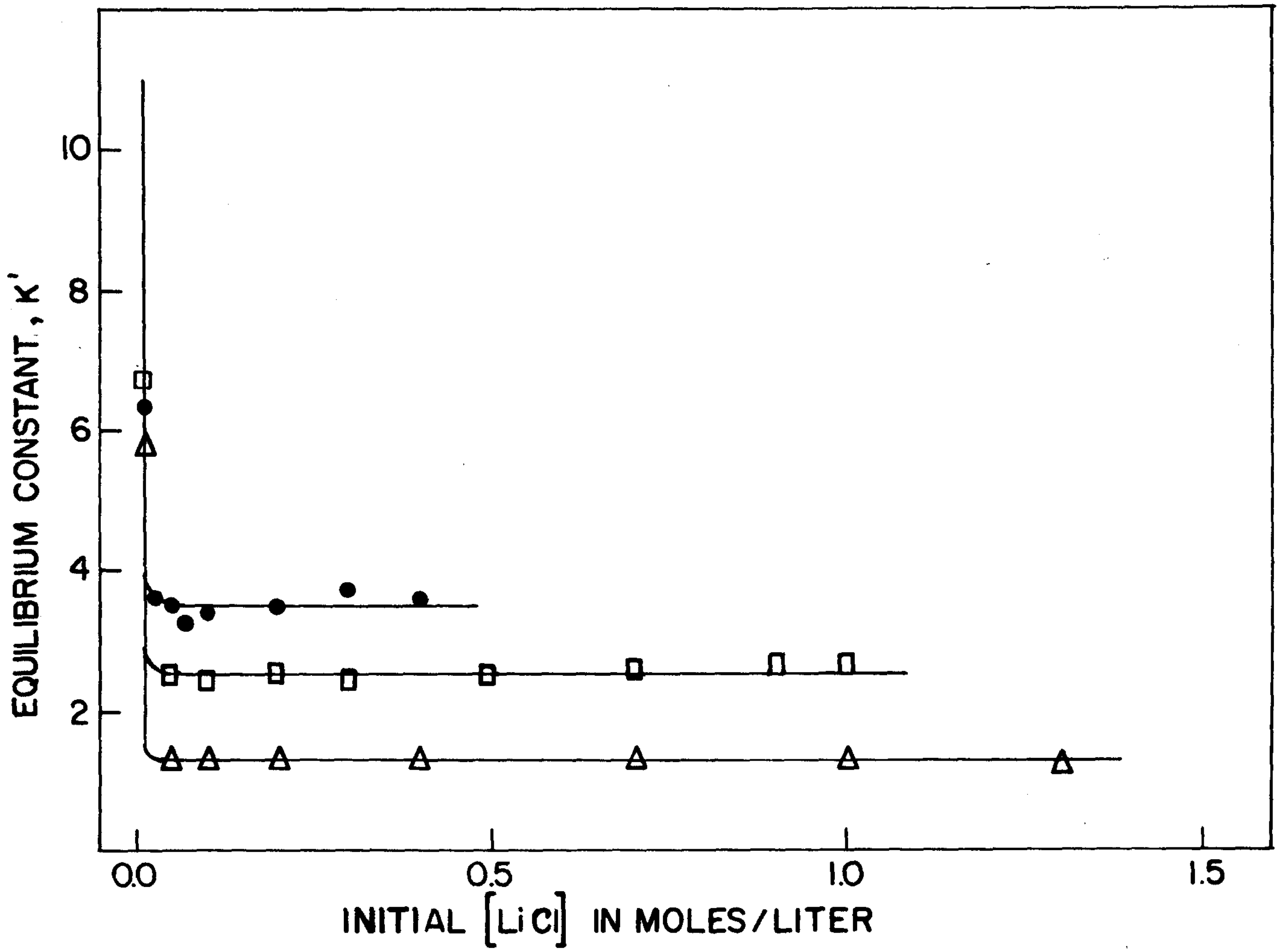


Figure 12. Dependence of K' upon [LiCl] at constant acid concentration for ionic strength equal to 2.0.

● - 1.6 M. $HClO_4$, □ - 1.0 M. $HClO_4$, △ - 0.4 M. $HClO_4$.

The constant value of K' indicated the validity of the assumption that the amount of thallium extracted was directly proportional to the aqueous activity of $TlCl_4^-$. Also this constant K' at high LiCl concentrations proved the validity of the assumption concerning the formation of the penta-cholo complex, $TlCl_5^{-2}$, in the aqueous phase which does not extract into the ether phase at the acid and chloride concentrations employed in this investigation.

However, once again the sharp increase in the K' values was noted at the very low LiCl concentrations. This increase was again contributed to two possible factors. The extraction of $TlCl_3$ seems very possible at these low LiCl concentrations thus giving rise to apparently large values of K'. Also at these low etheral concentrations of $HTlCl_4$ the ionization of $HTlCl_4$ in the ether phase becomes very important. This inoization would result in the calculation of large values of K' from the method employed.

3. Total salt and acid concentration equal to 3.0 M.

The extraction equilibrium was studied at a total salt and acid concentration of 3.0 M. for four different $HClO_4$ concentrations; 0.4 M., 1.0 M., 1.6 M. and 2.2 M. The LiCl concentration was varied for each $HClO_4$ concentration keeping the total salt and acid concentration at 3.0 M. by the addition of required amounts of standard $LiClO_4$ solutions. There was no noticeable difference in the initial and final etheral and aqueous volumes. The results of this investigation are shown in Figure 13 and Tables 19, 20, 21 and 22.

The plots of K_T against the initial LiCl concentration have the

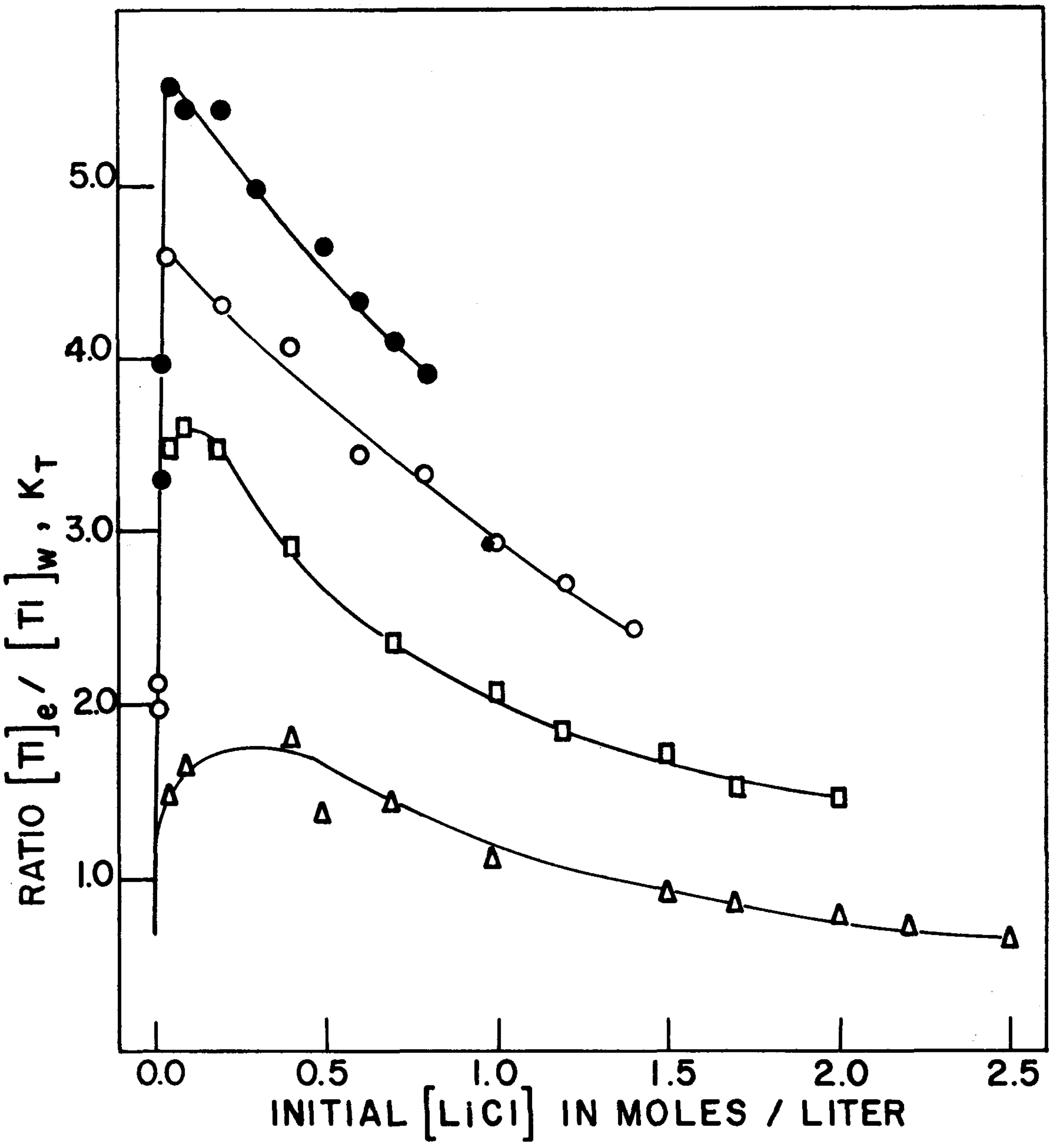


Figure 13. Extraction at total salt and acid concentration of 3.0 M.

● – 2.2 M. $HClO_4$ ☐ – 1.0 M. $HClO_4$
○ – 1.6 M. $HClO_4$ △ – 0.4 M. $HClO_4$

Table 19

I. Extraction Data for 3.0 M. Total Salt and Acid Concentration[a]

Initial Aqueous $HClO_4$ Concentration = 2.2 M.
Initial Aqueous $Tl(ClO_4)_3$ Concentration = 1.06×10^{-3} M.
Temperature = 30° C.

Initial Aqueous [LiCl]	K_T	Varying γ_{Cl^-}	K' values for γ_{Cl^-} equal to Varying γ_{Cl^-}	0.850
0.005	2.11	0.962	109.	138.
0.01	3.95	0.922	19.9	22.1
0.05	5.55	0.829	9.20	9.15
0.10	5.42	0.794	8.56	8.62
0.20	5.42	0.763	8.84	9.00
0.30	4.95	0.759	8.57	8.72
0.50	4.64	0.753	8.91	9.18
0.60	4.30	0.762	8.68	9.00
0.70	4.07	0.770	8.62	8.91
0.80	3.90	0.780	8.70	9.00

[a] Average to two runs.

Table 20

II. Extraction Data for 3.0 M. Total Salt and Acid Concentration[a]

Initial Aqueous $HClO_4$ Concentration = 1.6 M.
Initial Aqueous $Tl(ClO_4)_3$ Concentration = 1.06×10^{-3} M.
Temperature = 30° C.

Initial Aqueous [LiCl]	K_T	Varying γ_{Cl^-}	K' values for γ_{Cl^-} equal to Varying γ_{Cl^-}	0.850
0.005	1.91	0.962	98.5	125.
0.01	3.27	0.922	18.3	18.9
0.05	4.58	0.829	7.39	7.34
0.20	4.30	0.763	7.01	7.14
0.40	4.05	0.756	7.37	7.57
0.60	3.42	0.762	6.87	7.12
0.80	3.32	0.780	7.40	7.65
1.00	2.93	0.802	7.25	7.45
1.20	2.69	0.834	7.37	7.45
1.40	2.42	0.868	7.33	7.26

[a] Average of two runs

Table 21

III. Extraction Data for 3.0 M. Total Salt and Acid Concentration[a]

Initial Aqueous $HClO_4$ Concentration = 1.0 M.
Initial Aqueous $Tl(ClO_4)_3$ Concentration = 1.06×10^{-3} M.
Temperature = 30° C.

Initial Aqueous [LiCl]	K_T	Varying γ_{Cl^-}	K' values for γ_{Cl^-} equal to Varying γ_{Cl^-}	0.850
0.05	3.47	0.829	5.55	5.55
0.10	3.61	0.794	5.67	5.92
0.20	3.45	0.763	5.62	5.72
0.40	2.90	0.756	5.31	5.42
0.70	2.35	0.770	4.99	5.18
1.00	2.09	0.802	5.18	5.31
1.20	1.85	0.828	5.07	5.13
1.50	1.72	0.867	5.41	5.36
1.70	1.51	0.885	5.18	5.06
2.00	1.46	0.957	5.80	5.38

[a] Average of two runs.

Table 22

IV. Extraction Data for 3.0 M. Total Salt and Acid Concentration[a]

Initial Aqueous $HClO_4$ Concentration = 0.4 M.
Initial Aqueous $Tl(ClO_4)_3$ Concentration = 1.06×10^{-3} M.
Temperature = 30° C.

Initial Aqueous [LiCl]	K_T	Varying γ_{Cl^-}	K' values for γ_{Cl^-} equal to	
			Varying γ_{Cl^-}	0.850
0.05	1.48	0.829	2.39	2.39
0.10	1.64	0.794	2.58	2.59
0.40	1.81	0.756	3.29	3.38
0.50	1.40	0.750	2.67	2.77
0.70	1.45	0.760	3.06	3.17
1.00	1.10	0.816	2.74	2.79
1.50	0.924	0.845	2.87	2.87
1.70	0.837	0.868	2.84	2.79
2.00	0.770	0.927	3.00	2.84
2.20	0.705	1.000	3.07	2.77
2.50	0.638	1.050	3.15	2.71

[a] Average of two runs.

same general shape for the extraction at the four acid concentrations. A maximum in K_T was observed at LiCl concentrations of approximately 0.05 - 0.20 M. The width of the peak decreased quite markedly as the concentration of $HClO_4$ was increased. At LiCl concentrations below 0.05 M. the values of K_T decreased very rapidly. There was a decrease in K_T at higher LiCl concentrations, an initial large decrease followed by a more gradual decrease.

As in the case of 2.0 M. total salt and acid concentration the concentrations of the thallium-chloride complexes were very small in every case and their activity coefficients were calculated from the extension of the Debye-Huckel theory. Neglecting the concentrations of the thallium-chloride complexes, since they were very small, the ionic strength was essentially 3.0 and the value of the constant A was taken as 0.5130 at 30° C. The calculated values of the activity coefficients of the thallium-chloride complexes are shown in Table 23.

Using the method outlined in Chapter IV the varying activity coefficients of chloride were calculated from the values of the mean activity coefficients of HCl and LiCl. The constant value of the chloride activity coefficient which appears to give the most constant value of K' was 0.850.

The values of K' calculated using the extraction data and the values of the chloride activity coefficients are presented in Tables 19, 20, 21 and 22. At the low LiCl concentrations there is very little difference in the K' values calculated from the varying and the constant chloride activity coefficient. However, at the higher LiCl concentrations the values of K' calculated from the varying chloride activity coefficient

Table 23

Activity Coefficients of Thallium-Chloride
Complexes at Ionic Strength = 3.0 M.

Complex	Charge	$-\log \gamma_i$	γ_i
$TlCl_5^{-2}$	2	0.573	0.267
$TlCl_4^-$	1	0.144	0.718
$TlCl_3$	0	0.000	1.000
$TlCl_2^+$	1	0.144	0.718
$TlCl^{+2}$	2	0.573	0.267
Tl^{+3}	3	1.290	0.051

increase slightly, whereas the values calculated with the chloride activity coefficient equal to 0.850 remain remarkably constant. The constancy of the values of K' calculated with the chloride activity coefficient equal to 0.850 are shown in Figure 14 in a graph of K' versus the initial LiCl concentrations. However, it should be noted that the values of K' calculated from the varying chloride activity coefficient do not vary enough to say that this method is not correct. From the data present it was not possible to tell which method of determining the activity coefficient of the chloride ion in the solution was the best.

Since the values of K' were constant over such a wide range of LiCl concentrations it is felt that the initial assumptions about the

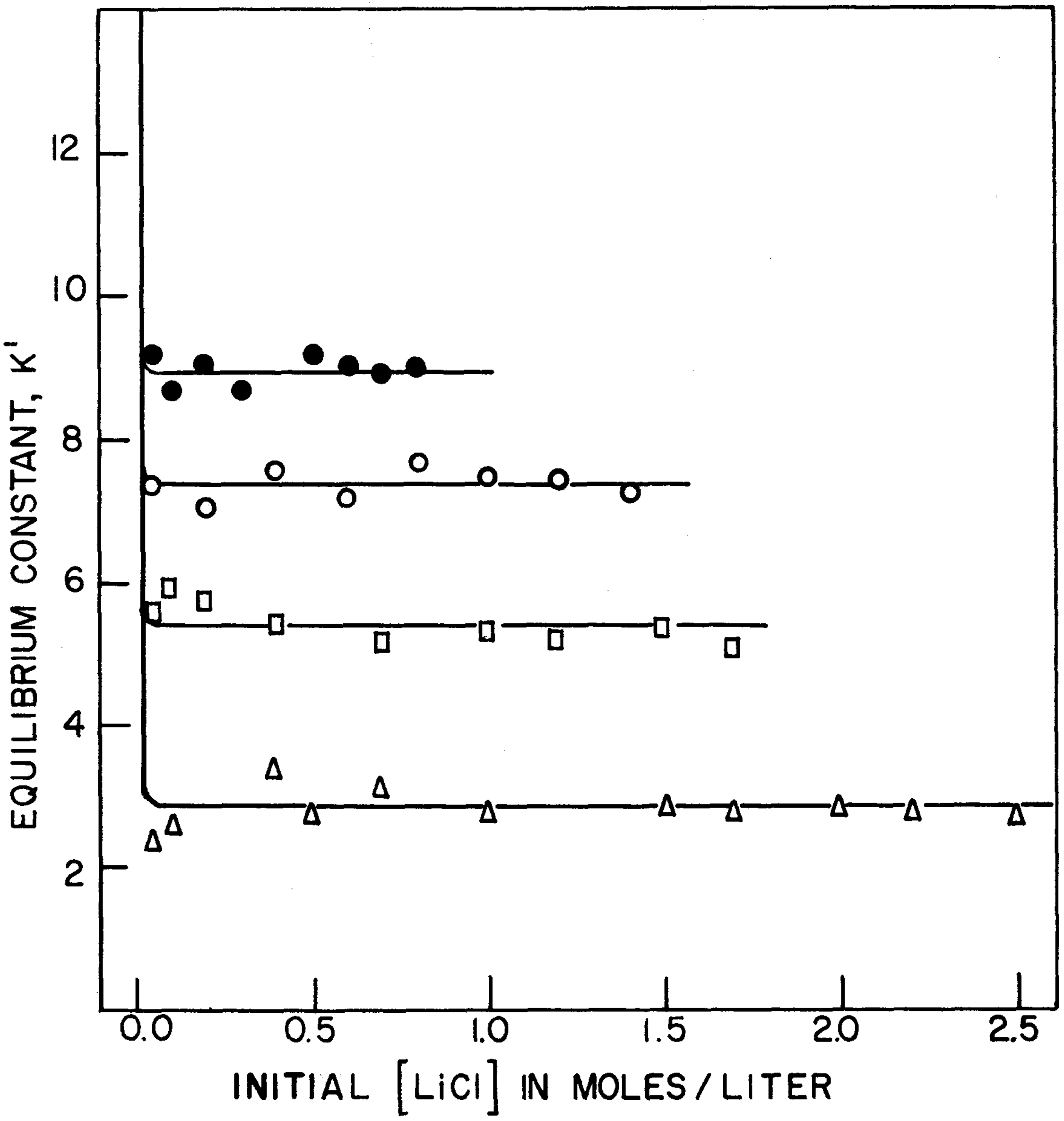


Figure 14. Dependence of K' upon LiCl at constant acid concentration for ionic strength equal to 3.0.

● - 2.2 M. $HClO_4$　　□ - 1.0 M. $HClO_4$

○ - 1.6 M. $HClO_4$　　△ - 0.4 M. $HClO_4$

equilibrium were correct. The amount of thallium extracted was directly proportional to the aqueous activity of $TlCl_4^-$. Since the values of K' would not be constant without including the term with K_5, the assumption that a penta-chloro complex, $TlCl_5^{-2}$, was formed in the aqueous phase and was not extractable into the ether phase over the range of LiCl and $HClO_4$ concentrations employed in this investigation was proven a valid assumption.

The sharp rise in the K' values at low LiCl concentrations was observed again, and once again this increase could be explained by the extraction of $TlCl_3$ and/or the ionization of $HTlCl_4$ in the ether phase.

H. Dependence of the Extraction upon Acid Concentration

In order to determine the effect of acid concentration the extraction was studied at a series of constant $HClO_4$ concentrations and constant ionic strength. The results of this investigation are shown in Table 24. In Figures 15 and 16 the values of K_T are plotted against the concentration of $HClO_4$ at the total salt and acid concentrations equal to 3.0 M. and 2.0 M., respectively.

If the plot of the extraction equilibrium constant against the activity of hydrogen ion is a straight line, the equilibrium constant must be a function of the hydrogen ion activity to the first power. The relationship will be of the order:

$$K = a(H^+) + b$$

where a is the slope of the plot and b is the intercept of the plot on the "y" axis.

Table 24

Extraction as a Function of $HClO_4$ Concentration
of Total Salt and Acid Concentration
Equal to 3.0 M. and 2.0 M.

Initial	Total Salt and Acid = 3.0 M. K' at $[HClO_4]$ equal to				Total Salt and Acid = 2.0 M. K' at $[HClO_4]$ equal to		
[HCl]	0.4 M.	1.0 M.	1.6 M.	2.2 M.	0.4 M.	1.0 M.	1.6 M.
0.05	-	-	-	-	0.794	1.49	2.12
0.10	1.64	3.61	4.50	5.42	0.860	1.58	2.19
0.20	1.72	3.45	4.30	5.42	-	-	-
0.40	1.81	2.90	4.05	4.74	0.744	1.42	2.00
0.70	1.45	2.35	3.42	4.07	-	-	-
1.00	1.20	2.09	2.93	-	-	-	-
1.20	1.07	1.85	2.69	-	-	-	-
1.40	0.97	1,72	2.42	-	-	-	-

If the plot of the logarithm of the equilibrium constant against the logarithm of the activity of hydrogen ion is a straight line, then the slope of that line will determine the power to which the equilibrium constant is a function of the hydrogen ion activity.

For those cases in which the activity coefficient was not known it was not possible to use the hydrogen ion activity in these plots. One can then use the acid concentration in place of the activity of the hydrogen ion and make use of the resulting graphs to guide in making assumptions about the activity coefficients and their variation with

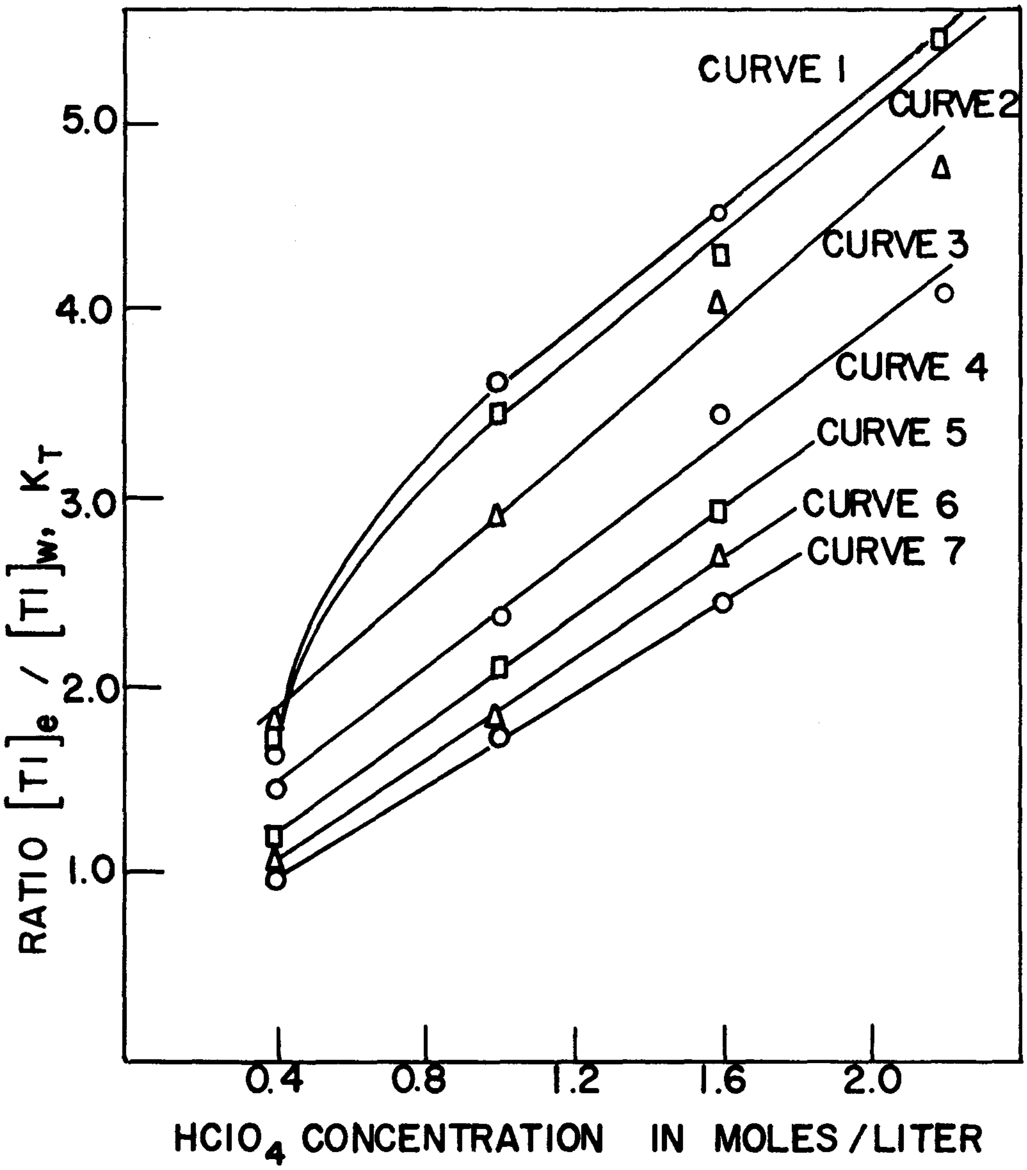


Figure 15. Extraction as a function of concentration of $HClO_4$ for total salt and acid concentration of 3.0 M.

Curve 1	0.10 M. LiCl	Curve 5	1.00 M. LiCl
Curve 2	0.20 M. LiCl	Curve 6	1.20 M. LiCl
Curve 3	0.40 M. LiCl	Curve 7	1.40 M. LiCl
Curve 4	0.70 M. LiCl		

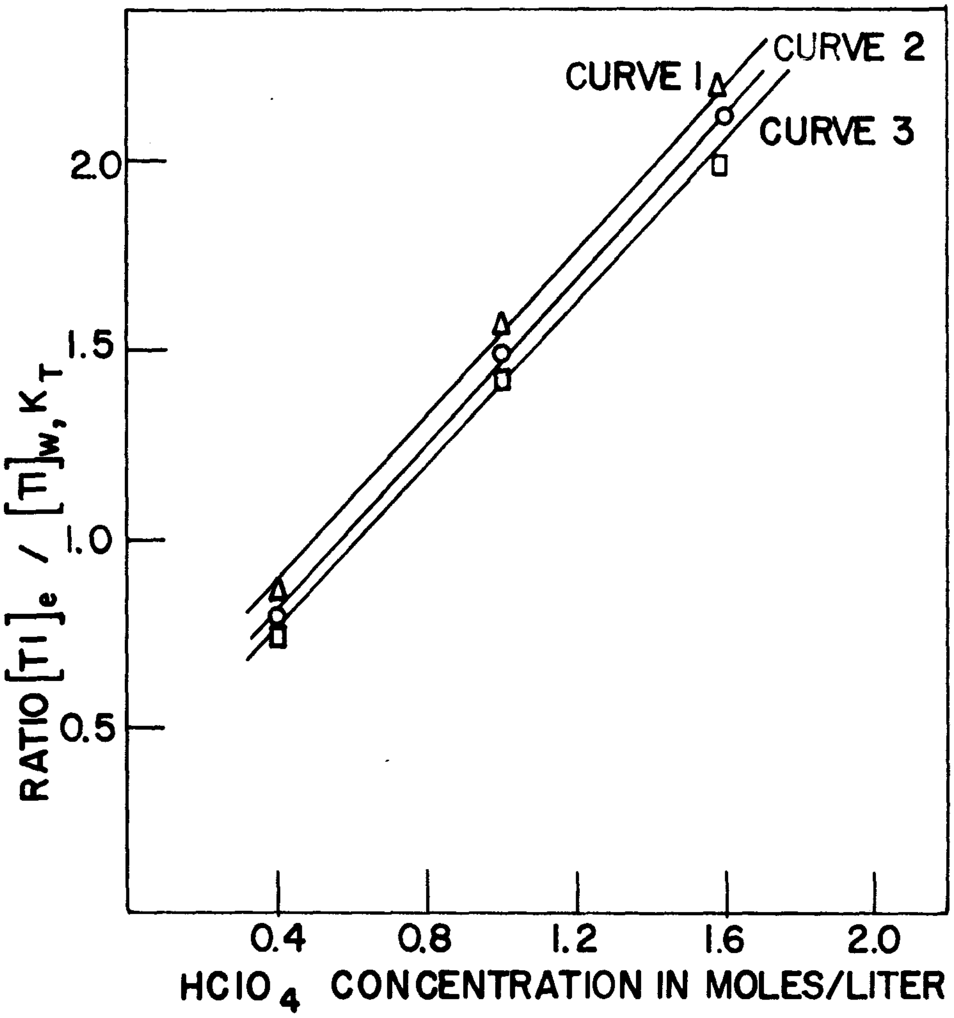


Figure 16. Extraction as a function of concentration of $HClO_4$ for total salt and acid concentration of 2.0 M.

Curve 1 - 0.10 M. LiCl
Curve 2 - 0.05 M. LiCl
Curve 3 - 0.40 M. LiCl

concentration.

It will be noted in Figure 15 that the plots of K_T against $HClO_4$ concentrations for total salt and acid concentrations equal to 3.0 M. gave straight lines at the high concentrations of LiCl. At low LiCl concentrations the plots were straight lines at high $HClO_4$ concentrations but deviated negatively at a low $HClO_4$ concentrations. These results have indicated two conclusions. At high LiCl concentrations and over the range of $HClO_4$ concentrations employed in this investigation K_T was found to be proportional to the concentration of $HClO_4$, to the first power. At low LiCl concentrations and $HClO_4$ concentrations greater than 1.0 M. K_T showed a first power dependence on the concentration of $HClO_4$, but at lower $HClO_4$ concentrations was proportional to the concentration of $HClO_4$ to some higher power. The dependence of K_T on the concentration of $HClO_4$ to the first power indicated that the species extracted contained one hydrogen and was probably $HTlCl_4$, but the dependence upon higher powers of $HClO_4$ concentrations indicated that another process was being observed. This higher power dependence could be due to the dependence of the extraction, at low LiCl concentrations, upon the ionization of $HTlCl_4$ in the ether phase and/or the extraction of $TlCl_3$ into the ether.

The extraction at 2.0 M. total salt and acid concentrations appeared to be dependent upon the concentration of $HClO_4$ to the first power over the range of $HClO_4$ and LiCl concentrations employed as is indicated by the straight line plots in Figure 16. The higher power $HClO_4$ concentration dependence was not observed at the lower LiCl concentrations, however it may be present at LiCl concentrations lower than those employed in this investigation. Again this first power $HClO_4$

concentration dependence indicated the extraction of $HTlCl_4$.

Using the constant values of K' as reported in Section G of this chapter, it will be noted from Figure 17 that K' was dependent upon the $HClO_4$ concentration to the first power at total salt and acid concentrations equal to 2.0 M. and 3.0 M. This first power dependence of K' upon the $HClO_4$ concentration indicated the extraction of $HTlCl_4$, since only one hydrogen ion is involved in the equilibrium constant. The linear dependence of K' upon the $HClO_4$ concentration also indicated that the activity coefficient of hydrogen ion was constant for a given total salt and acid concentration.

However, the true equilibrium constant should be constant at different acid concentrations. In order to explain this acid dependence two new constants were defined for the following equilibriums.

$$H^- - TlCl_4^- \rightleftarrows HTlCl_4^w$$

$$HTlCl_4^w \rightleftarrows HTlCl_4^e$$

where w and e designate $HTlCl_4$ in the aqueous and ether phases, respectively. The equilibrium constants for these equilibriums:

$$K_a = \frac{[HTlCl_4]_w}{[H^+]\ [TlCl_4^-]} \quad x \quad \frac{\gamma_{HTlCl_4}}{\gamma_{H^+} \cdot \gamma_{TlCl_4^-}}$$

and

$$K_x = \frac{[HTlCl_4]_e}{[HTlCl_4]_w} \quad x \quad \frac{\gamma^e_{HTlCl_4}}{\gamma_{HTlCl_4}} \quad .$$

Multiplying K_a by K_x one obtains:

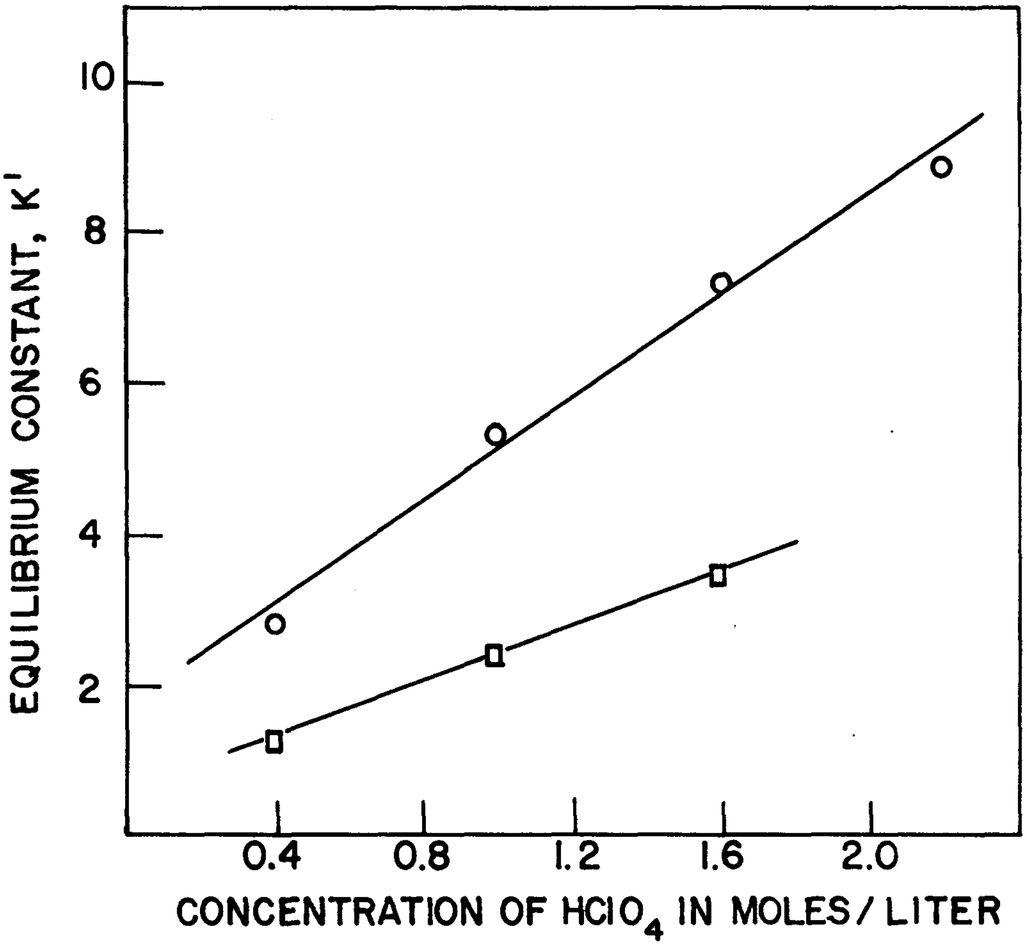


Figure 17. Dependence of K' upon $HClO_4$ concentration.

○ - 3.0 M. total salt and acid concentration.
□ - 2.0 M. total salt and acid concentration.

$$K_aK_x = K = \frac{(HTlCl_4)_e}{(H^+)\quad(TlCl_4^-)} \qquad (1).$$

From the acid dependence study the following was observed:

$$K' = \frac{K\,(H^-)}{\gamma^e_{HTlCl_4}} = \alpha\,(H^+) = \alpha\,[H^+]\,\gamma_{H^+} \qquad (2).$$

Rearranging equation (2) yields:

$$\alpha = \frac{K}{\gamma^e_{HTlCl_4}} = \frac{K'}{[H^+]\,\gamma_{H^+}} \qquad (3).$$

Assuming that the activity coefficient of hydrogen ion is constant for a given total salt and acid concentration yields:

$$\alpha\,\gamma_{H^+} = K'' = \frac{K'}{[H^+]} = K_x\,\frac{K_a\,\gamma_{H^+}}{\gamma^e_{HTlCl_4}} \qquad (4).$$

The value of K'' should be constant for the different $HClO_4$ concentrations at a given total salt and acid concentration if the activity coefficients of hydrogen ion and of $HTlCl_4$ in the ether phase are constant.

Therefore at constant acid and varying LiCl concentrations K' is proportional to the true extraction equilibrium constant, K_x, for a given total salt and acid concentration. However, at varying acid concentrations K_x should be inversely proportional to the acid concentration as is shown in equation (4).

Equation (2) is not quite true but should have added to it the term β, a constant which is determined by the intercept on the "y" axis of the plot of K' versus $HClO_4$ concentrations. Since the term is not zero, it might be considered as a measure of the dependence of the extraction equilibrium constant upon the ionization of $HTlCl_4$ in the ether phase or upon the extraction of $TlCl_3$ into the ether phase at low LiCl and $HClO_4$ concentrations.

From equation (4) it is noted that the ratio of K' to hydrogen ion concentration should be constant. In Table 25 the values of the ratio $K' / [HClO_4]$ have been calculated for total salt and acid concentrations of 2.0 M. and 3.0 M. It will be noted from Table 25 that for both total concentrations the ratio $K' / [HClO_4]$ is fairly constant at $HClO_4$ concentrations greater than 1.0 M. At $HClO_4$ concentrations below 1.0 M. the ratio is larger due to the fact that the term β influences the ratio to a greater degree. For the explanation for this increase in the ratio it might be recalled that at low $HClO_4$ concentrations other factors may influence the extraction equilibrium constant, such as the extraction of $TlCl_3$ or the ionization of $HTlCl_4$ in the ether phase.

In this investigation the true extraction equilibrium constant, K_x, was not determined. Rather terms which were proportional to K_x were calculated. In order to determine the value of K_x the concentration of $HTlCl_4$ in the aqueous phase or the value of K_a would have to be known. The activity coefficients of $HTlCl_4$ in ether and of hydrogen ion in the aqueous phase at the given total salt and acid concentration would also have to be known. These values would have to be acquired by independent measurements.

It was believed that the various thallium-chloride complexes might absorb light at different wave lengths and that the concentration of each complex could be determined by the amount of absorption at a given wave length. An absorption spectrum was determined on a solution of $Tl(ClO_4)_3$

Table 25

Determination of Ratio K' / $[H^+]$

1. 3.0 M. Total Salt and Acid Concentrations

K'	$[HClO_4]$	K' / $[HClO_4]$
2.80	0.4	7.0
5.35	1.0	5.4
7.35	1.6	4.6
8.90	2.2	4.1

2. 2.0 M. Total Salt and Acid Concentrations

K'	$[HClO_4]$	K' / $[HClO_4]$
1.30	0.4	3.2
2.52	1.0	2.5
3.50	1.6	2.2

in HCl by a Cary Spectrophotometer. However, only a wide absorption band was observed over the range employed with no sharp or characteristic peaks. The range of the Cary was 190 to 2800 $M\mu$. There may be characteristic absorption bands, however, in other regions.

No attempt was made to measure the formation constant of $HTlCl_4$ in the aqueous phase because of the very complex system present.

VI. SUMMARY AND CONCLUSIONS

A radiochemical study was made of the extraction of thallium-chloride complexes into iso-propyl ether from aqueous solutions of mixtures of $LiCl$, $LiClO_4$, $HClO_4$ and $Tl(ClO_4)_3$. To ensure complete equilibrium, both thermal and extraction, and separation between the ether and aqueous phases the proper rate of shaking, time of contact and time of separation were selected. The extraction was observed to be markedly influenced by the ionic strength and the investigations were performed at a given total salt and acid concentration, hence constant ionic strength.

The temperature dependence of the extraction was measured at two initial aqueous $HClO_4$ concentrations, 0.4 M. and 0.6 M., for varying LiCl concentrations maintaining a constant total salt concentration with additions of $LiClO_4$. Using the van't Hoff equation and a graphical method the partial molar heats of extraction were calculated as -9.5 kcal. / mole and -9.9 kcal. / mole for extraction from 0.4 M. and 0.6 M. $HClO_4$ solutions, respectively.

The variation of the distribution coefficient, K_T, with varying LiCl concentrations followed essentially the same pattern for the different values of total salt and acid concentration employed in this investigation. As the LiCl concentration was increased from zero there is a sharp increase in K_T and it reached a maximum at 0.1 to 0.2 M. LiCl. At higher LiCl concentrations the values of K_T decreased.

The formation of a pentachloro-thallium complex in the aqueous phase was postulated to explain the decrease in the extraction at high LiCl concentrations. The formation constant, K_5, for $TlCl_5^{-2}$:

$$K_5 = \frac{(TlCl_5^{-2})}{(Tl^{+3})\ (Cl^-)^5} ,$$

was calculated from the extraction data using the constants reported by Benoit (38) for the mono-, di-, tri- and tetrachloro-thallium complexes. The value for K_5 of 3.6×10^{17} was determined by evaluation with successive approximations.

The empirical formula of the thallium compound in the ether phase was calculated for the total salt and acid concentrations equal to 2.0 M. and 3.0 M. by analyzing the ether phase for the thallium, chloride and ionizable hydrogen ion contents. After correcting the analyses for the solubility of LiCl and $HClO_4$ in ether the empirical formula was observed to be essentially $HTlCl_4$. Actually the ratio of Cl^-/Tl in the ether phase was slightly greater than 4.0, but sufficiently close to be within the limits of error of the methods employed.

The extraction was studied at very low LiCl concentrations, up to 9×10^{-3} M. with 1.06×10^{-3} M. $Tl(ClO_4)_3$, for two $HClO_4$ concentrations, 0.4 M. and 1.0 M., while the total salt and acid concentrations were maintained at 1.0 M. For these conditions the equilibrium constant for the extraction at constant acid, K', was observed to vary quite markedly with the LiCl concentration. At the higher LiCl concentrations the value of K' tended toward a constant value, but K' increased to quite large values at the lower LiCl concentrations. These large values of K' might be explained by the extraction of $TlCl_3$ and/or the ionization of $HTlCl_4$ in ether at low etheral concentrations of thallium.

At total salt and acid concentrations equal to 5.0 M., 4.0 M. $HClO_4$ and 1.0 M. for the sum of LiCl and $LiClO_4$ concentrations, a three phase system, "light" ether, "heavy" ether and aqueous phases, were observed. The changing volumes of the three phases with varying LiCl concentrations made interpretation of this data quite difficult. In every case 89 to 96 percent of the original thallium appeared in the "heavy" ether phase. It has been suggested that the formation of the third phase, the "heavy" ether phase, was due to the formation of polymers of the form H_xTlCl_y in the ether phase, where x and y are greater than 1.0 and 4.0, respectively; such as H_2TlCl_5, H_3TlCl_6, etc.

At these low concentrations of thallium, 0.001 to 0.01 M. in the "heavy" ether phase, it is difficult to believe that the thallium has much influence in the gross behavior of the ether. In fact such three phase systems are observed in the absence of metal ions, such as thallium and iron. The formation of the third phase is most likely due to the solubility of hydrochloric acid, perchloric acid and their alkali salts in the isopropyl ether.

The extraction was studied at total salt and acid concentrations equal to 2.0 M. and 3.0 M. For the investigation at 3.0 M. the extraction was performed in 0.4 M., 1.0 M., 1.6 M. and 2.2 M. $HClO_4$ and at 2.0 M. in 0.4 M., 1.0 M. and 1.6 M. $HClO_4$ with varying LiCl concentrations. At LiCl concentrations greater than 0.1 M. the equilibrium constant, K', was fairly constant for a given acid concentration. The marked increase in K' at the low LiCl concentrations was again postulated as an indication that the extraction process at low etheral concentrations was dependent upon the extraction of $TlCl_3$ and/or the ionization of $HTlCl_4$ in the ether phase.

In the study of the dependence of the extraction upon acid concentration it was observed that the extraction equilibrium constant was proportional to the $HClO_4$ concentration to the first power. It was assumed from this first power dependence upon the concentration that the activity coefficient of hydrogen ion was constant at a given total salt and acid concentration.

It was concluded that the true extraction equilibrium between the aqueous and ether phases was:

$$HTlCl_4^w \rightleftharpoons HTlCl_4^e$$

for which:

$$K_x = \frac{(HTlCl_4)_e}{(HTlCl_4)_w}$$

Also in the aqueous phase the following equilibrium was postulated:

$$H^+ + TlCl_4^- \rightleftharpoons HTlCl_4^w$$

for which:

$$K_a = \frac{(HTlCl_4)_w}{(H^+) \quad (TlCl_4^-)}$$

Using the above assumptions it was shown that the true extraction equilibrium constant, K_x, was inversely proportional to the hydrogen ion concentration, assuming the activity coefficient of hydrogen ion is constant at a given total salt and acid concentration.

The true extraction equilibrium constant could not be calculated from the data reported. The value of K_a or some independent measurement of the concentration of one or more of the thallium-chloride complexes in the aqueous phase would be needed to calculate K_x. However, it has been shown that K_x is proportional to the etheral concentration of $HTlCl_4$ and inversely proportional to the aqueous concentration of $HClO_4$ and the aqueous activity of $TlCl_4^-$ at a given ionic strength.

VII. LITERATURE CITED

1. Waggaman, W. H., Heffner, G. G., and Gee, E. H., U.S. Bur. Mines Inform. Circ., No. 7553, (1950).

2. Howe, H. E., and Smith, Jr., A. A., J. Electrochem. Soc., 97, 167C-170C (1950).

3. Crookes, W., Chem. News, 3, 193-203 (1861); Bull. soc. chim., 3, 211-289 (1861).

4. Lamy, A., Ann. chim. phys., 4, 67, 385, 418 (1862).

5. Hopkins, B. S., "Chapters in the Chemistry of the Less Familiar Elements", Volume 1, Stipes Publishing Co., Champaign, Ill., 1939.

6. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis", Second Edition, John Wiley and Sons, Inc., New York, 1953.

7. Noyes, A. A., Bray, W. C., and Spear, E. B., J. Am. Chem. Soc., 30, 489, 515, 559 (1908).

8. Browning, P. E., and Hutchins, G. P., Am. J. Sci., /4/ 8, 460 (1899).

9. Mach, F., and Lepper, W., Z. anal. Chem. 68, 41 (1926).

10. Werther, G., Z. anal. Chem., 3, 1 (1864).

11. Noyes, A. A., and Bray, W. C., "A System of Qualitative Analysis of the Rare Elements", The Macmillan Co., New York, 1927.

12. Rothe, Stahl and Eisen, 12, 1052 (1892); 13, 333 (1893).

13. Langmuir, A. C., J. Am. Chem. Soc., 22, 102 (1900).

14. Kern, E. F., J. Am. Chem. Soc., 23, 689 (1901).

15. Speller, Chem. News, 83, 124 (1901).

16. Swift, E. H., J. Am. Chem. Soc., 46, 2375 (1924).

17. Wada, I., and Ishii, R., Bull. Inst. Phys. Chem. Res. Tokyo, 13, 264 (1934); /C. A., 28, 3334 (1934)./

18. Irving, H. M., Quart. Rev., 5, 200 (1951).

19. Edwards, F. C., and Voigt, A. F., *Analyt. Chem., 21,* 1204 (1949).

20. Irving, H. M., and Rossotti, F. J. C., *Analyst. 77,* 801 (1952).

21. Irving, H. M., Rossotti, F. J. C., and Drysdale, J. G., *Nature (London), 169,* 619 (1952).

22. Grahame, D. C., and Seaborg, G. T., *J. Am. Chem. Soc., 60,* 2524 (1938).

23. Nachtrieb, N. H., and Fryxell, R. E., *J. Am. Chem. Soc., 81,* 4035 (1949).

24. Nachtrieb, N. H., and Conway, J. G., *J. Am. Chem. Soc., 70,* 3547 (1948).

25. Nernst, W., *Z. physikal. Chem., 8,* 110 (1891).

26. Dodson, R. W., Forney, G. J., and Swift, E. H., *J. Am. Chem. Soc., 58,* 2573 (1936).

27. Axelrod, J., and Swift, E. H., *J. Am. Chem. Soc., 62,* 33 (1940).

28. Kato, J., and Isii, R., *Sci. Papers Inst. Phys. Chem. Research Tokyo, 36,* 82-96 (1939).

29. Nachtrieb, N. H., and Fryxell, R. E., *J. Am. Chem. Soc., 70,* 3552 (1948).

30. Nachtrieb, N. H., and Fryxell, R. E., *J. Am. Chem. Soc., 74,* 897 (1952).

31. Myers, R. J., Metzler, D. E., and Swift, E. H., *J. Am. Chem. Soc., 72,* 3767 (1950).

32. Myers, R. J., and Metzler, D. E., *J. Am. Chem. Soc., 72,* 3772 (1950).

33. Metzler, D. E., and Myers, R. J., *J. Am. Chem. Soc., 72,* 3776 (1950).

34. Lidofsky, L., Macklin, P., and Wu, C. S., *Phys. Rev., 87,* 391 (1952).

35. Horrocks, D. L., and Voigt, A. F., *Phys. Rev., 95,* 1205 (1954).

36. Kleinberg, J., "Collected Radiochemical Procedures", A. E. C. Document LA - 1721, Los Alamos Scientific Laboratory, (1954).

37. Willard, H. H., and Smith, G. M., *Ind. Eng. Chem., Anal. Ed., 11,* 186 (1939).

38. Benoit, R., *Bull. soc. chim. France, 1949,* 518 - 24.

39. Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions", Second Edition, Reinhold Publishing Corporation, New York, 1950.

40. Stokes, R. H., and Robinson, R. A., <u>J. Am. Chem. Soc., 70</u>, 1870 (1948).

VIII. ACKNOWLEDGEMENTS

The author appreciates, and wishes to express thanks for, the suggestions and encouragement received from Professor Adolf F. Voigt throughout the course of this research. He wishes to thank Dr. Robert S. Hansen for his advice on the assumptions of the activity coefficients. Thanks are also given to Mr. Edwin Klehr and Miss Marcia Potter for their great help in counting of the thallium samples.

Acknowledgement is made to the Ames Laboratory of the Atomic Energy Commission for providing funds and necessary facilities for the research.