

THE LIQUID-LIQUID EXTRACTION  
OF METAL PERCHLORATES  
BY 2-OCTANOL

By

Roy J. Laran

Bachelor of Science

Loyola University of the South

New Orleans, Louisiana

1952

Submitted to the faculty of the Graduate School of  
the Oklahoma Agricultural and Mechanical College  
in partial fulfillment of the requirements  
for the degree of  
MASTER OF SCIENCE

August 1957

OKLAHOMA  
STATE UNIVERSITY  
LIBRARY

OCT 1 1957

THE LIQUID-LIQUID EXTRACTION  
OF METAL PERCHLORATES  
BY 2-OCTANOL

Thesis Approved:

*Low E. Moore*

Thesis Adviser

*O. D. Derringer*

*John M. Mowbray*

Dean of the Graduate School

385475

#### ACKNOWLEDGEMENT

The author wishes to extend his sincere thanks to Dr. Thomas E. Moore for his continued guidance during the course of this investigation.

The author also wishes to thank Dr. Paul C. Yates whose inspiration and advice greatly aided the investigation.

Acknowledgement is made to the Research Foundation of Oklahoma Agricultural and Mechanical College for financial aid in the form of an Atomic Energy Commission Research Fellowship.

## TABLE OF CONTENTS

|     |   | Page |
|-----|---|------|
| I   | INTRODUCTION . . . . .                  | 1    |
| II  | HISTORICAL . . . . .                    | 3    |
| III | EXPERIMENTAL . . . . .                  | 18   |
| IV  | DISCUSSION . . . . .                    | 31   |
| V   | RESULTS AND TREATMENT OF DATA . . . . . | 42   |
| VI  | SUMMARY AND CONCLUSIONS . . . . .       | 62   |
| VII | BIBLIOGRAPHY . . . . .                  | 64   |

## LIST OF TABLES

| Table   | Page |
|---|------|
| 1. $\text{Co}(\text{ClO}_4)_2$ -2-Octanol Spectrophotometric Standards . . .  | 26   |
| 2. $\text{Co}(\text{ClO}_4)_2$ -LiCl-2-Octanol Spectrophotometric Standards . . . . .   | 26   |
| 3. $\text{Co}(\text{ClO}_4)_2$ -H <sub>2</sub> O Spectrophotometric Standards . . . . .   | 27   |
| 4. Water Activity of Aqueous LiCl Solutions and H <sub>2</sub> O Content of Corresponding 2-Octanol Phases Before Extraction Occurred . . . . . | 38   |
| 5. $\text{Co}(\text{ClO}_4)_2$ Hydration Data . . . . .   | 38   |
| 6. $\text{Ni}(\text{ClO}_4)_2$ Hydration Data . . . . .   | 39   |
| 7. Data on $\text{Co}(\text{ClO}_4)_2$ Unpromoted Extraction . . . . .  | 43   |
| 8. Data on $\text{Ni}(\text{ClO}_4)_2$ Unpromoted Extraction . . . . .  | 47   |
| 9. Data on $\text{CoCl}_2$ Unpromoted Extraction . . . . .  | 48   |
| 10. Data on $\text{Co}(\text{ClO}_4)_2$ - $\text{Ca}(\text{ClO}_4)_2$ Promoted Extraction . . . . .   | 52   |
| 11. Data on Distribution Constants ( $K_M$ ) and Distribution Coefficients ( $k_m$ ) . . . . .  | 54   |
| 12. Data on $\text{Co}(\text{ClO}_4)_2$ -LiClO <sub>4</sub> Promoted Extraction . . . . .   | 57   |
| 13. Data on $\text{Co}(\text{ClO}_4)_2$ -Al(ClO <sub>4</sub> ) <sub>3</sub> Promoted Extraction . . . . .                                       | 59   |
| 14. Data on $\text{CoCl}_2$ -CaCl <sub>2</sub> Promoted Extraction . . . . .  | 61   |

## LIST OF ILLUSTRATIONS

| Figure  | Page |
|---|------|
| 1. $\text{Co}(\text{ClO}_4)_2$ -2-Octanol Spectrophotometric Standard Curve . . . . .   | 28   |
| 2. $\text{Co}(\text{ClO}_4)_2$ -LiCl-2-Octanol Spectrophotometric Standard Curve . . . . .  | 29   |
| 3. $\text{Co}(\text{ClO}_4)_2$ -H <sub>2</sub> O Spectrophotometric Standard Curve . . . . .  | 30   |
| 4. Activity of H <sub>2</sub> O of Aqueous LiCl Solutions vs. H <sub>2</sub> O Content of Corresponding 2-Octanol Phases Before Extraction Occurred . . . . . | 40   |
| 5. $\text{Co}(\text{ClO}_4)_2$ and $\text{Ni}(\text{ClO}_4)_2$ Hydration Number Curves . . . . .  | 41   |
| 6. Extractibility Curves of Several Metal Perchlorates . . . . .  | 44   |
| 7. Mean Activity Coefficient Curve for $\text{Co}(\text{ClO}_4)_2$ and $\text{Ni}(\text{ClO}_4)_2$ in 2-Octanol . . . . .                                     | 45   |
| 8. Promotion of $\text{Co}(\text{ClO}_4)_2$ by $\text{Ca}(\text{ClO}_4)_2$ , $\text{LiClO}_4$ , and $\text{Al}(\text{ClO}_4)_3$ . . . . .                     | 53   |
| 9. Distribution Constant ( $K_M$ ) and Distribution Coefficient ( $k_m$ ) Curves . . . . .  | 55   |

## INTRODUCTION

The study of the liquid-liquid extraction of inorganic salts into 2-octanol was begun in 1949 by Garwin and Hixson (36,37). This investigation, initially largely one of engineering interest has been continued in the chemistry department of Oklahoma A. and M. College in order that it might be studied not only from an industrial point of view, but also from a theoretical standpoint.

The application of solvent extraction to the separation of salts is a theoretically complex field. Even in a relatively simple system where only one salt is involved, there will be at equilibrium both salt and water distributed in the non-aqueous phase as well as organic solvent transferred into the aqueous phase. It consequently is very difficult to find out what type of ion or molecule is transferred into the non-aqueous medium.

The original study was restricted to the extractions of cobalt and nickel chlorides, together with certain other chlorides which affect the distribution of these salts between the aqueous and non-aqueous phases. It is believed that both of these salts form complex ions and molecules to some extent in the 2-octanol phase (13). This complicates the problem considerably because of the uncertainty as to what ion or ions exist, and the relative importance of such complexing. Therefore, in an effort to avoid the complications involved in having complex ions present, it was decided that an investigation

be carried out on the extraction of perchlorates, where anion complexing is unlikely, because of the fact that the perchlorate ion is very large and relatively non-polarizable. This thesis is based upon the results of experiments having to do with the extraction of cobalt perchlorate into 2-octanol and the effect of various other metal perchlorates upon the distribution.



## HISTORICAL

The partition of substances between two immiscible solvent layers has long been known and recognized as an analytical tool. The literature contains a wealth of information on liquid-liquid extraction, but only recently has phase partition become prominent enough to be recognized as an important separational method for inorganic compounds.

Within the last three years there have been a number of excellent reviews on solvent extraction. Treybal (100, 101) has reviewed the extraction of both inorganic and organic substances and has also discussed various methods which have been used. Morrison (68) and Craig (24) have covered the extractions of inorganic salts. Sandell (82), and Lewis (57) have discussed the theoretical aspects of extraction, covering many points of interest. The extraction and separation of the rare earth elements has been discussed by Bock (15), while West (110) has surveyed the extraction and separation of many elements, with emphasis being placed on the organic solvents used in the separations. One of the most significant recent reviews on liquid-liquid extraction has been written by Irving (46), in which is discussed the theory of extraction, the extraction and separation of salts, and the extraction of chelate complexes.

In an effort to present a more connected review of the literature on liquid-liquid extraction, the remainder of this section will be devoted to a discussion of the solvent extrac-

tion of various metals. These metals are uranium, iron, cerium and other rare earths, and thorium. A survey of the extraction literature on many other elements will then be given.

#### Extraction of Uranium as $UO_2(NO_3)_2$

As long ago as 1842, uranium was extracted into diethyl ether. It was Peligot (77) who first extracted uranyl nitrate into ether as a means of purification. With the exception of Misciatelli's work in 1930 (63) on the distribution of  $UO_2(NO_3)_2$  between water and ether, the most important work on uranium extraction has been done in the past four years.

In an investigation carried out to determine optimal conditions for the ether extraction of aqueous solutions of uranyl nitrate, Neeb (75) has shown that the ether extraction increased with the aqueous nitrate concentration. According to this investigation  $Ca(NO_3)_2$  is the most beneficial nitrate to have present.

Furman, Mundy, and Morrison (33,34) have carried out extractions of  $UO_2(NO_3)_2$  from aqueous solutions into diethyl ether while Warner (106) compared the distribution coefficient of  $UO_2(NO_3)_2$  between water and diethyl ether with that obtained using 18 other organic solvents. Solvents of low molecular weight possessing sterically unhindered oxygen atoms gave the most favorable extractions.

Katzin and Hellman (51) have investigated the extraction of strong aqueous solutions of  $UO_2(NO_3)_2$  into diethyl ether. From the apparently strong electrolytic behavior of  $UO_2(NO_3)_2$ , it was inferred that the hexahydrate reacts with ether, losing three waters and forming a compound  $UO_2(NO_3)_2 \cdot 3H_2O \cdot C_4H_{10}$ .

Gluekauf, McKay, and Mathieson (39) used a circulating solvent extraction method for the measurement in aqueous mixtures of  $\text{NaNO}_3$  of the activity coefficients of  $\text{UO}_2(\text{NO}_3)_2$ . Later, these same investigators (40) proposed a partition law into solvents in which the solute is hydrated to a constant degree. In concentrated solutions this law necessitated the use of the activity coefficient of the hydrated  $\text{UO}_2(\text{NO}_3)_2$  in the organic phase. Using this law, the variation of activity coefficient with concentration was studied. Ternary systems of  $\text{UO}_2(\text{NO}_3)_2$ - $\text{H}_2\text{O}$ -organic solvent were investigated by Katzin and Sullivan (52) in which seven organic solvents were studied. The water content of the non-aqueous phase was determined and plotted against the concentration of  $\text{UO}_2(\text{NO}_3)_2$  in the organic phase to give a slope whose value was correlated with the number of solvated molecules in the coordination sphere of the cation in the organic phase.

McKay and Mathieson (61) studied the hydration of  $\text{UO}_2(\text{NO}_3)_2$  in various organic phases by using the procedure of Katzin and Sullivan (52). Later, however, Gardner, McKay, and Warren (35) developed a more theoretically sound method of determining the hydration number of  $\text{UO}_2(\text{NO}_3)_2$  in the organic phase after extraction. This method is an isopiestic one in which the equilibrium was established through the vapor phase between organic solutions and aqueous solutions of known water activity. The number of water molecules per molecule of  $\text{UO}_2(\text{NO}_3)_2$  found represented the total water minus the "free" water divided by the number of moles of  $\text{UO}_2(\text{NO}_3)_2$ . By this method it was found that a solution of  $\text{UO}_2(\text{NO}_3)_2$  in the organic phase contained a

mixture of hydrates.

Solvent extraction has also been used in the separation of uranium. Scott (84) has found that 99% uranium can be recovered if it is extracted from an aqueous solution of 3N  $\text{HNO}_3$  and 1M  $\text{Fe}(\text{NO}_3)_3$ . The  $\text{Fe}(\text{NO}_3)_3$  was shown to be an effective promoting salt for the extraction of uranium. Lindh and Rynning (58) extracted small amounts of  $\text{UO}_2(\text{NO}_3)_2$  with diethyl ether, and found that the salt could be quantitatively separated from other elements, especially iron, even up to a ratio (by weight) of Fe:U of 25,000 to 1. The efficiency of the extraction, however, depends upon the concentration of nitrate ion and free nitric acid. In an attempt to find a generally applicable procedure for the solvent extraction of uranium, Helger and Rynning (43) have shown that sulfates and phosphates interfere with the ether extraction and must be removed. The Chemical Research Laboratory in England has also shown (23) that the diethyl ether extraction of  $\text{UO}_2(\text{NO}_3)_2$  cannot be used to separate uranium from other elements when large amounts of sulfate ion are present.

The findings of the investigators discussed above on the liquid-liquid extraction of  $\text{UO}_2(\text{NO}_3)_2$  represent one of the most important and thoroughly investigated sections in the field.

#### The Extraction of Iron as $\text{FeCl}_3$

It is a well known fact that  $\text{FeCl}_3$  is very soluble in many organic solvents, especially ethers. In 1892, it was Rothe (79) who found that  $\text{FeCl}_3$  could be extracted from an HCl solution into isopropyl ether. Since that time the  $\text{FeCl}_3$ -HCl-

ether system has been investigated many times. Dodson, Forney, and Swift (26) compared the extractions of the  $\text{FeCl}_3$ -HCl solutions in diethyl and diisopropyl ethers and showed that diisopropyl ether is far superior as an extracting solvent because it gives a more efficient extraction over a wider range of acid concentrations. Ishibashi and Yamamoto (48) have shown that  $\text{FeCl}_3$ , at a concentration of 2 grams per liter in 6N HCl solution could be completely removed from the aqueous phase by five successive extractions with diethyl ether. Iron and aluminum could be separated by this method with no effects due to the presence of sulfate or phosphate ions. Using amyl acetate as the extracting solvent, Well and Hunter (109) found that 99.6% of the  $\text{FeCl}_3$  in concentrated HCl solutions could be removed from the aqueous phase. If concentrated sulfuric or phosphoric acid is added, the degree of separation is further increased. The distribution of  $\text{FeCl}_3$  between HCl and dichlorodiethyl ether solutions was investigated by Axelrod and Swift (5). It was shown that  $\text{FeCl}_3$  could be quantitatively extracted from solutions greater than 7N in HCl. It was also shown that one molecule of HCl and 4 or 5 molecules of  $\text{H}_2\text{O}$  are present for each iron molecule present in the ether. From the spectral studies of Kato and Isii (50) of extracted diethyl ether solutions of  $\text{FeCl}_3$  from aqueous HCl solutions, the compound extracted is believed to be  $\text{FeCl}_3 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ .

Nachtrieb and Fryxell (73) interpreted their results as indicative that a salting-out of the  $\text{FeCl}_3$  in the aqueous phase occurs. This is used to explain the increased extraction with increasing total iron concentration rather than the

assumption of polymerization in the ethereal phase. But later, an investigation of the distribution of  $\text{FeCl}_3$  between water and isopropyl ether was undertaken by Myers, Metzler, and Swift (70) for the purpose of determining the formula of the iron complex extracted. The dependence of the distribution ratio on the aqueous iron concentration was qualitatively explained by polymerization of the ethereal iron. In continuation of this work, Myers and Metzler (69) evaluated the effective polymerization of the ethereal iron, and determined the effect of the acid on the apparent polymerization.

Nachtrieb and Conway (72) have estimated the rate of attainment of equilibrium of the diethyl ether and aqueous phase of the  $\text{FeCl}_3$ -HCl extraction to be about 30 minutes. They have shown that the distribution coefficient, which is a ratio of non-aqueous to aqueous phase concentration, increased rapidly with HCl concentration and approached a maximum at about 9M in the aqueous phase. The compound extracted from various aqueous phase concentrations was found to be  $\text{HFeCl}_4$ . Bassett et al (8), and Campbell (20) have also investigated the nature of the  $\text{FeCl}_3$  complex in diethyl ether and have found it to be a singly charged anion with the hydrated proton as the transfer mechanism. From visible and ultraviolet absorption spectra, Friedman (32) also has given evidence for the existence of the  $\text{FeCl}_4^-$  complex ion.

Using a continuous extraction procedure with isopropyl ether, Ashley and Murray (2) have completely separated  $\text{FeCl}_3$  from aqueous solutions. The extraction was performed in the dark since there was some evidence of photochemical reduction

of the ether solution. Wolfe and Fowler (112) have used the isopropyl ether extraction to separate iron from many other metals. After extraction with isopropyl ether of solutions having known impurities present in the amount of 0.1% each a spectrographic analysis of the ether-phase contents showed the greatest remaining impurity was cobalt at a concentration of 0.003%.

Besides the extractions carried out on  $\text{FeCl}_3$ , some investigations have been performed on  $\text{Fe}(\text{SCN})_3$  and  $\text{Fe}(\text{NO}_3)_3$ . McDonald, Mitchell, and Mitchell (60) have investigated the distribution of  $\text{Fe}(\text{SCN})_3$  between water and ether and have found many aqueous phase complexes, varying from  $\text{Fe}(\text{SCN})_2^+$  to  $\text{Fe}(\text{SCN})_6^{3-}$ . Babko and Kodenskaya (6) have investigated the extraction of  $\text{Fe}(\text{NO}_3)_3$  in acid solutions of  $\text{NH}_4\text{SCN}$  by ethyl and butyl acetates. The degree of extraction was found to depend on the absolute concentration of  $\text{SCN}^-$ .

The above discussion on the extraction and separation of iron constitutes all of the important extraction research on iron.

#### Extraction of Cerium and Other Rare Earths

Inre (44) investigated the distribution of  $\text{Ce}(\text{NO}_3)_4$  between water and diethyl ether. The extraction was carried out from aqueous solutions which were 10.5N in  $\text{HNO}_3$ . Warf (102) extracted  $\text{Ce}(\text{NO}_3)_4$  into tri-n-butyl phosphate and recovered 98-99% when equal volumes were used, regardless of  $\text{NH}_4\text{NO}_3$  or  $\text{HNO}_3$  concentrations. Sulfate ion was found to interfere with the extraction efficiency. Several years later Warf (103) extracted  $\text{Ce}(\text{NO}_3)_4$  into nitromethane. The Ce(IV) salt in the

nitromethane phase was reduced to Ce(III) and back extracted with water and recovered. Bock and Bock (17,18) have obtained pure cerium nitrate in high yields by a diethyl ether extraction from 4.5N HNO<sub>3</sub> solutions.

Gryder and Dodson (42) have separated radioactive Ce(III) from inactive Ce(IV) by extracting their nitrates from a HNO<sub>3</sub> solution into diethyl ether. It was found that the active Ce(III) did not extract, while the extraction of the inactive Ce(IV) was essentially complete. The extraction and separation of cerium from iron, zirconium, lanthanum, and others of the rare earths has been successfully carried out by Warf (104, 105) using tri-n-butyl phosphate. Conditions for an efficient extraction were not critical, and the extraction efficiency was not affected by acetates or perchlorates, but sulfates did interfere. Wylie (113) has separated Ce(NO<sub>3</sub>)<sub>4</sub> from mixtures of other rare earth nitrates by extraction of Ce(NO<sub>3</sub>)<sub>4</sub> from 5-6N HNO<sub>3</sub> solutions into diethyl ether. It was found that the other rare earth nitrates present were beneficial in that they acted as promoting agents. The cerium complex in the ether phase was shown to consist of H<sub>2</sub>(Ce(NO<sub>3</sub>)<sub>6</sub>) or H(Ce(NO<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O), determined by titration of the HNO<sub>3</sub> in the ether phase after back-extraction into water.

There has been much work done on the extraction and separation of rare earths. The most important research done along these lines will be discussed here.

Fisher, Dietz, and Jubermann (31) have shown that the principle of phase distribution may be applied to the separation of the rare earths. According to these investigators,



the rare earth halides will distribute themselves between water and alcohols, ethers, ketones and many other solvent types.

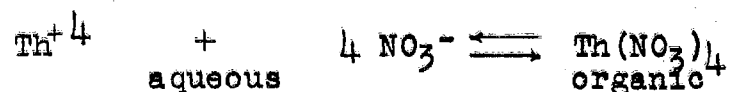
By extracting the rare earth nitrates from aqueous solutions into n-hexyl alcohol, Templeton (90) found that the extraction increased with increasing atomic number of the rare earth elements. Peppard, Faris, Gray, and Mason (78) also found that the extraction increased with increasing atomic number using tri-n-butyl phosphate as the extracting solvent. In an effort to separate a mixture of lanthanum and neodymium nitrates, Appleton and Selwood (1) extracted them into n-hexyl alcohol and obtained good separation factors. In fact the nitrates of these two rare earth elements, when extracted into n-hexyl alcohol, give a separation factor ten times greater than when the thiocyanates of the same metals are extracted into n-butyl alcohol. Topp (98) has separated neodymium and samarium nitrates from 12N  $\text{HNO}_3$  solution using tri-n-butyl phosphate. Samarium nitrate had a distribution coefficient 2.5 times greater than  $\text{Nd}(\text{NO}_3)_3$ . An attempt was made by Asselin, Audrieth and Comings (3) to separate the rare earth chlorides using n-butyl alcohol, but it was found that they extract only slightly. The rare earth nitrates were shown to extract to a significant extent in n-butyl alcohol, as had been found by previous investigators (1). Gadolinium oxide has been obtained better than 95% pure from a countercurrent extraction process carried out by Weaver, Kappelmann, and Topp (107) using tri-n-butyl phosphate.

One can see therefore, from the above discussion that solvent extraction has become very important in recent years

as a method of separating and isolating the rare earth elements.

#### Extraction of Thorium as $\text{Th}(\text{NO}_3)_4$

Templeton and Hall (94) have investigated the solubility of  $\text{Th}(\text{NO}_3)_4$  in various organic solvents in order that some qualitative predictions could be made regarding the extraction of this salt. It was found that oxygen-containing solvents dissolve  $\text{Th}(\text{NO}_3)_4$  while others do not. Distribution coefficients were obtained for the extraction of  $\text{Th}(\text{NO}_3)_4$  into several ketones and alcohols by Rothschild, Templeton, and Hall (97), and it was found that the concentration of  $\text{Th}(\text{NO}_3)_4$  in the aqueous phase must be very near to saturation for any appreciable extraction to occur. A year later, Templeton, Rothschild, and Hall (97) attempted to extract aqueous solutions of  $\text{Th}(\text{NO}_3)_4$  into various esters. Ethyl butyrate showed about the same extraction properties as alcohols and ketones of comparable weight. It is believed by these investigators that  $\text{Th}(\text{NO}_3)_4$  is dissociated to a great extent in the aqueous phase but undissociated in the organic phase, corresponding to:



The distribution obtained when a common ion (nitrate) is added seems to support the above hypothesis. Bock and Bock (17,18) found further that  $\text{Th}(\text{NO}_3)_4$  could be extracted by various organic solvents from dilute nitric acid solutions containing high concentrations of nitrate salts. Misciatelli (64) studied the distribution of  $\text{Th}(\text{NO}_3)_4$  between diethyl ether and water to establish the necessary conditions for the separation of uranium and thorium. Lending support to an earlier

investigation (80), Templeton and Hall (95) separated thorium from the rare earths using several different alcohols and ketones, but found that it was necessary for the aqueous phase to contain a near-saturation concentration of  $\text{Th}(\text{NO}_3)_4$ . A fractional solvent extraction method with reflux was employed by Asselin and Comings (4) to separate thorium from neodymium in a solution of their nitrates using n-amyl alcohol as the extracting solvent. Ammonium thiocyanate, present in the aqueous phase, was used as a separating agent, and it was found that the selectivity of the alcohol in preferentially extracting thorium increased as the thiocyanate ion concentration in the aqueous phase increased. Asselin, Audrieth, and Comings (3) found that  $\text{Th}(\text{NO}_3)_4$  was extracted to a much greater extent by n-pentanol than were the rare earth nitrates, and it could easily be separated from them in the presence of thiocyanate ion.

#### Extraction of Other Elements

Solvent extraction has been attempted as a means of separation and purification of many elements. Diisopropyl ketone was used by Stevenson and Hicks (86) to separate tantalum from niobium in an aqueous phase consisting of mineral acid-hydrofluoric acid mixture. Bassett and his coworkers (7,9,10,11) have attempted by several physical methods to correlate the structure of various organic solvents with their ability to extract inorganic ions. Taylor (89), back in 1925, in a discussion of hydration and solution showed that the presence of salts did not effect the distribution of HCl between water and benzene. He concluded from his work that there

appeared to be no dissimilarity between "free" and combined water, but later work has cast many doubts on the authenticity of Taylor's work.

Bonner (19) has separated Sb(V) from radioactive Sb(III) by extraction of their chlorides from aqueous HCl solutions into diisopropyl ether. He found that 98% of the Sb(V) went into the ether phase from 6 and 12N HCl solutions of the salts. Edwards and Voigt (27) have also separated Sb(V) from Sb(III) using diisopropyl ether and have found that 100% of the Sb(V) passes into the ether phase from aqueous 7-8N HCl solutions of the salts. Weinhardt and Hixson (108) have discovered that V(V) and Cr(VI) may be separated by liquid-liquid extraction using methylisobutyl ketone as the solvent. Sodium dichromate was separated from vanadic acid in aqueous HCl solutions of less than 3N HCl and a separation factor of greater than 4000 to 1 in favor of the sodium salt was obtained.

Gold has also been separated and purified by liquid-liquid extraction. McBryde and Yoe (59) separated gold from numerous other metals by extracting it as  $\text{HAuBr}_4$  from aqueous HBr solutions into diisopropyl ether. Lenher (55) in an early investigation found that many solvents would extract gold from aqueous solutions. Several years later Lenher and Kao (56) successfully separated gold from all of the common chlorides in aqueous HCl solutions using ethyl acetate as the selective solvent.

The distribution coefficients of minute (tracer) quantities ( $10^{-12}$  to  $10^{-15}$  gm.) of several radioactive metal halides between liquid phases have been reported by Grahme and Sea-

borg (41) to be quantitatively the same as those observed for the same substances at ordinary small (micro) concentrations. Nachtrieb and Fryxell (74) have shown that the distribution of  $\text{GaCl}_3$  between HCl solutions and isopropyl ether follows the simple Nernst partition law (76) at low gallium concentrations. Swift (88) in an earlier investigation extracted 97% of the  $\text{GaCl}_3$  from 5.5N HCl solutions into ether.

Templeton and Daly (92,93) and Templeton (91) have carried out extractions of many bivalent and trivalent transition-metal nitrates using n-hexanol as the extracting solvent. These investigators attempted to determine the hydration numbers of the various metal ions in the alcohol phase by the method of Katzin and Sullivan (52). The results were not very satisfying, however, and it was concluded that only a relative measure of the hydration of the cation could be obtained from such a method.

Kylander and Garwin (54) effectively separated  $\text{CoCl}_2$  from  $\text{NiCl}_2$  using 2-octanol in a spray tower in the presence of such promoting electrolytes as HCl and  $\text{CaCl}_2$ . The distribution was shown to be a function of the total chloride ion concentration. Yates and Moore (115) have investigated the extraction of various cobalt and nickel salts by 2-octanol in the presence of different extraction-promoting salts. The purpose of this investigation has been to determine the factors influencing liquid-liquid extraction and to obtain some information about the nature of the extracting species.

Bock (16) in a recent investigation has studied the distribution of the metal thiocyanates of Be, Co, Zn, Al, Sc, Ga,

In, Fe(III), Ti(III), Ti(IV), V(IV), Sn(IV), Mo(V), and V(VI) between water and diethyl ether. Cavanagh (22) has determined the activity coefficients of LiCl in very dilute amyl alcohol solutions. From a study of the distribution of LiCl between water and amyl alcohol, there are indications that the LiCl is completely dissociated in sufficiently dilute solutions. The distribution of LiCl between water and amyl alcohol was also studied by Dhar and Datta (25) who measured the amount of undissociated LiCl in amyl alcohol, both conductometrically and from distribution laws. Mylius and Huttner (71), two of the pioneer investigators in the field of liquid-liquid extraction, have studied the extraction of a large number of metal chlorides into diethyl ether from dilute aqueous solutions containing varying amounts of HCl. Campbell and Laurene (21) have studied the extraction systems consisting of inorganic chlorides, aqueous HCl solutions, and diethyl ether and have confirmed the already known fact that the optimum extraction occurs over a narrow range of HCl concentrations. Irving and Rosotti (47) have extracted radioactive group IIB metal halides into ether over a wide range of corresponding halogen acid concentrations. Indium iodide can be extracted quantitatively from HI solutions of low concentration, and may be separated from  $\text{GaI}_3$  in this way. The distribution of  $\text{MgBr}_2$  between water and diethyl ether has been investigated by Rowley and Reed (81) and they report that although there was practically no distribution of this salt between water and diethyl ether, the anhydrous salt was considerably soluble in ether. Other physical measurements indicated association and

very little ionization of the anhydrous salt in ether, factors which may partially explain the very small distribution coefficient of the salt.

Fischer and Chalybaeus (29), and Fischer, Chalybaeus, and Zumbusch (30) have separated zirconium from hafnium by diethyl ether extraction from aqueous solutions of  $\text{NH}_4\text{SCN}$  and  $\text{HSCN}$ . Hafnium could be obtained 99.6% pure in the ether phase after a series of eight distributions starting with a 60-95% hafnium sample.

Elson, et al (28) extracted protoactinium, obtained from aqueous waste, from a fluoride-complexed aqueous solution by diisopropylcarbinol. After further purifications with diisopropylketone, the final protoactinium was spectrochemically pure. Maddock and Stein (62) extracted trace amounts of protoactinium from concentrated chloride solutions by a variety of organic solvents, using  $\text{AlCl}_3$  as a promoting agent. The extraction and isolation of radioactinium by ether was investigated by Imre (45). This investigation studied the influence of  $\text{HNO}_3$  on the partition of thorium and radioactinium into diethyl ether.

In summarizing the status of the problems involved in solvent extraction of salts from aqueous solutions, there appears to be a need for more attention given to the chemical nature of the organic phases, the action of extraction-promoting agents, and the thermodynamic properties of the aqueous solutions. Individual systems need reexamination and further correlative studies made of the factors known to influence the distribution coefficients.

## EXPERIMENTAL

### Reagents

Cobalt and nickel perchlorates were prepared from the C. P. grade metal carbonates and hot diluted reagent grade perchloric acid. The carbonate was added until the solution was neutral, and a slight excess was then added to insure a complete reaction. The excess was subsequently filtered off, leaving a clear neutral stock solution of the salt, which was then used in preparing the solutions.

Anhydrous silver perchlorate, which was used in preparing an anhydrous solution of cobalt perchlorate in 2-octanol, was obtained by pulverizing the C.P. grade salt and drying at 120°C. Slight decomposition was noted.

Anhydrous cobalt chloride, also used in preparing the cobalt perchlorate solution, was prepared by pulverizing the C.P. grade hexahydrate and drying at 120°.

Anhydrous cobalt perchlorate in 2-octanol, used in preparing the spectrophotometric standards, was obtained by metathesis, following the method of Trevorrow (99), using 2-octanol solutions of anhydrous silver perchlorate and cobalt chloride.

Aqueous solutions of lithium perchlorate and aluminum perchlorate, used in preparing solutions for the promoted extractions, were also obtained by metathesis, using aqueous solutions of barium perchlorate and the corresponding sulfates.

The 2-octanol used throughout the investigation was the



best grade of anhydrous reagent from the Matheson Company.

A saturated solution of lithium chloride in 2-octanol was prepared from C.P. grade anhydrous lithium chloride and 2-octanol by shaking overnight with an excess of salt followed by filtration.

All other chemicals used either in preparing solutions for extraction, or in chemical analysis, were of C.P. grade, and were used without further purification.

#### Preparation of Solutions

Solutions of varying concentrations of  $\text{Co}(\text{ClO}_4)_2$ ,  $\text{Ni}(\text{ClO}_4)_2$ , and  $\text{CoCl}_2$ , were prepared by diluting aqueous stock solutions of these salts with distilled water. These solutions were weighed out to the nearest tenth of a gram only, and no attempt was made to accurately determine their concentrations before extraction. The object of this rather approximate method of preparing the solutions was to obtain a suitably distributed range of concentration varying from dilute solutions to the concentrated stock solutions.

Stock solutions of  $\text{Co}(\text{ClO}_4)_2$ - $\text{Ca}(\text{ClO}_4)_2$ ,  $\text{Co}(\text{ClO}_4)_2$ - $\text{LiClO}_4$ , and  $\text{Co}(\text{ClO}_4)_2$ - $\text{Al}(\text{ClO}_4)_3$ , used in the promoted extractions, were prepared by adding calculated weights of the  $\text{Co}(\text{ClO}_4)_2$  stock solution to the stock solutions of the other perchlorates, so as to obtain a constant  $\text{Co}(\text{ClO}_4)_2$  (0.243 m) concentration in each of the mixtures. A solution of 0.243 m  $\text{Co}(\text{ClO}_4)_2$  was then prepared from the concentrated  $\text{Co}(\text{ClO}_4)_2$  stock solution and used in diluting the solutions of promoting salts, i.e.,  $\text{LiClO}_4$ ,  $\text{Ca}(\text{ClO}_4)_2$ , and  $\text{Al}(\text{ClO}_4)_3$ , in the corresponding stock mixtures. In this manner the  $\text{Co}(\text{ClO}_4)_2$  concentration was

kept constant. By extracting solutions of this kind, the effect of varying the concentration of the promoting electrolyte on the extraction of  $\text{Co}(\text{ClO}_4)_2$  could be studied.

The  $\text{CoCl}_2$ - $\text{CaCl}_2$  stock mixture was prepared in a similar manner, and diluted with a 0.243 m  $\text{CoCl}_2$  solution.

#### Extraction Procedure

Early work was done using 250-ml. Erlenmeyer flasks and tinfoil covered corks. The stock solution, water or diluting solution, and 2-octanol were weighed directly into these flasks. The solutions were first fastened securely to a mechanical shaker and shaken overnight at room temperature and then placed in a 30° water bath to allow equilibration of the phases to take place. It was noticed, however, that these flasks not only leaked, but in some cases there was evidence of a reaction between the 2-octanol and the tinfoil, so these flasks were replaced by 250-ml. ground glass stoppered flasks. The liquid phases were separated with the aid of separatory funnels and placed in suitable air-tight containers until analyses could be performed.

#### Analytical Procedures

Most of the analytical procedures used in the investigation are, for the most part, common methods and are tabulated below along with some pertinent references.

The spectrophotometric method of analysis for cobalt and nickel using the Beckman Model B spectrophotometer was the most important analytical tool used, and the procedure for the cobalt analysis shall be discussed in detail.

Early spectrophotometric analyses on the octanol phases

were obtained with reference to standards of cobalt perchlorate in 2-octanol which were prepared from the hydrated salt. Since standards prepared in this way might be expected to differ greatly from extraction conditions in which the 2-octanol phase is saturated with  $H_2O$ , it was decided that an investigation should be made to determine the effect of water on the absorption and molar extinction coefficient of  $Co(ClO_4)_2$  in 2-octanol.

To anhydrous solutions of  $Co(ClO_4)_2$  in 2-octanol, prepared by metathesis as described above, various amounts of water were added by means of a hypodermic syringe, and the spectra of these solutions studied with the spectrophotometer. It was found that the presence of varying amount of  $H_2O$  up to saturation, did not change appreciably the wave length of maximum absorption, but the absorption peak was flattened considerably in solutions of high water concentrations. The molal extinction coefficient was found to increase with decreasing concentrations of  $Co(ClO_4)_2$  in both anhydrous solutions and solutions containing approximately a 10:1 mole ratio of  $H_2O:Co$ . In investigating the spectra of the anhydrous solutions it was found that the maximum absorption occurred at 525-530 millimicrons, while in the hydrous solutions regardless of the  $H_2O$  concentration it occurred at 510 millimicrons. So in an effort to approximate extraction conditions as much as possible, a new set of standards was prepared from an anhydrous  $Co(ClO_4)_2$ -2-octanol solution and a saturated  $H_2O$ -octanol mixture. Although each solution prepared would contain different amounts of  $H_2O$ , all would contain sufficiently large

quantities that the spectra would not be greatly affected, and extraction conditions would be more closely resembled than with the old standards.

If a great excess of chloride ion is added to the 2-octanol solutions of  $\text{Co}(\text{ClO}_4)_2$ , an intensely blue cobalt chloride complex develops which enables the spectrophotometric procedure to be extended down to  $10^{-5}$  molal. A saturated solution of LiCl in 2-octanol was used to prepare these solutions. Equal weights of the LiCl-2-octanol solution and the dilute  $\text{Co}(\text{ClO}_4)_2$ -2-octanol solution were mixed. This corresponded to a Cl:Co concentration ratio of greater than 1000:1. In order to be able to employ this complex as a means of determining cobalt concentration in very dilute solutions, it was necessary to consider the effect of  $\text{H}_2\text{O}$  upon the spectra of the 2-octanol solutions of the cobalt chloride complex. Beaver (12) has shown, however, that if the ratio of Cl:Co is 100:1 or greater, water will have little effect upon the absorption spectra. This was quickly verified by preparing a series of solutions containing LiCl-2-octanol and  $\text{Co}(\text{ClO}_4)_2$  in a solution-weight ratio of 1:1, with various amounts of water, and observing the spectra. It was found that both the anhydrous and all the hydrous solutions had a maximum absorption peak at 680 millimicrons. Since the molar extinction coefficient for these  $\text{Co}(\text{ClO}_4)_2$ -LiCl solutions was slightly higher for the solutions containing water than for the anhydrous solution, it was then decided that this set of standards, which would be used to cover the concentration range  $10^{-3}$  to  $10^{-5}$ , should also be prepared using 2-octanol satu-

rated with water as the solvent.

Tables 1 and 2 list data for the cobalt perchlorate "pink" standards in the 2-octanol phase, and also the "blue" standard cobalt perchlorate-lithium chloride data. In Figures 1 and 2 the data are plotted for the "pink" and "blue" standards respectively. Table 3 lists data for standard aqueous solutions of cobalt perchlorate and Figure 3 illustrates this data. The aqueous standards and the "blue" 2-octanol standards were found to follow Beer-Lambert's Law, but a slight curvature is exhibited by the "pink" 2-octanol standards indicating a slight deviation from this law.

The volume concentration (molarity) obtained from the curves was converted to a weight concentration (molality) by means of the density which was determined for each solution after extraction. The 2-octanol phase molality of all the extracted solutions was expressed as moles of salt per 1000 grams of mixed solvent (octanol and H<sub>2</sub>O).

By means of these new standard curves all previous extraction concentrations were corrected, and in many cases a considerable difference in concentration resulted.

The weight of solution used in analyzing the phases after extraction depended, of course, on the salt concentration in the solution. Duplicate analyses were always carried out on the extracted solutions with a precision of  $\pm 1\%$ . In the very dilute 2-octanol phases sometimes only a single large sample could be taken for analysis in order to be able to obtain an adequate quantity of salt. In these cases there was no way of knowing the magnitude of the error involved. In

most cases the contents of the 2-octanol phases were back-extracted with three portions of water and concentrated to a small volume prior to analysis or dried carefully to the crystals. In some of the more concentrated 2-octanol solutions, the perchlorate precipitation analyses were performed directly in the 2-octanol phase, because it was found possible to check such direct determinations with the results obtained on the analysis of back-extracted samples.

Summary of Analytical Methods

| System   | Aqueous Phase   | 2-octanol Phase  |
|--|---|--|
| $\text{Co}(\text{ClO}_4)_2\text{-H}_2\text{O-2-octanol}$                           | Co: Spectrophotometer   | Co: Spectrophotometer<br>H <sub>2</sub> O: Karl Fisher Method (65)                         |
| $\text{Ni}(\text{ClO}_4)_2\text{-H}_2\text{O-2-octanol}$                           | Ni: Spectrophotometer   | Ni: Spectrophotometer<br>Ni: Polarograph (53)<br>H <sub>2</sub> O: Karl Fisher Method (65) |
| $\text{Co}(\text{ClO}_4)_2\text{-Ca}(\text{ClO}_4)_2\text{-H}_2\text{O-2-octanol}$ | Co: Spectrophotometer<br>Ca: Calcium oxalate-<br>KMnO <sub>4</sub> titration (38) | Co: Spectrophotometer<br>Ca*: Calcium oxalate-<br>KMnO <sub>4</sub> titration (38)         |
| $\text{CoCl}_2\text{-H}_2\text{O-2-octanol}$                                       | Cl: AgNO <sub>3</sub> -dichloro-<br>fluorescein ind.                              | Co: Spectrophotometer.   |
| $\text{CoCl}_2\text{-GaCl}_2\text{-H}_2\text{O-2-octanol}$                         | Co: Electrolysis (83)<br>Ca: Calcium oxalate-<br>KMnO <sub>4</sub> titration (38) | Co: Spectrophotometer  |
| $\text{Co}(\text{ClO}_4)_2\text{-LiClO}_4\text{-H}_2\text{O-2-octanol}$            | Co: Spectrophotometer<br>Li: Total Perchlorate<br>Precipitation (85)              | Co: Spectrophotometer<br>Li: Total Perchlorate<br>Precipitation (85)                       |
| $\text{Co}(\text{ClO}_4)_2\text{-Al}(\text{ClO}_4)_3\text{-H}_2\text{O-2-octanol}$ | Co: Spectrophotometer<br>Al: Total Perchlorate<br>Precipitation (85)              | Co: Spectrophotometer<br>Al: Total Perchlorate<br>Precipitation (85)                       |

\* Low calcium concentrations determined by disodium ethylenediaminetetraacetate dihydrate titration using Eriochrome Black T as the indicator.

TABLE 1

Co(ClO<sub>4</sub>)<sub>2</sub>-2-Octanol Spectrophotometric Standard;

$$\lambda = 510 \text{ m}\mu$$

| M x 10 <sup>3</sup> | m x 10 <sup>3</sup> | O.D.  |
|---------------------|---------------------|-------|
| 1.63                | 1.99                | 0.015 |
| 2.26                | 2.76                | 0.024 |
| 5.79                | 7.06                | 0.040 |
| 11.6                | 14.2                | 0.072 |
| 23.4                | 28.6                | 0.136 |
| 33.6                | 41.2                | 0.195 |
| 59.4                | 70.2                | 0.328 |
| 80.6                | 98.7                | 0.469 |
| 97.7                | 120.                | 0.576 |
| 122.                | 150.                | 0.737 |
| 130.                | 160.                | 0.796 |
| 146.                | 181.                | 0.920 |
| 172.                | 212.                | 1.133 |

TABLE 2

Co(ClO<sub>4</sub>)<sub>2</sub>-LiCl-2-Octanol Spectrophotometric Standards

$$\lambda = 680 \text{ m}\mu$$

| M x 10 <sup>4</sup> | m x 10 <sup>4</sup> | O.D.  |
|---------------------|---------------------|-------|
| 0.38                | 0.47                | 0.011 |
| 0.69                | 0.85                | 0.028 |
| 1.26                | 1.56                | 0.070 |
| 1.91                | 2.34                | 0.111 |
| 4.53                | 5.55                | 0.282 |
| 6.77                | 8.31                | 0.392 |
| 9.42                | 11.6                | 0.596 |
| 19.3                | 23.7                | 0.998 |
| 29.3                | 36.1                | 1.480 |
| 33.1                | 40.7                | 1.740 |
| 59.1                | 72.7                | 3.029 |



TABLE 3

 $\text{Co}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  Spectrophotometric Standards

$$\lambda = 510 \text{ m}\mu$$

| M       | O.D.  | $\epsilon$        |
|---------|-------|-------------------|
| 0.0108  | 0.054 | 5.00              |
| 0.0216  | 0.105 | 4.86              |
| 0.0432  | 0.205 | 4.75              |
| 0.0863  | 0.410 | 4.75              |
| 0.108   | 0.509 | 4.71              |
| 0.270   | 1.32  | 4.89              |
| 0.540   | 2.67  | 4.94              |
| 1.08    | 5.48  | 5.07              |
| 2.16    | 10.83 | 5.01              |
| Average |       | $\epsilon = 4.89$ |

Figure 1

$\text{Co}(\text{ClO}_4)_2$ -2-Octanol Spectrophotometric Standard Curve

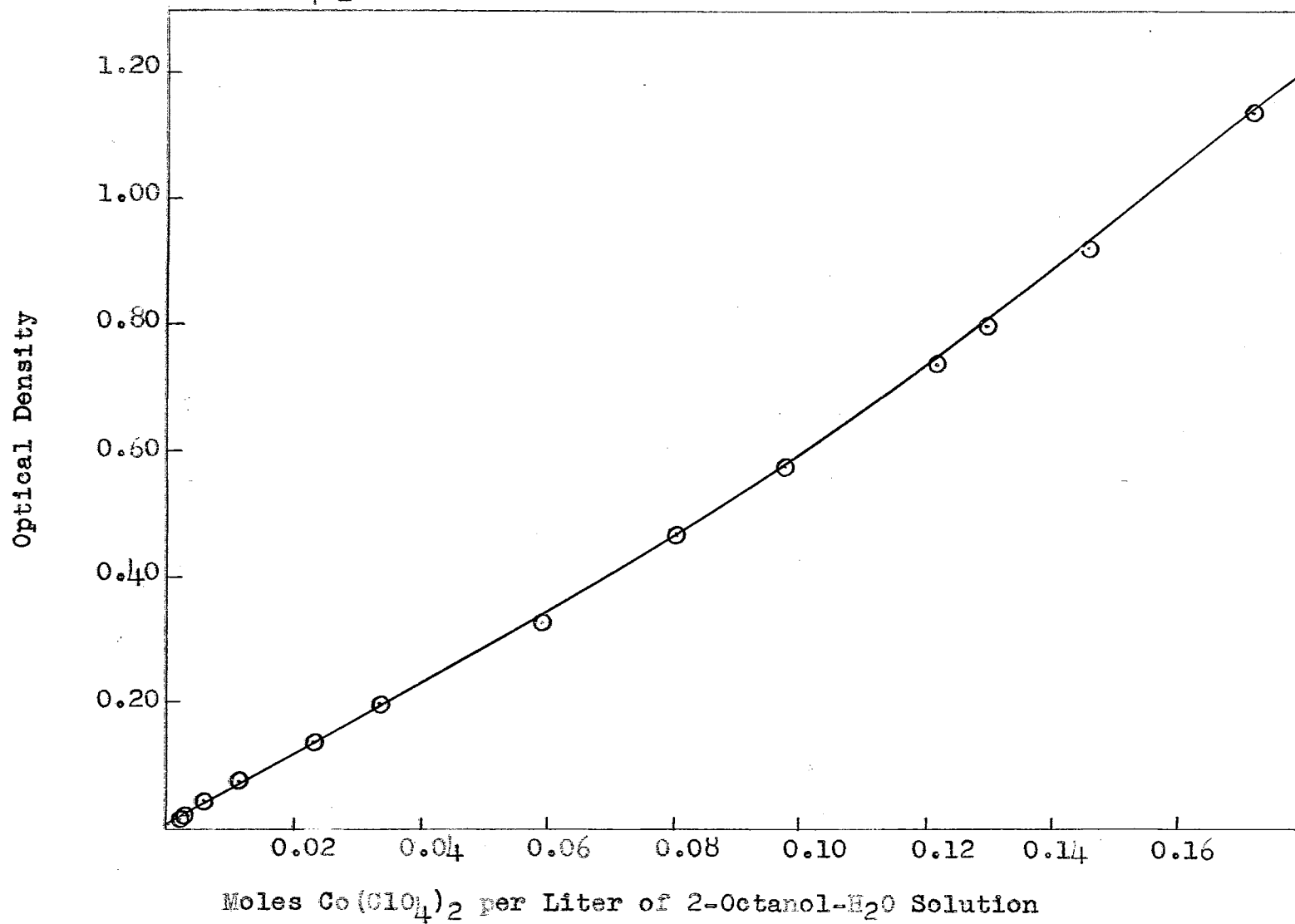


Figure 2

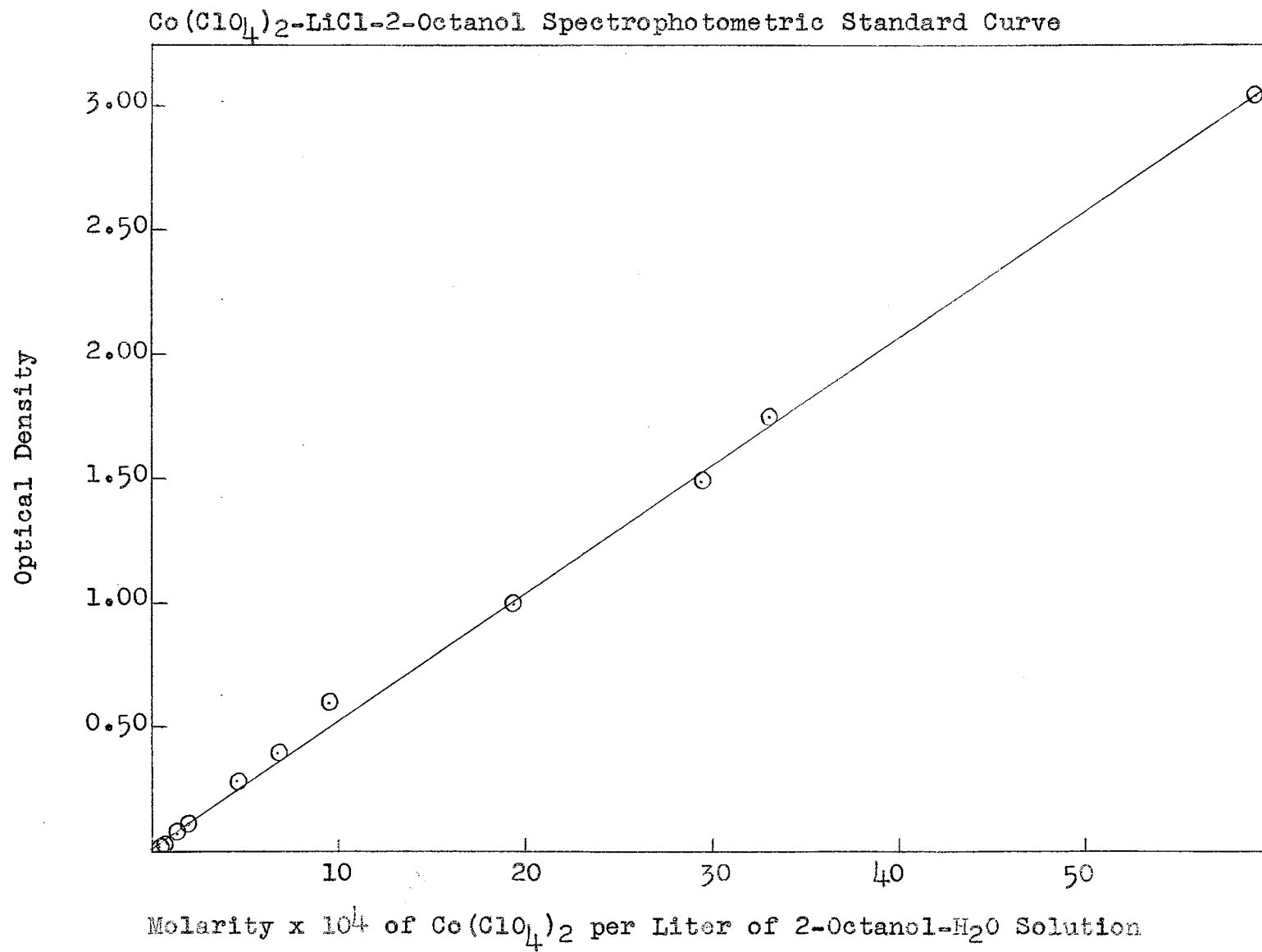
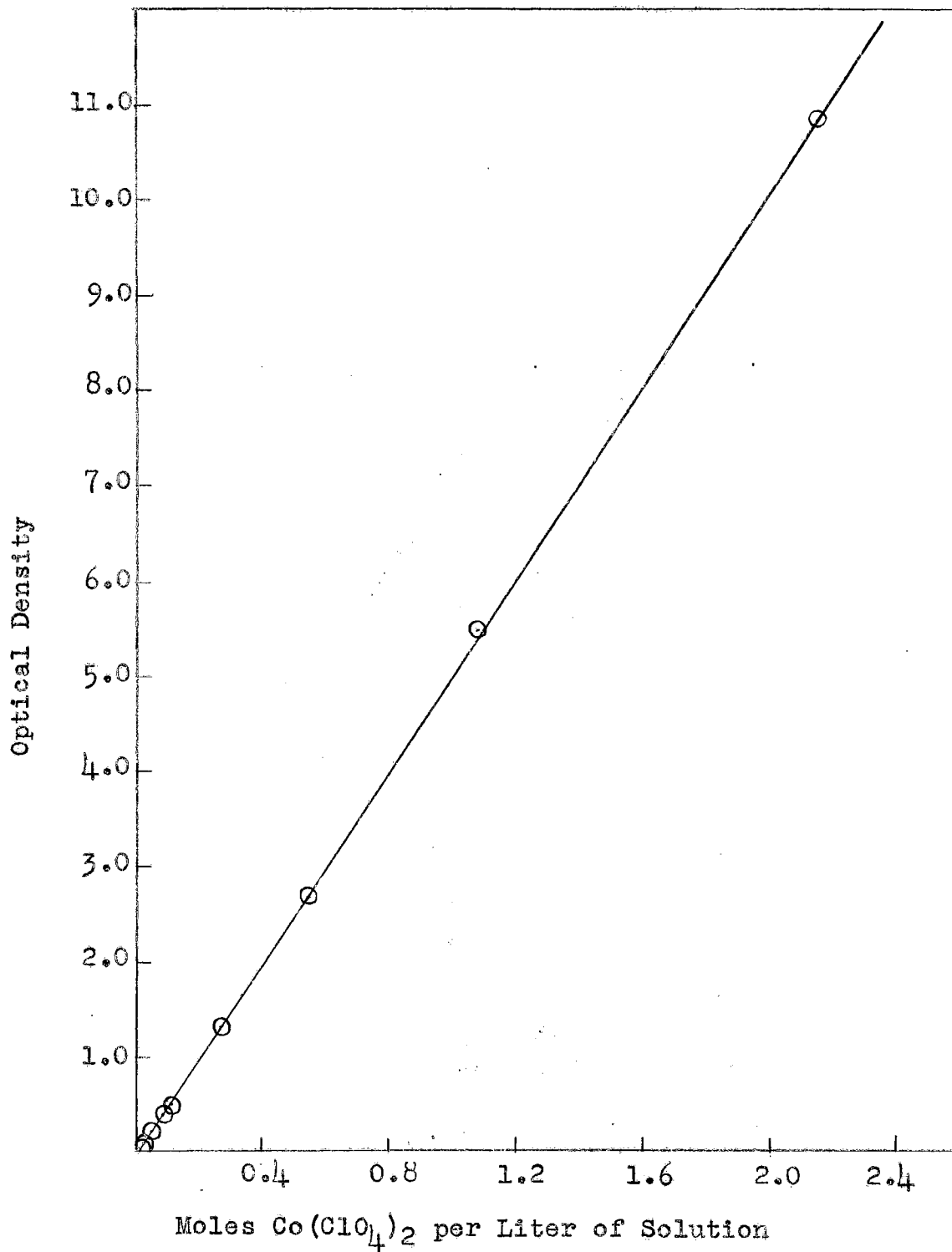


Figure 3

$\text{Co}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  Spectrophotometric Standard Curve



## DISCUSSION

### The Behavior of Perchlorates in Extraction

The high solubility of the metal perchlorates both in water and in many organic solvents is a well known fact (111), and therefore it seems logical to suppose that there should be some connection between solubility in, and extractibility into organic solvents. Experimentally this has been found.

Generally speaking, perchlorates seem to lack individualistic behavior when compared to chlorides (66). This is indicated by the uniformly high activity coefficients of many metal perchlorates in aqueous solutions and also by the non-specific promoting effect exhibited in solvent extraction found in this investigation.

The greater extractibility of cobalt chloride compared to nickel chloride (into 2-octanol) is believed to be due to the fact that cobalt chloride forms more stable complexes in the alcohol solution than does nickel chloride (67). The perchlorates, however, form no complex ions, as was mentioned earlier, and their high extractibility may be attributed to much smaller cation-anion interaction and to the solvent characteristics of the 2-octanol-water mixture. The perchlorate ion is unlikely to form complexes because it is a large ion which is composed of a highly electronegative central chlorine atom that holds firmly the electrons of the four oxygen atoms. The excess of one negative charge is spread out in its effect over a relatively large anion and as a result the perchlorate ion is not

easily distorted or polarized by a positive field; consequently, there is little tendency to form covalent bonds.

The relatively very high hydration numbers found for the perchlorates investigated (114) also indicates a lack of the type of specific cation and anion interaction which characterizes the chlorides. Presumably the cation is effectively masked by a sheath of water molecules and close approach to the anion is prevented. This is another example of the great difference between the extraction properties of the perchlorates and the chlorides. This apparent lack of specificity in perchlorate extractions is further supported by the fact that little difference exists in the extractibility of manganese, cobalt, nickel, copper, and cadmium perchlorates at equivalent concentrations (117).

It was pointed out in earlier discussions that the promoting action of perchlorates was governed largely by mass-action effects. It must also be pointed out that while this effect is a very important one in the promotion of perchlorates, there is another factor which also plays an important role in the promotion of extraction. This factor is the decrease in dielectric constant in the aqueous phase with concentration. As the salt concentration of a system increases the dielectric constant of that system decreases, and this lowering of the dielectric constant in aqueous phase favors an increase in extraction because the free energy of transfer is also lowered. The energy of association in the non-aqueous phase will then more nearly balance that lost in transferring the ions (116).

In general, the degree of extraction is determined by such factors as the energy of solvation of the ions in each phase, the nature and extent of interionic attractive forces, and the structure and stability of associated entities. It might be expected that these latter two factors play a part of less importance in the extraction of perchlorates than in the extraction of chlorides for reasons discussed earlier. The magnitude of these factors is determined by the charge, size, configuration, and polarizability of the ions, and the dielectric constant of the medium along with the solvating characteristics of the solvents.

While the evaluation of all of these factors is practically impossible, this investigation has revealed some of the important differences in the behavior of cobalt chloride and cobalt perchlorate which probably exist to an equal degree in other metal chlorides compared to the corresponding metal perchlorates.

#### Hydration Studies and Henry's Law

Hydration studies were made on unpromoted perchlorate extractions in an effort to find out how many water molecules may be regarded as associated with the salt in the non-aqueous phase.

Before discussing the method used here (114) it is worth noting that Katzin and Sullivan (52) had introduced a procedure for determining the extent of hydration of salts in non-aqueous media. Their method consisted of evaluating the slope of the curves obtained by plotting the total moles of water found in the non-aqueous phase vs. the number of moles of salt extracted

into that phase. These investigators assumed that all water in the organic phase had been transferred into it as hydrate water. Their plots, however, were not linear and exhibited a minimum in the dilute regions which was thought to be due to the lowering of the water activity in the aqueous phase before a sufficient amount of hydrated salt had been extracted to offset this effect. This is because solutions of low salt concentrations have high water activities, and since little salt extraction occurs from such solutions, all the water that is extracted may be regarded as free water. The hydration curve accordingly begins high, falls as the aqueous water activity decreases without significant extraction occurring, reaches a minimum, and finally rises as hydrated salt is extracted.

The two main objections to this method of determining hydration numbers are:

(1) Even after enough hydrate water has been extracted to offset the effect of the lowered water activity, there is no reason to believe that this effect ceases to operate as a factor in determining the total water transferred.

(2) The difficulty which arises in choosing the concentration range of the plot from which the slope is determined.

The following method was proposed by Yates and Moore (115) in an effort to overcome some of the objections to Katzin and Sullivan's method by attempting to determine the "free" or uncombined water in the non-aqueous phase. A similar procedure was independently suggested by Gardner, McKay and Warren (35).

Assume that the activity of the "free" water in the non-aqueous phase is related to its mole fraction by Henry's Law



by the relation

$$a'_w = kN'_w \quad (1)$$

where  $k$  is Henry's Law constant.

From thermodynamics the expression for the partition of water between phases is:

$$\frac{a'_w}{a_w} = K \quad (2)$$

where  $a_w$  is the water activity in the aqueous phase. Substituting into (2) the value of  $a'_w$  given in (1) one has

$$\frac{kN'_w}{a_w} = K \quad (3)$$

or

$$N'_w = \frac{K}{k} a_w = \underline{\underline{K}} a_w \quad (4)$$

From equation (4) it is seen that upon evaluation of the constant  $\underline{\underline{K}}$ , the mole fraction of "free" water in the non-aqueous phase may be obtained from a knowledge of the corresponding water activity in the aqueous phase.

The justification for using Henry's Law and the subsequent evaluation of  $\underline{\underline{K}}$  follows from the following consideration. Henry's Law could be expected to hold only in solutions of low water concentration in the non-aqueous or 2-octanol phase. This corresponds in general to a high aqueous phase salt concentration, i.e., one in which the water activity has been lowered considerably by the salt. It was necessary, therefore to find a salt which would not extract from highly concentrated aqueous solutions, thereby assuming that all of the water extracted was "free" water. This salt is lithium chlo-

ride. It was found that practically no extraction of lithium chloride occurred from a 5 molal solution while correspondingly the water activity of such a solution was 0.68. Water activities of aqueous solutions of lithium chloride (49) were plotted vs. moles of water extracted obtained from Karl Fisher analyses (65). This plot (Figure 4) was a curve which gradually approached a straight line as the aqueous lithium chloride concentration increased, i.e., decreasing water activity in aqueous phase as listed in Table 4. From equation (4) it is seen that Henry's Law predicts a straight line of slope  $1/\underline{K}$  (where  $\underline{K}$  is  $K/k$ ). Calculations of this slope for decreasing water concentrations gave values which gradually approached a constant value. The constant  $\underline{K}$  was actually evaluated at a point of lowest water activity without extraction of lithium chloride occurring. It was assumed that at all water activities in the aqueous phases lower than one at which Henry's Law constant was evaluated, the "free" water extracted would follow this law, and could be calculated by equation (4).

In making calculations of this kind, the mole fraction of "free" water partitioned from any solution of known water activity was determined either by Henry's Law calculations, or if the activity was too high, from the plot of water activities vs. moles of water extracted as obtained from the lithium chloride data.

Actually the majority of "free" water concentrations were determined graphically since most of the aqueous phase water activities were higher than 0.68. To make these calculations with the unpromoted-extraction data of cobalt and nickel per-

chlorates the water activities of zinc perchlorate solutions were used at equivalent salt concentrations rather than those of cobalt or nickel perchlorate solutions which were unavailable. The similarity in the activity coefficients of 2:1 metal perchlorates support this approximation.

After computing the "free" or uncombined water concentrations by the method discussed above, the values were subtracted from the corresponding total water values which had been determined by the Karl Fisher water analysis method and the moles of hydrate water were obtained. These are tabulated in Tables 5 and 6 and are shown graphically in Figure 5. The value of 12.5 was taken as the hydration number of cobalt perchlorate from this graph.

Similarly the value of the nickel perchlorate hydration number was found to be about 12.5 in the dilute range of concentrations, but the value decreased at higher concentrations. The similarity in the hydration numbers found for these salts is not surprising in view of their close physical and chemical properties.

TABLE 4

Water Activity of Aqueous LiCl Solutions and H<sub>2</sub>O Content of Corresponding 2-Octanol Phases Before Extraction Occurred

| m(aq) | a <sub>H2O</sub> | M <sub>w</sub> |
|-------|------------------|----------------|
| 0.00  | 1.00             | 2.15           |
| 1.03  | 0.976            | 2.00           |
| 2.60  | 0.898            | 1.66           |
| 4.12  | 0.812            | 1.39           |
| 5.97  | 0.689            | 1.12           |

TABLE 5

Co(ClO<sub>4</sub>)<sub>2</sub> Hydration Data

| M <sub>T</sub> | M <sub>F</sub> | M <sub>H</sub> | m <sub>Co(ClO<sub>4</sub>)<sub>2</sub></sub> x 10 <sup>3</sup><br>(oct) |
|----------------|----------------|----------------|---|
| 2.03           | 1.96           | 0.07           | 0.51  |
| 1.97           | 1.85           | 0.12           | 1.66  |
| 1.88           | 1.67           | 0.21           | 5.29  |
| 1.83           | 1.57           | 0.26           | 16.8  |
| 1.99           | 1.52           | 0.47           | 33.6  |
| 2.46           | 1.32           | 1.14           | 84.3  |
| 3.32           | 1.23           | 2.09           | 162.  |
| 3.91           | 1.18           | 2.73           | 211.  |

M<sub>T</sub> = Moles of Total Water

M<sub>F</sub> = Moles of Free Water

M<sub>H</sub> = Moles of Hydrate Water

TABLE 6  
 $\text{Ni}(\text{ClO}_4)_2$  Hydration Data

| $M_T$ | $M_F$ | $M_H$ | $m_{\text{Ni}(\text{ClO}_4)_2} \times 10^3$<br>(oct) |
|-------|-------|-------|--|
| 2.03  | 1.93  | 0.01  | 1.08   |
| 1.94  | 1.80  | 0.14  | 3.21   |
| 1.88  | 1.65  | 0.23  | 11.4   |
| 2.01  | 1.49  | 0.52  | 18.  |
| 2.37  | 1.32  | 1.05  | 64.  |
| 3.45  | 1.16  | 2.29  | 174.   |
| 4.97  | 0.99* | 3.98* | 346.   |
| 5.66  | 0.91* | 4.75* | 445.   |
| 6.32  | 0.80* | 5.52* | 553.   |

\* Determined by Henry's Law

$M_T$  = Moles of Total Water

$M_F$  = Moles of Free Water

$M_H$  = Moles of Hydrate Water

Figure 4

Activity of H<sub>2</sub>O of Aqueous LiCl Solutions vs. H<sub>2</sub>O Content of Corresponding 2-Octanol Phases Before Extraction Occurred

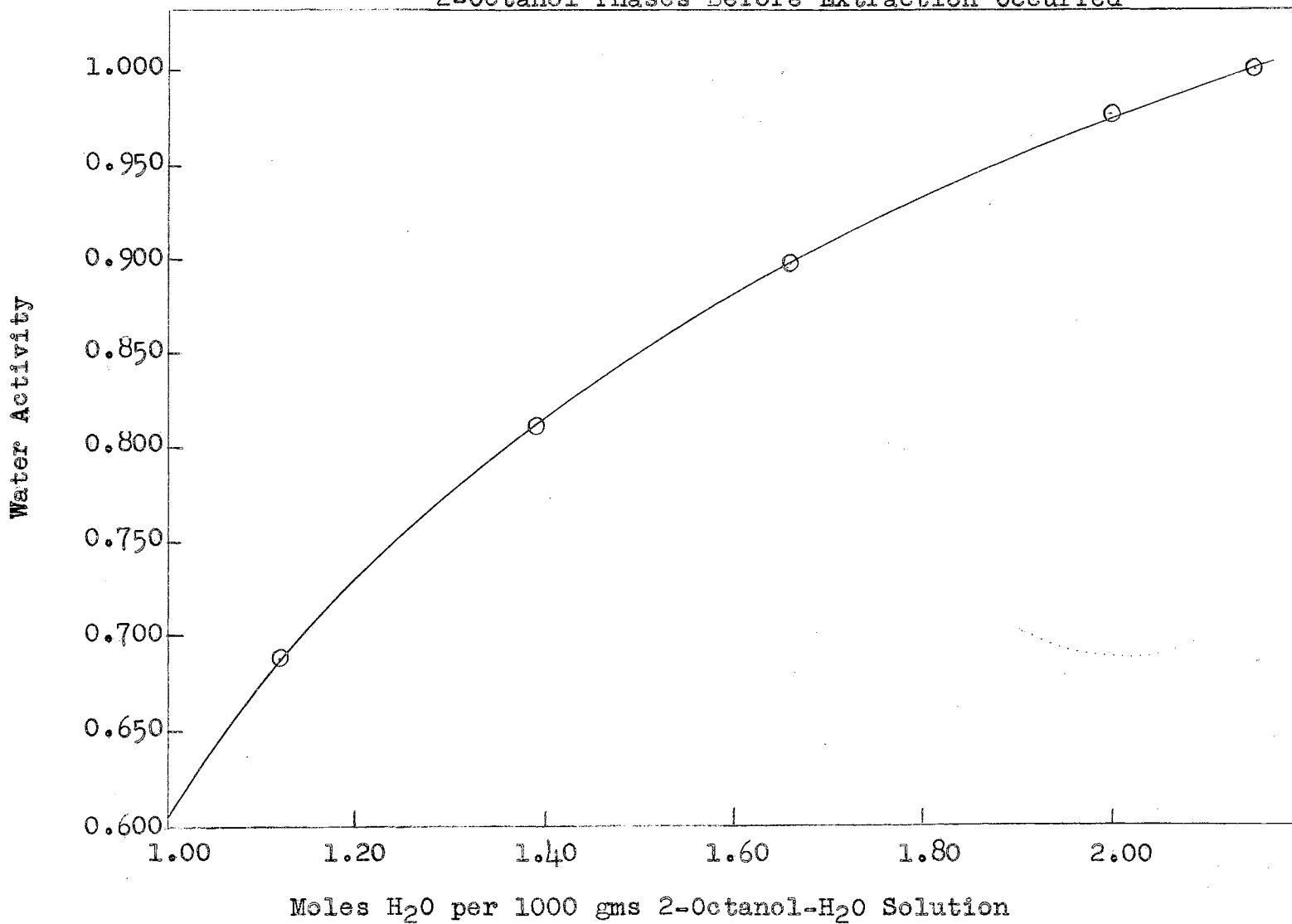
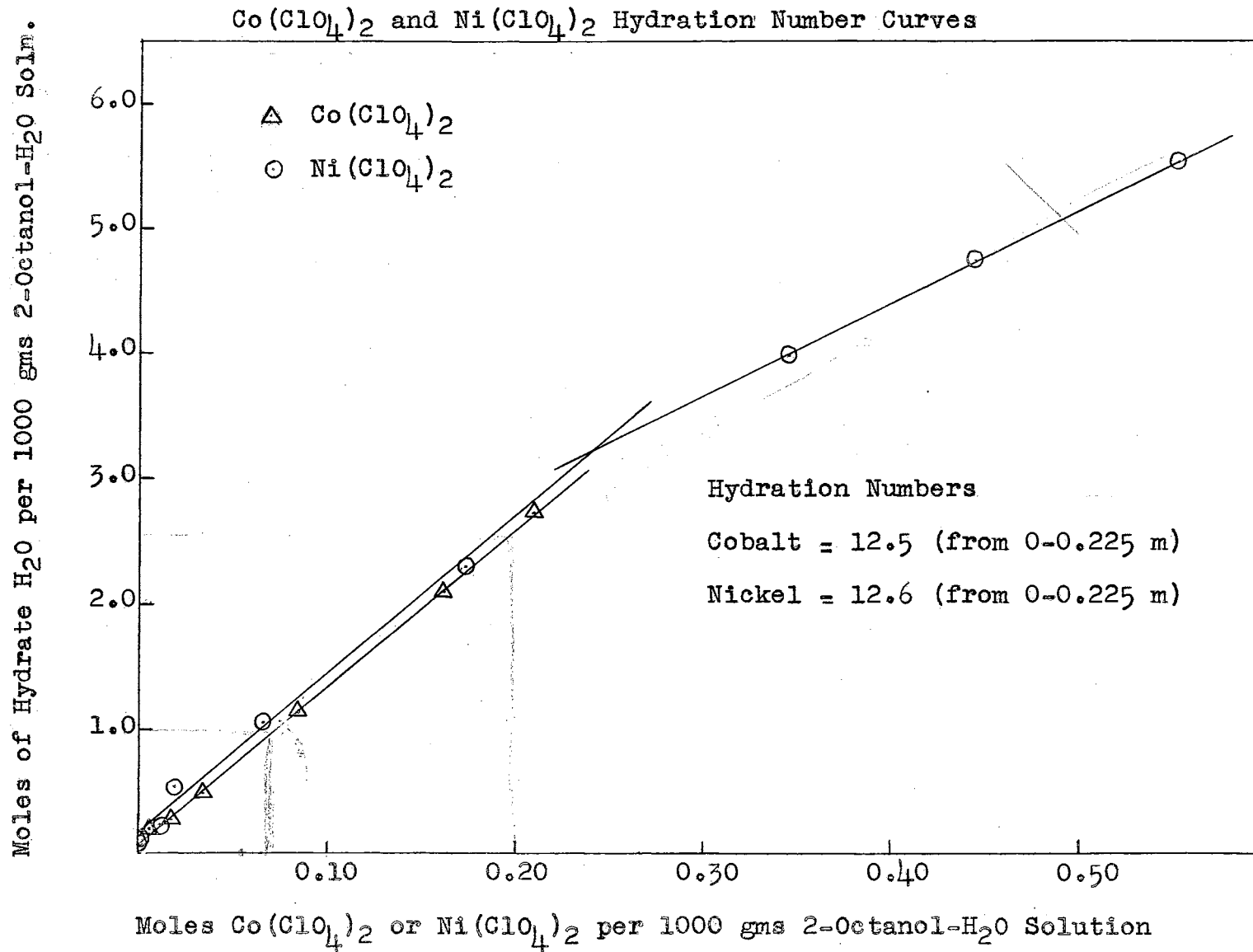


Figure 5



## RESULTS AND TREATMENT OF DATA

The discussion and interpretation of the data may be accomplished best by considering individual series of extraction experiments, and the significant tables and graphs relating to each series.

### The Cobalt Perchlorate Unpromoted Extraction

Most of the investigation was centered around the extraction of cobalt perchlorate into 2-octanol. Cobalt perchlorate like many metal perchlorates is very soluble in water, and quite concentrated solutions can be obtained. The extent of extraction is of course dependent upon the aqueous phase concentration, and the data obtained over a ten-fold variation in aqueous phase concentration is listed in Table 7. From the equilibrium aqueous and 2-octanol phase concentrations a useful quantity called the distribution coefficient ( $K_d$ ) has been calculated. This quantity is defined as the ratio of 2-octanol to the aqueous phase concentrations, and if  $K_d$  is plotted vs. equivalents of perchlorate ion in the aqueous phase, a curve like the  $\text{Co}(\text{ClO}_4)_2$  curve of Figure 6 is obtained. As shown by the tabulated data and plot, cobalt perchlorate extracts to a relatively high degree from aqueous solutions. The graph also illustrates that  $K_d$  is not constant as predicted by a simple Nernst Law distribution and that a more complex extraction law is followed. This was found to be true for all of the perchlorates in this investigation.

In order to study the change in mean activity coeffici-



ents in the 2-octanol phase with concentration, mean activity coefficients of aqueous solutions of zinc perchlorate (82) were used as an approximation to those of cobalt perchlorate and the  $\gamma_{\pm}$  values in the 2-octanol phase were calculated by means of the equation

$$K_a = \frac{(a_{\pm})_{\text{oct}}^3}{(\epsilon_{\pm})_{\text{aq}}^3} = \frac{(\gamma_{\pm})_{\text{oct}}^3 [\text{Co}^{++}] [\text{ClO}_4^-]_{\text{oct}}^2}{(\gamma_{\pm})_{\text{aq}}^3 [\text{Co}^{++}] [\text{ClO}_4^-]_{\text{aq}}^2}$$

$K_a$  was evaluated by arbitrarily setting  $(\gamma_{\pm})_{\text{oct}} = 1$  for the most dilute solution. Using this value and approximate  $(\gamma_{\pm})_{\text{aq}}$  values the  $(\gamma_{\pm})_{\text{oct}}$  values were determined at all of the other concentrations (Table 7). A plot of  $(\gamma_{\pm})_{\text{oct}}$  vs. moles of salt extracted is also shown in Figure 7.

TABLE 7

Data on  $\text{Co}(\text{ClO}_4)_2$  Unpromoted Extraction

| $m(\text{aq.})$ | $m \times 10^3$<br>(oct.) | $K_d \times 10^3$ | $\text{ClO}_4^-$ eq.<br>(aq.) | $\gamma_{\pm}$<br>(aq.) | $\gamma_{\pm}$<br>(oct.) | $a_{\text{H}_2\text{O}}$<br>(aq.) |
|-----------------|---------------------------|-------------------|-------------------------------|-------------------------|--------------------------|-----------------------------------|
| 0.593           | 0.51                      | 0.85              | 1.19                          | 0.65                    | 1.00                     | 0.966                             |
| 0.863           | 1.66                      | 1.92              | 1.73                          | 0.75                    | 0.51                     | 0.944                             |
| 1.27            | 5.29                      | 4.18              | 2.54                          | 1.15                    | 0.36                     | 0.903                             |
| 1.52            | 16.8                      | 11.0              | 3.04                          | 1.55                    | 0.18                     | 0.873                             |
| 1.64            | 33.6                      | 20.5              | 3.28                          | 1.80                    | 0.12                     | 0.857                             |
| 2.17            | 84.3                      | 38.8              | 4.34                          | 3.40                    | 0.11                     | 0.781                             |
| 2.39            | 162.                      | 67.9              | 4.78                          | 4.65                    | 0.090                    | 0.744                             |
| 2.57            | 211.                      | 82.0              | 5.14                          | 6.00                    | 0.096                    | 0.717                             |

Figure 6

## Extractability Curves of Several Metal Perchlorates

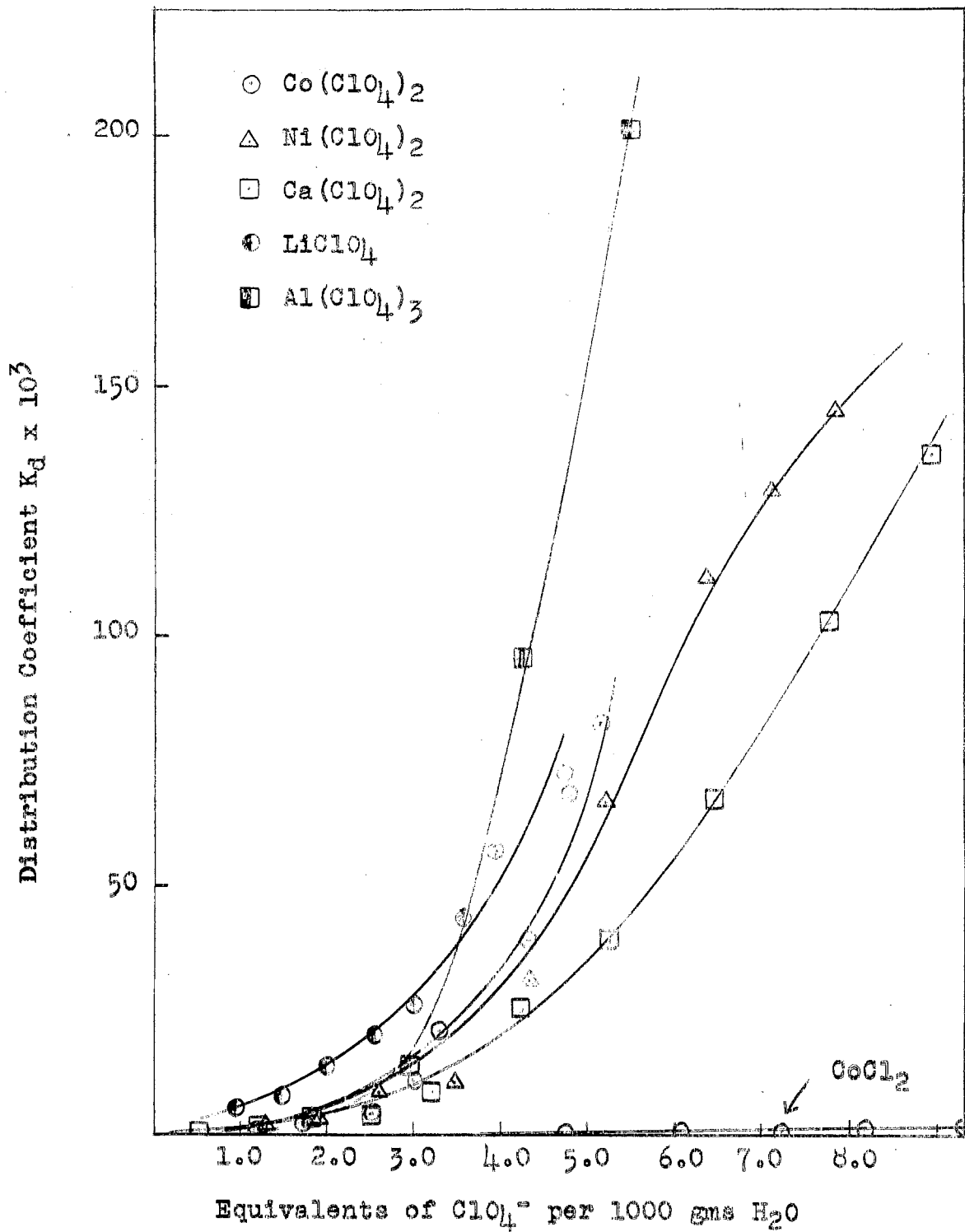
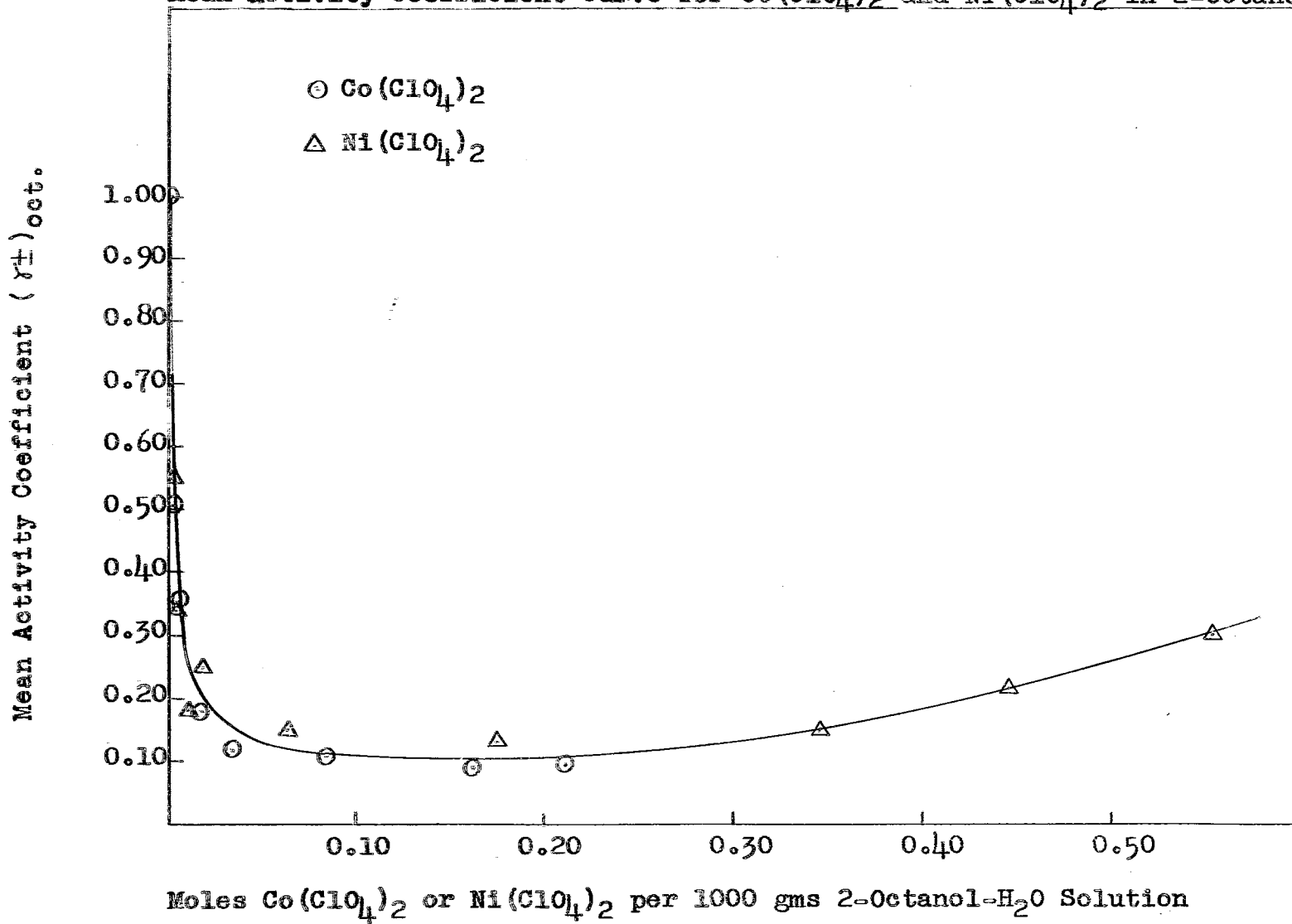


Figure 7

Mean Activity Coefficient Curve for  $\text{Co}(\text{ClO}_4)_2$  and  $\text{Ni}(\text{ClO}_4)_2$  in 2-Octanol



### The Nickel Perchlorate Unpromoted Extraction

The extraction of nickel perchlorate into 2-octanol was undertaken in order that this salt and cobalt perchlorate could be compared with the corresponding chlorides upon extraction. The extraction data for nickel perchlorate is tabulated in Table 8. It should also be noticed that this salt extracts to a high degree. Figure 6 illustrates the increase in extraction with increasing aqueous phase concentration and it is seen that nickel perchlorate like cobalt perchlorate does not follow a simple Nernst distribution.

A set of mean activity coefficients for nickel perchlorate in the 2-octanol phase was calculated with the aid of an expression similar that of the equation above. The K value used was selected to be identical with that for  $\text{Co}(\text{ClO}_4)_2$  in order that the two sets of values might be put on a comparable basis. This data is also listed in Table 8 and is illustrated in Figure 7. It is seen that the  $\gamma_{\pm}$  values for cobalt and nickel perchlorates appear to be about the same, lending support to the assumption that 2:1 metal perchlorates have the same  $\gamma_{\pm}$  values at equivalent concentrations.

TABLE 8

Data on Ni(ClO<sub>4</sub>)<sub>2</sub> Unpromoted Extraction

| m(aq.) | m x 10 <sup>3</sup><br>(oct.) | K <sub>d</sub> x 10 <sup>3</sup> | ClO <sub>4</sub> <sup>-</sup> eq.<br>(aq.) | γ±<br>(aq.) | γ±<br>(oct.) | a <sub>H<sub>2</sub>O</sub><br>(aq.) |
|--------|-------------------------------|----------------------------------|--|-------------|--------------|--------------------------------------|
| 0.65   | 1.1                           | 1.7                              | 1.30                                       | 0.70        | 0.55         | 0.961                                |
| 0.97   | 3.2                           | 3.3                              | 1.94                                       | 0.85        | 0.34         | 0.935                                |
| 1.31   | 11.4                          | 8.7                              | 2.62                                       | 1.20        | 0.18         | 0.898                                |
| 1.73   | 18.0                          | 10.4                             | 3.46                                       | 2.00        | 0.25         | 0.846                                |
| 2.17   | 64.0                          | 29.5                             | 4.34                                       | 3.40        | 0.15         | 0.782                                |
| 2.62   | 174.                          | 66.4                             | 5.24                                       | 6.50        | 0.13         | 0.708                                |
| 3.16   | 346.                          | 110.                             | 6.32                                       | 12.6        | 0.15         | 0.617                                |
| 3.44   | 445.                          | 129.                             | 6.88                                       | 21.6        | 0.22         | 0.567                                |
| 3.81   | 553.                          | 145.                             | 7.62                                       | 33.2        | 0.30         | 0.510                                |

### The Cobalt Chloride Unpromoted Extraction

This extraction was carried out using fairly concentrated solutions (2.4-4.6 m) because of the small degree of extraction of this salt into 2-octanol. Even from these concentrated solutions little extraction was obtained as can be seen from Table 9 and Figure 6. In this plot, the great difference in extractibility of cobalt chloride and the perchlorates is clearly shown. From a saturated aqueous solution, cobalt chloride extracts only  $6.3 \times 10^{-3}$  m, which is at least several hundred times less than any of the perchlorates studied at equivalent concentrations.

TABLE 9

Data on the  $\text{CoCl}_2$  Unpromoted Extraction

| m(aqueous) | m(oct.) $\times 10^3$ | $K_d \times 10^3$ | Equivalents aqueous $\text{Cl}^-$ |
|------------|-----------------------|-------------------|-----------------------------------|
| 2.38       | 0.77                  | 0.33              | 4.77                              |
| 3.03       | 1.06                  | 0.35              | 6.06                              |
| 3.61       | 2.16                  | 0.60              | 7.21                              |
| 4.15       | 3.91                  | 0.94              | 8.30                              |
| 4.65       | 6.38                  | 1.37              | 9.30                              |

### The Cobalt Perchlorate-Calcium Perchlorate-Promoted Extraction

These extraction experiments were carried out under conditions of gradually increasing concentrations of calcium perchlorate (from 0-4.2 m) while keeping the cobalt perchlorate concentration constant. This made it possible to study the effect of increasing promoting salt concentration. As seen in

Table 10 the increase in extraction arising from the addition of about 4.2 moles of calcium perchlorate is about 500 times greater than if no calcium perchlorate had been added. Also listed in Table 10 is the calcium perchlorate extraction data. In Figure 6 there is plotted the extraction of calcium perchlorate itself, and it too is seen to extract very well. The increase in extraction of cobalt perchlorate with increasing aqueous phase perchlorate concentration is plotted in Figure 8. The data used in making this plot is given in Table 10.

The promotion of the cobalt perchlorate by calcium perchlorate is due in part to a common-ion effect. Although this promoting action does not follow the simple mass-action law there is sufficient evidence to believe that it is partially due to a mass-action effect. Part of this evidence lies in the fact that the degree of extraction of cobalt perchlorate is determined largely by the aqueous phase total perchlorate concentration and is not very sensitive to the type of promoting salt cation. Figure 8 bears out this conclusion.

The calculation of mass-action distribution coefficients ( $k_m$ ) and mass-action distribution constants ( $K_M$ ) also provide evidence showing that the promotion of cobalt perchlorate by calcium perchlorate is partly a mass-action effect. In Table 10 there is a list of concentrations of both cobalt and calcium perchlorates along with corresponding mean activity coefficients in both phases. As has been pointed out activity data for cobalt perchlorate solutions are unavailable and the values for zinc perchlorate solutions were again employed. The activity coefficients of cobalt perchlorate were calcu-

lated from the zinc perchlorate values at concentrations corresponding to the total calcium and cobalt perchlorate concentrations in the aqueous phase and from the octanol extraction data on cobalt perchlorate alone at concentrations equal to the total calcium and cobalt concentrations in the octanol phase. In Table 11 the expressions used to calculate the  $K_M$  and  $k_m$  values are given along with a tabulation of these values at each concentration. Since the  $K_M$  expression is essentially an activity ratio, it should be theoretically constant. From the table it is seen that the values are reasonably constant over the range of concentrations studied, especially when compared with the corresponding  $k_m$  values, which are calculated from a concentration mass-action type expression. It is significant to note that while the  $K_M$  values vary about 37% from the average, in a random manner, the values obtained from the  $k_m$  expression vary about ten million times, steadily increasing with concentration. This is best shown in Figure 9 in which these values are plotted against the total aqueous phase concentration. The perchlorate concentrations used in the calculation of these values represent those of both cobalt and calcium in each phase. In order to calculate the  $K_M$  values, values of  $\gamma_{\pm}$  in the octanol phase had to be determined first. To do this the following assumptions were made: (1) values of  $\gamma_{\pm}$  for 2:1 metal perchlorates alone are approximately the same at the same concentration, both in water and in 2-octanol solution, (2) at the same total concentration, the mean activity coefficient of cobalt perchlorate in a mixture of 2:1 metal perchlorates



is independent of its concentration and depends only on the total mixed-salt concentration. That is, the  $\gamma^{\pm}$  for  $\text{Co}(\text{ClO}_4)_2$  in a mixture with  $\text{Ca}(\text{ClO}_4)_2$  can be taken as equal to that of  $\text{Co}(\text{ClO}_4)_2$  alone at the same concentration as the total concentration of the mixture. These values are plotted in Figure 7 for  $\text{Co}(\text{ClO}_4)_2$  and for  $\text{Ni}(\text{ClO}_4)_2$  in 2-octanol. Activity coefficients can be obtained for  $\text{Co}(\text{ClO}_4)_2$  in  $\text{Co}(\text{ClO}_4)_2$ - $\text{Ca}(\text{ClO}_4)_2$  mixtures by adding the  $\text{Ca}(\text{ClO}_4)_2$  concentration. From the curves given in Figure 8 and Figure 9 one concludes that the assumptions are justified and that the promotion of cobalt perchlorate by calcium perchlorate is governed in a large part by mass-action effect.

TABLE 10

Data on  $\text{Co}(\text{ClO}_4)_2$ - $\text{Ca}(\text{ClO}_4)_2$  Extraction

| $\text{Co}(\text{ClO}_4)_2$ |                          |                                  |                       |                        | $\text{Ca}(\text{ClO}_4)_2$ |                          |                                  | $\text{ClO}_4^-$ | Total                       |
|-----------------------------|--------------------------|----------------------------------|-----------------------|------------------------|-----------------------------|--------------------------|----------------------------------|------------------|-----------------------------|
| m(aq)                       | m(oct) x 10 <sup>3</sup> | K <sub>d</sub> x 10 <sup>3</sup> | $\frac{Y}{X}$<br>(aq) | $\frac{y}{x}$<br>(oct) | m(aq)                       | m(oct) x 10 <sup>3</sup> | K <sub>d</sub> x 10 <sup>3</sup> | Aq. Eq.          | $\text{ClO}_4^-$<br>Aq. Eq. |
| 0.249                       | 0.14                     | 0.55                             | 0.63                  | 1.00                   | 0.273                       | 0.20                     | 0.72                             | 0.546            | 1.04                        |
| 0.249                       | 0.45                     | 1.81                             | 0.84                  | 0.56                   | 0.634                       | 0.92                     | 1.45                             | 1.27             | 1.77                        |
| 0.252                       | 1.03                     | 4.08                             | 1.09                  | 0.40                   | 0.922                       | 1.95                     | 2.11                             | 1.84             | 2.35                        |
| 0.247                       | 2.22                     | 8.09                             | 1.50                  | 0.30                   | 1.22                        | 4.56                     | 3.73                             | 2.44             | 2.94                        |
| 0.245                       | 5.29                     | 21.6                             | 2.30                  | 0.22                   | 1.62                        | 13.4                     | 8.28                             | 3.23             | 3.74                        |
| 0.234                       | 12.2                     | 52.1                             | 4.4                   | 0.10                   | 2.11                        | 52.4                     | 24.8                             | 4.23             | 4.69                        |
| 0.215                       | 27.4                     | 127.                             | 8.4                   | 0.10                   | 2.62                        | 102.                     | 38.9                             | 5.24             | 5.67                        |
| 0.181                       | 46.2                     | 255.                             | 16.4                  | 0.10                   | 3.18                        | 212.                     | 66.6                             | 6.37             | 6.73                        |
| 0.138                       | 65.3                     | 473.                             | 44*                   | 0.23                   | 3.95                        | 403.                     | 102.                             | 7.90             | 8.18                        |
| 0.102                       | 73.1                     | 717.                             | 84*                   | 0.43*                  | 4.46                        | 607.                     | 136.                             | 8.92             | 9.13                        |

\* Extrapolated Values

Figure 8

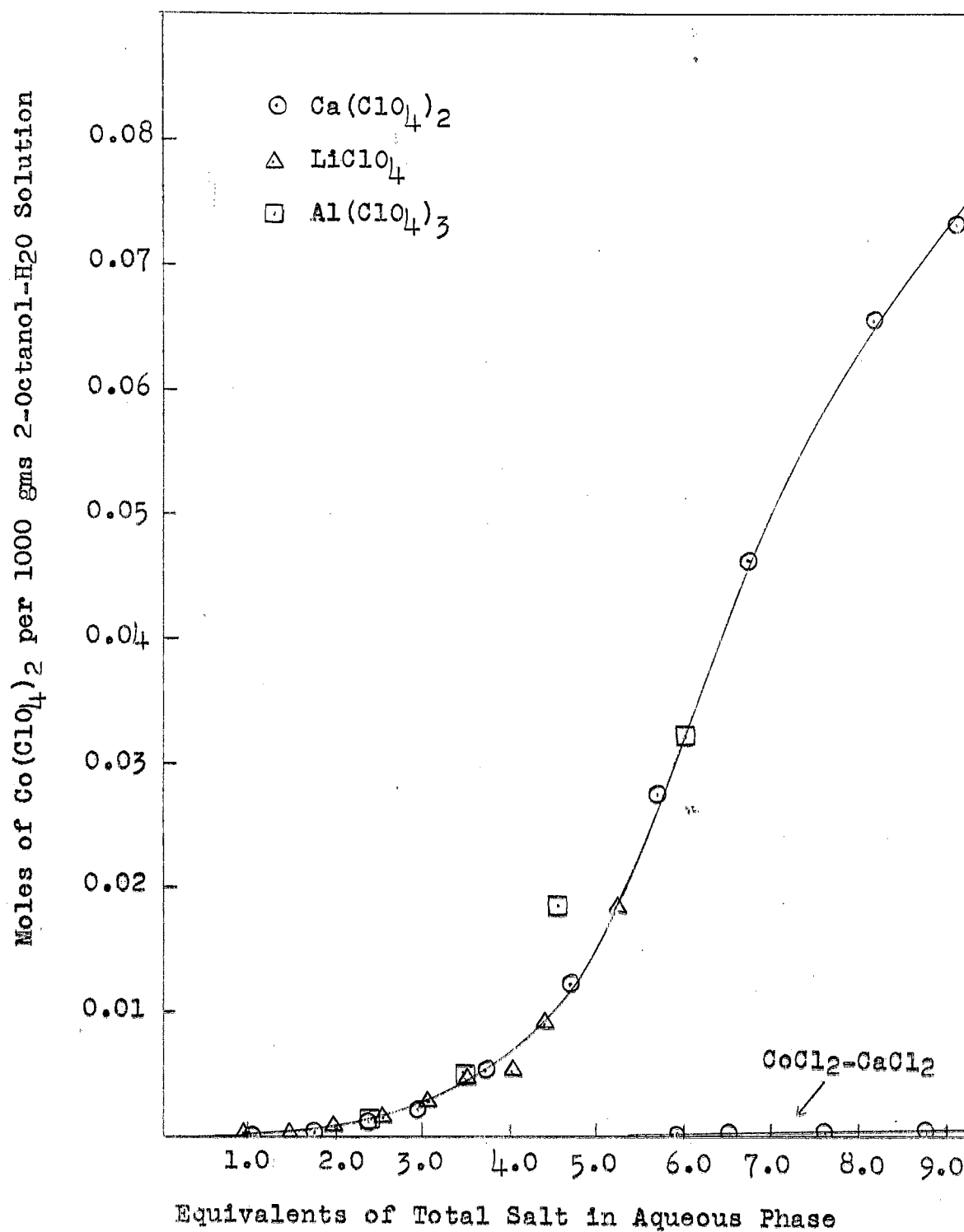
Promotion of  $\text{Co}(\text{ClO}_4)_2$  by  $\text{Ca}(\text{ClO}_4)_2$ ,  $\text{LiClO}_4$  and  $\text{Al}(\text{ClO}_4)_3$ 

TABLE 11

K<sub>M</sub> and k<sub>m</sub> Data

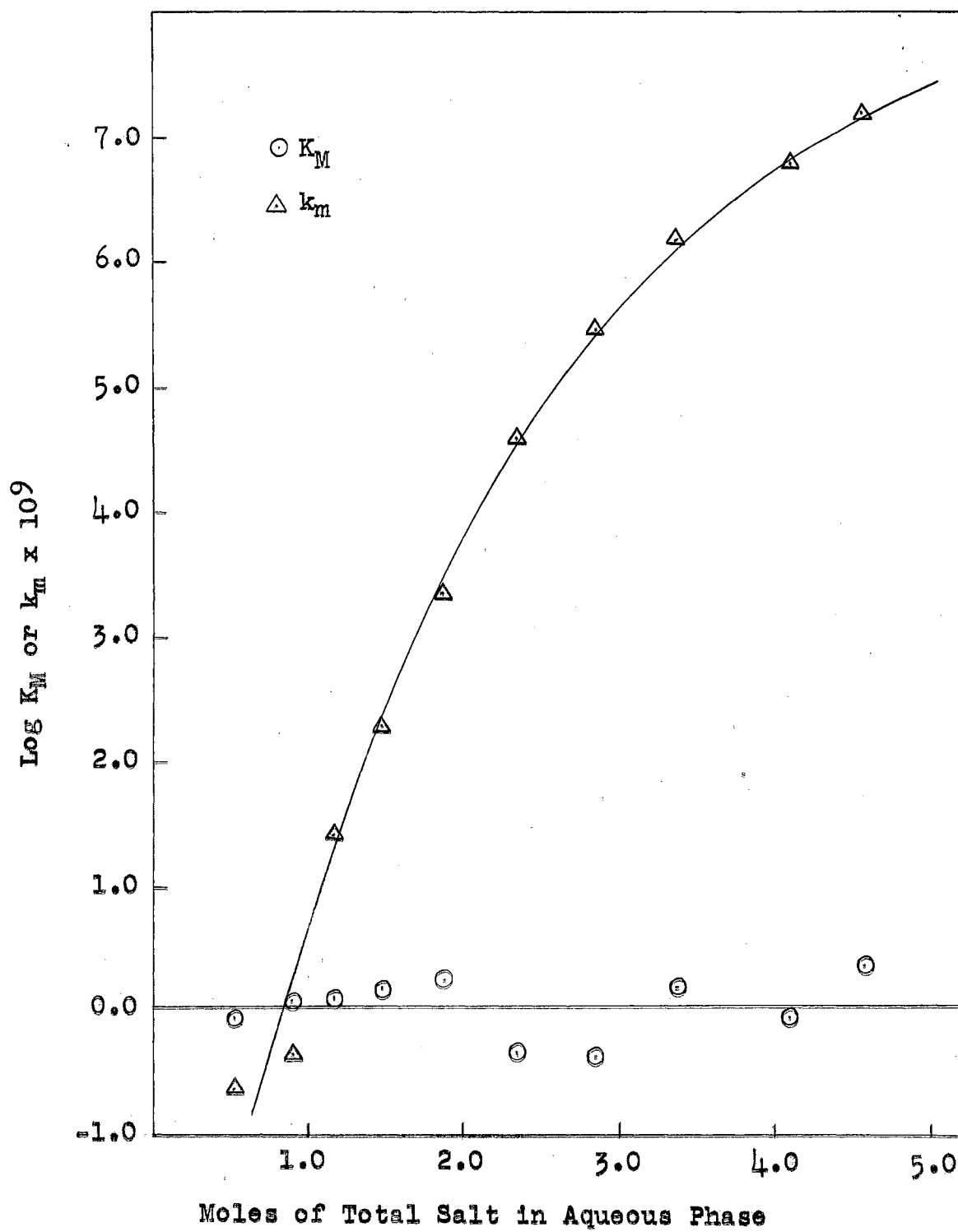
$$K_M = \frac{(\gamma_{\pm})^3_{\text{oct.}} [\text{Co}^{++}] [\text{ClO}_4^-]_{\text{oct.}}^2}{(\gamma_{\pm})^3_{\text{aq.}} [\text{Co}^{++}] [\text{ClO}_4^-]_{\text{aq.}}^2}$$

$$k_m = \frac{[\text{Co}^{++}] [\text{ClO}_4^-]_{\text{oct.}}^2}{[\text{Co}^{++}] [\text{ClO}_4^-]_{\text{aq.}}^2}$$

| K <sub>M</sub> x 10 <sup>9</sup> | k <sub>m</sub> x 10 <sup>9</sup> | Total Aq. Molality |
|----------------------------------|----------------------------------|--------------------|
| 0.91                             | 0.23                             | 0.522              |
| 1.29                             | 0.44                             | 0.883              |
| 1.31                             | 2.65 x 10 <sup>1</sup>           | 1.17               |
| 1.53                             | 1.93 x 10 <sup>2</sup>           | 1.47               |
| 1.92                             | 2.19 x 10 <sup>3</sup>           | 1.86               |
| 0.46                             | 3.93 x 10 <sup>4</sup>           | 2.35               |
| 0.44                             | 2.92 x 10 <sup>5</sup>           | 2.84               |
| 1.59                             | 1.50 x 10 <sup>6</sup>           | 3.36               |
| 0.89                             | 6.20 x 10 <sup>6</sup>           | 4.09               |
| 2.22                             | 1.59 x 10 <sup>7</sup>           | 4.56               |

Figure 9

Distribution Constant ( $K_M$ ) and Distribution Coefficient ( $k_m$ ) Curves



## The Cobalt Perchlorate-Lithium Perchlorate Promoted Extraction

This series of extractions was carried out in order to obtain a variation in the cationic charge of the promoting salt. The extraction experiments were made in a manner similar to that of the calcium perchlorate-promoted extractions. The concentration of cobalt perchlorate was kept constant at the same concentration as in the calcium perchlorate-promoted extractions, and the lithium perchlorate varied from zero to about 4.8 m (Figure 6). The results of the extraction are tabulated in Table 12 where concentrations of both cobalt and lithium perchlorates are listed. The increase in extraction with increasing promoting salt concentration isn't quite as pronounced here as it is with the calcium promotion and this is due mainly to the fact that the promoting salt is monovalent and contains only half the perchlorate concentration of a similar solution of calcium perchlorate. However, when the data is arranged in equivalent form, as in Figure 8, it is seen that the two sets of data superimpose one another. This supports again the conclusion that the degree of promotion is almost independent of the promoting salt cation and that the extent of promotion is principally dependent upon the total perchlorate concentration.

TABLE 12

Data on  $\text{Co}(\text{ClO}_4)_2\text{-LiClO}_4$  Extraction

| $\text{Co}(\text{ClO}_4)_2$ |                       |                   | $\text{LiClO}_4$ |                       |                   | Total Aqueous                |
|-----------------------------|-----------------------|-------------------|------------------|-----------------------|-------------------|------------------------------|
| m(aq.)                      | m(oct.) $\times 10^3$ | $K_d \times 10^3$ | m(aq.)           | m(oct.) $\times 10^3$ | $K_d \times 10^3$ | Equivalents $\text{ClO}_4^-$ |
| 0.257                       | 0.19                  | 0.74              | 0.472            |                       |                   | 0.986                        |
| 0.257                       | 0.42                  | 1.61              | 0.960            | 4.78                  | 4.98              | 1.47                         |
| 0.259                       | 0.75                  | 2.88              | 1.47             | 11.2                  | 7.60              | 1.99                         |
| 0.259                       | 1.64                  | 6.41              | 2.01             | 27.0                  | 13.4              | 2.52                         |
| 0.249                       | 2.74                  | 11.0              | 2.55             | 50.1                  | 19.7              | 3.05                         |
| 0.241                       | 4.58                  | 19.0              | 3.03             | 77.9                  | 25.8              | 3.51                         |
| 0.232                       | 5.21                  | 22.5              | 3.56             | 153.                  | 43.0              | 4.02                         |
| 0.215                       | 9.02                  | 42.0              | 3.94             | 222.                  | 56.3              | 4.37                         |
| 0.238                       | 18.3                  | 76.9              | 4.77             | 346.                  | 72.6              | 5.24                         |

The Cobalt Perchlorate-Aluminum Perchlorate Promoted Extrac-  
tion

The extraction of cobalt perchlorate promoted with aluminum perchlorate was the last of three promoted perchlorate extractions designed to test further the hypothesis that the extraction of perchlorates is largely governed by mass-action effects, and that the extraction is independent of the promoting salt cation. The results are shown in Figure 8 where it is seen that the extraction of cobalt perchlorate promoted by the three different ion-type perchlorates fall on the same line. The extraction data are listed in Table 13, and the distribution coefficients for aluminum perchlorate are plotted in Figure 6.



TABLE 13  
Data on  $\text{Co}(\text{ClO}_4)_2$ - $\text{Al}(\text{ClO}_4)_3$  Extraction

| $\text{Co}(\text{ClO}_4)_2$ |                       |                   | $\text{Al}(\text{ClO}_4)_3$ |                       |                   | Aq. $\text{ClO}_4^-$ | Total Aq.               |
|-----------------------------|-----------------------|-------------------|-----------------------------|-----------------------|-------------------|----------------------|-------------------------|
| m(aq.)                      | m(oct.) $\times 10^3$ | $K_d \times 10^3$ | m(aq.)                      | m(oct.) $\times 10^3$ | $K_d \times 10^3$ | Equiv.               | Equiv. $\text{ClO}_4^-$ |
| 0.253                       | 1.08                  | 4.27              | 0.626                       | 1.84                  | 2.94              | 2.94                 | 2.38                    |
| 0.250                       | 5.03                  | 20.1              | 0.994                       | 13.0                  | 13.1              | 2.98                 | 3.48                    |
| 0.244                       | 18.5                  | 75.8              | 1.42                        | 135.                  | 95.0              | 4.26                 | 4.75                    |
| 0.248                       | 32.2                  | 130.              | 1.84                        | 370.                  | 201.              | 5.51                 | 6.01                    |

### The Cobalt Chloride-Calcium Chloride Promoted Extraction

The promoted extraction of cobalt chloride by calcium chloride was studied so as to be able to compare the extraction and promotion of cobalt chloride with the extraction and promotion of cobalt perchlorate under similar conditions. It was pointed out earlier that unpromoted cobalt chloride extracts very little by comparison with cobalt perchlorate. The results obtained in the calcium chloride-promoted extraction of cobalt chloride show that in spite of the addition of as much as 4.2 m calcium chloride the extractibility of cobalt chloride still doesn't compare with that of cobalt perchlorate. The cobalt chloride was kept constant at the same concentration as in the promoted cobalt perchlorate extractions (0.24 m) and the calcium chloride was maintained at approximately the same concentration as calcium perchlorate in an effort to provide a suitable basis for comparison. Figure 8 compares the small degree of promotion of the cobalt chloride extraction to that of cobalt perchlorate. The extraction data are listed in Table 14. Although calcium chloride doesn't seem to promote the extraction of cobalt chloride very much at this low concentration of the cobalt salt, it is known that calcium chloride if present in higher concentrations does promote the extraction of more concentrated cobalt solutions into 2-octanol to a considerable degree.

TABLE 14

Data on  $\text{CoCl}_2$  in  $\text{CoCl}_2\text{-CaCl}_2$  Extraction

| $m(\text{aqueous})$ | $m(\text{oct.}) \times 10^3$ | $K_d \times 10^3$ | Total Aq. Equiv. $\text{Cl}^-$ |
|---------------------|------------------------------|-------------------|--------------------------------|
| 0.278               | 0.11                         | 0.41              | 5.90                           |
| 0.270               | 0.14                         | 0.51              | 6.50                           |
| 0.249               | 0.24                         | 0.98              | 7.60                           |
| 0.257               | 0.41                         | 1.60              | 8.78                           |

## SUMMARY AND CONCLUSIONS

A study of the extraction of cobalt perchlorate into 2-octanol and the promotion of this extraction with the perchlorates of calcium, lithium, and aluminum was undertaken. It was found that cobalt perchlorate is extracted to a high degree and that this extraction is greatly promoted by the addition of other perchlorates. This promotion was found to be caused in part by a common-ion or mass-action effect. At the same equivalent perchlorate concentration the promotion of the extraction was independent of the cation of the promoting perchlorate salt. A set of mean activity coefficients for cobalt perchlorate were found which satisfactorily account for variations in the extracted concentrations. The degree of extraction of nickel perchlorate into 2-octanol was also determined. It was found that all of the perchlorates studied extract to a high degree from aqueous solutions.

The degree of hydration of cobalt and nickel perchlorate in the unpromoted extractions of these salts into octanol was determined. It was found that these two salts both have about the same average hydration number, 12.5, in the dilute concentration regions. The hydration number of nickel perchlorate was found to fall below this value in the more concentrated solutions.

The degree of extraction of cobalt chloride and the extent of its promotion by calcium chloride at the same concentrations as those of the perchlorates was determined, and

it was found that cobalt chloride extracts to a much smaller degree than cobalt perchlorate; furthermore, its promotion by calcium chloride was also comparatively small.

## BIBLIOGRAPHY

1. Appleton and Selwood, J. Am. Chem. Soc. 63, 2029 (1941).
2. Ashley and Murray, Ind. Eng. Chem., Anal. Ed., 10, 367 (1938).
3. Asselin, Audrieth, and Comings, J. Phys. and Colloid Chem. 54, 640-8 (1950).
4. Asselin and Comings, Ind. Eng. Chem. 42, 1198 (1950).
5. Axelrod and Swift, J. Am. Chem. Soc. 62, 33 (1940).
6. Babko and Kodenskaya, Trudy Komissii Anal. Khim. Akad. Nauk. S.S.S.R. 3, 162-77 (1951) by way of C.A. 47, 2575 f. (1953).
7. Bassett, Bauer, Clark, Wiberly, and Savolainen, NYO 610 (1950) by way of N.S.A. 4, 840 (1950), abstract 5642.
8. Bassett, Bauer, Clark, Wiberly, Savolainen, and Laurene, NYO 612 (1950) by way of N.S.A. 5, 786 (1951), abstract 5055.
9. Bassett, Wiberly, and Savolainen, AECU 380 (1949) by way of N.S.A. 3, 442 (1949), abstract 1874.
10. Bassett, Wiberly, Savolainen, and Clark, NYO 607 (1950) by way of N.S.A. 4, 571 (1950), abstract 3912.
11. Bassett, Wiberly, Savolainen, Clark, and Ross, RPIB 3, (1949) by way of N.S.A. 4, 315 (1950), abstract 1957.
12. Beaver, Master's Thesis, Oklahoma A. and M. College 1953.
13. Beaver, Trevorrow, Estill, Yates, and Moore, J. Am. Chem. Soc. 75, 4556-60 (1953).
14. Betz and Noll, J. Am. Waterworks Assoc. 42, 49 (1950).
15. Bock, Angew. Chem. 62A, 375-82 (1950).
16. Bock, Z. Anal. Chem. 133, 110-35 (1951).
17. Bock and Bock, Z. Anorg. Allgem. Chem. 263, 146-68 (1950).
18. Bock and Bock, Naturwissenschaften 36, 344 (1949).
19. Bonner, J. Am. Chem. Soc. 71, 3909-14 (1949).

20. Campbell, AECU 2313 (1952) by way of N.S.A. 7, 63 (1953), abstract 616.
21. Campbell and Laurene, NYO 614 (1952) by way of N.S.A. 6, 465 (1952), abstract 3766.
22. Cavanagh, Proc. Roy. Soc. (London) 106A, 243-50 (1924) by way of C.A. 19, 203 (1924).
23. Chemical Research Laboratory, Chem. Age 63, 648-50 (1950).
24. Craig, Anal. Chem. 23, 41-44 (1951).
25. Dhar and Datta, Z. Elektrochem. 19, 583-5 (1913) by way of C.A. 8, 3564 (1913).
26. Dodson, Forney and Swift, J. Am. Chem. Soc. 58, 2573 (1936).
27. Edwards and Voigt, Anal. Chem. 21, 1204-5 (1949).
28. Elson, Mason, Peppard, Sellars, and Studier, J. A. Chem. Soc. 73, 4974-5 (1951).
29. Fischer and Chalybaeus, Z. Anorg. Chem. 255, 79-100 (1949) by way of C.A. 43, 2883c (1949).
30. Fischer, Chalybaeus, and Zumbusch, Z. Anorg. Chem. 255, 277-86 (1949) by way of C.A. 43, 288d (1949).
31. Fischer, Dietz, and Jubermann, Naturwissenschaften 25, 348 (1937) by way of C.A. 32, 28595 (1938).
32. Friedman, J. Am. Chem. Soc. 74, 5 (1952).
33. Furman, Mundy, and Morrison, AECD 286 (1950) by way of N.S.A. 4, 735 (1950), abstract 4866.
34. Furman, Mundy, and Morrison, AECD 2938 (1950) by way of N.S.A. 4, 983 (1950), abstract 6716.
35. Gardner, McKay, and Warren, Trans. Faraday Soc. 48, 997-1004 (1952).
36. Garwin and Hixson, Ind. Eng. Chem. 41, 2298-2303 (1949).
37. Ibid., 41, 2303-10 (1949).
38. Garwin and Hixson, Anal. Chem. 21, 1215-16 (1949).
39. Gluekauf, McKay and Mathieson, J. Chem. Soc. 1949, 5299-302 (1949).
40. Gluekauf, McKay, and Mathieson, Trans. Faraday Soc. 47, 437-39 (1951).

41. Grahme and Seaborg, J. Am. Chem. Soc. 60, 2524-8 (1938).
42. Gryder and Dodson, J. Am. Chem. Soc. 71, 1894-5 (1949).
43. Helger and Rynn timer, Svensk. Kem. Tid. 61, 189-96 (1949)  
by way of N.S.A. 5, 94 (1951), abstract 594.
44. Imre, Z. Anorg. Allgem. Chem. 164, 214-8 (1927) by way  
of C.A. 21, 3322 (1927).
45. Ibid., 166, 1-15 (1927) by way of C.A. 22, 1094 (1928).
46. Irving, Quat. Rev. 5, 200 (1951).
47. Irving and Rossotti, Analyst 77, 801-12 (1952).
48. Ishibashi and Yamamoto, J. Chem. Soc. Japan, Pure Chem.  
Sect. 73, 665-8 (1952) by way of C.A. 47, 4781g (1953).
49. Johnson and Molstad, J. Phys. and Colloid Chem. 55, 257  
(1951).
50. Kato and Isii, Sci. Papers Inst. Phys. Chem. Research,  
(Japan) 36, 82-96 (1939) by way of C.A. 33, 7232<sup>6</sup>  
(1939).
51. Katzin and Hellman, AECD 2758 (1949).
52. Katzin and Sullivan, J. Phys. and Colloid Chem. 55, 356  
(1951).
53. Kolthoff and Lingane, Polarography, Interscience Pub-  
lishers Inc., New York, 1941, p.281.
54. Kylander and Garwin, Chem. Eng. Progress 47, 186-90 (1951).
55. Lenher, J. Am. Chem. Soc. 35, 346 (1913).
56. Lenher and Kao, J. Phys. Chem. 30, 126 (1926).
57. Lewis, AERE-CE/R-910 (1950) by way of N.S.A. 7, 169 (1953),  
abstract 1398.
58. Lindh and Rynn timer, Svensk. Kem. Tid. 61, 180-8 (1949)  
by way of N.S.A. 5, 94 (1951), abstract 593.
59. McBride and Yoe, Anal. Chem. 20, 1094 (1948).
60. McDonald, Mitchell, and Mitchell, J. Chem. Soc. (1951),  
1574-81.
61. McKay and Mathieson, Trans. Faraday Soc. 47, 428-36 (1951).
62. Maddock and Stein, J. Chem. Soc. Supplement No. 2, (1949)  
258-9.



63. Misciatelli, Gazz. Chim. Ital. 60, 839-42 (1930) by way of C.A. 25, 1453 (1931).
64. Ibid., 60, 833-8 (1930) by way of C.A. 25, 1452 (1931).
65. Mitchell and Smith, Aquametry, Interscience Publishers Inc., New York, 1941.
66. Moore, Interim Progress Report No. 2, A.E.C. Contract No. AT(11-1)-71 Project 1, August 1, 1953.
67. Moore and Yates, Interim Progress Report No. 1, A.E.C. Contract No. AT(11-1)-71, Project 1, May 1, 1953.
68. Morrison, Anal. Chem. 22, 1388-93 (1950).
69. Myers and Metzler, J. Am. Chem. Soc. 72, 3772-76 (1950).
70. Myers, Metzler and Swift, J. Am. Chem. Soc. 72, 3767-72 (1950).
71. Mylius and Huttner, Ber. 44, 1315 (1911).
72. Nachtrieb and Conway, J. Am. Chem. Soc. 70, 3547-52 (1948).
73. Nachtrieb and Fryxell, J. Am. Chem. Soc. 70, 3552-7 (1948).
74. Ibid., 71, 4035-9 (1949).
75. Neab, Forsvarets Forskningsinstitut Arbok II, 367-72, 1948-49 by way of N.S.A. 5, 441 (1951), abstract 2743.
76. Nernst, Z. Phys. Chem. 8, 110 (1891) by way of Quat. Rev. 5, 200 (1951).
77. Pelligot, Ann. Chim. Phys. 5, 7, 42 (1842) by way of J. Phys. and Colloid Chem. 55, 346 (1951).
78. Peppard, Faris, Gray and Mason, ABCD 3327 by way of N.S.A. 6, 336 (1950), abstract 2632.
79. Rothe, Chem. News 66, 182 (1892) by way of J. Am. Chem. Soc. 58, 2573 (1936).
80. Rothschild, Templeton and Hall, J. Phys. and Colloid Chem. 52, 1006-20 (1948).
81. Rowley and Reed, Proc. Okla. Acad. Sci. 31, 129-33 (1950).
82. Sandell, Anal. Chim. Acta 4, 504-12 (1950).
83. Scott, Standard Methods of Chemical Analysis, 5th Ed., Vol. I., D. Van Nostrand Co., New York, 1939, p. 315.

84. Scott, *Analyst* 74, 486-91 (1949).
85. Smeets, *Natuurw. Tijdsch.* 16, 262-6 (1934) by way of C.A. 29, 2883<sup>7</sup> (1935).
86. Stevenson and Hicks, URCL 2009 (1952) by way of N.S.A. 7, 170 (1953), abstract 1399.
87. Stokes, *Trans. Faraday Soc.* 44, 295 (1948).
88. Swift, *J. Am. Chem. Soc.* 46, 2375 (1924).
89. Taylor, *J. Phys. Chem.* 29, 995-1003 (1925).
90. Templeton, *J. Am. Chem. Soc.* 71, 2187-90 (1949).
91. Templeton, *J. Phys. and Colloid Chem.* 54, 1255-69 (1950).
92. Templeton and Daly, *J. Am. Chem. Soc.* 73, 3989-91 (1951).
93. Templeton and Daly, *J. Phys. Chem.* 56, 215-17 (1952).
94. Templeton and Hall, *J. Phys. and Colloid Chem.* 51, 1441-9 (1947).
95. *Ibid.*, 54, 958-63 (1950).
96. Templeton and Peterson, *J. Am. Chem. Soc.* 70, 3967 (1948).
97. Templeton, Rothschild and Hall, *J. Phys. and Colloid Chem.* 53, 838-45 (1949).
98. Topp, ONRL 1409 (1952).
99. Trevorrow, Master's Thesis, Oklahoma A. and M. College, 1952.
100. Treybal, *Ind. Eng. Chem.* 43, 79-85 (1951).
101. *Ibid.*, 44, 53-63 (1952).
102. Warf, *J. Am. Chem. Soc.* 71, 3257-8 (1949).
103. Warf, U.S. Patent 2,523,892 by way of C.A. 45, 1314a (1951).
104. Warf, AECD. 2524 (1949).
105. Warf, U.S. Patent 2,564,241 by way of C.A. 46, 696e (1952).
106. Warner, *Australian J. Appl. Sci.* 3, 156-72 (1952) by way of C.A. 46, 89371 (1952).
107. Weaver, Kappelman, and Topp, ONRL 1408 (1952).
108. Weinhardt and Hixson, *Ind. Eng. Chem.* 43, 1676 (1951).

109. Wells and Hunter, *Analyst* 73, 671 (1948).
110. West, *Metallurgia* 43, 41-46 (1951).
111. Willard and Smith, *J. Am. Chem. Soc.* 45, 286 (1923).
112. Wolfe and Fowler, *J. Am. Opt. Soc.* 35, 86 (1945).
113. Wylie, *J. Chem. Soc.* (1950) 1474-80.
114. Yates, Laran, Williams, and Moore, *J. Am. Chem. Soc.* 75, 2212 (1953).
115. Yates and Moore, *AECU* 1669 (1951).
116. Yates and Moore, *AECU* 2246 (1952).
117. Yates and Moore, Paper presented at the Gordon Conference, New Hampton School, New Hampton, New Hampshire.

## VITA

Roy J. Laran  
candidate for the degree of  
Master of Science

**Thesis:** THE LIQUID-LIQUID EXTRACTION OF METAL PERCHLORATES  
BY 2-OCTANOL

**Major:** Inorganic Chemistry

**Biographical and Other Items:**

**Born:** March 11, 1931, New Orleans, Louisiana

**Undergraduate Study:** Loyola University of the South,  
New Orleans, Louisiana, 1947-52.

**Graduate Study:** Oklahoma A. and M. College, Stillwa-  
ter, Oklahoma, 1952-

**Experience:** Research Fellow, Oklahoma A. and M. Col-  
lege, 1952-

**Member of the American Chemical Society, Phi Lambda Upsilon,  
Associate Member of the Society of Sigma Xi.**