

March 8, 1958

To the Graduate Council:

I am submitting herewith a dissertation written by Frank Falkoner Dyer entitled "Studies of the Solvent Extraction of Cadmium and Silver Dithizonates." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Geo. K. Schweitzer
Major Professor

We have read this dissertation
and recommend its acceptance:

John A. Dean
W. J. Jancich
Robert H. Doyle
A. Deuelman

Accepted for the Council:

Rob. Hanting
Dean of the Graduate School

STUDIES OF THE SOLVENT EXTRACTION OF CADMIUM AND SILVER DITHIZONATES

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by

Frank Falkoner Dyer

March, 1958

To Marjorie

ACKNOWLEDGEMENT

For financial aid during this work the author wishes to acknowledge the following sources: the U. S. Atomic Energy Commission which provided a Research Assistantship during the first few months of the study, the University of Tennessee which appointed the author Graduate Assistant for one year and gave assistance through the Rhenium Research Fund at various times, and Union Carbide Nuclear Company from which the author received for one year their annual Chemistry Fellowship to the University of Tennessee.

The author wishes to express his sincere gratitude to Dr. George K. Schweitzer for his guidance throughout this study. He would like to extend a special thanks for Dr. Schweitzer's invaluable assistance in the preparation of this dissertation.

It is the author's pleasure to acknowledge his indebtedness to his wife whose patience, help, and understanding have been of inestimable value.

TABLE OF CONTENTS

CHAPTER	PAGE
I. HISTORY.	1
A. Dithizone and Metal Dithizonates	1
1. Dithizone.	1
2. Metal Dithizonates	6
3. Solvent Extraction of Metal Dithizonates	17
B. Theory and Treatment of Data	22
1. Simple Solvent Extraction Systems.	22
2. Complex Solvent Extraction Systems	29
C. Extraction Data for Dithizone and Metal Dithizonates	37
D. Complexes of Cadmium and Silver(I)	37
1. Cadmium Complexes.	37
2. Silver(I) Complexes.	40
E. Proposed Problem	45
II. EXPERIMENTAL PROCEDURES.	49
A. Reagents	49
1. Water.	49
2. Cadmium and Silver Solutions	49
3. Dithizone.	50
4. Organic Solvents	50
5. Other Chemicals.	51
6. Silver Dithizonate	51

CHAPTER

PAGE

II. (Continued)

B. Apparatus.	52
1. pH Measurements.	52
2. Stirring and Temperature	52
3. Radioactivity Measurements	53
C. General Procedure for Extractions.	54
1. Preparation of Solutions	54
2. Equilibration.	55
3. Sampling	56
D. Solubility Measurements.	56
III. RESULTS.	58
A. Cadmium Experiments.	58
1. Non-Masked Experiments	58
2. Masked Experiments	61
3. Dithizone Concentration and Ionic Strength Changes.	62
B. Silver Experiments	62
1. Non-Masked Experiments	62
2. Masked Experiments	64
3. Organic Solvent Changes.	84
4. Dithizone Concentration Changes.	84
5. Temperature Changes.	90
6. Silver Dithizonate Solubilities.	90

CHAPTER	PAGE
IV. CALCULATIONS AND DISCUSSIONS.	92
A. Presentation of Data and Calculated Quantities. . .	92
B. Extraction Equations.	97
1. Non-Masked Experiments.	97
2. Masked Experiments.	97
C. Cadmium Experiments	99
1. Calculation of Extraction Constant.	99
2. Prediction of Effect of Masking Agents.	100
3. Prediction of Effect of Dithizone Concentration Change.	103
4. Prediction of the Value of n	104
D. Silver Experiments.	104
1. Calculation of Extraction Constants from Data of Non-Masked Extractions	104
2. Calculation of Extraction Constants from Data of Masked Extractions	105
3. Calculation of pH Values for Masked Extractions	106
4. Calculation of Stability Constants of Masking Complexes	109
5. Prediction of Effect of Dithizone Concentration Changes	110
6. Prediction of the Value of n	111
7. Calculations Involving Solubility Measurements.	112
8. Treatment of the Effect of Temperature Change .	114

CHAPTER

PAGE

IV. (Continued)

E. Activity Considerations	117
F. Conclusions	118
1. Determination of Extraction Constants	118
2. Prediction of the pH of Extraction of Masked Extractions	119
3. Calculation of Stability Constants of Masking Complexes	120
4. Prediction of Solvent Change Effect	120
5. The Effect of Temperature Change.	121
6. Suggestions for Further Work.	121
V. SUMMARY	124
BIBLIOGRAPHY	128

LIST OF TABLES

TABLE		PAGE
I.	Absorption Maxima of Metal Dithizonates in Various Solvents.	15
II.	Extraction Data for Dithizone and Metal Dithizonates. . .	38
III.	Complexes of Cadmium and Silver	41
IV.	Definition of Symbols	47
V.	Data and Calculated Quantities for Cadmium Extractions at 30° into Chloroform.	93
VI.	Data and Calculated Quantities for Silver Extractions from Perchloric Acid.	94
VII.	Data and Calculated Quantities for Silver Extraction at 30°	95

LIST OF FIGURES

FIGURE	PAGE
1. Typical Extraction Curve	20
2. Extractions of Cd from Perchlorate, Chloride, and Iodide Solutions into Chloroform.	59
3. Extractions of Cd from Perchlorate, Chloride, and Bromide Solutions into Chloroform.	60
4. Extractions of Ag from Perchloric Acid Solutions into Chloroform	63
5. Extractions of Ag from Chloride Solutions into Chloro- form	66
6. Extractions of Ag from Chloride Solutions into Carbon Tetrachloride.	68
7. Extractions of Ag from Bromide Solutions into Carbon Tetrachloride.	69
8. Extractions of Ag from 0.01-M. Bromide Solutions into Chloroform	71
9. Extractions of Ag from 0.05-M. Bromide Solutions into Chloroform	72
10. Extractions of Ag from 0.08-M. Bromide Solutions into Chloroform	73
11. Extractions of Ag from 0.1-M. Bromide Solutions into Chloroform	74
12. Extractions of Ag from 0.1-M. Bromide Solutions into Chloroform	75

FIGURE

PAGE

13.	Extractions of Ag from 0.2-M. Bromide Solutions into Chloroform.	76
14.	Extractions of Ag from 0.01-M. Iodide Solutions into Benzene	77
15.	Extractions of Ag from 0.1-M. Iodide Solutions into Benzene	78
16.	Extractions of Ag from 0.01-M. and 0.05-M. Thiocyanate Solutions into Chloroform	80
17.	Extractions of Ag from 0.1-M. Thiocyanate Solutions into Chloroform	81
18.	Extractions of Ag from 0.2-M. Thiocyanate Solutions into Chloroform	82
19.	Extractions of Ag from 1×10^{-5} -M. Thiosulfate Solutions into Chloroform	83
20.	Extractions of Ag from 0.1-M. Bromide Solutions into Dichloromethane	85
21.	Extractions of Ag from 0.1-M. Bromide Solutions into Toluene	86
22.	Extractions of Ag from 0.1-M. Bromide Solutions into Benzene	87
23.	Extractions of Ag from 0.1-M. Bromide Solutions into Chlorobenzene	88
24.	Extractions of Ag from 0.1-M. Bromide Solutions into Bromobenzene.	89
25.	Plots of $\log K$ <u>versus</u> $1/T$	115

CHAPTER I

HISTORY

A. Dithizone and Metal Dithizonates

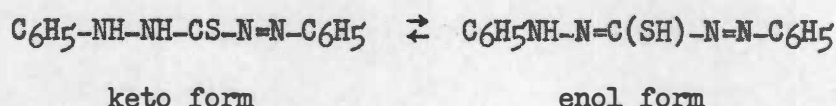
1. Dithizone

Dithizone (diphenylthiocarbazone) was first prepared and studied by Emil Fischer.^{1,2} He observed that dithizone dissolved in many organic solvents to form intense green solutions, and that it had an acidic character in water. He also reported that dithizone reacts with the ions of zinc, silver, mercury(II), and lead, and that the zinc compound produces a red solution in chloroform. Fischer gave a preparation of dithizone, and this preparation was repeated by Welcher.³ Billman and Cleland⁴ reported an improved procedure which is also repeated by Welcher. In reporting the preparation of dithizone tagged with sulfur-35, Irving and Bell⁵ reviewed a number of different methods for synthesizing the compound.

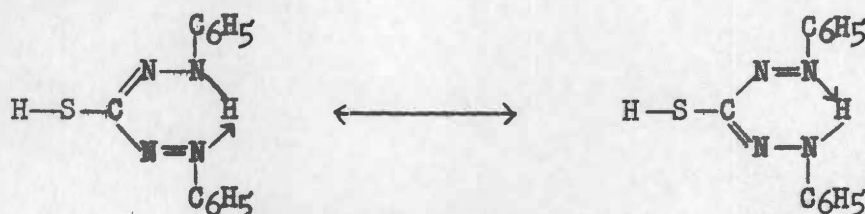
Sandell⁶ gave two methods for the purification of dithizone and Welcher³ gave one method. The more used of the two methods involves an extraction of the dithizone from an organic solution (usually chloroform) into an aqueous solution of ammonia, a separation of the two phases, an acidification of the aqueous phase, and a reextraction into an organic phase. Morrison and Freiser⁷ reported that if hydroxylamine is added to the ammoniacal solution, the dithizone might be less subject to oxidation.

Various procedures have been presented^{6,8} to make solutions of dithizone stable enough to be kept over a number of months. Sandell⁶ stated, however, that the ordinary solutions are fairly stable for a few weeks if they are stored in a cool dark place.

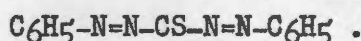
Most authors^{6,7,9} agree that the structure of dithizone can be written in terms of two tautomeric forms as follows:



It has been reported¹⁰ that dithizone may have internal hydrogen bonding leading to resonance stabilization of the enol form represented as:



Dithizone in organic solvents is very easily attacked by oxidizing agents. The product of oxidation is diphenylthiocarbadiazone with the structure



Diphenylthiocarbadiazone does not have replaceable hydrogens and does not react with metal ions. This author does not know whether or not solid dithizone decomposes slowly at room temperature. Sandell⁶ advised that when dithizone is dried of organic solvent the temperature should not go above 50°. Irving, Cooke, Woodger, and Williams¹⁰ reported that there was no decomposition of dithizone in chloroform when it was kept at 60° for ten minutes. Welcher³ reported that the decomposition range is 120-140°. Others⁷ reported that dithizone decomposes sharply at 165-169°.

Dithizone was found to be quite unstable in molten naphthalene,¹¹ and to have a rate of decomposition in molten naphthalene which is first order. From measurements of the rate of decomposition in molten naphthalene at temperatures of 100°, 110°, and 137°, it was possible to calculate an activation energy for the decomposition of 18 kcal./mole. Rate constants for the decomposition at these temperatures are 0.07, 0.14, and 0.28 min.⁻¹ respectively. This corresponds to half-times of 9.9, 5.0, and 2.5 min. respectively for these temperatures. Sandell⁶ reported that direct sunlight rapidly bleaches dithizone in carbon tetrachloride and chloroform solutions at relatively high temperatures. Clifford⁸ stated that when dithizone is dissolved in chloroform direct sunlight produces phosgene from the chloroform, and the phosgene then oxidizes the dithizone. Sandell⁶ gave some methods for preparing solvents free of oxidizing agents.

Irving and others¹⁰ have investigated the stability of dithizone in a 1.5-N. ammonium hydroxide solution by a spectrophotometric method. They reported that the absorbing specie was decomposed at a rate of 20-30 per cent per hour. The rate of decomposition was not much affected by increased illumination or total exclusion of light. Exclusion of air or a steady introduction of oxygen bubbles had no appreciable effect on the rate of decomposition. However they reported that hydroxylamine and traces of metals caused an increase in the rate of decomposition. Sulfite ions appeared to have no influence. It was stated that the rate of decomposition was much slower in 0.15-N. ammonium hydroxide. From the effect of the alkalinity on the rate of decomposition they postulated

a hydrolysis or base catalyzed dismutation of the dithizone.

Sandell⁶ reported that the solubility of dithizone in chloroform at room temperature is 7×10^{-2} moles/l. and in carbon tetrachloride 1.7×10^{-3} mole/l. Honaker¹³ appears to be the only one who has determined the solubility of dithizone in a number of solvents at a definite temperature. Honaker's data in moles/l. at 30° are as follows: chloroform, 7.9×10^{-2} ; dichloromethane, 4.9×10^{-2} ; benzene, 1.4×10^{-2} ; chlorobenzene, 9.8×10^{-3} ; carbon tetrachloride, 2.9×10^{-3} . Fischer² noted that dithizone was relatively insoluble in neutral aqueous solutions but was soluble in alkaline aqueous solutions. Geiger and Sandell¹² obtained the solubility of dithizone in water to be equal to approximately 1×10^{-7} moles/l. at 25° .

Dithizone in the solid state is a very dark purple substance. The color of dilute solutions in chloroform and in carbon tetrachloride is reported⁶ to be green. Sandell repeated what Fischer¹⁴ reported: that dithizone in highly polar solvents such as nitrobenzene gives a yellow solution. Honaker,¹³ however, has shown that nitrobenzene and nitromethane solutions of dithizone are green. He reported that after hours of standing the dithizone is oxidized, and a yellow solution is formed. Honaker also says that a dichloromethane solution of dithizone has a blue color. He explained this color in terms of the height of an absorption peak in the visible range (600 mu.).

Many have reported the spectrum of dithizone in various solvents. The typical curve shows two peaks, one around 450 mu. and the other around 620 mu. The position of the peaks in mu. have been reported in

chloroform (435,610),¹⁵ carbon tetrachloride (450,620),^{3,6} tetrachloroethylene (—,620),¹⁶ iso-amyl alcohol (460,580),¹⁸ methyl ethyl ketone (460,590),¹⁸ carbon disulfide (450,650),¹³ nitrobenzene (450,620),¹³ chlorobenzene (450,620),¹³ and dichloromethane (440,610).¹³

Dithizone though only very slightly soluble in water does dissolve and ionize to a small degree. Fischer² found acidic properties for dithizone, and Buch and Koroleff¹⁹ describe conditions under which it acts as a monobasic acid. Irving, Cook, Woodger, and Williams¹⁰ made a study of the acidic properties of dithizone and reported that it acts as a monobasic acid up to a pH of 12. Sandell¹⁶ gave a good survey of the equilibria associated with dithizone and said that even though dithizone acts as a monobasic acid up to a pH of 12 it must be assumed that it has a slight tendency to ionize as a dibasic acid. If one represents the formula of dithizone as HD, one can symbolize the equilibrium which exists in water between the unionized dithizone, hydrogen ion H^+ , and dithizonate ion D^- as



Following the convention of Irving and Williams,²⁰ the equilibrium constant for Eq. 1 can be represented as K_r , so that we write

$$K_r = \frac{(H)(D)}{(HD)}. \quad \text{Eq. 2}$$

In this work the charges of ions will be omitted when they occur in equations. The parenthesis indicate concentrations expressed in moles per liter,^{6,20} K_r then has the units of moles/l. The first value of K_r , obtained in 1949¹⁰ from extraction experiments, was 2×10^{-6} moles/l. at 20°. By showing that the acid strength of dithizone lies between the

acid strengths of methyl-red and bromthymolblue in a monophasic water-ethanol-chloroform, these same investigators¹⁰ were able to estimate K_r to be 3×10^{-6} moles/l. at 20° . Sandell²¹ in 1950 obtained a value of K_r equal to 1.5×10^{-5} moles/l. at 25° which obviously was not in agreement with the previous values. Sandell allowed dithizone to partition between carbon tetrachloride nearly saturated with dithizone and water which was either 0.1-N. or 0.01-N. in hydrochloric acid to obtain K_r . Irving and Bell²² in 1952 rejected previous values of K_r ¹⁰ and using an improved technique obtained a value of K_r equal to 3×10^{-5} moles/l. at 20° . These experiments by Irving and Bell consisted of extractions of dithizone from cyclohexane, carbon tetrachloride, and chloroform into an aqueous phase which was 0.1-N. in hydrochloric acid and 0.14-N. in sodium nitrate. In this same year Dyrssen and Hok²³ employed a radiotracer technique to obtain K_r to be 3×10^{-5} moles/l. at 25° .

Due to the fact that dithizone is slightly soluble and ionizes in water, a solubility product constant may be written. This constant has been obtained by Sandell²¹ to be 3×10^{-12} moles²/l.² at 25° . Dyrssen and Hok²³ gave a value of 9×10^{-10} moles²/l.² at 25° . The solubility product constant is defined as

$$K_{sp} = (H)(D). \quad \text{Eq. 3}$$

2. Metal Dithizonates

The discovery of the metal dithizonates must be an honor given to Emil Fischer,^{1,2} for as previously stated he found that dithizone reacts with the ions of zinc, lead, mercury(II), and silver. H. Fischer and others working with him observed reactions between dithizone and the

following ions: manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc, palladium(II), silver, cadmium, indium, tin(II), platinum(II), gold(I), mercury(II), thallium(I), lead, and bismuth. These reactions along with the determinations of these elements with dithizone are reported in two excellent papers by Fischer.¹³ Sandell⁶ summarized Fischer's data and said that iron(II), tin(II), and platinum(II) will react with dithizone, but that iron(III), tin(IV), and platinum(IV) will not react. Other authors^{24,25,26} have extended the list of metals above to include polonium(II). Filipenko²⁷ was unable to obtain a reaction between gallium(III) and dithizone.

Two methods are available for the preparation of metal dithizonates. The method most commonly used^{3,6} consists of shaking an aqueous solution of a metal ion in contact with a solution of dithizone in an organic solvent. The metal dithizonate is then obtained in the organic phase. To recover the solid compound, the organic phase can be separated from the aqueous phase and evaporated. The second method of preparation is the one used by Wasserman and Ssuprunowitsch²⁸ for the preparation of zinc dithizonate. In this method an aqueous solution of metal ions is mixed with an ammoniacal aqueous solution of dithizone to precipitate the metal dithizonate. Honaker¹³ used this method to prepare zinc dithizonate and found considerable amounts of impurity in the products which he removed by dissolving the zinc dithizonate in chloroform.

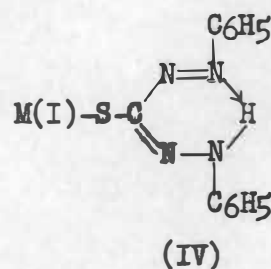
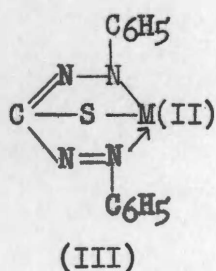
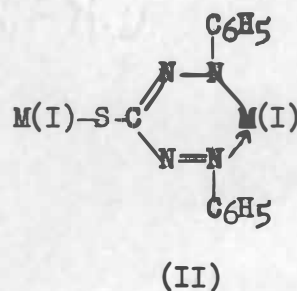
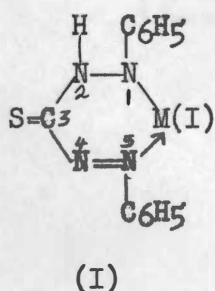
Since, as Sandell⁶ points out, dithizone may have two replaceable hydrogens, it cannot be decided a priori how many dithizonate groups are attached to a metal ion. By chemical analysis of silver and zinc dithizonates, Emil Fischer and Emil Besthorn² showed that there was one dithizonate

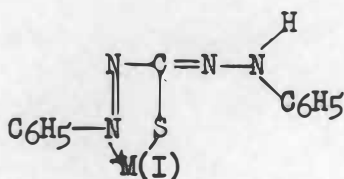
group attached to a silver ion and two attached to a zinc ion. H. Fischer²⁸ was led early to advance his ideas of the composition and structure of enol and keto dithizonates. The meanings of the terms keto and enol as applied to metal dithizonates are today misleading. The terms will be explained below in connection with the discussion of the structures of metal dithizonates. Fischer's ideas of the structure and composition of metal dithizonates seem to have arisen from his knowledge of the structure of dithizone and composition of the copper(II) and silver dithizonates, for he was able to chemically analyze the solid metal dithizonates. Fischer said that a keto dithizonate was formed from a metal ion and dithizonate ions which were formed by the loss of one hydrogen ion. This means that a metal ion with a valence n would react with n singly charged dithizonate ions to form the keto form of the metal dithizonate. In order for the enol form to result Fischer maintained that dithizone would have to lose two hydrogen ions. Therefore, a metal ion with a charge of n would react with $n/2$ doubly charged dithizonate ions to yield the enol form of the metal dithizonate. Fischer believed at the time of his work that the keto forms of all metal dithizonates exist but that the enol form of many metals were not known. One can see that the composition of the aqueous phase, e. g., pH or buffer concentration, determines to a large degree which form, enol or keto, will be obtained. Sandell⁶ stated that copper, silver, and mercury(II) readily form both monobasic and dibasic dithizonates. According to Sandell monobasic dithizonates preferentially form in an acidic solution, and dibasic dithizonates form when the solution is alkaline or when there is a deficiency of dithizone.

A large number of experiments have been performed in order to determine the stoichiometry of metal dithizonates. Liebhafsky and Winslow³⁰ extracted lead dithizonate from an ammoniacal aqueous solution into carbon tetrachloride, separated the phases, extracted the excess dithizone from the carbon tetrachloride with an ammonia solution, and determined the amount of dithizone bound to the lead by extracting the lead into an acid solution, leaving the dithizone in the carbon tetrachloride phase for spectrophotometric determination. A ratio of lead to dithizone in the complex was reported as one to one. In this same paper the formula of copper dithizonate was reported to be CuD_2 . The initial extraction of copper into carbon tetrachloride was performed using an aqueous phase which was 0.3-N. in perchloric acid. Clifford and Wichman³¹ extracted lead dithizonate from a slightly basic aqueous solution and identified the extracted specie as PbD_2 . Cooper and Hibbits³² using the method of continuous variations obtained results which showed lead dithizonate to have the formula PbD_2 when extracted from an aqueous buffer with a pH of 9.5. Miyakawa and Uemura,³³ using a modified form of the method of continuous variation, have identified the species CoD_2 , NiD_2 , and AuD . The cobalt and nickel dithizonates were extracted from an acetate buffer with a pH of 6.0. Cooper and Sullivan³⁴ established the formulas ZnD_2 , HgD_2 , PbD_2 , and AgD . In this case, lead and zinc dithizonates were extracted from an aqueous phase with a pH of approximately 8, silver dithizonate was extracted from an aqueous phase which was 0.1-M. in ammonium nitrate, and mercury dithizonate was extracted from a dilute ammonia solution. Chernitskaya¹⁸ has prepared

silver dithizonate and found it to be AgD . Pilipenko³⁵ has studied the dithizonates of mercury(II), bismuth, copper(II), silver, cobalt(II), nickel, tin(II), iron(II), and manganese(II) and found the following formulas: HgD_2 , BiD_3 , CuD_2 , AgD , CoD_2 , NiD_2 , SnD_2 , FeD_2 , and MnD_2 . Previously Pilipenko³⁶ reported the formulas of thallium(I) and indium dithizonates to be TlD and InD_3 . Polonium dithizonate has also been extracted from fairly acid solutions.^{37,38} The formula of the specie extracted was estimated to be either PoD_2 or PoOD_2 . Irving, Risdon, and Andrew³⁹ have extracted lead, silver, mercury(II), and bismuth dithizonates and found formulas of PbD_2 , HgD_2 , BiD_3 , and AgD . The very extensive solvent extraction studies which have been done with zinc dithizonate^{40,42,43} show it to have two dithizonate groups bound to one zinc ion. The conditions under which copper(II), mercury(II), and silver form both primary and secondary dithizonates have been quantitatively explained.^{42,43}

The structural formula of metal dithizonates have been written a number of ways:

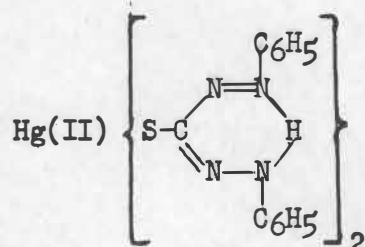




(V)

Structures I, II, IV, and V are shown with a monovalent metal. It is understood that the structure of a divalent metal dithizonate would be changed only to include two dithizonate groups attached to the metal ion. Structures I, II, and III are the ones proposed by Fischer²⁹ in 1934. Fischer believed that the keto form of dithizone could lose the hydrogen in the one position (numbered as I is numbered) and form I. This structure he called the "keto" form. If the aqueous phase in which the metal ion is dissolved is sufficiently alkaline or if the dithizone is present in deficient amounts, then Fischer believed the second hydrogen could enolize to the sulfur and then ionize allowing structure II to be formed. This structure Fischer called the enol metal dithizonate. In the case of a divalent metal ion Fischer represented the enol form by structure III. Various authors^{11,42} have very recently written the structures of the metal dithizonates as Fischer wrote them, and the reports of metal dithizonates which have previously used the Fischer formulas are too numerous to mention. It is unfortunate that Fischer had very little, if any, experimental information upon which to base the structures which he reported. In 1949 Irving, Cooke, Woodger, and Williams¹⁰ began to draw attention to the lack of experimental data about the structures of the metal dithizonates. These investigators reported that dithizone may be stabilized by internal hydrogen bonding and that

the first hydrogen to ionize may come from the thiol group and result in a dithizonate ion similarly stabilized. Consequently mercury(II) dithizonate was written as



This represents a divalent metal dithizonate corresponding to IV for a monovalent metal dithizonate. It was stated¹⁰ that previous workers had not considered the part which resonance plays in the structures of metal dithizonates. Irving and Bell^{9,41} later expanded on their reasons for postulating structure IV and added experimental evidence in favor of this formulation. They argued that if I is formed the second hydrogen should migrate to the sulfur resulting in resonance stabilization. In that event the thiol group should show acidic properties which they said had not been observed. Replacing the hydrogen on the thiol group of the enol form of dithizone, forming 3-methylthio-1,5-diphenylformazan, resulted in a compound which was insoluble in alkaline solutions and which would not react with metal ions under conditions which ordinarily lead to metal dithizonates. This evidence though not completely conclusive lent great support to the validity of IV. Irving and Bell⁹ said that next they would try N-alkyl derivatives of dithizone to see if the thiol group would be acidic and complex with metal ions. This author has not found the published results of that research. Morrison and Freiser⁷ have taken the data and ideas of Irving and Bell¹⁰ and have written what amounts to V for the structure of metal dithizonates. Martell and

Calvin⁴⁵ had previously written the structure given by Morrison and Freiser as a possible structure of a metal dithizonate. It appears that in V the contribution of the resonance energy would be lost. These same authors⁷ stated that the "enol" form of the dithizonates would probably involve dithizone as a tridentate chelating agent. The word "enol" appears in quotations because obviously the terms "keto" and "enol" do not now have the same meaning which Fischer²⁹ intended for them. Many authors⁶ now use the terms "primary" and "secondary" or "monobasic" and "dibasic" to designate metal dithizonates which form when a metal ion reacts with singly or doubly charged dithizonate ions respectively. It remains to be shown, however, whether the primary metal dithizonates are chelates or unidentate complexes.

It appears that the stability of metal dithizonates either in solution or in the solid state toward oxidizing agents and heat has been investigated very little. H. Fischer⁴⁶ reported that at high temperatures solid dithizonates would decompose explosively. Pariand and Archinard⁴⁷ made a thermogravimetric analysis of the so-called keto dithizonates of silver, lead, copper(II), and zinc. Silver dithizonate was found to decompose very little, if any, up to a temperature of 120°; the decomposition then became more rapid as the temperature increased to 180°. At 180° the decomposition was almost explosive. Lead dithizonate was stable up to 80°, and was found to decompose very rapidly at 215°. Zinc dithizonate was stable to 120°, and decomposed very rapidly at 225°. Copper dithizonate was found to be stable at 75° and to decompose almost explosively at 150°. Sandell⁶ stated that dithizonates are sometimes quite

unstable when they are extracted from a strongly basic medium, and that the color fades rapidly. One might suppose that the metal dithizonates are more stable toward heat than dithizone since it was possible to obtain the spectra of metal dithizonates in molten naphthalene at elevated temperatures and impossible to obtain a good spectrum of dithizone due to decomposition.¹¹

Solubility measurements of metal dithizonates in organic solvents are scant indeed. Geiger and Sandell¹² reported the solubilities in carbon tetrachloride at 25° of primary and secondary copper(II) dithizonates to be 5.3×10^{-4} and 1.2×10^{-3} mole/l. respectively. Honaker¹³ gave the following solubilities of zinc dithizonate at 30° in the designated solvents: chloroform, 3.7×10^{-2} mole/l.; dichloromethane, 2.8×10^{-2} mole/l.; benzene, 4.0×10^{-3} mole/l.; chlorobenzene, 8.1×10^{-3} mole/l.; carbon tetrachloride, 1.3×10^{-3} mole/l. Metal dithizonates were found by E. Fischer² to be relatively insoluble in water.

Fischer⁴⁸ was the first to make a detailed study of the spectra of metal dithizonates. The typical spectrum usually shows at least one absorption maximum in the visible range, two maxima being reported⁴⁸ in some cases. Table I gives some of the absorption maxima in μ . (10^{-7} cm.) for metal dithizonates in several solvents.

The metal dithizonates, though usually classified as insoluble in water, will dissolve to a slight extent to establish the equilibrium



The metal dithizonate and the metal ion with a valence of $n+$ are represented by MD_n and M^{n+} respectively. Following the conventions of Irving

TABLE I

ABSORPTION MAXIMA OF METAL DITHIZONATES IN VARIOUS SOLVENTS

Metal Dithizonate	Absorption Maximum(a)	Solvent	Reference Number
Silver ^a	480	Carbon tetrachloride	48
Silver ^a	480	Carbon tetrachloride	50
Silver ^a	460	Carbon tetrachloride	51
Silver ^a	450	<u>Iso-amyl</u> alcohol	51
Nickel (II)	510	Carbon tetrachloride	48
Cobalt (II)	560	Carbon tetrachloride	48
Tin (II)	505	Carbon tetrachloride	48
Tin (II)	520	Molten naphthalene	11
Bismuth	505	Carbon tetrachloride	48
Bismuth	505	Molten naphthalene	11
Bismuth	490	Carbon tetrachloride	50
Lead	520	Carbon tetrachloride	48
Lead	522	Carbon tetrachloride	50
Lead	525	Carbon tetrachloride	51
Lead	505	<u>Iso-amyl</u> alcohol	51
Thallium (I)	510,620	Carbon tetrachloride	48
Mercury (II) ^b	500	Carbon tetrachloride	48
Mercury (II) ^b	490	Molten naphthalene	11
Mercury (II) ^b	310,483	Carbon tetrachloride	50
Mercury (II) ^b	530	Carbon tetrachloride	51
Mercury (II) ^b	530	Carbon tetrachloride	48
Mercury (II) ^b	300,500	Carbon tetrachloride	50
Mercury (II) ^a	490	<u>Iso-amyl</u> alcohol	51
Zinc	530	Carbon tetrachloride	48
Zinc	280,520,635	Carbon tetrachloride	50
Zinc	535	Carbon tetrachloride	51
Zinc	535	Chlorobenzene	13
Zinc	535	Benzene	13
Zinc	535	Dichloromethane	13
Zinc	505	<u>Iso-amyl</u> alcohol	51
Cadmium	505	Carbon tetrachloride	48
Cadmium	520	Carbon tetrachloride	49
Cadmium	280,540	Carbon tetrachloride	50
Cadmium	510	Carbon tetrachloride	51
Cadmium	500	<u>Iso-amyl</u> alcohol	51

TABLE I

ABSORPTION MAXIMA OF METAL DITHIZONATES IN VARIOUS SOLVENTS (Continued)

Metal Dithizonate	Absorption Maximum(a)	Solvent	Reference Number
Copper (II) ^a	560	Carbon tetrachloride	48
Copper (II) ^a	310,555	Carbon tetrachloride	50
Copper (II) ^a	510	Carbon tetrachloride	51
Copper (II) ^a	500	<u>Iso</u> -amyl alcohol	51
Copper (II) ^b	450	Carbon tetrachloride	48
Copper (II) ^b	308,455	Carbon tetrachloride	50
Antimony (III)	510	Molten naphthalene	11

^aPrimary metal dithizonate.^bSecondary metal dithizonate.

and Williams²⁰ the equilibrium constant for this equilibrium may be written as

$$K_c = \frac{(M)(D)^n}{(MD_n)} \quad \text{Eq. 5}$$

This constant has been determined only for copper(II).¹² A value was given equal to approximately $10^{-23} \text{ moles}^2/\text{l}^2$ at 25° . The units of K_c in general will be $\text{moles}^n/\text{l}^n$.

3. Solvent Extraction of Metal Dithizonates

Most of the early research on solvent extraction of metal dithizonates had the following objectives: to define conditions under which a particular metal dithizonate would form and extract, and to define conditions under which two or more metals could be separated from each other by this extraction technique. The technique employed in extracting a metal dithizonate usually consisted of shaking together an organic phase (most often chloroform or carbon tetrachloride) containing dithizone and an aqueous phase containing the metal ion. The amount of metal dithizonate extracted was then determined colorimetrically, gravimetrically, or by destroying the dithizonate and determining the metal by some other means. The conditions needed to extract a particular metal dithizonate or separate two or more metal ions were obtained in an almost totally empirical manner. Determination of these conditions involved finding optimum values for the pH of the aqueous phase, the concentration of dithizone in the organic phase, the relative volumes of the two phases, and the concentration of complexing salts (or masking agents as they are usually now called) if these salts were needed. Separations were usually

effected by proper adjustments of these variables. The literature is replete with detailed empirical procedures for the separation of metal ions by extraction with dithizone. Hellmut Fischer in 1937¹⁴ published a review of the subject which listed 74 references. Welcher³ in 1947 gave 212 references dealing mainly with the solvent extraction of metal dithizonates. Welcher summarized in great detail the preparation of special solutions (adjusting the various controlling factors listed above) to allow the solvent extraction of metal dithizonates. The use of the masking agents (such as citrate, tartrate, cyanide, thiocyanate, thiosulfate, iodide, chloride, and bromide) along with the adjustment of the acidity so as to allow certain metals to extract while complexing or masking others were discussed fully by Welcher.

The placing of the solvent extraction of metal dithizonates on a systematic or theoretical basis was begun in 1939⁵² when Wichmann published his survey. In that paper Wichmann called to the attention of physical chemists the need for further investigation of the equilibria involved in these extractions. Great emphasis was placed on the value of obtaining equilibrium curves of per cent of metal extracted versus pH of the aqueous phase. From the work which had previously been done with lead³¹ and from "bits of information picked here and there from the literature" provisional equilibrium curves (per cent extraction versus pH) were drawn for the ions of silver(I), mercury(II), tin(II), bismuth, copper, zinc, lead, cadmium, and thallium(I). Wichmann made no claim of accuracy for these curves but used them to illustrate how separations might be predicted and explained if the true equilibrium curves were known. Wichmann said that complicated equilibria were involved in the

extractions, and he made comments about how factors which affect these equilibria would affect these equilibrium curves.

A typical equilibrium or extraction curve for a monovalent metal is shown in Figure 1. The abscissa is plotted in terms of pH units measured from the point of 50 per cent extraction. The pH of 50 per cent extraction is designated by $\text{pH}_{\frac{1}{2}}$. For a divalent or trivalent metal ion the curve is much steeper, and extraction goes from low to high percentages in a much smaller pH range. These extraction curves will be analyzed in much greater detail later. Wichmann⁵² stated that an increase or decrease of dithizone concentration in the organic phase or metal ion concentration in the aqueous phase would result in a family of curves displaced to lower or higher pH ranges respectively. Wichmann reported that in general the more noble the metal the lower would be the pH of extraction. He gave the following order of extraction as the pH is increased: gold(I), platinum(II), palladium(II), silver(I), mercury(II), tin(II), copper, bismuth, zinc, cobalt(II), nickel(II), lead, thallium(I), and cadmium. It was stated, however, that there were numerous co-extractions. Hydrolysis of some metal ions at high pH values will cause these ions to revert into the aqueous phase. Wichmann gave a treatment of hydrolysis and showed the reversion of tin(II), bismuth, zinc, and lead in his provisional equilibrium curves. Wichmann predicted that extraction curves with carbon tetrachloride would be shifted approximately one pH unit to the left of the corresponding curves in chloroform.

Kolthoff and Sandell⁴⁰ in 1941 considered the extraction of a divalent metal dithizonate. Equations were derived to describe the extraction for the case in which the metal ion is not hydrolyzed and for the

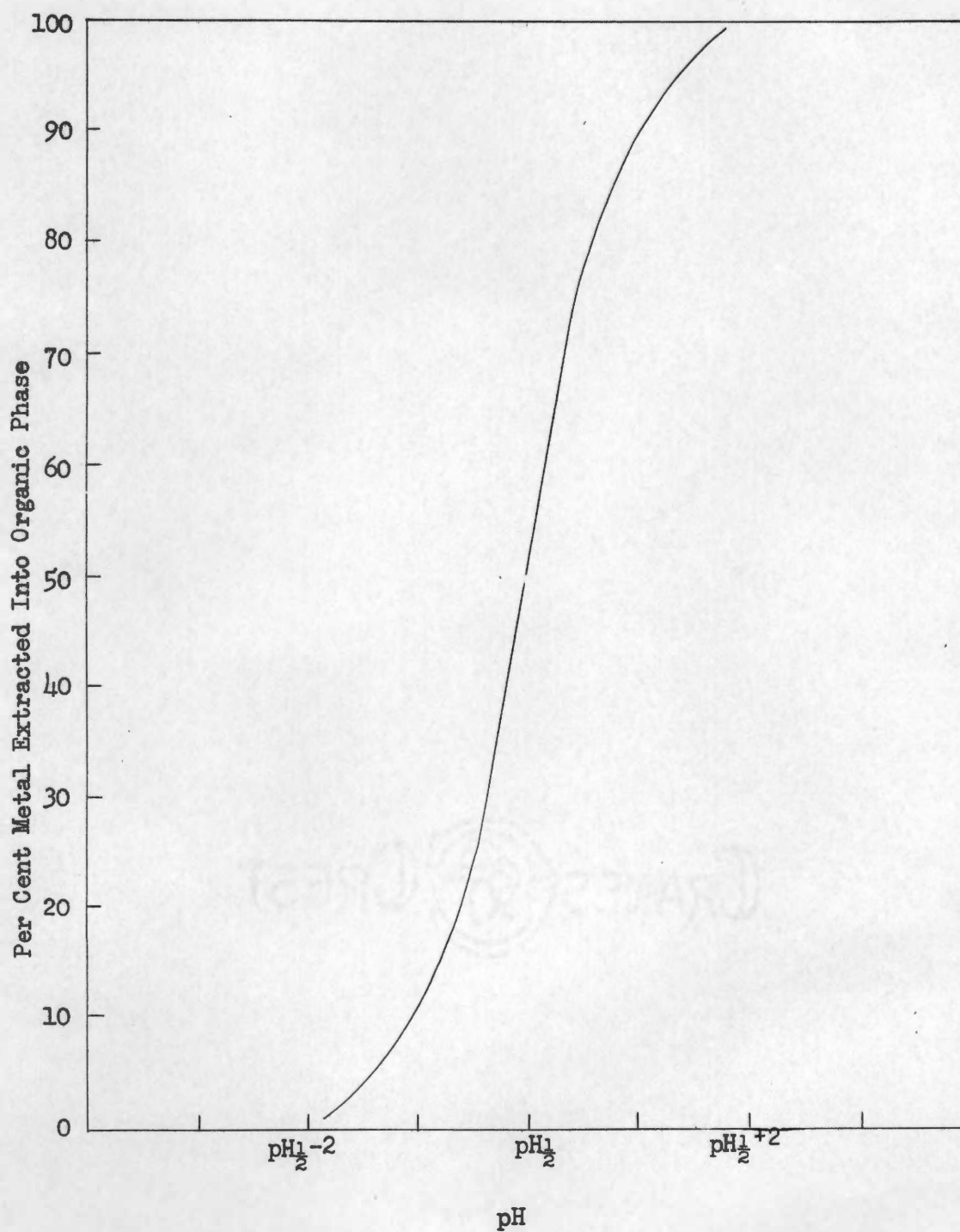


Figure 1. Typical Extraction Curve of Metal(I) Dithizonate.

case in which the metal ion is hydrolyzed. Experimentally, zinc was the ion investigated. The pH was not varied enough to obtain a complete extraction curve. Equilibria were attained, however, at a few definite pH values, and the equation for the case of no hydrolysis was found to apply.

Concepts involved in the solvent extraction of metal dithizonates or systems similar to metal dithizonates with a metal of valence n were expanded and generalized by Irving and Williams²⁰ in 1949. The variables considered were: pH, concentration of dithizone or complexing reagent in the organic phase, organic solvent, valence of the metal ion, and nature of chemical species present in terms of relevant equilibrium constants.

The effects of the variation of temperature and ionic strength on the solvent extraction of metal dithizonates have not been investigated. Work of this type can be found for some other systems. Waggener and Stoughton⁵³ investigated the chloride complexing of thorium as a function of ionic strength by a solvent extraction method. The per cent of extraction of complexes of uranium(IV) and high molecular weight amines from an aqueous phase into kerosene has been reported to decrease as the temperature is increased.⁵⁴ Increasing the temperature was also found to decrease the solvent extraction of the thiocyanate complexes of iron(III), chromium(III), aluminum, and titanium(III).⁷

B. Theory and Treatment of Data

1. Simple Solvent Extraction Systems

In almost all cases of solvent extraction only electrically neutral chemical species will extract into the organic phase so that usually in the solvent extraction of metal complexes only one or two chemical species containing the metal ion will exist in the organic phase. Sometimes, however, a number of chemical species both charged and uncharged which contain the metal ion will exist in the aqueous phase. As the number of chemical species containing the metal ion increases in the aqueous phase the equations which describe the extraction become correspondingly more and more complicated. The systems to be described in this section are those with a very few (sometimes essentially only one) such species in the aqueous phase.

For the solvent extraction of dithizonates of divalent metal ions Kolthoff and Sandell⁴⁰ in 1941 derived the following expression for the ratio of the concentration of metal dithizonate in the organic phase to the metal ion concentration in the aqueous phase:

$$\frac{(\text{MD}_2)_o}{(\text{M})} = \frac{K(\text{HD})_o^2}{(\text{H})^2} \quad \text{Eq. 6}$$

The subscript o represents the organic phase; all other species are in the aqueous phase. This ratio was designated the extractability. Kolthoff and Sandell called K the equilibrium constant for the extraction. In this work the constant will be known as the extraction constant. Sandell⁶ has stated that for expressions such as Eq. 6 to be strictly accurate, thermodynamic activities should be used in place of concentra-

tions. Concentrations (which are accurate enough for most purposes) will be used in most equations in this dissertation. Sandell⁶ also stated that two divalent metal ions may be separated fairly satisfactorily by the solvent extraction of their dithizonates if the extraction constants differ by a factor of 1000.

Sandell⁶ later derived the expression for K simply by writing an equation for the equilibrium which exists for the over-all extraction and is given by



The equilibrium constant for this reaction is the extraction constant K. In this same work⁶ Sandell also gave a derivation of K which was similar to the derivation given by Kolthoff and Sandell.⁴⁰ Experimentally Eq. 6 is tested by varying the concentration of dithizone in the organic phase or the hydrogen ion concentration in the aqueous phase. If the value of K remains reasonably constant when these quantities are varied, the equation is assumed to be valid for the system or to be valid at least over the ranges of $(HD)_o$ and (H) investigated. Kolthoff and Sandell⁴⁰ extracted zinc dithizonate from an aqueous solution buffered with phthalate into chloroform and found a value of K equal to approximately 3. However, they did not vary the hydrogen ion concentration to a very large degree. It is obvious from Eq. 6 that for the equation to be valid the metal in the aqueous phase must be present essentially only as the metal ion.

Kolthoff and Sandell⁴⁰ also derived an expression for the ratio of the total concentration of metal (metal in all chemical species) in the organic phase to the total concentration of metal in the aqueous phase

for the case in which hydrolysis of the metal ion takes place in the aqueous phase. This ratio is given by

$$\frac{(MD_2)_o}{(M)_t} = \frac{K(HD)_o^2}{(H)^2 + K_{1h}(H) + K_{2h}} \quad \text{Eq. 8}$$

The quantity $(M)_t$ equals the total metal concentration in the aqueous phase and is given by

$$(M)_t = (M) + (MOH) + (M(OH)_2) \quad \text{Eq. 9}$$

The constants K_{1h} and K_{2h} are defined by

$$K_{1h} = \frac{(MOH)(H)}{(M)} \quad \text{Eq. 10}$$

and

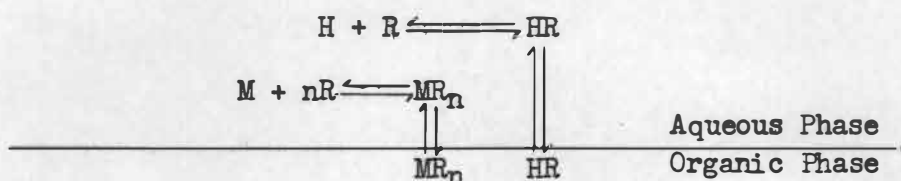
$$K_{2h} = \frac{(M(OH)_2)(H)^2}{(M)} \quad \text{Eq. 11}$$

If hydrolysis is complete, that is to say if all of the metal in the aqueous phase is present as $M(OH)_2$, then Eq. 8 reduces to

$$\frac{(MD_2)_o}{(M)_t} = \frac{K(HD)_o^2}{K_{2h}} \quad \text{Eq. 12}$$

Eq. 12 predicts that the extraction is independent of pH or hydrogen ion concentration whenever all of the metal in the aqueous phase is present as $M(OH)_2$. Kolthoff and Sandell⁴⁰ did not test Eq. 8 and Eq. 12.

Irving and Williams²⁰ and Furman, Mason, and Pekola⁵⁵ in 1949 expanded on the work of Kolthoff and Sandell⁴⁰ by taking into consideration the presence of metal complex in the aqueous phase. Irving and Williams diagrammatically represented the solvent extraction of a complex of a metal with a valence n as follows:



The reagent, HR, partitions into the aqueous phase and ionizes; the ion, R^- , then reacts with the metal ion, M^{n+} , to form the metal complex, MR_n , which then partitions into the organic phase. Equilibrium constants for the four equilibria are the ionization constant for the reagent, K_r , the dissociation constant of the complex, K_c , the partition coefficient for the reagent, P_r , and the partition coefficient for the metal complex, P_c . The constants K_r and K_c are given by Eq. 2 and Eq. 5 respectively when the complexing reagent is dithizone. The constants P_r and P_c may be written as

$$P_r = \frac{(\text{HR})}{(\text{HR})_o} \quad \text{Eq. 13}$$

and

$$P_c = \frac{(\text{MR}_n)}{(\text{MR}_n)_o} \quad \text{Eq. 14}$$

Irving and Williams called the ratio of the total metal concentration in the organic phase to the total metal concentration in the aqueous phase the true extractability, symbolizing it E_t . The true extractability is thus given by

$$E_t = \frac{(\text{MR}_n)_o}{(\text{MR}_n)_o + (\text{M})} \quad \text{Eq. 15}$$

Irving and Williams then made the following derivations. Dividing the numerator and denominator of Eq. 15 by the numerator one obtains

$$E_t = \frac{1}{P_C + \frac{(M)}{(MR_n)_o}} \quad \text{Eq. 16}$$

The following relations hold for the second member of the denominator of Eq. 16.

$$\frac{(M)}{(MR_n)_o} = \frac{(M)(MR_n)(R)^n(H)^n(HR)^n(HR)_o^n}{(MR_n)_o(MR_n)(R)^n(H)^n(HR)^n(HR)_o^n} = \frac{P_C K_C (H)^n}{P_R^n K_R^n (HR)_o^n}$$

The true extractability now becomes

$$E_t = \frac{1}{P_C + \frac{P_C K_C (H)^n}{P_R^n K_R^n (HR)_o^n}} \quad \text{Eq. 17}$$

Since the complex is usually much more soluble in the organic phase than in the aqueous phase the quantity P_C is quite small. Thus P_C as the first member of the denominator of Eq. 17 does not become significant in the equation until E_t becomes quite large. It is thus possible to omit P_C in this position allowing one to write what Irving and Williams called the extractability, E .

$$E = \frac{P_R^n K_R^n (HR)_o^n}{P_C K_C (H)^n} \quad \text{Eq. 18}$$

Eq. 18 is equivalent to

$$\frac{(MR_n)_o}{(M)} = \frac{P_R^n K_R^n (HR)_o^n}{P_C K_C (H)^n} \quad \text{Eq. 19}$$

By analogy with Eq. 6 it is seen that

$$E = \frac{K(HR)_o^n}{(H)^n} \quad \text{Eq. 20}$$

where K is the extraction constant of Eq. 6. The relation between the true extractability and the extractability can be easily shown to be

$$E_t = \frac{E}{1 + P_C E} . \quad \text{Eq. 21}$$

Irving and Williams expressed the opinion that the reason that various metal dithizonates extract at widely different pH values is due to different values of K_C and that the constants P_C do not vary significantly.

Irving and Williams wanted not only to show the effect on the extractability of the presence of the metal complex in the aqueous phase but also to derive an expression for the per cent extraction as a function of pH. This relationship was obtained in the following manner. By taking the logarithm of Eq. 20 one obtains

$$\log E = \log K + n \log (HR)_0 + npH . \quad \text{Eq. 21}$$

By applying the definition of $pH_{\frac{1}{2}}$ which was previously given, Eq. 21 at 50 per cent extraction becomes

$$0 = \log K + n \log (HR)_0 + npH_{\frac{1}{2}} . \quad \text{Eq. 22}$$

If one subtracts Eq. 21 from Eq. 22, one obtains

$$-\log E = n(pH_{\frac{1}{2}} - pH) . \quad \text{Eq. 23}$$

From the following relation between per cent extraction designated x and the extractability

$$E = \frac{x}{100 - x} ,$$

one may write Eq. 23 as

$$\log \frac{100 - x}{x} = n(pH_{\frac{1}{2}} - pH) . \quad \text{Eq. 24}$$

This is an equation expressing a relation between the per cent extraction x and the difference between the pH of 50 per cent extraction and the pH.

Irving and Williams also obtained a more direct relation between x and the quantity $(pH_{\frac{1}{2}} - pH)$ by taking the inverse of Eq. 24. The relation is

given by

$$x = 50 \left[1 - \tanh 1.15 \ln(\text{pH}_2 - \text{pH}) \right] \quad \text{Eq. 25}$$

The typical extraction curve for a monovalent metal is obtained with either Eq. 24 or Eq. 25 if n is set equal to one. Figure 1 shows this curve. Between 25 per cent and 75 per cent extraction, it has been shown that the following expression describes the typical extraction curve,¹⁰

$$x = -57.57(\text{pH}_2 - \text{pH} - 0.87) . \quad \text{Eq. 26}$$

Eq. 25 was differentiated with respect to pH by Irving and Williams to give

$$\frac{dx}{d(\text{pH})} = 57.57n \left[1 - \tanh^2 1.15 \ln(\text{pH}_2 - \text{pH}) \right] . \quad \text{Eq. 27}$$

The middle portion of extraction curves, near pH_2 , (see Figure 1) is almost a straight line. If the pH in Eq. 27 is set equal to the pH_2 , the slope of the straight line portion of the curve is seen to be equal to $57.57n$ in units of per cent metal extracted/ pH unit.

In addition to the equations above, Irving and Williams²⁰ were able to obtain other very interesting relations which allowed them to make some important predictions. By taking the partial derivatives of Eq. 21 first with respect to pH while holding the concentration of the reagent constant, and second with respect to the concentration of reagent while holding the pH constant, it was shown that

$$\left(\frac{\partial \log E}{\partial \text{pH}} \right)_{(\text{HR})_0} = \left(\frac{\partial \log E}{\partial (\text{HR})_0} \right)_{\text{pH}} . \quad \text{Eq. 28}$$

Eq. 28 shows that a change of pH of one unit is equivalent to a change by a factor of ten in the concentration of the reagent. Irving and Williams also derived the following equation relating the hydrogen ion

concentrations when equal extractions are obtained for two different organic solvents when equal concentrations of chelating reagent are employed

$$\left(\frac{H}{H'}\right)^n = \frac{(P_R/P_R')^n}{P_C/P_C'} , \quad \text{Eq. 29}$$

where the primed quantities refer to one solvent system, and the unprimed quantities refer to another solvent system. It should be pointed out that whenever the concentration of reagent is involved in an equation such as Eq. 29, the concentration under equilibrium conditions is the quantity intended. Irving and Williams did not test Eq. 29. Honaker¹³ modified Eq. 29 to the following approximate form

$$\left(\frac{H}{H'}\right)^n = \frac{(S_R'/S_R)^n}{S_C'/S_C} , \quad \text{Eq. 30}$$

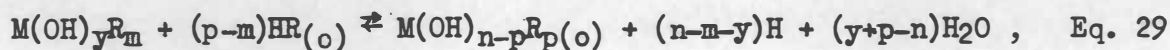
where the symbol S is used to mean molar solubility in the organic phase. Honaker measured the solubility of dithizone and zinc dithizonate in the solvents chloroform, dichloromethane, chlorobenzene, benzene, and carbon tetrachloride but was only able to confirm Eq. 30 qualitatively.

2. Complex Solvent Extraction Systems

Connick and McVey⁵⁶ extended the work of Kolthoff and Sandell³⁹ and Irving and Williams¹⁹ to include the effect on extractions of the presence of various intermediate and mixed complexes in the aqueous phase. Connick and McVey extracted from an aqueous solution into benzene the complex formed between zirconium(IV) and the ion of thenoyltrifluoroacetone (TTA) which has a unit negative charge due to the loss of one hydrogen ion. In this work the equations developed by Connick and McVey will be

shown in terms of a metal ion M^{n+} and a complexing reagent HR so that the results may be compared more easily to previous developments.

It was stated that the extraction might possibly be represented by an equation such as Eq. 2, where in the case of zirconium the coefficient of the reagent is four instead of two. However, it was felt that the complex in the organic phase might contain hydroxyl ligands as well as reagent ligands, the only requirement being that the complex in the organic phase be electrically neutral. Due to this possibility the following general equation was written for the extraction



and the equilibrium constant for this reaction was defined by

$$K_{myp} = \frac{(M(OH)_{n-p} R_p)_o (H)^{n-m-y} (H_2O)^{y+p-n}}{(M(OH)_y R_m)(HR)_o^{p-m}}. \quad \text{Eq. 30}$$

Connick and McVey used activities in most of their expressions; concentrations are used in this work. One objective which Connick and McVey had was to show which species exist in the aqueous phase and which species extract into the organic phase. They obtained this information in the following manner. The extractability for the system was written as

$$E = \frac{\sum_p (M(OH)_{n-p} R_p)_o}{\sum_y \sum_m (M(OH)_y R_m)}, \quad \text{Eq. 31}$$

where the summation is used to include all species involved. From certain combinations of constants obtained from Eq. 30, it is possible to obtain the following expression for the extractability

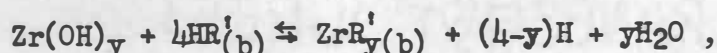
$$E = \frac{\sum_p \frac{(H_2O)^{n-p} K_{oop}}{(HR)_o^{n-p} K_{oon}}}{\sum_m \sum_y \frac{(H)^{n-m-y} (H_2O)^y}{K_{my n} (HR)^{n-m}}} \quad \text{Eq. 32}$$

It is then possible to take the partial derivative of the logarithm of Eq. 32 with respect to the concentration of the reagent in the organic phase.

For the case in which n equals four and the coordination number of M^{4+} is equal to eight, as is the case with zirconium(IV), this partial derivative was symbolized as

$$\frac{\partial \ln E}{\partial \ln (HR)_o} = -4f_0 - 3f_1 - 2f_2 - f_3 + 4f'_0 + 3f'_1 + 2f'_2 + f'_3 \quad \text{Eq. 33}$$

where each f is the fraction of total metal concentration in one phase for a particular specie containing the metal. The subscripts represent the number of reagent groups bound to the metal ion; the unprimed f 's refer to the organic phase; and the primed f 's refer to the aqueous phase. In order to obtain the partial derivative of Eq. 33 the activities of the water and hydrogen ion must remain constant. For the system they investigated, Connick and McVey made a plot of $\log E$ versus $\log (HR)_o$ and obtained a straight line with a slope of four. It was stated that this value of the slope was possible only if all the values of the f 's in Eq. 33 are zero except f'_0 which must be unity. This means that p equals 4 and m equals 0, and Eq. 29 may be written for this system as



where R' represents the thenoyltrifluoroacetate ion, and (b) represents the benzene phase. By varying the acidity of the aqueous phase, Connick

and McVey were able to obtain in a similar manner the number of hydroxyl groups bound to the zirconium(IV) ion at various acidities.

Complex formation between zirconium(IV) and sulfate and fluoride ions was also studied by the extraction technique. The presence of sulfate ion in the aqueous phase modifies the extractability to give

$$E = \frac{(ZrR_4)_0}{\sum_y \sum_m (Zr(OH)_y(SO_4)_m) + \sum_p (Zr(OH)_p)} \quad \text{Eq. 34}$$

The number of sulfate groups bound to the zirconium at various concentrations of sulfate ion was obtained by the same method as was used to obtain the number of TTA groups bound to the zirconium.

Connick and McVey⁵⁶ were able to obtain stability constants for the complexes $ZrSO_4^{2+}$, $Zr(SO_4)_2$, $Zr(SO_4)_3^{2-}$, ZrF^{3+} , ZrF_2^{2+} , and ZrF_3^+ which were formed in the aqueous phase. It was reported that these constants were obtained by the use of an equation which Leden⁵⁷ developed in 1941. Leden's equation is given by

$$\frac{(M)_t - (M)}{(M)(X)} = K_1 + K_2(X) + K_3(X)^2 \quad \text{Eq. 35}$$

where X represents a complexing anion, and the K constants are given by

$$K_i = (MX_i)(M)^{-1}(X)^{-i} \quad \text{Eq. 36}$$

where i equals 1, 2, 3. The term on the left side of Eq. 35 given in terms of the extractability used by Connick and McVey is

$$\frac{E_0 - E}{E(X)}$$

where E_0 equals the extractability in the absence of complexing anion X, and E is the extractability in the presence of X. Apparently Connick and McVey used plots involving the logarithm of the expression above versus

the term $\log(X)$ in order to obtain the stability constants. However, they did not give details of their calculations.

In 1950 Rydberg⁵⁸ published a work which dealt with the complex formation between thorium and acetylacetone. An extraction technique was used with benzene being the organic phase. Shown in terms of a metal ion M^{n+} , and complexing reagent HR, Rydberg's work is as follows. Rydberg considered the effect on the extractability E of the formation and existence in the aqueous phase of various complexes $MR_p^{(n-p)+}$ and various hydrolysis products $M(OH)_y^{(n-y)+}$. Rydberg found that by working with very low concentrations of metal ion in the aqueous phase the formation of polymers represented by $M_mR_p^{(mn-p)+}$ and $M_m(OH)_y^{(mn-y)+}$ could be neglected. No evidence of mixed complexes $MR_p(OH)_y^{(n-p-y)+}$ was found. For the possibility in which polymerization takes place Rydberg wrote the extractability as

$$E = \frac{P_C(R)^n}{1 + \sum_m \sum_p mK_{mp}(M)^{m-1}(R)^p + \sum_m \sum_y mB_{my}(M)^{m-1}(OH)^y} \quad \text{Eq. 37}$$

where the stability constants K_{mp} and B_{my} are given by

$$K_{mp} = (M_mR_p)(M)^{-m}(R)^{-p} \quad \text{Eq. 38}$$

and

$$B_{my} = (M_mOH_y)(M)^{-m}(OH)^{-y} . \quad \text{Eq. 39}$$

It should be noted that the complexes $MR_p^{(n-p)+}$ in the water phase are complexes of the metal ion and the anion of the complexing reagent HR, and that no additional complexing anions such as sulfate, chloride, etc. are present in the water phase. Rydberg found that for the system he investigated only the specie MR_n was present in the organic phase.

Rydberg found that hydrolysis and polymerization could be neglected so that he could write

$$E = \frac{P_0(R)^n}{\sum_{p=0}^n K_p(R)^p} \quad \text{Eq. 40}$$

where K_0 equals 1. Eq. 40 is summed only up to p equals n so that no negative complexes are considered; Rydberg summed above n to allow for the formation of negative complexes. No evidence for negative complexes was found in his system.

Rydberg obtained values for the constants in Eq. 40 by two methods. In the first method he used the following expression for the mean number of ligands attached to a metal atom in the water phase

$$\bar{n} = \frac{\sum_p p(MR)_p}{(M)_t} \quad \text{Eq. 41}$$

which is also given by

$$\bar{n} = n' + \frac{d(\log MR_{n'})}{d(p(R))} \quad \text{Eq. 42}$$

where $p(R)$ equals $-\log(R)$, and $MR_{n'}$ is any complex between the metal ion and the ion R^- which can be experimentally measured. The value of n' was taken as n (the valence of the metal ion) so that Eq. 42 could be written as

$$\bar{n} = n + \frac{d(\log E)}{d(p(R))} \quad \text{Eq. 43}$$

From experimental values of E and (R^-) a smoothed curve of $\log E$ versus $\log(R)$ was made. By graphical differentiation of this curve, it was possible to obtain values of $\bar{n}$ at various values of (R^-) . Eq. 41 was

then transformed to the following equation

$$\bar{n} + (\bar{n}-1)K_1(R) + (\bar{n}-2)K_2(R)^2 + \dots + (\bar{n}-n)K_n(R)^n = 0. \quad \text{Eq. 44}$$

In Rydberg's system n was equal to four. Since Rydberg could determine experimentally all quantities in Eq. 44 except the stability constants, he was able to solve four simultaneous equations for the four constants.

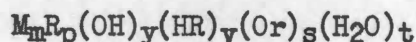
Connick and Reas⁶⁰ in 1951 adapted solvent extraction methods to the study of the polymerization of hydrolyzed species of zirconium(IV) in an aqueous solution. Thenoyltrifluoroacetone was the complexing reagent, and benzene was the organic phase. The extractability was measured as a function of the total concentration of zirconium in the aqueous phase. Using symbols which have been previously used, the extractability was given by

$$E = \frac{(MR_n)_o}{\sum_m m(M_m)} \quad \text{Eq. 45}$$

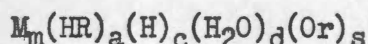
where the summation is equal to $(M)_t$. After modifying Eq. 45 it was possible to differentiate the logarithm of the extractability with respect to the logarithm of the total concentration of zirconium in the aqueous phase. From this derivative it was possible to interpret a plot of $\log E$ versus $\log (M)_t$ in terms of the approximate degree of polymerization of the zirconium. Some ideas were obtained about the magnitude for the equilibrium constants for the reactions leading to the polymers. Also the average number of hydroxyl groups per zirconium atom in the polymers was estimated.

In 1955 Irving, Rossotti, and Williams⁶¹ and Rydberg⁶² independently treated the solvent extraction analysis of complicated complexes which

may be written as



where Or represents a molecule of the organic solvent. The electrical charge of the complex is equal to the quantity ($mn - p - y$). The two papers approach the subject somewhat differently. Irving, Rossotti, and Williams derived their expressions in terms of complexes of average composition whereas Rydberg used summation expressions to derive pertinent equations. Rydberg showed that equilibrium measurements would not distinguish between isomers of the formula above and the following form



which has a charge of ($mn + c$). Irving, Rossotti, and Williams showed that from the function

$$\frac{\partial \log E}{\partial \log (Y)}$$

the average compositions of the species could be determined, where (Y) is equal to (M)_t, (R), or (H). In this respect their work can be considered as an extension of the work of Connick, McVey, and Reas.^{56,57}

Rydberg has applied the equations which he developed⁶² to the study of complexes formed between acetylacetone and thorium(IV) and uranium(V). The literature dealing with the solvent extraction of acetylacetone complexes is very extensive. McKaveney⁶³ and Krishen⁶⁴ have recently studied acetylacetone as an extracting reagent. McKaveney listed 167 references in his work, and Krishen listed 113. Rydberg⁶⁵ gave a short summary of the history of the principles involved in solvent extraction in a paper dealing with some actinide complexes of acetylacetone. Dyrssen⁶⁶ recently published a paper dealing with the use of var-

ious chelating agents for the extraction of lanthanide and actinide elements. The reference work in Dyrssen's paper is very extensive.

C. Extraction Data for Dithizone and Metal Dithizonates

Though the constant K_r for dithizone is now fairly accurately established and P_r has been obtained for a few solvents, the constants involving the metal dithizonates K_c and P_c have been determined only for copper dithizonate. The amount of data for the extraction constants K is also very small. Table II gives a summary of what is now available in the literature plus a few values which have been calculated from literature data.

D. Complexes of Cadmium and Silver(I)

1. Cadmium Complexes

The cadmium ion reacts with many anions, neutral molecules, and chelating agents to form complex compounds. A fairly complete review of the chemistry of cadmium containing some basic information on its complex-forming abilities has been given by Sidgwick.⁶⁸ Block⁶⁹ indicates that cadmium(II) with a coordination number of four shows a tetrahedral geometry. In general, oxy-complexes of cadmium are much less stable than those in which nitrogen or sulfur acts as the electron-donating atom. One exception to this statement is represented by the extreme stabilities of the versene complexes. It has been noted that the stabilities of the halide complexes of cadmium increase as the atomic number of the halide goes up.

TABLE II^a

EXTRACTION DATA FOR DITHIZONE AND METAL DITHIZONATES

Dithizonate	K	K_R or K_C^b	P_R or P_C^c	Organic Phase for K , P_C , and P_R	t °C	Ref.	Date
H ⁺		2 x 10 ⁻⁶	6 x 10 ⁻⁴	CCl ₄	20	10	1949
H ⁺			1 x 10 ⁻⁵	CHCl ₃	20	10	1949
H ⁺		2 x 10 ⁻⁵	9 x 10 ⁻⁵	CCl ₄	25	21	1950
H ⁺		3 x 10 ⁻⁵	1 x 10 ⁻⁵	CHCl ₃	20	22	1952
H ⁺			5 x 10 ⁻⁵	C ₆ H ₁₂	20	22	1952
H ⁺			7 x 10 ⁻⁵	CCl ₄	20	22	1952
H ⁺			1 x 10 ⁻⁵	C ₆ H ₆	20	22	1952
H ⁺		3 x 10 ⁻⁵			25	23	1952
H ⁺		3 x 10 ⁻⁵	9 x 10 ⁻⁵	CCl ₄	25	12	1953
M ⁺			2 x 10 ⁻⁶	CH ₂ Cl ₂	30	13 ^d	1957
H ⁺			1 x 10 ⁻⁵	C ₆ H ₅ Cl	30	13 ^d	1957
Zn ⁺⁺	3 x 10 ⁰			CHCl ₃	25	40	1941
Zn ⁺⁺	4 x 10 ⁰			CCl ₄		6 ^f	1950
Zn ⁺⁺	4 x 10 ⁰			CHCl ₃	25	41	1952
Zn ⁺⁺	6 x 10 ⁻²			CHCl ₃	30	13	1957
Zn ⁺⁺	1 x 10 ⁰			CH ₂ Cl ₂	30	13	1957
Zn ⁺⁺	1 x 10 ¹			C ₆ H ₆	30	13	1957
Zn ⁺⁺	2 x 10 ¹			C ₆ H ₅ Cl	30	13	1957
Zn ⁺⁺	5 x 10 ¹			CCl ₄	30	13	1957
Cu ⁺⁺	~10 ¹⁰			CCl ₄	--	6	1950
Cu ⁺⁺	1 x 10 ¹⁰	1 x 10 ⁻²³	1 x 10 ⁻⁵	CCl ₄	25	12	1953
Cu ⁺⁺	3 x 10 ¹⁰			CCl ₄	18	43	1954
Ag ⁺	~10 ⁷			CCl ₄	--	6	1950
Ag ⁺	4 x 10 ⁷			CCl ₄	18	43	1954
Hg ⁺⁺	7 x 10 ²⁶			CCl ₄	--	42	1956

TABLE II^a

EXTRACTION DATA FOR DITHIZONE AND METAL DITHIZONATES (Continued)

Dithizonate	K	K_r or K_c ^b	P_r or P_c ^c	Organic Phase for K , P_c , and P_r	t °C	Ref.	Date
Po ⁺⁺	3×10^7 ^e			CHCl ₃	—	23	1952

^aAll values are given to one significant number.

^b K_r applies to H⁺ and K_c applies to M⁺ⁿ.

^c P_r applies to H⁺ and P_c applies to M⁺ⁿ.

^dValues approximated by S/So. S was taken from Geiger and Sandell¹² and So was taken from Honaker.¹³

^eCalculated assuming all polonium species to be Po⁺⁺. The value of K is not changed if all polonium species are assumed to be PoO⁺⁺.

^fValue calculated by Sandell⁶ from Buch's data.⁶⁷

In connection with the present work, it was of interest to locate values for the stepwise stability constants for complexes of cadmium with simple inorganic anions and a few organic anions, mainly those which yielded water-soluble complexes. Some constants for cadmium-ammonia complexes have also been found. Table III presents a selection of values which were deemed to be pertinent. The constants as given here are defined in terms of Eq. 36.

2. Silver(I) Complexes

According to Sidgwick⁶⁸ silver(I) forms complexes in which the electron-donating group may be carbon, nitrogen, phosphorous, arsenic, oxygen, or the halogens. Unidentate or chelate complexes may be formed. Silver(I) forms tetrahedral complexes whenever the coordination number is four.⁷⁰ Silver(I) also forms complexes in which the coordination number is two and complexes in which the coordination number is three.⁷¹ It has been shown^{71,72} that the complexes $\text{Ag}(\text{NH}_3)_2^+$ and $\text{Ag}(\text{CN})_2^-$ are linear.

Some complexes of silver(I) in which the electron-donating atom is carbon, nitrogen, or sulfur are very stable. The cyanide complexes of silver(I) are very stable, and the donor atom is thought to be carbon.⁶⁸ Schwarzenbach and others working with him^{73,74,75} have made many studies of the stabilities of silver(I)-amine complexes. Of the electron-donating atoms listed above oxygen forms the least stable complexes with silver(I).

It was also of interest to obtain stepwise stability constants for some silver(I) complexes which are water-soluble. Table III gives a collection of the stability constants which were thought to pertain to the

TABLE III^a

COMPLEXES OF CADMIUM AND SILVER

Ligand	K ₁	K ₂	K ₃	K ₄	u	t °C	Ref.	Date
Cadmium Complexes:								
Cl ⁻	1 x 10 ²				0.02	18	76 ^b	1930
Cl ⁻				8 x 10 ²	0.5		78 ^c	1930
Cl ⁻	1 x 10 ²	4 x 10 ²	5 x 10 ²	1 x 10 ³	2.0 ^d	18	77 ^c	1932
Cl ⁻	9 x 10 ¹				1.0 ^e	25	79 ^c	1936
Cl ⁻	4 x 10 ¹	2 x 10 ²	3 x 10 ²		3.0	25	57 ^c	1941
Cl ⁻	3 x 10 ¹	2 x 10 ²	3 x 10 ²		3.0	25	83 ^h	1949
Cl ⁻	2 x 10 ¹	6 x 10 ¹			0.5	25	80 ^c	1953
Cl ⁻	2 x 10 ¹	6 x 10 ¹	2 x 10 ¹		1.0	25	80 ^c	1953
Cl ⁻	3 x 10 ¹	9 x 10 ¹	6 x 10 ¹		2.0	25	80 ^c	1953
Cl ⁻	4 x 10 ¹	2 x 10 ²	2 x 10 ¹		3.0	25	80 ^c	1953
Cl ⁻	1 x 10 ²	5 x 10 ²	1 x 10 ²		0.0	25	80 ^f	1953
Cl ⁻	4 x 10 ¹	1 x 10 ²	3 x 10 ²		3.0	25	81 ^g	1953
Cl ⁻	2 x 10 ¹	2 x 10 ¹	3 x 10 ¹		2.0		82	1953
Br ⁻	2 x 10 ²	1 x 10 ³	3 x 10 ³	1 x 10 ⁴	2.0 ^d	18	77 ^c	1932
Br ⁻	1 x 10 ²				0.1	30	84	1939
Br ⁻	6 x 10 ¹	2 x 10 ²	2 x 10 ³	5 x 10 ³	3.0	25	57 ^c	1941
Br ⁻	6 x 10 ¹	3 x 10 ²	2 x 10 ³	5 x 10 ³	3.0	25	81 ^g	1953
Br ⁻	3 x 10 ¹	1 x 10 ²	1 x 10 ²	5 x 10 ²	2.0		82	1953
I ⁻				2 x 10 ⁶	0.9 ⁱ		78 ^c	1930
I ⁻	3 x 10 ²	3 x 10 ³	1 x 10 ⁵	1 x 10 ⁶	2.0 ^d	18	77 ^c	1932
I ⁻	2 x 10 ²	8 x 10 ³	1 x 10 ⁵	1 x 10 ⁶	0.01	25	85 ^c	1938
I ⁻	1 x 10 ²	5 x 10 ²	1 x 10 ⁵	3 x 10 ⁶	3.0	25	57 ^c	1941
I ⁻				8 x 10 ⁵	0.1	25	87 ^g	1949
I ⁻	1 x 10 ²	2 x 10 ³		4 x 10 ⁵	2.0		82	1953
I ⁻	6 x 10 ¹	2 x 10 ²	3 x 10 ³	4 x 10 ⁴	3.0	25	86 ^c	1956
SCN ⁻	2 x 10 ¹	1 x 10 ²	4 x 10 ²		3.0	25	57 ^c	1941
SCN ⁻	1 x 10 ¹	6 x 10 ¹	6 x 10 ⁰	6 x 10 ¹	2.0	30	88 ^g	1951
NO ₃ ⁻	1 x 10 ⁰				3.0	25	57 ^c	1941
NO ₃ ⁻	1 x 10 ⁰					25	80	1953
SO ₄ ²⁻	2 x 10 ²				0.02	18	76 ^b	1930
SO ₄ ²⁻	8 x 10 ⁰				3.0	25	57 ^c	1941
SO ₄ ²⁻	7 x 10 ⁰				3.0	20	89 ^k	1953
S ₂ O ₃ ²⁻			2 x 10 ⁶		0.1	25	87 ^g	1949
NH ₃				1 x 10 ⁷			90 ^c	1903
NH ₃		4 x 10 ⁴		4 x 10 ⁶		25	91 ^j	1925
NH ₃				1 x 10 ⁷	0.1	25	87 ^g	1949

TABLE III^a

COMPLEXES OF CADMIUM AND SILVER (Continued)

Ligand	K ₁	K ₂	K ₃	K ₄	u	t °C	Ref.	Date
Cadmium Complexes:								
CN ⁻	3 x 10 ⁵	4 x 10 ¹⁰	2 x 10 ¹⁵	6 x 10 ¹⁸	3.0	25	92 ^h	1944
CN ⁻		3 x 10 ⁶	8 x 10 ⁹	8 x 10 ¹¹		25	93 ^g	1955
CN ⁻	2 x 10 ⁵	4 x 10 ⁹	8 x 10 ¹³	1 x 10 ¹⁷		25	93 ^c	1955
EDDA ¹	6 x 10 ⁸				0.1	30	94 ^c	1955
HEDTA ¹	1 x 10 ¹³				0.1	30	94 ^c	1955
EDTA ¹	3 x 10 ¹⁶				0.1	20	95 ^c	1951
NTA ¹	1 x 10 ⁹				0.1		96 ^g	1950
NTA ¹	6 x 10 ⁸				0.2		96 ^g	1950
NTA ¹	4 x 10 ⁸				0.3		96 ^g	1950
Cl ⁻		1 x 10 ⁸			0.1	20	97	1950
Silver Complexes:								
Cl ⁻		2 x 10 ⁵	5 x 10 ⁵	2 x 10 ⁵	0.1	25	101 ^o	1921
Cl ⁻	3 x 10 ³	2 x 10 ⁵	5 x 10 ⁵				104 ^o	1937
Cl ⁻			4 x 10 ⁵	1 x 10 ⁵		20	103 ^{o,p}	1946
Cl ⁻	2 x 10 ³	2 x 10 ⁵			0.2	25	98 ^m	1952
Cl ⁻	1 x 10 ³	1 x 10 ⁵	1 x 10 ⁵	2 x 10 ⁵	0	25	99 ⁿ	1953
Cl ⁻	7 x 10 ²	5 x 10 ⁴	1 x 10 ⁵	8 x 10 ⁵	0.2	25	99 ^c	1953
Cl ⁻	1 x 10 ³	3 x 10 ⁵	2 x 10 ⁶	4 x 10 ⁵	5.0	25	99 ^c	1953
Cl ⁻		2 x 10 ⁵				25	100	1953
Br ⁻	1 x 10 ⁴	1 x 10 ⁷	9 x 10 ⁷	8 x 10 ⁸	0.1	25	105 ^c	1953
Br ⁻			8 x 10 ⁸	1 x 10 ⁹	5.0	25	105 ^c	1953
Br ⁻		2 x 10 ⁸	1 x 10 ⁹	2 x 10 ⁹	5.0	25	105 ^h	1953
Br ⁻	1 x 10 ⁵	5 x 10 ⁷	6 x 10 ⁸	8 x 10 ⁸			106	1953
Br ⁻			7 x 10 ⁸	1 x 10 ⁹			107 ^o	1953
I ⁻				1 x 10 ¹⁴			109 ^o	1900
I ⁻				6 x 10 ¹⁵		18	108 ^c	1904
I ⁻			8 x 10 ¹⁴				113 ^o	1941
I ⁻				3 x 10 ¹⁴			112	1946
I ⁻			4 x 10 ¹³	1 x 10 ¹⁴			115 ^o	1951
I ⁻			1 x 10 ¹⁴				110	1953
I ⁻			7 x 10 ¹³	2 x 10 ¹⁴	4.0	25	111 ^c	1956
I ⁻	1 x 10 ⁸				4.0	25	114	1956
SCN ⁻		6 x 10 ⁹		1 x 10 ¹¹		18	108 ^c	1904
SCN ⁻		4 x 10 ⁷	1 x 10 ⁹	1 x 10 ¹⁰	2.2	25	116 ^g	1953
SCN ⁻		2 x 10 ⁸	4 x 10 ⁹	8 x 10 ⁹	0	25	116 ⁿ	1953
SCN ⁻	4 x 10 ⁴	2 x 10 ⁸	1 x 10 ¹⁰	2 x 10 ¹¹	4.0	25	117 ^c	1955
SCN ⁻	4 x 10 ⁴	1 x 10 ⁸	4 x 10 ⁹	3 x 10 ¹⁰	0.1	25	117 ^c	1955
SCN ⁻	6 x 10 ⁴	2 x 10 ⁸	3 x 10 ⁹	5 x 10 ⁹	0	25	117 ⁿ	1955

TABLE III^a

COMPLEXES OF CADMIUM AND SILVER (Continued)

Ligand	K ₁	K ₂	K ₃	K ₄	u	t °C	Ref.	Date
Silver Complexes:								
F ⁻	0.5					25	118	1952
N ₃ ⁻	3 x 10	1 x 10 ⁴	2 x 10 ⁴	9 x 10 ³	4.0	25	119	1954
CN ⁻		9 x 10 ²¹				18	108 ^c	1904
CN ⁻		2 x 10 ²¹					120 ^c	1932
CN ⁻			6 x 10 ²¹	4 x 10 ²⁰		21	121 ^g	1954
OCN ⁻		1 x 10 ⁵			0.01	30	122 ^b	1954
S ₂ O ₃ ²⁻		3 x 10 ¹³	1 x 10 ¹⁴			20	107 ⁿ	1953
SO ₃ ²⁻		2 x 10 ⁸				29	124 ⁿ	1951
SO ₃ ²⁻	4 x 10 ⁵	5 x 10 ⁸	1 x 10 ⁹				123	1956
G ¹		5 x 10 ⁶				19	125 ^c	1949
G ¹	3 x 10 ⁴	4 x 10 ⁴					126 ⁿ	1951
NH ₃	1 x 10 ³	1 x 10 ⁷			2.0	22	59	1941
EDTA	2 x 10 ⁷						127	1957

^aValues of constants are expressed with one significant number.

^bConductometric method.

^cPotentiometric method.

^du varied from 0.07 to 2.0 M.

^eu varied from 0.0005 to 1.0 M.

^fValues of constants were calculated for an ionic strength of 0.

^gPolarographic method.

^hSolubility method.

ⁱu varied from 0.1 to 0.9 M.

^jVapor pressure method.

^kIon exchange method.

^lEDDA designates ion of ethylenediaminediacetic acid, HEDTA designates ion of N-hydroxyethylenediaminetriacetic acid, EDTA designates ion of ethylenediaminetetraacetic acid, G designates ion of glycine.

TABLE III^a

COMPLEXES OF CADMIUM AND SILVER (Continued)

^mSolubility method using radiotracer.

ⁿCalculated thermodynamic constants.

^oConstants were calculated by Kratochvill, Tezak and Vouk.¹⁰²

^p μ varied greatly.

^qInfrared method.

present research. The constants given in Table III are defined by Eq. 36.

E. Proposed Problem

The present research was undertaken with the followings ends in view. (1) Since no determination of the extraction constants for cadmium dithizonate apparently has been made and only two values of the extraction constant are available for silver dithizonate, it was thought that the determination of these constants for a number of solvents would be significant. (2) Systematic studies of the effect of masking agents upon extractions are few.^{13,53,64,128} The effect of masking agents on extractions such as the extraction of metal dithizonates in terms of extraction curves (see Figure 1) is to cause a shift of the extraction curves to higher pH values. Since the position of extraction curves determines how well metal ions may be separated by pH adjustments, the possibility of predicting the pH of extraction presents some very intriguing ideas. It was thought that if the pH of extraction of cadmium and silver dithizonates could be predicted by the use of stability constants of complexes of cadmium and silver(I) which are formed by masking agents such as those listed in Table III, an important contribution would be made to the field of solvent extraction. The present writer knows of no other work which approaches this subject in this manner. (3) Also it would be of value to know the effect upon these extractions of small changes of ionic strength in the aqueous phase. (4) Since some investigators who have studied the solvent extraction of metal dithizonates have worked at

different temperatures (see Table II) it was considered that valuable results might be obtained by an investigation of some extraction constants as a function of temperature.

TABLE IV

DEFINITION OF SYMBOLS

Symbol	Definition
M^{n+} , M	Metal ion with a positive valence of n
HR	Complexing or extracting reagent
R^- , R	Anion of complexing reagent
MD	Dithizone
D^- , D	Anion of dithizone
MR_n	Metal complex which has no charge and may exist in either the aqueous or organic phases
MD_n	Metal dithizonate which has no charge
X	Complexing group of masking reagent in the aqueous phase
MX_i	Metal complex formed between M^{n+} and X usually but not necessarily insoluble in the organic phase ($i = 1, 2, 3, 4$)
$(M)_t$	Total concentration of metal in the aqueous phase
o	A subscript used to designate that a chemical specie is in the organic phase
P_r	Partition coefficient of complexing reagent
K_r	Ionization constant of complexing reagent
P_c	Partition coefficient of metal complex, MR_n
K_c	Instability constant of metal complex, MR_n
K	Extraction constant of metal complex, MR_n

TABLE IV

DEFINITION OF SYMBOLS (Continued)

Symbol	Definition
K_{1h} , K_{2h} , B_{my}	Stability constants of hydrolysis species of the metal ion
n	Mean number of ligands attached to a metal ion

CHAPTER II

EXPERIMENTAL PROCEDURES

A. Reagents

1. Water

All aqueous solutions were prepared from water which was first distilled in a copper still and then allowed to run through a column of Amberlite MB-3 resin. The height and diameter of the column were 63 cm. and 3.5 cm. respectively. The water was allowed to run through the column at a rate of 1 drop every three or four seconds. Extraction tests with dithizone showed this water to be sufficiently free of heavy metals for these experiments.

2. Cadmium and Silver Solutions

Cadmium-115 and silver-110 as nitrates in solutions were obtained from Oak Ridge National Laboratory. The cadmium had a specific activity of approximately 5 mc./g. Most of the experiments with silver were made using silver with a specific activity of approximately 1000 mc./g. In a few experiments silver with a specific activity of 409 mc./g. was used. As obtained, both the cadmium and the silver solutions contained a small amount of nitric acid.

Stock solutions of the radiotracers were prepared by diluting the samples obtained from Oak Ridge to such an extent that a drop of the stock solutions added to 20 ml. of water produced a solution such that

a 0.1-ml. aliquot taken from the 20 ml. gave a radioassay of approximately 1000 counts/min. A few mg. of sodium perchlorate was added to the stock solution to prevent the cadmium or silver from adsorbing on the glass wall of the container.

3. Dithizone

Eastman's White Label grade dithizone was purified for all experiments. The purification method used was essentially the one given by Welcher³ and previously outlined in this work (see page 1). Dithizone was dissolved in chloroform and extracted into redistilled 1:99 ammonium hydroxide. The aqueous extract was filtered and acidified with dilute perchloric acid. The precipitated dithizone was then dissolved in chloroform, and this solution was washed two or three times with water. To obtain the dry solid dithizone the chloroform was evaporated with a stream of air, and the dithizone was allowed to remain in an evacuated desiccator over Ascarite for four or five hours. The purified dithizone was stored in the dark in a brown bottle. An extractive titration with a standard silver nitrate solution of the purified dithizone dissolved in chloroform gave a 99 plus per cent assay for the dithizone.

4. Organic Solvents

All organic solvents were of U. S. P. grade or better. Due to the fact that such a large quantity of chloroform was used some of it was recovered. The recovery procedure was the one outlined by Welcher³ as modified by Honaker.¹³ The used chloroform which contained dithizone

was separated from aqueous solution present and distilled to remove the dithizone. The distillate of chloroform was washed with concentrated sulfuric acid. After separating the sulfuric acid phase, the chloroform was distilled over calcium oxide into a brown bottle which contained enough ethanol to make the final chloroform distillate contain approximately 1 per cent by volume of ethanol. The role of the ethanol is to inhibit the formation of phosgene.

5. Other Chemicals

All other chemicals were of reagent grade. In cases in which the salt was found to contain heavy metal ions which would react with dithizone, the solutions of these salts were purified by extracting the heavy metals with dithizone dissolved in chloroform.

6. Silver Dithizonate

Radioactive silver dithizonate was prepared in order to measure the solubility of silver dithizonate in various solvents. A solution of silver nitrate approximately 0.1 M., which contained some silver-110 was prepared and adjusted to a pH of approximately 5. This silver nitrate solution was shaken in a 1-l. separatory funnel in contact with small portions of a 0.0005-M. solution of dithizone in chloroform. The chloroform phase turned red almost immediately, but shaking was continued for each portion of dithizone solution for one-half hour. It should be mentioned that very dilute solutions, 10^{-5} M. or less, of primary silver dithizonate in organic solvents appear yellow, but as the silver dithizonate becomes more concentrated, the solutions acquire a progressively deeper red color.

After shaking for one-half hour the two phases were separated. Successive portions of the dithizone solution were shaken with the silver nitrate solution until between 0.5 and 1.0 g. of primary silver dithizonate was prepared. The chloroform was then evaporated from the silver dithizonate, and the silver dithizonate was allowed to dry over Ascarite in an evacuated desiccator.

B. Apparatus

1. pH Measurements

All pH measurements were made with a Beckman Model H2 pH meter equipped with miniature electrodes. The instrument was standardized against a buffer solution which has a pH of 7.01 at 25° and against a 0.05-M. solution of potassium acid phthalate which has a pH of 4.01 at 25°. For measurements below a pH of 5 the latter buffer was used; above a pH of 5 the former was used.

2. Stirring and Temperature

Magnetic stirring was used to equilibrate all samples in 25-ml. glass-stoppered Erlenmeyer flasks. A device was constructed which consisted of twelve small horseshoe magnets mounted vertically on aluminum shafts with a copper tray placed directly over and very close to the magnets. Pulleys were placed on the shafts, and a narrow leather belt pulled by a small motor mounted on the end of the unit turned the magnets. When stirring was desired, the Erlenmeyer flasks with small stirring bars inside were placed in the tray over the magnets, and the motor was started.

In this way it was possible to equilibrate twelve samples in one experiment. Stirring bars were made by sealing pieces of iron wire in 3 mm. glass tubes.

To maintain a constant temperature, water from a constant-temperature bath was circulated through the tray. It was found that the temperature in the tray could be maintained with a consistency of 0.5° or better.

3. Radioactivity Measurements

All radioactivity measurements were made with a Tracerlab "Thousand Scaler" using an end window GM tube. A count of the background radiation was taken occasionally, and this count was subtracted from all measurements.

Due to the fact that radioactive decay is a random process there is a random error associated with all radiation measurements. The standard deviation of radioactivity measurements is given by the square root of the total number of counts. All samples which were equilibrated in the present work contained enough radiotracer to give at least 600 counts/min. when 50 per cent extraction was obtained. A total 5-minute count was recorded for each measurement. At very low per cent extraction, the count of the organic phase is small; at high per cent extraction, the count of the aqueous phase is small. Although the error for these low counts becomes quite significant, the resulting error in the calculated per cent extraction is small. It can be shown that the mean variation $\bar{x}$ in the calculated per cent extraction which is caused

by a random variation in the radioactivity is given by

$$\bar{x} = \frac{100C_o}{C_t}, \quad \text{or } \bar{x} = \frac{100C_o}{C_t}$$

where C_o is the total count of the organic phase sample, and C_t is the sum of the total counts of the organic and aqueous phase samples. Thus it can be seen that in extractions of this type the mean variation in the calculated per cent extraction which is due to randomness in the radioactivity is small when the total count, C_t , is large.

C. General Procedure for Extractions

1. Preparation of Solutions

Salt solutions in water were prepared by weighing on an analytical balance the amount of appropriate salt required to produce a solution of a predetermined molarity. The salt was placed in a volumetric flask and diluted to the capacity of the flask. Dithizone solutions in organic solvents were also prepared by weighing a quantity of dithizone necessary to produce a solution of a predetermined molarity. The dithizone was placed in a volumetric flask, and the flask was filled to capacity with the required solvent. The accuracy of the weighing was to within a few tenths of a milligram. In no case was the amount of dithizone less than 32 mg. To obtain solutions of dithizone which had molarities as low as 10^{-5} aliquots were taken with a pipette from the more concentrated solutions, and dilutions were made with an organic solvent.

Samples were prepared for the extractions in the following manner. For each extraction an interval of pH values was prechosen. A little

more than 120 ml. of the required salt solution was placed in a beaker, and the pH was adjusted to the highest value of the chosen pH interval. Ten ml. of this solution was pipetted into a 25-ml. glass-stoppered Erlenmeyer flask. The pH of the solution in the beaker was then adjusted with dilute perchloric acid, and the process above was repeated until twelve samples were obtained which covered the chosen pH interval. A quantity of radiotracer solution (approximately 0.05 ml.) from the radiotracer stock solution was added to each sample. The quantity of radiotracer added was such that when 0.1 ml. was taken from any of the samples and dried on a planchet at least 1200 counts/min. were obtained. Ten ml. of dithizone solution in an organic solvent was added to each of the 10-ml. samples above. In all experiments, the concentration of the dithizone in the organic solvent was so much in excess of the metal ion in the aqueous phase that the difference between the initial and final dithizone concentrations was negligible. After placing stirring bars in the flasks and stoppering them, the solutions were equilibrated.

2. Equilibration

Each set of twelve solutions was placed in the constant temperature bath, stirred for two hours, and allowed to stand for two hours. At first some experiments were made varying the time of stirring, and it was found that for most solutions one hour of stirring was sufficient to bring about equilibrium. However, a few instances were noted in which equilibration did not seem to be quite established in this time. Thus all solutions were stirred for at least two hours.

3. Sampling

After equilibrium was attained, 0.1-ml. samples were taken from each phase of every flask, placed on separate planchets, dried with a drying lamp, and counted. A 0.1-ml. (100 lambda) micro-pipette was used to take the samples. Watch glasses 25 mm. in diameter were used as counting planchets. It was found that these watch glasses could be cleaned and reused.

In three experiments with cadmium in which the aqueous phase contained either 1-M. sodium chloride, 1-M. potassium bromide, or 1-M. sodium perchlorate, it was necessary to measure the per cent of radiation loss due to the absorption of radiation by the dried salt. This measurement was made by adding an accurately measured amount of radiotracer to 10 ml. of solution containing only a small amount of salt and adding the same amount of radiotracer to 10 ml. of the 1-M. salt solution. After sampling and counting each solution the per cent of radiation loss was calculated. This per cent was added to the counts of all samples taken from solutions which were 1-M. in salt.

D. Solubility Measurements

The solubility of silver dithizonate in various organic solvents was measured by the use of the radioactive silver dithizonate. More than enough silver dithizonate to saturate 5 ml. of the organic solvent was placed in a 25-ml. glass-stoppered Erlenmeyer flask. Five ml. of the organic solvent was added along with a stirring bar. The flasks were stoppered, placed on the constant temperature bath, and stirred

for five hours. The solutions were sampled immediately. A 0.1-ml. sample was withdrawn through a cone of filter paper into a micro-pipette. The sample was placed on a planchet, allowed to dry, and counted. By counting a 0.1-ml. sample from a solution of the radioactive silver dithizonate of a known concentration, it was possible to obtain the unknown concentrations of the saturated solutions. The solution of known concentration was prepared by weighing a quantity of the silver dithizonate, placing it in a volumetric flask, and diluting with chloroform to the capacity of the flask.

CHAPTER III

RESULTS

A. Cadmium Experiments

1. Non-Masked Experiments

It was assumed that cadmium does not form complexes with the perchlorate ion. If this assumption is correct, it should be possible to make extractions of cadmium from perchlorate solutions without any masking effect taking place.

Experiments were made in which cadmium dithizonate was extracted from sodium perchlorate solutions into chloroform which contained dithione. The results of these experiments are shown in Figures 2 and 3. In all experiments with cadmium the concentration of cadmium was approximately 7×10^{-5} M., and the temperature was 30° . Also in each cadmium experiment, chloroform was the organic phase. Figures 2 and 3 show the data plotted according to the usual extraction curves. Theoretically the extraction curves for cadmium should show a slope at $\text{pH}_{\frac{1}{2}}$ of 11.5 per cent cadmium extracted/pH unit. The curves for the cadmium extractions have been drawn by the following method. The experimentally determined points were placed at their respective coordinates. A point was selected which was thought to be the best value for the coordinate (50 per cent $\text{pH}_{\frac{1}{2}}$ extraction), and a short straight line of theoretical slope was drawn through this point. The straight line was extended for a few tenths of a pH unit on both sides of the selected point. The curve was

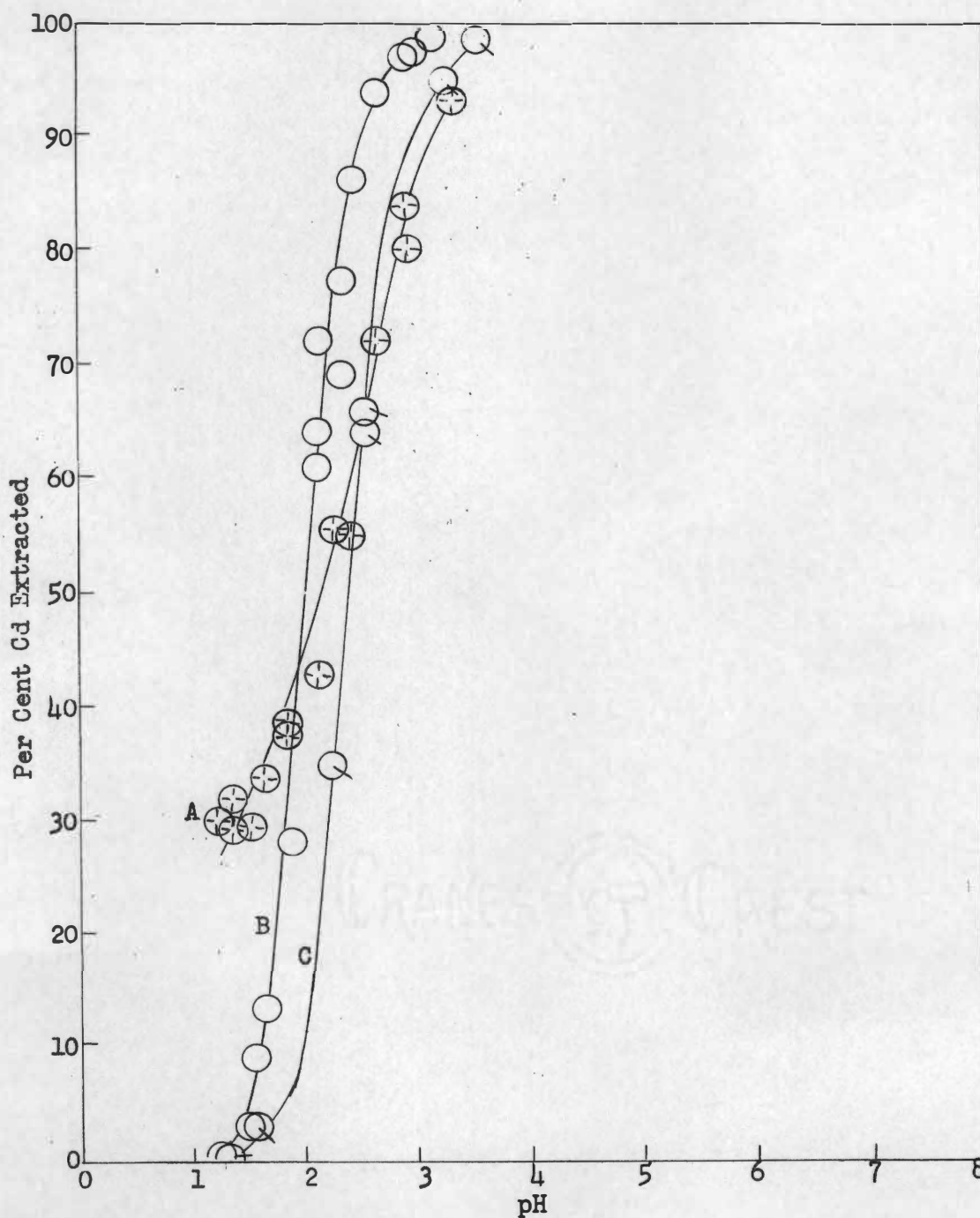


Figure 2. Plots of per cent Cd extracted versus final pH. Initial aqueous phases: HClO_4 , $7 \times 10^{-5}\text{-M}$ is $\text{Cd}(\text{ClO}_4)_2$, (A) 0.1-M . KI, (B) 0.1-M . NaClO_4 , (C) 0.1-M . KCl. Initial CHCl_3 phase: 5×10^{-3} HD. $t = 30^\circ$.

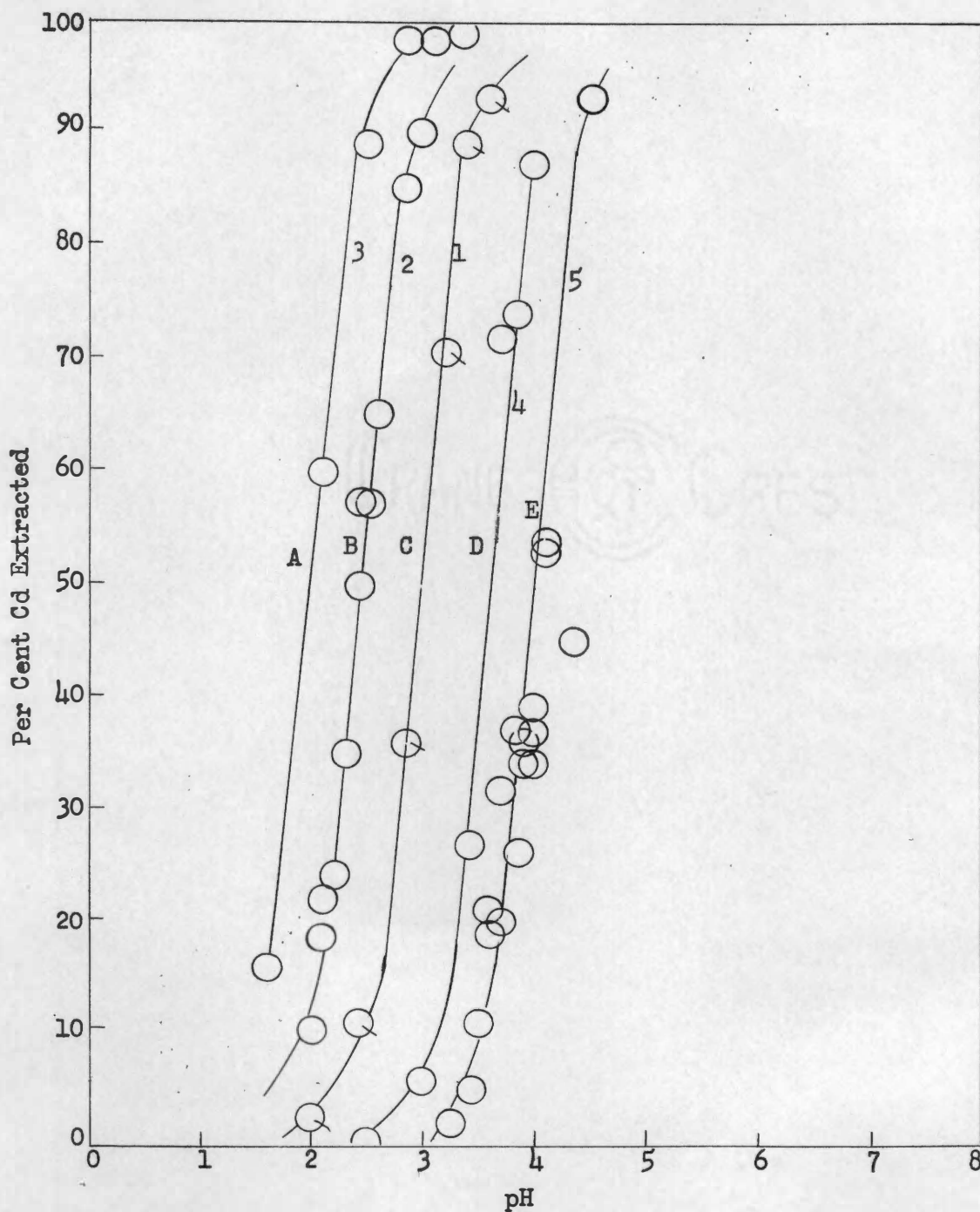


Figure 3. Plots of per cent Cd extracted versus final pH. Initial aqueous phases: HClO_4 , 7×10^{-5} -M. is $\text{Cd}(\text{ClO}_4)_2$, (A) 1.0-M. NaClO_4 , (B) 0.1-M. NaClO_4 , (C) 0.1-M. KBr , (D) 1.0-M. KCl , (E) 1.0-M. KBr . Initial CHCl_3 phase: 2×10^{-3} -M. HD. $t = 30^\circ$.

completed by drawing the remainder of it through the points by a more or less free-hand method.

Figure 2 shows the extraction of cadmium from a 0.1-M. sodium perchlorate solution. The dithizone concentration was 5×10^{-3} M. A $\text{pH}_{\frac{1}{2}}$ was obtained equal to 2.0. Figure 3 shows the extraction of cadmium from a 0.1-M. sodium perchlorate solution and from a 1.0-M. sodium perchlorate solution. In each case the dithizone concentration was equal to 2×10^{-3} M. The $\text{pH}_{\frac{1}{2}}$ values obtained were 2.5 and 2.1 respectively.

2. Masked Experiments

Figures 2 and 3 also show extractions of cadmium from aqueous solutions which contained some masking agents. Cadmium was first extracted from a 0.1-M. potassium chloride solution and from a 0.1-M. potassium iodide solution. The results are shown in Figure 2. In these two experiments the dithizone concentration was 5×10^{-3} M. The $\text{pH}_{\frac{1}{2}}$ of extraction from the chloride solution was obtained to be equal to 2.4. This represents a shift from the comparable non-masked extraction of 0.4 pH unit. The extraction from the iodide solution was found to give a curve which was shifted from the non-masked extraction curve at the higher extractions, but which crossed the non-masked curve at approximately 40 per cent extraction and a pH of 1.9. A slope at $\text{pH}_{\frac{1}{2}}$ was obtained for the extraction from the chloride solution which was approximately the theoretical value; the slope of the curve in the iodide case was much smaller than the theoretical value at $\text{pH}_{\frac{1}{2}}$.

Figure 3 shows the extraction of cadmium from 0.1-M. potassium bromide, 1.0-M. potassium chloride, and 1.0-M. potassium bromide. The

concentration of the dithizone in all cases was 2×10^{-3} M. The $\text{pH}_{\frac{1}{2}}$ values for these three extractions were obtained to be equal to 3.0, 3.5, and 4.1 respectively.

3. Dithizone Concentration and Ionic Strength Changes

The concentration of dithizone was equal to 5×10^{-3} M. for those extractions shown in Figure 2 and equal to 2×10^{-3} M. for those extractions shown in Figure 3. The effect of this change can be compared for the extractions from 0.1-M. sodium perchlorate solutions. For this system the change from 5×10^{-3} -M. to 2×10^{-3} -M. dithizone produced a shift of the $\text{pH}_{\frac{1}{2}}$ from 2.0 to 2.5, a difference of 0.5 pH unit.

B. Silver Experiments

1. Non-Masked Experiments

It is believed that the silver ion does not complex with the perchlorate ion. Thus it was thought that non-masked extractions of silver dithizonate might be made from aqueous perchlorate solutions into organic solvents which contain dithizone. Extraction curves for such extractions should closely resemble the typical extraction curve previously shown (see Figure 1), and therefore should have a slope at pH which is close to 57 per cent silver extracted/pH unit.

The usual curve (per cent metal extracted versus pH) for the extraction of silver dithizonate was not obtained. Figure 4, however, shows the results obtained for the extraction at 0° and 30° of silver dithizonate from fairly concentrated perchloric acid solutions into

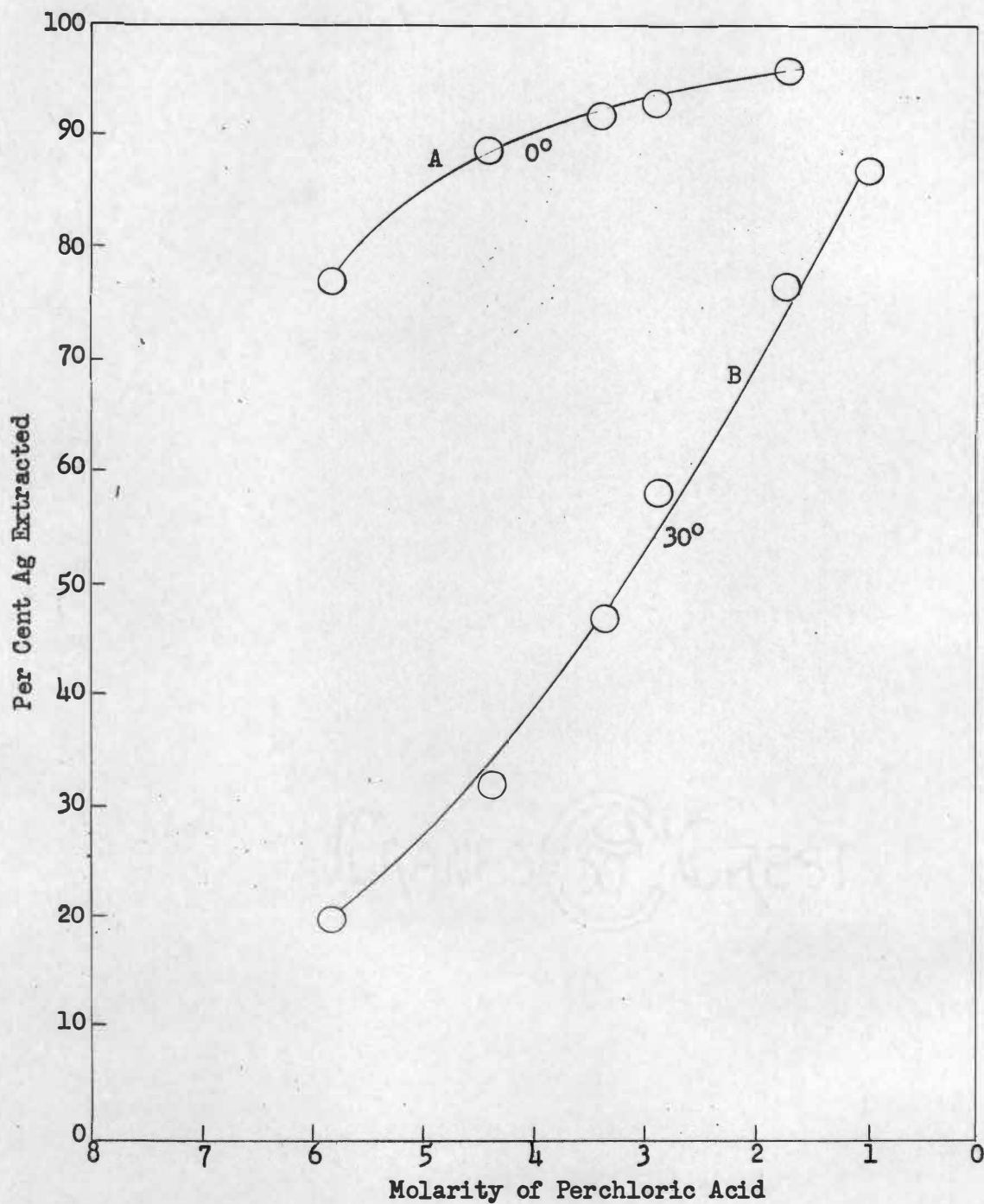


Figure 4. Plots of per cent Ag extracted versus final acid molarity. Initial aqueous phases: HClO_4 , $1 \times 10^{-7}\text{-M}$. AgClO_4 . Initial CHCl_3 phase: $1 \times 10^{-5}\text{-M}$. HD. (A) $t = 0^\circ$. (B) $t = 30^\circ$.

chloroform. The dithizone concentration was 1×10^{-5} M. The ordinate of Figure 4 is in terms of per cent silver extracted into the organic phase, and the abscissa is in terms of molarity of perchloric acid in the aqueous phase. It can be seen that at 30° a 50 per cent extraction was obtained at approximately 3.2-M. perchloric acid. Other extractions were made at other temperatures from 1.0-M. perchloric acid, but these will be discussed under the section dealing with temperature changes.

2. Masked Experiments

Extractions at 30° of silver dithizonate into chloroform were carried out for cases in which the aqueous phase contained one of the following substances: 1.0-M. acetic acid, 0.1-M. tartaric acid, 0.1-M. citric acid, 0.1-M. glycine, 1×10^{-3} -M. ethylenediaminetetraacetic acid, 1×10^{-3} -M. nitrilotriacetic acid, and 0.5-M. sulfuric acid. No masking effect was found for any of these substances. It was observed that if the aqueous phase contained 1.0-M. perchloric acid along with any one of the substances listed above at the designated concentration, the per cent extraction obtained was approximately the same as that obtained if only the perchloric acid was in the aqueous phase. The per cent extraction obtained in all cases was approximately 90. In all of these extractions the dithizone concentration was 1×10^{-5} M.

The substances potassium chloride, potassium bromide, potassium iodide, sodium thiocyanate, and sodium thiosulfate was found to mask the extraction of silver dithizonate. It was observed that the usual extraction curves (per cent metal extracted versus pH) could be obtained for the extractions of silver dithizonate if a sufficient amount of

masking agent was present in the aqueous phase to cause the extractions to take place at much lower acidities. Each of the five masking agents was employed for extractions into chloroform. Potassium bromide and potassium chloride were also used to mask extractions into carbon tetrachloride. In addition, potassium iodide was used to mask extractions of silver dithizonate into benzene. Masking agents were used for extractions into other solvents, but these extractions will be discussed under the section dealing with organic solvent changes.

Figure 5 shows the data which were obtained for the extraction of silver dithizonate from 0.1-M. and 0.2-M. potassium chloride solutions into chloroform containing dithizone. Some extractions were made in which the aqueous phase contained 0.1-M. potassium chloride along with 0.1-M. potassium nitrate. The results of these experiments are also shown in Figure 5. The results obtained for the extractions from the solutions containing potassium nitrate did not appear to be different from the results of the extractions from solutions containing only potassium chloride. The concentration of dithizone was 1×10^{-5} M. A $\text{pH}_{\frac{1}{2}}$ of 2.4 was obtained for the extraction from the 0.1-M. chloride solution; with the 0.2-M. chloride solution a $\text{pH}_{\frac{1}{2}}$ of 3.1 was obtained.

The method used to draw the curves which represent the silver dithizonate extractions was similar to the method used to draw the cadmium extraction curves. The experimental points were placed at their respective coordinates, and a value of $\text{pH}_{\frac{1}{2}}$ which was thought to represent the best value was chosen. A cardboard template which had the shape theoretically predicted for extraction curves of monovalent metal dithizonates

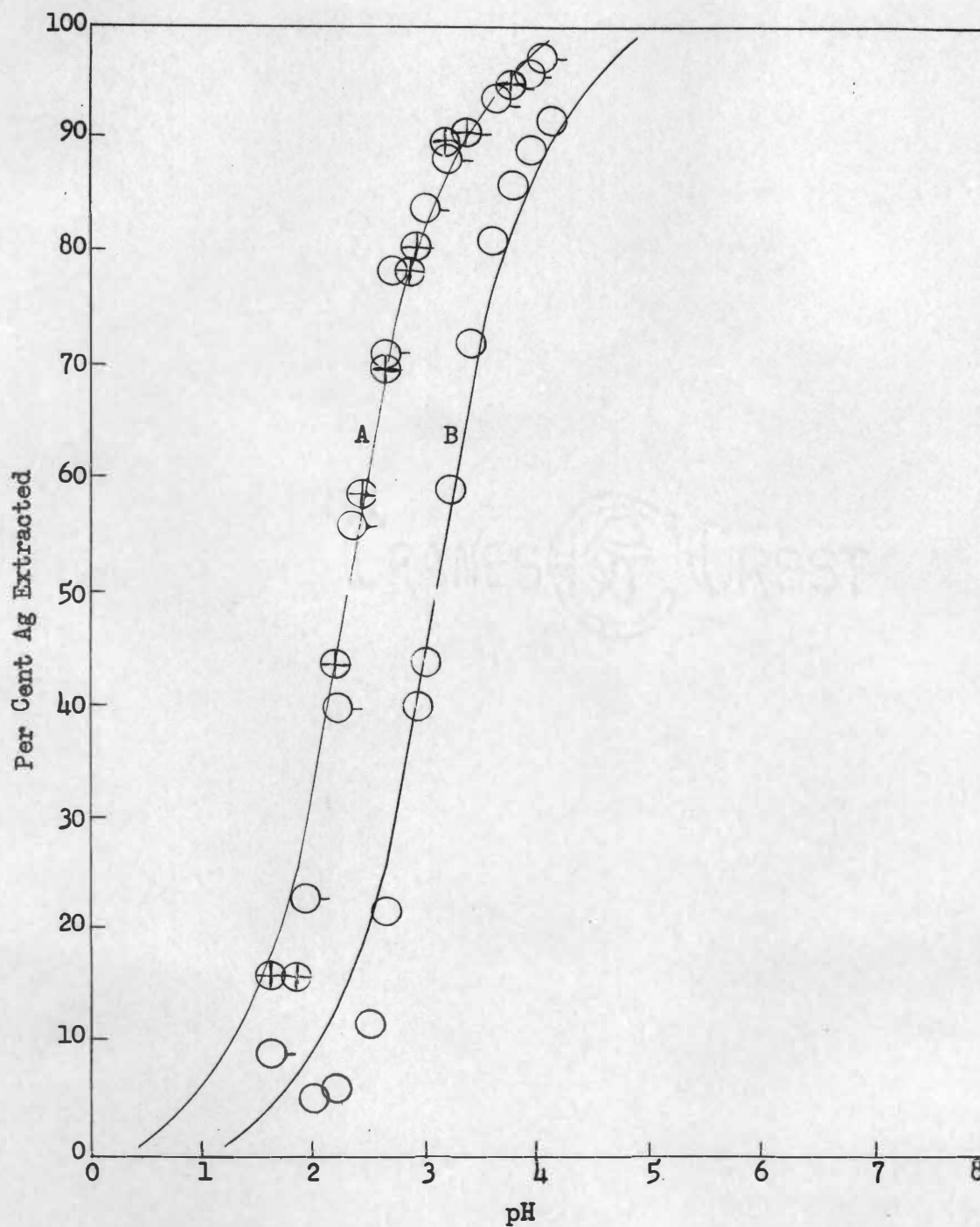


Figure 5. Plots of per cent Ag extracted versus final pH. Initial aqueous phases: HClO_4 , 1×10^{-7} -M. AgClO_4 , (A) ○ 0.1-M. KCl, ⊕ 0.1-M. KCl, + 0.1-M. KNO_3 , (B) 0.2-M. KCl. Initial CHCl_3 phase: 1×10^{-5} -M. HD.

was then placed on the graph with its $\text{pH}_{\frac{1}{2}}$ and 50 per cent extraction coordinate corresponding to the same point of the experimental curve. The curve was then drawn by the use of the template.

Since the usual extraction curve was not obtained for non-masked extractions of silver dithizonate into chloroform, it is impossible to strictly compare the masked extractions to those extractions from concentrated perchloric acid solutions. However, it can be seen that the chloride ion exerts a pronounced masking effect, and that 0.1-M. potassium chloride caused a shift in $\text{pH}_{\frac{1}{2}}$ of greater than 2.0 pH units. The shift produced by 0.2-M. potassium chloride was greater than 3.0 pH units.

Figure 6 shows the results for the extraction of silver dithizonate from 0.1-M. and 0.2-M. potassium chloride solutions into carbon tetrachloride containing dithizone. The $\text{pH}_{\frac{1}{2}}$ values were found to be equal to 1.3 and 1.9 respectively.

Figure 7 shows the results obtained for the extraction of silver dithizonate from 0.1-M. potassium bromide solutions into carbon tetrachloride solutions of dithizone. The dithizone was 5×10^{-5} M. The $\text{pH}_{\frac{1}{2}}$ was found to be 3.1. The effect of increasing the dithizone concentration in the organic phase is to shift the extraction curves to lower pH values. Even though the dithizone was 5 times more concentrated in the extractions from 0.1-M. potassium bromide solutions than in the extractions from the 0.1-M. chloride solutions, the $\text{pH}_{\frac{1}{2}}$ for the former extraction was much higher (3.1) than for the latter (1.3). Thus it is seen that for silver extractions the bromide ion is a much more effective

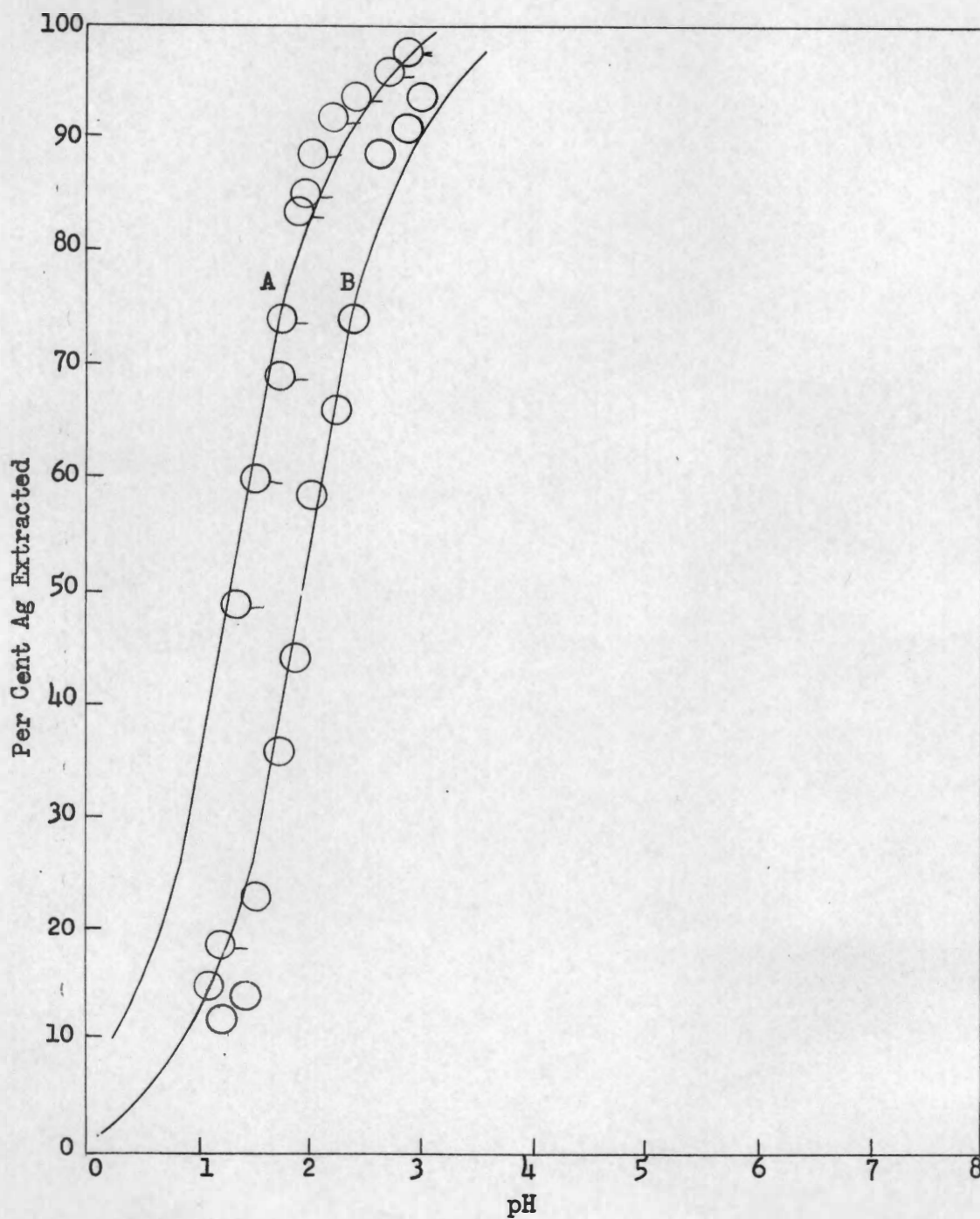


Figure 6. Plots of per cent Ag extracted versus final pH. Initial aqueous phases: HClO_4 , 1×10^{-7} -M. AgClO_4 , (A) 0.1-M. KCl , (B) 0.2-M. KCl . Initial CCl_4 phase: 1×10^{-5} -M. HD.

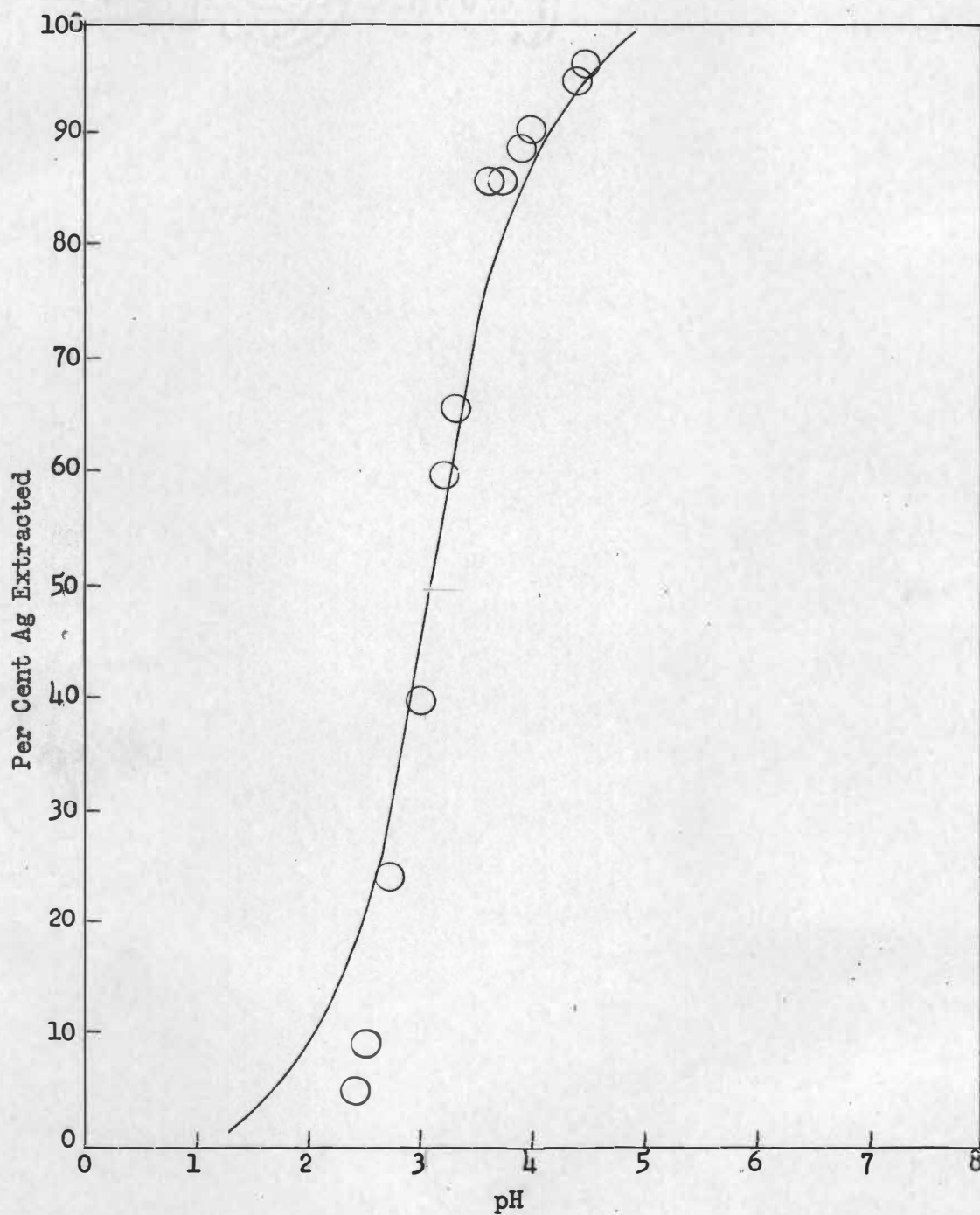


Figure 7. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.1-M. KBr . Initial CCl_4 phase: 5×10^{-5} -M. HD.

masking agent than the chloride ion.

A large number of extractions of silver dithizonate into chloroform were made using potassium bromide as the masking agent. Figures 8, 9, 10, 11, 12, and 13 show the results obtained for these extractions. The respective molarities of potassium bromide in these extractions were 0.01, 0.05, 0.08, 0.1, 0.1, and 0.2, and the corresponding molarities of the dithizone were 1×10^{-5} , 1×10^{-5} , 1×10^{-5} , 5×10^{-4} , 1×10^{-5} , and 5×10^{-4} . Some extractions were made from aqueous solutions which contained either sodium perchlorate or potassium nitrate in addition to the potassium bromide. These electrolytes were present in the extractions which are represented by Figures 8, 9, and 11. The effect of these electrolytes on the extractions represented by Figures 8 and 11 was to produce a slight shift in the curve to lower pH values. Values for pH_2 were found for the extractions represented by Figures 8, 9, 10, 11, 12, and 13 to be equal to 2.9, 4.1, 4.7, 2.9, 5.0, and 3.8 respectively.

The results of the experiments using potassium iodide to mask extractions into benzene which contained dithizone are shown in Figures 14 and 15. Figure 14 gives the results for extractions from 0.01-M. potassium iodide solutions into benzene containing 1×10^{-3} -M. dithizone. The pH_2 was found to be 3.7. However, mass balance of silver was not obtained in these extractions. The data presented by Figure 15 were obtained from extractions from 0.05-M. potassium iodide solutions into benzene which contained 4×10^{-3} -M. dithizone. A pH_2 value equal to 4.5 was obtained. Due to the fact that the solvent was changed, the masking ability of the iodide ion on silver extractions cannot be directly compared to the masking abilities of the chloride and bromide ions.

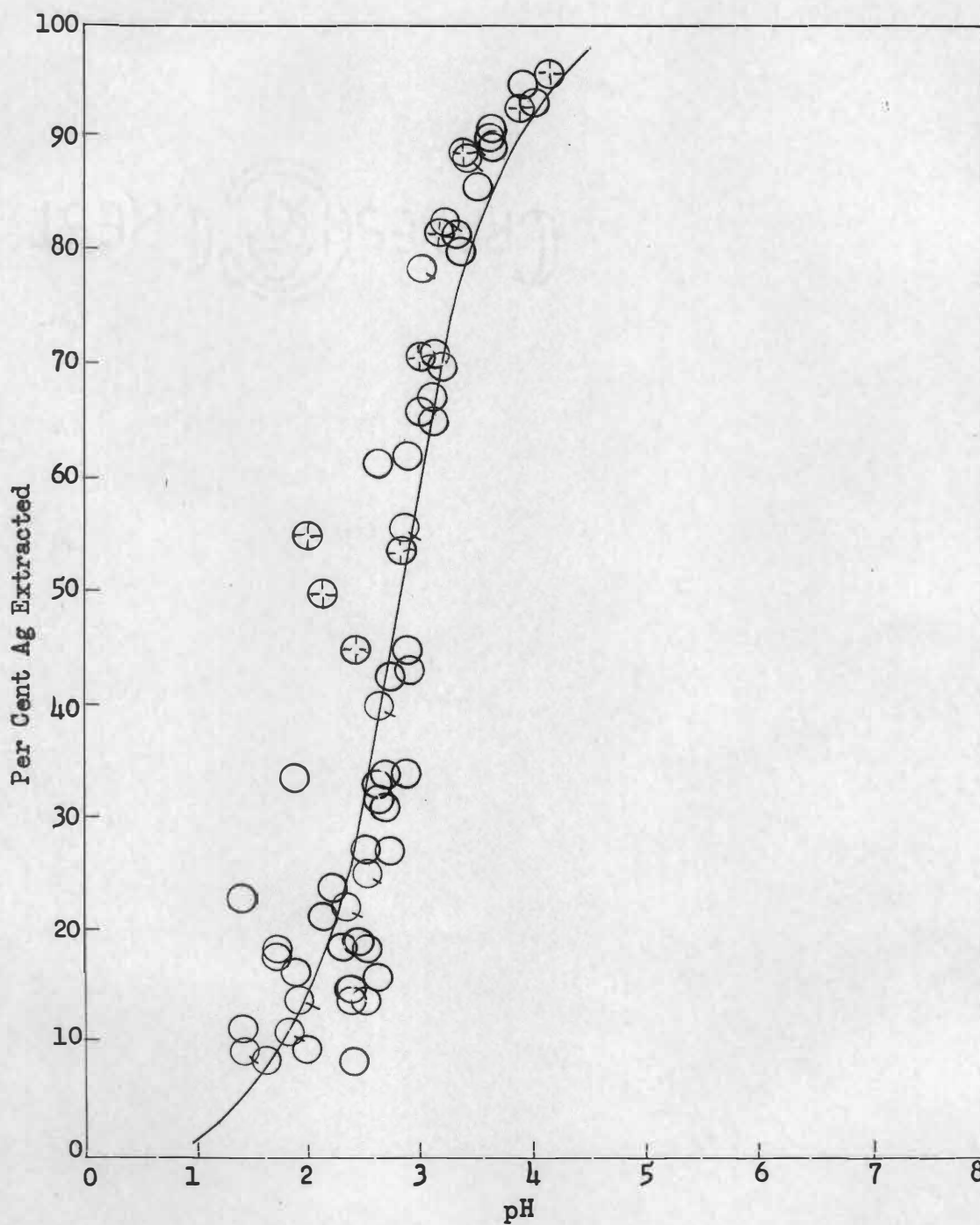


Figure 8. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , ○ 0.1-M. KBr, ⊗ 0.01-M. KBr + 0.2-M. NaClO_4 , ⊕ 0.01-M. KBr + 0.2-M. KNO_3 . Initial CHCl_3 phase: 1×10^{-5} -M. HD.

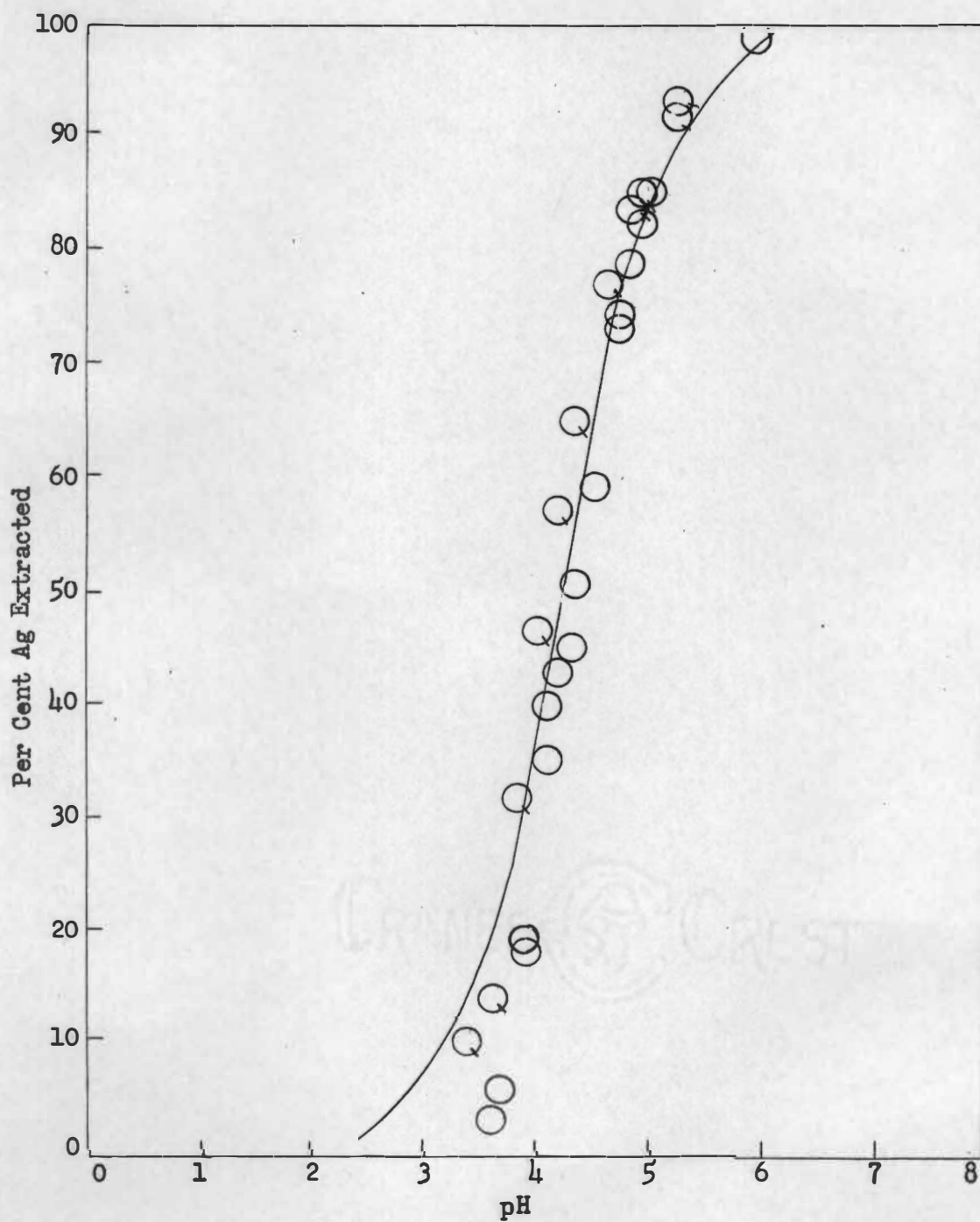


Figure 9. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , $\bigcirc$ 0.05-M. KBr , $\bigcirc$ 0.05-M. KBr + 0.15-M. NaClO_4 . Initial CHCl_3 phase: 1×10^{-5} -M. HD.

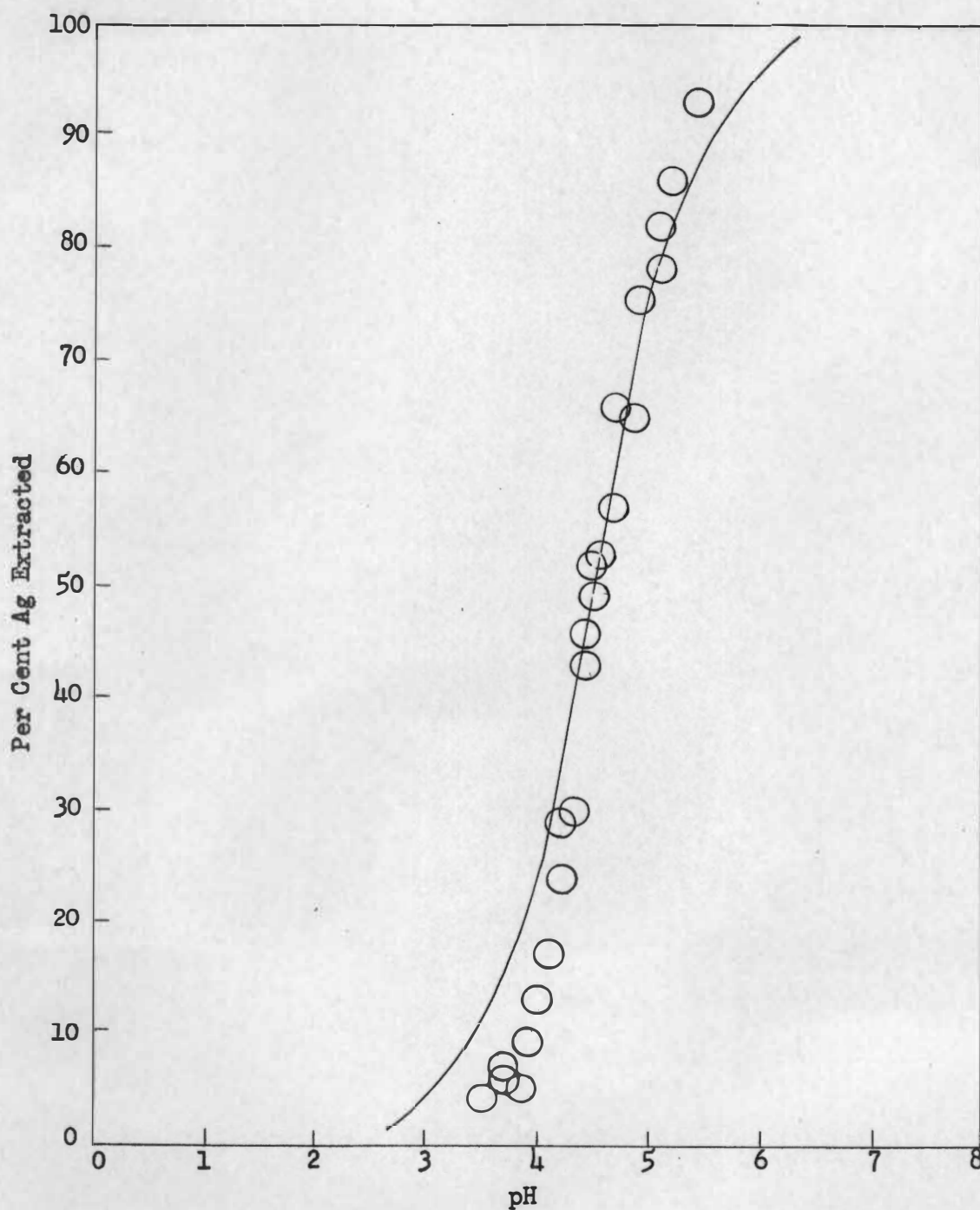


Figure 10. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.08-M. KBr , 0.12-M. NaClO_4 . Initial CHCl_3 phase: 1×10^{-5} -M. HD.

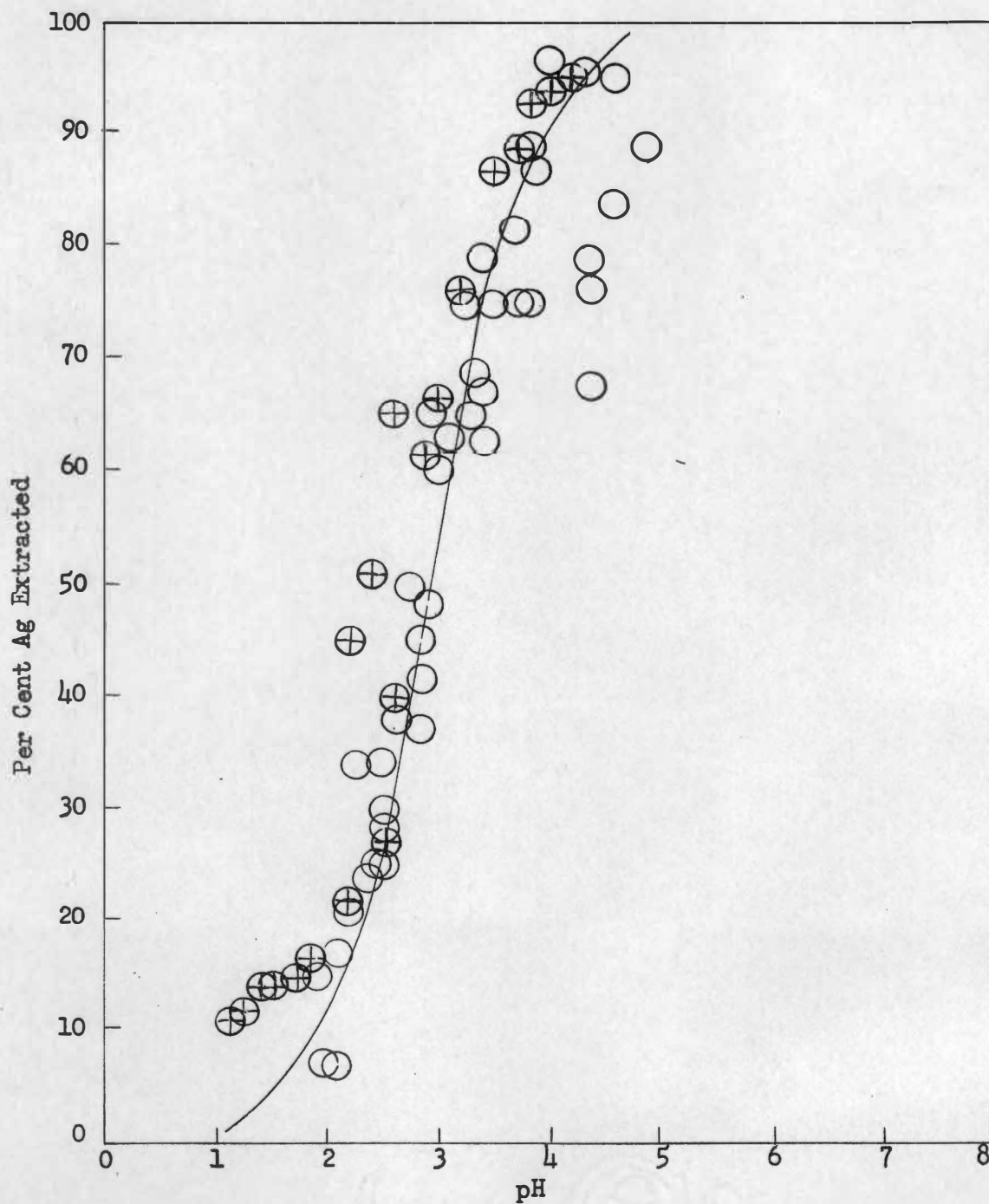


Figure 11. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , $\bigcirc$ 0.1-M. KBr, $\oplus$ 0.1-M. KBr + 0.1-M. NaClO_4 . Initial CHCl_3 phase: 5×10^{-4} -M. HD.

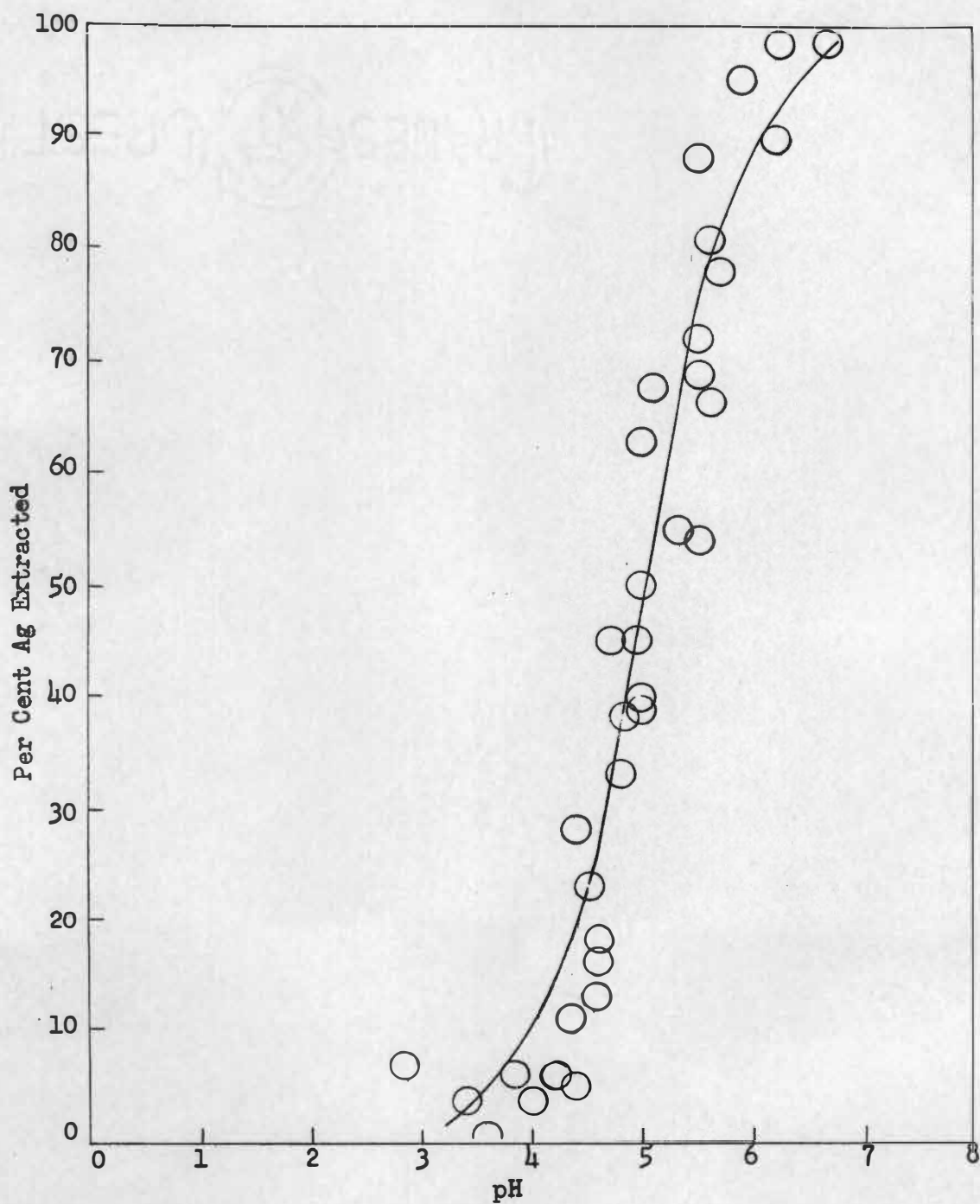


Figure 12. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.1-M. KBr . Initial CHCl_3 phase: 1×10^{-5} -M. HD.

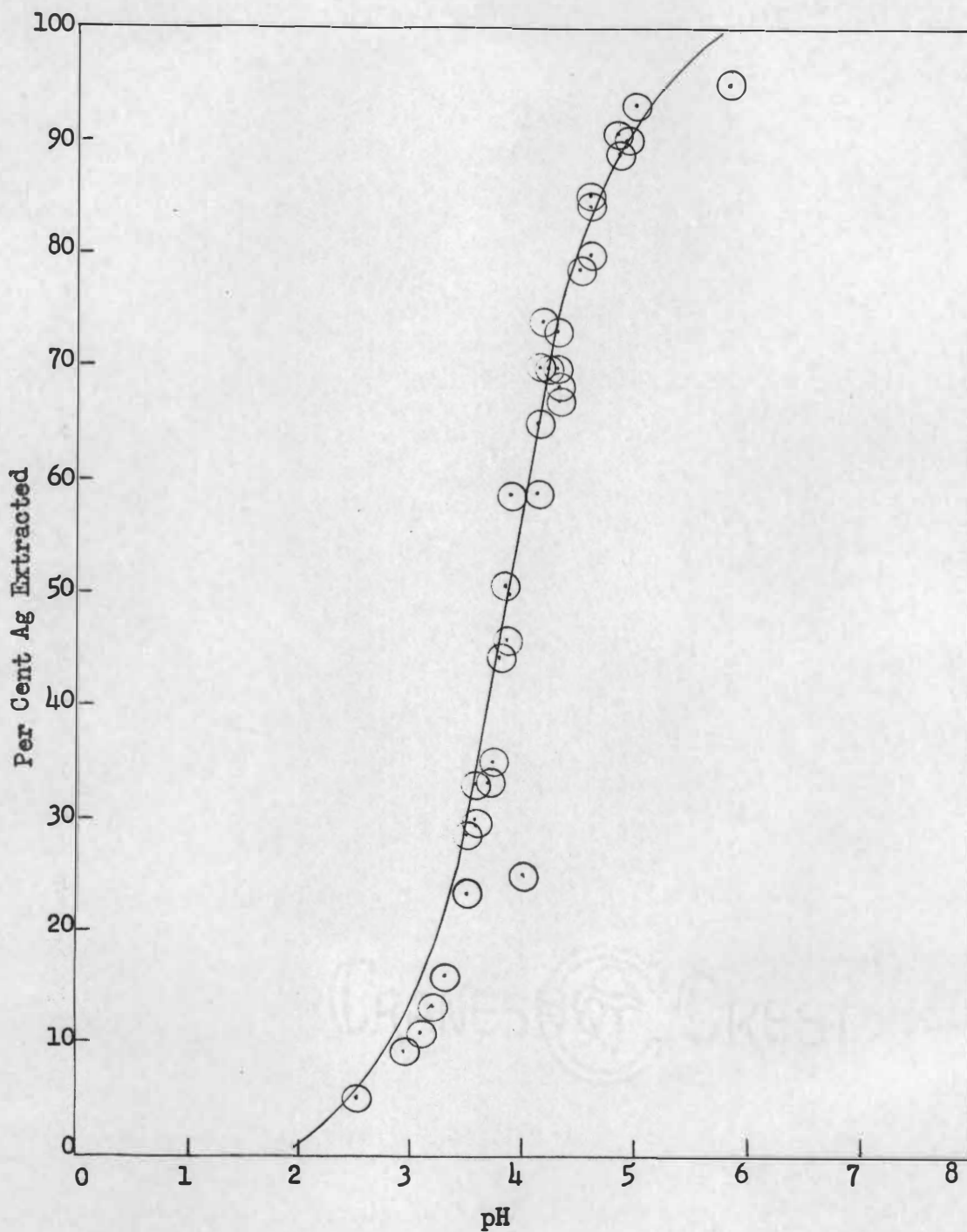


Figure 13. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.2-M. KBr . Initial CHCl_3 phase: 5×10^{-4} -M. HD.

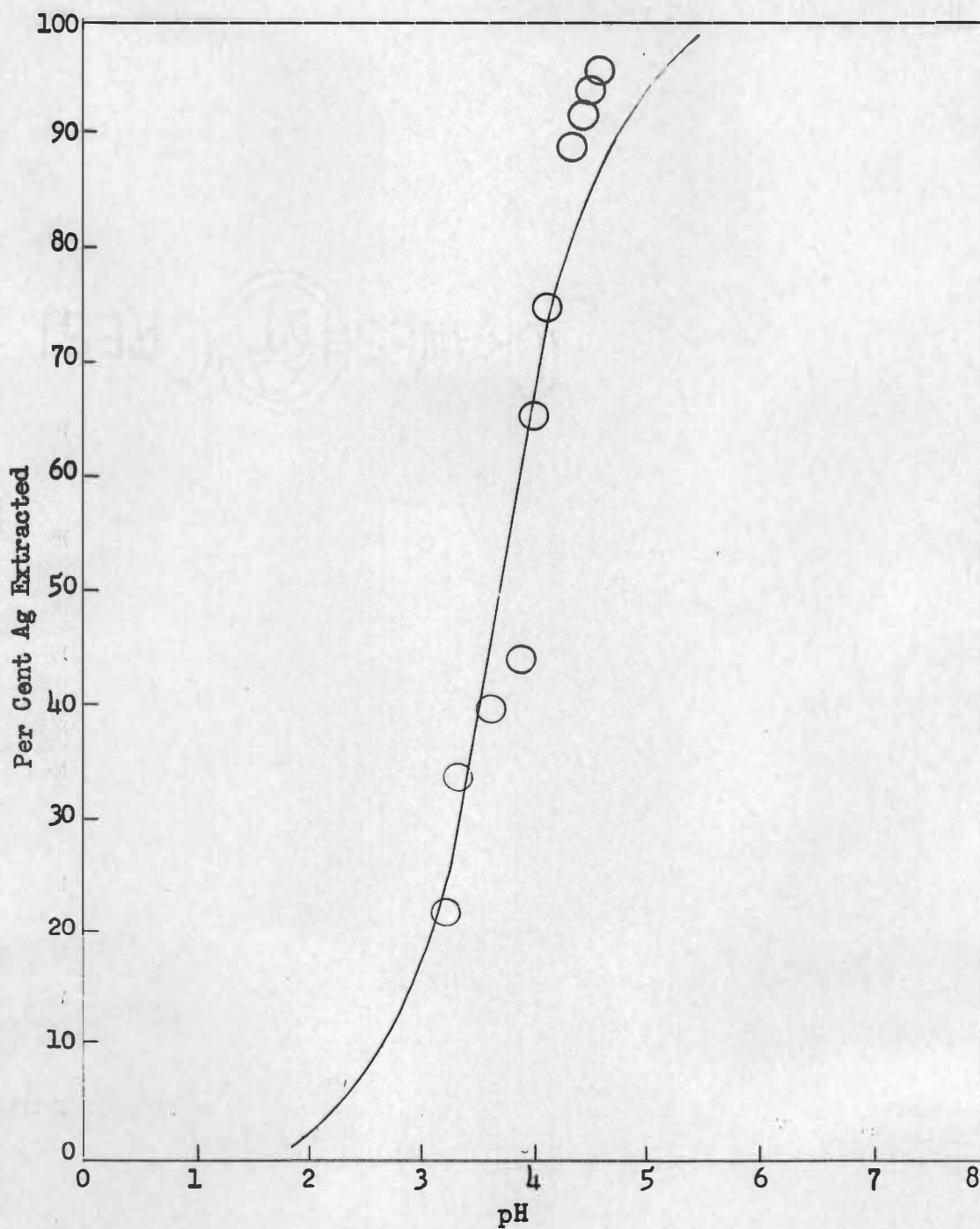


Figure 14. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.01-M. KI . Initial C_6H_6 phase: 1×10^{-3} -M. HD.

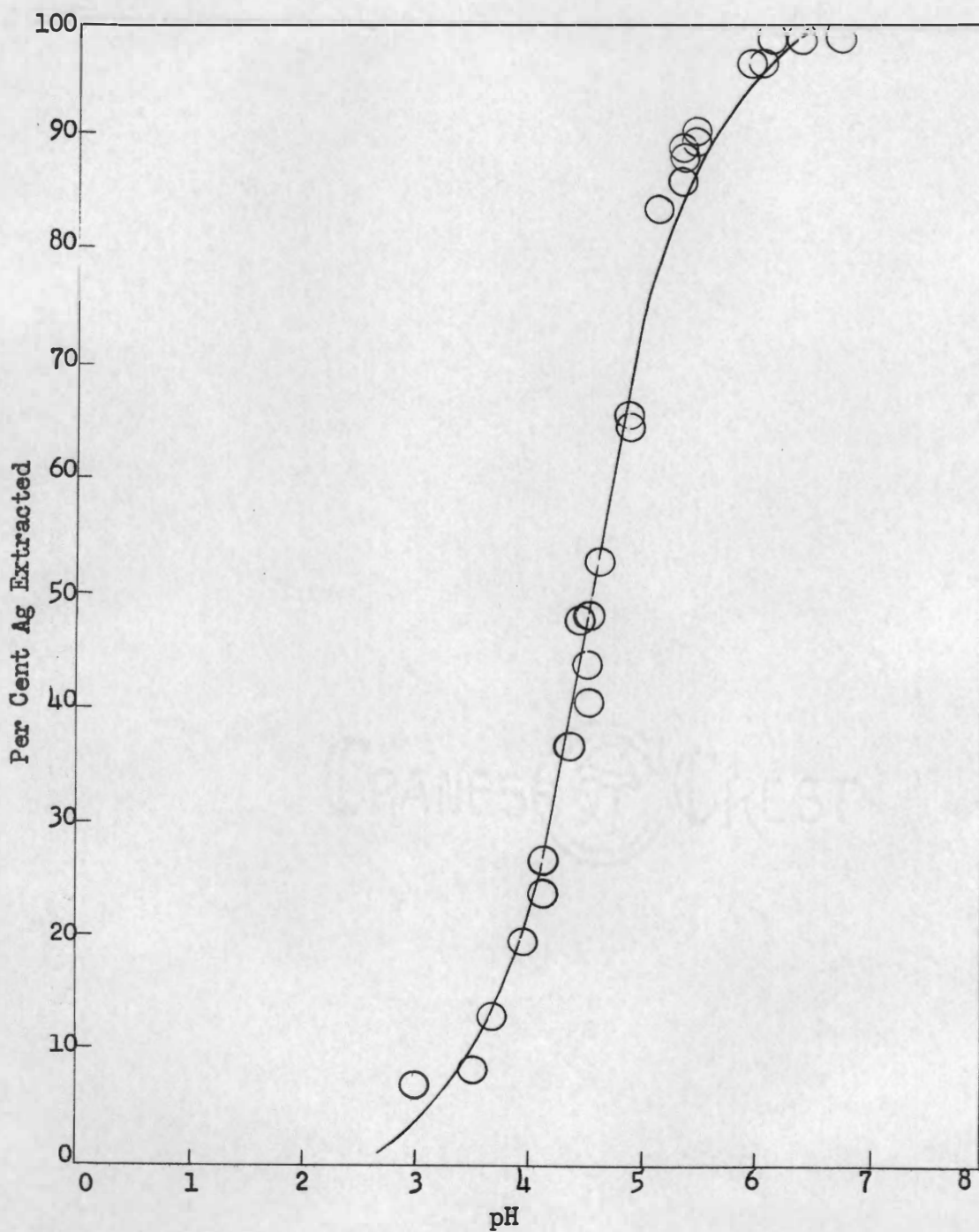


Figure 15. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.05-M. KI. Initial C_6H_6 phase: 4×10^{-3} -M. HD.

Figures 16, 17, and 18 present the results obtained from extractions of silver dithizonate from aqueous solutions of sodium thiocyanate into chloroform solutions of dithizone. Some extractions were made from aqueous solutions which contained 0.01-M. sodium thiocyanate and 0.09-M. sodium perchlorate. The effect of this increase in ionic strength does not seem to have been experimentally detected. Figure 16 gives the results obtained for extractions from 0.01-M. and 0.05-M. sodium thiocyanate solutions. In each case the dithizone concentration was 1×10^{-5} M. Values of $\text{pH}_{\frac{1}{2}}$ for the two curves are 3.5 and 5.4 respectively. Figure 17 shows the extraction of silver dithizonate from 0.1-M. sodium thiocyanate solutions. Extractions were made using two concentrations of dithizone. For the case in which dithizone was 1×10^{-5} M., a $\text{pH}_{\frac{1}{2}}$ equal to 6.2 was obtained. A $\text{pH}_{\frac{1}{2}}$ equal to 3.7 was obtained for the case in which the dithizone was 5×10^{-4} M. Silver dithizonate was also extracted into chloroform from 0.2-M. sodium thiocyanate solutions. Figure 18 shows the results of these experiments. The dithizone was 1.6×10^{-3} M. A $\text{pH}_{\frac{1}{2}}$ equal to 4.1 was obtained.

It can therefore be seen by comparing the results obtained for extractions from chloride, bromide, and thiocyanate solutions that the masking abilities of these ions increase in the order: chloride < bromide < thiocyanate.

Sodium thiosulfate was found to exert a very great masking effect upon the extraction of silver dithizonate. Figure 19 shows the results for the extraction of silver dithizonate from 1×10^{-5} -M. sodium thiosulfate solutions into chloroform which was 1×10^{-5} M. with dithizone. The $\text{pH}_{\frac{1}{2}}$ obtained was 2.6.

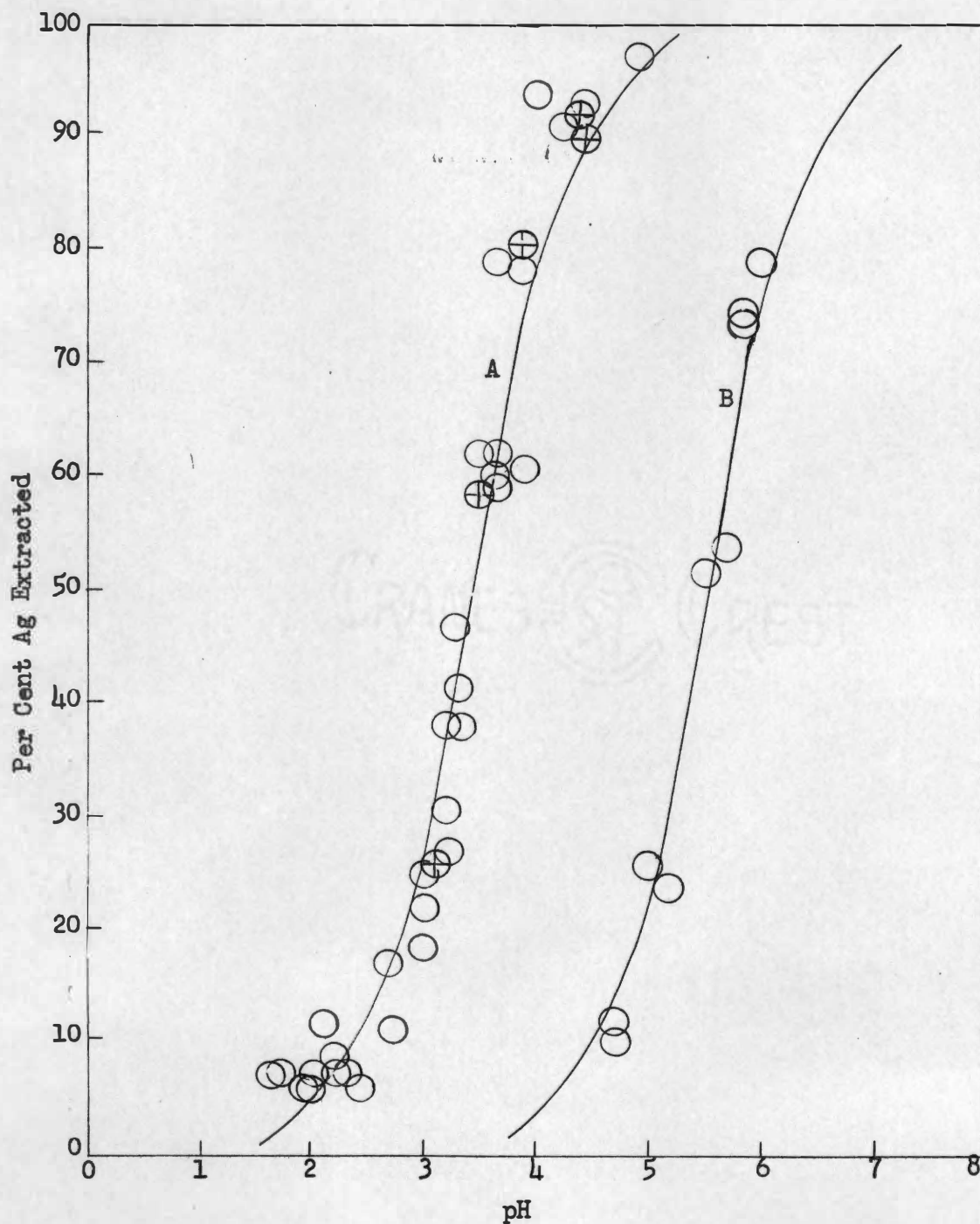


Figure 16. Plots of per cent Ag extracted versus final pH. Initial aqueous phases: HClO_4 , 1×10^{-7} -M. AgClO_4 , (A) $\bigcirc$ 0.01-M. NaSCN , $\oplus$ 0.01-M. $\text{NaSCN} + 0.09$ -M. NaClO_4 , (B) 0.05-M. NaSCN . Initial CHCl_3 phase: 1×10^{-5} -M. HD.

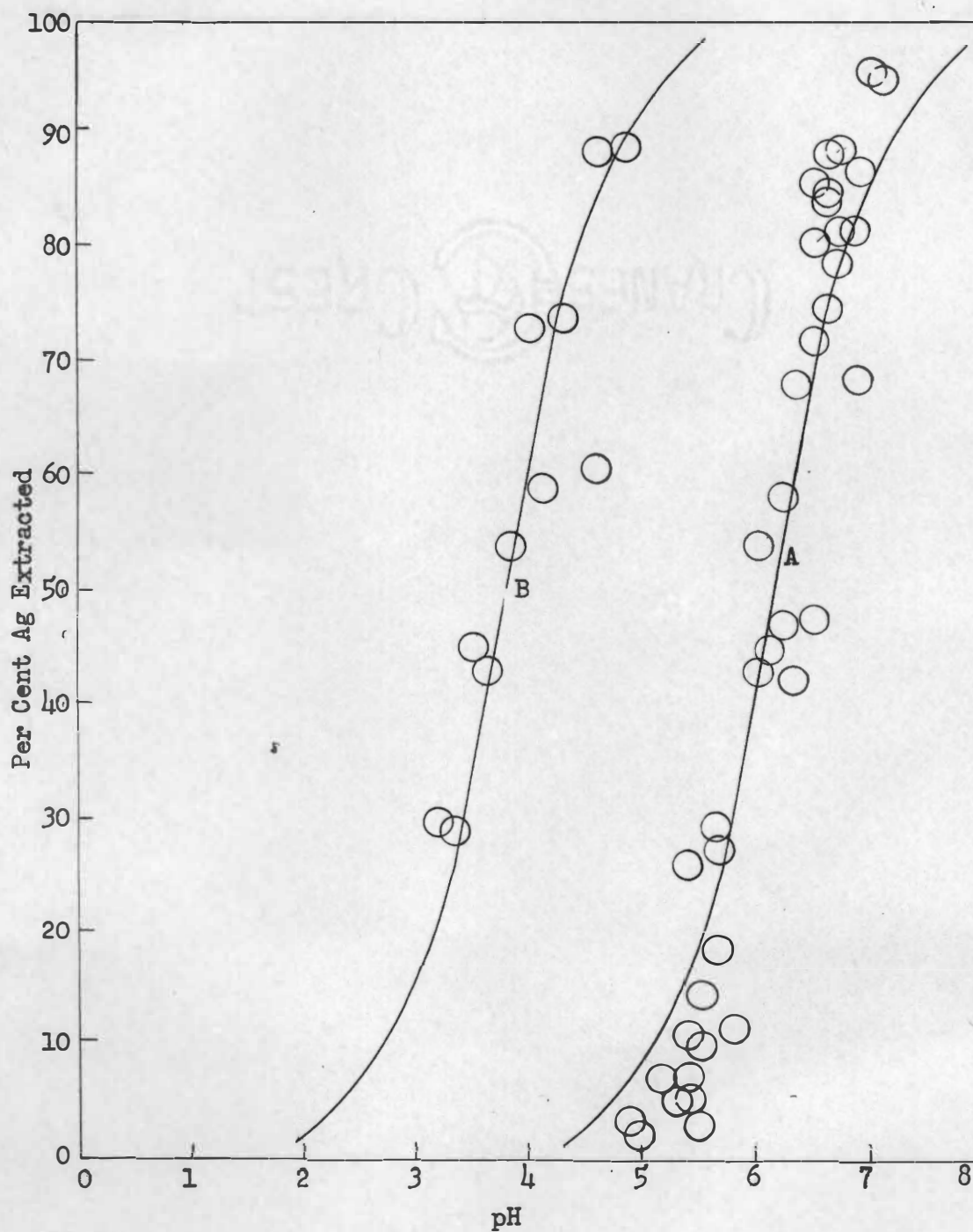


Figure 17. Plots of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.1-M. NaSCN . Initial CHCl_3 phase: (A) 1×10^{-5} -M. HD, (B) 5×10^{-4} -M. HD.

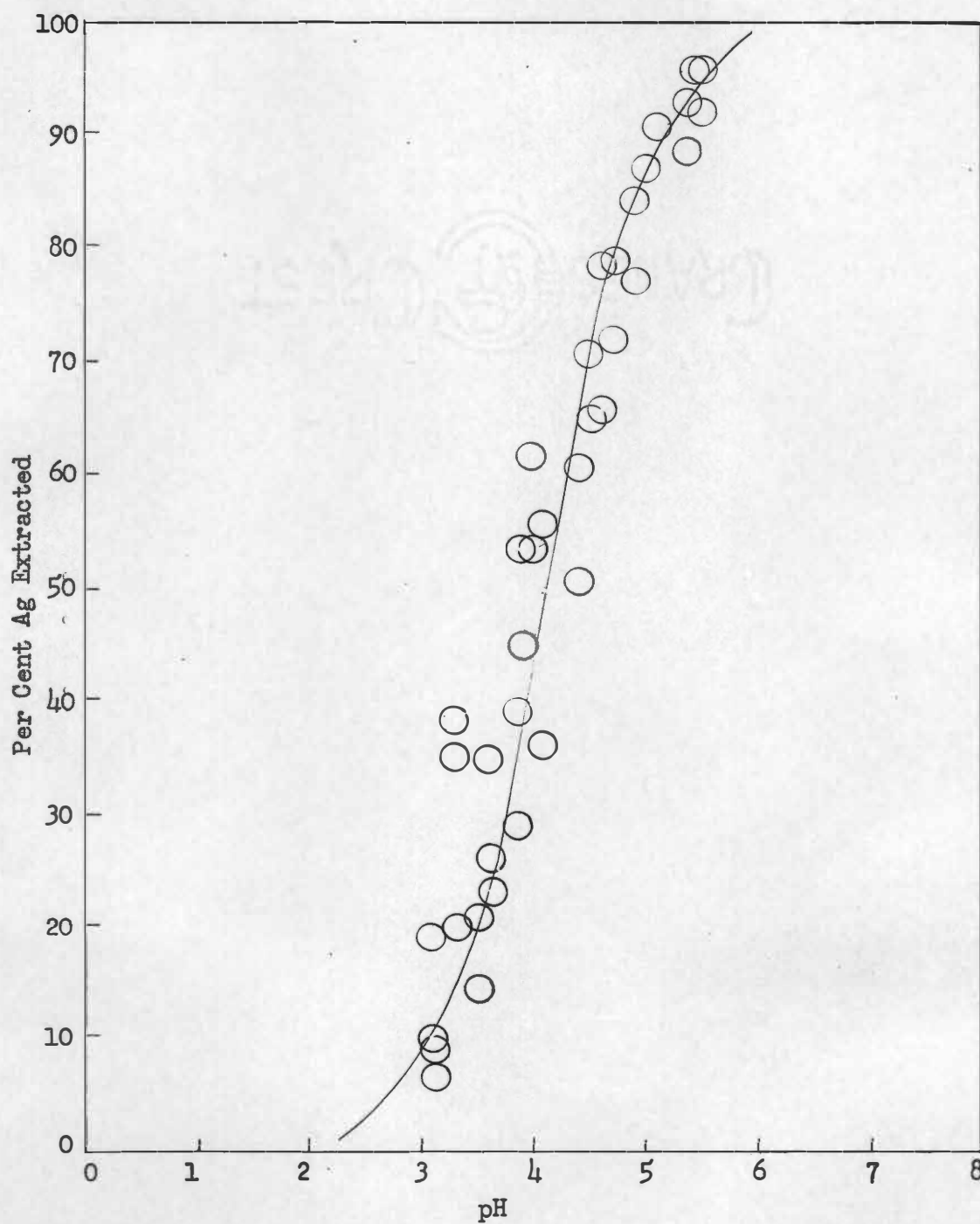


Figure 18. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.2-M. NaSCN . Initial CHCl_3 phase: 1.6×10^{-3} -M. HD.

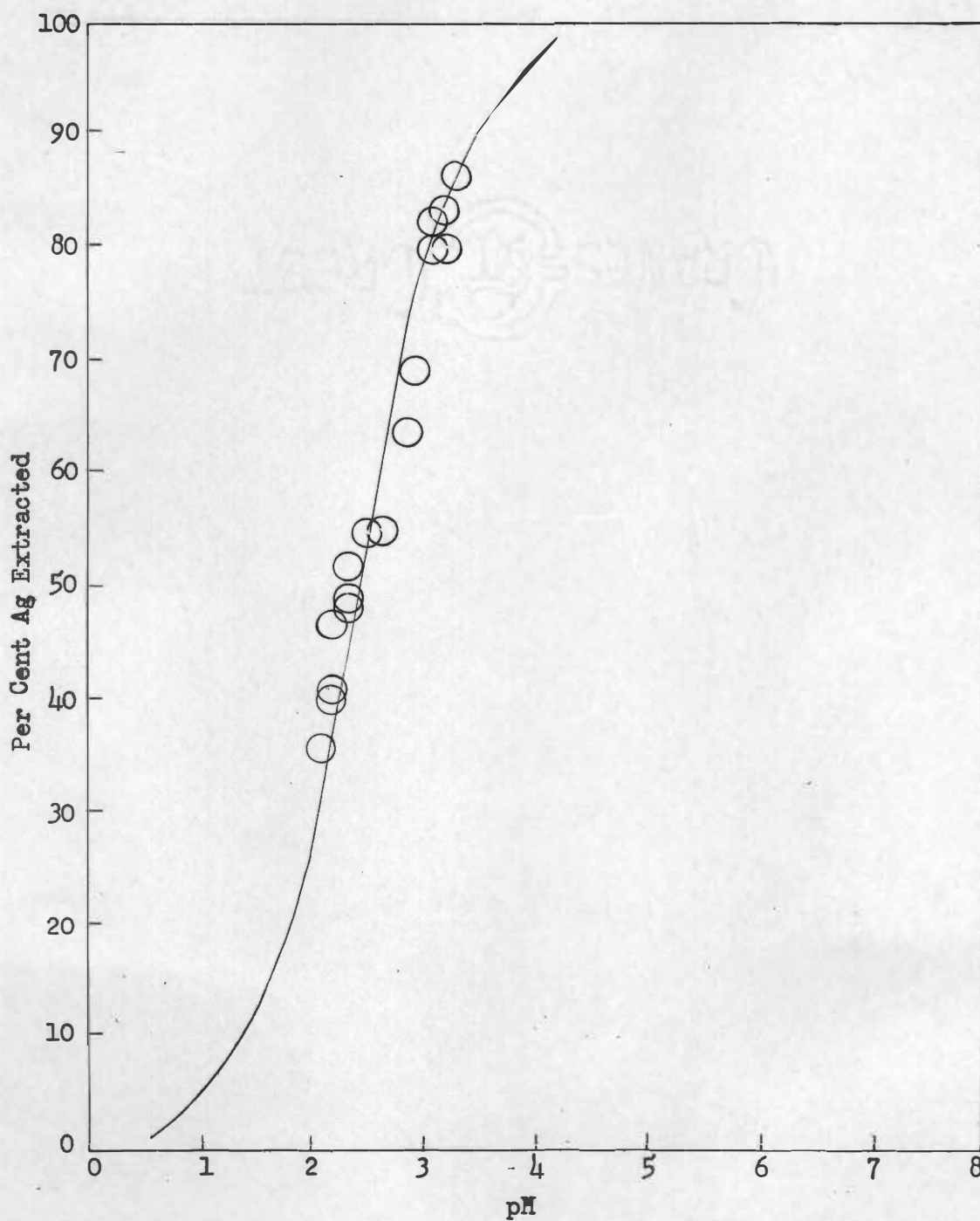


Figure 19. Plot of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 1×10^{-5} -M. $\text{Na}_2\text{S}_2\text{O}_3$. Initial CHCl_3 phase: 1×10^{-5} -M. HD.

3. Organic Solvent Changes

For all organic solvents investigated it was found that at 30° and with a dithizone concentration of 1×10^{-5} M. the non-masked extractions of silver dithizonate occurred at such large perchloric acid concentrations it was impossible to obtain the usual extraction curves. Experimental factors prevented the use of lower dithizone concentrations so that the curves might lie in higher pH ranges. Extractions were therefore carried out from aqueous solutions which contained 0.1-M. potassium bromide into the organic solvents which contained 5×10^{-5} -M. dithizone. The corresponding extractions into carbon tetrachloride has already been described, and the results are shown in Figure 7.

The results for extractions into dichloromethane, toluene, benzene, chlorobenzene, and bromobenzene are shown in Figures 20, 21, 22, 23, and 24 respectively. The respective pH_2 values which were found for these extractions are 3.5, 3.4, 3.4, 3.2, and 3.1. A corresponding extraction was attempted using carbon disulfide as the organic phase. However, when counts were made on both phases it was found that very little radioactivity remained in either phase. Thus the silver in some chemical form had either precipitated or adsorbed on the walls of the flask or on the interface of the two phases or both.

4. Dithizone Concentration Changes

Various concentrations of dithizone were used to obtain the data shown in Figures 4 to 23. However, for results of extractions in which the dithizone concentration is changed to be immediately meaningful, all other factors must be held constant. This requirement is met in the ex-

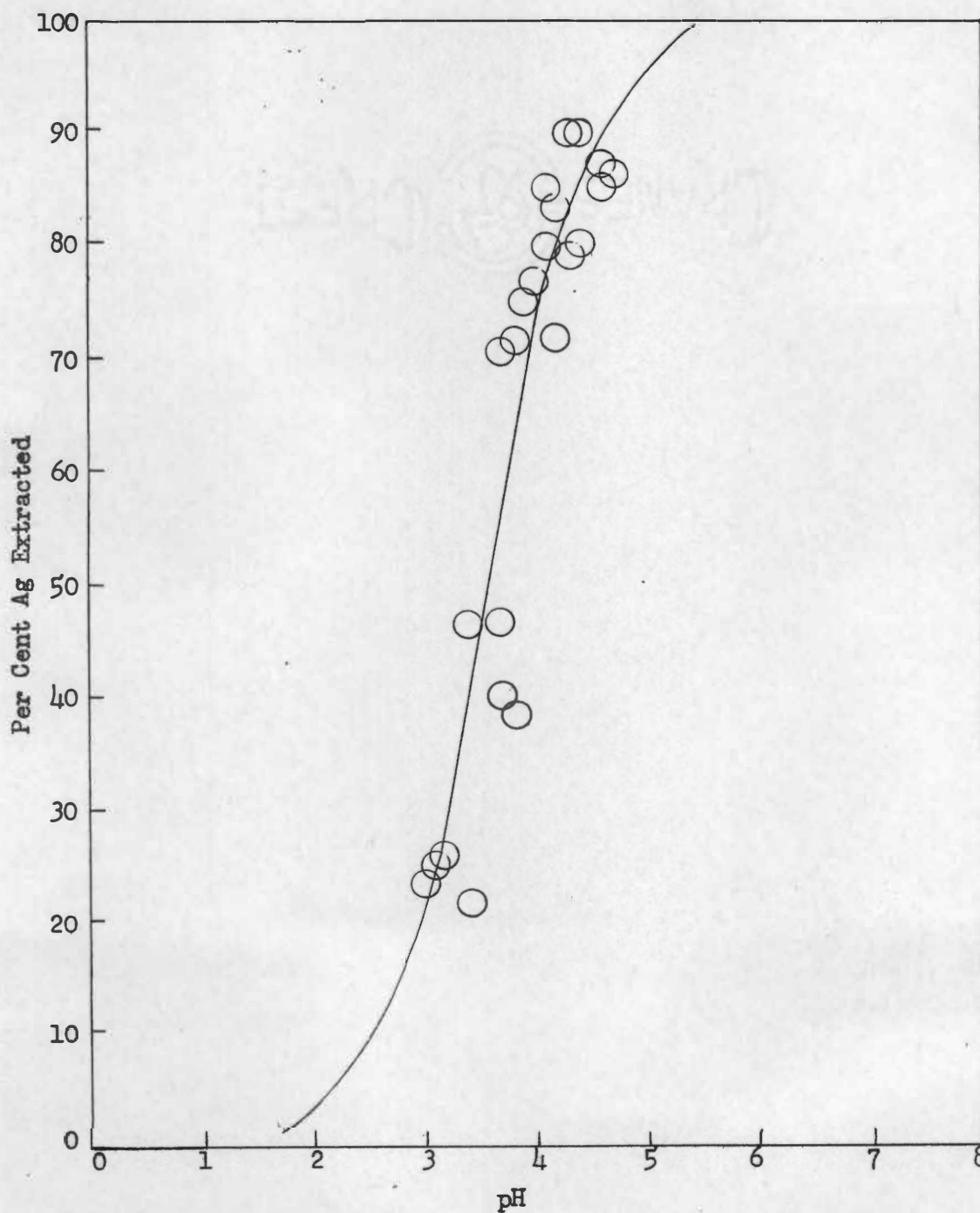


Figure 20. Plots of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.1-M. KBr. Initial CH_2Cl_2 phase: 5×10^{-5} -M. HD.

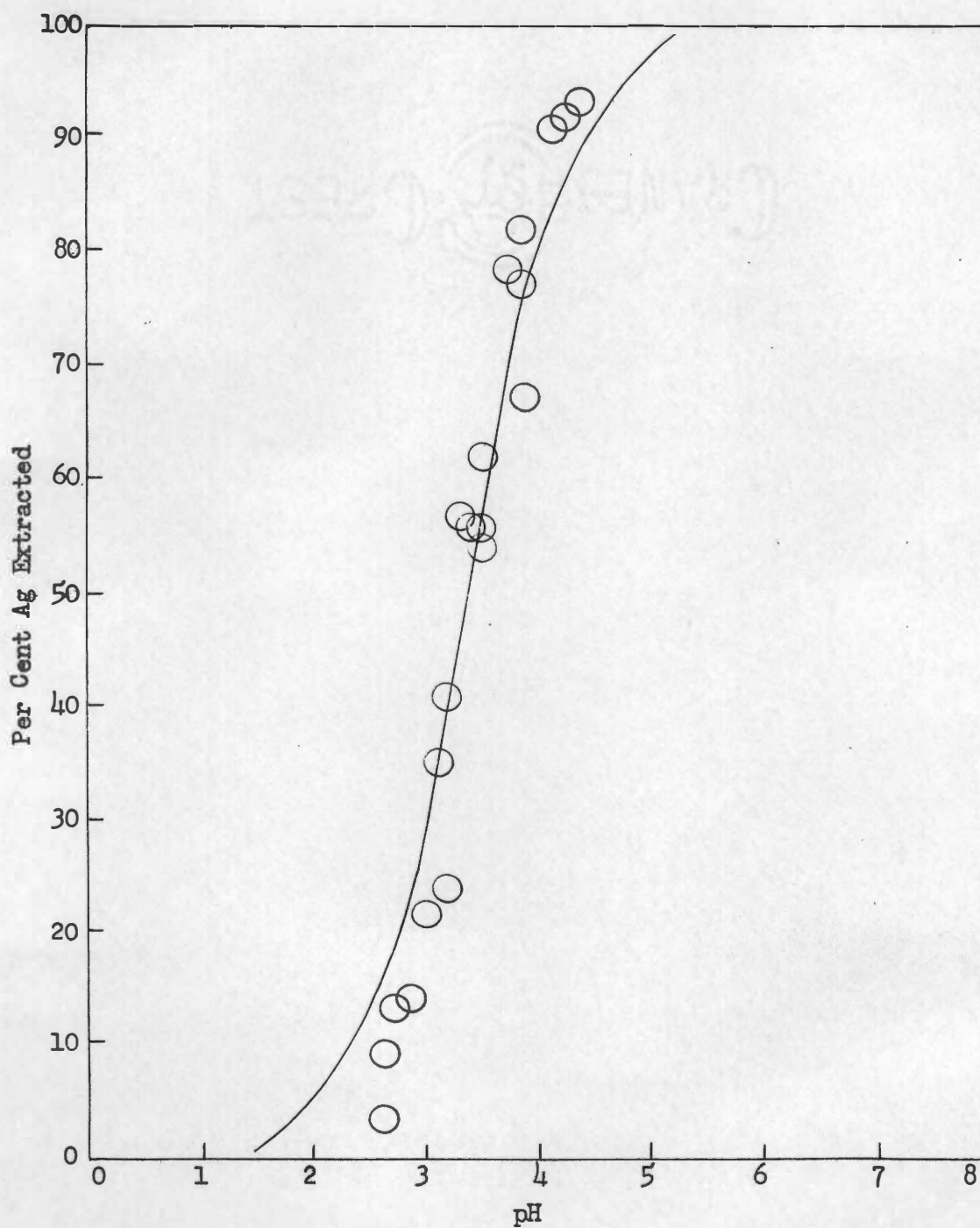


Figure 21. Plots of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.1-M. KBr . Initial $\text{C}_6\text{H}_5\text{CH}_3$ phase: 5×10^{-5} -M. HD.

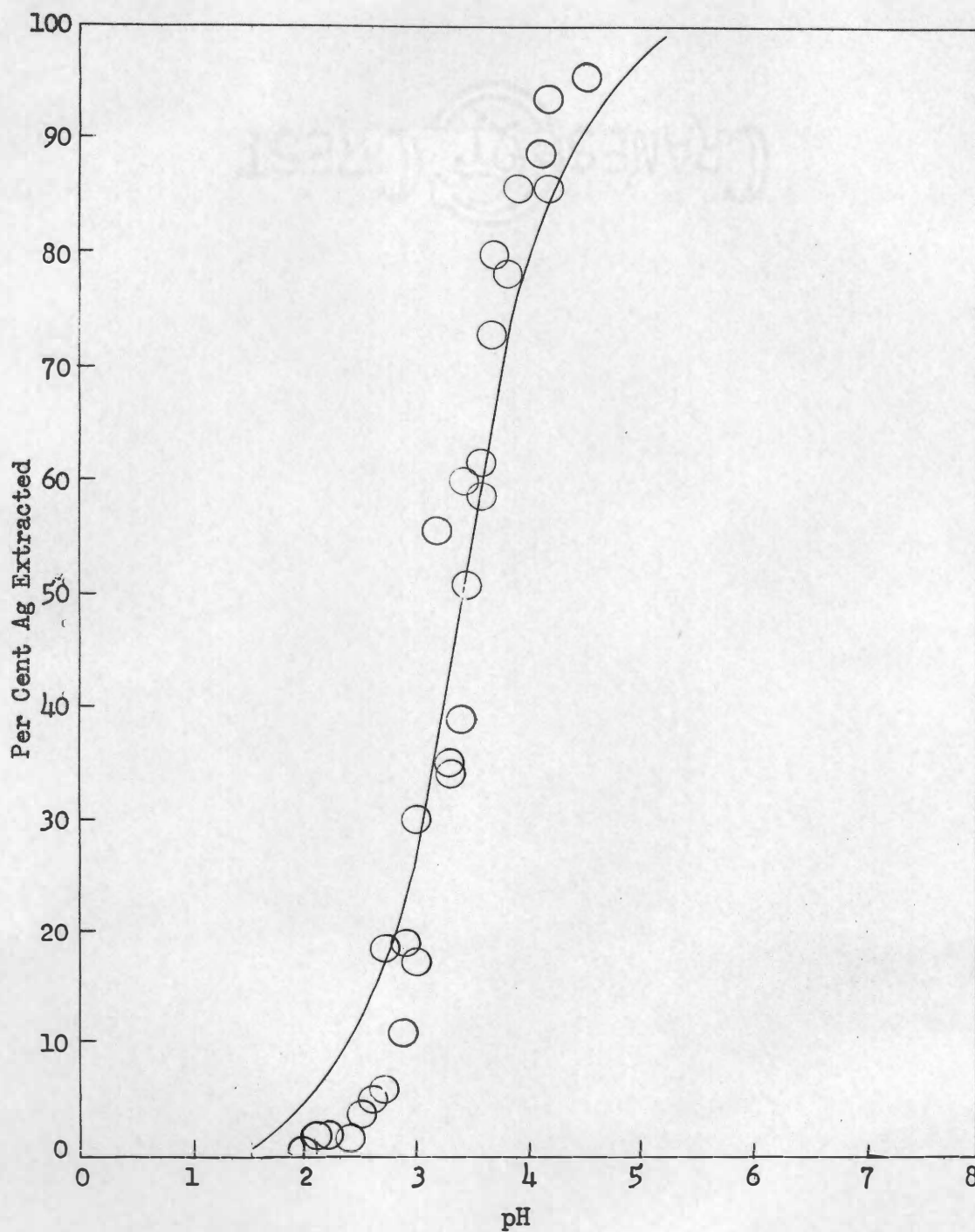


Figure 22. Plots of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.1-M. KBr. Initial benzene phase: 5×10^{-5} -M. HD.

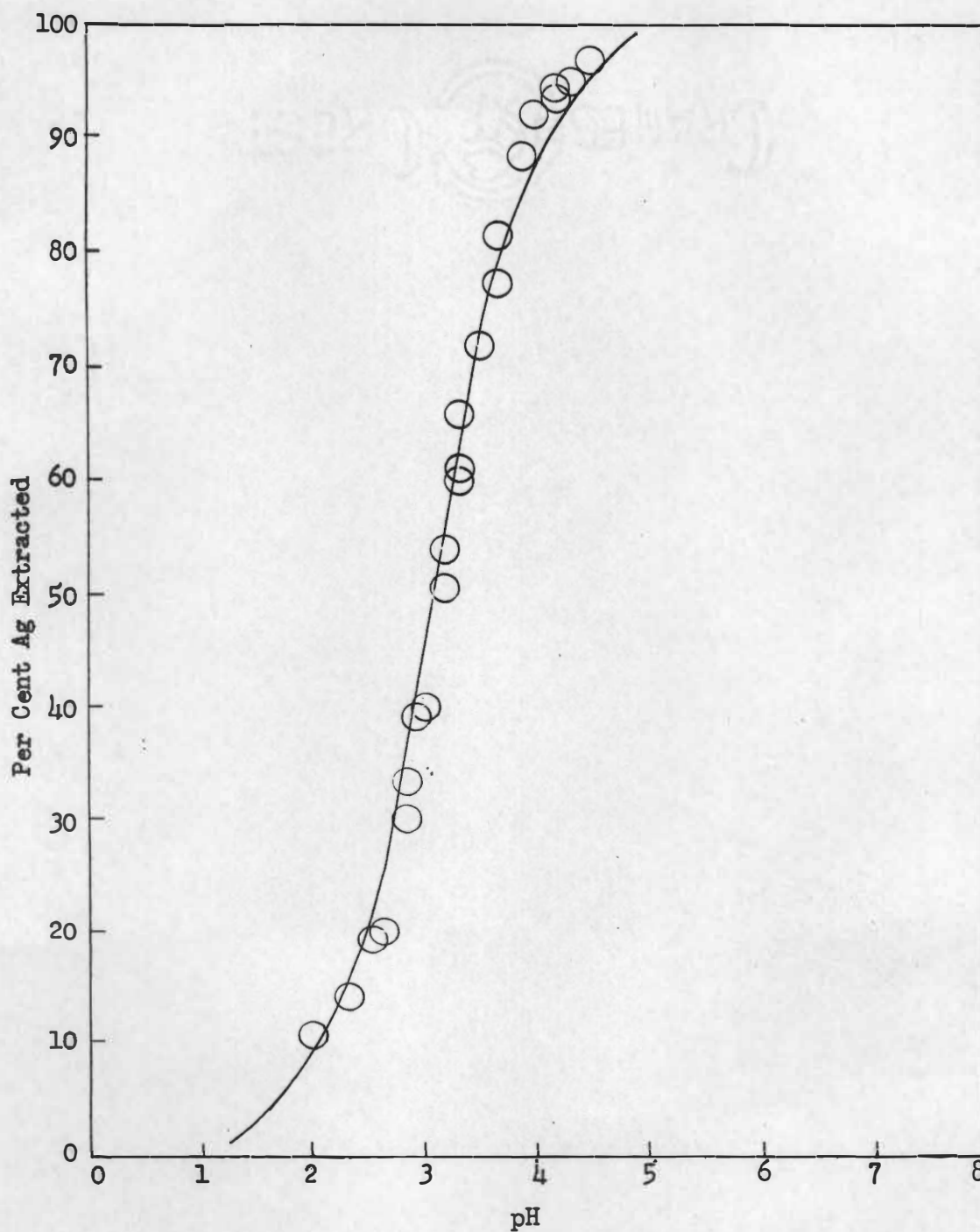


Figure 23. Plots of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.1-M. KBr. Initial $\text{C}_6\text{H}_5\text{Cl}$ phase: 5×10^{-5} -M. HD.

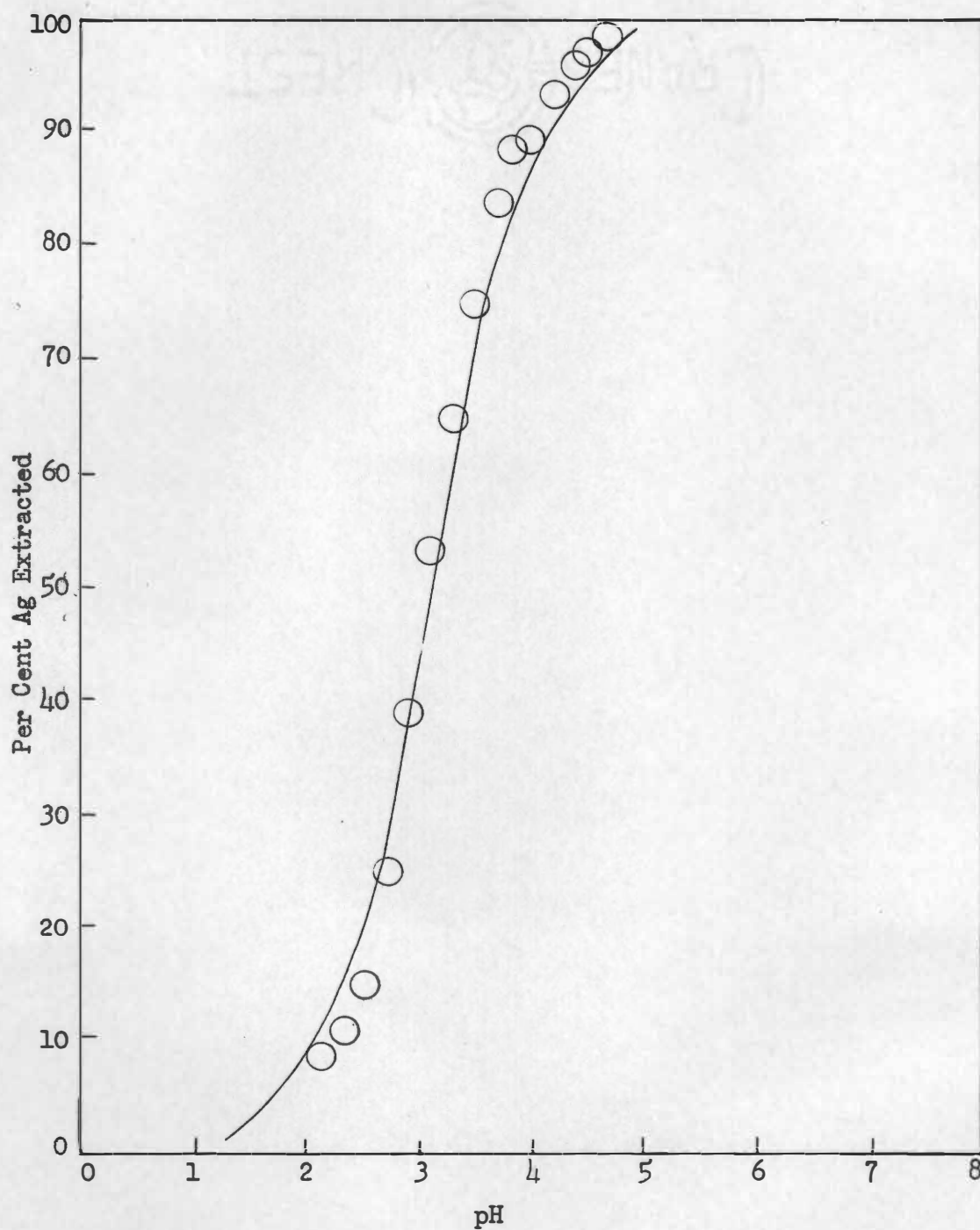


Figure 24. Plots of per cent Ag extracted versus final pH. Initial aqueous phase: HClO_4 , 1×10^{-7} -M. AgClO_4 , 0.1-M. KBr. Initial $\text{C}_6\text{H}_5\text{Br}$ phase: 5×10^{-5} -M. HD.

tractions represented in Figures 11 and 12, and in Figure 17. Figures 11 and 12 show the extractions made from 0.1-M. potassium bromide solutions. A change from a dithizone concentration of 1×10^{-5} M. to 5×10^{-4} M. lowers the $\text{pH}_{\frac{1}{2}}$ from 5.0 to 3.0. Figure 17 shows extractions from 0.1-M. sodium thiocyanate solutions. A change in the dithizone concentration from 1×10^{-5} M. to 5×10^{-4} M. lowers the $\text{pH}_{\frac{1}{2}}$ from 6.2 to 3.7.

5. Temperature Changes

Extractions of silver dithizonate from 1-M. perchloric acid solutions 1×10^{-7} M. in silver perchlorate into carbon tetrachloride 1×10^{-5} M. in dithizone gave the following results: at 35° , 94 per cent extraction. Corresponding extractions into chloroform at 25° , 30° , 35° , 40° , 45° , 50° , 55° , gave the following per cents extractions respectively: 88, 86, 77, 65, 55, 42, and 38.

6. Silver Dithizonate Solubilities

The solubility of silver dithizonate was measured at 30° in the organic solvents: chloroform, dichloromethane, carbon disulfide, bromobenzene, benzene, chlorobenzene, toluene, and carbon tetrachloride. The solubility of silver dithizonate in these solvents was found to be respectively in moles/l.: 1.6×10^{-2} , 1.2×10^{-2} , 1.1×10^{-2} , 1.1×10^{-2} , 0.82×10^{-2} , 0.74×10^{-2} , 0.46×10^{-2} , and 0.37×10^{-2} . An attempt was also made to measure at 30° the solubility of silver dithizonate in cyclohexane. It was found that the solubility was so low in this solvent that the radioactivity count of the samples taken was not above the back-

ground count. Indeed, the silver dithizonate did not impart any color to the cyclohexane. This datum indicates an extremely low solubility, since color probably would be detectable down to a concentration of 10^{-6} moles/l. One additional measurement was made at 50° with chloroform as the solvent. A solubility of 3.5×10^{-2} moles/l. was found. Thus the solubility of silver dithizonate in chloroform at 50° is more than twice its solubility at 30° .

CHAPTER IV

CALCULATIONS AND DISCUSSIONS

A. Presentation of Data and Calculated Quantities

To simplify the presentation of data for calculations of pertinent quantities, the information from the extractions are listed in Tables V, VI, and VII. So that easy reference may be made to the data and calculated values for a particular extraction, each extraction given in Tables V, VI, and VII is classified by a system number. Throughout this chapter these extractions will be referred to by their system numbers.

Table V shows the data which were obtained from cadmium extractions for which the usual extraction curves (pH versus per cent metal extracted) were obtained. The following information is given in Table V for each extraction curve: initial molarity of dithizone in the organic phase, composition of the aqueous phase, and the value of the pH for an extraction of 50 per cent, pH_2 . Also included in Table V are values of extraction constants, values of the logarithms of the extraction constants, and values of pH_2 which are calculated throughout this chapter. The data obtained for extractions of silver dithizonate from the more concentrated perchloric acid solutions are given in Table VI. The usual extraction curves were not obtained for these extractions, and each system in Table VI represents an extraction at only one acidity. The quantities listed in Table VI are organic phase, initial molarity of dithizone in the organic phase, molarity of perchloric acid in the aqueous phase, extractability E, temperature, cal-

TABLE V

DATA AND CALCULATED QUANTITIES FOR CADMIUM EXTRACTIONS AT 30° INTO CHLOROFORM^a

System No.	Initial (HD) ₀	Composition of Aqueous Phase	Observed	Calculated		
			pH _{1/2}	pH _{1/2}	K ^b	log K
1	5 x 10 ⁻³	HClO ₄ , 0.1-M. NaClO ₄	2.0		4	0.6
2	2 x 10 ⁻³	HClO ₄ , 0.1-M. NaClO ₄	2.5		3	0.5
3	2 x 10 ⁻³	HClO ₄ , 1.0-M. NaClO ₄	2.1		10	1.0
4	5 x 10 ⁻³	HClO ₄ , 0.1-M. KCl	2.4	2.4		
5	2 x 10 ⁻³	HClO ₄ , 1.0-M. KCl	3.5	3.2		
6	5 x 10 ⁻³	HClO ₄ , 0.1-M. KI	2.2	3.3		
7	2 x 10 ⁻³	HClO ₄ , 0.1-M. KBr	3.0	3.2		
8	2 x 10 ⁻³	HClO ₄ , 1.0-M. KBr	4.1	4.3		

^aThe initial concentration of cadmium perchlorate in the aqueous phase was 7 x 10⁻⁵ M.^bValues are expressed with one significant number.

TABLE VI

DATA AND CALCULATED QUANTITIES FOR SILVER EXTRACTIONS
FROM PERCHLORIC ACID SOLUTIONS^a

System No.	Organic Phase	HClO ₄ Molarity	Observed E	Calculated		t° C
				K x 10 ⁻⁵ b	log K	
9	CHCl ₃	1.0	7.5	8	5.9	25
10	CHCl ₃	1.0	6.2	6	5.8	30
11	CHCl ₃	1.0	3.3	3	5.5	35
12	CHCl ₃	1.0	1.9	2	5.3	40
13	CHCl ₃	1.0	1.2	1	5.0	45
14	CHCl ₃	1.0	0.7	0.7	4.8	50
15	CHCl ₃	1.0	0.6	0.6	4.9	55
16	CHCl ₃	1.7	3.4	6	5.8	30
17	CHCl ₃	2.9	1.4	4	5.6	30
18	CHCl ₃	3.4	0.9	3	5.5	30
19	CHCl ₃	4.4	0.5	2	5.3	30
20	CHCl ₃	6.0	0.2	1	5.0	30
21	CHCl ₃	1.7	22	40	6.6	0
22	CHCl ₃	2.9	14	40	6.6	0
23	CHCl ₃	3.4	12	40	6.6	0
24	CHCl ₃	4.4	8.8	40	6.6	0
25	CHCl ₃	6.0	3.2	20	6.3	0
26	CCl ₄	1.0	17	20	6.3	35
27	CCl ₄	1.0	6.0	6	5.8	45
28	CCl ₄	1.0	1.5	2	5.3	55

^aThe initial concentration of silver perchlorate in the aqueous phase was 1×10^{-7} M.

^bValues are expressed with one significant number.

TABLE VII

DATA AND CALCULATED QUANTITIES FOR SILVER EXTRACTIONS AT 30° a

System No.	Organic Phase	Initial (HD) ₀	Composition of Aqueous Phase	Observed pH _{1/2}	Calculated	
					pH _{1/2} K x 10 ^{-5b}	log K
29	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.1-M. KCl	2.4	2.1	
30	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.2-M. KCl	3.1	2.8	
31	CCl ₄	1 x 10 ⁻⁵	HClO ₄ , 0.1-M. KCl	1.3		
32	CCl ₄	1 x 10 ⁻⁵	HClO ₄ , 0.2-M. KCl	1.9		
33	CCl ₄	5 x 10 ⁻⁵	HClO ₄ , 0.1-M. KBr	3.1		30 6.5
34	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.01-M. KBr	2.9	2.3	
35	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.01-M. KBr, 0.2-M. NaClO ₄	2.6	2.3	
36	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.05-M. KBr	4.1	3.8	
37	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.05-M. KBr, 0.15-M. NaClO ₄	4.0	3.8	
38	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.08-M. KBr, 0.12-M. NaClO ₄	4.7	4.3	
39	CHCl ₃	5 x 10 ⁻⁴	HClO ₄ , 0.1-M. KBr	2.9	2.9	5 5.7
40	CHCl ₃	5 x 10 ⁻⁴	HClO ₄ , 0.1-M. KBr, 0.1-M. NaClO ₄	2.8	2.9	
41	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.1-M. KBr	5.0	4.6	
42	CHCl ₃	5 x 10 ⁻⁴	HClO ₄ , 0.2-M. KBr	3.8	4.4	
43	C ₆ H ₆	1 x 10 ⁻³	HClO ₄ , 0.01-M. KI	3.7	4.3	
44	C ₆ H ₆	4 x 10 ⁻³	HClO ₄ , 0.05-M. KI	4.5	4.8	
45	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.01-M. NaSCN	3.5	3.4	
46	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.05-M. NaSCN	5.4	5.1	
47	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 0.1-M. NaSCN	6.2	6.1	
48	CHCl ₃	5 x 10 ⁻⁴	HClO ₄ , 0.1-M. NaSCN	3.7	4.4	

TABLE VII

DATA AND CALCULATED QUANTITIES FOR SILVER EXTRACTIONS AT 30° a (Continued)

System No.	Organic Phase	Initial (HD) ₀	Composition of Aqueous Phase	Observed pH _{1/2}	Calculated	
					pH _{1/2}	K x 10 ^{-5b} log K
49	CHCl ₃	2 x 10 ⁻³	HClO ₄ , 0.2-M. NaSCN	4.1	4.8	
50	CHCl ₃	1 x 10 ⁻⁵	HClO ₄ , 1 x 10 ⁻⁵ -M. Na ₂ S ₂ O ₃	2.6	2.7	
51	CH ₂ Cl ₂	5 x 10 ⁻⁵	HClO ₄ , 0.1-M. KBr	3.5		10 6.0
52	C ₆ H ₅ CH ₃	5 x 10 ⁻⁵	HClO ₄ , 0.1-M. KBr	3.4		20 6.3
53	C ₆ H ₆	5 x 10 ⁻⁵	HClO ₄ , 0.1-M. KBr	3.4		20 6.3
54	C ₆ H ₅ Cl	5 x 10 ⁻⁵	HClO ₄ , 0.1-M. KBr	3.2		30 6.5
55	C ₆ H ₅ Br	5 x 10 ⁻⁵	HClO ₄ , 0.1-M. KBr	3.1		30 6.5

^aThe initial concentration of silver in the aqueous phase was 1 x 10⁻⁷ M.

^bValues are expressed with one significant number.

culated values of the extraction constants, and logarithms of the calculated extraction constants. Table VII contains the data for the silver dithizonate extractions for cases in which the usual extraction curves were obtained. Listed are the organic phase, the initial molarity of the dithizone in the organic phase, the composition of the aqueous phase, the experimental values of pH_2 , calculated values of pH_2 , extraction constants, and logarithms of extraction constants.

B. Extraction Equations

1. Non-Masked Experiments

The principal use of the data obtained from the non-masked extractions of cadmium and silver dithizonates was for the determination of extraction constants. Modifications of Eq. 20 and Eq. 22 were used for these calculations. Eqs. 20 and 22 may be rewritten in terms encountered in extractions of metal dithizonates. Rewriting Eq. 20 one obtains

$$K = \frac{E(H)^n}{(HD)_O^n} ; \quad \text{Eq. 46}$$

for Eq. 22 one may write

$$\log K = -n\text{pH}_2 - n\log (HD)_O . \quad \text{Eq. 47}$$

It will be assumed that the value of n for the cadmium extractions is 2, and that the value of n for the silver extractions is 1. Eqs. 46 and 47 were used to calculate quantities for the non-masked extractions.

2. Masked Extractions

For the masked extractions, the extractability was written as

$$E = \frac{(MD_n)_O}{(M) + (MX) + (MX_2) + (MX_3) + (MX_4)} \quad \text{Eq. 48}$$

where MD_n is either cadmium or silver dithizonate, M is either the cadmium or silver ion, and the quantities MX , MX_2 , MX_3 , MX_4 are complexes between either the cadmium or silver ion and the masking agent. Eq. 48 is essentially the reciprocal of the relation used by Waggener and Stoughton.⁵³ Throughout the remainder of this work, the complexes formed between the metal ion and the masking agent will be referred to as the masking complexes. In writing Eq. 48 the following assumptions were made: (1) that the contribution of the concentration of the specie MD_n in the aqueous phase could be neglected, (2) that no significant amounts of intermediate metal dithizonates such as MD_{n-1} are formed, (3) that the masking complexes are insoluble in the organic phase, (4) that no hydrolysis species of the metal are formed, (5) that no polymeric species of the metal ion are formed, and (6) that the maximum number of ligands attached to the masking complexes is four. By the use of the stability constants of the masking complexes (see page 32) it is possible to modify Eq. 48 to the following form:

$$E = \frac{(MD_n)_o}{(M) + K_1(M)(X) + K_2(M)(X)^2 + K_3(M)(X)^3 + K_4(M)(X)^4} \quad \text{Eq. 49}$$

By factoring the term (M) from the denominator and dividing the numerator and denominator by the term $(MD_n)_o$ in Eq. 49, one obtains

$$E = \frac{1}{\frac{(M)}{(MD_n)_o} [1 + K_1(X) + K_2(X)^2 + K_3(X)^3 + K_4(X)^4]} \quad \text{Eq. 50}$$

The ratio $(M)/(MD_n)_o$ has previously been shown to be given by (see page 16)

$$\frac{(M)}{(MD_n)_o} = \frac{(H)^n}{K(HD)_o^n} \quad .$$

Thus Eq. 50 can be written in the following form

$$E = \frac{1}{\frac{(H)^n}{K(HD)_0} [1 + K_1(X) + K_2(X)^2 + K_3(X)^3 + K_4(X)^4]} \quad \text{Eq. 51}$$

The writing of Eq. 51 is made shorter by employing the definition

$$F = \sum_{i=0}^4 K_i(X)^i \quad \text{Eq. 52}$$

One may then write

$$E = \frac{K(HD)_0^n}{(H)^{nF}} \quad \text{Eq. 53}$$

By taking the logarithm of Eq. 53 the following relation at 50 per cent extraction is obtained

$$\log K + n \log (HD)_0 + npH_{\frac{1}{2}} - \log F = 0 \quad \text{Eq. 54}$$

Eq. 54 is the form of the extraction equation which was used to treat the data obtained from the masked extractions. The equation is important from three aspects. If the quantities F , n , and $(HD)_0$ are known for an extraction, one may with a knowledge of the value of either one of the terms K or $pH_{\frac{1}{2}}$, calculate the other term. The possibility of determining the stability constants of the masking complexes also presents itself.

C. Cadmium Experiments

1. Calculation of Extraction Constant

Non-masked extractions of cadmium dithizonate were made into chloroform from 0.1-M. sodium perchlorate solutions. Systems 1 and 2 give the data for these extractions. Details for the calculation of the

extraction constant using the data from system 1 are as follows. The pertinent data are: $(HD)_0 = 5 \times 10^{-3}$ M., $pH_{\frac{1}{2}} = 2.0$, and $n = 2$. Inserting these values into Eq. 47 there results

$$\begin{aligned}\log K &= -2(2.0) - 2\log (5 \times 10^{-3}) \\ &= -4.0 - (-4.6) \\ &= 0.6 .\end{aligned}$$

Taking the antilogarithm, a value of 4 is obtained for K. A value of 3 is obtained for K by the use of the data from system 2. These two extractions are thus in quite good agreement.

System 3 gives data for the extraction of cadmium dithizonate from 1.0-M. sodium perchlorate solutions. In this case a value of $\log K$ is found to be 1.0 giving an extraction constant equal to 10. It should be noted that throughout this work extraction constants are expressed by one significant number affixed to the nearest order of ten magnitude.

2. Prediction of Effect of Masking Agents

As previously stated the effect of masking agents on the extractions was to produce a shift in the extraction curves to higher pH values. In all experiments except the extractions from 0.1-M. potassium iodide solutions, the curves for the masked extractions were roughly parallel to the non-masked curves. It was thought that the $pH_{\frac{1}{2}}$ for the masked extractions might be estimated by the use of Eq. 54. In section B-2 of this chapter it was stated that if the quantities F , $(HD)_0$, n , and K are known, the term $pH_{\frac{1}{2}}$ in Eq. 54 could be calculated. The value of F may be obtained if values of the stability constants of the masking complexes are available. For calculations in this work, the values of

these stability constants are taken from Table III. The values of the constants in Table III have not in each case been determined at the temperature at which these extractions were made; it is believed, however, that the error caused by this difference is slight in most cases.

System 4 shows the data for the extraction of cadmium dithizonate from 0.1-M. potassium chloride solutions into chloroform. Before calculations are made, the value of F is needed for a 0.1-M. chloride solution. From Table III it is seen that no values of the stability constants of the cadmium-chloride complexes were found for an ionic strength of 0.1 M. In view of this fact, a set of constants were chosen which gave a calculated $pH_{\frac{1}{2}}$ in agreement with the experimental $pH_{\frac{1}{2}}$. The chosen constants taken from the work of King⁸³ are as follows: $K_1 = 30$, $K_2 = 200$, and $K_3 = 300$. A value of K_4 was not given. In a number of calculations which involve the term F throughout this chapter, some of the constants K_1 , K_2 , K_3 , and K_4 could not be found in the literature. Nonetheless, calculations have been made with the constants which were available. It appears to be impossible to predict the error which is caused in the value of F by the omission of one or more of these constants. However, in most cases in the present calculations, it is thought that such errors are slight in view of the fact that other factors such as the effect of temperature upon the value of F are not considered. Pertinent data for the extraction are: $(HD)_0 = 5 \times 10^{-3}$ M., $(KCl) = 0.1$ M., $F = 5$, and $K = 3$. If n is assumed to have a value of 2, the value of $pH_{\frac{1}{2}}$ is calculated with Eq. 54 as follows:

$$2\text{pH}_{\frac{1}{2}} = -\log K - 2\log (\text{HD}) + \log F$$

$$2\text{pH}_{\frac{1}{2}} = -\log 3 - 2\log (5 \times 10^{-3}) + \log 5$$

$$= -0.4 + 4.6 + 0.7$$

$$= 4.9 .$$

Thus the $\text{pH}_{\frac{1}{2}}$ is equal to 2.4. A value of 2.4 was also obtained experimentally.

System 5 shows data for the extraction of cadmium dithizonate from 1.0-M. potassium chloride solutions into chloroform. The cadmium-chloride complexes have been studied at an ionic strength of 1.0 M.⁸⁰ Values of the stability constants at an ionic strength of 1.0 M. are: $K_1 = 20$, $K_2 = 60$, and $K_3 = 20$. Therefore a value of 100 is obtained for F . The dithizone concentration was 2×10^{-3} M. If the value of $\log K$ is taken to be 1.0 (the value obtained for extractions from 1.0-M. sodium perchlorate solutions) the following calculations may be made:

$$2\text{pH}_{\frac{1}{2}} = -1.0 - 2\log (2 \times 10^{-3}) + \log 100$$

$$= -1.0 + 5.4 + 2.0$$

$$= 6.4 .$$

The calculated value of $\text{pH}_{\frac{1}{2}}$ is thus 3.2, and the experimental value is 3.5, a difference of 0.3 pH unit.

Although the cadmium dithizonate extraction from 0.1-M. potassium iodide solutions did not behave as the other masked extractions, the $\text{pH}_{\frac{1}{2}}$ value for this curve was found to be 2.2. This value is entered under system 6 in Table VI. The following values for the cadmium-iodide complexes were taken from the literature⁸⁵ and entered in Table III: $K_1 = 2 \times 10^2$, $K_2 = 8 \times 10^3$, $K_3 = 1 \times 10^5$, and $K_4 = 1 \times 10^6$. The value of F for a 0.1-M. iodide solution is equal to 300. Pertinent data taken from

system 6 are: $(\text{HD})_0 = 5 \times 10^{-3} \text{ M.}$, and $(\text{KI}) = 0.1 \text{ M.}$ Using a value of 3 for K and 2 for n , the $\text{pH}_{\frac{1}{2}}$ for this extraction is calculated to be 3.3. Thus the predicted $\text{pH}_{\frac{1}{2}}$ is much larger than the observed value. It was thought that a possible explanation for the peculiar behavior of this extraction might well be that the specie CdI_2 extracts into the chloroform phase. However, this possibility was not tested.

The data for extractions from 0.1-M. potassium bromide solutions are shown under system 7. Stability constants for the masking complexes were not found for an ionic strength of 0.1 M. However, there was reasonably good agreement among the values of the stability constants found. The constants determined by Riley and Gallafent⁷⁷ were chosen. Values of the constants are: $K_1 = 200$, $K_2 = 1000$, $K_3 = 3000$, and $K_4 = 10,000$. The value of F is 3.4. Data for system 7 are: $(\text{HD})_0 = 2 \times 10^{-3} \text{ M.}$, and $(\text{KBr}) = 0.1 \text{ M.}$ The calculated value of $\text{pH}_{\frac{1}{2}}$ is found to be 3.2. Experimentally 3.0 was obtained for this value. Using these same stability constants for the masking complexes, a value of $\log K$ equal to 1.0, and the data from system 8, the calculated $\text{pH}_{\frac{1}{2}}$ for the extraction of cadmium dithizonate from 1.0-M. potassium bromide solutions is 4.3. The observed $\text{pH}_{\frac{1}{2}}$ was 4.1.

3. Prediction of Effect of Dithizone Concentration Change

The effect produced on the extractions by a change of the dithizone concentration may be evaluated by comparing the data of systems 1 and 2. In Chapter I it was shown (see Eq. 28) that one might expect that if the dithizone concentration is changed by a factor of 10, the effect upon the per cent extraction is equivalent to a change of pH of 1.0 unit. Al-

though the difference of $(HD)_0$ between systems 1 and 2 is small, the expected difference between the $pH_{\frac{1}{2}}$ values is approximately obtained. The difference between the $pH_{\frac{1}{2}}$ values for the two systems is 0.5; the numerical difference between the logarithms of the dithizone concentrations is 0.4.

4. Prediction of the Value of n .

The value of n is equal to the number of dithizonate ions which react with the cadmium ion to form a neutral cadmium dithizonate molecule. It has been shown in Chapter I that for n equal to 2, the extraction curve should show a slope at 50 per cent extraction of 115 per cent metal extracted/pH unit. Since all of the cadmium extraction curves except the extraction from 0.1-M. iodide solution approximate this slope closely at 50 per cent extraction, it appears that the assumption that n equals 2 is justified.

D. Silver Experiments

1. Calculation of Extraction Constants from Data of Non-Masked Extractions

System 9 gives an averaged value of the extractability from data which were obtained for extractions at 25° of silver dithizonate from 1.0-M. perchloric acid solutions into chloroform. Eq. 46 may be used in conjunction with the data of system 9 to calculate the extraction constant. Pertinent data for the calculation are: $E = 7.5$, $(HD)_0 = 1 \times 10^{-5}$ M., and $(HClO_4) = 1.0$ M. For all extractions of silver the value of n was assumed to be 1. The calculation of the extraction constant using Eq. 46 is made as follows:

$$K = \frac{7.5(1.0)}{1 \times 10^{-5}} = 8 \times 10^5$$

The value of $\log K$ is 5.9. The values of K and $\log K$ are entered in Table VI. Systems 10 through 25 show data which were obtained for extractions of silver dithizonate from various perchloric acid concentrations. The temperature at which each extraction was made is given in Table VI. The extraction constants for these systems have been calculated and are shown in Table VI. Also some extractions were made into carbon tetrachloride. The concentration of perchloric acid was 1.0 M. The data for these extractions are shown in systems 26, 27, and 28. The extraction constants for these three systems have been calculated and are entered in the corresponding system in Table VI.

2. Calculation of Extraction Constants from Data of Masked Extractions

It was previously shown that if the quantities F , $(HD)_0$, n , and pH_2 are known for a masked extraction, Eq. 54 may be used to calculate a value of the extraction constant. Extractions of silver dithizonate have been made from 0.1-M. potassium bromide solutions into these organic solvents: chloroform, carbon tetrachloride, dichloromethane, toluene, benzene, chlorobenzene, and bromobenzene. Using the constants, $K_1 = 1 \times 10^4$, $K_2 = 1 \times 10^7$, $K_3 = 9 \times 10^7$, and $K_4 = 8 \times 10^8$ for the masking complexes as determined by Berne and Leden,¹⁰⁵ a value of F is obtained to be 2×10^5 . Using this value of F along with data from systems 39, 33, 51, 52, 53, 54, and 55 extraction constants for extractions at 30° into chloroform, carbon tetrachloride, dichloromethane, toluene, benzene, chlorobenzene, and bromobenzene were obtained to be respectively 5×10^5 ,

3×10^6 , 1×10^6 , 2×10^6 , 2×10^6 , 3×10^6 , and 3×10^6 . These constants and the logarithms of these constants are entered in Table VIII.

3. Calculation of $pH_{\frac{1}{2}}$ Values for Masked Extractions

The extraction constants which have been determined may now be used so that $pH_{\frac{1}{2}}$ values for other masked extractions may be predicted. Systems 29 and 30 show data for extractions of silver dithizonate from 0.1-M. and 0.2-M. potassium chloride solutions respectively. Details for the calculation of the $pH_{\frac{1}{2}}$ for system 29 are as follows: Pertinent data are: $K = 6 \times 10^5$, $(HD)_0 = 1 \times 10^{-5}$ M., $(KCl) = 0.1$ M., $K_1 = 7 \times 10^2$, $K_2 = 5 \times 10^4$, $K_3 = 1 \times 10^5$, and $K_4 = 8 \times 10^5$. The value of K was taken from system 10, and the quantities K_1 , K_2 , K_3 , and K_4 are those determined by Berne and Leden.⁹⁹ The value of F is equal to 8×10^2 . Eq. 54 for $n = 1$ states that

$$pH_{\frac{1}{2}} = -\log K - \log (HD) + \log F.$$

Inserting appropriate quantities into this equation there is obtained

$$\begin{aligned} pH_{\frac{1}{2}} &= -\log (6 \times 10^5) + -\log (1 \times 10^{-5}) + \log (8 \times 10^2) \\ &= -5.8 + 5.0 + 2.9 \\ &= 2.1 . \end{aligned}$$

The experimental $pH_{\frac{1}{2}}$ was found to be 2.4. Making use of the same values of K , K_1 , K_2 , K_3 , and K_4 and the data of system 30, a $pH_{\frac{1}{2}}$ was calculated to be 2.8. The observed $pH_{\frac{1}{2}}$ is 3.1.

Systems 31 and 32 show data for the extractions of silver dithizonate from 0.1-M. and 0.2-M. potassium chloride solutions into carbon tetrachloride. The pertinent extraction constant was previously determined to be 3×10^6 . Making use of the values of K_1 , K_2 , K_3 , and K_4

which were used to calculate values of pH_2 for systems 29 and 30, a pH_2 was obtained for system 31 to be 1.4. The observed value is 1.3. A pH_2 of 2.1 was calculated for system 32; a value of 1.9 was observed.

Systems 34, 35, 36, 37, 38, and 42 give data for extractions from 0.01-M., 0.05-M., 0.08-M., and 0.2-M. potassium bromide solutions into chloroform. The following values for the stability constants of the masking complexes were chosen: $K_1 = 1 \times 10^4$, $K_2 = 1 \times 10^7$, $K_3 = 9 \times 10^7$, and $K_4 = 8 \times 10^8$. These constants were determined by Berne and Leden.¹⁰⁵ The values of $\log F$ were calculated to be 3.1, 4.6, 5.1, and 6.9 for the corresponding extractions listed above. For these extractions pH_2 values were calculated to be 2.3, 3.8, 4.3, and 4.4. Experimentally these quantities were found to be 2.9, 4.1, 4.7, and 3.8 respectively. The pH_2 was observed to shift to slightly lower values in cases in which the aqueous phase contained small amounts of sodium perchlorate. Values for the pH_2 for these extractions have been estimated and are listed in Table VII.

Extractions from 0.1-M. potassium bromide solutions were made, and the data are listed in systems 39, 40, and 41. For systems 39 and 40 the dithizone concentrations were 5×10^{-4} M.; for system 41 the dithizone was 1×10^{-5} M. A value for the pH_2 may be calculated for systems 39 and 40 to be 2.9. A pH_2 equal to 2.9 was observed. For system 41 the calculated pH_2 is 4.6; the observed value is 5.2. It should be pointed out that even though agreement between calculated and observed pH_2 values is reasonably good, better agreement might possibly be obtained if other values of K_1 , K_2 , K_3 , and K_4 listed in Table III were used. Also one

should note that the temperatures listed in Table III do not in all cases correspond exactly with the temperatures at which these extractions were performed.

Systems 43 and 44 list data for extractions from 0.01-M. and 0.05-M. potassium iodide solutions into benzene. If values of K_1 , K_3 , and K_4 are chosen from Table III to be 1×10^8 , 4×10^{13} , and 1×10^{14} respectively, a pH_2 is calculated for system 43 to be 4.3. A value of K_4 was not found. A pH_2 equal to 3.7 was observed. The pH_2 for system 44 was calculated to be 4.8. A value of 4.5 was observed. An extraction constant equal to 2×10^6 was used to make these calculations.

Mass balance was not obtained in the extraction from the 0.01-M. potassium iodide solutions. The radioactivity measurements of the aqueous phase were very erratic. It was suspected that the solubility product of silver iodide had been exceeded in these solutions. This idea might have been tested by taking the samples through a filter cone; however, this procedure was not followed. A search of the literature was made for solubility measurements of silver iodide in water which was saturated with benzene. No such work was found, however.

Values of pH_2 were calculated for the extractions which were carried out from sodium thiocyanate solutions into chloroform. Systems 45, 46, 47, 48, and 49 list these extractions; the pH_2 values were calculated to be 3.4, 5.1, 6.1, 4.4, and 4.8. The corresponding observed values were found to be 3.5, 5.4, 6.2, 3.7, and 4.1. In order to make these calculations the quantities K_1 , K_2 , K_3 , and K_4 were taken from the work of Leden and Nilsson.¹¹⁷ The values of these constants are 4×10^4 ,

1×10^8 , 4×10^9 , and 3×10^{10} respectively.

System 50 gives data for the extraction of silver dithizonate from 10^{-5} -M. sodium thiosulfate solutions into chloroform. The quantities $K_2 = 3 \times 10^{13}$ and $K_3 = 1 \times 10^{14}$ are given in Table III. Values of K_1 and K_4 were not found. Using values of K_2 and K_3 , a $\text{pH}_{\frac{1}{2}}$ for this extraction was calculated to be 2.7. The observed $\text{pH}_{\frac{1}{2}}$ was found to be 2.6.

4. Calculation of Stability Constants of Masking Complexes

In order to obtain values for the stability constants of the complexes MX , MX_2 , MX_3 , and MX_4 (assuming that these complexes form) from extraction data, a large amount of extraction data must be obtained. At the very minimum four accurate values of the per cent extraction at four different concentrations of the masking agent must be obtained. These four extractions must be carried out at concentrations of masking agent so that at least at one of the per cent extractions, each of the complexes is effective in determining this per cent extraction. Obviously, at very high concentrations of the masking agent one could learn very little about K_1 unless, of course, it was possible to accurately determine the concentration of MX .

Sufficient extraction data were obtained for the extractions of silver dithizonate from potassium bromide solutions into chloroform so that it was possible to use Eq. 54 to calculate values for the stability constants of the complexes formed between the silver ion and the bromide ion. It should be noted that even though Eq. 54 contains the term $\text{pH}_{\frac{1}{2}}$, data from extractions at other pH values may be used with slight modifications of the extraction equation.

In order to calculate values for K_1 , K_2 , K_3 , and K_4 , the data from four systems in Table VII were chosen so that four simultaneous equations could be written. Systems 35, 37, 40, and 42 were chosen to provide the data for these equations. The ionic strength of the aqueous phase in each of these systems was approximately 0.2 M. Experimental values of pH_2 , $(\text{HD})_0$, and (KBr) for these systems are respectively: system 35, 2.6, 1×10^{-5} M., and 0.01 M.; system 37, 4.0, 1×10^{-5} M., and 0.05 M.; system 40, 2.8, 5×10^{-4} M., and 0.1 M.; system 42, 3.8, 5×10^{-4} M., and 0.2 M. By inserting these data into Eq. 54, the following four symbolic equations may be written:

$$\log F_a = 3.4$$

$$\log F_b = 4.8$$

$$\log F_c = 5.3$$

$$\log F_d = 6.3$$

where the subscripts a, b, c, and d refer to the molarities 0.01, 0.05, 0.1, and 0.2 of the potassium bromide respectively. These equations have been rewritten in terms of the constants K_1 , K_2 , K_3 , and K_4 , and the values of these constants were solved for by the method of determinants. The corresponding values of the constants were found to be 3×10^4 , 3×10^7 , 6×10^7 , and 2×10^9 . These values compare quite well with those found in the literature and given in Table III.

5. Prediction of Effect of Dithizone Concentration Changes

If the only difference of composition between two extractions is that the organic phase of one contains more or less dithizone than the other, the resulting pH_2 values should be simply and directly related by the following expression:

$$\text{pH}_2' - \text{pH}_2 = \log \frac{(\text{HD})_0'}{(\text{HD})_0}$$

where the primed quantities refer to one of the extractions, and the unprimed quantities refer to the other extraction. This relation may be obtained from either Eq. 47 or Eq. 54. Thus it makes no difference whether or not the aqueous phases contain masking agent. Two pairs of extractions of silver dithizonate were carried out for which calculations may be made. These two pairs of extractions are listed in systems 39 and 41 and systems 47 and 48. For systems 39 and 41 the difference in the pH_2' values was found to be 2.3. The value of $\log (\text{HD})_0'/(\text{HD})_0$ was calculated to be 1.7. The difference between the pH_2' values for systems 47 and 48 was found to be 2.5. The logarithm function was calculated to be 1.7.

6. Prediction of the Value of n

It was shown in Chapter I (see page 28) that the extraction curves for non-masked extractions should have slopes at pH_2 equal to $57.57n$. The same result may easily be obtained for the extraction curves of masked extractions if the quantity F is not a function of the pH viz. if the masking agent, X , is not an anion of a weak acid. Since all of the masked extractions of silver gave extraction curves with slopes very near 57, it appears that the assumption that $n = 1$ is justified.

There has been some controversy in the literature about whether or not thiocyanic acid, HSCN , is a strong acid. Data from pH measurements of thiocyanic acid solutions have led previous workers to conclude that it is a strong acid.¹²⁹ The fact that the extraction curves in this work

show slopes very near 57 at $\text{pH}_{\frac{1}{2}}$ adds further support to the contention that thiocyanic acid is a strong acid.

7. Calculations Involving Solubility Measurements

In his study of the solvent extraction of zinc dithizonate, Honaker¹³ gave an expression which was supposed to relate at equal extractabilities for two extractions into two different organic solvents the hydrogen ion concentrations to the solubilities of complexing reagent, HR, and metal complex, MR_n , in the organic solvents (see page 29). The assumptions leading to this derivation were that the partition coefficients of the complexing reagent and metal complex, P_r and P_c , could be approximated by the ratios of the molar solubilities of the complexing reagent and metal complex in water to their solubilities in the organic solvents. Expressed in equation form for one organic solvent, these assumptions are:

$$P_r = \frac{S_{rw}}{S_r} \quad \text{Eq. 55}$$

and

$$P_c = \frac{S_{cw}}{S_c} \quad \text{Eq. 56}$$

where S_{rw} and S_{cw} are the solubilities of the complexing reagent and metal complex respectively in water, and S_r and S_c are the corresponding solubilities of these species in the organic solvent.

If equal extractabilities are obtained for two extractions into different solvents and if all factors except the organic solvents are equal, then the following relation should hold:

$$\frac{K(HR)_0^n}{(H)^n} = \frac{K'(HR)_0^n}{(H')^n}$$

where the primed and unprimed quantities refer to different solvents.

By cancelling the term $(HR)_0^n$ one may obtain

$$\frac{K}{K'} = \frac{(H)^n}{(H')^n} \quad \text{Eq. 57}$$

By the use of Eq. 30 and Eq. 57 the following expression is obtained

$$K \frac{S_r^n}{S_c} = K' \frac{S_r'^n}{S_c'} \quad \text{Eq. 58}$$

One may therefore write

$$K \frac{S_r^n}{S_c} = C \quad \text{Eq. 59}$$

where the quantity C should be approximately constant. The term C will be called the solvent factor.

Thus it should be possible to obtain approximate values of extraction constants for a particular complex extraction into other organic solvents by the use of solubility measurements, once the value of the solvent factor has been established for the complex and some solvent. The consistency of Eq. 59 has been tested using solubilities of silver dithizonate and extraction constants for silver dithizonate extractions which were determined in this study and solubilities of dithizone which were determined by Honaker. Honaker's data are reported on page 4. Values of the solvent factor were obtained at 30° as follows: chloroform, 3×10^6 ; dichloromethane, 4×10^6 ; benzene, 3×10^6 ; chlorobenzene, 4×10^6 ; and carbon tetrachloride, 2×10^6 . Thus it is seen that for silver dithizonate extractions the solvent factor is obtained to be approximately constant.

The data which were given by Honaker for zinc dithizonate extractions was used to calculate the solvent factor for zinc dithizonate extractions. Numerical values were obtained as follows: benzene, 0.5; carbon tetrachloride, 0.3; chlorobenzene, 0.2; dichloromethane, 0.09; and chloroform, 0.01. Thus an approximately constant value of the solvent factor was obtained for all of these extractions except the extraction into chloroform.

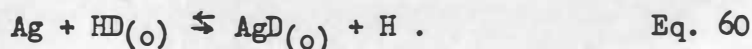
8. Treatment of the Effect of Temperature Change

Extractions of silver dithizonate were made at several temperatures from 1.0-M. perchloric acid solutions into chloroform and carbon tetrachloride. It was found that if the values of $\log K$ for the extractions were plotted versus the reciprocal of the absolute temperature straight lines were obtained. These plots are shown in Figure 25. The values of $\log K$ are listed in Table VI. It was found for extractions into chloroform that for every rise of 5° the value of $\log K$ decreased approximately 0.2. The slope for this curve was found to be 3.5×10^3 $^{\circ}\text{C}$. By the use of the value of the slope it is possible to obtain an equation of the straight line which relates $\log K$ and $1/T$ as follows:

$$\log K = (3.5 \times 10^3)/T - 5.9 \quad \text{Eq. 59}$$

Thus a value of the extraction constant for the extraction into chloroform may be obtained for any temperature in the interval 25° to 55° . Presumably extrapolations could be made to higher or lower temperatures.

The overall reaction for the extraction of silver dithizonate into an organic phase is given by



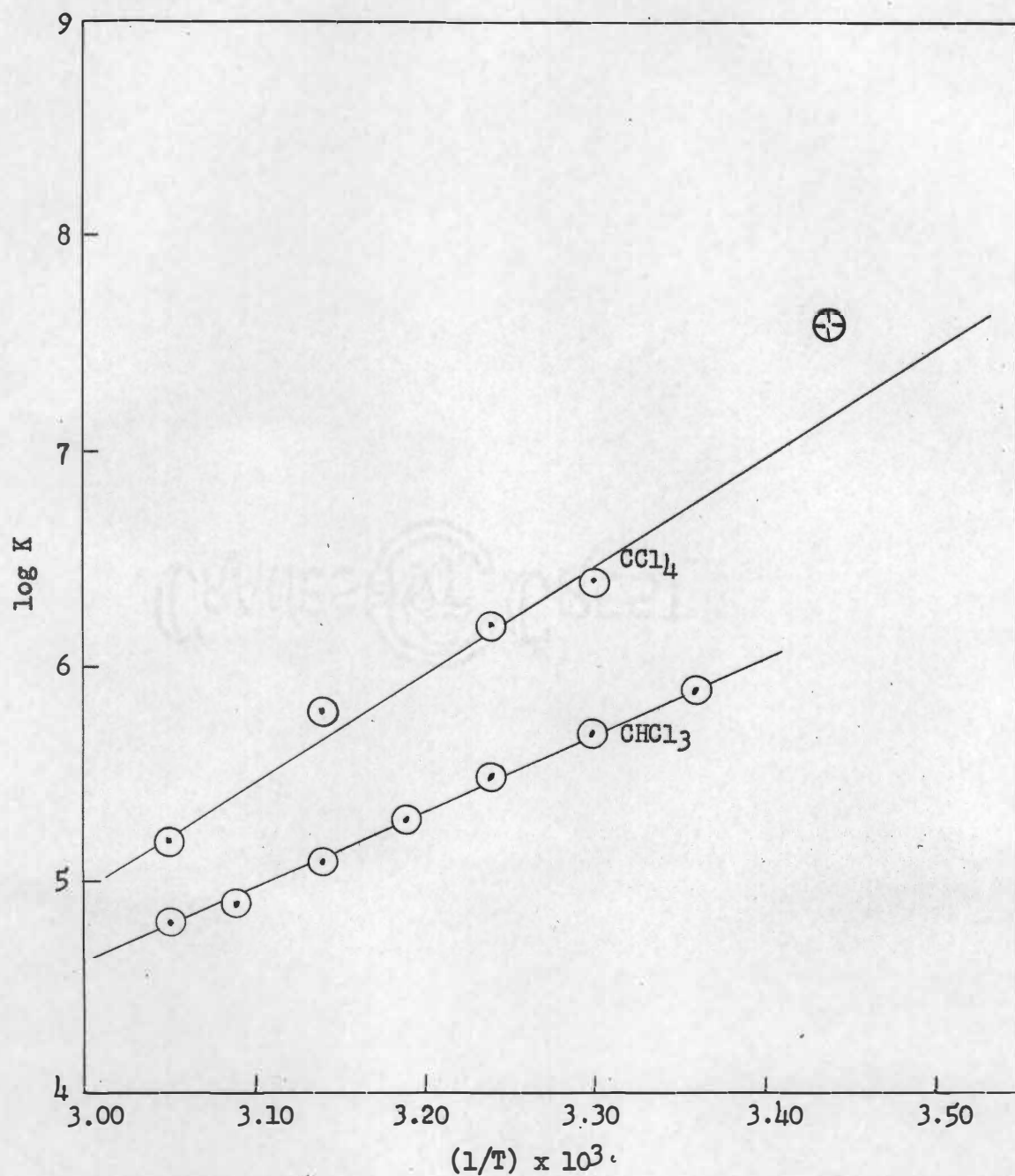


Figure 25. Plots of $\log K$ versus $1/T$ for extractions into chloroform and carbon tetrachloride. $\oplus$ Value obtained by Tremillon.⁴³

The enthalpy of this reaction may be calculated from the slope of the line represented by Eq. 59 as follows:

$$\begin{aligned}\Delta H^{\circ} &= -2.3R(\text{slope}) \\ &= -2.3 \times 1.98 \times 3.5 \times 10^3 \\ &\approx -16 \text{ kcal./mole.}\end{aligned}$$

It is possible to calculate values of the free energy for the reaction of Eq. 60 from the equation

$$\Delta F^{\circ} = -2.3RT \log K \quad \text{Eq. 61}$$

and values of the entropy from

$$\Delta S^{\circ} = (\Delta H^{\circ} - \Delta F^{\circ})/T. \quad \text{Eq. 62}$$

The value of ΔF° is -8.0 kcal./mole at 25° and -7.2 kcal./mole at 55°. The value of ΔS° is approximately -30 entropy units over the temperature range 25° to 55°.

Extractions of silver dithizonate from 1.0-M. perchloric acid into carbon tetrachloride were made at 35°, 45°, and 55°. Figure 25 contains a point at 30° which was calculated using data which were obtained from extractions from 0.1-M. potassium bromide solutions. Also included is a value of $\log K$ which was determined by Tremillon.⁴³ Tremillon's value lies slightly above the line which is extrapolated from the values determined in this study.

The straight line for the extractions into carbon tetrachloride can be represented by

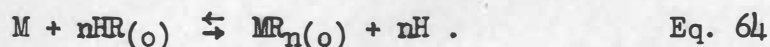
$$\log K = (5.3 \times 10^3)/T - 11.0. \quad \text{Eq. 63}$$

The value of ΔH° for these extractions over the interval 35° to 55° is found to be -24 kcal./mole. The quantities ΔF° and ΔS° are fairly

constant over this interval and are equal to approximately -8 kcal./mole and -50 e.u. respectively.

E. Activity Considerations

Irving and Williams²⁰ gave the generalized equation for the extraction of a metal complex such as a metal dithizonate as:



By considering activity coefficients as was done by Furman, Mason, and Pekola,⁵⁵ one may write the thermodynamic or true extraction constant as follows:

$$K' = \frac{(MR_n)_o(H)^n f_{MR_n}^n f_H^n}{(M)(HR)_o^n f_M^n f_{HR}^n} \quad \text{Eq. 65}$$

where f_{MR_n} , f_H , f_M , and f_{HR} are the activity coefficients of the species indicated by the subscripts. For extractions in which the concentrations of reagent HR and complex MR_n in the organic phase are quite low, the ratio f_{MR_n}/f_{HR}^n would probably be near unity especially if n is equal to 1. If it is assumed that this ratio is near unity, then it follows that

$$K' = \frac{(MR_n)_o(H)^n f_H^n}{(M)(HR)_o^n f_M^n} \quad \text{Eq. 66}$$

The extraction constant, K , which has previously been given and calculated may now be written as:

$$K = K' \frac{f_M}{f_H^n} \quad \text{Eq. 67}$$

Eq. 67 shows how activity coefficients of aqueous species affect the value of the extraction constant as determined by Eqs. 20 and 46. In

general the values of f_M and f_H are not known making it impossible to calculate a true extraction constant. One might suspect that for aqueous solutions having an ionic strength of a few tenths molar the ratio f_M/f_H^n should be near unity.

How the consideration of activity coefficients affect extraction constants which are determined by Eqs. 22 and 47, should also be indicated. In Eqs. 22 and 47 concentration and activity terms are mixed. Values of $pH_{\frac{1}{2}}$ were used for calculations with these equations. Since pH determinations with a pH meter involve the mean activity of the hydrogen ion, the calculated extraction constant may be written as follows:

$$K = K'f_M \quad \text{Eq. 68}$$

Therefore constants which are determined by Eqs. 22 and 47 may differ more from the true extraction constant than constants which are calculated by Eqs. 20 and 46. This consideration may partially explain the difference between the constants determined by systems 1 and 3.

One method of avoiding the mixing of concentration and activity terms is to calibrate all pH determinations in terms of concentration of hydrogen ion. This procedure was not followed in this study.

F. Conclusions

1. Determination of Extraction Constants

It has been shown that it is possible to determine extraction constants from data derived from masked extractions by the use of a theoretical equation involving the stability constants of the complexes formed

in the aqueous phase between the metal ion and the masking agents. Moreover it has been shown that the values of constants determined by this method are in agreement with constants determined from data of non-masked extractions. A variation of the method employing masking agents was previously used⁴² for determining the extraction constant of mercury dithizonate.

Thus it appears that a very promising method is available for the determination of extraction constants. Determinations of extraction constants for some metal dithizonates have been complicated by the fact that the metals extract at such high acid concentrations. Silver dithizonate extraction into carbon tetrachloride is such an example. However, by suitable adjustment of the concentrations of dithizone and masking agent, extraction may be made to proceed at any acidity which is desired. The data from the masked extractions may then be used to calculate extraction constants.

2. Prediction of the pH of Extraction of Masked Extractions

It has been shown that it is possible to predict by the use of a theoretical equation the pH of 50 per cent extraction for the extraction of metal complexes from aqueous solutions containing masking agents into organic solvents which contain the complexing reagent. Since the masked extraction curves were shown to behave as the non-masked extraction curves (that is, to have the same slope and shape), it is therefore possible to predict the pH of any other per cent extraction. Also the small amount of data which were obtained for systems in which the ionic strength was varied slightly appears to indicate that such variations do not de-

crease the accuracy of predictions.

If it were possible to make such predictions for any metal complex, the gains derived for analytical purposes would be great indeed. Although much more data would have to be available before such predictions could be made, it is felt that the present study constitutes a significant step in that direction.

3. Calculation of Stability Constants of Masking Complexes

The data for extractions of silver dithizonate from aqueous solutions of potassium bromide have been used to determine the stability constants of complexes formed between the silver ion and bromide ions. In order to obtain these constants, four equations were solved simultaneously. It appears that many factors limit such a treatment, and that to determine such constants in general it would probably be a better procedure to resort to one of the many graphical methods which are available in the literature.⁵⁸

4. Prediction of Solvent Change Effect

A function has been derived which is approximately constant for the extraction of a particular metal dithizonate into any organic solvent. The function, the solvent factor, is expressed in terms of the solubilities of the dithizone and the metal dithizonate in the organic solvent and in terms of the extraction constant. The function was tested using data from this work and the study made by Honaker. Use of the function should enable one to approximate the extraction constant of a metal complex once the function has been established for one solvent.

5. The Effect of Temperature Change

The effect of temperature change on the extraction constant has been shown to be very important. Thus it is necessary when comparing values of extraction constants, to take into consideration any differences of temperature which might exist. Certainly, when extractions are carried out for purposes of calculating various quantities some provision should be made to keep the temperature approximately constant. It is of interest to note that the entropy changes obtained for these reactions are somewhat larger than values observed for most ordinary chemical reactions.

6. Suggestions for Further Work

From insights gained in this work a large number of ideas for other studies have been obtained which it is believed would add considerably to the principles of solvent extraction and separations of metal ions as well as be of interest from an academic standpoint.

The author is of the opinion that the study concerned with the determination of extraction constants of a large number of metal dithizonates is long overdue. Eighteen and possibly more metals react with dithizone. Methods should now be available to obtain extraction constants for most of these metal dithizonates.

Since apparently no really satisfactory quantitative method is available for the determination of microquantities of tin, a comprehensive study of tin dithizonate might prove very fruitful.

Investigations with complexing reagents other than dithizone along the same lines of approach used in this study would be of interest from the standpoint of predicting pH_2 values and determining extraction constants.

Extractions of silver dithizonate into carbon disulfide from 0.1-M. potassium bromide solutions could not be made because the silver would not stay in either phase even though silver dithizonate as well as dithizone are soluble in carbon disulfide. One might make such extractions by mixing chlorobenzene with the carbon disulfide. If various mole ratios of chlorobenzene and carbon disulfide were used, and extrapolations were made to pure carbon disulfide, it might be possible to determine the extraction constant. By measuring the solubility of dithizone in carbon disulfide and using the value of the solubility of silver dithizonate which was determined in this work, it should be possible to estimate the extraction constant. Comparison of the constants determined by the two methods would be of interest.

Investigations of the effects of high concentrations of electrolytes in the aqueous phase on extractions such as metal dithizonate extractions would doubtlessly be a fertile field. The author suggests the approach of determining activity coefficient ratios from solvent extraction data and comparing these ratios with values obtained by electromotive force measurements. Cadmium would appear to be an excellent metal with which to make such studies since the cadmium amalgam electrode is well known.

Especially, an extensive study should be made of the effect of temperature on extractions. This subject has too long been neglected. The literature contains statements that some organic solvents are better than others for certain separations of metal ions.²⁰ It might well be that if such is the case the ease of separation could be reversed at

some other temperature. Such peculiar behavior could be represented by plots of $\log K$ versus $1/T$. If the slopes of such plots were different for two different metals extracted into the same solvent, then certainly separations of the metals could be made better at some temperatures than others. It remains to be seen how a change of organic solvent would affect the ease of separation.

CHAPTER V

SUMMARY

Studies of masked and non-masked extractions of cadmium and silver dithizonates have been made from aqueous solutions into various organic solvents containing dithizone. The term, masked extraction, was used to designate extractions from aqueous solutions containing chemical species which complex with the ions of silver and cadmium. The term, non-masked extraction, was applied to extractions from aqueous solutions containing the perchlorate ion which was assumed not to form complexes with the ions of silver and cadmium. Cadmium dithizonate extractions were made from aqueous solutions into chloroform, and silver dithizonate extractions were made from aqueous solutions into chloroform, carbon tetrachloride, dichloromethane, benzene, toluene, chlorobenzene, and bromobenzene. The initial compositions of the aqueous solutions varied with regard to hydrogen ion concentration, masking agent, and ionic strength; the initial concentrations of cadmium and silver ions remained constant at values of 7×10^{-5} M. and 1×10^{-7} M. respectively. The initial compositions of the organic solutions varied only with respect to the dithizone concentration.

In many cases it was possible to obtain the usual S-shaped extraction curve of per cent metal extracted into the organic phase versus the pH of the aqueous phase.

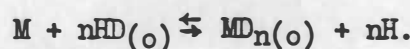
It was found that the equations

$$K = \frac{E(H)^n}{(HD)_o^n}$$

and

$$pH_{\frac{1}{2}} = -\log K - n \log (HD)_o$$

were applicable to the non-masked extractions where E is the extractability or the ratio of metal in the organic phase to the metal in the aqueous phase, $(HD)_o$ is the concentration of dithizone in the organic phase, (H) is the concentration of the hydrogen ion in the aqueous phase, $pH_{\frac{1}{2}}$ is the pH of 50 per cent extraction, and n is the valence of the metal ion. The constant K is the equilibrium constant for the extraction reaction expressed as follows:



Charges of ions have been omitted in equations to simplify the writing.

The constant K is therefore expressed as

$$K = \frac{(MD_n)_o (H)^n}{(M)(HD)_o^n}$$

where the subscript o has been used to designate that the specie is in the organic phase, other species being in the aqueous phase. The quantities M and MD_n refer to the metal ion and the metal dithizonate respectively.

It was found that the equation

$$pH_{\frac{1}{2}} = -\log K - n \log (HD)_o + \log [1 + K_1(X) + K_2(X)^2 + K_3(X)^3 + K_4(X)^4]$$

was applicable to the masked extractions where the constants K_1 , K_2 , K_3 , and K_4 are the stability constants of the complexes formed in the aqueous phase between the masking agent and the metal ion. The quantity X designates the masking agent. It was shown that extraction constants could

be obtained from masked extractions as well as from non-masked extractions.

A value of $\log K$ for the extraction at 30° of cadmium dithizonate into chloroform was obtained to be equal to 0.4. Values of $\log K$ for the extraction at 30° of silver dithizonate was obtained for cases in which the organic solvent varied; the values are as follows: chloroform, 5.8; carbon tetrachloride, 6.5; dichloromethane, 6.0; benzene, 6.3; toluene, 6.3; chlorobenzene, 6.5; bromobenzene, 6.5. Values of $\log K$ for extractions of silver dithizonate into chloroform at temperatures other than 30° are: 0° , 6.6; 25° , 5.9; 35° , 5.5; 40° , 5.3; 45° , 5.0; 50° , 4.9; 55° , 4.8. For extractions into carbon tetrachloride, the values of $\log K$ at 35° , 45° , and 55° were obtained to be 6.3, 5.8, and 5.3 respectively.

A large tabulation of values of K_1 , K_2 , K_3 , and K_4 for cadmium and silver complexes was made from values obtained in the literature. These quantities were used to make calculations of pH_2 and K for masked extractions.

A limited study was made of the effect of small changes of ionic strength on the extractions. No large effect was found.

It was found that if values of $\log K$ were plotted versus $1/T$ straight lines were obtained for both the extractions into chloroform and the extractions into carbon tetrachloride. The slope of the line obtained for extractions into chloroform was found to be 3.5×10^3 $^\circ\text{C}$. For these extractions it was possible to obtain values of the enthalpy, free energy, and entropy for the extraction. These quantities were found to be approximately constant over the temperatures investigated and were

equal to -16 kcal./mole, -8 kcal./mole, and -30 e.u. respectively. A slope of 5.3×10^3 °C. was obtained for the plot for extractions into carbon tetrachloride. Values of the enthalpy, free energy, and entropy for these extractions were obtained to be approximately -24 kcal./mole, -8 kcal./mole, and -50 e.u. respectively. It was shown that temperature is a very important and interesting factor in such extractions.

An extensive historical survey was made of the studies which have treated dithizone and metal dithizonates. Much detail was devoted to the mathematical methods which have been used to treat data derived from solvent extraction.

The solubility of silver dithizonate in various organic solvents was measured by a radiotracer technique. An expression was derived to relate the extraction constant of a metal dithizonate to the solubilities of dithizone and metal dithizonate in various organic solvents. The equation was given as

$$K \frac{S_r^n}{S_c} = C$$

where S_r and S_c are the solubilities of dithizone and metal dithizonate in the organic solvent, and C is a constant. The consistency of the expression was tested for silver dithizonate using data for S_c and K from this study and data for S_r from the literature. The expression was found to be approximately constant with an average value of C equal to 3×10^6 . Using data from the literature, an average value of C was found for zinc dithizonate to be approximately 0.2.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. E. Fischer, Ann. Chem. Liebig's, 190, 118-122 (1878).
2. E. Fischer and E. Besthorn, Ann. Chem. Liebig's, 212, 316-324 (1881).
3. F. J. Welcher, "Organic Analytical Reagents," Vol. 3, D. Van Nostrand Company, Inc., New York, New York, 1953, pp. 463-550.
4. J. H. Billman and E. S. Cleland, J. Am. Chem. Soc., 65, 1300 (1943).
5. H. M. Irving and C. F. Bell, J. Chem. Soc., 3538-3543 (1953).
6. E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd ed., Interscience Publishers, Inc., New York, New York, 1950, pp. 107-110.
7. G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley and Sons, Inc., New York, 1957, pp. 173-177.
8. P. A. Clifford, J. Assoc. Agr. Chem., 21, 695 (1938).
9. H. M. Irving and C. F. Bell, J. Chem. Soc., 4253-4256 (1954).
10. H. M. Irving, S. J. Cooke, S. C. Woodger and R. J. P. Williams, J. Chem. Soc., 1847-1855 (1949).
11. J. K. Carlton, W. C. Bradbury and R. Kruh, Anal. Chim. Acta, 12, 101-106 (1955).
12. R. W. Geiger and E. B. Sandell, Anal. Chim. Acta, 8, 197-208 (1953).
13. C. B. Honaker, Ph. D. Thesis, University of Tennessee, 1957, to be published in Anal. Chim. Acta (1958).
14. H. Fischer, Angew. Chem., 50, 919-932 (1937; H. Fischer, Angew. Chem., 46, 442-446 (1933).
15. J. Cholak, D. M. Hubbard and R. E. Burkey, Anal. Chem., 15, 754-759 (1943).
16. B. G. Malmstrom and D. Glick, Anal. Chem., 23, 1699-1703 (1951).
17. B. L. Vallee, Anal. Chem., 26, 914-917 (1954).
18. R. E. Chernitskaya, Zhur. Obshchei Khim., 22, 408-414 (1952).
19. K. Buch and F. Koroleff, Finska Kemistsamfundets Medd., 54, 98 (1945).

20. H. M. Irving and R. J. P. Williams, J. Chem. Soc., 1841-1847 (1949).
21. E. B. Sandell, J. Am. Chem. Soc., 72, 4660-4661 (1950).
22. H. M. Irving and C. F. Bell, J. Chem. Soc., 1216-1220 (1952).
23. D. Dyrssen and B. Hok, Svensk Kem. Tidskr., 64, 80-85 (1952).
24. G. Bouissieres and C. Ferrandini, Anal. Chim. Acta, 4, 610-614 (1950).
25. K. W. Bagnall and D. S. Robertson, J. Chem. Soc., 509-512 (1957).
26. T. Ishimori, Bull. Chem. Soc. Japan, 27, 520-522 (1954).
27. A. T. Pilipenko, Zhur. Anal. Chim., 5, 14-20 (1950).
28. E. S. Wasserman and I. B. Ssuprunowitsch, Ukrain. Khem. Zhur., 9, 33-40 (1934); Chem. Zentr., II, 106, 3268 (1935).
29. H. Fischer, Angew. Chem., 47, 685-692 (1934).
30. H. A. Liebhafsky and E. H. Winslow, J. Am. Chem. Soc., 59, 1966 (1937).
31. P. A. Clifford and H. J. Wichman, J. Assoc. Official Agr. Chem., 19, 134 (1936).
32. S. S. Cooper and J. O. Hibbits, J. Am. Chem. Soc., 75, 5084 (1953).
33. S. Miyakawa and T. Uemura, Bull. Chem. Soc. Japan, 24, 25-27 (1951).
34. S. S. Cooper and M. I. Sullivan, Anal. Chem., 23, 613 (1951).
35. A. T. Pilipenko, Zhur. Anal. Chim., 8, 286-292 (1953).
36. A. T. Pilipenko, Zhur. Anal. Chim., 5, 14-20 (1950).
37. T. Ishimori, Bull. Chem. Soc. Japan, 27, 520-522 (1954).
38. K. W. Bagnall and D. S. Robertson, J. Chem. Soc., 509-512 (1957).
39. H. Irving, E. J. Risdon and G. Andrew, J. Chem. Soc., 537-541 (1949).
40. I. M. Kolthoff and E. B. Sandell, J. Am. Chem. Soc., 63, 1906-1908 (1941).
41. H. M. Irving, C. F. Bell and R. J. P. Williams, J. Chem. Soc., 356-369 (1952).
42. M. Brent, Bull. soc. chim. France, 948-951 (1956).

43. B. Tremillon, Bull. soc. chim. France, 1156-1160 (1954).
44. H. M. Irving and C. F. Bell, Nature, 169, 756 (1952).
45. A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice Hall, Inc., New York, New York, 1952, p. 52.
46. H. Fischer, Wiss. Veroffentl. Siemens-Konzern, 12, 44-60 (1933).
47. J. C. Pariand and P. Archinard, Rec. trav. chim., 71, 634-638 (1952).
48. H. Fischer and W. Weyl, Wiss. Veroffentl. Siemens-Konzern, 14, No. 2, 41 (1935).
49. W. B. Schaap, H. Farber, I. J. Andrews, and J. W. Gates, Jr., U. S. Atomic Energy Commission Report, AECD-4180 (1945).
50. T. Uemura and S. Miyakawa, Bull. Chem. Soc. Japan, 22, 115-120 (1949).
51. R. E. Chernitskaya, Zhur. Obshchei Khim., 22, 408-414 (1952).
52. H. J. Wichman, Ind. Eng. Chem. Anal. Ed., 11, 66-72 (1939).
53. W. C. Waggener and R. W. Stoughton, J. Phys. Chem., 56, 1-5 (1952).
54. K. B. Brown, C. F. Coleman, D. J. Crouse, J. O. Denis, and J. G. Moore, U. S. Atomic Energy Commission Report, ORNL-1734.
55. N. H. Furman, W. B. Mason, and J. S. Pekola, Anal. Chem., 11, 1325 (1949).
56. R. E. Connick and W. H. McVey, J. Am. Chem. Soc., 71, 3182-3191 (1949).
57. I. Leden, Z. Physik. Chem., 188A, 160-181 (1941).
58. J. Rydberg, Acta Chem. Scand., 4, 1503-1522 (1950).
59. J. Bjerrum, "Metal Amine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 22.
60. R. E. Connick and W. H. Reas, J. Am. Chem. Soc., 73, 1171-1176 (1951).
61. H. M. Irving, F. J. C. Rossotti, and R. J. P. Williams, J. Chem. Soc., 1906-1919 (1955).
62. J. Rydberg, Arkiv Kemi, 8, 101-112 (1955).
63. J. P. McKaveney, "Use of Acetylacetone Extractions in Ferrous Analysis," U. S. Atomic Energy Commission Document, NYO-6507, Office of Technical Service, Department of Commerce, Washington, 1957.

64. A. Krishen, "A Systematic Study of Solvent Extraction With Acetyl-acetone," U. S. Atomic Energy Commission Document, NYO-6498, Office of Technical Service, Department of Commerce, Washington, 1957.
65. J. Rydberg, Svensk Kem. Tidskr., 67, 499-512 (1955).
66. D. Dyrssen, Svensk Kem. Tidskr., 68, 212-246 (1956).
67. K. Buch, Finska Kemistamfundets Medd., 63, 25-37 (1944).
68. N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 1, Oxford University Press, London, 1950, pp. 262-284.
69. B. P. Block in J. C. Bailar, Jr., "The Chemistry of Coordination Compounds," Reinhold Publishing Corp., New York, New York, 1956, p. 373.
70. J. C. Bailar, Jr., "The Chemistry of Coordination Compounds," Reinhold Publishing Corp., New York, New York, 1956, pp. 371-385.
71. R. B. Corey and R. W. G. Wyckoff, Z. Krist., 87, 264 (1934).
72. J. L. Hoard, Z. Krist., 84, 231 (1933).
73. G. Schwarzenbach, B. Maissen, and H. Ackerman, Helv. Chim. Acta, 35, 2333-2336 (1952).
74. G. Schwarzenbach, B. Maissen, H. Ackerman, and G. Anderegg, Helv. Chim. Acta, 35, 2337-2343 (1952).
75. G. Schwarzenbach, Helv. Chim. Acta, 36, 23-36 (1953).
76. E. C. Righellato and C. W. Davis, Trans. Faraday Soc., 26, 592 (1930).
77. H. L. Riley and V. Gallafent, J. Chem. Soc., 514 (1932).
78. W. Knoblock, Lotos, 78, 110 (1930).
79. H. Harned and M. Fitzgerald, J. Am. Chem. Soc., 58, 2624-2629 (1936).
80. C. E. Vanderzee and H. J. Dawson, Jr., J. Am. Chem. Soc., 75, 5659-5663 (1953).
81. L. Eriksson, Acta Chim. Scand., 7, 1146-1154 (1953).
82. D. N. Hume, L. B. Rogers, B. Rossi, R. W. Williams, H. S. Bridges, and J. R. Zacharias, U. S. Atomic Energy Commission Report, AECU-2616 (1953).

83. E. L. King, J. Am. Chem. Soc., 71, 319-322 (1949).
84. R. Bates, J. Am. Chem. Soc., 61, 308-315 (1939).
85. R. Bates and W. Vosburgh, J. Am. Chem. Soc., 60, 137 (1938).
86. M. Quintin and S. Pellitier, Compt. rend., 242, 768-770 (1956).
87. A. G. Stromberg and I. E. Bykov, Zhur. Obschei Khim., 19, 245-257 (1949).
88. D. N. Hume, D. D. DeFord, and G. C. B. Cave, J. Am. Chem. Soc., 73, 5321-5325 (1951).
89. R. A. Whiteker and N. Davidson, J. Am. Chem. Soc., 75, 3081-3085 (1953).
90. H. Euler, Ber., 36, 3400 (1903).
91. H. Wijs, Rec. trav. Chim., 44, 663 (1925).
92. I. Leden, Svensk Kem. Tidskr., 1, 31-56 (1944).
93. S. N. Fleggs, U. S. Atomic Energy Commission Translation, AEC-tr-2829 from Chim. Chronika 20A, 127-135 (1955).
94. S. Chaberek, Jr., and A. E. Martell, J. Am. Chem. Soc., 77, 1477-1480 (1955).
95. G. Schwarzenbach and E. Freitag, Helv. Chim. Acta, 34, 1492-1502, 1503-1508 (1951).
96. J. Koryta and I. Kossler, Experientia, 6, 36-37 (1950).
97. A. Albert, J. Biochem., 46, Proc. of Soc., XXXIX (1950).
98. J. H. Jonte and D. S. Martin, J. Am. Chem. Soc., 74, 2052-2054 (1952).
99. E. Berne and I. Leden, Svensk Kem. Tidskr., 65, 88-97 (1953).
100. V. V. Formin, Zhur. Fiz. Khim., 27, 1280-1286 (1953).
101. G. S. Farbe and H. I. Cole, J. Am. Chem. Soc., 43, 2492 (1921).
102. J. Kratochvill, B. Tezak, and V. B. Vouk, Arktiv Kemi, 26, 191-209 (1954).
103. S. Jaques, Helv. Chim. Acta, 29, 1041 (1946).
104. A. Pinkus and A. Timmermans, Bull. soc. chim. Belges., 46, 46 (1937).

105. E. Berne and K. Leden, Z. Naturforsch., 8A, 719-726 (1953).
106. V. B. Vouk, J. Kratochvill, and B. Tezak, Arkiv Kemi, 25, 219-224 (1953).
107. H. Chateau and J. Pourdier, Science et inds. phot., 24, 129-140 (1953).
108. G. Bolander and W. Eberline, Z. anorg. Chem., 39, 197 (1904).
109. H. Hellwig, Z. anorg. Chem., 25, 157 (1900).
110. A. M. Golub, Ukrain. Khim. Zhur., 19, 467-472 (1953).
111. I. Leden, Acta Chem. Scand., 10, 540-547 (1956).
112. I. M. Korenman, Zhur. Obschei Khim., 16, 157 (1946).
113. W. Erber, Z. anorg. u. allgem. Chem., 248, 36 (1941).
114. I. Leden and C. Parck, Acta Chem. Scand., 10, 535-539 (1956).
115. K. Schulz and B. Tezak, Arhiv Kem., 23, 200 (1951).
116. G. C. B. Cave and D. N. Hume, J. Am. Chem. Soc., 75, 2893-2897 (1953).
117. I. Leden and R. Nilsson, Z. Naturforsch., 10A, 67-76 (1955).
118. I. Leden and I. E. Marthen, Acta Chem. Scand., 6, 1125 (1952).
119. I. Leden and N. H. Schoon, Trans. Chalmers Univ. Technol. Gothenburg, No. 144, 3-17 (1954).
120. H. T. S. Britton and E. N. Dodd, J. Chem. Soc., 1940-1954 (1932).
121. L. H. Jones and R. A. Penneman, J. Chem. Phys., 22, 965-970 (1954).
122. R. Cohen-Adad, Compt. rend., 238, 810-812 (1954).
123. H. Chateau, M. Durante, and B. Hervier, Science at inds. phot., 27, 81-90, 257-262 (1956).
124. E. L. Jahn and H. Stoude, Z. Naturforsch., 6A, 385-387 (1951).
125. S. Valladas-Dubois, Ann. chim., 4, 548-591 (1949).
126. C. B. Monk, Trans. Faraday Soc., 47, 285-297 (1951).
127. J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, "Stability Constants of Metal-Ion Complexes, Part I, Organic Ligands," The Chemical Society, London, Special Publication No. 6, 1957.

128. R. A. Day, Jr. and R. W. Stoughton, J. Am. Chem. Soc., 72, 5662-5666 (1950).
129. M. Garman and J. Connell, J. Am. Chem. Soc., 69, 2063-2064 (1947).

VITA

Frank Falkoner Dyer was born near Webbers Falls, Oklahoma, on November 18, 1931. He graduated from Webbers Falls High School in May, 1949. In June, 1949 he entered Oklahoma Agricultural and Mechanical College (now Oklahoma State University) and was graduated with a B. S. degree with a major in chemistry in May, 1953. He continued his studies at Oklahoma Agricultural and Mechanical College and obtained the M. S. degree with a major in chemistry in May, 1955. He was provided financial assistance while obtaining the M. S. degree in the form of a research assistantship. In November, 1954, he went to the University of Tennessee to work toward the doctorate degree in chemistry. He was provided financial aid for his studies at the University of Tennessee in the following forms: Research Assistantship on an Atomic Energy Commission project, Research Grant from the Rhenium Research Fund, Graduate Assistantship, Fellowship from Union Carbide Nuclear Company.

The author married the former Miss Marjorie Lee Williams of Knoxville, Tennessee on March 16, 1957.

The author is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, and Pi Mu Epsilon.