AN INVESTIGATION OF COMPLEX SPECIES
IN SILVER CHLORIDE SOLUTIONS
I. SOLUBILITY MEASUREMENTS
II. ION EXCHANGE METHODS

A THESIS
SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
BRIGHAM YOUNG UNIVERSITY

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
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May, 1959
This Thesis by Harry G. Hecht is accepted in its present form by the Department of Chemistry as satisfying the thesis requirement for the degree of Master of Science.

Signed:

April 30, 1959

Date
PREFACE

The work reported in this Thesis is part of a research project at Brigham Young University titled, "Detection of Molecular Species in Ionic Equilibria." From this work, which is supported by the National Science Foundation, it is anticipated that improved methods of study for complex systems will be developed.

My sincere gratitude is extended to Dr. Keith P. Anderson and Dr. Eliot A. Butler for their direction of this work. I would also like to express my gratitude to Dr. Richard L. Snow, who assisted in programming calculations for the IBM 650 Data Processing System.

I would like to acknowledge my appreciation for financial assistance by the National Science Foundation, Brigham Young University Chemistry Department, Kennecott Copper Corporation, and Woodrow Wilson National Fellowship Foundation.
# TABLE OF CONTENTS

LIST OF TABLES .................................................. v

LIST OF ILLUSTRATIONS ........................................ vi

## PART I.

I. INTRODUCTION ................................................. 1

II. EXPERIMENTAL ............................................... 4

Preparation of Solutions
Temperature Control
Analysis of Solutions
Radioassay Techniques

III. RESULTS AND CALCULATIONS ................................. 11

IV. CONCLUSIONS ................................................ 16

## PART II.

V. INTRODUCTION ................................................ 17

VI. THEORY OF ION EXCHANGE EQUILIBRIA ..................... 19

VII. EXPERIMENTAL .............................................. 25

Preparation of Resin
pH Control
Separation of Resinous and Aqueous Phases

VIII. RESULTS AND CALCULATIONS ............................... 28

Determination of \( \lambda_0 \)
Sorption of AgCl\( (aq) \)
Determination of the Degree of Association of the Sorbed Species

IX. CONCLUSIONS ................................................. 36

X. REFERENCES CITED ............................................ 37
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Experimental Data From Solubility Measurements of AgCl at 25.00°C</td>
<td>11</td>
</tr>
<tr>
<td>2. Activity Coefficient of a Singly Charged Species</td>
<td>14</td>
</tr>
<tr>
<td>3. Effect of Varying the Amount of Sodium Resin Upon the Concentration of Silver and Sodium Ions in Solution</td>
<td>29</td>
</tr>
<tr>
<td>4. Effect of the Chloride Concentration Upon the Concentration of Silver in Solution</td>
<td>31</td>
</tr>
<tr>
<td>5. Effect of the Concentration of AgCl(aq) on the Amount of Silver Chloride Sorbed on Amberlite IR-120</td>
<td>32</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Mercury Expansion Thermoregulator</td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>Thyatron Tube Relay</td>
<td>7</td>
</tr>
<tr>
<td>3.</td>
<td>Solubility of AgCl at 25.00°C</td>
<td>13</td>
</tr>
<tr>
<td>4.</td>
<td>Effect of the Weight of Resin Upon the Equilibrium pH</td>
<td>27</td>
</tr>
<tr>
<td>5.</td>
<td>Effect of the Centrifugation Time Upon the Amount of Radiotracer in Solution</td>
<td>27</td>
</tr>
<tr>
<td>6.</td>
<td>Effect of Varying the Amount of Sodium Resin Upon the Concentrations of the Silver and Sodium Ions in Solution</td>
<td>30</td>
</tr>
<tr>
<td>7.</td>
<td>Sorption of Silver Chloride Molecules by Amberlite IR-120</td>
<td>34</td>
</tr>
</tbody>
</table>
PART I.

SOLUBILITY MEASUREMENTS
I. INTRODUCTION

Complex silver chloride solutions have been investigated by a number of workers, beginning with the first major study of this system in 1911 by Forbes.\(^1\) Forbes postulated the existence of the following complex species in aqueous solutions from data obtained by solubility measurements in the presence of excess chloride ion: \(\text{AgCl}_3\), \(\text{AgCl}_4\), and \(\text{AgCl}_5\). The existence of the dichloro-complex species, \(\text{AgCl}_2\), was also indicated by later work of Forbes and Cole.\(^2\)

The next work of major interest concerning the complex silver chloride system was reported in a series of papers by Pinkus and his co-workers.\(^3, 4, 5\) It was concluded that AgCl dissolves in the colloidal state in dilute chloride solutions, since filtration through a nitrocellulose membrane apparently resulted in a high loss of AgCl in the solution.

Berne and Leden calculated dissociation constants for a number of complex silver chloride species from solubility data.\(^6\) Radioassay

---

\(^3\) A. Pinkus and M. Haugen, \textit{Bull. soc. chim. Belg.}, 45, 693 (1936) [C. A., 31, 2965 (1937)].
techniques were employed on solutions which had been filtered through an ultra colloid filtering medium. Less reproducible results in a chloride ion concentration range near 0.001 molar led these workers to suggest either a peptization effect of chloride ions in this concentration range, or a polymerization of the type: \( n\text{AgCl} = (\text{AgCl})_n \). Berne and Leden also showed that at equal concentrations of silver ion and chloride ion, about 1% of the total solubility of AgCl is contributed by AgCl molecules (These data are taken from investigations at 25°C).

Jonte and Martin have also studied this system.\(^7\) These workers employed radioassay techniques on saturated AgCl solutions which had been centrifuged. The results were interpreted in terms of equilibria involving the following species: \( \text{Ag}^+ \), \( \text{AgCl(aq)} \), \( \text{AgCl}_2^- \), and \( \text{AgCl(s)} \) (The notations, \( \text{AgCl(aq)} \) and \( \text{AgCl(s)} \), refer to the silver chloride molecules in aqueous solution and the solid silver chloride, respectively). Determinations at various temperatures permitted calculations of thermodynamic data, as well as the equilibrium constants involved.

Lieser has used the same techniques that were employed by Jonte and Martin to extend the data to higher chloride ion concentrations, as well as to other halide systems.\(^8\) In addition to the species dealt with in the Jonte and Martin work, the trichloro-complex, \( \text{AgCl}_3^{12-} \), was also studied by Lieser.

This phase of the present investigation consists of a study of the complex silver chloride system in a manner similar to that of Jonte

and Martin. $\text{Ag}^{110}$ is used as a radiotracer in the determination of the concentration of silver in saturated silver chloride solutions which contain excess chloride ion. From the data obtained in this manner, it is possible to calculate the equilibrium constants involved.
II. EXPERIMENTAL

Ten millicuries of Ag$^{110}$ were obtained from the Oak Ridge National Laboratory in the silver nitrate form to be used as a radiotracer in this investigation. Ag$^{110}$ decays with a half life of approximately 270 days to form Cd$^{110}$, both beta and gamma rays being emitted.

All chemicals used were of reagent grade purity. Water used in the preparation of solutions was re-distilled from alkaline permanganate.

Three or four millicuries of Ag$^{110}$ were combined with 0.2821 gram of inactive AgNO$_3$ in 15 ml. of a 1.5 F solution of KCN. This solution was then electrolyzed at approximately 3.5 volts. The weighed quantity of silver on the cathode was dissolved in dilute HNO$_3$, and the resulting solution evaporated almost to dryness three times with 2 ml. portions of HClO$_4$. This solution was diluted to volume in a calibrated 1000 ml. volumetric flask. A clear-point titration with iodide was used to check the concentration of silver. Ten milliliter aliquots of this solution were diluted to 100 ml. in volumetric flasks. The 100 ml. solutions were used in the preparation of saturated silver chloride solutions. The stock solutions thus prepared were stored in glass-stoppered reagent bottles within a lead shield.

Chloride solutions were prepared by diluting a weighed portion of dried NaCl to volume in a calibrated flask. The concentration of the chloride in these solutions was checked by a Mohr titration.

Saturated AgCl solutions of varying chloride ion concentrations were prepared by the addition of appropriate volumes of the above silver
and chloride solutions to 125 ml. glass-stoppered Erlenmeyer flasks, enough water being added to make the total volume 30 ml. in each case. The flasks containing the AgCl solutions were heated to 35°C or cooled to 15°C, and then thermostated at 25°C. The smooth curve produced by plotting the data obtained from these samples was taken as an indication that equilibrium had been attained. It was found, by taking samples over various periods of time, that these solutions reached equilibrium in approximately one week with continuous shaking in a constant temperature water bath.

The water bath used in this investigation was constructed of the components common to laboratory temperature controlling devices, i.e., a cooling coil, heater, stirrer, sensing element, and a relay. The sensing element employed was a mercury expansion thermoregulator, constructed according to Figure 1. The circuit diagram for the thyratron tube relay used is shown in Figure 2. The temperature of the water bath was 25.00°C, as determined with a National Bureau of Standards calibrated thermometer; the precision of control was within ±0.01°C. The continuous shaking of the samples was accomplished by attaching the sample support to the reciprocating rod of an electric windshield wiper motor, which was powered by a 6-volt power supply.

An air bath consisting of the same basic components as those used in the water bath was also constructed. The temperature maintained in the air bath was within ±0.2°C of 25.0°C. Control of the temperature during the sampling of the AgCl solutions was necessary to prevent precipitation or solution of AgCl while samples were being withdrawn.

The AgCl solutions were centrifuged prior to the pipetting of samples, so that finely divided silver chloride would not remain suspended.
Figure -1-

MERIDY EXPANSION THERMOREGULATOR
Figure 2

THYRATRON TUBE RELAY
One milliliter samples were pipetted from the centrifuged solutions into stainless steel planchets. Preliminary investigations showed that reproducible results could not be obtained using a 0.1 ml. micropipettor. The high surface area per unit volume in this instrument suggests the possibility of an adsorption phenomenon, although a satisfactory explanation has not been formulated. The centrifuge and pipet were mounted inside the constant temperature air bath.

The planchets containing the one ml. samples were then dried under an infra-red lamp. A Tracerlab SC-51 Autoscaler, equipped with a Tracerlab SC-6D Automatic Sample Changer and a Tracerlab SC-5F Printing Interval Timer, was used to count the planchets in which the solutions had been dried. It was possible to calculate the total concentration of silver in each of the solutions sampled by comparison of the count rate with that of a standard prepared from the silver stock solution.

The used planchets were treated with chromic acid cleaning solution. The cleaned planchets were counted, and those which were within approximately ten counts per minute of the background rate were used again.

Analysis of the AgCl solutions was completed by a determination of the pH, which was necessary for the calculation of the activity coefficients. A Beckman Model G pH Meter was used for this purpose. It was necessary to use a salt bridge in determining the pH's, to eliminate the possibility of the formation of a precipitate at the junction between the silver ion in the solution and the chloride ion in the calomel electrode. One formal NH₄NO₃ was employed as the electrolyte, agar being used to jell a portion of the solution in a glass tube to act as a contact between the two solutions. The glass electrode was placed in the solution whose pH was being determined, and the calomel electrode was placed in
the 1 F NH₄NO₃ solution.

It was necessary in some cases to correct the observed count rates for coincidence losses, since there was a large difference in the activity of the various solutions. A linear approximation of the coincidence loss, \( R = r(1+rt) \), was used in which \( R \) is the corrected count rate, \( r \) is the observed count rate, and \( t \) is the resolution time of the Geiger tube.

Self absorption of radiation was determined to be the cause of a large discrepancy in the count rates of certain samples containing large concentrations of NaCl or NaClO₄. Attempts were made to correct for this effect by shielding the beta radiation with a thin sheet of aluminum foil placed over the end of the Geiger tube. The total count rate of the solution was reduced to such an extent that this procedure was not considered practical, although the error due to self absorption was virtually eliminated. Consequently, it was necessary to make standards of approximately the same ionic strength as the samples being counted.

Certain precautions were observed in handling the radiotracers which are not encountered in ordinary laboratory procedures. Calculation of the radiation level was necessary, to determine the length of time which could be spent in working with the radioactive silver without exceeding the maximum permissible dose.⁹ Landsverk Model L-24 Dosimeters were worn to determine actual exposure. Tongs were used in handling the radioactive substances whenever their use was not prohibited by the experimental procedures.

The laboratory was monitored periodically to determine the level of radiation present in various working areas. Monitoring was also necessary when stock solutions were prepared. A Tracerlab Model Su5A Survey Meter and a Nuclear-Chicago Model 1613A Monitor were used for this purpose.

Valuable suggestions for further precautions, as well as methods useful in cleaning contaminated equipment, have been compiled elsewhere.  

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III. RESULTS AND CALCULATIONS

The experimental results obtained are tabulated in Table 1. The

<table>
<thead>
<tr>
<th>[Cl(^-)]</th>
<th>pH</th>
<th>(\mu^3)</th>
<th>(\log a_{\text{Cl}^-})</th>
<th>(\log [\text{Ag}_{\text{tot}}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.83 x 10(^{-5})</td>
<td>6.70</td>
<td>8.30 x 10(^{-3})</td>
<td>4.321</td>
<td>5.379</td>
</tr>
<tr>
<td>6.23 x 10(^{-5})</td>
<td>2.97</td>
<td>3.41 x 10(^{-2})</td>
<td>4.223</td>
<td>5.445</td>
</tr>
<tr>
<td>1.23 x 10(^{-4})</td>
<td>3.23</td>
<td>2.72 x 10(^{-2})</td>
<td>3.927</td>
<td>5.732</td>
</tr>
<tr>
<td>1.97 x 10(^{-4})</td>
<td>3.23</td>
<td>2.86 x 10(^{-2})</td>
<td>3.721</td>
<td>5.879</td>
</tr>
<tr>
<td>3.56 x 10(^{-4})</td>
<td>3.51</td>
<td>2.60 x 10(^{-2})</td>
<td>3.489</td>
<td>6.063</td>
</tr>
<tr>
<td>8.00 x 10(^{-4})</td>
<td>6.10</td>
<td>2.88 x 10(^{-2})</td>
<td>3.112</td>
<td>6.256</td>
</tr>
<tr>
<td>1.62 x 10(^{-3})</td>
<td>2.62</td>
<td>6.35 x 10(^{-2})</td>
<td>2.819</td>
<td>6.225</td>
</tr>
<tr>
<td>2.44 x 10(^{-3})</td>
<td>2.82</td>
<td>6.31 x 10(^{-2})</td>
<td>2.629</td>
<td>6.357</td>
</tr>
<tr>
<td>3.27 x 10(^{-3})</td>
<td>2.71</td>
<td>7.24 x 10(^{-2})</td>
<td>2.518</td>
<td>6.351</td>
</tr>
<tr>
<td>4.09 x 10(^{-3})</td>
<td>2.74</td>
<td>7.71 x 10(^{-2})</td>
<td>2.422</td>
<td>6.372</td>
</tr>
</tbody>
</table>

equililibria involved can be expressed by the following equations, considering Ag\(^+\), AgCl\(_{\text{aq}}\), and AgCl\(_2\)\(^-\) as the only silver-containing species in these solutions.

\[
\text{AgCl}_s = \text{Ag}^+ + \text{Cl}^- \quad (1)
\]
\[
\text{Ag}^+ + \text{Cl}^- = \text{AgCl}_{\text{aq}} \quad (2)
\]
\[
\text{Ag}^+ + 2\text{Cl}^- = \text{AgCl}_2^- \quad (3)
\]
The equilibrium constants can be represented by (4), (5), and (6), in which \( \gamma_1 \) and \( \gamma_0 \) refer to the activity coefficients of a singly charged and neutral species, respectively.

\[
K_{sp} = [Ag^+] \gamma_1 a_{Cl^-} \quad (4)
\]

\[
K_1 = \frac{[AgCl(aq)] \gamma_0}{[Ag^+] \gamma_1 a_{Cl^-}} \quad (5)
\]

\[
K_2 = \frac{[AgCl^-]}{[Ag^+] a_{Cl^-}} \quad (6)
\]

The total concentration of silver in the solutions, the logarithm of which is shown in Figure 3 as a function of the logarithm of the chloride ion activity, can be written as the sum of the three silver-containing species in solution.

\[
[Ag_{tot}] = [Ag^+] + [AgCl(aq)] + [AgCl^-] \quad (7)
\]

Substituting into (7) from (4), (5), and (6), this expression becomes

\[
[Ag_{tot}] = \frac{K_{sp}}{\gamma_1 a_{Cl^-}} + \frac{K_1 K_{sp}}{\gamma_0 \gamma_1 a_{Cl^-}} + \frac{K_2 K_{sp} a_{Cl^-}}{\gamma_1 a_{Cl^-}} \quad (8)
\]

The activity coefficient of the neutral species, \( AgCl(aq) \), is taken as unity, since the concentrations involved are quite small. The magnitude of \( \gamma_1 \) is a function of the ionic strength, the values of which are tabulated in Table 2.

The values of \( [Ag_{tot}] \) were determined by the count rates of the various AgCl solutions. The chloride ion concentrations were taken to be approximately equal to the initial chloride added to the solutions minus that precipitated as AgCl, the latter quantity being determined by the difference in the count rates of the solutions before and after chloride
SOLUBILITY OF AgCl AT 25.00°C
was added. Multiplication of the concentration term by $r_1$ yields the corresponding activity.

**TABLE 2.**

<table>
<thead>
<tr>
<th>$\mu^2$</th>
<th>$r_1$</th>
<th>$\mu^2$</th>
<th>$r_1$</th>
<th>$\mu^2$</th>
<th>$r_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>0.945</td>
<td>0.300</td>
<td>0.790</td>
<td>0.550</td>
<td>0.730</td>
</tr>
<tr>
<td>0.100</td>
<td>0.905</td>
<td>0.350</td>
<td>0.775</td>
<td>0.600</td>
<td>0.720</td>
</tr>
<tr>
<td>0.150</td>
<td>0.870</td>
<td>0.400</td>
<td>0.760</td>
<td>0.650</td>
<td>0.710</td>
</tr>
<tr>
<td>0.200</td>
<td>0.835</td>
<td>0.450</td>
<td>0.750</td>
<td>0.700</td>
<td>0.705</td>
</tr>
<tr>
<td>0.250</td>
<td>0.810</td>
<td>0.500</td>
<td>0.735</td>
<td>0.750</td>
<td>0.700</td>
</tr>
</tbody>
</table>

These data can be treated by the method of least squares to find the best values of the constants, $K_1$ and $K_2$. Accordingly, we can write the following expression for the residual corresponding to the first experimental point.

$$r_1 = [A_{\text{tot}}]_1 - \frac{K_1}{r_1} \frac{sp}{a_{Cl}} - \frac{K_2}{r_1} \frac{sp}{Cl} - \frac{K}{r_1} \frac{a}{Cl}$$  \hspace{1cm} (9)

The following expressions are obtained by differentiating the sum of the squares of the residuals of all experimental points with respect to $K_1$ and $K_2$, and equating these derivatives to zero.

\[C. E. Crouthamel and D. S. Martin, J. Am. Chem. Soc., 73, 569 (1951).\]
\[
\sum_{n=1}^{n} [Ag_{tot}]_n = K_{sp} \sum_{n=1}^{n} \frac{1}{(\gamma_1)_n a_{Cl^-} n} + nK_1K_{sp} + K_2K_{sp} \sum_{n=1}^{n} \frac{a_{Cl^-} n}{(\gamma_1)_n} \quad (10)
\]

\[
\sum_{n=1}^{n} \frac{[Ag_{tot}]_n a_{Cl^-} n}{(\gamma_1)_n} = K_{sp} \sum_{n=1}^{n} \frac{1}{(\gamma_1)_n^2} + K_1K_{sp} \sum_{n=1}^{n} \frac{a_{Cl^-} n}{(\gamma_1)_n} + K_2K_{sp} \sum_{n=1}^{n} \frac{(a_{Cl^-} n)^2}{(\gamma_1)_n^2} \quad (11)
\]

These two equations can be solved simultaneously for \(K_1\) and \(K_2\).

The value of \(K_{sp}\) reported by Owen, \(1.77 \times 10^{-10}\), was assumed in the calculations.\(^{12}\) The following values of the constants have been determined by solving Equations (10) and (11): \(K_1 = 1.99 \times 10^3\), \(K_2 = 2.98 \times 10^4\).

IV. CONCLUSIONS

A constant for the formation of the aqueous silver chloride molecular species, $\text{AgCl}_2^{-}$, has been determined at 25.00°C, the value of which is $1.99 \times 10^3$. This is in excellent agreement with the value, $2.04 \times 10^3$, reported by Jonte and Martin.7

A value of the formation constant for the dichloro-complex, $\text{AgCl}_2^{-}$, has also been determined at 25.00°C. The reliability of the value determined for this constant is somewhat questionable, due to the low range of chloride ion concentration investigated. The value determined is $2.98 \times 10^4$; the corresponding value reported by Jonte and Martin is $1.76 \times 10^5$.7
PART II.

ION EXCHANGE METHODS
V. INTRODUCTION

An ion exchanger is defined as an insoluble material containing labile ions which will exchange reversibly with other ions in a surrounding medium without any physical change occurring in the material. The ion exchangers in most common use today are organic polymers to which functional groups which ionize in solution, e.g., \(-\text{SO}_3\text{H}, \text{PO}(\text{OH})_2, \text{COOH},\) \(-\text{OH}, \text{NR}_3^+, \text{NH}_2, \text{NHR},\) and \(-\text{NR}_2\), are attached. It is these functional groups which take part in the exchange reaction.

Ion exchange is a very useful tool for the study of electrolytic solutions. This tool has been used in the past for many different types of investigations. Included among these are such studies as the determination of dissociation constants of complex ions, the measurement of activity coefficients, and the determination of the charge of a species in solution.

This phase of the present investigation is a study of the complex species in silver chloride solutions by cation exchange methods. Amberlite IR-120 is used as the ion exchanger, and Ag\(^{110}\) is employed as a radiotracer for the determination of the silver concentrations in the various solutions.

An independent determination of the formation constants of the complex silver chloride species has not been accomplished in this work. Very fundamental to the development of the theory by which this investigation was pursued is the assumption that no neutral species are sorbed by the ion exchange resin. This assumption has been found to be invalid.
for this particular system.

Although it has been found that the sorption of the neutral species can be treated by a simple adsorption relationship, this topic is not discussed in the development of the theory in Chapter VI. One is led to the conclusion that silver chloride molecules are sorbed from the solution when the data are interpreted in terms of the erroneous assumption that only silver ion reacts with the ion exchanger.
Equations expressing ion exchange equilibria arise primarily from two considerations: the exchange may be viewed as a simple adsorption process, or as a displacement reaction to which the law of mass action applies. A great number of equations which support either one view or the other are reported in the literature. In this investigation a displacement type reaction is assumed.

The following metathesis reaction represents a simple cation exchange process.

\[ A^+ + BR = AR + B^+ \]  \hspace{1cm} (12)

The symbols, \( A^+ \) and \( B^+ \), represent univalent cations, and \( R \) is a cation exchange resin.

The thermodynamic equilibrium constant for this reaction can be represented as,

\[ K_a = \frac{(a_{B^+})(a_{AR})}{(a_{A^+})(a_{BR})} \]  \hspace{1cm} (13)

in which the \( a \)'s are activities.

X-ray diffraction studies have indicated a random distribution of the metal cations throughout the resinous phase, which suggests the formation of a completely miscible solid solution of \( AR \) in \( BR \).\(^{13}\)

The activities of the components, AR and BR, can be written in terms of mole fractions if it is assumed that the resinous phase may be treated as an ideal solid solution. If only univalent cations of approximately the same radii are involved, the activities are equal to the mole fractions.

\[
K_a = \frac{(a_A^+)(\frac{m_{AR}}{m_{AR} + m_{BR}})}{(a_B^+)(\frac{m_{BR}}{m_{AR} + m_{BR}})} = \frac{(a_A^+)(m_{AR})}{(a_B^+)(m_{BR})} \quad (14)
\]

\[m_{AR} \quad \text{and} \quad m_{BR} \quad \text{represent the moles of the A and B forms of the resin, respectively.}
\]

An empirical method based on the Duhem-Margules equation has been developed by Kielland for systems to which this simple treatment of the activity of the resinous phase is not applicable. The following expressions can be written in which C is a constant which is characteristic of the particular system involved, and \(n_{AR}\) and \(n_{BR}\) are the mole fractions of the A and B forms of the resin, respectively.

\[
\log \gamma_{AR} = C n_{BR}^2
\]
\[
\log \gamma_{BR} = C n_{AR}^2
\quad (15)
\]

Therefore,

\[
\log K_a = \log \frac{(a_A^+)(n_{AR})}{(a_B^+)(n_{BR})} + C(n_{BR}^2 - n_{AR}^2) \quad (16)
\]

If $K'_c$ is defined as

$$K'_c = \frac{(a_B^+)(n_{AR})}{(a_A^+)(n_{BR})}, \quad (17)$$

equation (16) becomes

$$\log K'_c = \log K_a - C(n_{BR}^2 - n_{AR}^2). \quad (18)$$

The value of $C$ may be obtained by noting that $\log K'_c$ is a linear function of $(n_{BR}^2 - n_{AR}^2)$, the slope of which is $C$, and that $\log K'_c$ is equal to $\log K_a$ when $n_{BR}$ is equal to $n_{AR}$. The activity coefficients can then be calculated by Equations (15), using the value of $C$ thus determined.

In very dilute solutions where the Debye-Hückel limiting law is valid, the activity coefficients of $A^+$ and $B^+$ are equal, since the law states that the mean activity coefficient is a function only of the charge of the ions and the ionic strength, $\mu$, of the solution.

$$\log \gamma^+_t = -A(z_+)(z_-)\mu^{1/2} \quad (19)$$

Inspection of the Debye-Hückel equation as it applies to more concentrated solutions,

$$\log \gamma^+_t = \frac{-A(z_+)(z_-)\mu^{1/2}}{1 + \frac{e^2}{a_B\mu^{1/2}}} \quad (20)$$

shows that the mean activity coefficient is also a function of the ionic radii, which indicates that the activity coefficients of $A^+$ and $B^+$ are
equal only if their radii are equal. Harned and Owen have pointed out that the activity coefficient of a strong electrolyte in a solution of another electrolyte is primarily a function of the total ionic strength. Therefore, the ratio of the activity coefficients is a constant at constant ionic strength.

Equation (14) can be written as

\[ K_a = \frac{[B^+]_{\text{m}} \gamma_{B}^+}{[A^+]_{\text{m}} \gamma_{A}^+} \quad (21) \]

The following expression is obtained by taking the logarithm of Equation (21), and rearranging the terms.

\[ \log \frac{[B^+]_{\text{m}}}{[A^+]_{\text{m}}} = \log K_a + \log \frac{\gamma_{B}^+}{\gamma_{A}^+} \quad (22) \]

The last two terms in this expression are constants at a given ionic strength. The linearity of a plot of \( \log \frac{[B^+]_{\text{m}}}{[A^+]_{\text{m}}} \) versus \( \log K_a \) is an indication that the assumptions made in the derivation of this expression are valid. If this condition is satisfied for Equation (22), the ion exchange process can be treated as a metathesis reaction.

In the present investigation, the sodium form of a cation exchanger is equilibrated with silver chloride solutions.

\[ \text{Ag}^+ + \text{NaR} = \text{AgR} + \text{Na}^+ \quad (23) \]

---

Equation (22) takes the following form when applied to this system.

\[
\log \frac{\text{m}_{\text{NaR}}}{\text{m}_{\text{AgR}}} = \log \frac{[\text{Na}^+]}{[\text{Ag}^+]} - \log K_a + \log \frac{\gamma_{\text{Na}^+}}{\gamma_{\text{Ag}^+}}
\]  

(24)

The equilibrium constant for the exchange reaction [Equation (23)], expressed in terms of concentrations, is

\[
K_c = \frac{[\text{AgR}][\text{Na}^+]}{[\text{Ag}^+][\text{NaR}]}
\]  

(25)

A new constant, the adsorption isotherm, can be defined as follows if the concentration of sodium ion is large compared to the silver ion concentration, and if the amount of ion exchanger used is large compared to the quantity of silver ion to be exchanged.

\[
\lambda_o = \frac{K_c[\text{NaR}]}{[\text{Na}^+]} = \frac{[\text{AgR}]}{[\text{Ag}^+]}
\]  

(26)

This constant can also be expressed,

\[
\lambda_o = \frac{\% \text{ tracer sorbed} \times \text{ volume of solution}}{\% \text{ tracer not sorbed} \times \text{ weight of resin}}
\]  

(27)

Furthermore, if the volume of the solution and the quantity of resin used in each determination are the same, these factors can be included in the adsorption isotherm to obtain a new constant, \( \lambda'_o \).

\[
\lambda'_o = \frac{\text{total counts per minute} - \text{counts per minute in solution}}{\text{counts per minute in solution}}
\]  

(28)
The calculation of the constant, $K_1$, for the formation of the $\text{AgCl(aq)}$ species requires the existence of the following conditions in solution.

1. The concentration of the chloride ion in solution is small, therefore, no $\text{AgCl}_2^-$ forms.

2. Constant values of the sodium ion concentration and ionic strength of the solution are maintained by a large concentration of $\text{NaClO}_4$ relative to the concentration of the silver.

3. The silver ion concentration is very small, compared to both the sodium ion concentration and the chloride ion concentration. This condition insures a constant value of $\frac{[\text{AgR}]}{[\text{Ag}^+]^2}$, as well as providing that the chloride ion concentration at equilibrium is the same as the initial chloride ion concentration.

4. The pH and volume of the solution, as well as the weight of the resin are the same for all solutions.

5. The resin is initially saturated with sodium ion.

6. There is no sorption of neutral or negative species.

If the above conditions are assumed, the constant for the formation of $\text{AgCl(aq)}$ can be expressed as follows:

$$K_1 = \frac{\lambda_0 (\text{cpm} \text{ sol.} - \frac{\text{cpm} \text{ sor.}}{\lambda_0})}{(\text{cpm} \text{ sor.})[\text{Cl}^-]}$$  \hspace{1cm} (29)

cpm \text{ sol.} and cpm \text{ sor.} represent the activities of the tracer (in counts per minute) in solution and the tracer sorbed by the ion exchanger, respectively.
VII. EXPERIMENTAL

Amberlite IR-120 is a strongly acidic cation exchange resin of the nuclear sulfonic acid type. Reagent grade beads of 0.45 - 0.60 millimeter diameter in the hydrogen form were converted to the sodium form by treatment with 5 F NaOH. The treated resin was rinsed with distilled water until the sodium in the rinsing water was virtually eliminated, as indicated by the absence of the characteristic sodium color of a flame test. The resin was air dried for two days, and stored in a dust-proof container.

A solution which was approximately 0.4 F with respect to NaClO\textsubscript{4} was prepared by diluting 70 ml. of 71 % HClO\textsubscript{4} to one liter. 500 ml. of this solution, which was standardized against KIO\textsubscript{3}, was neutralized with NaOH. The resulting NaClO\textsubscript{4} solution was diluted to volume in a one liter volumetric flask. Sodium chloride and silver perchlorate solutions were prepared as described in Part I.

Silver chloride solutions were prepared by adding 10.00 ml of the NaClO\textsubscript{4} solution and a few drops of 0.8 F HClO\textsubscript{4} to appropriate volumes of the NaCl and AgClO\textsubscript{4} solutions, the acid being added to adjust the pH. The total volume in each case was 20.0 ml. These solutions were prepared in 125 ml. Erlenmeyer flasks. Following the addition of a weighed quantity of ion exchange resin, the samples were shaken in the constant temperature water bath until equilibrium was reached.

Determinations of the activity of the radiotracer in solutions after various periods of time indicated that 24 hours was a sufficient
period to insure the attainment of equilibrium.

Preliminary investigations of the control of the pH of these solutions indicated a linear variation of the equilibrium pH as a function of the weight of resin used in solutions of the same initial pH. This relationship is shown graphically in Figure 4. These data are taken as evidence for the homogeneity of the resin used. The data also provide a means by which the pH may be eliminated as a variable in these solutions.

Centrifugation of samples as a method of separation of the resinous and aqueous phases was also investigated. Figure 5 shows that the activity of the radiotracer in the solution was changing even after 10 minutes of continuous centrifugation. A much more effective means of separation was provided by filtration through a glass fiber filtering pad with slight suction. The activity of the solution agreed with that of the original sample within 0.7 % after 10 ml. of solution had been filtered through the pad.

With the exception of the few procedures mentioned here which specifically involve the ion exchange resin, the methods employed were the same as those described in Chapter II.
Figure 4

EFFECT OF THE WEIGHT OF RESIN UPON THE EQUILIBRIUM pH

Figure 5

EFFECT OF CENTRIFUGATION TIME UPON THE AMOUNT OF RADIOTRACER IN SOLUTION
VIII. RESULTS AND CALCULATIONS

The ion exchange reaction between silver ion and the sodium form of Amberlite IR-120 can be treated as a metathesis reaction to which the law of mass action applies. Evidence for this conclusion is shown by the data of Table 3, and is illustrated graphically in Figure 6.

This experimental verification of Equation (24) was accomplished by measuring the initial and equilibrium activities of the radiotracer in solutions to which varying portions of resin had been added. The number of moles of the sodium form of the resin were calculated using the exchange capacity of Amberlite IR-120, i.e., 4.25 milliequivalents per gram of dry resin. There was no chloride ion present in these solutions.

The constant, $\lambda_0$, defined by Equation (28), was found to be independent of the pH in the range, $2 < \text{pH} < 7$, within the limits of experimental error. The value of this constant was calculated from determinations of the activities of the radiotracer before and after the attainment of equilibrium in solutions of varying pH. A constant weight of resin, 0.200 gram, was used in these solutions which contained no chloride ion. The average value of $\lambda_0$ was found to be 1.44, with a probable error of ± 0.10.

The data found in Table 4 are equilibrium concentrations of solutions in which the initial silver ion concentration was the same, i.e., $2.7 \times 10^{-7}$ moles per liter. The ionic strength of these solutions was 0.215, and the pH was 2.9, within approximately 0.1 of a pH unit.
### TABLE 3

**EFFECT OF VARYING THE AMOUNT OF SODIUM RESIN UPON THE CONCENTRATION OF THE SILVER AND SODIUM IONS IN SOLUTION**

<table>
<thead>
<tr>
<th>Grams of Sodium Resin</th>
<th>0.1119</th>
<th>0.1455</th>
<th>0.1533</th>
<th>0.2506</th>
<th>0.3555</th>
<th>0.4010</th>
<th>0.5436</th>
<th>0.6888</th>
<th>1.1020</th>
</tr>
</thead>
</table>

**INITIALLY**

<table>
<thead>
<tr>
<th>Moles of Sodium Resin</th>
<th>4.76x10^{-4}</th>
<th>6.18x10^{-4}</th>
<th>6.52x10^{-4}</th>
<th>1.07x10^{-3}</th>
<th>1.51x10^{-3}</th>
<th>1.70x10^{-3}</th>
<th>2.31x10^{-3}</th>
<th>2.93x10^{-3}</th>
<th>4.68x10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Na⁺] in Sodium</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
</tr>
<tr>
<td>[Ag⁺] in Solution</td>
<td>1.47x10^{-5}</td>
<td>1.47x10^{-5}</td>
<td>1.47x10^{-5}</td>
<td>1.47x10^{-5}</td>
<td>1.47x10^{-5}</td>
<td>1.47x10^{-5}</td>
<td>1.47x10^{-5}</td>
<td>1.47x10^{-5}</td>
<td>1.47x10^{-5}</td>
</tr>
</tbody>
</table>

**AT EQUILIBRIUM**

<table>
<thead>
<tr>
<th>Moles of Sodium Resin</th>
<th>4.76x10^{-4}</th>
<th>6.18x10^{-4}</th>
<th>6.52x10^{-4}</th>
<th>1.07x10^{-3}</th>
<th>1.51x10^{-3}</th>
<th>1.70x10^{-3}</th>
<th>2.31x10^{-3}</th>
<th>2.93x10^{-3}</th>
<th>4.68x10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles of Silver Resin</td>
<td>1.86x10^{-7}</td>
<td>2.04x10^{-7}</td>
<td>2.14x10^{-7}</td>
<td>2.41x10^{-7}</td>
<td>2.56x10^{-7}</td>
<td>2.59x10^{-7}</td>
<td>2.75x10^{-7}</td>
<td>2.88x10^{-7}</td>
<td>2.88x10^{-7}</td>
</tr>
<tr>
<td>[Na⁺] in Solution</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
<td>0.190</td>
</tr>
<tr>
<td>[Ag⁺] in Solution</td>
<td>5.40x10^{-6}</td>
<td>4.46x10^{-6}</td>
<td>3.98x10^{-6}</td>
<td>2.64x10^{-6}</td>
<td>1.86x10^{-6}</td>
<td>1.72x10^{-6}</td>
<td>9.20x10^{-7}</td>
<td>2.79x10^{-7}</td>
<td>2.60x10^{-7}</td>
</tr>
<tr>
<td>log ([Na⁺] / [Ag⁺])</td>
<td>4.546</td>
<td>4.629</td>
<td>4.677</td>
<td>4.856</td>
<td>5.008</td>
<td>5.043</td>
<td>5.314</td>
<td>5.832</td>
<td>5.862</td>
</tr>
<tr>
<td>log (m_{NaR} / m_{AgR})</td>
<td>3.408</td>
<td>3.481</td>
<td>3.484</td>
<td>3.645</td>
<td>3.770</td>
<td>3.817</td>
<td>3.924</td>
<td>4.210</td>
<td>4.211</td>
</tr>
</tbody>
</table>
Figure 6

EFFECT OF VARYING THE AMOUNT OF SODIUM RESIN UPON
THE CONCENTRATION OF THE SILVER AND SODIUM
IONS IN SOLUTION
TABLE 4.
EFFECT OF THE CHLORIDE CONCENTRATION UPON THE CONCENTRATION OF SILVER IN SOLUTION

<table>
<thead>
<tr>
<th>[Cl(^-)]</th>
<th>[Ag(_{\text{tot}})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.84 x 10(^{-5})</td>
<td>7.9 x 10(^{-8})</td>
</tr>
<tr>
<td>5.50 x 10(^{-5})</td>
<td>8.0 x 10(^{-8})</td>
</tr>
<tr>
<td>7.70 x 10(^{-5})</td>
<td>7.0 x 10(^{-8})</td>
</tr>
<tr>
<td>8.24 x 10(^{-5})</td>
<td>7.8 x 10(^{-8})</td>
</tr>
<tr>
<td>1.10 x 10(^{-4})</td>
<td>7.6 x 10(^{-8})</td>
</tr>
<tr>
<td>1.65 x 10(^{-4})</td>
<td>8.3 x 10(^{-8})</td>
</tr>
<tr>
<td>2.18 x 10(^{-4})</td>
<td>7.3 x 10(^{-8})</td>
</tr>
<tr>
<td>3.27 x 10(^{-4})</td>
<td>7.9 x 10(^{-8})</td>
</tr>
<tr>
<td>2.82 x 10(^{-4})</td>
<td>7.1 x 10(^{-8})</td>
</tr>
<tr>
<td>6.22 x 10(^{-4})</td>
<td>5.6 x 10(^{-8})</td>
</tr>
</tbody>
</table>

It will be observed by inspection of Table 4 that a trend which is expected on the basis of previous work is not present. The concentration of the total silver in solution is expected to increase with increasing chloride ion concentration. The basis of this expectation is the decrease of the silver ion concentration in equilibrium with the ion exchange resin by the formation of AgCl\(_{\text{(aq)}}\).

A plausible explanation of this effect can be formulated by assuming the sorption of a silver-containing species other than the silver ion. The sorption of AgCl\(_{\text{(aq)}}\) is postulated on the basis of the following considerations.

1. Polynuclear species are not expected to exist to any signi-
significant extent in these solutions, which contain a large excess of chloride ion.

2. Sorption of anionic species, if such species exist to a significant extent, is considered unlikely on a cation exchange resin.

3. Sorption of the silver-containing species (other than $\text{Ag}^+$) is seen to increase with the chloride ion concentration.

The value of the silver ion concentration thus determined, together with the exchange constant, $\lambda_0$, can be used to calculate the quantity of silver exchanged from solution as the silver ion. The quantity of silver sorbed as $\text{AgCl}(\text{aq})$ is the difference in the quantity of silver exchanged from solution as the silver ion, and the total silver on the resin.

The results of these calculations are shown in Table 5.

**Table 5.**

| Effect of the Concentration of $\text{AgCl(}\text{aq})$ on the Amount of Silver Chloride Sorbed on Amberlite IR-120 |
|---|---|---|---|---|
| $[\text{Cl}^-]$ | $[\text{Ag}^+]$ | $[\text{AgCl(}\text{aq})]$ | Moles $\text{AgCl}$ Sorbed |
| $3.84 \times 10^{-5}$ | $7.60 \times 10^{-8}$ | $3.20 \times 10^{-9}$ | $8.2 \times 10^{-9}$ |
| $5.50 \times 10^{-5}$ | $7.54 \times 10^{-8}$ | $4.56 \times 10^{-9}$ | $8.1 \times 10^{-9}$ |
| $7.70 \times 10^{-5}$ | $6.45 \times 10^{-8}$ | $5.47 \times 10^{-9}$ | $1.07 \times 10^{-8}$ |
| $8.24 \times 10^{-5}$ | $7.15 \times 10^{-8}$ | $6.48 \times 10^{-9}$ | $8.9 \times 10^{-9}$ |
| $1.10 \times 10^{-4}$ | $6.78 \times 10^{-8}$ | $8.20 \times 10^{-9}$ | $9.6 \times 10^{-9}$ |
| $1.65 \times 10^{-4}$ | $7.02 \times 10^{-8}$ | $1.28 \times 10^{-8}$ | $8.6 \times 10^{-9}$ |
| $2.18 \times 10^{-4}$ | $5.90 \times 10^{-8}$ | $1.41 \times 10^{-8}$ | $1.12 \times 10^{-8}$ |
| $3.27 \times 10^{-4}$ | $5.81 \times 10^{-8}$ | $2.09 \times 10^{-8}$ | $1.07 \times 10^{-8}$ |
| $3.82 \times 10^{-4}$ | $5.00 \times 10^{-8}$ | $2.10 \times 10^{-8}$ | $1.27 \times 10^{-8}$ |
| $6.22 \times 10^{-4}$ | $3.32 \times 10^{-8}$ | $2.28 \times 10^{-8}$ | $1.66 \times 10^{-8}$ |
The Freundlich adsorption isotherm applied to this system is of the following form:

$$\frac{\text{moles } \text{AgCl} \cdot \text{R}}{\text{grams of resin}} = k[\text{AgCl}_{(aq)}]^\frac{1}{n}$$  \hspace{1cm} (30)

where $n$ and $k$ are empirical constants in this expression, and $\text{moles } \text{AgCl} \cdot \text{R}$ is used to denote the number of moles of the silver chloride molecules sorbed.

The following equation is obtained by taking the logarithm of Equation (30).

$$\log \frac{\text{moles } \text{AgCl} \cdot \text{R}}{\text{grams of resin}} = \frac{1}{n} \log [\text{AgCl}_{(aq)}] + \log k$$  \hspace{1cm} (31)

It is apparent that $\log \frac{\text{moles } \text{AgCl} \cdot \text{R}}{\text{grams of resin}}$ is a linear function of $\log [\text{AgCl}_{(aq)}]$, the slope of which is $\frac{1}{n}$. The constant, $k$, can be evaluated from the intercept.

A graphical representation of the data in the manner of Equation (31) is shown in Figure 7. The constants, $n$ and $k$, were calculated by the method of least squares to be 4.158 and $8.68 \times 10^{-7}$, respectively.

The magnitude of the constant, $n$, in the Freundlich equation suggests the possibility of the sorption of an associated species. The Langmuir adsorption equation for monomeric silver chloride molecules can be written,

$$\frac{[\text{AgCl}_{(aq)}]}{\text{moles } \text{AgCl} \cdot \text{R}} = \frac{1}{a} + \frac{b}{a} [\text{AgCl}_{(aq)}]$$  \hspace{1cm} (32)

where $a$ and $b$ are constants in this expression.

To determine the degree of association of the sorbed silver...
Figure 7

SORPTION OF SILVER CHLORIDE MOLECULES
BY AMBERLITE IR-120
chloride, the Langmuir equation can be re-written as

\[
\frac{[\text{AgCl}(aq)]^x}{\text{moles AgCl}\cdot \text{R}} = \frac{1}{a} + \frac{b}{a} \left[\text{AgCl}(aq)\right]^x
\]  

(33)

The value of the parameter, \( x \), which gives the best fit of this equation to the experimental data is an indication of the degree of association of the sorbed species.

Calculations were made in which the value of the parameter, \( x \), was varied from 1 to 8. It was found that if \( x \) assumed the values of 4, 5, or 6, Equation (33) was a distinctly better representation of the experimental data.

Preliminary investigations at higher chloride ion concentrations suggest the possibility of a calculation of the constant for the formation of the dichloro-complex, \( \text{AgCl}_2^- \), by ion exchange studies. This method assumes the previously determined values of \( K_1 \) and the constants, \( n \) and \( k \), in the Freundlich equation, as well as careful control of the ionic strength and sodium ion concentration of the solution.
IX. CONCLUSIONS

The exchange reaction between silver ion and the sodium form of Amberlite IR-120 has been found to be a metathesis reaction. A constant for this exchange has been determined at 25.00°C for a particular set of solution conditions applicable to this investigation.

Attempts to calculate a constant for the formation of AgCl(aq) indicated the sorption of silver chloride molecules by the resin. This sorption has been found to follow the Freundlich adsorption isotherm.

Treatment of the data by a modified form of the Langmuir adsorption equation suggests that the species sorbed on the ion exchange resin is associated AgCl(aq); the degree of association being about 4, 5, or 6.
X. REFERENCES CITED


AN INVESTIGATION OF COMPLEX SPECIES
IN SILVER CHLORIDE SOLUTIONS

I. SOLUBILITY MEASUREMENTS
II. ION EXCHANGE METHODS

ABSTRACT OF THESIS
SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
BRIGHAM YOUNG UNIVERSITY

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Harry G. Hecht
May, 1959
ABSTRACT

The complex species in silver chloride solutions have been investigated by solubility measurements and by ion exchange methods in this work.

The solubility of silver chloride in solutions of varying chloride ion concentrations was determined by radioassay techniques. The method of least squares was used to evaluate the constants for the formation of the aqueous silver chloride and the dichloro-complex species; the values being $1.99 \times 10^3$ and $2.98 \times 10^4$, respectively, at 25.00 °C.

Aqueous silver chloride has been shown to be sorbed by Amberlite IR-120 from silver chloride solutions which have an ionic strength of 0.2. This sorption has been found to follow the Freundlich, as well as the Langmuir adsorption equations. The sorbed species is postulated to be associated silver chloride molecules, the degree of association being about 4, 5, or 6.

Signed:

April 30, 1957
Date