[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE SOLUBILITY OF SILVER CHLORIDE IN CHLORIDE SOLUTIONS AND THE EXISTENCE OF COMPLEX ARGENTICHLORIDE IONS.

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It has long been known that silver chloride is fairly soluble in concentrated solutions of various chlorides. Reinsch[1] speaks of its solubility in concentrated hydrochloric acid. Vogel,[2] who appears to have made the first quantitative study of the reaction, gives solubilities in acid of specific gravity 1.165 to which varying proportions of water had been added, and also speaks of the increase of solubility with the temperature. Mulder[3] studies its solubility qualitatively in other chlorides. These and other references to early work on the subject are found in Comey's "Dictionary of Solubilities," pages 372–3. The only attempt to find numerical regularities seems to have been made by Barlow[4] who, while seeking errors in a method for determining sulfur, titrated solutions of sodium chloride, or of hydrochloric acid, or of both together, with silver nitrate. He concludes: "The figures show that the solubility of sodium chloride falls off (at a gradually diminishing rate) with diminishing concentration." He investigated only one concentration of hydrochloric acid. The solubilities as observed by Barlow appear roughly proportional to the concentration of sodium chloride. Noyes and Bray,[5] perhaps with these figures in mind, stated that a complex anion like $AgCl_2'$ probably exists in such solutions.

Researches concerning reactions between other pairs of halides are numerous. Of those most closely related to the present research may be mentioned that by Hellwig,[6] who prepared in solid form many complex compounds of silver halides with silver nitrate, also with alkali halides including thiocyanates. He failed to isolate a complex salt between silver chloride and other chlorides, and did not study the reaction further. This field was next investigated by Bodländer,[7] who found evidence of complex anions of the type AgX_4, and by Krym,[8] who dealt with the iodides of sodium and silver. Important work on halides of mercury and copper will be referred to in the discussion of results below.

The theory of such complex compounds has been discussed at length by Abegg.[9]

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[1] *J. prakt. Chem.*, 13, 133.

[2] *N. Rep. Pharm.*, 23, 355.

[3] *Loc. cit.*

[4] THIS JOURNAL, 28, 1446 (1906).

[5] *Ibid.*, 29, 166 (1907).

[6] *Z. anorg. Chem.*, 25, 157 (1900).

[7] *Ber.*, 36, 2878 (1903).

[8] *J. Russ. Phys. Chem. Ges.*, 41, 382 (1909); abstracted in *Chem. Zentr.*, 1909, II, 681.

[9] *Z. anorg. Chem.*, 20, 453–499 (1899).

The present research aimed to determin the solubility of silver chloride in a large variety of aqueous chloride solutions; to find what complex ions, if any, were indicated by the data, and to draw conclusions if possible regarding the relative "activities"[1] of the chloride ion in such solutions.

Very concentrated indeterminate solutions of the chlorides were prepared and carefully filtered. The ammonium chloride was barely acidified with hydrochloric acid to avoid hydrolysis. The purity of the materials is discussed below after recording the effect of impurities intentionally introduced. Silver chloride was precipitated from weighed portions diluted with much water and weighed on platinum Gooch crucibles with the usual precautions. Dilute solutions of silver nitrate, one about hundredth normal, the other about quarter normal, also one of silver sulfate for use with hydrochloric acid, about fortieth normal, were made and analyzed with equal care.

The determinations were carried out in flat-bottomed glass cylinders of about 60 cc. capacity, except in the case of the most dilute solutions, where deep beakers holding 600 cc. were used. These were set on a porcelain plate covered with black glazed paper and immersed to a suitable depth in a thermostat electrically regulated to maintain a temperature (corrected) of 25.06° within a few hundredths of a degree. The solutions were examined for opalescence in horizontal light reflected by an immersed forty-five degree mirror from an incandescent lamp supported above the thermostat.

The method was as follows: The dry cylinder was counterpoised, then carefully weighed with a convenient amount of chloride solution. Water, or in some cases the solid salt, was added and the additional weight found as before. A silver solution was next run in from a weight buret until equilibrium was nearly reached at some temperature between 24° and 26°. The vessel was then immersed in the thermostat and ten minutes allowed for the final adjustment of temperature—ample time, as proved by special experiments. Hundredth normal silver nitrate was added drop by drop until the faintest opalescence visible persisted after careful stirring. Immediately after the final adjustment the cylinder was wiped and weighed with the stirrer. Then the true density was determined within one part in five thousand by a pycnometer. All effects of evaporation or change of volume on mixing were thus avoided.

The above end point was proved sufficiently near the true equilibrium by the following considerations: Concentrated chloride solutions nearly saturated with silver chloride show a surprizing degree of supersaturation on cooling; this can be promptly relieved by adding, on the end of a stirring rod, quantities of precipitated silver chloride so minute as to produce no visible turbidity in 50 cc. of pure water. In such concentrated

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[1] Lewis, *Proc. Am. Acad.*, **43**, 288 (1907).

chlorides the precipitation of silver chloride is very prompt; larger quantities of it are required to produce visible opalescence in these solutions than in very dilute ones. The precipitate looks coarser from the start, and becomes rapidly more so, therefore it should not be allowed to stand more than a few minutes. Various chloride solutions at 25° were treated with successive drops of hundredth normal silver nitrate, seeding after each drop with minute portions of silver chloride. This seeding never produced any effect in solutions which had been cleared by stirring, hence such solutions were not supersaturated. If the last drop of silver nitrate produced a permanent precipitate, this was dissolved by heat and the solution quickly cooled to 25°, after which seeding *always* produced a precipitate. These experiments eliminated the danger that solutions which had failed to dissolve all the silver chloride formed in them were unsaturated, for if this had been the case, no precipitate would have been produced on seeding at 25° after cooling. Thus it was proved that the solutions at 25°, in which the faintest cloud remained, were saturated, and that the excess hardly exceeded that derived from the last drop. Such an excess in 50 cc. was equivalent to 6×10^{-6} mole per liter, the maximum probable error in the silver concentrations given below.

After much consideration it was decided to record all concentrations in gram equivalents per liter. As ample evidence was available that the chloride ion was the active agent, it seemed that the cations and the undissociated molecules with their possible hydrate water might well count as free space. Concentrations could hardly be calculated on such a basis for lack of any means of determining the volume occupied by the chlorine ion. Trial calculations showed that the conclusions drawn from the following figures would be substantially unchanged if concentrations were reckoned in equivalents per thousand grams of water. The table gives the total concentration of dissolved silver, and of the chloride in each case, the symbols being [Ag] and [MCl] where M is a gram equivalent of any metal. $K_m = [\text{Ag}]/[\text{MCl}]^m$ where m is a small whole number:

TABLE I.

Sodium Chloride.

$[\text{Ag}] \times 10^3$.	[NaCl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.
0.086	0.933	0.98	1.05
0.130	1.190	0.92	0.77
0.184	1.433	0.90	0.63
0.245	1.617	0.94	0.58
0.348	1.871	0.99	0.53
0.446	2.094	1.04	0.50
0.570	2.272	1.10	0.486
0.684	2.449	1.14	0.466
0.851	2.658	1.20	0.453
1.040	2.841	1.29	0.453

TABLE I (*continued*).

Sodium Chloride.

[Ag] × 10^3.	[NaCl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.
1.194	3.000	1.33	0.442
1.583	3.270	1.48	0.453
1.897	3.471	1.57	0.454
2.462	3.747	1.75	0.468
2.879	3.977	1.82	0.458
3.335	4.170	1.92	0.460
3.810	4.363	2.05	0.458
4.298	4.535	2.09	0.461
6.039	5.039	2.38	0.472

Calcium Chloride.

[Ag] × 10^3.	[$CaCl_2$/2].	$k_2 \times 10^4$.	$k_3 \times 10^4$.
0.289	1.748	0.95	0.54
0.501	2.201	1.03	0.47
0.900	2.741	1.20	0.44
1.463	3.264	1.37	0.42
2.182	3.737	1.56	0.418
2.802	4.033	1.72	0.427
4.175	4.538	2.03	0.447
5.823	5.005	2.32	0.464

Ammonium Chloride.

[Ag] × 10^3.	[NH_4Cl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_4 \times 10^4$.
0.042	0.513	1.59	2.46	...
0.113	0.926	1.33	1.43	...
0.172	1.141	1.32	1.16	...
0.365	1.574	1.47	0.94	...
0.842	2.143	1.80	0.86	...
1.425	2.566	2.16	0.84	...
2.160	2.918	2.54	0.87	...
2.795	3.162	....	0.88	0.280
4.029	3.510	....	0.93	0.265
9.353	4.363	....	1.13	0.258
14.92	4.902	....	1.27	0.258
24.04	5.503	....	1.44	0.262
30.17	5.764	....	1.57	0.273

Strontium Chloride.

[Ag] × 10^3.	[$SnCl_2$/2].	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_4 \times 10^4$.
0.033	0.550	1.10	2.00	...
0.092	0.989	0.94	0.95	...
0.173	1.359	0.94	0.69	...
0.236	1.572	0.95	0.61	...
0.284	1.698	0.98	0.58	...
0.348	1.818	1.05	0.58	...
0.510	2.140	1.11	0.52	...
0.747	2.476	1.22	0.49	...
1.252	2.992	1.40	0.47	...
2.018	3.494	1.65	0.47	...
3.594	4.152	2.08	0.50	0.121
8.174	5.216	3.00	0.58	0.110
12.04	5.775	3.61	0.62	0.108

TABLE I (*continued*).

Potassium Chloride.

[Ag × 10^3].	[KCl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_4 \times 10^4$.
0.141	1.111	1.11	1.02	...
0.235	1.425	1.16	0.81	...
0.391	1.713	1.33	0.78	...
0.616	2.022	1.51	0.74	...
1.050	2.396	1.84	0.763	...
1.390	2.628	....	0.766	0.291
1.845	2.850	....	0.797	0.280
2.435	3.081	....	0.83	0.270
3.602	3.424	....	0.90	0.262
5.725	3.843	....	1.01	0.262

Hydrochloric Acid.

[Ag × 10^3].	[HCl].	$k_2 \times 10^4$.	$k_3 \times 10^4$.
0.032	0.649	0.76	1.18
0.126	1.300	0.75	0.57
0.266	1.911	0.73	0.38
0.374	2.149	0.81	0.38
0.610	2.569	0.86	0.325
0.814	2.975	0.92	0.309
1.358	3.576	1.06	0.297
2.147	4.182	1.23	0.294
3.168	4.735	1.41	0.298
5.126	5.508	1.69	0.307

Barium Chloride

[Ag] × 10^3.	$BaCl_2/2$.	$k_2 \times 10^4$.	$k_3 \times 10^4$.
0.186	1.248	1.20	0.96
0.339	1.610	1.31	0.81
1.274	2.676	1.78	0.67
2.366	3.260	2.20	0.67

Since silver chloride is virtually insoluble in concentrated mercuric chloride solution, the chloride ion, and not the undissociated molecules, must be responsible for its solubility in the cases studied above. In the rather feebly dissociated zinc chloride its solubility is small, 0.000364 mole per liter of 4.777 normal solution as compared with 0.0135 mole in ammonium chloride equally concentrated. Richards and Archibald[1] found mercurous chloride unchanged by concentrated cadmium chloride solutions, although highly dissociated chlorides decomposed it into mercuric chloride and mercury. They similarly attributed the lack of action to the low concentration of the chloride ion.

Bodländer and Storbeck[2] proved very conclusively that the complex anion $CuBr_2'$ is present in a solution of cuprous bromide in potassium bromide. Richards and Archibald[2] concluded that the ion $HgCl_4''$ was

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[1] *Proc. Am Acad.*, **37**, 347 (1902).

[2] *Z. anorg. Chem.*, 31, 1 (1902).

formed according to the reaction $Hg_2Cl_2 + 2Cl' \rightleftarrows HgCl_4'' + Hg$. The results presented above are now completely explained by assuming the existence of complex anions of the type $(AgCl)_xCl^{n'}$, where x is probably one by analogy with the very similar cuprous bromide. If $AgCl + mCl' \rightleftarrows AgCl^{m'}_{m+1}$, then according to the so-called law of mass action, if this may be assumed to hold in spite of the high concentration, $[Ag] = k[Cl']^m$ in a solution saturated with silver chloride. If next the further assumption is made, as no better could be devized, that the activity of the chloride ion is nearly proportional to the total chloride concentration throughout moderate ranges of the latter, the figures in Table I may be explained. The values of k_2, in the third column, are constant from 1.5n down to the smallest concentrations studied; that is, solubility is closely proportional to the square of the chloride concentration. Support is thus lent to the hypothesis that the ion $AgCl_3''$ exists in such solutions. No evidence of the ion $AgCl_2'$ is to be found.[1] In the fourth column the values of k_3 are very constant from 2.5n upward, that is, solubility is closely proportional to the cubes of the concentrations, hence the ion $AgCl_4'''$ is suggested, except in the cases of potassium and ammonium chlorides, where this ion appears to be present from 1.5n to 3.0n, above even which a third ion, $AgCl_5''''$, is suspected from the data.

That m is really integral throughout considerable ranges of concentration, and does not increase continuously except in those solutions where no single complex predominates, is also shown by plotting the common logarithms of the chloride concentrations as abscissas against the common logarithms of the silver concentrations as ordinates. The equation of any graph is found by taking the logarithm of each side of the equation $[Ag] = km[MCl]^m$ for the corresponding salt. The result is: $\log [Ag] = \log km + m \log [MCl]$, which is the equation of a straight line if m is a constant. Now all the graphs are seen to consist of straight parallel lines connected by shorter curved portions, which shows that m is constant and also the same for different salts throughout given ranges of concentration. The values of $\frac{\Delta \log [Ag]}{\Delta \log [MCl]}$, which must be numerically equal to m, are seen to be almost exactly equal to 2, 3 or 4, according to the concentration region in which the straight lines lie. Thus it is shown graphically that complex ions of silver chloride molecules with two, three or perhaps even four chlorine ions exist in well defined concentration intervals.

Is it possible to connect the solubility of silver chloride more closely with the true concentration of the chloride ion? Not only is the latter uncertain, but also the degree of association of the complex anions with

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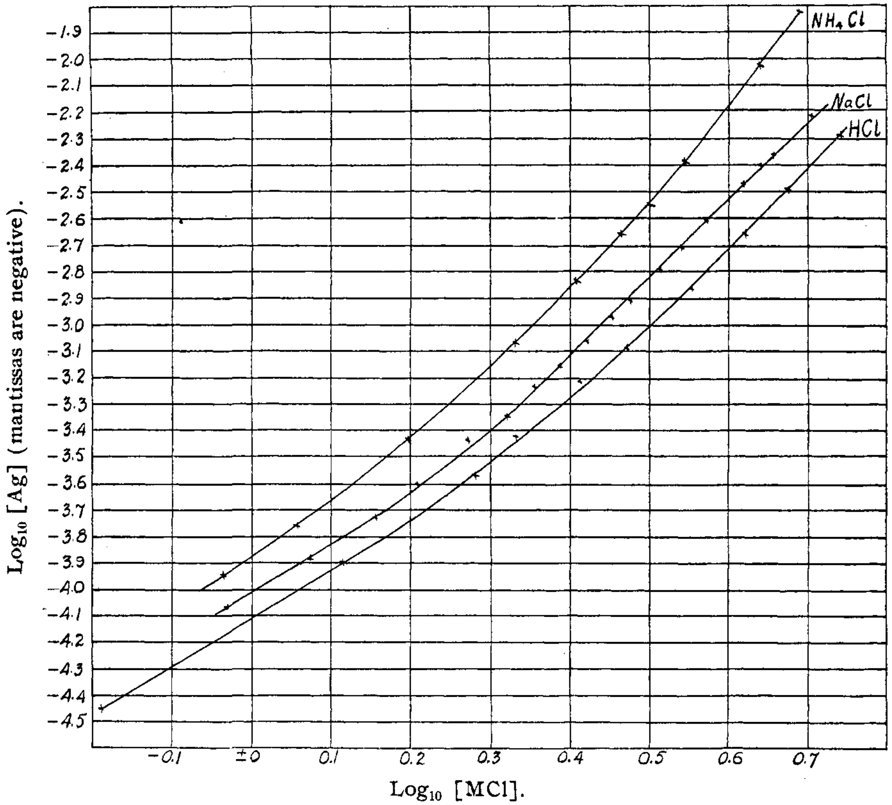
[1] The increase in k_2 at the smallest concentrations is to be attributed largely to the excess of silver chloride used to produce opalescence.

cations is entirely unknown. The work of Le Blanc and Noyes[1] on the conductance and catalytic power of hydrochloric acid containing mercuric chloride, and the experiments of Richards and Archibald[2] on the conductance of sodium chloride containing mercuric chloride led them to conclude that any well dissociated chloride, MCl, and the complex compound M_2HgCl_4 are about equally dissociated up to normal concentration of the former. Thus the total mercury could be written as $C+C(1-\alpha)/\alpha$ or C/α, where C represented the concentration of the ionized portion. Then by the law of mass action $C/\alpha = kx^m/\alpha$, where x is the specific conductance of chloride and m the number of chloride ions entering the complex. To find whether a corresponding relation existed in the case of silver chloride, sodium nitrate was added to sodium chloride solution before running in silver solution. If in the case of the silver complex we can write $C/\alpha = kx^m/\alpha$, any repression of ionization should *lower* the total solubility, since the complex ion must decrease as the m^{th} power of the



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[1] Le Blanc and Noyes, *Z. physik. Chem.*, 6, 389, et seq. (1890).

[2] *Proc. Am. Acad.*, 37, 347 (1902).

chloride ion, while the associated part increases only as the first power of the same. Consider now Table II; the k' values are interpolated for equal concentrations of pure chloride:

TABLE II.

$[Ag] \times 10^3$.	[NaCl].	$[NaNO_3]$.	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_2' \times 10^4$.	$k_3' \times 10^4$.
2.457	3.743	0.00	1.75	0.469	....	...
2.493	3.592	0.84	1.93	0.538	1.65	0.461
2.538	3.462	1.50	2.12	0.611	1.57	0.454

The addition of sodium ion increases the constants, and hence the solubility also. Neglecting the change in the medium produced by so much sodium nitrate, it would appear that the concentration of at least the trivalent anion $AgCl_4'''$ is lowered relatively much more than that of the chloride ion by adding sodium ion, for the increase in $[M_3AgCl_4]$ far more than compensates for the loss in $[AgCl_4''']$. Therefore the hypothesis of equal dissociation of MCl and M_3AgCl_4 was abandoned, and in despair of evaluating the many unknown variables, the activity of the chloride ion was taken as roughly proportional to total chloride concentration for moderate increments of the latter.

Richards and Archibald[1] suggested that the extent of action of chlorides on mercurous chloride might possibly be used to determin the concentration of the chloride ion. If the extent of action in the case of each such complex is an explicit function of the activity of the chloride ion, a mere comparison of constants ought to show whether complex formation is a measure of the relative activities in various solutions. In normal solutions, where the same type of complex ion is formed from both mercuric and silver chlorides, k_2 may be calculated from the data of Richards and Archibald, $k_2 = \frac{[\text{Hg}]\text{ dissolved}}{[\text{MCl}]^2}$.

	HCl.	NaCl.	$CaCl_2$.	$BaCl_2$.
$k_2 \times 10^4$ for $HgCl_2$	2.4	2.0	1.7	2.2
$k_2 \times 10^4$ for $AgCl_2$	0.75	0.97	0.9	1.2

The ratio between the hydrochloric acid constants differs so widely from the other ratios that the difference cannot be attributed to errors in experiment or extrapolation. Redistillation of the acid failed to increase the values of its constants. It must therefore be concluded that complex formation by mercurous and silver chlorides is not proportional to the activity of the chloride ion unless perhaps a single salt is considered at a time. Possibly the undissociated portions of the chlorides, while incapable of direct combination with silver chloride, support or hinder the action of the chloride ion in varying degrees.

One equilibrium was determined in the presence of a known amount of sodium bromide:

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[1] *Proc. Am. Acad.*, 37, 359 (1902).

$[Ag] \times 10^3$.	$[CaCl_2/2]$.	$[NaBr]$.	$k_2 \times 10^4$.	$k_3 \times 10^4$.	$k_2' \times 10^4$.	$k_3' \times 10^4$.
5.62	5.074	0.0018	2.18	0.430	2.37	0.467

These figures, together with those on sodium nitrate, show pretty conclusively that the purest commercial preparations, such as were used in this research, could hardly have contained impurities of serious consequence to the results. Bromide and iodide were the only anions capable of forming highly insoluble silver compounds which were likely to be present. No test for these could be obtained, and yet a fifth of the above concentration of bromide can be detected under the same conditions with carbon disulfide and chlorine water. Of other salts it appeared likely, in view of the results with sodium nitrate, that even a whole per cent. would have had a negligible effect.

The temperature coefficient of the solubility was investigated in thrice normal potassium and calcium chlorides, salts widely different in most respects, at 1.0°, 25.0° and 35.0°. Silver nitrate was first introduced at 1.0° until equilibrium was attained; then the solution was warmed to 25.0° and more silver nitrate added; then a further addition was made at 35.0°. The normality of the chloride was changed by each addition of silver solution, so that in order to compare solubilities at the *same* concentration but at different temperatures extrapolation was necessary. Table I shows that for these concentrations $[Ag]/[KCl]^4 = k_4$ and $[Ag]/[CaCl_2/2]^3 = k_3$ at 25.0°. Assuming these equations to hold at 1.0° and 35.0°, take the logarithm of each side and differentiate. $\Delta \log [Ag] = 4\Delta \log [KCl]$ and $\Delta \log Ag = 3\Delta \log [CaCl_2/2]$. The solubilities in 3.083*n* KCl and in 3.320*n* $CaCl_2$ may now be calculated at 1.0° and 35.0°. The "primes" indicate values obtained with the help of this artifice.

t.	$[Ag] \times 10^3$.	$[KCl]$.	$[Ag]' \times 10^3$.	$[KCl]'$.	$\log[Ag]'_{t_2} - \log[Ag']_{t_1}$.	$\frac{\log[Ag]'_{t_2} - \log[Ag]'_{t_1}}{t_2 - t_1}$.
1.0°	1.734	3.325	1.283	3.083		
					0.2747	0.0113
25.0°	2.415	3.083	2.415	3.083		
					0.1356	0.0136
35.0°	2.786	2.955	3.300	3.083		

t.	$[Ag] \times 10^3$.	$[CaCl_2/2]$.	$[Ag]' \times 10^3$.	$[CaCl_2/2]'$.	$\Delta \log [Ag]'$.	$\Delta \log [Ag]'/\Delta t$.
1.0°	0.964	3.512	0.814	3.320		
					0.2694	0.0112
25.0°	1.514	3.320	1.514	3.320		
					0.1156	0.0116
35.0°	1.806	3.221	1.976	3.320		

The increase in solubility with temperature is roughly logarithmic, about three per cent. change for one degree, hence the variations of a few hundredths of a degree were permissible in the determinations. The activity of the chloride ion seems to vary with temperature to about the same extent in both salts, the differences being perhaps due to unequal changes in dissociation with temperature.

The data obtained in the research incidentally make it possible to calculate what excess of chloride will make silver chloride most insoluble—an imporant question in analytical work. As the solubility product of silver chloride at 25° is nearly 2×10^{-10},[1] the concentration of silver in solution due to incomplete repression of ionization is given by the equation $[Ag]_1 = 2 \times 10^{-10}/[MCl]$, assuming complete dissociation of MCl. The concentration of silver in solution due to complex ion formation is given by the equation $[Ag]_2 = 10^{-4} [MCl]^2$, where 10^{-4} is the average value of k_2 at low concentrations. Total dissolved silver is the sum of the above: $[Ag] = 2 \times 10^{-10}/[MCl] + 10^{-4} [MCl]^2$. Differentiating, $d[Ag]/d[MCl] = -2 \times 10^{-10}/[MCl]^2 + 2 \times 10^{-4} [MCl]$. If the left hand side of the equation becomes zero, $2 \times 10^{-10}/[MCl]^2 = 2 \times 10^{-4} [MCl]$ whence $[MCl] = 10^{-4}$. Hence silver chloride ought to be most insoluble in hundredth normal chloride solutions.

One determination was also made of the solubility of silver chloride in concentrated silver nitrate.[2] This salt was recrystallized from fifty per cent. nitric acid, whirled on a centrifugal, fused in a platinum dish, and dissolved to form a solution about twice normal. A cloud was produced in 40 cc. by 0.09 cc. of 0.014 *N* KCl, that is, by a concentration of 3×10^{-5} gram equivalent or 0.001 gram of chlorine per liter, less than one-tenth the solubility of silver chloride in a twice normal chloride solution.

Summary.

The solubility of silver chloride in concentrated solutions of various chlorides was determined mainly at 25°.

The solubility is nearly doubled in going from 0° to 25°, the rate of increase above and below 25° being nearly logarithmic.

The solubility is sharply proportional to integral powers of the chloride concentration throughout considerable ranges, a fact explained by assuming the existence of the complex anions $AgCl_3''$, $AgCl_4'''$ and possibly $AgCl_5''''$. No evidence of the ion $AgCl_2'$ is found.

The extent of complex formation by mercurous and silver chlorides cannot be used as a measure of the activity of the chloride ion in concentrated solutions.

Silver chloride should be most insoluble, at 25°, in hundredth normal chloride solutions.

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[1] Data from Goodwin, *Z. physik. Chem.*, 13, 645 (1894).

[2] Hellwig, *Z. anorg. Chem.*, 25, 177 (1900), states that 100 cc. of thrice normal silver nitrate dissolved 0.08 gram of silver chloride, a quantity which fell off *very* rapidly with dilution.