future, bearing in mind the precautions to which attention has been called in this paper.

In conclusion, we are glad to express our indebtedness to the Carnegie Institution of Washington for some of the apparatus employed in this research.

Summary.

In the course of a series of determinations of capillary constants by measuring the capillary rise in fine tubes, the following precautions have been esspecially emphasized:

First, inequalities in the glass tubes employed were detected and corrected by the use of reversible apparatus.

Secondly, the capillary rise was referred to an unrestricted flat surface 38 mm. in diameter, which is larger than that usually used. It was shown that smaller surfaces are too small and that the insertion of a capillary in the middle of a larger tube causes appreciable error by increasing the capillary effect of the large tube.

Thirdly, special care was taken that the true bottom of the meniscus should be read.

Fourthly, the weight of the fine meniscus was in each case allowed for, and a new approximate formula suggested for its calculation, depending upon the observed height of the meniscus.

Heeding these precautions, determinations of the capillary constants of several important liquids were determined at 20° as follows: water 14.861, benzene 6.721, toluene 6.743, methyl alcohol 5.832, ethyl alcohol 5.765, isobutyl alcohol 5.823, ethyl butyrate 5.704.

CAMBRIDGE, MASS., U. S. A.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE POTENTIAL OF SILVER AGAINST SILVER ION IN CONCENTRATED SOLUTIONS OF POTASSIUM AND OF SODIUM CHLORIDE, AND ITS RELATION TO THE ACTIVITIES OF SUCH SOLUTIONS.

BY GEORGE SHANNON FORBES AND FREDERICK OSBAND ANDEREGG.

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The present paper records the measurement of the potential of cells of the type Ag | dilute $AgNO_3$ | KNO_3 | AgCl in conc. MCl | Ag, and an attempt to calculate from the data the activity of chloride ion at high concentrations—a problem of great importance. This work, carried out in the academic year 1912–13, has been left unpublished in the hope of an opportunity to extend the experiments. Because this hope has not yet been fulfilled, the following statement of results is to be regarded, in a sense, as preliminary in character:

Although there exist numerous careful measurements[1] of the potential of silver electrodes against dilute chloride solutions saturated with silver chloride, some of which, as Jahn's, were made to determine concentration of chloride ion, none to our knowledge traverse systematically the field of high concentrations. Nor has anyone investigated solutions unsaturated with silver chloride—a field where results of great interest are obtainable.

Three difficulties are mainly responsible—lack of definiteness in the metallic electrodes, and lack of knowledge of the variation of the solubility product and of the potential at the liquid junction with concentration.

Of the various methods[2] of preparing electrodes, that suggested by Lewis, to pack pure moist silver oxide into a spiral of platinum wire and then to ignite at 450° (we used an electric oven), proved most satisfactory. Crystalline silver deposits produced on cathodes of platinum foil in silver nitrate served well when carefully prepared. Bell and Feild[2] have recently used such electrodes with success. But in all cases electrodes for use in a given cell had to be left short-circuited in silver nitrate solution for days, and then carefully washed before using; otherwise they often showed considerable potentials against each other in any single solution of silver ions. If a cell contains two similar silver electrodes thus equalized, the specific peculiarities of their surface energy should cancel out, and this condition was insured throughout the work. But our experiences would lead us to view with distrust values obtained by opposing any silver electrode to another of different character—a calomel electrode for instance, where the surface energy effect would be uncompensated.

After Nernst,[3] in 1889, first proposed the principle of the solubility product, Rudolphi[4] pointed out its tendency to increase with concentration. Stieglitz[5] pointed out obstacles to applying the law of con-

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[1] Nernst, *Z. physik. Chem.*, **4**, 155 (1899); Goodwin, *Ibid.*, **13**, 641 (1894); Thiele, *Z. anorg. Chem.*, **26**, 1 (1900); Jahn, *Z. physik. Chem.*, **33**, 545 (1900) and **35**, 1 (1900); Sackur, *Ibid.*, **48**, 129 (1904); Broensted, *Ibid.*, **50**, 481 (1904), and Tolman and Ferguson, THIS JOURNAL, **34**, 232 (1912). While the proof of this article was being read, there appeared the interesting article by MacInnes and Parker, *Ibid.*, **37**, 1445 (1915), on potassium chloride concentration cells, ingeniously contrived to avoid transference, including solutions as concentrated as half normal. While opportunity for extended comment is lacking, it may be noted that the abnormally low "activities" of the ions in the solutions investigated by them are continued in still more striking fashion at higher concentrations as measured by us.

[2] See 1, also Richards and Lewis, *Z. physik. Chem.*, **28**, 1 (1899); Lewis, THIS JOURNAL, **28**, 166 (1906); Bell and Feild, *Ibid.*, **35**, 715 (1913); Gibbons and Getman, *Ibid.*, **36**, 1630 (1914); Jones, *Ibid.*, **37**, 756 (1915).

[3] Nernst, *Z. physik. Chem.*, **4**, 372 (1889).

[4] Rudolphi, *Ibid.*, **17**, 385 (1895).

[5] Stieglitz, THIS JOURNAL, **30**, 946 (1908).

centration effect, but considered it a good empirical approximation due to compensation of opposing errors. Washburn[1] has apparently derived a sound theoretical basis for treatment of the solubility product from the original viewpoint, but the solutions must be "sufficiently dilute." Noyes[2] and his associates have shown the variations in the solubility product to increase with the solubility and valences of a salt. According to this conclusion, the product should be more constant in the case of silver chloride than with almost any other salt. The danger of assuming constancy is fully realized, but our results must show at least the effect of superposing changes in activities and in solubility product at different concentrations. As for the most probable value of solubility product times 10^{10} at 25°, omitting Hollemann's[3] early work, Kohlrausch and Rose[4] give 2.13; Goodwin's[5] value, 1.56, is raised to 1.73 if $F = 96,540$ and viscosity corrections are made; Thiele[6] obtains 2.00; Kohlrausch[7] later finds 1.75; from measurements of Melcher[8] we calculate 1.93; Böttger[9] upholds 1.99; and finally, Glowczynski,[10] titrating the silver chloride in solution at 25° with NH_4CNS, finds 1.44. He believes that previous investigators have had impure AgCl, but as his original paper is not accessible, his very low value is not for the present taken instead of the above array of concordant data. The average of the six accepted determinations is 1.92×10^{-10}.

Potassium and sodium chlorides were purified by precipitation from water solution of hydrochloric acid gas made by heating the pure concentrated acid. The precipitates were washed, dried, ignited, and dissolved in redistilled water almost to saturation. These solutions were also saturated with precipitated silver chloride. On dilution with a known volume of water, a precipitate appeared, and the solution, after settling, was still saturated with silver chloride. Concentrations of alkali chloride were calculated from analyses, those of silver chloride by interpolation on a large curve drawn from data obtained by one of us.[11] Solutions unsaturated with silver chloride, but containing it in constant concentration, were also used. To prepare these, equal volumes of alkali chloride and of water were treated with a volume of silver nitrate

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[1] Washburn, THIS JOURNAL, **32,** 467, 653 (1910).

[2] Noyes and Associates, *Ibid.*, **33,** 1643, 1650, 1663, 1673, 1807, 1827, 1836 (1911).

[3] Holleman, *Z. physik. Chem.*, **12,** 132 (1893).

[4] Kohlrausch and Rose, *Ibid.*, 12, 242 (1893).

[5] Goodwin, *Ibid.*, **13,** 641 (1894).

[6] Thiele, *Z. anorg. Chem.*, **24,** 57 (1900).

[7] Kohlrausch, *Z. physik. Chem.*, **64,** 129 (1908).

[8] Melcher, THIS JOURNAL, **32,** 50 (1910).

[9] Böttger, *Z. physik. Chem.*, **56,** 83 (1906).

[10] Glowczynski, *C. A.*, **1915,** 741.

[11] Forbes, THIS JOURNAL, **33,** 1937 (1911).

identical in both cases, and on mixing known amounts of the products, solutions constant in silver content were obtained, until precipitation occurred.

Solutions of 0.01 *N* silver nitrate and of alkali chloride containing silver chloride were contained in separate wide-mouthed bottles immersed in a thermostat kept at 25.0°. As a precipitate would form on mixing, the junction could not be made and calculated in the manner usually applied to concentration cells with transference. Siphons of pure concentrated potassium nitrate in agar-agar were, therefore, used to connect the solutions. Sackur[1] has found the electromotive force of such cells independent of the concentration of the nitrate. Our chloride solutions were much more concentrated than his, but as the mobilities of all the ions involved (except sodium) were very nearly equal, the error introduced by junctions at the boundaries of the concentrated potassium nitrate solutions should be inconsiderable.

The possibility of variable oxidation of the electrodes by dissolved air was tested by measuring the potentials of given cells in air, in pure nitrogen from an apparatus used in atomic weight investigation, and in carbon dioxide. As the only variations were traced to the stirring of the solutions by bubbles, subsequent measurements were made in air. Stirring the chloride solutions greatly disturbed the potential of the cells. Tolman[2] has reviewed the hypotheses made to account for such effects, and has advanced a plausible one of his own. Kistiakowsky[3] holds that stirring is necessary, in the case of solid electrodes, to submerge the slight differences in potential between different points on the same electrode. This would be particularly true of metals in which a gas film tended to form. The disturbances noted by us increased with the speed of stirring, and failed to approach limiting values with any speed that we could attain. Therefore, the solutions, after brisk stirring, were allowed to stand at rest until the potential assumed a value constant for hours within a few tenths of a millivolt.

The total potential of each cell was measured to one-tenth millivolt, without interpolation, by the compensation method. The potentiometer was calibrated, and the corrections applied. The standard cadmium cell was carefully made up, and checked at intervals against cells kindly loaned by other investigators.

Tables I and II exhibit data and results of calculations for solutions saturated with silver chloride. Concentrations are expressed in mols per liter and in mol fractions. As each molecule of silver chloride combines with two of alkali chloride up to 1.5 *N*, and with three above 1.5

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[1] Sackur, *Z. physik. Chem.*, **48**, 129 (1904).

[2] Tolman, This Journal, **33**, 1836 (1911); **36**, 466 (1914).

[3] Kistiakowsky, *Z. Elektrochem.*, **14**, 113 (1908).

TABLE I.—POTASSIUM CHLORIDE SATURATED WITH SILVER CHLORIDE. PART I.

[KCl], Mols/Liter.	Density. 25°/4°.	[KCl] × 10^2, Mol Fraction.	Total [Ag] × 10^3. Mols/Liter.	Total [Ag] × 10^4, Mol Fraction.	[KCl] — [Ag] × *m*, Mols/Liter.	[[KCl] — [Ag] × *m*] × 10^2, Mol Fraction.	Potential Found, $[Ag^{\cdot}]_1 = 0.009314$.
3.917	1.1657	7.476	6.185	1.179	3.898	7.441	0.4759
3.926	1.1674	7.482	6.245	1.189	3.907	7.446	0.4752
3.797	1.1610	7.428	5.722	1.089	3.780	7.395	0.4753
3.890	1.1661	7.395	6.024	1.145	3.872	7.361	0.4737
3.154	1.1340	5.837	2.644	0.4967	3.146	5.822	0.4668
2.677	1.1131	4.990	1.493	0.2807	2.672	4.982	0.4590
2.508	1.1061	4.679	1.198	0.2234	2.504	4.672	0.4586
1.976	1.0833	3.663	0.601	0.1113	1.974	3.660	0.4526
1.952	1.0819	3.619	0.580	0.1073	1.950	3.616	0.4518
1.820	1.0791	3.353	0.467	0.0860	1.819	3.350	0.4453
1.648	1.0690	3.147	0.352	0.0650	1.647	3.145	0.4446
1.383	1.0526	2.556	0.219	0.0405	1.383	2.556	0.4413
0.977	1.0496	1.767	0.121	0.0219	0.977	1.767	0.4328
0.853	1.0402	1.545			0.853	1.545	0.4296
0.758	1.0357	1.374			0.758	1.374	0.4269
0.381	1.0193	0.686			0.381	0.686	0.4145

TABLE I.—POTASSIUM CHLORIDE SATURATED WITH SILVER CHLORIDE. PART II.

[KCl], Mols/Liter.	Potential calc., $[Ag^{\cdot}]_1 = 1.000$.	$[Ag^{\cdot}] \times 10^{10}$, Gram Ion/Liter.	$[Ag^{\cdot}] \times 10^{12}$, Mol Fraction.	$\frac{\Lambda}{150.6}$	$\frac{\Lambda}{150} \times \frac{\eta}{\eta_0}$.	$\frac{1.92 \times 10^{-10}}{[Ag^{\cdot}][KCl] \text{ corr.}}$	$\frac{1.92 \times 10^{-10}}{[Ag^{\cdot}][KCl]} \div \frac{\Lambda\eta}{150\,\eta_0}$.	$\frac{1.92 \times 10^{-10}}{[Ag^{\cdot}][KCl]} \div \frac{\Lambda}{150.6}$.
3.917	0.5960	0.834	1.59	0.634	0.637	0.591	0.927	0.932
3.926	0.5953	0.854	1.62	0.634	0.637	0.575	0.903	0.907
3.797	0.5954	0.857	1.63	0.636	0.639	0.593	0.928	0.932
3.890	0.5938	0.909	1.73	0.635	0.637	0.546	0.856	0.860
3.154	0.5869	1.187	2.23	0.649	0.652	0.514	0.789	0.793
2.677	0.5791	1.610	3.03	0.660	0.663	0.446	0.673	0.676
2.508	0.5787	1.636	3.05	0.664	0.667	0.469	0.705	0.708
1.976	0.5727	2.067	3.83	0.684	0.682	0.471	0.690	0.688
1.952	0.5719	2.130	3.95	0.685	0.683	0.462	0.677	0.674
1.820	0.5654	2.739	5.05	0.691	0.689	0.385	0.559	0.557
1.648	0.5647	2.820	5.20	0.700	0.697	0.413	0.593	0.592
1.383	0.5614	3.211	5.93	0.717	0.713	0.432	0.607	0.603
0.977	0.5529	4.461	7.92	0.751	0.745	0.441	0.591	0.588
0.853	0.5497	5.065	9.18	0.759	0.753	0.444	0.590	0.586
0.758	0.5470	5.616	10.18	0.767	0.761	0.451	0.593	0.587
0.381	0.5346	9.112	16.55	0.801	0.796	0.553	0.695	0.692

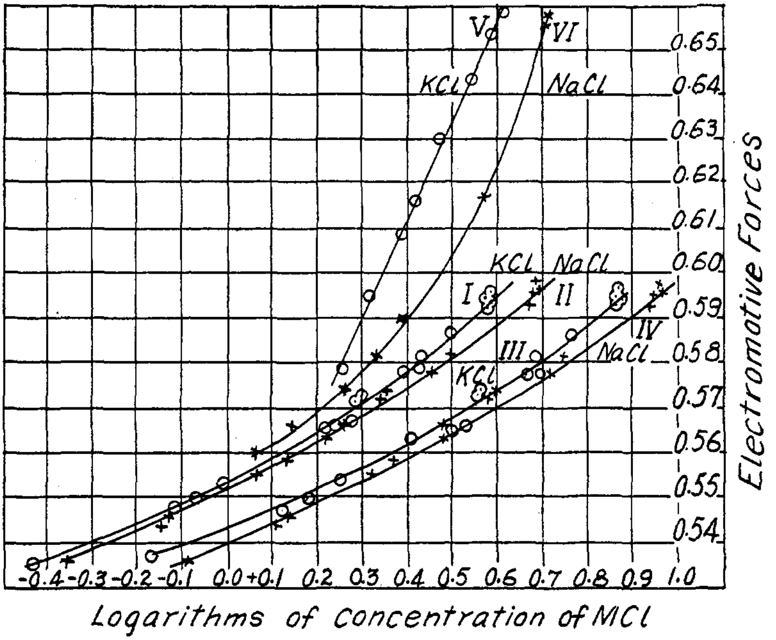
TABLE II.—SODIUM CHLORIDE SATURATED WITH SILVER CHLORIDE. PART I.

[NaCl], Mols/Liter.	Density, 25°/4°.	[NaCl] × 10^2, Mol Fraction.	Total [Ag] × 10^3, Mols/Liter.	Total [Ag] × 10^4, Mol Fraction.	[NaCl] — [Ag] × m. Mols/Liter.	[[NaCl]—[Ag] × m] × 10^2, Mol Fraction.	Potential Found. $[Ag^\cdot]_1 = 0.009314$.
5.013	1.1841	9.196	5.936	1.0890	4.895	9.163	0.4776
4.992	1.1837	9.152	5.925	1.0860	4.974	9.119	0.4768
4.895	1.1802	8.975	5.510	1.0100	4.878	8.945	0.4758
4.781	1.1758	8.761	5.085	0.9318	4.766	8.733	0.4736
3.080	1.1123	5.613	1.297	0.2364	3.076	5.606	0.4611
2.815	1.1025	5.114	0.988	0.1817	2.812	5.108	0.4586
2.171	1.0761	3.954	0.500	0.0907	2.169	3.951	0.4537
2.121	1.0680	3.877	0.470	0.0861	2.119	3.884	0.4517
1.700	1.0603	3.086	0.280	0.0508	1.699	3.084	0.4451
1.640	1.0579	2.978	0.257	0.0467	1.639	2.977	0.4432
1.393	1.0486	2.517	0.174	0.0316	1.393	2.517	0.4404
1.300	1.0450	2.358	0.159	0.0288	1.300	2.358	0.4379
1.154	1.0390	2.094	0.121	0.0220	1.154	2.094	0.4350
0.758	1.0247	1.376			0.758	1.376	0.4264
0.719	1.0232	1.301			0.719	1.301	0.4260
0.441	1.0126	0.798			0.441	0.798	0.4147

TABLE II.—SODIUM CHLORIDE SATURATED WITH SILVER CHLORIDE. PART II.

[NaCl], Mols/Liter.	Potential calc.; $[Ag^\cdot]_1 = 1.000$.	$[Ag^\cdot] \times 10^{10}$, Gram Ion/Liter.	$[Ag^\cdot] \times 10^{-12}$. Mol Fraction.	$\frac{\Lambda}{127.0}$.	$\frac{\Lambda}{125.0} \times \frac{\eta}{\eta_0}$.	$\frac{1.92 \times 10^{-10}}{[Ag^\cdot]\,[NaCl]\text{ corr.}}$.	$\frac{1.92 \times 10^{-10}}{[Ag]\,[NaCl]} \div \frac{\Lambda\eta}{125\,\eta_0}$.	$\frac{1.92 \times 10^{-10}}{[Ag^\cdot]\,[NaCl]} \div \frac{\Lambda}{127}$.
5.013	0.5977	0.780	1.43	0.396	0.684	0.493	0.720	1.242
4.992	0.5969	0.805	1.47	0.397	0.685	0.479	0.700	1.204
4.895	0.5959	0.837	1.53	0.401	0.686	0.470	0.685	1.173
4.781	0.5937	0.911	1.67	0.406	0.686	0.442	0.645	1.088
3.080	0.5812	1.482	2.70	0.499	0.695	0.422	0.607	0.845
2.815	0.5787	1.634	2.97	0.516	0.698	0.418	0.599	0.813
2.171	0.5738	1.977	3.60	0.566	0.713	0.448	0.627	0.792
2.121	0.5718	2.138	3.91	0.568	0.714	0.424	0.594	0.746
1.700	0.5652	2.775	5.04	0.599	0.717	0.407	0.568	0.680
1.640	0.5633	2.976	5.40	0.609	0.724	0.394	0.544	0.647
1.393	0.5605	3.320	6.02	0.632	0.734	0.415	0.566	0.657
1.300	0.5580	3.660	6.64	0.642	0.737	0.404	0.548	0.630
1.154	0.5551	4.096	7.43	0.659	0.746	0.406	0.544	0.616
0.758	0.5465	5.727	10.38	0.710	0.772	0.442	0.573	0.623
0.719	0.5461	5.816	10.52	0.713	0.774	0.459	0.593	0.644
0.441	0.5438	9.032	16.31	0.756	0.800	0.482	0.603	0.636

N,[1] the silver concentration must be multiplied by two, or three, and subtracted from that of the alkali chloride in each case. Observed potentials are given, also those calculated for cells containing normal silver ion by adding 0.05913 log 1.000/0.009314, or 0.1201 volt, to observed values, where the dissociation of 0.01 N silver nitrate is taken as 93.14% at 25°. Curves I, II exhibit the latter potentials plotted against log mols/liter, and II, IV the same plotted against log mol fractions × 10^2.



All these solutions were saturated with silver chloride. Next in order are tabulated silver ion concentrations calculated from the formula log $[Ag^{\cdot}] = \log 0.009314 - \pi/0.05913$. The error is 4% per millivolt in all cases. Degree of dissociation is calculated in two ways, first as Λ_v/Λ_∞, using 150.6 and 127.0, the customary values, respectively, of Λ_∞ at 25°; second by extrapolating Λ to infinite dilution by the method of Kraus and Bray,[2] we found 150.0 for potassium chloride, and 125.0 for sodium chloride, and multiplied the conductance ratio by the ratio of the viscosities[3] rather than by any power of the same. In the case of the potassium chloride, reliable data[4] for viscosities were found and

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[1] Forbes, THIS JOURNAL, **33**, 1937 (1911).

[2] Kraus and Bray, *Ibid.*, **35**, 1315 (1913).

[3] See Sutherland, *Phil. Mag.*, **3**, 161 (1902); Bousfield, *Z. physik. Chem.*, **53**, 257 (1905); Washburn, THIS JOURNAL, **33**, 1469 (1911).

[4] Wagner, *Z. physik. Chem.*, **5**, 31 (1890); Reyer, *Ibid.*, **2**, 744 (1888); Brueckner, *Ann. physik.*, **42**, 294 (1891); Hoskings, *Phil. Mag.*, [6] **17**, 502 (1909). Hosking's

applied up to 2.0 N only. Data for viscosity and degree of dissociation were interpolated on smoothed curves drawn on a large scale. Because of the length of the process for calculating the corrected values, these are given below without comment. By dividing 1.92×10^{-10} by $[Ag^{\cdot}]$ we obtain the apparent effective concentration or activity of the chloride ion, and by dividing also by [MCl] corrected for complex formation, we obtain a new set of figures for effective degree of dissociation. The succeeding column gives the ratio between these figures and the corrected degree of dissociation. It will be noted that the activity of the chloride ion in relation to concentration decreases as concentration increases from small values up to 1.7 N, and the minima attained—0.385 and 0.394 are almost identical for both chlorides. These minima are not to be attributed to any decrease in the solubility product of silver chloride as concentration increases, for Noyes[1] has shown the product to increase. Nor can the decreases be mainly due to absence of correction for the liquid junctions, because the decrease is smaller in the case of sodium chloride, where the difference in ionic mobilities is far more pronounced than in potassium chloride. In passing through the concentration, 1.7, the formula of the complex changes from M_2AgCl_3 to M_3AgCl_4,[2] showing this region to be worthy of careful study. As the concentration is increased beyond this point the change in the nature of the medium seems to prevail over the tendencies which have acted to lower the relative activity of the chloride ion. A sharp rise in the ratio of activity to concentration takes place as higher concentrations are approached, which is much more pronounced in the case of potassium chloride, corresponding to the greater power of this salt to dissolve AgCl.

In the last column we have the ratio between the effective degree of dissociation, calculated from the solubility product, and the degree of dissociation calculated in the usual simple fashion. With potassium chloride the values follow the same trend as in the column before, but with sodium a huge increase is noted at high concentrations, imputing to the solution an activity 24% greater than could be explained by complete dissociation. The viscosity correction appears, therefore, to yield more reasonable figures in calculating dissociation from conductivity.

Measurements were also made in solutions where the concentration of the alkali chloride was varied, as described above, without changing that of the total dissolved silver, at least when expressed in mols per liter. Curve V in the graph shows the results in potassium chloride, and

values were interpolated between 20° and 30°, while Brueckner's were extrapolated from 15° and 20° to 25°.

[1] Noyes and associates, This Journal, **33**, 1643, 1650, 1663, 1673, 1807, 1827, 1836 (1911).

[2] Forbes, *Ibid.*, **33**, 1937 (1911).

TABLE III.—CONSTANT [AgCl], VARIABLE [KCl].

[MCl], Mols/Liter.	Potential found, $[\mathrm{Ag}^{\cdot}]_1 = 0.009314$.	Potential calc., $[\mathrm{Ag}^{\cdot}] = 1.000$.	$[\mathrm{Ag}^{\cdot}] \times 10^{10}$, Mols/Liter.	$\frac{\Lambda}{\Lambda_\infty}$.	[Cl'].	$[\mathrm{Ag}^{\cdot}]\,[\mathrm{Cl}']^4 \times 10^{10}$.	$[\mathrm{Ag}^{\cdot}]\,[\mathrm{Cl}']^3 \times 10^{10}$.
4.064	0.5385	0.6586	0.0736	0.632	2.563	3.17	..
3.474	0.5225	0.6426	0.1357	0.641	2.222	3.34	..
2.968	0.5100	0.6301	0.2209	0.650	1.395	3.06	..
2.624	0.4957	0.6158	0.3565	0.658	1.727	3.17	..
2.476	0.4890	0.6091	0.500	0.663	1.642	3.63	..
2.055	0.4738	0.5939	0.904	0.679	1.395	3.43	..
1.824	0.4591	0.5792	1.603	0.689	1.257	4.00	..

TABLE IV.—CONSTANT [AgCl], VARIABLE [NaCl].

5.143	0.5378	0.6579	0.0748	0.389	2.000	1.20	..
5.080	0.5357	0.6558	0.0812	0.392	1.991	1.28	..
3.690	0.4968	0.6169	0.1868	0.463	1.708	1.59	..
3.262	0.4875	0.6076	0.3410	0.488	1.592	2.19	..
2.504	0.4705	0.5906	1.028	0.539	1.350	3.41	..
2.454	0.4694	0.5895	1.098	0.543	1.332	3.46	..
2.159	0.4617	0.5818	1.448	0.565	1.220	3.21	..
1.808	0.4540	0.5741	1.955	0.592	1.070	2.57	..
1.394	0.4458	0.5659	2.690	0.632	0.881	..	1.46
1.180	0.4405	0.5606	3.307	0.656	0.774	..	1.53
0.943	0.4348	0.5549	4.128	0.685	0.646	..	1.11

Curve VI those in sodium chloride, plotting potentials calculated as against normal silver ions against concentrations in mols per liter only, as the mol fraction curves would cut Curves I and II in a confusing fashion. In the potassium chloride (Table III) total silver was 1.43×10^{-4}, and in the sodium chloride (Table IV) 3.73×10^{-5} mol/liter. The constants in the last column are derived as follows, using the unmodified Law of Concentration Effect for this first approximation:

$$[\mathrm{Ag}^+]\,[\mathrm{Cl}^-] = k_1\,[\mathrm{AgCl}]$$

$$[\mathrm{AgCl}]\,[\mathrm{Cl}^-]^n = k_2\,[\mathrm{AgCl}_{n+1}^{n-}]$$

Eliminating (AgCl) between the equations,

$$\frac{[\mathrm{Ag}^+]\,[\mathrm{Cl}^-]}{k_1} = \frac{k_2\,[\mathrm{AgCl}_{n+1}^{n-}]}{[\mathrm{Cl}^-]^n}$$

But as the total silver is constant, and almost equal to $(\mathrm{AgCl}_{n+1}^{n-})$, as practically all the silver is in the form of the complex ion, we have

$$[\mathrm{Ag}^+]\,[\mathrm{Cl}^-]^{n+1} = \mathrm{K}_n$$

The complex ion existing above 1.7 *N* has been found by one of us[1] to be AgCl_4''', whence $n = 3$. The degree of dissociation is taken as

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[1] Forbes, THIS JOURNAL, **33**, 1937 (1911).

Λ/Λ_∞. If the values corrected for viscosity were used, the results for potassium chloride would be little changed, but no approach to a constant could be obtained in the case of sodium chloride. This work with constant silver concentration was interrupted when barely begun, but it promises to be of much interest, as also determinations in which chloride concentration is kept constant, but total silver is varied, which would help greatly in the interpretation. No conclusion can at present be drawn as to the significance of the difference in shape, slope, or position of the two curves given.

Summary.

The activity of chloride ion in concentrated solutions of sodium and of potassium chloride saturated with silver chloride is calculated from potential measurements, using silver electrodes, and a junction of concentrated potassium nitrate, to eliminate diffusion potentials. The solubility product, for want of a better hypothesis, is assumed constant, and evidence is offered to show that its variations do not greatly affect the conclusions.

The values obtained by this method are always smaller than those calculated from conductivities except in the most concentrated solutions of sodium chloride. The dissociation calculated from them reaches a minimum at 1.7 *N*.

Solutions variable in alkali chloride, but constant in silver chloride, afford results supporting the hypothesis that the complex K_3AgCl_4 exists in concentrations above 1.7 *N*.

CAMBRIDGE, MASS.

EQUILIBRIUM IN THE SYSTEM DISODIUM HYDROGEN ARSENATE, LEAD NITRATE, AND WATER AT 25° C.

BY B. E. CURRY AND T. O. SMITH.

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In the course of an investigation of commercial lead arsenates the writers experienced the need of more definite information than the literature affords concerning the theoretical compounds of lead and arsenic acid. The compounds reported by previous workers have evidently been formed under ordinary synthetic rather than equilibrium conditions. The methods of preparation in most cases have apparently been selected with the view of duplicating those used by the manufacturer.

The most important source of arsenic used in the preparation of commercial lead arsenate is disodium hydrogen arsenate. This is the cheapest source of arsenic in suitable form. The lead salts used are the nitrate and the acetate. The nitrate is given the preference because it is the cheaper salt on the basis of lead content; also, because the product formed from the nitrate under manufacturing conditions possesses more desirable physical