SOLUBILITY RELATIONS OF SILVER CHLORIDE IN AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES

BY EDWARD W. NEUMAN[1]

In an earlier article[2] a method·was described for the determination of the solubility of inorganic precipitates in aqueous solutions of strong electrolytes. The method was applied to silver chloride in solutions of various nitrates and it was shown that the activity coefficients calculated from the measurements obeyed, at least approximately, the limiting law of Debye and Hückel. The method has here been extended to include solubility measurements of silver chloride in solutions of various valence type sulfates, and the data on some of the nitrate solvent salts, previously investigated, have been extended to higher concentrations.

Theoretical

Solubility measurements are analogous to vapor pressure measurements, in that in one case the solute escapes into a solvent, and in the other into a vacuum. When the solute in the saturated solution is in equilibrium with the solid phase, the activity of the solute in solution is fixed; so that, if foreign substances are added to the solution in equilibrium with the solid, the stoichiometric solubility S may change, but the activity A of the solute must remain constant. Hence for a series of solutions, 0, 1, 2, ... n

$$A = f_0 S_0 = f_1 S_1 = f_2 S_2 = \ldots\ldots = f_n S_n \qquad (1)$$

where f_1 is the activity coefficient of the solute in a given solution of the system. If $f_0 S_0$ denotes the activity of the solute in the otherwise pure solvent and fS its activity in the same solvent containing also an electrolyte, then, by determining the solubility of the solute at various concentrations of the added electrolyte, it is possible to evaluate f and f_0 from the relation

$$f_0 S_0 = fS$$

or, more conveniently[3]

$$-\log f = \log (S/S_0) - \log f_0 \qquad (2)$$

The value of $\log f_0$ may be evaluated by extrapolation, to zero concentration, of a plot of $\log (S/S_0)$ against some linear function of the total concentration.

Debye and Hückel[4] have developed a theory of solutions of strong

---

[1] National Research Fellow in Chemistry.

[2] Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853 (1930).

[3] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[4] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

electrolytes. Their equation for the activity coefficient of a salt in a solution is

$$-\log_e f_{[1]} = \frac{\alpha(-Z_1 Z_2)(\mu)^{1/2}}{1 + a\kappa} \tag{3}$$

Here α is a constant depending on the dielectric constant D of the solvent, the absolute temperature T, and various universal constants, and is defined for decadic logarithms by

$$\alpha = \frac{\epsilon^3 (2\pi n)^{1/2}}{2.3026 \; (DkT)^{3/2}} \tag{4}$$

The reciprocal of κ is an important quantity in this theory. It has the dimensions of distance and its introduction avoids some of the difficulties encountered by many investigators. It is defined by

$$\kappa^2 = \frac{\epsilon^2 \; 4\pi n\mu}{DkT} \tag{5}$$

The quantity a is the distance of closest approach of the ions and is expressed in Ångström units; ϵ is the unit charge in E. S. U., k is Boltzmann's constant; n is Avogadro's number; and μ is the ionic strength of the solution, based on moles per unit volume of solution, and defined by

$$\mu = {}^1\!/_2 \sum C_i Z_i^2 \tag{6}$$

where C_i is the number of moles per liter of solution, and Z_i is the valence of an ion of the i-th kind. For aqueous solutions at $25°$, $\alpha = 0.5066$,[5] and $\kappa = 0.3287^5 (\mu)^{1/2} 10^8$.

The relation (3) seems to have been generally accepted for aqueous solutions of low valence type salts up to about 0.2μ, but is inadequate for most high valence-type salts and for many non-aqueous solutions. If constancy of the value of a, calculated from the experimental data, be taken as a criterion for applicability of the theory, it will be shown that this relation holds only as a first approximation, if at all, for solutions of a uni-univalent salt in the presence of relatively simple valence-type electrolytes at concentrations as low as 0.002μ. From the form of the equation it may readily be seen that deviations of observed values derived from formula (2), when positive, can only be accounted for in equation (3) by physically absurd negative values of a.

The formula of Debye and Hückel was based on the first approximation of the solution of the Poisson–Boltzmann equation. Gronwall, La Mer and Sandved[6] have succeeded in obtaining a complete solution of this equation. They derived additional terms in powers of a for equation (3) and proposed, for the activity coefficient of a salt, the relation

[5] The numerical values of the constants used in the computation of these factors are: $n = 6.061 \times 10^{23}$; $k = 1.372 \times 10^{-16}$; $T = 298.1$; $\epsilon = 4.774 \times 10^{-10}$; $D = 78.54$. The value for D, the dielectric constant for water, is that given by Wyman, *Phys. Rev.*, **35**, 623 (1930).

[6] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

$$\log_e f_{[5]} = \frac{-\epsilon^2 Z^2 x}{2aDkT(1+x)} + \sum \left[\frac{\epsilon^2 Z^2}{aDkT}\right]^{2m+1} [\tfrac{1}{2}X_{2m+1}(x) + 2m Y_{2m+1}(x)] \qquad (7)$$

where $x = a\kappa$, and κ is defined as in (5). For aqueous solutions[7] at 25° this formula becomes

$$-\log_{10} f_{[5]} = \frac{0.5043(\mu)^{1/2}}{1 + 0.3283a(\mu)^{1/2}} - 0.15382 \; F_3(x)10^3/a^3$$
$$- 0.007700 \; F_5(x)10^5/a^5 \qquad (8)$$

when m is extended to $m = 2$. The first term on the right of equation (7) is the well-known Debye approximation, (equation 3). The X and Y terms are complicated functions of x, and have been evaluated over a wide range of x values. This formula is applicable only to electrolytes of the symmetric valence type in both the solute and the solvent salt and has been evaluated to the fifth approximation.[6]

Recently La Mer, Gronwall and Greiff[8] have extended the treatment to include unsymmetric valence type electrolytes. The computations have been extended to the third approximation. In the case of the activity coefficient of a solute electrolyte in aqueous solution at 25° in the presence of one other electrolyte, their formula becomes

$$-\log_{10} f_{[3]} = -Z_1 Z_2 \left\{ \frac{1.53636}{a(1+x)} x + \frac{0.12740}{a^2} q_2^2 [\tfrac{1}{2}X_2(x) - Y_2(x)]10^2 + \right.$$

$$\frac{0.43480}{a^2} q_2(Z_1 + Z_2 - q_2)Y_2(x)10^2 - \frac{0.15382}{a^3} q_2^2 q_3 [\tfrac{1}{2}X_3^*(x) - 2Y_3^*(x)]10^3 -$$

$$\frac{0.15382}{a^3} q_3^2 [\tfrac{1}{2}X_3(x) - 2Y_3(x)]10^3 - \frac{0.15382}{a^3} q_2[2(Z_1 + Z_2)q_3 +$$

$$(Z_1^2 + Z_1 Z_2 + Z_2^2)q_2 - 3q_2 q_3]Y_3^*(x)10^3 -$$

$$\left. \frac{0.30764}{a^3} q_3 [(Z_1^2 + Z_1 Z_2 + Z_2^2) - q_3]Y_3(x)10^3 \right\} \qquad (9)$$

The X and Y factors are again complicated functions of x and have been evaluated and tabulated by the authors so that the formula readily yields to computation of values of $\log f_{[3]}$ for comparison with experiment. The factor Z_1 is the valence of the cation, and Z_2 is the valence of the anion of the solute salt. The a value, appearing in Ångström units in the formula, has the same significance as before. In this relatively simple case of only two electrolytes, q_ν has the form

$$q_\nu = \frac{n[\nu_1 Z_1^{\nu+1} + \nu_2 Z_2^{\nu+1}] + n'[\nu_3 Z_3^{\nu+1} + \nu_4 Z_4^{\nu+1}]}{n[\nu_1 Z_1^2 + \nu_2 Z_2^2] + n'[\nu_3 Z_3^2 + \nu_4 Z_4^2]} \qquad (10)$$

wherein n is the number of moles of solute consisting of ν_1 cations of valence Z_1 and ν_2 anions of valence Z_2; and n' is the number of moles of solvent salt consisting of ν_3 cations of valence Z_3 and ν_4 anions of valence Z_4. In

[7] Drude's value for the dielectric constant of water was used [*Ann. Physik*, **59**, 61 (1896)]: $D = 88.23 - 0.4044 t + 0.001035 t^2$.

[8] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

the symmetric case of both salts, q_2 is zero and formula (9) simplifies accordingly.

When using the extended formulas for the calculation of a values which are to fit the experimental points, recourse must be had to methods of interpolation, since the forms of the x functions do not readily yield to a direct solution for values of a. Thus, for each total concentration there is a value of κ and a series of x values corresponding to the assumed values of a in Ångström units, for which values the functions $x_2(x)$, $Y_2(x)$, etc., may be found by interpolation on large-scale charts of the tables already computed. The values of $\log f_{[3]}$ or $\log f_{[5]}$ for each assumed a value are then obtained by substitution in formula (8) or (9), as the case may be, and the value of a, corresponding to the experimentally determined $\log f$, obtained by interpolation on the curve $\log f_{[3]}$ or $\log f_{[5]}$ against a.

The formula (9) is given as correct to terms of the third order inclusive. The development is based, in part, on the assumption that $a_1 = a_2 = a_3 = a_4 = a$ in a solution of two electrolytes; that $\log f_{0[3]}$ is equal to $\log f_{0[1]}$; and that there is no specific interaction among the various ions of the two electrolytes such as would result in an alteration of the number of ions from that required by a complete dissociation. This obviates the effects of Bjerrum's[9] ion association and lends the extended theory pertinent significance in view of the theory of complete dissociation of strong electrolytes.

Materials

Water.—Twice distilled, second distillation through a block tin condenser. Specific conductivity, 1.2×10^{-6} mhos. Used in all final recrystallizations, in the preparation of all solutions, and in all experimental work.

Silver Salts.—The nitrate was thrice recrystallized. The sulfate was prepared according to Richards and Jones.[10] During purification and subsequent storage the salts were protected from light as much as possible. As a result no photodecomposition could be noted. Stock solutions were analyzed gravimetrically, and experimental solutions containing 1×10^{-4} mole of Ag^+ per liter were prepared by dilution.

Acids.—Hydrochloric and sulfuric acids were subjected to two distillations retaining only the middle one-third.

Salts.—All salts were carefully purified by two, and in some cases three, recrystallizations. The calcium salts were prepared from pure calcium carbonate. The concentrations of all solutions were checked by analysis. All solutions of the solvent electrolytes were tested for chlorides under the conditions obtaining in the experimental runs. The lanthanum salts were tested for cerium by the hypochlorite method. Only a trace was found in lanthanum chloride and, since the concentration of this salt was never more than 2×10^{-6} M per liter, the effects of cerium salts were disregarded.

Experimental

A series of solutions containing a constant quantity of the solvent electrolyte and varying, but equivalent, amounts of silver nitrate or sulfate

[9] Bjerrum, *Kgl. Danske Videnskab. Selskab, Det, Mathk.-fys. Medd.*, VII, No. 9, 1926.

[10] Richards and Jones, THIS JOURNAL, **29**, 831 (1907).

and the metallic chloride, corresponding to the solvent salt used, were made up in 100-cc. oil sample bottles. The bottles were sealed with corks, which had been soaked in chloride-free paraffin, and were agitated in a water thermostat at 25° until equilibrium was attained. The solutions were examined, at intervals of about eight hours, for turbidity in a Tyndallometer. The standard for comparison was a solution similar in composition to the solutions of the series but containing no silver ions.

The bottles in which the solutions were prepared and examined were carefully selected so that they all had a minimum, and equal, point of reflection when filled with twice distilled water and examined in the Tyndallometer. When used thereafter they were always examined in the calibrated position. The shaker for the bottles was arranged so that the bottles were held upright. This prevented the solutions from coming in contact with the corks and decreased the chances of contamination.

The solutions of the series were measured with calibrated burets. Chloride and silver solutions were measured with micro burets having a capacity of 20 cc. and readable to 0.005 cc. All glass apparatus was washed with cleaning solution, rinsed with distilled water ten times, and finally rinsed five times with redistilled water before use. The temperature of the room was kept at about $25 \pm 1°$ during the preparation.

The solubility of the salt was taken to lie at some point between the concentration showing no turbidity, and the first concentration showing the Tyndall beam. By preparing another series having smaller increments of the concentration of silver chloride and having a range, between and overlapping, for purposes of a more certain control, the last clear and first turbid concentration, it was possible to fix the solubility within still narrower limits. The smallest increments employed at the lowest concentration of solvent electrolytes were 4×10^{-8} M per liter, and 5×10^{-8} M per liter at the higher concentrations. The preliminary series for the approximate location of the point of solubility were usually prepared with increments of 2×10^{-6} M per liter, or more. Table I gives data for one of the experimental points illustrating the preliminary and the final location of the solubility.

TABLE I

DATA ILLUSTRATING METHOD OF OBTAINING THE END-POINT FROM THE TYNDALLOMETER INDICATION

0.001295 M La$_2$(SO$_4$)$_3$					
Preliminary Series A		Preliminary Series B		Final Series	
Molality of AgCl × 10^5	Turbidity	Molality of AgCl × 10^5	Turbidity	Molality of AgCl × 10^5	Turbidity
1.470	− − − −	1.490	− − −	1.500	− − − −
1.490	− − − −	1.500	− − −	1.505	− − − −
1.510	− + − −	1.510	− − −	1.510	− − − −
1.530	− + + +	1.520	+ + +	1.515	− − + +
1.550	+ + + +	1.530	+ + +	1.520	+ + + +

In series A, the solubility lies between 1.510 and 1.530; in series B, which has narrower limits, the solubility is located between 1.510 and 1.520; and, finally, in the last series having the narrowest limits the solubility is fixed between 1.510 and 1.515.

The criterion for equilibrium was that the Tyndallometer readings became constant. The readings given in Table I extend, for each series, over a period of about seventy-two hours. The first readings were taken at the end of twenty-four hours. It was found that more time was required for the solutions to come to equilibrium in the case of the higher concentrations of the solvent electrolytes. Sulfuric acid proved most troublesome in this respect, and, in addition, the turbidities occurring in solutions of the acid were much less sharply defined than in the case of the salts. Generally, when first prepared, all of the solutions were clear when examined in the Tyndallometer, and in most cases at least twelve hours was required for the first signs of turbidity. In general, solutions that had been cooled until all were turbid, after first having come to equilibrium at 25°, returned to the original state when again agitated in the thermostat at 25°.

The Tyndallometer used for detecting the first appearance of turbidity in the solutions has already been described.[2] Light from a 150-watt, compact-filament tungsten bulb entered the solution through the side of the oil sample bottles. Light, scattered by the solid phase, passed through the bottom of the bottles, whence it was reflected through the optical system of the Macbeth illuminometer and thence to the eye. The illuminometer light was adjusted so that the field of the telescope had a uniform intensity when the standard solution was placed in the apparatus. The color of the reflected light was blue and in order accurately to match the two fields of the telescope it was necessary to insert an appropriate filter in the light path of the illuminometer. Since the amount of solid phase which is formed in the neighborhood of the end-point is necessarily very small, the intensity of the reflected light is very low, necessitating working in a dark room. Occasional solutions which exhibited a relatively bright Tyndall beam were rejected as contaminated and the experiment was repeated.

Data and Discussion

The solubility of silver chloride was determined in aqueous solutions of sulfuric acid, potassium sulfate, calcium sulfate, magnesium sulfate, lanthanum sulfate, potassium nitrate, barium nitrate and lanthanum nitrate. The concentration range covered was from the amount of the solvent electrolyte equivalent to the solute salt, to about 0.04μ, except in the case of calcium sulfate, where the highest concentration was about 0.01μ. The range for potassium and for barium nitrate was from 0.01 to 0.04μ, extending the measurements of Popoff and Neuman. The five lowest points on lanthanum nitrate were measured in the Chemical Laboratory

of the State University of Iowa with the collaboration of Professor Stephen Popoff.

The value of S_0, the solubility of silver chloride in otherwise pure water, can only be obtained by methods of extrapolation from this type of experimental data. This is due to the fact that there is always present, in the solutions, an amount of solvent salt equivalent to the amount of solute salt, or silver chloride. Values of S_0' were determined from the data below 0.01μ for each solvent electrolyte and the results averaged to give the value S_0. The lower portions of the curves S vs. $(M)^{1/2}$, where M is the moles of solvent salt per liter of solution, approximated a straight line, and, by assuming the function

$$S = S_0' + A(M)^{1/2} \tag{12}$$

the S_0' values were readily evaluated by the method of moments. Similarly, the values of $\log f_0'$ were determined by assuming the function

$$\log (S/S_0) = (\log f_0') + b(\mu)^{1/2} \tag{13}$$

The arithmetic mean of S_0' and of f_0' was taken as the most probable value of the solubility and activity coefficient, respectively, of silver chloride in water at 25°.

The value of S_0 (mean) is 1.273×10^{-5} as compared to the value of 1.30×10^{-5} mole/liter reported in the "International Critical Tables."[11] Assuming that f_0 (mean) $= 0.9985 = f_+ f_-$ the activity product constant for silver chloride becomes 1.616×10^{-10}.

While not strictly the most accurate method of extrapolation in view of the peculiarities of some of the curves, as will be seen later, the treatment at least eliminates the uncertainties of individual error in graphical extrapolation. The parameters of the statistical equations (12, 13) are given in Table II.

TABLE II

EMPIRICAL PARAMETERS FROM STATISTICAL TREATMENT OF DATA

Solvent electrolyte	$S_0' \times 10^5$	$A \times 10^5$	$A \times 10^5/1.5$	$-\log f_0'$	f_0'	b
HNO₃	1.274	1.527 ⎫	1.02	0.00075	0.9983	0.5076
KNO₃	1.279	1.455 ⎬	0.970	.00130	.9970	.5004
NaNO₃	1.273	1.540 ⎭	1.03	.00061	.9986	.5081
Ba(NO₃)₂	1.273	2.613	1.74	.00069	.9984	.5005
La(NO₃)₃	1.273	3.757	2.50	.00053	.9988	.5045
H₂SO₄	1.268	2.759 ⎫	1.84	.00023	.9995	.5176
K₂SO₄	1.278	2.687 ⎭	1.79	.00108	.9975	.5200
CaSO₄	1.268	3.406 ⎫	2.27	.00029	.9993	.5534
MgSO₄	1.267	3.430 ⎭	2.29	.00064	.9985	.5596
La₂(SO₄)₃	1.274	6.167	4.11	.00026	.9994	.5141
Mean	1.273	...	..	.00064	.9985	.5186
NO₃⁻	1.274	...	..	.00077	.9982	.5042
SO₄⁻	1.271	...	..	.00050	.9988	.5329

11 "International Critical Tables," 1929, Vol. VI, p. 256.

The values of b in the last column of the data are analogous to the factor α in the limiting Debye equation, $-\log f = \alpha\mu^{1/2}$, and as such should very closely approximate the value 0.5066, assuming that the dielectric constant of Wyman is correct, and that the limiting law is obeyed in the region below 0.01μ. The average value from the nitrate solvent salts seems to be in good agreement with the theoretical and it might be said that, for the nitrates at least, the limiting law is obeyed below 0.01μ. The mean slope for the sulfates, however, is about 4% higher than the theoretical, a rather significant deviation. The ratios[12] in the middle column, although proportional to the square roots of 1, 3, 4, 6 and 15, in the case of $(1, -1)$, $(1, -2)$, $(2, -1)$, $(2, -2)$, $(3, -1)$, and $(3, -2)$ valence type electrolytes, respectively, have much greater deviations in the case of the sulfates than in the case of the nitrates.

The experimental data appear in Table III. The mean values, $S_0 = 1.274 \times 10^{-5}$ and $\log f_0 = -0.00064$ are used throughout for the calculation of $-\log f(\text{obs.})$. The values $-\log f_{[1]}$ were calculated from the limiting law of Debye and Hückel, $\log f_{[1]} = -0.5066\mu^{1/2}$. The apparent ionic diameters $a_{[1]}$ are from the Debye first approximation (3) arranged according to the formula

$$a_{[1]} \text{ (in Ångström units)} = \frac{0.5066\mu^{1/2} + \log f(\text{obs.})}{-\log f(\text{obs.}) \times 0.3287\mu^{1/2}}$$

The apparent ionic diameters, $a_{[5]}$, are obtained to the fifth approximation from the Gronwall, La Mer and Sandved[6] treatment for the case of symmetrical valence type solvent salts, and the diameter $a_{[3]}$ are obtained to the third approximation from the La Mer, Gronwall and Greiff[8] treatment for unsymmetrical cases.

The differences between $f(\text{obs.})$ and $f(\text{L.L.})$ [limiting law] tabulated in the column headed Δ clearly indicate a peculiar mode of deviation from the limiting law. In the case of the unsymmetrical sulfates the change of sign in the deviations is in the order $+, -, +, -$, with increase in concentration of the solvent salt, and leads to a series of maxima and minima in the experimental curve $-\log f/\mu^{1/2}$, shown in Fig. 1. This phenomenon has not

[12] The value 1.5 is an approximation, for purposes of comparison, of the theoretical parameter A in the equation for the solubility of a slightly soluble $(1, -1)$ salt in a solution of ionic strength μ, given by

$$S = S_0 + A\mu^{1/2} + B\mu + C\mu^{3/2} + \ldots\ldots$$

The terms after the second are assumed to be negligible. The equation may be established from the limiting law and from equation (1) as follows: From (1), $Sf = \zeta$ (a constant), and from the limiting law, $-\log_{10} f = \alpha\mu^{1/2}$, or $f = 10^{-\alpha\sqrt{\mu}}$: then, $S = \zeta 10^{\alpha\sqrt{\mu}}$. Expanding the exponential, we have

$$S = \zeta + \frac{\zeta\alpha\log_e 10\mu^{1/2}}{1!} + \frac{\zeta\alpha^2(\log_e 10)^2\mu}{2!} + \frac{\zeta\alpha^3(\log_e 10)^3\mu^{3/2}}{3!} + \ldots\ldots$$

Since S_0 is of the order of 10^{-5}, f_0 is almost unity and the difference between ζ and S_0 may be disregarded for purposes of approximation.

TABLE III

SOLUBILITY RELATIONS OF SILVER CHLORIDE IN AQUEOUS SOLUTIONS OF SULFATES AND NITRATES AT 25°

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	

Solvent: Water (by extrapolation)

| 1.273 | 0. | 0.003568 | 0.00064 | −0.0027 | + | |

(1, −2) Solvent: Sulfuric Acid Solutions

						$a_{[s]}$
1.278	0.00000639	0.005652	0.00234	−0.0012	+120	>6
1.289	.00003644	.01106	.00606	+ .0011	− 21	0.8
1.310	.0002065	.02515	.01308	+ .0008	− 3.14	2.53
1.340	.0007067	.04621	.02291	− .0011	+ 1.44	3.86
1.371	.001507	.06734	.03285	− .0026	+ 1.73	2.67
1.384	.002207	.08146	.03695	− .0090	+ 4.37	6.10
1.420	.003107	.09662	.04810	− .0018	+ 0.556	2.70
1.473	.004807	.12017	.06401	+ .0062	− 1.24	3.00
1.485	.005402	.12736	.06754	+ .0059	− 1.07	1.66
1.505	.006484	.13952	.07335	+ .0052	− 0.794	1.78
1.515	.007021	.14518	.07622	+ .0052	− .734	1.72
1.530	.008100	.15594	.08050	+ .0029	− .364	1.85
1.535	.009179	.16599	.08192	− .0041	+ .486	2.22
1.540	.010258	.17578	.08333	− .0108	+ 1.19	2.56
1.552	.010392	.17662	.08670	− .0052	+ 0.552	2.20
1.551	.010794	.18002	.08642	− .0090	+ 0.935	2.37
1.570	.012488	.19356	.09171	− .0117	+ 1.09	2.34
1.580	.013495	.20125	.09447	− .0137	+ 1.20	2.42

(1, −2) Solvent: Potassium Sulfate Solutions

						$a_{[s]}$
1.281	0.000006405	0.005659	0.00336	+0.0011	− 78	0.7
1.291	.00003645	.01106	.00674	+ .0026	− 46	0.4
1.314	.0002065	.02515	.01441	+ .0037	− 14	0.81
1.336	.0007067	.04619	.02162	− .0038	+ 5.42	5.8
1.364	.001507	.06734	.03062	− .0074	+ 5.15	5.9
1.386	.002207	.08146	.03757	− .0077	+ 3.68	4.26
1.413	.003107	.09662	.04595	− .0062	+ 2.06	3.29
1.475	.004807	.12017	.06460	+ .0074	− 1.46	2.94
1.503	.006511	.13984	.07277	+ .0038	− 0.577	1.83
1.526	.008593	.16060	.07936	− .0038	+ .477	2.21
1.550	.010674	.17899	.08614	− .0085	+ .896	2.35
1.576	.013276	.19961	.09337	− .0142	+ 1.27	2.50

(2, −2) Solvent: Calcium Sulfate Solutions

						$a_{[s]}$
1.281	0.000006405	0.00620	0.00336	+0.0005	− 32	0.8
1.287	.00003168	.01128	.00539	− .0014	+ 28.7	>3.
1.306	.0001075	.02105	.01175	+ .0024	− 13.4	0.7
1.344	.0005119	.04539	.02421	+ .0026	− 3.38	1.26
1.372	.001017	.06389	.03316	+ .0017	− 1.13	1.54
1.395	.001522	.07811	.04038	+ .0017	− 0.78	1.62
1.436	.002532	.10070	.05296	+ .0040	− 1.11	1.35
1.467	.002037	.11028	.06224	+ .0129	− 2.82	0.8

TABLE III   *(Continued)*

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[s]}$

(2, −2) Solvent: Magnesium Sulfate Solutions

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[s]}$
1.276	0.00000638	0.006188	0.00166	−0.0034	+433.	
1.286	.00003144	.01177	.00505	− .0020	+ 47.	
1.301	.0001065	.02095	.01009	− .0012	+ 7.48	>3
1.319	.0002266	.03118	.01605	+ .0006	− 1.52	1.85
1.340	.0005067	.04517	.02291	+ .0001	− 0.882	2.16
1.377	.0010069	.06357	.03474	+ .0055	− 3.50	1.00
1.402	.0015072	.07774	.04256	+ .0067	− 2.92	1.08
1.438	.0025072	.10022	.05357	+ .0057	− 1.59	1.26
1.454	.0030073	.10974	.05837	+ .0057	− 1.32	1.38
1.489	.005207	.14437	.06870	− .0087	+ 1.36	2.18
1.525	.007608	.17449	.07908	− .0177	+ 2.06	2.52
1.544	.010008	.20012	.08446	− .0315	+ 3.05	2.30

(3, −2) Solvent: Lanthanum Sulfate Solutions

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[s]}$
1.282	0.00000214	0.006702	0.00370	+0.0007	−37	0.8
1.292	.00000660	.01058	.00707	+ .0039	−69	0.95
1.309	.00002440	.01947	.01275	+ .0064	−35	0.75
1.338	.0001033	.03954	.02227	+ .0049	− 7.74	1.60
1.362	.0002467	.06094	.02999	− .0019	+ 1.47	3.20
1.387	.0004132	.07882	.03789	− .0043	+ 2.08	2.98
1.426	.0006690	.10025	.04993	− .0018	+ 0.523	2.39
1.475	.0009589	.12000	.06460	+ .0076	− 1.50	1.72
1.512	.0012950	.13943	.07536	+ .0092	− 1.36	1.42
1.562	.0019048	.16900	.08949	+ .0073	− 0.779	1.42
1.575	.0022853	.18519	.09309	− .0014	+ .129	1.55
1.598	.0026655	.20000	.09939	− .0047	+ .295	1.42

(3, −1) Solvent: Lanthanum Nitrate Solutions

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[s]}$
1.280[a]	0.00000427	0.00620	0.00302	−0.0003	+20	>4
1.305[a]	.00007626	.02169	.01142	+ .0009	− 5.28	3
1.317[a]	.0001438	.02960	.01540	+ .0009	− 2.67	3.02
1.367[a]	.0005780	.05910	.03158	+ .0035	− 2.67	2.39
1.404[a]	.001155	.08333	.04318	+ .0020	− 0.812	2.65
1.432	.001660	.09988	.05175	+ .0024	− 0.677	2.43
1.477	.0028072	.12984	.06519	− .0012	+ 0.212	2.47
1.505	.0038264	.15157	.07335	− .0067	+ 0.941	2.55
1.538	.0051003	.17498	.08277	− .0111	+ 1.23	2.52
1.563	.0066290	.19947	.08977	− .0209	+ 1.92	2.80

[a] Values in braces done at State University of Iowa, not published.

(2, −1) Solvent: Barium Nitrate Solutions

$S \times 10^5$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[s]}$
1.450	0.004402	0.11602	0.05718	−0.0032	+0.734	2.56
1.467	.005600	.12967	.06224	− .0069	+1.30	2.95
1.503	.008396	.15875	.07277	− .0147	+2.02	3.10
1.526	.011193	.18328	.07936·	− .0255	+2.82	3.56
1.542	.013989	.20490	.08389	− .0379	+3.55	4.07

TABLE III   (*Concluded*)

$S \times 10^6$	Mol. solvent electrolyte	$\mu^{1/2}$	$-\log f$(obs.)	Δ	$a_{[1]}$	$a_{[s]}$
		(1, −1) Solvent:	Potassium Nitrate Solutions			
1.453	0.013695	0.11708	0.05808	−0.0025	+0.550	1.88
1.469	.016431	.12825	.06283	− .0042	+0.808	1.92
1.488	.020064	.14175	.06841	− .0068	+1.086	2.00
1.516	.027376	.16550	.07651	− .0141	+1.76	2.35
1.537	.033760	.18378	.08248	− .0199	+2.15	2.58
1.552	.040144	.20040	.08670	− .0274	+2.59	2.90

hitherto been recorded.   The symmetrical sulfates and lanthanum nitrate behave quite differently, the curves exhibiting but one maximum above the
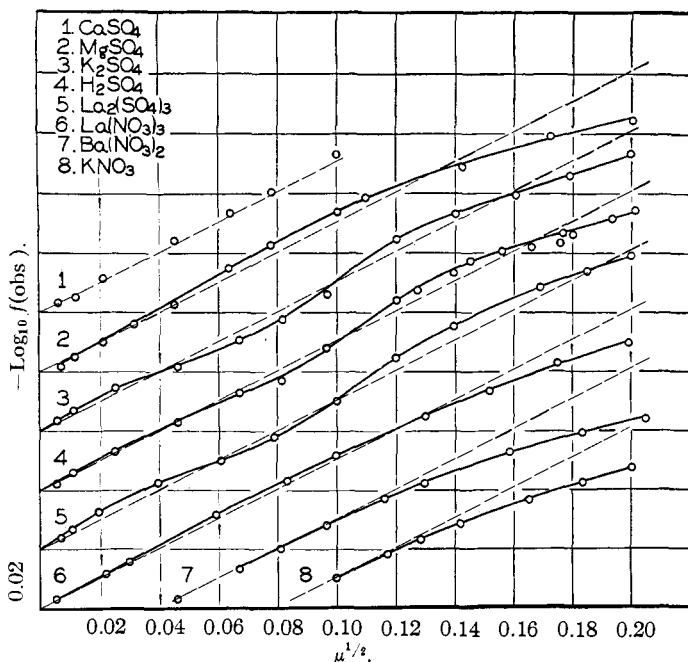

Fig. 1.—Activity relations of silver chloride in aqueous solutions of electrolytes at 25°.   The ordinates, $-\log f$ (obs.), have been separated by 0.02 unit (one square).   The scale is the same for all curves.   1, Calcium sulfate; 2, magnesium sulfate; 3, potassium sulfate; 4, sulfuric acid;   5, lanthanum sulfate;   6, lanthanum nitrate;   7, barium nitrate; 8, potassium nitrate.

slope of the limiting law.   A similar tendency is only very slightly indicated, if at all, in the case of barium and potassium nitrate.   "Deviations" of this nature have already been widely noted, chiefly by La Mer and his co-workers.[13]

[13] La Mer and Mason, THIS JOURNAL, **49**, 410 (1927);   La Mer and Goldman, *ibid.*, **51**, 2632 (1929).

The characteristics of the curves are clearly illustrated in the graphs of Fig. 1. In this figure the ordinates for each curve, representing $-\log f(\text{obs.})$, have been separated 0.02 unit in order to bring out the characteristics of each curve without the confusion of crowding. The scale is the same for all salts and has the same magnitude as the scale of the abscissas. The broken lines represent the slope of the Debye limiting law, and are identical for all of the salts. The points on curves 7 and 8 below 0.1μ are points already published[2] and are here included merely to indicate the degree of agreement of the later data at higher concentrations. The variation in sign is still more strikingly brought out in the $a_{[1]}$ values, a clear indication that the Debye formula fails to apply to the data even in most dilute cases, except as a rough first approximation. The formulas of Gronwall and La Mer are in good agreement with the data. None of the $a_{[3]}$ or $a_{[5]}$ values assume a negative sign and the magnitudes, while small, are not altogether impossible. They exhibit, however, a decided trend in the cases of all of the solvent salts, and the theoretical treatment, in so far as it has been developed, does not account for the first positive and negative "humps" of the unsymmetric sulfate curves. It should be noted, before criticizing the theory too severely, that with decreasing concentration of the solvent salt, very small errors in the value of $\log f(\text{obs.})$ are increasingly magnified in the values of "a," whether derived from the Debye theory or from the extended treatments of Gronwall and La Mer.

In Table IV appear the points of maximum and minimum deviation of the experimental curves from the limiting law. These values expressed in $\Delta = \log f(\text{obs.}) - \log f(\text{L.L.})$ were read directly from large scale graphs of the experimental curves appearing in Fig. 1.

TABLE IV

MAXIMUM AND MINIMUM DEVIATION FROM CURVES

Solvent	$\mu^{1/2}$	Δ	Solvent	$\mu^{1/2}$	Δ
H_2SO_4	0.0	0.00	$MgSO_4$	0.00	+ ...
	.03	+ .0008		.04	0.00
	.046	.00		.085	+ .0034
	.08	− .0030		.125	.00
	.107	.00		(0.20)	− .015
	.13	+ .0034	$La_2(SO_4)_3$	0.03	+0.003
	.163	.00		.056	.00
	(0.20)	− .008		.082	− .0024
				.103	.00
K_2SO_4	0.0	0.00		.140	+ .005
	.02	+ .0016		.188	.00
	.038	.00		(0.20)	− .002
	.07	− .0036	$La(NO_3)_3$	0.04	0.00
	.103	.00		.08	+ .0014
	.125	+ .0036		.125	.00
	.151	.00		(0.20)	− .0113
	(0.20)	− .008			

Predictions based on the assumption that sulfuric acid is incompletely dissociated, and the calculations of Sherrill and Noyes,[14] would indicate that curve 4 in Fig. 1 should lie somewhat lower than it does. Actually the acid seems to have the same effect as potassium sulfate.

The author wishes to acknowledge the helpful criticism and suggestions of Professors A. A. Noyes and S. J. Bates of the California Institute of Technology, and is indebted to Professor Victor K. La Mer of Columbia University for his valuable criticisms and suggestions in the interpretation of the data.

Summary and Conclusions

The solubilities of silver chloride at 25° in aqueous solutions of the sulfates of hydrogen, potassium, calcium, magnesium and lanthanum, and of the nitrates of potassium, barium and lanthanum, were determined by a synthetic method. The solubility of the chloride in water was approximated statistically and found to be 1.273×10^{-5} mole per liter, and its activity coefficient was found to be 0.9985.

The activity coefficients of silver chloride in the various solutions were calculated from the experimental data. Marked deviations from the Debye–Hückel limiting law as well as from the first approximation formula appear, even at the lowest concentrations, in the case of the sulfates and lanthanum nitrate. The unsymmetric sulfates exhibit positive, negative, positive and finally negative deviations from the limiting law when the logarithm of the observed activity coefficient is plotted against the square root of the ionic strength. The symmetric sulfates show only one such positive deviation, and a similar deviation is barely, if at all, indicated in the case of potassium and barium nitrates.

Apparent ionic diameters, a, calculated on the basis of the Debye first approximation indicate that the theory is inadequate for silver chloride in the presence of the substances studied even at the lowest concentrations. The a values calculated on the basis of the Gronwall and La Mer extensions of the theory are in good agreement with experiment in the case of the symmetrical sulfates and nitrates. These extensions do not explain, however, the peculiar behavior of the unsymmetrical valence type sulfates, except possibly as a first approximation.

PASADENA, CALIFORNIA

---

[14] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926).