for thallium amalgams obtained by Richards and Daniels and by Hilde-brand and Eastman.   It has been shown how the heat of solution of solid thallium and of supercooled liquid thallium in a large excess of mercury may be obtained, and later how these quantities may be used for cal-culating the heat of fusion of thallium.   The activities of thallium and of mercury in amalgams of various compositions are given at 20° C. and at 325° C., and these values, resting upon independent measurements, are compared by simple thermodynamic methods.   The effect of tempera-ture upon the abnormality of solutions is discussed, and it is shown that the vapor pressure of amalgams at 325° may be calculated from the mea-surement of electromotive force at 20° by 2 methods, between which 2 results the true value must lie.   Thus in 40% amalgam the vapor pressure was found by one method to be 1% higher and by the other to be 2% lower than the measured value.

BERKELEY, CAL.

THE DISTRIBUTION OF A STRONG ELECTROLYTE BETWEEN BENZENE AND WATER.

BY ARTHUR E. HILL.

In the effort to determine the degree of dissociation of a strong electro-lyte in water, distribution experiments should be of use.   Such experi-ments have rarely been performed, probably because of the difficulty in finding strong electrolytes which possess suitable solubility in a non-aqueous solvent which is itself immiscible with water.   The distribution of picric acid between water and benzene has been studied by Kuriloff,[1] Walden,[2] Rothmund and Drucker,[3] and Herz and Fischer,[4] and that of lithium chloride between water and amyl alcohol by Dhar and Data.[5] Other cases have not been found.

The theory by which such experiments may be interpreted is well known.   According to Berthelot and Jungfliesch[6] and as elaborated by Nernst,[7] the distribution law states that a solute will be partitioned be-tween 2 immiscible solvents in a ratio which is independent of the concen-trations used, and which is the ratio of its solubility in the 2 pure sol-vents, provided that the solvents are immiscible in each other, that the

[1] Kuriloff, Z. physik. Chem., **25**, 425 (1898)

[2] Walden, Ber., **34**, 419 (1901).

[3] Rothmund and Drucker, Z. physik. Chem., **46**, 827 (1903).

[4] Herz and Fischer, Ber., **37**, 4746 (1904); ibid., **38**, 1138 (1905).

[5] Dhar and Data, Z. Elektrochem., **19**, 583 (1913).

[6] Berthelot and Jungfliesch, Ann. chem. phys., [4] **26** ,396 (1872).

[7] Z. physik. Chem., **8**, 110 (1891).

total concentrations are small, and that the solute has the same molecular weight in each phase. If the solute undergoes electrolytic dissociation in the aqueous phase, or association in the non-ionizing phase, it is assumed that the unchanged molecules are distributed in accordance with the law as stated, and in the mathematical expression

$$\frac{C_1}{C_2} = K$$

the terms C_1 and C_2 represent concentrations of simple molecules in the 2 phases. Corrections of this kind have been made for the distribution of a considerable number of weak electrolytes, such as acetic acid or benzoic acid, where the electrolytic dissociation in water is taken from conductance experiments, and the association in the non-aqueous phase has been determined by cryoscopic experiments. In the case of the strong electrolyte picric acid, Rothmund and Drucker[1] showed the compound to be monomolecular in benzene, and calculated its dissociation in water by assuming the constancy of the distribution ratio and the validity of the Ostwald dilution law for its electrolytic dissociation. If the distribution law may be relied upon to give the concentration of undissociated molecules in the aqueous phase, we may calculate the ionization from the equation $C_2 = 1 - \alpha/v$, where C_2 is the molecular concentration, v the dilution, that is, the volume (in liters) containing one mole of the electrolyte as determined analytically, and α the degree of dissociation.

The salt silver perchlorate is well suited to distribution experiments. That it acts as a strong electrolyte in aqueous solution was determined by Loeb and Nernst,[2] who made use of it in their classic investigation of the migration velocity of the silver ion. Its solubility in benzene was made known to us by M. Gomberg. We have found that it possesses a moderate solubility also in toluene, nitrobenzene, chlorobenzene, glycerine, and glacial acetic acid; it is insoluble in chloroform, carbon tetrachloride and in ligroin. Benzene has been chosen as the non-aqueous solvent for the distribution experiments because its solvent effect is greater than that of the other substances mentioned, and its miscibility with water very small In the following pargaraphs will be given an account of the solubility of silver perchlorate in water and in benzene, its molecular condition in benzene, and its distribution between the 2 sol·vents, together with some statement of the properties of the salt; with the data thus obtained we have been able to draw certain conclusions as to the molecular condition of silver perchlorate in water.

I. Properties of Silver Perchlorate.

The literature of this interesting salt is scanty. First prepared by

[1] *Loc. cit.*

[2] Loeb and Nernst, *Z. physik. Chem.*, **2**, 948 (1888).

Serullas,[1] it was found to be deliquescent in character,[2] soluble in water, alcohol and ether; it melts at 480°,[3] and explodes at about 800°, in aqueous solution conducts the electric current well,[4] and is sensitive to the action of light.

The deliquescence of the salt is so marked that samples show a visible dampness and stickiness in the short time that they are exposed to the air of the laboratory during transfer from one receptacle to another; small particles liquefy completely in a few minutes. In order to compare its rate of absorption of water with that of the common drying agents, a rough experiment was conducted by placing 5 g. of the powdered salt in a desiccator over water, with 5 g. of powdered anhydrous calcium chloride and 5 g. of conc. sulfuric acid; during a period of 36 hours the silver perchlorate gained in weight at about 55% of the rate shown by the calcium chloride, and about 70% of that of the sulfuric acid. The salt liquefied completely in a few hours, at which time the calcium chloride was but slightly moist upon the surface, the difference being due to the higher solubility of the silver perchlorate.

On account of this hygroscopic property of the silver perchlorate, especial pains are necessary to keep the salt entirely water-free. In our work reported here, the salt to be used was heated in an electric oven at 110–115° for 2 hours, and then kept in a desiccator over phosphorus pentoxide; the samples taken for analysis or for experiment were weighed from stoppered flasks or tubes directly into the reaction vessels. Under these conditions, our analyses of the salt showed a silver content, by Volhard's method or gravimetrically, corresponding to a purity varying between 99.24% and 99.68%. In our later work, the salt was heated at 120–125° for 24 hours directly before using, and transferred into oven-dried receptacles immediately before use; under these conditions of work, the analyses gave figures corresponding to 99.97% to 100.37% purity.

The sensitivity of the salt to light and heat appears to be much less than in the case of the commoner silver salts. Samples which had been heated at 120° for several days showed only the slightest coloration. Crystals covered by water became colored on exposure to light only after long intervals of time, and the large, transparent crystals which can be obtained from benzene solution are not visibly changed after several days of exposure.

The solubility of the salt in the various organic solvents mentioned above was found to be considerable, probably one to 3 g. per hundred cc. in each case; quantitative data will be submitted at a later time. It is to

[1] Serullas, *Ann. chim. phys.*, **46**, 307 (1831).

[2] Abegg, "Hand. der anorg. Chem.," II, **1905**, p. 712.

[3] Carnelley, *J. Chem. Soc.*, **45**, 409 (1884).

[4] Gore, *Chem. News*, **50**, 150 (1884); Loeb and Nernst, *loc. cit.*

be noted that the small amounts of water usually present in these solvents cause a great increase in the apparent solubility, making it necessary to use care in their dehydration if any exact information is to be sought.

The silver perchlorate used in our experiments was prepared from c. p. silver nitrate. About 200 g. of this salt was dissolved in 500 cc. of water, and a slight excess of pure sodium hydroxide dissolved in 500 cc. of water was added. The precipitated silver oxide was filtered upon a Büchner funnel and washed repeatedly with distilled water; it was then transferred to a beaker with a little water and treated with a slight excess of 60% perchloric acid. The solution was filtered from a small residue of silver chloride and evaporated in a porcelain dish upon the water-bath until crystals began to appear upon the surface. After cooling the hot solution, the material was filtered in a Richards' centrifuge, from which the crystals could be taken in a condition nearly dry; they were finally dried in an electric oven, as noted above. From the mother liquor a second crop of crystals could be obtained which showed by analysis no diminution in purity.

II. Molecular Condition of Silver Perchlorate in Benzene.

The cryoscopic method was used for determining the molecular weight of the silver perchlorate in benzene. The solvent used was prepared from a thiophene-free sample, which was cooled until about $1/2$ had solidified; the crystals were filtered with suction, melted, and the liquid kept in a stoppered bottle in contact with anhydrous calcium chloride. Its freezing point was found to be $5.44°$ (uncorrected).

The usual form of the Beckmann freezing-point apparatus was used for the experiments, the thermometer being a special instrument having a range from $0°$ to $6°$ with $0.01°$ divisions, and read by means of a magnifying glass to $0.001°$. In the outer vessel water for cooling was kept at $3°$ to $4°$. The silver perchlorate was in the first experiments weighed directly into the benzene after the freezing point of the pure solvent had been taken; in the latter cases an analyzed solution of the salt in benzene was used, in order to reduce the errors in weighing, and was added from a pipet, so that the same set-up of the apparatus could be used for a series of determinations. The weights of benzene used varied from 13 to 34 g., and those of the silver perchlorate from 0.0318 g. to 0.9534 g.

In the following table are given the results of the experiments, which were carried out by Mr. Joseph Schlesinger.

The molecular weights in Col. 4 were calculated by means of the formula

$$\text{M. W.} = \frac{50 \times w}{D}$$

in which w is the weight of silver perchlorate and D the observed freezing-point depression, 50 being taken as the constant for one gram equivalent weight of solute in 100 g. of benzene. The equivalent concentrations of Col. 6 were calculated by assuming the density of the benzene as 0.874, and disregarding the small volume of the dissolved salt, which would affect the volume less than 1% in the most extreme case.

<div align="center">TABLE I.</div>

<div align="center">Molecular Weight of AgClO$_4$ in C$_6$H$_6$.</div>

No.	G. AgClO$_4$ per 100 G. C$_6$H$_6$.	Depression of freezing point. ° C.	Mol. wt. of AgClO$_4$.	Average mol. wt.	Conc. of AgClO$_4$ in g. equiv. per liter.
1..............	0.140	0.035	200	...	..
	0.140	0.031	225	...	..
	0.140	0.034	206	210	0.0059
2..............	0.610	0.089	342	342	0.0257
3..............	1.045	0.139	376	...	..
	1.045	0.137	381	378	0.0440
4..............	1.370	0.171	400	...	..
	1.370	0.172	398	399	0.0578
5..............	1.820	0.221	412	412	0.0767
6..............	2.085	0.253	412	...	..
	2.085	0.251	415	414	0.0879
7..............	2.365	0.283	418	...	..
	2.385	0.280	426	...	..
	2.385	0.277	430	425	0.1001
8..............	2.425	0.280	433	433	0.1022
9..............	2.73	0.314	435	...	..
	2.73	0.311	439	...	..
	2.79	0.314	444	...	..
	2.79	0.311	448	442	0.1163
10..............	3.35	0.368	455	...	..
	3.35	0.363	461	458	0.1412
11..............	3.65	0.402	454	454	0.1538

The molecular weight of silver perchlorate, if monomolecular, would be 207.3. It thus appears that the true molecular weight is always greater than corresponds to single molecules, rising with the concentration to a value about 2.2 times as great at the equivalent concentration 0.1412. Before attempting to calculate the degree of association, it seemed best to apply the theory of least squares to the measurements, in order to secure figures approaching the true values more closely than the individual determinations. In Fig. 1 it will be seen that the average molecular weights, plotted against the equivalent concentrations, fall quite closely upon a smooth curve, with the exception of the 2 end points. These may be considered as affected by experimental errors, since at the lowest concentration the depression of freezing point is too small to be measured accurately, and at the highest concentration it is probable that salt also crystallized out, since the solution was known to be at or near to the saturation point. An effort to find an expression for this curve showed that a straight line could be drawn if the logarithms of the concentration and the molecular weight are plotted against each other. By the method of least squares[1] the best straight line was determined, and

[1] Expts. 1, 5, 8 and 11 were not used in calculating the constants of the straight line.

its slope measured and found to be expressed by the number 0.17. From this is obtained the empirical equation,

$$C^{0.17}/m.\,w. = 1.571(10)^{-3},$$

from which the molecular weight may be calculated at any concentration within the limits of the experiments.[1] In Table II are given the molecular weights calculated by this formula.

TABLE II.

Calculated Molecular Weight of Silver Perchlorate in Benzene.

No.	Equiv. conc. of AgClO₄.	Mol. wt. found.	Mol. wt. calculated.	Variation. %.
1..........	0.0059	(210)	(266.0)	...
2..........	0.0257	342	341.6	—0.1
3..........	0.0440	378	374.1	—1.0
4..........	0.0578	399	392.0	—1.7
5..........	0.0767	412	411.4	—0.1
6..........	0.0879	414	421.0	+1.7
7..........	0.1001	425	430.0	+1.1
8..........	0.1022	433	431.8	—0.3
9..........	0.1163	442	441.6	—0.1
10..........	0.1412	458	456.5	—0.3
11..........	0.1538	(454)	(463)	...

In order to use these figures in determining the extent of the association which obviously occurs, it is also necessary to know whether or not there is also any electrolytic dissociation. For this experiment apparatus was set up for measuring conductivity by means of the Wheatstone bridge
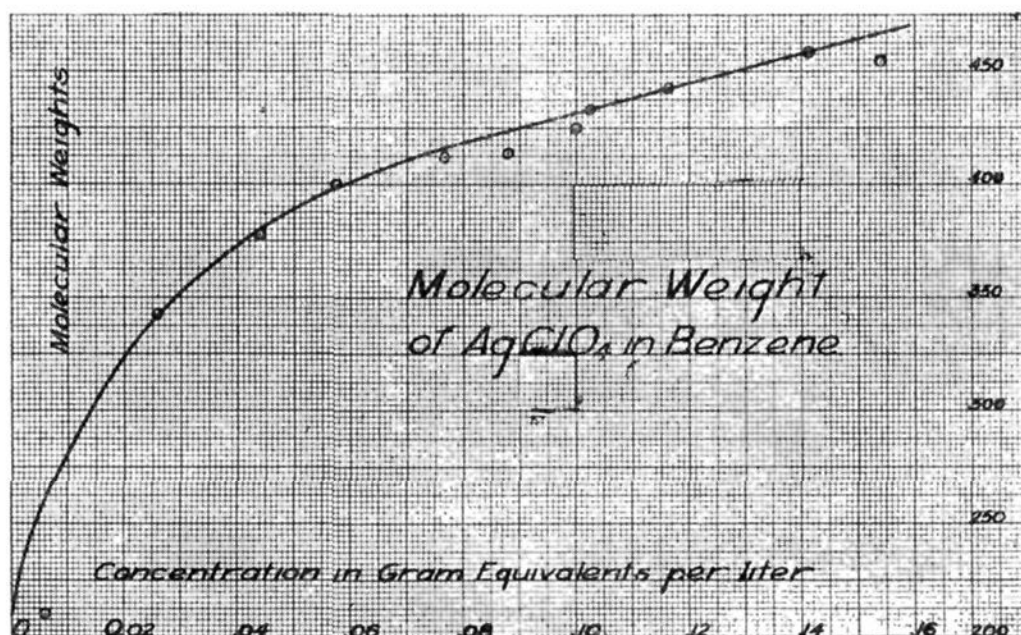

Fig. 1.

[1] In order to avoid the absurdity which results when this empirical equation is extrapolated to zero concentration, we may use an alternative form m. w. = 507 $C^{0.357}$ + 207, which gives nearly the same values for the molecular weight.

and telephone. In an electrolytic cell of which the constant was found to be 0.3641 by use of $0.1\,N$ potassium chloride solution, the pure benzene was first tested; using resistances up to 100,000 ohms, no minimum could be detected. A saturated solution of silver perchlorate was then tested at $25°$; using a resistance of 100,000 ohms, a minimum was obtained when the bridge read about $825/1000$, showing a conductivity[1] of 7.4×10^{-7}. This is about $^1/_5$ of the value for good conductivity water; it is of such small magnitude that it may be due to traces of unknown impurities in the salt or to dissociation caused by the traces of water carried in during the transfer of the salt into the apparatus. If it is considered to be a measure of the true electrolytic dissociation of the silver perchlorate in dry benzene, it indicates that the dissociation is of the same order of magnitude as that of pure water, and hence of too small a degree to affect the molecular weight determinations described above.

Further information as to the condition of the dissolved salt may be had by inspection of Fig. 1. The average molecular weight is less than 414 (which is twice the monomolecular weight 207) at all concentrations lower than $0.07\,N$, indicating that single molecules are present to a greater or less degree; at higher concentrations it is greater than 414, indicating the presence of triple molecules. The tendency of the curve to flatten out at the higher concentrations makes it probable that molecules of greater complexity are not present, at least within the limits investigated, so that it is probable that the salt exists in benzene solution as single, double and triple molecules.

The relative concentrations of these 3 species can not be determined by any single observation of the average molecular weight, but can be determined from any 2 such observations by means of very simple assumptions. We may take for a basis of calculation, first, that the weight of all the molecules of one kind present in unit volume added to the weight of all other kinds of molecules present will be equal to the total weight of solute, and, second, that the average molecular weight is equal to the total weight of solute in unit volume divided by the number of molecules present; and we may assume third, that the following equations represent the equilibria and that the mass law may be applied to them:

$$6AgClO_4 \rightleftarrows 3(AgClO_4)_2 \rightleftarrows 2(AgClO_4)_3.$$

We may thus derive for any single experiment the following 4 equations, of which Equation 1 expresses the first postulate, Equation 2 the second, and Equations 3 and 4 express the assumption of the mass law.

$$3x + 2y + z = C \qquad\qquad (1)$$

$$x + y + z \quad = \frac{207.34\,C}{w} = a \qquad\qquad (2)$$

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[1] The conductivity measurements were made by Mr. Rudolph Macy.

$$\frac{x^2}{y^3} = K_a \tag{3}$$

$$\frac{y^3}{z^6} = \text{const.} \ldots \quad \frac{y}{z^2} = \text{const.} = K_1. \tag{4}$$

In these equations x stands for the concentration of the triple molecules in gram-molecular weights per liter, y for the concentration of the double molecules, and z for the single molecules; c represents the total concentration in gram equivalents per liter, w the average molecular weight as found by experiment, and K_a and K_1 are concentration-law constants. For any second experiment we may write 4 similar equations:

$$3x_1 + 2y_1 + z_1 = C_1 \tag{5}$$

$$x_1 + y_1 + z_1 = \frac{207.34\,C_1}{w_1} = a_1 \tag{6}$$

$$\frac{x_1^2}{y_1^3} = K_a \tag{7}$$

$$\frac{y_1}{z_1^2} = K_1 \tag{8}$$

These 8 equations contain 8 unknown terms, the 6 molecular concentrations x, y, z, x_1, y_1, z_1, and the 2 mass-law constants K_a and K_1. Their algebraical solution is possible, but as it involves equations of higher degree it has seemed better to use a method of approximation. For this purpose the total equivalent concentrations $0.10\,N$ and $0.05\,N$ have been used, at which the average molecular weights were calculated by the formula, $m.w. = C^{0.17}/1.571 \times 10^{-3}$, giving the values 430 and 382.4 respectively. Considering now only Equations 1 to 4, and applying them to the lower concentration, a preliminary value for x was guessed. Corresponding values of y and z may then be calculated from Equations 1 and 2, and the constants K_a and K_1 from Equations 3 and 4. Now passing to the second set of equations, z_1 may be calculated from Equations 5, 6 and 7, by which it has the value $\frac{-1}{K_1} + \frac{1}{K_1}\sqrt{K_1\,(3a_1 - c_1) + 1}$. The value of y_1 may be taken from Equation 8, and that of x_1 from Equation 6. Finally, the vaue of K_a is calculated from Equation 7. This second value of K_a is of course not in agreement with the first value of K_a found, but by repeating the approximation with a new value of x, the 2 values may be made to approach each other. When the convergence has been established, the 2 values of K_a found by each trial may be plotted against values of x assumed, and by extrapolation of these 2 curves the x value determined which will give identical values for K_a. By carrying out this operation, the 2 constants were found to be as follows: $K_1 = 35.22$; $K_a = 386.4$.

With these 2 constants found, it becomes a much simpler matter to determine the value of x, y and z for any other concentration, which may be done by algebraic solution of Equations 1, 2 and 4. In the following table the figures are given for several round concentrations.

TABLE III.

Molecular Complexity of Silver Perchlorate in Benzene Solution at the Freezing Point.

No.	Total equiv. Conc.	Average mol. wt.	Conc. of single molecules(z).	Conc. of double mol.(y).	Conc. of triple mol.(x).
1...............	0.02	327.4	0.007901	0.002199	0.002567
2...............	0.03	350.7	0.009885	0.003441	0.004410
3...............	0.05	382.4	0.012779	0.005751	0.008573
4...............	0.075	409.8	0.015297	0.008240	0.014407
5...............	0.10	430.0	0.017148	0.010355	0.020713
6...............	0.14	455.6	0.019113	0.012865	0.031720

With these figures as a basis, Fig. 2 has been drawn so as to show the molecular concentration of the single, double and triple molecules of silver perchlorate at all total concentrations up to 0.14-equivalent normal, which is close to the saturation point at the freezing point of benzene.
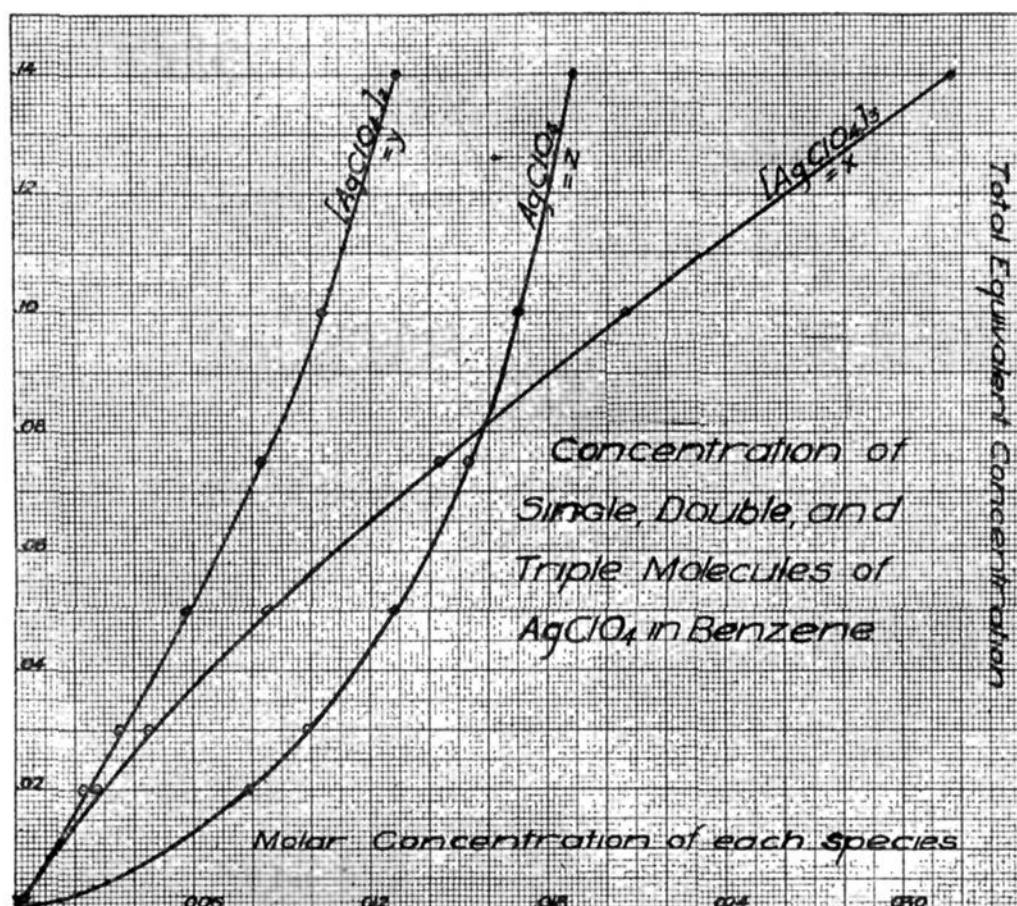

Fig. 2.

A rigid inspection of these figures will show that some one of the assumptions used is not wholly justified. The concentrations in Lines 1,

2, 4 and 6 have been calculated as described above, using the constant K_1 found at the concentrations of Lines 3 and 5. If the assumptions are wholly correct, it should be possible to re-calculate also the mass-law constant $K_a = x^2/y^3$ in Lines 1, 2, 4 and 6, since that equation was not used in deriving the data of those lines. The result of such a calculation follows in Table IV.

TABLE IV.

Mass-Law Constant for $AgClO_4$.

Total conc.	Const. $Ka = \dfrac{x^2}{y^3}$
0.02	620
0.03	477
0.05	386.4
0.075	371.0
0.10	386.4
0.14	472.0

It will be seen that there is a variation in the value of the constant. This may possibly be due to experimental error at the lowest concentration, but it is more probable that it is due either to a true variation from the mass law or to the presence of molecules of higher complexity than have been assumed. The actual effect of this variation upon the calculated molecular concentrations is, however, very slight; a change of 15 units in the constant corresponds to about 0.3% variation in the value of z, 0.25% in that of x, and 0.8% in that of y, so that in the extreme cases the error from this source amounts to only a few per cent.

III. Solubility of Silver Perchlorate in Water.

About 15 g. of silver perchlorate was put in a small glass-stoppered cylinder, covered with a small amount of water, and rotated in a thermostat at 25° for one hour. A sample was then withdrawn with a pipet delivering 1.014 cc., weighed into a flask and then analyzed for its silver content by Volhard's method, using a 0.1 N ammonium thiocyanate solution. To the original cylinder a further excess of the perchlorate was added, and the apparatus rotated for 2 hours longer. Analysis of a sample now taken agreed with the first within 0.2%, which is within the errors of measurement of the pipet. On account of the high solubility, experiments from supersaturation were not attempted. It was found that the density of the saturated solution was 2.806. The solubility in g. per liter of solution was found to be 2368, in g. per 100 g. of water, 540; and in g. equivalents per liter, 11.42.

The solubility of silver perchlorate is exceptionally high. The ordinary solubility tables do not show data for any salt with a solubility in water so great, expressed in per 100 g. of water, except in the case of antimony trichloride.[1] The molecular solubilities of hydrochloric acid and of the bases ammonia and potassium hydroxide are, however, somewhat higher.

IV. The Solubility of Silver Perchlorate in Benzene.

It was observed that the solubility of silver perchlorate in benzene is greatly increased by the presence of small amounts of water. Benzene

[1] Meerburg, Z. anorg. Chem., **33**, 299 (1903).

saturated with water, containing 0.211 part of water per hundred parts of benzene,[1] dissolves more than twice the amount of salt which can be dissolved in perfectly dry benzene, and if the amount of water present is increased the mutual solubility of all 3 components becomes enormously larger. The interesting conditions existing in this ternary system will be made the basis of a later publication.

In order to prevent errors in the solubility measurements due to traces of water, especial precautions were taken in drying both the solvent and the solute. The silver perchlorate was heated in an electric oven at 120° for 24 hours, transferred to a stoppered tube while still hot, and put immediately into the prepared solvent. The benzene was dried by contact with metallic sodium for several days. The 2 materials were put in glass-stoppered cylinders, the stopper paraffined, and the end of the cylinder covered with a close-fitting test-tube held to the cylinder by a piece of thin rubber tubing, the joints being again well paraffined; by these precautions leakage during the immersion in the thermostat was effectually prevented. One such cylinder was first heated and agitated at 40° by immersion in water until nearly all of the salt had dissolved, so as to insure a condition of supersaturation of 25°. The 2 cylinders were now rotated in the thermostat at 25° for 2 hours. Samples of 10 cc. of the solutions were pipetted out, the density determined by direct weighing and the silver content determined by titration with 0.1 N thiocyanate solution, in the presence of considerable water to extract the salt from the benzene solution. The results are given in Table V.

TABLE V.

Solubility of Silver Perchlorate in Benzene at 25°.

	Density.	Solubility in g. per liter.	Solubility in g. equivalents per liter.
From under saturation..............	0.9044	45.22	0.2181
From supersaturation..............	0.9062	45.36	0.2187
Average........................	0.9053	45.29	0.2184

V. Distribution of Silver Perchlorate between Water and Benzene.

In the distribution experiments pure benzene was shaken with aqueous solutions of the salt, and pure water with benzene solutions, the operations being conducted mechanically in a thermostat at 25°. It was found that equilibrium was reached from either direction in less than an hour. In order, however, to obtain reproducible results it was necessary to let the cylinders of the mixture stand upright for several hours, in order to avoid the occurrence of traces of the aqueous layer in suspension in the benzene layer, carrying with them traces of the salt. Samples of each layer were removed by a pipet and analyzed by titration with thiocyanate solution.

On carrying out experiments in which the final salt concentration in the aqueous layer was a fraction of a molar concentration, and up to a concentration of 2 M, the remarkable fact appeared that the silver perchlorate was absolutely lacking in the benzene layer, as far as could be determined by testing with 0.01 N thiocyanate solution. When samples of 10 or 20 cc. of the benzene solution were titrated, the first drop of the thiocyanate produced a red color with the iron indicator, showing that

[1] Herz, *Ber.*, **31**, 2669 (1898).

the concentration could not be expressed by figures larger than hundred thousandths normality. The figures in Table VI give the results when the concentration in the aqueous layer was at the high value of 2.3 N.

TABLE VI.
Distribution of Silver Perchlorate between Water and Benzene.

	Equiv. conc. in aqueous layer.	Equiv. conc. in benzene layer.	Ratio.
From water solution of salt........	2.31	Less than 0.0000562	41100
From benzene solution of salt......	2.34	Less than 0.0000450	52000
Average......................	2.325	Less than 0.0000506	46550

It appears, therefore, that the distribution ratio in favor of the aqueous layer is at least as high as 46550 to 1, at a concentration of 2.3 N. When the concentration in the water layer rises, the ratio falls; at a concentration of 4 N in the aqueous phase the salt becomes analytically detectible in the benzene, the ratio being 8000 to 1, and at still higher concentrations the ratio drops rapidly. In these latter cases, however, the mutual solubility of water and benzene has been found to be enormously increased, which fact will be dealt with in a later publication; under these conditions, however, we are no longer dealing with a distribution of the salt between pure water and benzene. By extrapolating toward the more dilute solutions, we may say that, at all concentrations in the aqueous phase lower than 2.3 N, the distribution ratio is higher than 46650, and we may regard the salt as being wholly in the water layer.

It is possible to compare this result with a rough calculation of what the distribution ratio would be expected to be, on the basis of the usual theory that the salt is partially dissociated in water and that the molecular species common to both phases is the unpolymerized molecule. The total concentration of the salt in benzene in saturated solution at 25° is 0.2184-gram equivalents. Using the figures for association at 4° + as approximately true for 25°, we may roughly extrapolate from Fig. 2 that the concentration of single molecules at that concentration is not far from 0.0216-gram equivalents. For the molecular concentration in the aqueous layer at saturation we may assume that the salt, dissociating as it does[1] to a degree similar to that of silver nitrate in dilute solution, has about the same degree of dissociation in more concentrated solution also. The degree of dissociation of this latter salt, at the highest concentration measured,[2] namely 7 N, is about 26%, as obtained by dividing its equivalent conductivity at that concentration by its equivalent conductivity at infinite dilution. If it is assumed that silver perchlorate is therefore, about 75% in the form of single molecules in its saturated solution, the concentration of single molecules is $0.75 \times 11.42 = 8.76$.

[1] Loeb and Nernst, loc. cit.
[2] Kohlrausch and Holborn, "Leit. der Electrolyte," 2nd Edition, 1916, p. 166.

We may then calculate the distribution ratio of the salt between water and benzene as follows,

$$K = \frac{\text{mol. conc. in sat. aqueous solution}}{\text{mol. conc. in sat. benzene solution}} = \frac{8.76}{0.0216} = 406.$$

Instead of this calculated distribution ratio of about 406, the experimental ratio is something greater than 46,650; that is, the concentration in the aqueous layer is more than 114 times greater than is to be expected on the basis of the usual theories as to the electrolytic dissociation of salts in water.

VI. Interpretation of Distribution Experiments.

From the distribution experiments, it seems clear that the water and the benzene solutions of silver perchlorate contain no molecular species in common, since the extraction of the salt by the water is complete up to a concentration of $2.3 \, N$. The species which may be assumed present in the one solvent or the other are the ions of the salt, the single, double and triple molecules of the same and hydrates or benzene-solvates of any of them. Of these, ions are present in the water and absent from the benzene, as shown by conductivity experiments. It therefore remains to interpret the conditions which might exist when no molecular form is found common to both solvents. The hypotheses possible are the following.

(1) Unpolymerized molecules may be present in both solvents, but those in the water are completely hydrated. That there should be hydration of the salt, either in its ionic or in its molecular form, is of course in conformity with the present views of many and perhaps of most chemists. Hantzsch and Sebaldt[1] and Hantzsch and Vogt,[2] in their valuable critique of the distribution law, explain the deviations from the distribution law as due to hydration, which they believe varies with the temperature, concentration or other conditions. This very plausible explanation seems unsuitable in the case under discussion, however, since it demands belief not in a partial hydration, but in a hydration that is complete. In an experiment with dimethylammonium chloride Hantzsch[3] found that "almost none of the salt goes into chloroform on shaking a very concentrated aqueous solution with chloroform." There is no information at hand that would lead us to believe that these 2 salts differ from the commoner compounds, where the evidence points toward a partial hydration, for which reason an explanation of these experiments by means of the assumption of hydration is not the most satisfactory.

[1] Hantzsch and Sebaldt, *Z. physik. Chem.*, **30**, 258 (1899).
[2] Hantzsch and Vogt, *ibid.*, **38**, 705 (1901).
[3] Hantzsch, *Chem.-Zentr.*, [2] **1906**, p. 922.

(2) The unpolymerized molecules in the benzene may be wholly combined with the solvent; $i. e.$, a benzene solution does not contain any unsolvated molecules. Such an explanation might be used to explain the apparent high molecular weight of silver perchlorate in that solvent, but leads to improbable ratios in the composition of the solvate. At the low concentration of 0.61 g. of salt per 100 g. of benzene (0.0257 N.) the calculated formula would be $AgClO_4.168C_6H_6$, and at higher concentrations the ratio is correspondingly higher. It is of course true that by assuming both polymerized and solvated molecules a lower ratio of salt to benzene would be found; no means are at hand to make possible a calculation of the formula upon the basis of this double hypothesis. A fact tending to make unsatisfactory the explanation of solvation is that the mass law leads us to expect that the ratio of benzene to salt in the solvate should increase with decrease in the salt concentration, whereas the apparent molecular weights point in the opposite direction; we should therefore have to complicate our hypothesis still further by assuming that, with increasing concentration, the tendency to polymerize more than counterbalances the tendency toward forming simpler solvates.

(3) The aqueous solution may contain no simple molecules; that is, the salt is completely ionized in water at all concentrations up to 2.3 N. This interpretation seems to be the most plausible, and is in agreement with views which have been expressed recently with some frequency. Milner[1] believes that strong electrolytes are completely dissociated, and Bjerrum[2] has arrived at the same conclusion. Ghosh[3] has built up "a complete theory of dilute solution," rejecting Arrhenius' theory of partial dissociation and reconciling the conductance ratios of salts and their abnormal molecular weight as determined by cryoscopic experiments with the assumption of complete dissociation. A. A. Noyes and MacInnes[4] find that neither the conductance ratio of strong electrolytes nor their activity coefficients are determined by the degree of dissociation, and that there is no known property of solutions of strong electrolytes which affords any direct evidence of the existence of non-ionized molecules up to moderate concentrations, for which reason they adopt the hypothesis that such substances are completely ionized. The distribution experiments here reported seem to us to be evidence pointing toward this same conclusion.

The evidence here proposed rests upon the assumption that the distribution law, as commonly interpreted, is qualitatively correct, though not necessarily quantitatively correct; that is, that the distribution of a sub-

[1] Milner, *Phil. Mag.*, **35**, 214 (1918).
[2] Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).
[3] Ghosh, *J. Chem. Soc.*, **113**, 449, 672, 707 (1918).
[4] Noyes and MacInnes, THIS JOURNAL, **42**, 239 (1920).

stance between 2 immiscible solvents is some function of the solubility of the common molecular species in the 2 solvents. Georgevics[1] rejects the distribution law, at least for those substances which fail to give a constant distribution ratio, and explains these abnormalities as due to adsorption, which is conditioned upon the affinity of the solute for the respective solvents. The acceptance of this view would invalidate all calculations of the ionization of weak electrolytes previously made, and likewise the present interpretation of the complete extraction of silver perchlorate and of dimethyl ammonium chloride from non-aqueous solvents by water.

Summary.

1. Silver perchlorate has been found to be soluble in chlorobenzene, glycerine, acetic acid, toluene and nitrobenzene.

2. Silver perchlorate is soluble in water at 25° to the extent of 2386 g. per liter of solution, and in anhydrous benzene to the extent of 45.29 g. per liter of solution.

3. In benzene solution, silver perchlorate is found to exist as single molecules and as polymerized molecules of double and triple molecular weight. The average molecular weight, up to a concentration of 0.14 N, is expressed by the equation m. w. $= \dfrac{C^{-0.17}}{1.571 \ (10)^{-3}}$. Electrolytic dissociation is not present, except possibly of the same order as that of pure water.

4. A method is proposed for calculating the concentration of the 3 different species of silver perchlorate molecules in benzene solution, and curves have been drawn for these concentrations.

5. Distribution experiments show that water extracts the salt completely from its benzene solution, up to a concentration of 2.3 N in the aqueous layer.

6. The experiments are interpreted as evidence that silver perchlorate, apparently a typical salt, is completely ionized in water at higher as well as at low concentration.

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[1] Georgevics, Z. physik. Chem., **84**, 353 (1913); **90**, 47 (1915).