flat-bottomed flask of about 100 cc. The flask is fitted with a single-bored cork, through which passes a fine, capillary tube about 4 inches long. The cork is pressed into the neck of the flask as far as it will go, and the capacity of the flask determined. The position of the cork is marked by a scratch on the neck of the flask.

The flask is thoroughly dried, and the cork containing the capillary tube is pressed into the neck until the lower end is even with the scratch. Using the capillary tube as a handle, the flask is immersed in a bath of boiling water. It is held in this position until the air in the flask has reached the temperature of the water. The temperature is then taken. The finger is moistened and placed over the end of the capillary tube, the apparatus is transferred to a bath of cold water, capillary end first, and the finger removed. As the apparatus cools, the water enters the flask, the quantity of water measuring the change in the volume of the air. From the data thus obtained, the law may be verified.

Care must be taken to handle the apparatus by means of the capillary tube so as to avoid the error due to the heat of the hand. The chief cause of error is that due to imperfect drying of the apparatus, especially the cork, capillary and the space between them.

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THE SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE SOLUTIONS.

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I. HYPOTHESES AS TO THE CAUSE OF THE SOLUBILITY-INCREASE.

IT IS A well-known fact, and one often made use of in chemical analysis, that lead sulphate, though difficultly soluble in water, dissolves in considerable quantity in a strong ammonium acetate solution. As to the magnitude of this solubility we have, however, been able to find only two quantitative statements, that of Long,[1] and that of Bischof,[2] both of which relate to very concentrated solutions of ammonium acetate.

[1] *Am. Chem. J.*, **22**, 217 (1899).

[2] Comey's "Dictionary of Solubilities."

There has, moreover, been offered no verified explanation of the large increase in solubility which ammonium acetate produces. It seems, however, probable that the effect arises from one of the three following causes, or from a combination of them: (1) lead acetate is a slightly ionized substance, and therefore, a large quantity of it is produced in the solution by metathesis; (2) intermediate cathions containing lead in combination with the acetate ion $PbC_2H_3O_2^{+}$ are formed; (3) complex cathions of the composition $Pb(NH_3)_x^{++}$ are produced by combination of the lead ion with the free ammonia resulting from the hydrolysis of the salt.

These three hypotheses can be tested by migration experiments, for, in the first case, the lead, being present only as an un-ionized compound, would not move at all, while in the second or third case, it would migrate with the positive current. The first and second hypotheses can further be tested by determining the degree of ionization of lead acetate and its change with the dilution by conductivity measurements or otherwise. Furthermore, both the first and second hypotheses evidently require that sodium acetate (or any other di-ionic acetate) have nearly the same effect on the solubility of lead sulphate as ammonium acetate, while, on the other hand, the third hypothesis would lead to the expectation that the sodium salt would have a much slighter effect. The third hypothesis may seem to be inconsistent with the fact that lead hydroxide is but little soluble in ammonium hydroxide, but it is not necessarily so, since in the latter solvent the hydroxyl-ion concentration may be large enough to keep down the concentration of the lead ion and therefore that of the complex ion, if this were not very stable. This hypothesis would, however, evidently require that neutral ammonium acetate, owing to its greater hydrolysis, be a much better solvent for lead sulphate than neutral ammonium nitrate or chloride; that these different salts behave nearly alike if a moderate proportion of ammonium hydroxide be added to their solutions; and that the addition of acetic acid greatly reduce the solvent power of ammonium acetate. These last requirements seem, indeed, to be at variance with analytical experience.

II. PREVIOUS MEASUREMENTS RELATING TO THE SUBJECT.

There already exists some evidence that lead acetate is much less ionized than other salts of the same type, and, therefore, that the first hypothesis furnishes the true explanation of the increase in the solubility of lead sulphate. Thus, the freezing-point measurements of Kahlenberg[1] indicate an ionization of only 19 per cent. in $\frac{1}{4}$ molal, and of 37 per cent. in $\frac{1}{8}$ molal solution. Moreover, an isolated measurement of the conductance of the salt in 1-40 molal (1-20 normal) solution at 25° by Trey,[2] gave a value corresponding to an equivalent conductivity of 32.0 in reciprocal ohms or to a degree of ionization of 28.4 per cent.; and a series by Ley[3] beginning with 1-32 normal gave at this concentration an equivalent conductivity of 37.6 reciprocal ohms corresponding to an ionization of 33.4 per cent. Evidence against the third hypothesis is furnished also by the results of Dibbitts,[4] who found that sodium acetate also increases greatly the solubility of lead sulphate; he found namely, that 100 cc. of a solution containing 2.05 grams sodium acetate dissolves 0.054 gram lead sulphate, and 100 cc. of one containing 8.20 grams sodium acetate dissolves 0.900 gram lead sulphate.

The subject seemed, however, to deserve fuller investigation, and we have, therefore, done some further work upon it. This has consisted in qualitative migration experiments with solutions of lead sulphate in ammonium acetate, measurements of the conductivity of aqueous solutions of pure lead acetate, accurate determinations of the solubility of lead sulphate in ammonium acetate solutions, and a single rough one in a sodium acetate solution. It is the purpose of this article to present the results, and discuss their significance.

III. CONDUCTIVITY OF LEAD ACETATE SOLUTIONS.

The sample of lead acetate used in our experiments was prepared by crystallizing the chemically pure commercial salt four times from hot water containing acetic acid, and once from pure water. It was dissolved in conductivity water, and the solution was standardized by precipitation with sulphuric acid and weighing the lead sulphate. Two solutions were so prepared at different times. The first contained 1.420 equivalents (0.710 mol) per

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[1] *Z. phys. Chem.*, **17**, 583 (1895).

[2] *Ibid.*, **22**, 433 (1897).

[3] *Ibid.*, **30**, 246 (1899).

[4] *Dingler polytech. J.*, **210**, 475; *Z. anal. Chem.*, **13**, 137.

liter. The second contained 0.5088 equivalent (0.2544 mol) per liter.

The measurements were made at 25° by the Kohlrausch method, using a resistance vessel of the Arrhenius type, the resistance capacity or cell-constant of which was determined by measurements with 0.01 normal potassium chloride solution. The results are all expressed in reciprocal ohms. The value of the equivalent conductivity (Λ_0) at infinite dilution (112.8) used in calculating the conductivity ratio (Λ/Λ_0), which corresponds to the degree of ionization, if the salt dissociates only into Pb^{++} and Ac^- ions, was calculated from the values for the individual ions at 18° given by Kohlrausch and Grüneisen[1] ($\Lambda_{Pb} = 61.1$ at 18°), and by Kohlrausch and Steinwehr[2]) ($\Lambda_{Ac} = 35.0$ at 18°), and from the temperature-coefficients computed by Kohlrausch.[3]

The first solution above referred to was diluted four times in succession with conductivity water by means of two graduated flasks in such a way that the concentration was each time reduced to one-fourth of its former value. The value of the cell-constant (or the factor by which the actual conductance must be multiplied to give the specific conductance) in this series of experiments was 0.1389.

A second series of measurements was carried out with greater care with the second solution, it being diluted in a somewhat different manner from the first. The stock solution was kept in a Jena flask, from which it was drawn as required, air being admitted through a soda-lime tube. Twofold dilutions were made by weighing, the volume concentrations being calculated with the help of a specific gravity determination. The value of the cell-constant was 0.1400 in the case of the first two measurements of the series, 0.1243 in the other cases.

The results of the measurements are given in Table I.

TABLE I.—CONDUCTIVITY OF LEAD ACETATE AT 25°.

Equivalents per liter.	Actual conductance.	Equivalent conductivity.	Conductivity ratio × 100.
		First Series.	
0.3550	0.03457	13.50	12.0
0.0888	0.01627	25.38	22.5
0.0222	0.007035	43.74	38.8
0.00555	0.002790	68.75	60.9

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[1] *Berliner Sitzungsber. d. Akad. d. Wissenschaften*, 1904, p. 1221.

[2] *Ibid.*, 1902, p. 587.

[3] *Ibid.*, 1901, p. 1026; *Z. phys. Chem.*, **43**, 511.

Equivalents per liter.	Actual conductance.	Equivalent conductivity.	Conductivity ratio × 100.
	Second Series.		
0.5088	0.04220	11.61	....
....	0.04209	11.58	....
....	0.04762	11.63	....
....	0.04772	11.66	....
....	0.04735	11.57	....
....	0.04770	11.65	....
....	Mean	11.62	10.3
0.2544	0.03345	16.34	....
....	0.03346	16.34	....
....	0.03345	16.34	....
....	0.03368	16.45	....
....	0.03361	16.42	....
....	0.03365	16.43	....
....	Mean	16.39	14.5
0.1272	0.02272	22.19	....
....	0.02274	22.21	....
....	0.02271	22.18	....
....	Mean	22.19	19.7

The mean values of the equivalent conductivity derived from these two independent series of experiments (after being corrected with help of the formula referred to just below, to a round dilution not differing much from that at which the measurements were made) and the above-mentioned results of Trey and of Ley (expressed in reciprocal ohms instead of in mercury-units as given by those authors) are for the purpose of better comparison, summarized in Table II. The table also contains the corresponding value of the conductivity-ratio ($\Lambda/\Lambda_0 = \gamma$) multiplied by 100, and the values of the empirical function $100\ (\gamma\ C)^2/C(1-\gamma)$ where C is the equivalent concentration, which function was found to be fairly constant when applied to our own data between ½ and $^1/_{12}$-normal.

TABLE II.—SUMMARY OF EQUIVALENT CONDUCTIVITY VALUES.

Liters per equivalent.	Investigator.	Equivalent conductivity.	Conductivity ratio × 100.	$\frac{100(\gamma)C^2}{(1-\gamma)C}$.
2	N. & W., 2nd Ser.	11.73	10.4	0.6019
3	N. & W., 1st Ser.	13.99	12.4	0.5808
4	N. & W., 2nd Ser.	16.47	14.6	0.6256
8	N. & W., 2nd Ser.	22.45	19.9	0.6148
12	N. & W., 1st Ser.	26.05	23.1	0.5800
20	Trey	32.00	28.4	0.5635
32	Ley	37.63	33.4	0.5234
48	N. & W., 1st Ser.	44.89	39.8	0.5461

Liters per equivalent.	Investigator.	Equivalent conductivity.	Conductivity ratio × 100.	$\frac{100(\gamma C)^2}{(1-\gamma)C}$.
64	Ley	46.98	41.7	0.4662
128	Ley	57.40	50.9	0.4121
192	N. & W., 1st Ser.	69.94	62.0	0.5264
256	Ley	68.23	60.5	0.3623
512	Ley	79.09	70.1	0.3209
1024	Ley	89.29	79.2	0.2947

It will be seen from the last column that the conductivity value of Trey corresponds well with ours, but that those of Ley are considerably less, especially in the dilute solutions (1/128 to 1/256 normal).

The results show clearly that lead acetate is much less ionized than is usual with unibivalent salts, which are commonly 70-75 per cent. ionized in 0.1 normal solution. The results of Ley with other acetates of this type show too that even these have a much higher conductivity than lead acetate; thus for 1/32-normal solutions he obtained the following equivalent conductivities in reciprocal ohms: barium acetate, 80.0; manganese acetate, 66.6; nickel acetate, 64.6; cobalt acetate, 65.9; zinc acetate, 62.3; and cadmium acetate, 54.5; while that of lead acetate is only 37.6.

The actual values of the conductivity-ratio given in the table are not to be regarded, however, as a true measure of the ionization, for it is very probable in view of its slight degree of ionization that this salt forms the intermediate ion $PbAc^+$ in large quantity. Moreover, since the Λ_0 value for dissociation into the two ions $PbAc^+$ and Ac^- would be very different from that for dissociation into the three ions Pb^{++} and $2Ac^-$, which last was assumed in computing the ratio, it is not proved by the constancy (in the stronger solution) of the function given in the last column that the former kind of ionization alone takes place, but only that the latter kind is not the exclusive one.

IV. MIGRATION EXPERIMENTS.

Two series of qualitative migration experiments were made. In one of these, the solutions, in order to avoid stirring, were gelatinized by the addition of agar; in the other, to eliminate the possibility of any influence of the agar upon the lead salt, difference in specific gravity was alone relied upon.

In the former series a U-tube 1.75 cm. in diameter and 15 cm. in height was used. The bend was filled with an agar jelly made up with a normal ammonium acetate solution and containing zinc sulphide in suspension. Above this in each arm of the tube were placed, first, a plug of jelly 0.5 cm. long with ammonium acetate solution alone; next, one also saturated with lead sulphate; then, another one 0.5 cm. long with ammonium acetate alone; then, one with this salt in solution and zinc sulphide in suspension; and finally, some ammonium acetate solution without agar, in which platinum-wire electrodes were placed. The tube was immersed in a bath of ice water. The electrodes were kept at a potential difference of 80 volts for two hours, but at no point did the zinc sulphide become blackened, showing that the lead did not migrate to an appreciable extent in either direction.

Of the experiments made with solutions without agar added, only the final and most conclusive one need be described. The apparatus used consisted essentially of two U-tubes connected by side-arms, one of the tubes being joined at the bottom of the bend to a glass tube of small bore. The tubes were completely filled with half-normal ammonium acetate solution; then both arms of one of them were tightly stoppered, and by means of suction applied to both arms of the other, a normal solution of ammonium acetate saturated with lead sulphate and strongly colored with rosaniline hydrochloride was slowly drawn up through the small glass tube at the bottom until the bend was sealed. The solutions had been brought to a constant temperature of 25° previous to the filling, which took place immediately over the thermostat. A difference of potential of 110 volts was applied and the current (of 0.2 ampere) was passed for two hours. The length of the column of solution was 73 cm., thus giving a drop in potential of 1.5 volts per centimeter. The color boundary remained sharp, and nearly stationary, showing there was no stirring. At the end of the experiment, successive portions were carefully withdrawn by means of a pipette from both arms of the tube containing the dissolved lead sulphate, almost down to the color boundary. To each of these portions was added potassium chromate, which furnishes a very delicate test for lead even in acetate solution. None of the portions from the cathode side gave any indication of lead, even down to the line of separation. In the portions on the anode side there was a trifling quantity of lead in the portion immediately adjoining the lead sulphate solution, but a portion 2.4 cm. away gave no precipitate whatever with the potassium chromate. An ordinary lead ion, for example, in a 0.2 normal lead nitrate solution, moves under a potential gradient of 1 volt per centimeter about 0.00040 cm. per second, so that under the conditions of our experiment, it would have moved about $0.00040 \times 1.5 \times 7200 = 4.3$ cm., while, in fact, no considerable quantity of the lead migrated more than a small fraction of a centimeter. On the other hand, the SO_4 ions migrated several centimeters in the same time, for a precipitate of barium sulphate was obtained in all the portions from the anode arm upon the addition of barium chloride and acidifying with hydrochloric acid, while the solution in the cathode arm gave no such indication of the presence of sulphate.

Both of these series of experiments lead to the same conclusion, namely, that substantially all the lead exists in the acetate solution in the form of un-ionized compound.

V. EXPERIMENTS ON THE SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE SOLUTIONS.

Since ammonium acetate is very hygroscopic, it is impracticable to obtain a solution of known strength by weighing out the salt. The solution was, therefore, prepared by the neutralization of ammonium hydroxide with acetic acid. Pure ammonia, free from amines, was prepared by the following method:[1] Commercial ammonium chloride, "free from hydrocarbons," was dissolved in enough boiling water to form a saturated solution. One-tenth of its volume of nitric acid (sp. gr. 1.42) was added, and the solution boiled until there was no further evolution of chlorine. The solution was then allowed to cool, the crystallized salt dissolved in water, one-twentieth of its volume of nitric acid added, and the solution again boiled as long as chlorine was given off. After diluting sufficiently to form a nearly saturated solution when cold, the salt was decomposed by lime. The ammonia was absorbed in conductivity water, carbon dioxide being carefully excluded by the use of soda-lime tubes. The ammonium hydroxide solution so obtained was standardized with the help of methyl orange against a solution of pure hydrochloric acid, whose strength had been determined by precipitation with silver nitrate. An acetic acid solution was prepared by diluting glacial acetic acid with water. It was standardized with the help of phenolphthalein against a barium hydroxide solution, which had been titrated against the

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[1] Bender u. Erdmann: "Praparatenkunde," p. 234.

hydrochloric acid. The standardizations were made by weight, so as to give the number of grams of acetic acid solution which were equivalent to 1 gram of ammonium hydroxide solution. The neutral ammonium acetate solution was then prepared by adding to a given weight of the latter solution the appropriate weight of the former. Taking into account also the specific gravity of the two solutions, the concentration of the ammonium acetate solution so obtained was calculated to be 0.4141 equivalent per liter. The lead sulphate used was prepared by precipitating the commercial chemically pure lead acetate from solution by sulphuric acid, dissolving the precipitate in pure ammonium acetate, and reprecipitating with sulphuric acid.

For the determination of the lead dissolved in the ammonium acetate solution, two methods were tested by using known weights of pure lead sulphate. The first consisted in precipitation as lead chromate from acetic acid solution, filtering upon a Gooch crucible and drying at 170°; the second in precipitation as lead sulphate by sulphuric acid, filtering upon a Gooch crucible, washing first with dilute sulphuric acid and then with 50 per cent. alcohol, and drying at 170°.

The former method gave results about 0.7 per cent. too high, owing probably to the carrying-down of an excess of chromic acid; the latter method gave results which trial analyses showed to be accurate within 0.05 per cent.

The solutions were saturated by rotating the ammonium acetate solutions with a large excess of solid lead sulphate for fifteen hours within a thermostat at 25° in the manner previously described[1]. In half the determinations (marked *s* in the table below) the equilibrium was approached from the supersaturated side, by cooling a solution which had been shaken with the salt at a higher temperature, while in the other half (marked *u* in the table) it was approached from the undersaturated side, by heating the solution from the room temperature to 25°. It will be seen that the two procedures gave substantially identical results.

Table III contains the results obtained, the solubility of the lead sulphate as well as the concentration of the ammonium acetate being expressed in the first three columns in millimols per liter. In the fourth column the solubility in grams per liter is added. For comparison, is included also the solubility in pure

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[1] Noyes: *Z. phys. Chem.*, 9, 606 (1892).

water, or rather the concentration of the ionized portion in the saturated solution in water, as determined by Böttger[1] by conductivity measurements.

TABLE III.—SOLUBILITY OF LEAD SULPHATE IN AMMONIUM ACETATE SOLUTIONS AT 25°.

	Solubility of $PbSO_4$.		
Concentration of $NH_4C_2H_3O_2$.	Separate determ.	Mean millimols per liter.	Mean gms. per liter.
0.0	....	0.134	0.041
103.5	2.10 *s*	2.10	0.636
.....	2.10 *u*		
207.1	4.54 *s*	4.55	1.38
.....	4.56 *u*		
414.1	10.12 *s*	10.10	3.06
.....	10.09 *u*		

It is seen from the table that the solubility is about fifteen times as great in 0.1 normal ammonium acetate solution as in water and that it increases with increasing concentration of the salt somewhat, but not very much, more rapidly than proportionality between solubility and concentration would require.

It seems certain from the conductivity and migration experiments above described that this increase of the solubility is mainly due to the formation of un-ionized lead acetate, accompanied, of course, by the production of an equivalent quantity of ammonium sulphate, which would exist partly as ions and partly as un-ionized molecules. Assuming now that the solubility product, $C_{Pb} \times C_{SO_4}$, retains the same value as in pure water, the solubility in any ammonium acetate solution might be computed if it were possible to determine the resulting concentration of un-ionized lead acetate,—a quantity which is substantially equivalent to that solubility. Unfortunately, however, our knowledge of the ionization-relations, not only of lead acetate itself, but also in general of mixtures of salts which do not conform to the mass-action law is still very imperfect, and any assumption that may be made, especially with regard to the slightly ionized lead acetate, is arbitrary. Nevertheless, it is perhaps not without interest to determine whether the solubility-change with the concentration is satisfactorily explained if it be assumed that this salt follows the mass action law (which may well be true in virtue of its small ionization tendency) and that ammonium sulphate follows

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[1] *Z. phys. Chem.*, **46**, 604 (1903).

the empirical law which has been shown to apply to mixtures of largely ionized salts[1]. We then have the equilibrium equations:

$$C_{Pb} \times C_{SO_4} = S_0^2;\; C_{Pb} \times C^2_{Ac} = K_1 C_{PbAc_2};\; \text{and}\; C_{Am} \times C_{SO_4} = K_2 C_{Am_2SO_4} C_i^m,$$

where S_0 is the solubility of lead sulphate in pure water, K_1 and K_2 are equilibrium-constants, m is an empirical exponent, and C_i is the total concentration of all the positive or negative ions in the solution. Furthermore, if S is the solubility of lead sulphate in a solution of ammonium acetate of concentration C and ionization γ, the following relations given by the conditions of the problem also hold true approximately:

$$C_{PbAc_2} = S;\; C_{SO_4} + C_{Am_2SO_4} = S;\; \text{and}\; C_{Am} = C_{Ac} = C_i = C\gamma.$$

Combining these equations we get:

$$S = \frac{S_0}{\sqrt{K_1}}(C\gamma)\left(1 + \frac{1}{K_2}(C\gamma)^{1-m}\right)^{\frac{1}{2}}$$

Now Kohlrausch's conductivity measurements at 18° with potassium sulphate, whose ionization relations may be assumed identical with those of ammonium sulphate, show that $m = 0.59$ and $K_2 = 0.881$ when computed for the concentrations between 0.1 and 0.5 normal. The preceding equation therefore becomes

$$S = \frac{S_0}{\sqrt{K}} C\gamma\left(1 + 1.135(C\gamma)^{0.41}\right)^{\frac{1}{2}}.$$

It will be seen at once that this equation requires that the solubility increase a little more rapidly than the ionic concentration of the salt. By means of it the solubility at the two concentrations, 0.1036 and 0.414 molal can be computed from that in the 0.207 molal solution, the value of $S_0/\sqrt{K_1}$ being first calculated from the data for the latter. For these purposes we have obtained γ from the conductivity data of Kohlrausch at 18° for sodium acetate, whose ionization relations doubtless correspond closely to those for ammonium acetate. We have thus calculated the solubility at the other two concentrations and found it to be that shown in the following table. The concentrations of the ammonium acetate are here expressed in equivalents and those of the lead sulphate in millimols per liter.

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[1] See Noyes: *Science*, **20**, 577 (1904); *Tech. Quart.*, 17, 293 (1904); This JOURNAL, **27**, R. 203.

TABLE IV.—OBSERVED AND CALCULATED SOLUBILITIES OF LEAD SULPHATE.

Concentration of $NH_4C_2H_3O_2$.	Ionization of $NH_4C_2H_3O_2$.	Solubility of $PbSO_4$. Observed.	Solubility of $PbSO_4$. Calculated.
0.1035	0.775	2.10	2.34
0.2071	0.724	4.55	....
0.4141	0.652	10.10	8.56

It will be seen that the change of solubility with the concentration is roughly, and only roughly, that required by the foregoing formula.

Finally it may be mentioned that, to determine whether the requirement of the hypothesis is fulfilled that sodium acetate has nearly the same effect on the solubility of lead sulphate as ammonium acetate, normal solutions of these two substances were shaken occasionally at room temperature for two days with an excess of solid lead sulphate, and a 100-cc. portion of each was analyzed for its lead-content. The ammonium acetate solution yielded 0.42 gram and the sodium acetate solution 0.45 gram of lead sulphate. These experiments were very rough ones, for the solutions were made up by weighing out the commercial "chemically pure" salts without thorough drying, the temperature was variable, and complete saturation may not have been reached. Still they certainly show that the two salts have, at least roughly, the same effect.

VI. SUMMARY.

New measurements of the conductivity of lead acetate solutions at 25° between 1/2- and 1/192-normal, have been presented, which show that this salt has an abnormally small degree of ionization (only about 22 per cent. at 0.1 normal, assuming that it dissociates directly into three ions).

Qualitative migration experiments made with a saturated solution of lead sulphate in normal ammonium acetate solution have been described, which show that the lead in this solution is not present to an appreciable extent in the form of either a positive or negative ion.

The solubility of lead sulphate (in millimols per liter) has been found to be 2.1 in 0.104 normal ammonium acetate solution, 4.55 in 0.207 normal, and 10.1 in 0.414 normal. The solubility is very much greater than that in pure water (0.134 millimol per liter according to Böttger), and is roughly proportional to the concentration of the ammonium acetate. Rough comparative experiments with sodium acetate and ammonium acetate showed that the solubility of lead sulphate in solutions of these two salts is of about the same magnitude.

These facts all indicate that the increased solubility of lead sulphate in acetate solutions arises mainly from the formation of unionized lead acetate by metathesis.

April, 1905.

NOTE.

A Method of Measuring Electric Currents in Solutions for Lecture Purposes.—In order to demonstrate the existence of electric currents in electrolytes it has always been necessary to use measuring instruments in an external metallic circuit. Such methods furnish but indirect information about the direction and intensity of the current in the solution.

The instrument described below, remedies these deficiencies. It permits the direct measurement of the currents passing through the interior of a cell, and renders it possible to demonstrate the analogy of electrolytic and metallic conduction by a simple and comprehensive lecture experiment.

The apparatus consists of two half-cells A_1 and A_2 which contain exchangeable electrodes E_1 and E_2 immersed in the electrolytes that are to be examined. A glass tube, having the shape of a solenoid with one or two coils, and filled with a well-conducting solution, furnishes the electrolytic connection between the cells; while the external current can be closed by means of a switch connected by wire with both electrodes. With the aid of this arrangement it is possible to construct any galvanic cell. If, for instance, EE_1 is a carbon plate in nitric acid, E_2 a zinc electrode in dilute sulphuric acid, the common Bunsen element is formed, the solenoid playing the rôle of a porous cell. If E_1 is lead, E_2 lead covered with peroxide, and the liquid throughout the cell sulphuric acid, a storage cell is obtained, etc. As soon as the external circuit is established, discharge of the ions takes place at the electrodes, and there is a continuous migration through the electrolyte in the solenoid. That the internal current thus formed is actually identical with the current in the metallic circuit (but of opposite direction, from the negative to the positive plate when used as a