CCCXCIV.—*Physico-chemical Studies of Complex Formation involving Weak Acids. Part II. The Constitution of Acetates in Solution.*

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Theory demands that in order that acetic acid should combine with a base as a soluble acetate, the base itself must be able to impart to the solution a concentration of hydrogen-ions of p_H higher than 6·7, this being 2 p_H units higher than that of the negative exponent of acetic acid (see Britton, "Hydrogen Ions," p. 138). In the case of a number of metallic bases, however, this is not possible, for, as Britton (J., 1925, **127**, 2110) has shown, the bases themselves are precipitated from solutions that are more acidic than p_H 6·7. On the other hand, normal lead and copper acetates can be crystallised from aqueous solutions in the pure condition, though it is significant that calculations, based on measurements of the equivalent conductivities of solutions of these salts, indicate abnormally small degrees of ionisation. Moreover, basic acetates of the metals, *e.g.*, lead, copper, aluminium, beryllium, thorium, zirconium, can be obtained which dissolve in water to give quite clear solutions. It is highly probable that normal acetates undergo considerable hydrolysis in solution, which might account for the

low conductivities. Failure to realise that acetates of weak metallic bases do not ionise in solution in a normal manner has undoubtedly led to erroneous theories regarding the existence of complex acetate ions. This applies to the current explanation of the ability of alkali and ammonium acetates to dissolve lead sulphate.

The following investigation was undertaken to ascertain the nature of typical metallic acetates in solution, and to correlate it with certain characteristic reactions. For this purpose, our studies have been confined to solutions of the acetates of lead, copper, aluminium, beryllium, and thorium.

EXPERIMENTAL.

The hydrogen-ion concentrations which are established during the progressive neutralisation of a weak acid, such as acetic, with a base may be found from $K_a = [\text{H}^\cdot][\text{A}']/[\text{HA}]$, or from $p_\text{H} = p_{K_a} + \log [\text{A}']/[\text{HA}]$, where $[\text{A}']$ is the concentration of the weak acid anions, and $[\text{HA}]$ that of undissociated acid. These mass-law expressions are applicable to the ionisation of acetic acid, and must therefore hold for all neutralisations in which that acid might participate, no matter what the base may be. Hitherto, it has been found to hold in the case of reactions with soluble bases, viz., alkalis, ammonium hydroxide, and organic bases. For dilute solutions, the above expression becomes

$$p_\text{H} = p_{K_a} + \log \left(\frac{\text{Fraction neutralised}}{\text{Fraction un-neutralised}} \right)$$

the assumptions involved being that the salt formed is completely ionised and that the concentration of undissociated acid is equal to that of the un-neutralised acid. The latter assumption becomes relatively true in the case of acetic acid soon after it has undergone 10% neutralisation.

I. *Metallic Acetate–Acetic Acid Solutions.*—In order to ascertain the mode of ionisation of acetates of sparingly soluble bases, several series of solutions were prepared, and in each series, the total concentration of acetic acid, *i.e.*, free and neutralised, was kept constant, whereas the concentrations of the base were varied so as to correspond to successive 10% stages of neutralisation. Instead of dissolving the sparingly soluble bases directly in the acid, the various solutions were prepared from solutions of the metallic acetates and acetic acid. The crystalline normal acetates of lead and copper were used, but since the acetates of beryllium, thorium, and aluminium have not yet been obtained in the pure state, solutions were made that contained these metals and acid in the stoicheiometric proportion by metathesis of their respective sulphates with

barium acetate. These solutions were thoroughly agitated mechanically for a day, allowed to stand until all the barium sulphate had settled, and the almost clear solution was then removed by decantation and filtered. In every case the solution was free from barium and sulphate ions, and only a very slight entrainment of the weak metallic bases by the precipitated barium sulphate occurred. The concentrations of the total acetic acid in the solutions were : $0.0197N$ in the case of the lead solutions; $0.01965N$, copper;

FIG. 1.

Acetic acid neutralised, %.
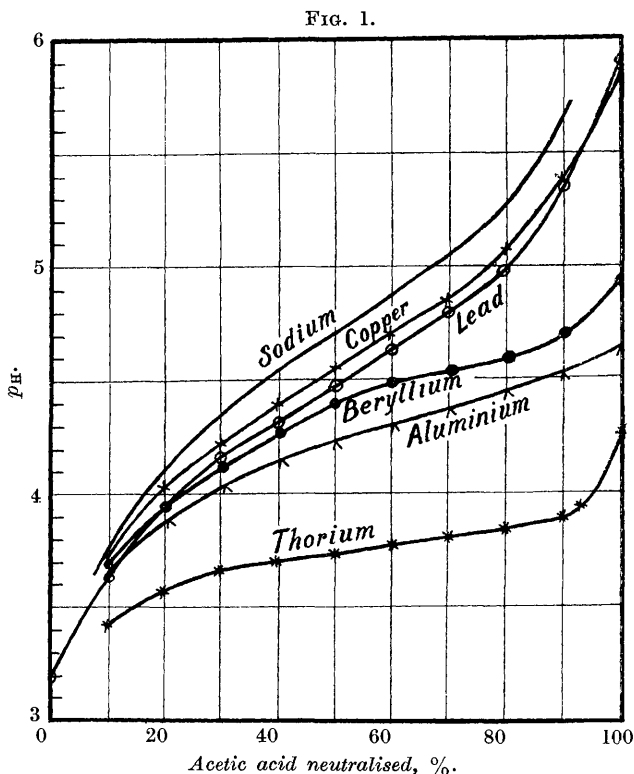
$0.0135N$, beryllium; $0.0213N$, aluminium; and $0.0170N$, thorium. The p_H measurements were made at room temperature, *viz.*, 18—20°, by means of the quinhydrone and the normal calomel electrode, and saturated solutions of either potassium chloride or nitrate were used as the junction liquid. The data are represented graphically in Fig. 1, and are recorded in col. 2 of Table I. (In this table, x represents the percentage degree of neutralisation, and v is the dilution, in litres, of the salt.) The curve " Sodium " is introduced for comparison and represents the course of neutral-

TABLE I.

x.	p_H, obs.	$\kappa \times 10^4$ mixt.	salt.	v.	Λ.	a.	p_H, calc.	$\kappa \times 10^4$ mixt., obs.	salt, calc.
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Lead.									
10	3·62	2·30	1·50	507·6	76·1	0·67	3·67	0·80	0·84
20	3·94	3·15	2·62	253·8	66·5	0·59	3·92	0·53	0·47
30	4·15	3·92	3·55	169·2	60·1	0·53	4·10	0·37	0·31
40	4·29	4·73	4·41	126·9	56·0	0·49	4·25	0·32	0·22
50	4·47	5·41	5·19	101·5	52·7	0·46	4·40	0·22	0·16
60	4·64	6·13	5·90	84·6	49·9	0·44	4·55	0·23	0·11
70	4·79	6·79	6·62	72·5	48·0	0·42	4·72	0·17	0·07
80	4·97	7·39	7·28	63·45	46·2	0·41	4·95	0·11	0·04
90	5·35	8·04	7·96	56·4	44·9	0·39	5·27	0·08	0·02
100	5·89	8·62	8·62	50·8	43·8	0·38	—	—	—
Copper.									
10	3·72	2·21	1·53	508·9	77·9	0·81	3·74	0·68	0·71
20	4·03	3·00	2·68	254·5	68·2	0·71	4·00	0·32	0·39
30	4·22	3·96	3·60	169·6	61·1	0·64	4·18	0·36	0·26
40	4·38	4·87	4·51	127·2	57·4	0·60	4·33	0·36	0·18
50	4·55	5·70	5·40	101·8	55·0	0·57	4·49	0·30	0·13
60	4·69	6·45	6·21	84·8	52·7	0·55	4·64	0·24	0·09
70	4·84	7·19	6·90	72·7	50·2	0·52	4·86	0·29	0·05
80	5·08	7·94	7·60	63·6	48·3	0·50	5·03	0·34	0·04
90	5·38	8·51	8·31	56·5	47·0	0·49	5·37	0·20	0·02
100	5·84	8·97	8·97	50·9	45·7	0·48	—	—	—
Beryllium.									
10	3·67	1·73	0·84	740·7	62·2	0·74	3·73	0·89	0·73
20	3·94	2·26	1·50	370·4	55·6	0·66	3·98	0·76	0·41
30	4·13	2·91	2·08	246·9	51·4	0·61	4·16	0·83	0·27
40	4·26	3·49	2·65	185·2	49·1	0·59	4·33	0·84	0·18
50	4·39	3·96	3·20	148·1	47·4	0·57	4·49	0·76	0·13
60	4·48	4·31	3·72	123·5	45·9	0·55	4·64	0·59	0·09
70	4·53	4·69	4·28	105·8	45·3	0·54	4·83	0·41	0·06
80	4·59	4·98	4·74	92·6	43·9	0·52	5·05	0·24	0·03
90	4·69	5·31	5·22	82·3	43·0	0·51	5·39	0·09	0·02
100	4·85	5·62	5·62	74·1	41·6	0·50	—	—	—
Aluminium.									
10	3·65	2·29	0·80	469·5	37·6	0·42	3·61	1·49	0·96
20	3·88	2·93	1·58	234·7	37·1	0·41	3·79	1·35	0·63
30	4·03	3·46	2·31	156·5	36·2	0·40	3·99	1·15	0·40
40	4·14	3·99	2·96	117·4	34·8	0·39	4·16	1·03	0·27
50	4·23	4·37	3·58	93·9	33·6	0·38	4·32	0·79	0·19
60	4·27	4·73	4·12	78·3	32·3	0·36	4·48	0·61	0·13
70	4·37	5·11	4·66	67·1	31·3	0·35	4·64	0·45	0·09
80	4·47	5·35	5·15	58·7	30·2	0·34	4·86	0·20	0·05
90	4·52	5·62	5·60	52·2	29·2	0·32	5·19	0·02	0·03
100	4·64	6·02	6·02	47·0	28·3	0·31	—	—	—
Thorium.									
10	3·41	1·67	0·32	591·7	18·9			1·35	
20	3·57	1·62	0·61	295·9	18·0			1·01	
30	3·66	1·61	0·85	197·2	16·8			0·76	
40	3·68	1·57	0·95	147·9	14·1			0·62	
50	3·73	1·55	1·04	118·3	12·3			0·51	
60	3·76	1·52	1·13	98·6	11·1			0·39	
70	3·81	1·50	1·22	84·5	10·3			0·32	
80	3·85	1·47	1·31	74·0	9·69			0·16	
90	3·88	1·46	1·39	65·7	9·13			0·07	
100	4·31	1·46	1·46	59·2	8·64			—	

isation of acetic acid of approximately the same concentration, viz., $0.0200N$. The specific conductivities of the various acetate solutions were determined at $25.0°$ and are given in col. 3 of Table I. The specific conductivities at $25°$ of the metallic acetates in aqueous solutions at comparable dilutions were also measured. These are given in col. 4, together with the corresponding equivalent conductivities, Λ (col. 6).

If the metallic acetates were normal as regards their mode of ionisation, and also underwent ionisation to the same extent as does sodium acetate, then it would be expected that all the curves given in Fig. 1 would be very similar and almost coincident. This is seen not to be the case. It is significant, however, that, with the exception of beryllium, the acetates of those hydroxides having the highest precipitation p_H values, viz., copper and lead, lie nearest to the sodium curve. The p_H at which copper ordinarily becomes precipitable as hydroxide is 5, whilst that for lead is approximately 6. Although beryllium hydroxide begins to precipitate at p_H 5.7. precipitation does not occur until at least 1 equivalent of alkali has been added, during the addition of which a considerable increase in p_H ensues. It is evidently this property of beryllium hydroxide that is reflected in the latter portion of the acetate curve in Fig. 1. The aluminium and thorium curves are still lower and lie in the order of the precipitation p_H values of the respective hydroxides, viz., 4.1 and 3.5. Another point of interest is that the cupric, aluminium, and thorium acetate solutions remained clear even though p_H values were established in many of their solutions which were higher than those at which their respective hydroxides are normally precipitated. Table I shows that this is particularly true of many of the solutions of thorium and aluminium. It is, of course, possible that these solutions were on the point of precipitation, but no sign of this was evident on keeping. If this be the case, then it is likely that some portion of the hydroxides was in the state of either a colloidal or a pseudo-colloidal solution which was stabilised by some kind of partial combination with the acetic acid.

The p_H data permit of calculations of the ratio of the concentration of acetate ions to that of undissociated acetic acid of the various solutions. Such calculations were made on the basis of $p_{K_{HOAc}} = 4.73$, and the results are given in Table II.

Compared with the ratios corresponding to the sodium acetate–acetic acid mixtures, those of the aluminium, thorium, and beryllium acetates are all extremely low. Those of lead and copper, although much smaller, show relatively less deviation. The acetates of copper and lead, having hydroxide precipitation p_H values which almost permit complete combination with acetic acid, would be

TABLE II.

Ratios [OAc′]/[HOAc].

x, %.	Na.	Pb.	Cu.	Al.	Th.	Be.
10	0·10	0·08	0·10	0·08	0·05	0·09
20	0·23	0·16	0·20	0·14	0·07	0·16
30	0·39	0·26	0·31	0·20	0·09	0·25
40	0·63	0·36	0·45	0·26	0·09	0·34
50	0·91	0·55	0·66	0·32	0·10	0·46
60	1·35	0·81	0·91	0·35	0·11	0·56
70	2·09	1·15	1·29	0·44	0·12	0·63
80	3·63	1·74	2·24	0·55	0·13	0·72
90	8·13	4·17	4·47	0·62	0·14	0·91
100	100	14·45	12·88	0·81	0·38	1·32

expected to approximate more closely to the ideal conditions represented by the sodium ratios.

Attention has already been directed to the fact that the equivalent conductivities of the acetates of the heavy metals lead to remarkably low degrees of dissociation. This will be apparent from a comparison of the data given in Table I for lead, copper, and beryllium acetates with those for sodium acetate in Table III.

TABLE III.

Equivalent Conductivities of Sodium Acetate at 25°.

v ...	19·8	20·9	22·3	26·4	29·7	34·6	42·8	87·0	108·8	250·0
Λ ...	80·0	80·3	80·7	81·0	81·4	82·5	82·6	82·7	83·8	85·0
a ...	0·87	0·88	0·88	0·88	0·89	0·90	0·90	0·90	0·91	0·93

The mobility of the sodium ion was taken as 50·9 (Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 1015). The equivalent conductivities of sodium acetate were determined experimentally, since the published values of Lorenz and Ostwald (*Z. anorg. Chem.*, 1920, **114**, 209) and of Jones and West (*Carnegie Inst. Publications*, 1912, No. 170) showed poor agreement. The specific conductivities of lead acetate solution at various dilutions have been determined by Noyes and Whitcomb (*J. Amer. Chem. Soc.*, 1905, **27**, 747) and by Jones (*loc. cit.*). Those for copper and beryllium acetate solutions have been determined by Ley (*Ber.*, 1909, **42**, 370) and by Sidgwick and Lewis (J., 1926, 2538) respectively. The experimental values obtained (col. 4 of Table I) agree reasonably well with those obtained by extrapolation (wherever possible) from the curves drawn from the above published data.

To ascertain whether the p_H values and the specific conductivities of the mixtures could be explained on the assumption that Λ_v/Λ_∞ gave a true measure of α, two series of calculations have been made. In the first set, the concentration of acetate ions arising from the metallic acetates was found, use being made of the values of α given in col. 7 of Table I. The equivalent conductivities at infinite

dilution at 25° of the acetates of lead, copper, beryllium, and aluminium were obtained from the mobilities of the respective ions, viz., $CH_3 \cdot CO_2' = 40 \cdot 8$ (Johnston, *loc. cit.*); $\frac{1}{2}Pb = 73$, $\frac{1}{2}Cu = 55$ (Landolt–Börnstein, "Tabellen," 3 Aufl., 1927); $\frac{1}{2}Be = 43$ (Sidgwick and Lewis, J., 1926, 1287), and $Al = 49 \cdot 2$ (Heyrovský, J., 1920, **117**, 19). Some doubt exists as to the accuracy of the last value, and no satisfactory value for the mobility of the thorium ion could be found. The acetate ions originate from both the metallic acetate and the free acetic acid. As the concentration of acetate ions due to the free acid is equal to the hydrogen-ion concentration of the solution, it follows that

$$K = 10^{-4 \cdot 73} = [H^{\bullet}]([H^{\bullet}] + [OAc'])/([HOAc] - [H^{\bullet}])$$

where [OAc'] represents the concentration of acetate ions supplied by the salt. Hence the p_H values of the various solutions can be computed from conductivity data, and values so obtained are recorded in col. 8 of Table I. In the case of the lead and copper solutions, the calculated p_H values compare remarkably well with those observed (col. 2). Too much weight, however, should not be placed on this agreement, for, as the curves in Fig. 1 show, the p_H values correspond to solutions that are extremely well buffered, so much so that these values will only be greatly affected by appreciable changes in [OAc']/[HOAc]. With the beryllium and aluminium solutions the agreement becomes poor with the diminishing concentrations of free acetic acid. Nevertheless, the agreement is surprisingly good in the case of the first four solutions in both instances, suggesting that, if beryllium and aluminium acetates ionise into their simple ions, they do so only in solutions containing relatively large amounts of acetic acid. Incidentally, the beryllium data may, perhaps, be regarded as supplying some confirmation of the mobility of the beryllium ion as determined by Sidgwick and Lewis (*loc. cit.*), and not of the value, *viz.*, 30, of Fricke and Schützdeller (*Z. anorg. Chem.*, 1924, **131**, 130). It should be mentioned, however, that, whilst Sidgwick and Lewis corrected their conductivity data of beryllium chloride for hydrolysis, no such correction was here possible, for, unlike the p_H values of beryllium chloride, those of beryllium acetate cannot, for obvious reasons, be used for the direct calculation of the hydrolysis, the extent of which, it is believed, must necessarily be considerable. In the second series of calculations, the contributions to the specific conductivities (col. 10, Table I) of the mixtures were computed and compared with the difference (col. 9) between the specific conductivities of the mixtures (col. 3) and the corresponding specific conductivities of the metallic acetates alone (col. 4). For this purpose, it was considered that,

4 z 2

whereas the acetic acid would have no great effect on the ionisation of the acetate, the relatively large concentration of acetate ions originating from the salt would repress the dissociation of the acetic acid and thereby diminish the contribution of the free acid to the specific conductivity of each mixture. The values given in col. 10 of Table I were therefore calculated by means of

$$K_{\text{(Acetic acid in mixture)}} = \frac{[\text{H}^{\bullet}]}{1000} \times (l_{\text{H}\cdot} + l_{\text{CH}_3\cdot\text{CO}_2'}) =$$
$$[\text{H}^{\bullet}](350 + 40\cdot8)/1000,$$

the mobility of the hydrogen ion being taken as 350 (Johnston, *loc. cit.*). Comparison of the data given in the last two columns of Table I reveals that, with the exception of those corresponding to about 90% of free acid, no agreement exists, and this is especially marked as the free acid contents became smaller. Moreover, the observed differences are greater than those which would have been expected on the basis of the normal ionisation of acetates. Hence, it appears from the p_{H} data that, although the ratio $[\text{OAc}']/[\text{HOAc}]$ is approximately equal to that required by simple theory, the majority of the solutions are more conducting than would be expected on these grounds. It would appear, therefore, that the concentrations of acetate ions and of undissociated acetic acid are greater than indicated by the conductivity data, though the actual ratios are similar. If this be the case, then, in aqueous solutions of these acetates and also in solutions containing small quantities of free acid, the metallic acetate must furnish the solution, by hydrolysis, with some free acetic acid; and the acetate, thereby rendered basic, must ionise to provide the solution with an enhanced concentration of acetate ions. Hence lead acetate in solution might be expected to behave thus:

$$\text{Pb(OAc)}_2 + \text{H}_2\text{O} \longrightarrow \text{Pb(OH)}_x(\text{OAc})_{2-x} + x\text{HOAc}$$
$$\text{Pb(OH)}_x(\text{OAc})_{2-x} \rightleftharpoons [\text{Pb(OH)}_2(\text{OAc})_{2-x-y}]^{\bullet} + y\text{OAc}'$$
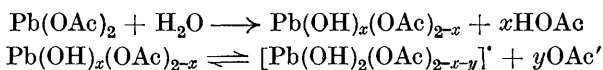
The conductivity of such a solution would thus be composite and due to the ionisation of a somewhat highly conducting soluble basic acetate and feebly conducting acetic acid. In addition, some ionisation as metallic ions of the basic kation would undoubtedly occur, the extent depending upon the complex nature of the ion itself.

II. *Solutions of Basic Acetates.*—It has long been known that soluble basic acetates of lead, copper, aluminium, beryllium, and thorium may exist in solution. As far back as 1854, Crum (*Annalen*, **89**, 156) obtained basic aluminium acetate, $\text{Al(OH)}(\text{CH}_3\cdot\text{CO}_2)_2,1\cdot5\text{H}_2\text{O}$, which was readily soluble in water, and Berzelius (*Pogg. Ann.*, **2**, 242) found that a cold solution of copper acetate could be treated with much ammonium hydroxide

before precipitation of a basic acetate began. Jackson (*J. Amer. Chem. Soc.*, 1914, **36**, 2347) isolated the basic lead acetates, $3Pb(CH_3 \cdot CO_2)_2, PbO, 3H_2O$ and $Pb(CH_3 \cdot CO_2)_2, 2PbO, 4H_2O$, which were exceedingly soluble in water, whilst Langecker (*Biochem. Z.*, 1921, **122**, 34) obtained lead acetate solutions which dissolved as much as 3 mols. of lead oxide. Relatively little enquiry of a physicochemical character has been made into the nature of these basic solutions, though Parsons (*J. Physical Chem.*, 1907, **11**, 659) observed that the freezing point of a lead acetate solution was raised somewhat on dissolution of lead hydroxide. From cryoscopic determinations, Blomberg (*Z. Elektrochem.*, 1915, **21**, 438) postulated that lead acetate ionises thus, $2Pb(OAc)_2 \rightleftharpoons PbOAc^{\cdot} + Pb(OAc)_3'$, and also showed that the lead-ion concentration of a normal solution was exceedingly small.

In order to obtain some insight into the mode of ionisation of basic lead acetate solutions, measurements were made of their conductivity, p_H values (by the quinhydrone electrode), and lead-ion concentrations, by means of $E.M.F.$'s of lead-N-calomel combinations in which saturated potassium nitrate solution was used as junction liquid. The basic lead acetate solutions were prepared by shaking fairly concentrated lead acetate solutions with various amounts of litharge for several days, filtering, and diluting the filtrates to suitable volumes. The lead concentrations were determined gravimetrically as lead sulphate, and the acetate contents by the method of Sandved (J., 1927, 2967). The lead electrodes were prepared by Glasstone's method (J., 1921, **119**, 1915), i.e., by electrodepositing finely divided lead on platinum wire or foil, and 0·122 volt was taken as the normal electrode potential of lead (see Lewis and Randall, " Thermodynamics," p. 424), on the hydrogen scale (i.e., N-$H^{\cdot} = 0$). In the basic lead acetate solutions here studied, the lead electrode gave steady and reproducible potentials. The specific conductivities of the solutions of the basic acetates and of normal lead acetate having the same lead content were determined at 25°. They are recorded in cols. 4 and 5 respectively of Table IV. In the penultimate column, i represents the percentage of lead which is ionised in the basic acetate. The electrometric work was performed at the ordinary temperature.

TABLE IV.

Conc. of Pb.	Conc. of soluble basic acetate, $Pb(OAc)_x(OH)_y$.		p_H.	100K of acetate.		$[Pb^{\cdot\cdot}] \times 10^3$.	i, %.	$[Pb^{\cdot\cdot}][OH']^2 \times 10^{17}$.
	$x =$	$y =$		Basic.	Normal.			
0·715M	1·974	0·026	6·13	8·69	8·78	4·79	0·67	0·05
0·728	1·814	0·186	6·38	8·39	8·82	2·95	0·41	0·09
0·428	1·068	0·932	7·60	6·25	7·62	0·28	0·07	2·34
0·574	1·046	0·954	7·38	7·28	8·27	0·68	0·12	2·04

The p_H values of the basic lead acetate solutions are seen from Table IV to increase as the acetate contents diminish and tend to exceed the p_H value at which lead hydroxide is normally precipitated. As the p_H values are determined by the ratio $[OAc'] : [HOAc]$, it follows that the higher p_H values are to be attributed to a diminution in the concentrations of hydrolysed acetic acid, consequent upon the dissolution of further amounts of lead oxide. Table IV reveals that the specific conductivities of the basic acetates are appreciably high in spite of the fact that the concentration of lead ions does not in any case exceed 1% of the total lead in solution. It also shows that the specific conductivity of a basic lead acetate solution is less than that of a normal lead acetate solution of the same lead concentration. Although the complex kation and anion theory of Blomberg might possibly explain the low lead-ion concentration of lead acetate solutions, it can scarcely be considered tenable in view of the evidence now advanced. The last column of Table IV contains the product of lead- and hydroxyl-ion concentrations of the basic acetate solutions. The solubility product of precipitated lead hydroxide does not appear to have been determined with certainty, though according to Applebey and Reid (J., 1922, **121**, 2129), from $E.M.F.$ determinations on alkali solutions of the red and the yellow form of lead oxide, the solubility product at 20° is either $4 \cdot 7 \times 10^{-16}$ or $9 \cdot 1 \times 10^{-16}$, depending on the oxide with which the solution is last in equilibrium. The data given in the last column show that the product $[Pb^{\cdot\cdot}] [OH']^2$ is less than the solubility product as determined by the above authors, but as the solutions become more basic this value becomes greater, as would be expected.