LI.—*The Quaternary System Lead Acetate–Lead Chloride–Acetic Acid–Water at 25°.*

BY KARL SANDVED.

IN a previous paper (J., 1927, 2967) the author directed attention to the exceptional character of the ternary system lead acetate–acetic acid–water. The high solubility of lead acetate in acetic acid and the failure to isolate any acid acetates were ascribed to the existence of complex ions in the solution. Symmetrical complex ions, in which the lead atom is surrounded entirely by acetate groups, might be expected to show a high solubility in acetic acid, due to the similarity between the solute and the solvent. In the present work, lead chloride was added as a sparingly soluble fourth component in order to introduce a certain dissimilarity between solute and solvent, and hence to render more probable the precipitation of complex compounds.

According to White (*Amer. Chem. J.*, 1906, **35**, 217), various compounds are obtained by mixing solutions of lead chloride and lead acetate, for in slightly acid solutions he obtained a precipitate of composition $PbCl{\cdot}C_2H_3O_2,Pb(C_2H_3O_2)_2,\frac{1}{2}C_2H_4O_2$, and in strongly acid solutions another of formula $(PbCl{\cdot}C_2H_3O_2)_2,C_2H_4O_2$. The phase-rule investigation now described confirms the existence of these compounds and affords information on the conditions governing their stability.

EXPERIMENTAL.

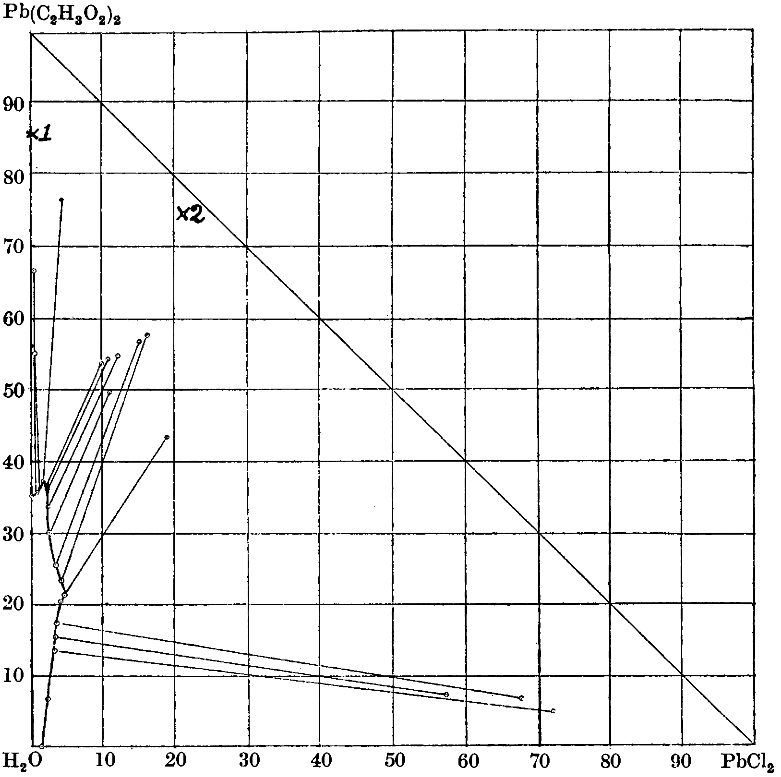
The usual procedure, described in the previous paper (*loc. cit.*), was employed for separating the liquid and the solid phase. The analytical method was the same as before, with the addition of a gravimetric determination of chlorine as silver chloride.

The purest quality of lead acetate from the British Drug Houses was used, and its analysis was in accord with the formula for the trihydrate. Lead chloride was precipitated from pure lead acetate solutions with distilled hydrochloric acid and twice recrystallised from hot water. Acetic acid was purified by three-fold freezing.

The System $Pb(C_2H_3O_2)_2$–$PbCl_2$–H_2O.

Precipitation of basic compounds always occurred on addition of lead chloride to neutral solutions of lead acetate. In his investigation of the system $Pb(C_2H_3O_2)_2$–PbO–H_2O, Jackson (*J. Amer. Chem. Soc.*, 1914, **36**, 2346) found that lead acetate trihydrate is stable as a solid up to a concentration of lead oxide equal to 15·9% ; the conditions are altered in presence of lead chloride, however, and since a study of the basic side of the diagram was beyond the scope of this work, it was found preferable to start at low concentrations of acetic acid, sufficient for dissolving the basic

FIG. 1.



compounds. This was effected in the following manner : Solutions of lead acetate and lead chloride without any acetic acid were saturated at 35°, and hydrolysis allowed to take place. After the precipitate had settled, the clear, slightly acid solutions were drawn off and cooled in a thermostat at 25°. This procedure led to complete equilibrium within 5 hours, and the crystalline solids subsided very quickly. The concentrations of free acetic acid in the solutions thus obtained were found to range between 1·4 and 1·6%. The system drawn in Fig. 1 is therefore, strictly speaking, not ternary, but rather "pseudo-ternary," for it contains a small but practically constant amount of a fourth and independent component. From Fig. 3, in which is shown the complete quaternary system, it may be seen that Fig. 1 does not give the curves lying on the $PbCl_2$–$Pb(C_2H_3O_2)_2$–H_2O triangle of the tetrahedron, but shows the curves lying in a plane parallel to this triangle at a distance corresponding to 1·4—1·6% of acetic acid.

TABLE I.

The System Lead Acetate–Lead Chloride–Water at 25°.

	Liquid.		Wet solid.	
No.	$PbCl_2$, %.	$PbAc_2$, %.	$PbCl_2$, %.	$PbAc_2$, %.
1	1·06	—	—	—
2	2·07	6·91	—	—
3	3·01	13·47	72·00	4·95
4	3·30	15·71	57·19	7·29
5	3·68	17·88	67·50	6·75
6	4·00	20·63	—	—
7	4·48	21·25	19·01	43·50
8	4·13	23·70	16·29	57·50
9	3·32	25·95	15·22	56·71
10	2·43	30·21	11·09	49·97
11	2·31	33·80	12·03	54·99
12	2·08	36·23	10·80	54·52
13	2·03	36·44	9·84	53·80
14	1·46	37·43	4·45	76·65
15	1·08	36·40	0·41	55·00
16	0·73	35·92	0·27	66·75
17	—	35·53	—	—

Fig. 1, constructed according to Lodočnikow's method (*Z. anorg. Chem.*, 1926, **151**, 185) from the experimental data in Table I, shows that three compounds are capable of existence at 25°, *viz.*, lead acetate trihydrate, a double compound of lead chloride and lead acetate, and finally, anhydrous lead chloride. The composition and appearance of the double compound agree with those given by White (*loc. cit.*); the silky tufts of crystals were, in fact, so characteristic that the compound was easily identified as soon as it had been precipitated. Similarly, the attainment of the invariant point between the trihydrate and the double compound was clearly marked, the large heavy needles of the former being detected without difficulty in presence of the latter.

The two invariant points of the system lie at 1·46% $PbCl_2$, 37·43% $Pb(C_2H_3O_2)_2$, and 4·48% $PbCl_2$, 21·25% $Pb(C_2H_3O_2)_2$. The solubility of lead acetate in pure water at 25° is 35·53% and that of lead chloride 1·06%.

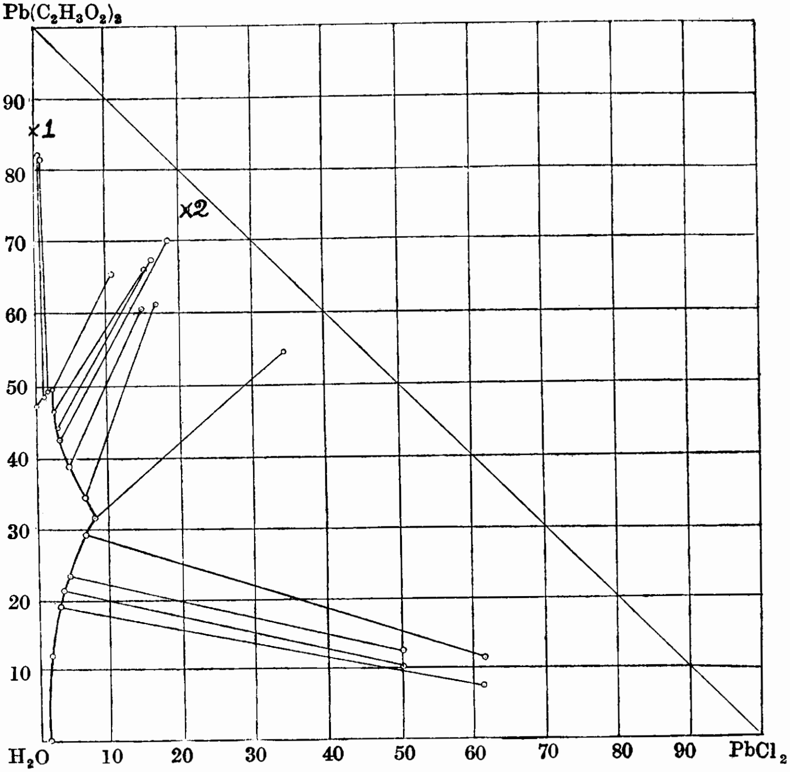
Table II and Fig. 2 represent the same system at 35°. Supersaturation was in this case effected at 42°, yielding 1·5—1·8% of acetic acid in the liquid phase. The shape of the curves is the same as in Fig. 1, and no new solid phase has appeared. The two invariant points lie at 2·17%$PbCl_2$,49·53%$Pb(C_2H_3O_2)_2$ and 7·72%$PbCl_2$,31·90%$Pb(C_2H_3O_2)_2$. The solubility of lead acetate at 35° is 47·40% and of lead chloride 1·30%.

TABLE II.

The System Lead Acetate–Lead Chloride–Water at 35°.

No.	Liquid. $PbCl_2$, %.	Liquid. $PbAc_2$, %.	Wet solid. $PbCl_2$, %.	Wet solid. $PbAc_2$, %.
1	—	47·40	—	—
2	1·18	48·83	0·65	82·30
3	1·67	49·32	0·76	81·83
4	2·17	49·53	10·87	65·70
5	2·31	46·70	15·06	66·10
6	3·00	44·15	16·10	67·70
7	3·11	42·97	18·50	70·03
8	4·70	39·01	14·98	60·80
9	6·81	34·81	16·80	61·30
10	7·72	31·90	34·25	54·55
11	6·87	29·55	61·50	11·51
12	4·25	23·90	50·03	12·42
13	3·61	21·60	50·07	10·17
14	3·33	19·05	61·05	7·91
15	1·71	12·41	—	—
16	1·30	—	—	—

FIG. 2.



The System $PbCl_2$–$C_2H_4O_2$–H_2O *at* 25°.

Hill (*J. Amer. Chem. Soc.*, 1917, **39**, 218; see also Sandved, *loc. cit.*) and Hertz and Martin (*Z. anorg. Chem.*, 1924, **140**, 339) have determined the solubility of lead chloride in acetic acid, but their values are all referred to unit of volume. The system has now been worked out on a weight basis, and Table III shows that pure lead chloride is the only solid capable of existence under the conditions chosen. The system is properly a quaternary system, in which lead acetate or hydrogen chloride acts as a fourth, independent component. The points obtained by determining the solubility of lead chloride in acetic acid, therefore, merely represent points in a limited area of the system given in Fig. 3. The assumption is made that the equilibrium $PbCl_2 + 2HC_2H_3O_2 \rightleftharpoons Pb(C_2H_3O_2)_2 + 2HCl$ is displaced so largely to the left as to render negligible the concentrations of the other products. Hence the total chlorine estimated is attributed entirely to lead chloride, and the curve based on the figures in Table III is taken to represent the line of intersection between the isothermal surface 5 in Fig. 3 and the $PbCl_2$–$C_2H_4O_2$–H_2O triangle of the tetrahedron.

FIG. 3.

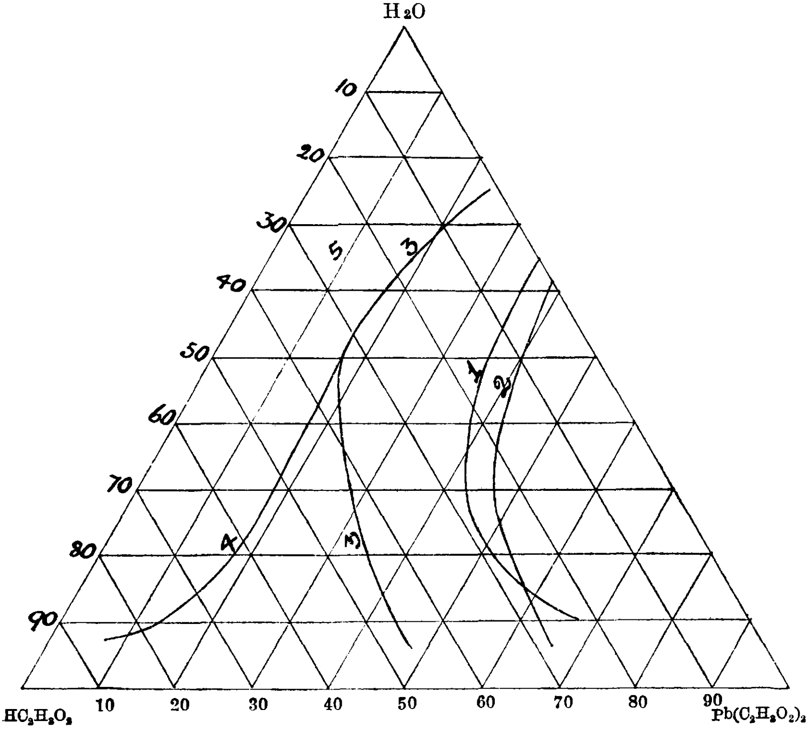


TABLE III.

The Solubility of Lead Chloride in Acetic Acid at 25°.

Liquid.		Wet solid.	
$PbCl_2$, %.	HAc, %.	$PbCl_2$, %.	HAc, %.
1·060	—	—	—
1·024	1·28	—	—
0·983	2·33	—	—
0·883	6·01	93·01	0·87
0·793	9·58	—	—
0·723	12·71	—	—
0·627	17·27	95·15	0·81
0·547	21·31	—	—
0·481	24·83	—	—
0·372	30·32	—	—
0·273	36·99	—	—
0·213	42·20	—	—
0·147	51·72	95·21	2·41
0·084	60·40	—	—
0·047	78·30	—	—
0·013	96·60	95·61	3·20

The System $PbCl_2$–$Pb(C_2H_3O_2)_2$–$C_2H_4O_2$–H_2O *at* 25°.

The relevant experimental data are set out in Table IV. The method of Jänecke (*Z. physikal. Chem.*, 1908, **64**, 343; 1912, **80**, 1) was found most convenient for plotting this type of quaternary system, for a rather confusing picture was obtained by Lodočnikow's method. Owing to the slight solubility of lead chloride, the various surfaces are more or less parallel to the $Pb(C_2H_3O_2)_2$–$C_2H_4O_2$–H_2O triangle of the tetrahedron, and for this reason it was found most convenient to project the entire system upon this plane as a base, as shown in Fig. 3. Only the intersection curves of the various surfaces are drawn, in order to make as clear as possible the stability conditions of each compound. The ternary system $Pb(C_2H_3O_2)_2$–$C_2H_4O_2$–H_2O, necessary for the construction of Fig. 3, has been described in a previous paper (*loc. cit.*). As pointed out there, it proved impossible to effect a satisfactory separation of the two phases at the highest concentrations of acetic acid by using the ordinary technique, and this part of the diagram has therefore not been covered.

From Fig. 3 it may be seen that four different solids, represented by four isothermal surfaces, are involved in this system, *viz.*,

Compound 1. Surface 1—2 : $Pb(C_2H_3O_2)_2,3H_2O$.
Compound 2. Surface 2—3 : $PbCl{\cdot}C_2H_3O_2,Pb(C_2H_3O_2)_2,\frac{1}{2}C_2H_4O_2$.
Compound 3. Surface 3—4 : $(PbCl{\cdot}C_2H_3O_2)_2,C_2H_4O_2$.
Compound 4. Surface 5 : $PbCl_2$.

The point representing the coexistence of 2, 3, and 4 lies at 1·44%$PbCl_2$,17·00%$Pb(C_2H_3O_2)_2$, and 32·82%$C_2H_4O_2$.

Compound 1.—At lower concentrations of acetic acid the solubility of lead acetate increases on addition of lead chloride. Fig. 3 shows that at higher concentrations of acetic acid just the opposite takes place, the solubility of lead acetate being diminished on addition of lead chloride.

Compound 2.—The solubility of this double compound increases

TABLE IV.

The System $Pb(C_2H_3O_2)_2$–$PbCl_2$–$C_2H_4O_2$–H_2O *at* 25°.

	Liquid.			Wet solid.		
No.	$PbCl_2$, %.	$PbAc_2$, %.	HAc, %.	$PbCl_2$, %.	$PbAc_2$, %.	HAc, %.
1	1·45	37·45	1·61	3·63	80·90	1·66
2	0·55	36·31	4·98	0·21	80·02	0·82
3	1·39	38·58	6·31	2·71	80·00	2·35
4	1·35	41·25	11·94	4·11	63·22	7·31
5	0·64	38·90	14·69	0·32	81·22	1·98
6	0·81	39·43	17·31	0·35	78·60	3·19
7	1·08	42·15	19·18	0·39	76·04	3·89
8	1·01	44·57	20·98	1·03	70·75	10·48
9	1·00	46·72	23·90	1·10	77·75	7·71
10	0·98	47·92	24·96	1·15	80·70	5·82
11	1·07	51·65	25·92	1·13	81·75	2·47
12	1·07	54·20	26·72	3·81	65·20	18·67
13	1·06	56·22	27·50	1·16	76·95	8·68
14	1·08	62·25	27·02	3·31	76·05	15·18
15	1·03	65·75	24·34	0·37	81·25	5·88
16	1·10	65·15	27·60	3·89	74·15	18·09
17	1·12	67·10	27·38	0·43	75·15	16·94
18	3·54	25·38	1·95	14·63	49·35	3·25
19	4·54	21·22	1·57	31·55	39·70	2·46
20	2·44	25·18	7·12	13·77	50·65	5·69
21	3·62	21·92	8·39	14·10	33·15	7·32
22	3·54	22·38	8·43	14·51	30·90	7·36
23	3·40	18·84	13·04	27·20	51·20	6·15
24	1·96	24·27	13·79	14·15	45·75	8·16
25	2·90	17·82	20·80	30·60	44·73	8·68
26	1·27	21·82	23·51	13·95	49·64	13·03
27	1·41	23·72	29·60	14·80	41·92	17·84
28	1·37	20·56	33·35	15·10	55·85	14·38
29	1·44	17·00	32·82	43·67	48·74	9·34
30	1·21	21·23	36·95	25·40	38·90	18·94
31	0·99	27·32	39·02	14·70	49·35	20·42
32	0·97	42·24	29·52	13·90	49·77	19·67
33	1·11	33·22	44·02	27·90	49·73	16·32
34	1·63	47·02	38·68	14·20	64·95	16·56
35	1·70	48·87	39·67	14·50	60·20	20·48
36	2·28	43·68	45·82	23·55	53·95	14·72
37	2·36	46·30	45·70	26·50	55·45	16·53
38	1·16	66·03	18·74	15·30	66·23	16·09
39	1·03	20·28	41·58	34·50	39·48	17·07
40	0·71	20·85	53·60	33·70	39·78	20·22
41	0·25	21·15	68·33	35·15	39·56	22·56
42	0·36	24·12	69·22	33·85	36·58	27·97
43	0·33	21·42	72·05	34·43	40·90	23·12
44	1·13	39·30	32·54	34·72	42·28	21·54
45	0·61	34·58	58·85	34·88	38·68	24·53
46	0·44	30·08	66·72	34·15	39·05	25·68
47	0·06	7·29	86·21	52·17	17·77	18·03
48	1·11	17·79	40·70	57·60	26·28	10·34
49	0·59	16·40	59·40	47·23	37·14	13·39
50	0·09	12·06	74·16	41·25	35·25	21·18
51	3·48	16·31	2·22	96·51	0·11	2·70
52	1·51	14·77	27·58	94·76	0·18	4·24
53	0·63	15·89	50·58	94·55	0·44	4·24
54	0·08	11·81	70·80	93·63	1·06	5·29

in just that same region where the solubility of lead acetate is subject to such a striking rise, and consequently the surface is twisted in a peculiar way, as shown in Fig. 3.

Compound 3.—This complex substance, which is sparingly soluble, is only stable over a certain range, for which the concentrations of acetic acid are high compared with those of lead acetate. At lower concentrations of acetic acid the compound becomes increasingly soluble and finally disappears as a solid through conversion into compound 2, whilst an addition of acetic acid is seen to diminish the solubility. The compound always separated as a finely divided powder, readily distinguishable from compound 2.

Compound 4.—The surface representing the solubility of lead chloride intersects the $PbCl_2$–$C_2H_4O_2$–H_2O triangle along a line corresponding to the values given in Table III. The solubility decreases on the first part of curve 3, but passes through a minimum at that point where the increase in the solubility of lead acetate occurs.

Both the type of double compound isolated and the corresponding solubility curves indicate a pronounced tendency of lead acetate to enter into reactions yielding various complex substances. The formation of the group $PbCl{\cdot}C_2H_3O_2$, involved in the two compounds, is well accounted for by the theory of Blomberg (*Chem. Weekblad*, 1914, **11**, 1030; *Z. Elektrochem.*, 1915, **21**, 438), in which the ion $Pb(C_2H_3O_2)^{\cdot}$ is supposed to play an important role (see Sandved, *loc. cit.*). This explanation is further supported by the parallelism between the solubility of lead acetate and of the double compound 2.

Summary.

The two systems $Pb(C_2H_3O_2)_2$–$PbCl_2$–H_2O and $PbCl_2$–$C_2H_4O_2$–H_2O have been studied at 25°, and the first also at 35°. Based upon these data, as well as upon the system $Pb(C_2H_3O_2)_2$–$C_2H_4O_2$–H_2O, an investigation of the quaternary system has been undertaken at 25°.

From the results, it is shown that the changes brought about by the introduction of lead chloride in these systems are in accord with the views upon lead acetate solutions advanced previously by the author.

The author's thanks are due to the Ramsay Memorial Fellowship Trust for placing a Fellowship at his disposal, and to Professor J. C. Philip, F.R.S., under whose interested direction this research was conducted.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, November 26th,* 1928.]