XCVII.—*Solubility of Lead Sulphate in Concentrated Solutions of Sodium and Potassium Acetates.*

By John Jacob Fox.

The investigation described in this paper was undertaken mainly with the object of ascertaining what changes, if any, take place in solid lead sulphate when brought into contact with aqueous solutions of sodium and potassium acetates; and, further, to what extent the solubility of the sulphate is influenced by increasing the concentration of the acetate.

Lead sulphate differs from the insoluble sulphates of barium, strontium, and calcium in the ease with which it may be dissolved in a variety of salt solutions. Of the three sulphates mentioned, calcium sulphate is the only one which can be dissolved by acetates to any degree comparable with that of lead sulphate, and it is also fairly readily soluble in ammonium sulphate; but as it is considerably more soluble in water than either barium, strontium, or lead sulphate, its increased solubility might be anticipated if we suppose that calcium acetate is formed, and that more sulphate is dissolved to restore the equilibrium of the solution. Such an explanation might, however, be equally applicable to barium and strontium sulphates, but breaks down, since these two are insoluble in aqueous ammonium acetate solutions.

A more probable explanation is the formation of complex ions (such as $Ca(NH_4)_n$), due to double salt formation. It has been shown that calcium sulphate dissolves in ammonium sulphate solution, and deposits crystals corresponding in composition with $Ca(NH_4)_2(SO_4)_2,2H_2O$ (Bell and Faber, *J. Physical Chem.*, 1907, **2**, 492). A similar observation has been made by the author in the case of the solubility of lead sulphate in ammonium acetate (Proc., 1907, **23**, 200). It was there shown that when the concentration of the ammonium acetate was about $3N$, crystals of ammonium lead sulphate, $Pb(NH_4)_2(SO_4)_2$, were deposited by the solution, the increase of solubility of the lead sulphate at the same time being most marked for stronger ammonium acetate. Now it is obvious that if some of the sulphate is deposited from the solution in the form of ammonium lead sulphate, whilst at the same time the solubility of the lead increases considerably, the equilibrium system cannot be one solely of the solubility of lead sulphate. In reality, it is an equilibrium system for the solubility of lead acetate or possibly ammonium lead acetate in the peculiar circumstances of having a solid phase or phases consisting of sulphates. The matter is still further complicated by the fact that lead sulphate is fairly soluble in ammonium sulphate. Since neither sodium nor potassium sulphate dissolves lead sulphate, it seemed possible that simpler systems would result from the investigation of the solubility in sodium and potassium acetates.

The only measurements of such solubilities made hitherto are those of Dibbits (*Zeitsch. anal. Chem.*, 1874, **13**, 139), and one experiment recorded by Noyes (*Amer. Chem. J.*, 1905, **27**, 747), who worked with solutions up to $0{\cdot}4$-N concentration. The formulæ deduced by Noyes from these dilute solutions do not apply to concentrated solutions.

The systematic determination of the solubility of lead sulphate in potassium and sodium acetates described below shows that the solubility increases regularly with increasing concentration of the acetates, but the increase of solubility is much greater than the corresponding increase in the concentration of the acetate. In other words, the solubility of the lead sulphate is not a linear function of the alkali acetate, and the nature of the curve suggests that the solubility of the lead is some function of the alkali acetate, involving powers higher than unity. Expressing the reaction by the equation:

$$PbSO_4 + 2RC_2H_3O_2 = R_2SO_4 + Pb(C_2H_3O_2)_2,$$

would give, as the simplest expression:

$$C_{PbSO_4} \times C^2{}_{Acetate} = k.C_{Sulphate} \times C_{Pb(C_2H_3O_2)_2}.$$

This expression would be modified by the decreased solubility of the alkali sulphate in the alkali acetate, evidence of which was obtained from the examination of the systems alkali acetate–alkali sulphate. However this might affect the main equation, the solubility expression would still include the square of the concentration of the alkali acetate, provided that the equation actually represents the reaction during dissolution. This matter was solved from the examination of the equilibria solutions for lead sulphate–potassium acetate. None of these solutions contained any sulphate, although the quantity of lead dissolved was fairly considerable, amounting in some cases to more than 19 per cent., calculated as lead acetate. It follows, therefore, that these solutions contained lead and potassium acetates only, and that the solubility of lead sulphate in potassium acetate is due exclusively to the formation of lead acetate and potassium sulphate.

The solid phase consists of lead potassium sulphate, which is practically insoluble as such in the acetate, careful tests showing that no lead acetate was present in the solid phase. The formation of the salt $PbK_2(SO_4)_2$ on mixing solutions of lead acetate and potassium sulphate may be accounted for by the preliminary formation of complex acetates, such as $PbK_2(C_2H_3O_2)_4$. This would then react with more potassium sulphate to give insoluble $PbK_2(SO_4)_2$. It is difficult otherwise to account for the uniform composition of the precipitate, even when an excess of potassium sulphate solution is used.*

The absence of sulphates in the equilibria solutions in the case of potassium acetate confirms Noyes's supposition that the solubility of lead sulphate is due to the formation of non-ionised lead acetate by metathesis, and it may not unreasonably be assumed that a similar explanation holds for both ammonium and sodium acetates.

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* Holmes and Sageman (Trans., 1907, **91**, 1611) conclude that potassium sulphate exists in solution as $(K_2SO_4)_2$. The formation of lead potassium sulphate would, on this view, take place thus:

$$Pb(C_2H_3O_2)_2 + (K_2SO_4)_2 = PbK_2(SO_4)_2 + 2C_2H_3O_2K.$$

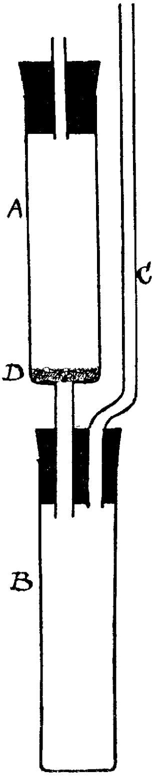
In the case of ammonium acetate, the formation of ammonium lead sulphate with the greater concentrations of acetate bears this out, but sodium acetate did not give rise to any double salt of this kind. In all the cases examined, the solid phases for the sodium acetate solutions consisted of lead sulphate. When the saturated solutions were separated from the solid and cooled, crystals of sodium sulphate decahydrate separated from the strongest solutions, pointing to the existence in the solution of lead acetate and sodium sulphate. The absence of the double salt in the solid phases in the sodium systems is especially interesting in view of the fact that the curve for the solubility of sodium sulphate in sodium acetate solutions is of an entirely different character from that of potassium sulphate in potassium acetate solutions. The amount of potassium sulphate which can be dissolved in potassium acetate solutions of increasing concentration reaches a point, in the stronger solutions, where it is far less than the equivalent quantity of lead dissolved in the acetates. But with sodium acetate the smallest amount of sodium sulphate found was 14·4 mols. per 1000 mols. of water; and this quantity is greater than any of the quantities of lead which could be dissolved in the acetate solutions. Consequently the sodium acetate–lead sulphate equilibrium solutions are never saturated as regards sodium sulphate, which therefore does not appear in the solid phases either alone or as double salt with lead sulphate.

EXPERIMENTAL.

The solubility determinations were carried out at a temperature of 25° ± 0·1°. In some cases dissolution was effected by shaking the lead sulphate in a well-stoppered bottle half filled with the cold solution, and completely immersed in the thermostat. In other cases, saturation was obtained by heating the solution in presence of excess of the solid at a higher temperature and placing the vessel in the thermostat at 25°, the solution being well shaken from time to time and then allowed to settle. The apparatus shown in Fig. 1 was used to obtain saturated solutions without stirring or shaking.

A tube about four inches in length and one inch in diameter, *A*, was drawn out as shown, and fitted by a rubber stopper into tube *B*, an air vent, *C*, being provided. The tube *A* was plugged with asbestos at *D*, and the solid was placed on the asbestos. The solvent was poured into *A*, and allowed to percolate slowly into *B*, which also contained some solid. After all the liquid had passed into *B*, it was transferred to *A* again. The whole apparatus was immersed in the thermostat as far as the stopper of *A*. The percolation was continued until the density of the solution became constant, the density being determined in a Meyerhoffer pipette (*Zeitsch. physikal. Chem.*, 1899, **28**, 466). In many cases, saturation was complete in a few hours, especially when the solid phase suffered no change. When, however, the solid altered, considerably longer periods were required, and in a few cases, more especially with the more concentrated solutions, two or three days were found to be necessary before the density of the solution became constant.

FIG. 1.



A point of some importance arose in connexion with the distilled water used. In one case ordinary distilled water, which had been boiled to expel dissolved gases, gave a solution of which the density was 1·16421. A similar experiment was carried out, except that the distilled water was prepared in a platinum still and condenser and collected in a well steamed-out Jena flask. The density of the resulting solution in this case was 1·16431. The difference is very small. In all the subsequent experiments distilled water, which had been previously boiled, was used. Although water of this kind is unsuitable for very dilute solutions, it is apparently sufficiently satisfactory for concentrated solutions.

The lead sulphate was prepared by treatment of a solution of lead acetate with sulphuric acid, the precipitate being washed with diluted sulphuric acid and finally with a little water; it was then dried, gently ignited, and powdered. Prepared in this way, one gram of the solid gave no alteration in weight on evaporation to dryness with sulphuric acid and gentle ignition.

For convenience of reference the solubilities in potassium and sodium acetates are treated separately.

Solubility of Lead Sulphate in Potassium Acetate Solutions at 25°.

The potassium acetate was prepared by treatment of potassium hydrogen carbonate with slightly diluted glacial acetic acid, in the proper proportion. The solution so obtained was evaporated to small bulk to expel carbon dioxide and diluted as required. It was usually found to be slightly acid to phenolphthalein, and the requisite quantity of potassium hydroxide solution (freed from impurities by alcohol) was added to yield a neutral solution. A less troublesome method was the use of pure potassium acetate, tested before use as to its neutrality to phenolphthalein and for impurities.

About 25 c.c. of potassium acetate solution were agitated for several days with excess of lead sulphate, the prolonged agitation being essential, since the preliminary dissolution of the lead sulphate which must take place is slow on account of the difficulty in dissolving sulphate in potassium acetate. When the saturation point is approached from a higher temperature, the liquid with the solid must be thoroughly agitated in the thermostat. Lead potassium sulphate is so little soluble in potassium lead acetate solutions that prolonged shaking is necessary to ensure equilibrium.

The composition of the solutions was ascertained by determining the proportions of lead and potassium, the precipitated sulphate being boiled for some time with diluted sulphuric acid in order to decompose any potassium lead sulphate which might be formed. A portion of the solutions was acidified with hydrochloric acid, raised to the boiling point to dissolve lead chloride, and treated with barium chloride solution. As no precipitate of barium sulphate formed even after long boiling, it was thought possible that complex acetosulphates might be formed, or that the inability to form sulphions might prevent the precipitation of barium sulphate, similar to the prevention of the precipitation of silver chloride from mercury solutions, described by Hewitt (Proc., 1907, **23**, 10).

A test was therefore made with lead sulphate and potassium acetate solution in large excess to ascertain whether the sulphate could be estimated under these conditions. 0·4272 Gram of lead sulphate was treated with 50 c.c. of potassium acetate solution; hydrochloric acid was added, and the whole was boiled until a clear solution resulted. The conditions are then similar to those

Composition of Saturated Solutions of System $KC_2H_3O_2 - Pb(C_2H_3O_2)_2$ *in Solution; Solid Phases,* $PbSO_4$ *and* $PbK_2(SO_4)_2$, *at* 25°.

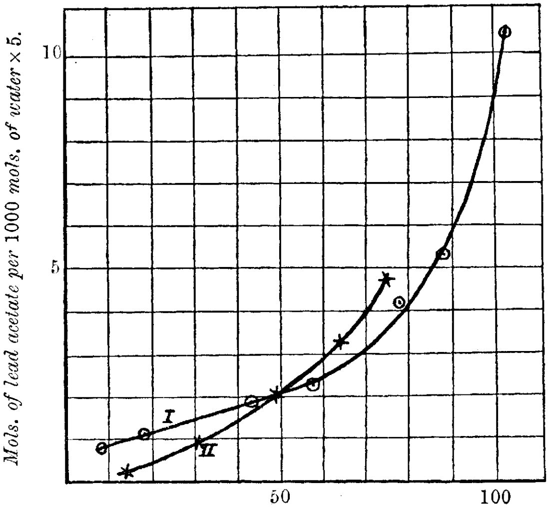
	Percentage.			Molecules per 1000 molecules H_2O.	
	Potassium acetate.	Lead acetate.	Water.	Potassium acetate.	Lead acetate.
1	4·33	2·54	93·13	8·53	1·51
2	9·03	3·55	87·42	18·95	2·25
3	17·81	5·43	76·76	42·57	3·92
4	22·07	5·95	71·98	56·27	4·58
5	26·58	9·83	63·59	76·69	8·57
6	28·82	11·40	59·78	88·45	10·57
7	28·93	19·41	51·66	102·80	20·82

which occur on attempting to estimate the sulphate, if present, in the actual solubility experiments. Barium chloride produced an immediate precipitate, which gave 0·3165 $BaSO_4$, equivalent to 0·4286 $PbSO_4$.

The results are plotted in Fig. 2, curve I, the curve being regular. The abscissæ are molecules of potassium acetate, and the scale of the ordinates is five times that of the abscissæ, the enlarged scale of the ordinates exaggerating the errors in the determinations.

The solid phases consisted of sulphates only, and were anhydrous, containing traces of adherent moisture only. The following are the results for the solids in two cases:

FIG. 2.



Mols. of alkali acetate per 1000 *mols. of water.*

I. *Solubility of lead sulphate in potassium acetate.*
II. ,, ,, *sodium acetate.*

0·9792 gave 0·6348 $PbSO_4$ = 64·83.
0·8668 ,, 0·6512 $PbSO_4$ = 75·13 per cent.

In neither case was there any alteration of weight on evaporation with sulphuric acid.

The double salt, potassium lead sulphate, was prepared by mixing a solution of lead acetate with a solution of potassium sulphate, having the lead acetate in excess. The solutions were well shaken for some time, and the solid collected, washed two or three times with a solution of potassium acetate, and finally with a little alcohol. The air-dried product, which is amorphous, gave on analysis the following results:

0·6482 gave 0·4108 $PbSO_4$ and 0·2370 K_2SO_4.

$PbSO_4$ = 63·38; K_2SO_4 = 36·36.

$PbK_2(SO_4)_2$ requires $PbSO_4$ = 63·48; K_2SO_4 = 36·52 per cent.

The same compound is formed when the amount of lead sulphate shaken with potassium acetate solution is not present in excess.

System: Potassium Acetate (Solution)–Potassium Sulphate at 25°.

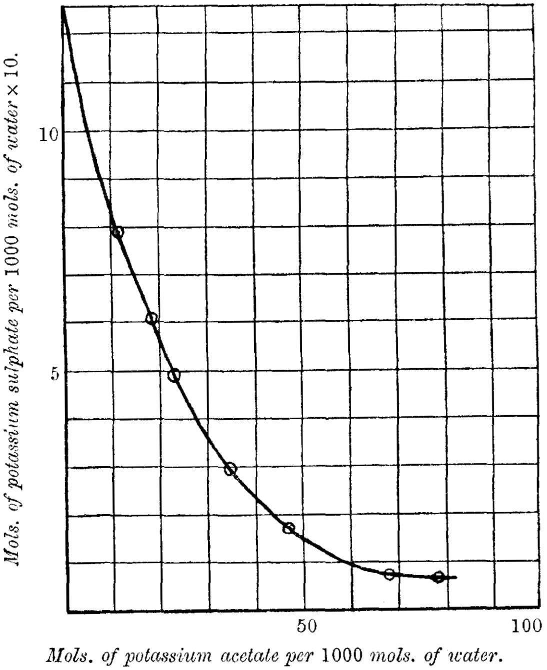
This system was investigated to ascertain the influence on the solubility of potassium sulphate of the increased concentration of the potassium acetate, for since potassium sulphate can be formed from the lead sulphate by metathesis, it seemed desirable to determine the extent to which it could remain dissolved. On mixing a saturated aqueous solution of potassium sulphate with a concentrated solution of potassium acetate, an immediate precipitate of potassium sulphate formed, so that obviously potassium sulphate is less soluble in potassium acetate solution than in water. The solutions for investigating this system were obtained by shaking with excess of solid potassium sulphate or by heating potassium acetate solution with potassium sulphate in a water-bath and allowing to cool in the thermostat, shaking frequently. The analysis of the saturated solutions presented no difficulty; but it was necessary to boil the precipitated barium sulphate for several hours to remove all the potassium chloride, barium sulphate having a tendency to retain sodium and potassium unless this is done.

Composition of the Solutions.

	Percentage.			Molecules of salt per 1000 molecules H_2O.	
	Potassium acetate.	Potassium sulphate.	Water.	Potassium acetate.	Potassium sulphate.
1	6·11	6·65	87·24	12·85	7·87
2	8·68	5·09	86·23	18·47	6·10
3	11·29	3·99	84·72	24·45	4·86
4	15·59	2·35	82·06	34·78	2·96
5	20·12	1·23	78·65	46·90	1·62
6	29·95	0·39	69·66	79·00	0·58

These results give a regular curve (Fig. 3), the scale for potassium sulphate being five times that of potassium acetate. The solubility of potassium sulphate in water is 10·75 per cent. (Seidell, *Solubilities of Inorganic and Organic Substances*), which is equivalent to 12·47 molecules of potassium sulphate per 1000 molecules of water. If the curve is produced it will be found to pass almost through the point on the ordinate corresponding with the solubility of potassium sulphate in water. The striking feature of this system is the rapid decrease in the solubility of potassium sulphate with increasing concentration of the acetate. To a certain extent the absence of sulphate in the liquid of the systems $[KC_2H_3O_2 + Pb(C_2H_3O_2)_2] - [PbSO_4 + PbK_2(SO_4)_2]$ is no doubt connected with the marked decrease of solubility of the sulphate in the potassium acetate. The solid phase in the system potassium acetate–potassium sulphate was found to consist of potassium sulphate containing a little adhering solvent.

FIG. 3.



It has already been shown that the solubility of lead sulphate in potassium acetate is due to the formation of lead acetate, the solubility being influenced in all probability by the solid sulphate phases. Whether the sulphates exerted any influence could be ascertained by determining the solubility of lead acetate in potassium acetate solutions. One or two such saturated solutions were obtained by using lead acetate, $Pb(C_2H_3O_2)_2,3H_2O$, with potassium acetate solutions. The solubility in water alone was determined, and found to be 35·9 per cent. of lead acetate (anhydrous).

Composition of the Solutions.

	Percentage.			Molecules per 1000 molecules H_2O.	
	Potassium acetate.	Lead acetate.	Water.	Potassium acetate.	Lead acetate.
1	13·87	38·05	48·06	52·97	43·90
2	15·40	36·91	47·69	59·25	42·88
3	0	35·90	64·10	0	31·03

A crystalline solid separated from the solutions on cooling, and was found to correspond with $Pb(C_2H_3O_2)_2,3H_2O$. The solubility of lead acetate in potassium acetate is seen to be greater than in water. These solubilities are not very different as percentages, but, expressed on the basis of a fixed quantity of water, the difference becomes marked.

If lead acetate in solutions gave rise to ions, the addition of potassium acetate, which is partly electrolytically dissociated, should result in a lowering of the solubility of lead acetate. Since, however, the solubility increases, the conclusion that lead acetate gives no ions receives additional support.

The ratio $C_2H_3O_2K/Pb(C_2H_3O_2)_2$ in this system is less than in the system potassium acetate–lead sulphate, the concentration of the lead being much less in the latter system. The difference must be ascribed to the presence of the sulphate solid phases, the tendency of which would be to lower the solubility of the lead.

Solubility of Lead Sulphate in Sodium Acetate Solutions at 25°.

The sodium acetate solutions were prepared from sodium hydrogen carbonate and acetic acid, as in the case of potassium acetate, or by using recrystallised sodium acetate. The analyses were conducted as in the previous cases, but as the solutions contained sulphate it was necessary to determine this constituent. In all the cases examined, the proportion of sulphate in solution corresponded with the amount of lead present, but was calculated to sodium sulphate, since sodium sulphate decahydrate crystallised from the solutions on cooling.

Composition of the Solutions.

	Percentage.				Molecules per 1000 molecules H_2O.		
	Sodium acetate.	Lead acetate.	Sodium sulphate.	Water.	Sodium acetate.	Lead acetate.	Sodium sulphate.
1	6·69	0·78	0·34 (0·38)	92·19	15·92	0·47	0·47
2	11·76	2·73	1·26 (1·26)	84·25	30·62	1·80	1·80
3	16·90	5·70	2·49 (2·58)	74·91	49·49	4·22	4·22
4	19·92	8·24	3·60 (3·70)	68·24	64·03	6·69	6·69
5	21·51	10·75	4·68 (4·77)	63·10	74·78	9·41	9·41
6	6·95	0·81	0·35 —	91·90	—	—	—

The figures in brackets are calculated from the barium sulphate obtained. The form of the curve (Fig. 2, curve II) somewhat resembles the curve for the solubility of lead sulphate in potassium acetate, the scale of ordinates being five times that of the abscissæ.

The fact that the amount of sulphate in solution is equivalent to the amount of lead necessitates that the solid phase should remain as lead sulphate, and this was found to be the case, the separated solid containing very small amounts of sodium salts and acetates due to the adhering solvent. No double salt of lead and sodium was obtained.

System: Sodium Acetate (Solution)–Sodium Sulphate Decahydrate at 25°.

This system was investigated similarly to the corresponding potassium salts, but some difficulty was experienced in obtaining representative portions of the liquid at 25°, owing to the tendency of the sodium sulphate to crystallise when the solution cooled slightly. The temperature-coefficient for the solubility of sodium sulphate in water in the neighbourhood of 25° is large (about 1·3 per cent.), and this renders it rather difficult to work with clear solutions.

Composition of the Solutions.

	Percentage.			Molecules per 1000 molecules H_2O.	
	Sodium acetate.	Sodium sulphate.	Water.	Sodium acetate.	Sodium sulphate.
1	0	21·9	78·1	0	35·5
2	4·10	17·72	78·18	11·5	28·7
3	7·71	16·48	75·81	22·3	27·5
4	12·58	13·50	73·92	37·4	23·1
5	16·26	11·50	72·24	49·4	20·2
6	20·63	8·10	71·27	63·5	14·4

The solubility of sodium sulphate decahydrate in water is taken from Seidell's *Solubilities of Inorganic and Organic Compounds.* It will be seen that the curve, ordinates and abscissæ being drawn to the same scale (Fig. 4), is nearly a straight line. In this respect the solubility of sodium sulphate is entirely different from that of potassium sulphate in potassium acetate, and largely explains the inability of sodium sulphate to form a double sulphate with lead.

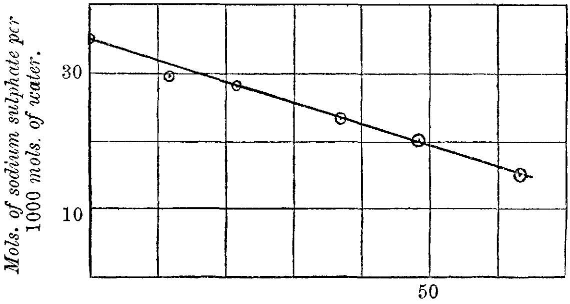
The solid phase in the system sodium acetate–sodium sulphate decahydrate consisted wholly of sodium sulphate decahydrate, which formed in large crystals on cooling.

One saturated solution of lead acetate in sodium acetate was prepared, with the following results:

12·58 per cent. of sodium acetate, 32·40 per cent. of lead acetate, and 55·02 per cent. of water; corresponding with 50·2 molecules of sodium acetate and 32·6 molecules of lead acetate per 1000 molecules of water.

The ratio sodium acetate/lead acetate is of the same order of magnitude as the ratio potassium acetate/lead acetate found before, and although one solubility only is here determined, it points to the conclusion that the reason for the solubilities of lead sulphate in the two acetates is the same despite the differences in the solid phases, namely, the formation of lead acetate in solution.

FIG. 4.



Mols. of sodium acetate per 1000 *mols. of water.*

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