My thanks are due to Professors P. C. Ray and J. B. Bhaduri for their encouragement in carrying on the above investigation.

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EQUILIBRIUM IN THE SYSTEM: LEAD ACETATE, LEAD OXIDE, WATER, AT 25°.

BY RICHARD F. JACKSON.

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The basic acetates of lead owe a considerable importance in applied chemistry to the fact that, for a large class of crude substances, they are the most effective and most convenient clarifying agents known. In the analysis of crude saccharine products the question of clarification is assuming an ever-increasing importance, as the sugar analysis approaches a continually higher precision. In order that further advances may rest upon a firm basis, it seems highly advisable that in place of acquiring more empirical data on the crude products themselves, we turn our attention to some of the more fundamental problems involved. The present work was undertaken in order to contribute to our very meager knowledge of the basic acetates themselves and their behavior in aqueous solution. Its application to the complicated problem of sugar clarification will form the subject of a special investigation.

A glance into the history of the study of this problem reveals the fact that while a number of compounds have been reported, no work has been done in the light of modern knowledge. Much of the work which has hitherto been accepted was done under assumptions which we now know to be radically erroneous. As an instance of this the work of Löwe[1] may be cited. This investigator boiled lead oxide and lead acetate for an arbitrary length of time and, upon obtaining a solution and a residue, he assumed that each represented a compound. In order to identify these compounds he used them to precipitate the insoluble basic nitrate of lead, which was then recrystallized before analysis. Its analysis was assumed to indicate the proportion of basic to neutral lead in the original compound. The conclusions based upon this procedure must be considered invalid.

In other instances investigators have attempted to isolate and purify the basic compounds and have reported the formulas on the basis of the direct analysis of these substances. In most cases the substance obtained must have been heterogeneous. Indeed, as will appear from the present work, it is almost, if not quite, impossible to isolate at least one of the basic compounds, while the danger of obtaining a mixture is so great that it makes this method of investigation unreliable.

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[1] *J. prakt. Chem.*, 98, 385 (1886).

The following compounds have been reported:

$Pb(C_2H_3O_2)_2.5PbO$[1]
$Pb(C_2H_3O_2)_2.2PbO$[2]
$Pb(C_2H_3O_2)_2.PbO$[3]
$3Pb(C_2H_3O_2)_2.2PbO$[4]
$2Pb(C_2H_3O_2)_2.PbO.H_2O$[5]

The U. S. Pharmacopoeia states that neutral lead acetate is soluble in two parts of water at 25°. Other than this, no measurement of the solubility of neutral or basic lead acetate has been made.

The present work has been intended to show what compounds exist and what are the limits of stability of each. For this purpose the problem was attacked from the standpoint of the Phase Rule.

Preparation of Reagents.

Lead Acetate.—Lead acetate, C. P., from Baker & Adamson, was recrystallized once from distilled water containing a slight excess of acetic acid. Two samples were tested by separating the lead quantitatively as sulfate and sulfide, respectively. The filtrate in each case yielded no significant residue.

Lead Hydroxide.—Recrystallized lead acetate was dissolved in water free from carbonic acid. A small quantity of this solution was added to a caustic alkali solution and the mixture allowed to stand several days to permit lead carbonate to settle. The solution was then filtered rapidly through asbestos and mixed with the remaining lead acetate solution. The lead hydroxide precipitate was thrown on a filter and washed with water free from carbon dioxide until free from sodium salts. The content of lead oxide was determined by ignition of a small sample. This procedure could not have accomplished the complete elimination of carbonate, but a few experiments showed that the presence of even a considerable amount of carbonate was without influence on the equilibrium.

Acetic Acid.—The C. P. reagent of commerce was redistilled and the middle portion of the distillate reserved for use.

Analytical Procedure.

The analytical processes were required to yield the percentages of neutral lead acetate and of basic lead present in the sample. These data were obtained by measuring the quantity of standard acid neutralized by the basic lead and the quantity of reagent required for the complete precipitation of lead. Two methods of estimation of total lead were utilized,

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[1] Wittstein and Kühn, *Büchner's Rep.*, 84, 181.

[2] Löwe, *Loc. cit.*; Pelouse, *Ann.*, 42, 206 (1842).

[3] Löwe, *Loc. cit.*

[4] "Brown's Handbook of Sugar Analysis," p. 207.

[5] Stolle, "Handbuch für Zuckerfabriks Chemiker," p. 527; Wöhler, *Ann.*, **29**, 63 (1839).

namely, precipitation by normal sulfuric acid[1] and precipitation by one-third normal sodium oxalate,[2]

To the weighed sample, in a 500 cc. volumetric flask, a slight excess of normal acetic acid was measured from a pipet. In the sulfate method the solution was diluted and sufficient normal sulfuric acid added for complete precipitation. The solution was made up to the calibration mark with water free from carbon dioxide, mixed and allowed to remain over night. Since the total precipitate of lead sulfate amounted to more than 15 grams, the quantity remaining in solution in the presence of the excess sulfuric acid was too small to be significant. Four 100 cc. aliquot portions of the clear supernatant liquid were drawn off in a pipet. Duplicate titrations were made with standard alkali to determine the excess of acid. The alkali was a solution of sodium hydroxide containing a little barium hydroxide. Phenolphthalein was used as an indicator. In the remaining two portions the excess of sulfuric acid was determined by precipitation with barium chloride. In this precipitation the precautions recommended by Allen and Johnson[3] were observed.

In the oxalate method the acetic acid was added in the same manner. An excess of third normal sodium oxalate was measured in and the solution made to volume, mixed, and allowed to settle. The aliquot portions of the supernatant liquid were titrated for free acetic acid with normal alkali and for excess of oxalate with potassium permanganate.[4] This method, on account of its greater convenience, was the main reliance. The two methods proved to be equally trustworthy. The lead oxalate is much less soluble than lead sulfate. The presence of the slight quantity of acetic acid did not appear to increase the solubility appreciably. The acetic acid was without influence upon the permanganate titration, provided it was purified by redistillation.

The volume of the precipitate was computed in every instance and deducted from the calibrated volume of the flask. For this purpose the data of Schröder[5] for the density of precipitated lead sulfate are available, but no data exist on that of lead oxalate. Consequently this was determined. The precipitated oxalate was washed by decantation and transferred to a calibrated pycnometer. The pycnometer was nearly filled with water, which was then brought to boiling in a vacuum to remove air. After adjustment and weighing, the contents of the pycnometer were transferred to a Gooch crucible and the weight of the dry precipitate

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[1] Fresenius-Cohn, "Quantitative Chemical Analysis," Vol. II, p. 599 (1904).

[2] Mohr's "Lehrbuch der Chemisch-Analytischen Titrirmethoden," 7th Aufl., p. 798; Sutton, "Volumetric Analysis," 10th ed., p. 245.

[3] THIS JOURNAL, 32, 588 (1910).

[4] The procedure was that recommended by McBride, *Bull. Bur. Standards*, 8, 611 (1912); THIS JOURNAL, 34, 393 (1912).

[5] *Pogg. Ann*, Erg., Bd. 6, 622 (1874).

was determined. From the data obtained the density of lead oxalate was found to be 5.28. In computing the total excess of reagent from the aliquot titer, the latter was multiplied by the ratio of the true volume of the solution to the actual volume delivered by the pipet.

Inasmuch as the computation of results was troublesome until it was condensed to routine, it is considered advisable to illustrate, by specific instance, the final method used.

Total normal acid added	58.37	
Excess of acid, by alkali titration	17.26	
Normal acid equivalent to basic lead	41.11	
$\text{PbO} = \frac{41.11 \times {}^1/_2 \text{ M. W. PbO}}{\text{Wt. of sample (28.86 g.)}}$		15.89%
Total $N/3$ oxalate added	400.32	
Excess oxalate by permanganate titration	16.36	
Oxalate equivalent to total lead	383.96	
Ditto in normal solution	127.99	
Total lead equivalent minus basic lead equivalent 127.99—41.11 =	86.88	
$\text{Pb(C}_2\text{H}_3\text{O}_2)_2 \text{ present} = \frac{\cdot 86.88 \times {}^1/_2 \text{ M. W. Pb(C}_2\text{H}_3\text{O}_2)_2}{\text{Wt. sample (28.86)}} =$		48.95%

The computation from the analysis as sulfate was similar, the total added acid being the sum of the acetic and sulfuric acids.

Synthesis of Basic Acetates.

The usual methods of preparing the basic lead acetates have consisted of boiling the neutral acetate with varying quantities of lead oxide. In the present work the compounds were made by the interaction of the neutral acetate and a suspension of lead hydroxide. These reactions were in many cases very striking and, in contrast to the long period of boiling required in the case of the oxide, they occurred with great rapidity.

A few instances will illustrate these phenomena:

In the preliminary work before the saturation curves had been located, a synthetic mixture was made up of about the composition 20% PbO and 15% $\text{Pb(C}_2\text{H}_3\text{O}_2)_2$. The hydroxide was added in the form of a suspension in water. On shaking up the mixture there was an immediate solution, with the exception of a slight turbidity. Then after a few minutes the entire solution stiffened to a solid mass. This was due to the crystallization of $\text{Pb(C}_2\text{H}_3\text{O}_2)_2.2\text{PbO}.4\text{H}_2\text{O}$.

Another synthetic mixture was made up of composition 20% PbO, 53% $\text{Pb(C}_2\text{H}_3\text{O}_2)_2$. In order to prepare a mixture containing little enough water it was necessary to dry both the neutral acetate crystals and the hydroxide suspension, the latter to a stiff paste, in a desiccator. On weighing out the components into a bottle the unmixed mass had the appearance of nearly dry solid material. After a few seconds' vigorous shaking the reaction occurred rapidly and the whole mass was transformed into a mobile liquid. At the same time there occurred a very considerable absorption of heat.

The Establishment and the Determination of the Equilibria.

The equilibria were established in long narrow flasks of thin glass which were agitated in a motor-driven rotating frame under the water

SUMMARY OF DATA.

Expt. No.	Solution.		Residue		Solid phase.	Density of solution. $D_{25/4}$.	Refractive index. n_D.
	PbO.	$Pb(C_2H_3O_2)_2$.	PbO.	$Pb(C_2H_3O_2)_2$.			
1.....	−0.27[1]	35.19			$Pb(C_2H_3O_2)_2$ $3H_2O$	1.326	
2.....	+0.10	35.60				1.334	1.380
3.....	1.01	37.14				1.367	
4.....	3.38	38.93				1.422	
5.....	6.01	41.95	2.85	64.34		1.531	
6.....	9.47	44.71				1.658	
7.....	14.22	47.88	9.44	60.68			
8.....	14.44	47.92				1.852	
9.....	15.89	48.95	14.10	60.99	Transition		1.456
10.....	15.90	48.42	16.68	58.84	$3Pb(C_2H_3O_2)_2$ PbO $3H_2O$	1.930	1.456
11.....	16.25	48.85	16.63	55.52		1.942	1.4605
12.....	16.29	48.87				1.941	
13.....	16.65	49.04				1.956	
14.....	18.83	48.71	18.61	58.98		2.024	1.467
15.....	22.23	48.52	20.50	60.05		2.161	1.4845
16.....	22.94	48.96	21.72	57.06		2.193	1.491
17.....	23.28	49.14	21.81	57.05			
18.....	23.53	49.01				2.220	
19.....	24.71	49.22	26.02	52.90	Transition	2.282	1.502
20.....	24.77	49.20	27.44	52.12	Transition	2.279	1.501
21.....	23.59	43.17			$Pb(C_2H_3O_2)_2$ 2PbO $4H_2O$	2.048	1.469
22.....	22.78	40.78	29.14	40.39		1.951	
23.....	19.63	31.40	25.14	32.60		1.657	
24.....	18.73	29.63				1.599	1.409
25.....	14.62	20.96	35.00	30.49		1.382	1.379
26.....	13.41	19.65				1.348	
27.....	10.66	12.99				1.229	
28.....	8.47	8.64				1.157	
29.....	8.08	8.07					
30.....	7.84	5.36					
31.....	7.87	5.27				1.119	
32.....	7.79	5.25				1.117	1.344
33.....	7.17	4.71			$Pb(OH)_2$		
34.....	6.84	4.31				1.100	1.343
35.....	6.54	4.25	68.60	1.39		1.095	
36.....	5.91	3.82				1.085	1.340
37.....	5.29	3.40				1.075	
38.....	0.20	0.11					

[1] Acidity expressed in terms of PbO.

of a thermostat for at least 48 hours. The temperature of the bath was constant to about 0.01°. All experiments were made at 25.00°. In order to determine with certainty whether equilibrium was reached in 48 hours, the time of agitation in a number of experiments was increased by varying amounts. In these instances practically identical results within the error of experiment were obtained. See Experiments 7 and 8, 11 and 12, 19 and 20, 31 and 32. Moreover, in general, the times of agitation were very varied, never less than 48 hours, frequently as long as seven days. The fact that smooth curves were obtained is further evidence that equilibrium was attained.

After the mixture had reached equilibrium the flask was placed in a rack in the thermostat to permit the solid phase to separate. In taking the sample the solution was drawn up into a pipet and a measured volume delivered into a weighed 500 cc. volumetric flask. The flask and substance were then weighed. This procedure gave the weight of the sample and, as the subsequent treatment was in the same flask, no further transfer of material was necessary. A knowledge of the volume and weight of the solution permitted a calculation of the density. The values to three decimals are given in the summary of data.

In studying the solid phase the indirect method of Schreinemakers[1] was employed. The supernatant solution was decanted and a portion of the solid with the adhering mother liquor shaken into the volumetric flask for analysis.

The Solid Phases.

As a study of the diagram, Fig. 1, will reveal, there are four solid phases which can exist in equilibrium with aqueous solutions of the two solid components.

The neutral lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$, consists of brilliant monoclinic prisms. It can exist in equilibrium with an aqueous solution containing dissolved substance of its own composition. It is also capable of existence in equilibrium with solutions containing as much as 15.9% basic lead, estimated as oxide. Its saturation curve is continuous with one extending into acid solutions.

The tetra-lead-monoxy-hexacetate,[2] $3Pb(C_2H_3O_2)_2.PbO.3H_2O$, consists of perfectly formed needles which may attain the length of 5 mm., but usually appear as small, lustrous, silky crystals whose form is difficult to recognize. It is exceedingly soluble in water and forms solutions of density, 1.93 to 2.28. It cannot exist in equilibrium with aqueous solutions of itself, but depends upon an excess of dissolved basic lead.

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[1] *Z. physik. Chem.*, **11**, 76; Bancroft, *J. Phys. Chem.*, **6**, 179; Findlay, "Phase Rule," 3rd ed., p. 305.

[2] For nomenclature see Hoffman, "Dictionary of Inorganic Compounds," Vol. I, p. 44.

On account of the small size and softness of the crystals, and the high density and viscosity of the mother liquor, it is practically impossible to isolate in pure form. It is probable that these experimental difficulties are responsible for the fact that its composition has not previously been correctly ascertained. To establish the formula of this compound six lines were determined. These gave rise to a large number of intersections, of which ten were at sufficiently large angle to be considered representative of the solid phase. The mean of these ten was the accepted value.

Calc. for $3Pb(C_2H_3O_2)_2.PbO.3H_2O$: $Pb(C_2H_3O_2)_2$, 77.9; H_2O, 4.3; found: 77.9 and 4.2.

The apparent precision of the accepted value is somewhat deceptive, as the individual determinations are slightly scattering.

The tri-lead-dioxy-diacetate, $Pb(C_2H_3O_2)_2.2PbO.4H_2O$, has been isolated previously and its formula, with respect to the two solid components, correctly ascertained. It has been hitherto described as an amorphous solid and, in fact, as it usually occurs, it has that appearance. Nevertheless, by slow evaporation of its clear solution it can be obtained in small, rather ill-formed, needles which leave no doubt of its crystalline character. Its saturation curve has a very great length, extending from 13% to 74% of dissolved substance. It is stable in contact with aqueous solutions of itself.

Calc. for $Pb(C_2H_3O_2)_2.2PbO.4H_2O$: PbO, 52.9; H_2O, 8.55; found: 52.5 and 8.6.

Lead hydroxide, $Pb(OH)_2$, is in equilibrium with solutions containing less than 4.8% of lead acetate.

The Quadruple Points.

At 25° there are three sharply defined quadruple points. The transition mixture at B was obtained by approaching it with successive additions of neutral acetate to the solution of the monoxy-acetate.

The transition mixture at C was reached in two separate experiments, one a new synthetic mixture which was filtered and allowed to concentrate in a desiccator, the other a mixture formed by addition of neutral lead acetate to a solution which was on the saturation curve CD. The solutions proved to be of identical composition; while the solid phases, as shown by the arrows, were mixtures in different proportions of the two solid phases in equilibrium with the two intersecting saturation curves.

At the point D, the dioxy-acetate and lead hydroxide can exist in contact with the same solution.

The Saturation Curves.

The saturation curves in equilibrium with the four respective solid phases are in some respects noteworthy. The curve AB, representing the solubility of neutral lead acetate in basic solutions, shows a remarkably high rate of increase of solubility of the solid phase. In order to cause such a rise in solubility there must occur a more deep-seated change in the solution than the mere admixture of two solutes. The curve is slightly convex toward the solid phase. The curve BC is approximately a straight line. The solution contains a nearly constant quantity of lead acetate with varying lead oxide content. Since the dioxy-acetate has a low temperature coefficient of solubility and the neutral acetate a high one it is conceivable that at some temperature in the neighborhood of 0° this small curve would be squeezed out of existence. At such temperature we should have three solid phases in equilibrium with the same solution and vapor and hence a nonvariant point. The curve CD in equilibrium with the dioxy-acetate shows again the great effect upon the solubility which a relatively slight change in the ratio of basic to neutral lead exerts. It is slightly concave toward the solid phase. The curve DE is practically linear.

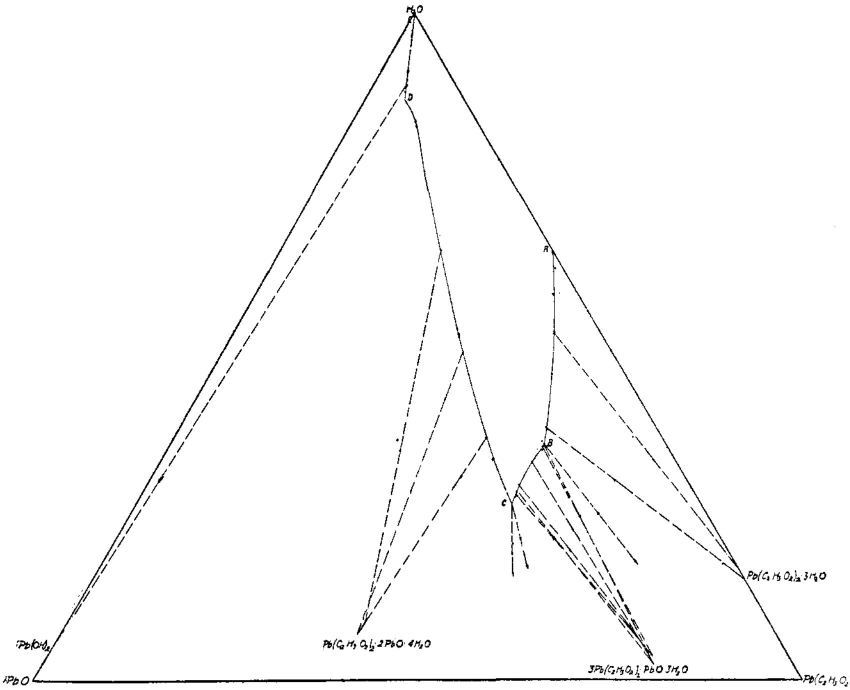

Fig. 1.—Isothermal equilibrium at 25°. The curves AB, BC, CD and DE represent the composition of the solution in equilibrium with the respective solid phases. The area ABCDE encloses the region of unsaturated solutions. Note the great increase of solubility of the neutral acetate in basic solutions, the high solubility and limited range of stability of the monoxy-acetate, and the very great range of stability of the dioxy-acetate. The data are computed with respect to weight per cent.

The plot, Fig. 1, was constructed with reference only to weight percentages. If the data are plotted in molecular percentages, a diagram of the same general form results, but of very much diminished area. On account of the high molecular weight of the lead compounds the molecular percentages become very low.

A study of the purely chemical equilibria enables us to understand some of the changes which occur in the solution and thus to predict, in some measure, the course of the saturation curves.

Starting at the point A of the diagram, we find neutral lead acetate crystals in equilibrium with a solution of neutral lead acetate. We may suppose that the first equilibrium is between whole molecules thus:

$$(1)\quad \overset{\text{solid}}{Pb(C_2H_3O_2)_2} \quad \rightleftarrows \quad \overset{\text{molecules in solution}}{Pb(C_2H_3O_2)_2}$$

neglecting the water of hydration.

Undoubtedly the dissolved salt is then to some extent both ionized and hydrolyzed. However, it must be equilibrium (1) which determines the solubility of the crystals and the constant of that equilibrium must be maintained whatever subsequent reactions occur.[1]

Upon addition of lead hydroxide the first basic acetate which makes its appearance has the formula $3Pb(C_2H_3O_2)_2.PbO.3H_2O$. The solution does not become saturated with respect to the solid phase until about 15% of lead oxide is dissolved. Here again, an equilibrium between whole molecules of solid and dissolved basic acetate must exist. The solution represented by the saturation curve AB of the neutral acetate must also contain this same molecular species although in a state of unsaturation. There must then be in the solution an equilibrium between the dissolved molecules of neutral acetate and those of the monoxy-acetate thus:

$$(2)\quad 3Pb(C_2H_3O_2)_2 + PbO \rightleftarrows [Pb(C_2H_3O_2)_2]_3.PbO$$

Now from this equation it appears that one molecule of lead hydroxide causes the disappearance of three molecules of neutral acetate. The equation would occur almost totally from left to right at the low concentrations of the basic acetate. If then we add lead hydroxide to a saturated solution of the neutral acetate we cause a disproportionately large quantity of dissolved lead acetate molecules to disappear. But now the original equilibrium between the neutral crystals and the dissolved neutral molecules must be maintained, hence a large quantity of neutral acetate must go into solution. This would account for the astonishing increase of solubility of the neutral acetate in basic solutions.

Of interest in this connection is the correlation of another phenomenon. Parsons[2] has shown that the freezing point of a lead acetate solution is

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[1] This must be rigorously true for minute changes in the solution.

[2] *J. Phys. Chem.*, 11, 659 (1907).

raised by the addition of basic lead even although more solid substance is in solution. In his discussion he very justly pointed out that no evidence of a molecular complex then existed. If, however, Equation 2 is substantially correct the addition of one molecule of lead hydroxide to three of acetate has caused the formation of but one molecule of the basic compound or a disappearance of three molecules. Since the lowering of freezing point depends only upon the number of dissolved particles, we should expect a rise and not a lowering upon the addition of basic lead.

If we make the assumption that the constancy of equilibrium (1) is rigidly maintained throughout the wide variation of conditions represented by the curve AB, we can make a further prediction in regard to the saturation curve. If we continue the addition of lead hydroxide, the concentration of the basic acetate continually increases and gradually Equation 2 becomes important in the sense from right to left. Thus at the farther end of the curve the addition of a small quantity of lead hydroxide must produce a smaller relative effect than at the low concentrations. In other words, the saturation curve should have, according to this theory, the convex shape which was found by experiment.

The nature of the solution represented by AB undergoes some variation between A and B in respect to basicity, viscosity, and density; and it seems at first somewhat violent to assume the constancy of Equation 1. On the other hand, if we calculate in molecular per cent. instead of weight per cent. we find that the point A corresponds to but 2.98% lead acetate and the point B to 6.93% lead acetate and 3.28% lead oxide. As far as molecular percentages are concerned, we are still dealing with fairly dilute solutions. This justifies, to some extent, our assumption.

The mechanism of the reaction cannot be supposed to be as simple as represented by Equation 2, but even so, we may say with certainty that the end members of the chain of reactions are just as represented, namely, neutral lead acetate molecules and basic lead acetate molecules, and whatever reasoning has been applied would be equally valid if the mechanism of the reaction included the products of ionization and hydrolysis.

With regard to the second saturation curve BC, *viz.*, that in equilibrium with the solid phase $[Pb(C_2H_3O_2)_2]_3.PbO$, let us suppose that we are following the curve from right to left. Neutral lead acetate has now acquired so great a solubility that the basic acetate is the more insoluble substance and separates from its own saturated solution. As we continue to add lead hydroxide the following reaction becomes important:

$$(3)\quad [Pb(C_2H_3O_2)_2]_3.PbO + 5PbO \rightleftharpoons 3[Pb(C_2H_3O_2)_2.2PbO]$$

Here it requires five molecules of lead hydroxide to cause the disappearance of one molecule of the monoxy-acetate and we should expect just what happens experimentally—a much slower increase of solubility of the solid phase with continued addition of lead hydroxide. Furthermore, since the dioxy-acetate is a relatively insoluble substance it must reach its saturation after a relatively small addition of lead hydroxide. As we pass down the saturation curve BC of the solid phase $3Pb(C_2H_3O_2)_2.PbO$ we gradually increase the concentration of the dioxy-acetate, namely, $Pb(C_2H_3O_2)_2.2PbO$, until at the quadruple point C we increase it to its saturation point and it begins to separate. Further addition of lead hydroxide converts the soluble monoxy-acetate into the relatively insoluble dioxy-acetate which immediately precipitates. Hence occurs the very rapid decrease of solubility as shown by the saturation curve CD.

The convexity of the curve CD may be explained if we make assumptions similar to those made with the curve AB. Let us start with the transition point D and approach C. This can be accomplished by adding neutral lead acetate to the saturated solution of the dibasic acetate. The reaction is then

$$(4)\ Pb(C_2H_3O_2)_2.2PbO + 5Pb(C_2H_3O_2)_2 \rightleftarrows 2[(Pb(C_2H_3O_2)_2)_3.PbO].$$

The increase of solubility would, according to our theory, depend upon the disappearance of the dissolved dioxy-acetate and the appearance of the very soluble monoxy-acetate. At first the concentration of the monoxy-acetate is low and the reaction proceeds almost entirely in the sense of the equation from left to right. As the concentration of monoxy-acetate increases the former reaction is opposed by the reverse equation and consequently the rate of increase of solubility diminishes. Thus the convexity toward the solid phase.

The slope of the saturation curve DE of lead hydroxide possesses some interest. Upon adding lead acetate the following reaction occurs:

$$(5)\ 2Pb(OH)_2 + Pb(C_2H_3O_2)_2 \rightleftarrows Pb(C_2H_3O_2)_2.2PbO + 2H_2O$$

Since, with lead hydroxide as the solid phase, we are far from the region of stability of the neutral acetate, the latter cannot remain in considerable concentration, and since the hydroxide itself has but slight solubility, we should expect the dissolved substance to consist almost entirely of the dioxy-acetate. In this compound the weight ratio of lead acetate to lead oxide is 0.73 while in the solution of the curve DE it is 0.64. This indicates a slight excess of dissolved lead hydroxide which apparently acquires an increased solubility in solutions of basic acetates.

If this latter conclusion is correct, reaction (5) will continue in the sense from left to right even after the point D has been passed and the solid phase has changed from the hydroxide to the dioxy-acetate. During the initial stages of the curve DC the addition of neutral acetate results only in an exhaustion of this dissolved hydroxide and makes no demands upon the dioxy-acetate. Consequently reaction (4) does not become predominant until lead hydroxide is exhausted. As a result of this we find at the upper end of CD a slight but unmistakable change of curvature.

In conclusion, it is a pleasure to acknowledge the kind assistance rendered by Dr. William Blum, of this Bureau, who made many valuable suggestions in regard to analytical procedure, and by Dr. John Johnston, who read the manuscript critically.

Summary.

1. The analysis of basic lead acetate was performed by measuring the volume of standard acid neutralized by the basic lead and the volume of reagent required for the complete precipitation of lead.

2. The synthesis of the basic acetates was accomplished by the interaction of lead acetate and lead hydroxide. Some of the accompanying phenomena are described.

3. A theory of the course of the saturation curves is proposed.

4. The solid phases capable of existence are:

$Pb(C_2H_3O_2)_2.3H_2O$, brilliant monoclinic crystals. It can exist in equilibrium with acid and neutral solutions and with basic solutions containing as much as 15.9% lead oxide. Its solubility in water is 35.50%.

$3Pb(C_2H_3O_2)_2.PbO.3H_2O$ crystallizes in needles. It is exceedingly soluble in water and forms solutions of density 1.93 to 2.28. The substance is unstable in contact with solutions of itself. For its existence in equilibrium with a solution there must be an excess of dissolved basic lead. The solutions contain at the extremes of the saturation curve 15.89% PbO, 48.95% $Pb(C_2H_3O_2)_2$ and 24.74% PbO, 49.21% $Pb(C_2H_3O_2)_2$.

$Pb(C_2H_3O_2)_2.2PbO.4H_2O$ consists of needles which may be so small as to seem amorphous. It is capable of existence in equilibrium with solutions of itself but under such conditions has a solubility of but 13.3%. Its saturation curve possesses a very great length. The extremes of solubility are 7.4% PbO, 4.8% $Pb(C_2H_3O_2)_2$ and 24.74% PbO, 49.21% $Pb(C_2H_3O_2)_2$.

$Pb(OH)_2$ is stable in equilibrium with solutions containing as much as 7.4% PbO and 4.8% $Pb(C_2H_3O_2)_2$.

Bureau of Standards,
Washington, D. C.

ON THE RHYTHMICAL PRECIPITATION OF FERROUS FERRICYANIDE AND FERROUS HYDROXIDE IN JELLY.

By Henry Jermain Maude Creighton.

Received September 23, 1914.

When a drop of silver nitrate solution is placed on a thin layer of gelatin containing potassium dichromate, silver chromate precipitates out in circles which are concentric to the drop of silver nitrate. Such precipitation of silver chromate has been investigated during the past few years