

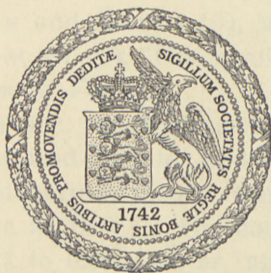
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THE ACID DISSOCIATION OF
THE HYDRATED LEAD ION AND THE
FORMATION OF POLYNUCLEAR IONS

THE PRECIPITATES FORMED
WHEN SOLUTIONS OF LEAD NITRATE AND SODIUM
HYDROXIDE ARE MIXED

BY

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KØBENHAVN

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ACID ARE MIXED

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K. M. JENSEN



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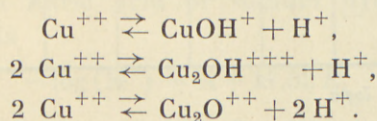
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Part I.

The Acid Dissociation of the Hydrated Lead Ion and the Formation of Polynuclear Ions.

In an earlier paper (1), the hydrogen ion concentrations of aqueous solutions of cupric nitrate were measured by means of the glass electrode. The following equilibria (omitting the water of hydration) were found:



In the present paper, a similar study of solutions of lead nitrate has been made.

The hydrogen ion concentrations of lead nitrate solutions were first measured by WALKER and ASTON (2) using the method of inversion of sucrose. The same method was applied by LONG (3) and by KULLGREN (4). The quinhydrone electrode was used by DENHAM and MARRIS (5), and the glass electrode by CRANSTON and BROWN (6). The results of the last two investigations are given in Fig. 1.

In the present paper, the hydrogen ion concentrations of aqueous solutions of lead nitrate, and of solutions containing both lead nitrate and barium nitrate, were measured by means of the glass electrode at 18.0° C. The concentration of lead nitrate varied from 0.4 to 0.005 molar, and both pure aqueous solutions and solutions containing small concentrations of sodium hydroxide or nitric acid were measured. In 0.4 and 0.1 molar lead nitrate, the greatest concentration of sodium hydroxide which gave no turbidity during the measurement was only about 0.4

per cent. of the lead ion concentration; in 0.01 molar lead nitrate, it was about 1 per cent. These examples show that only extremely weakly buffered solutions could be measured.

The preparations used were commercial pure lead nitrate, which was further recrystallized twice from water, and *pro analysi* barium nitrate, which was recrystallized once. The amount of acid or basic impurity in the recrystallized preparations was determined from the hydrogen ion concentrations of

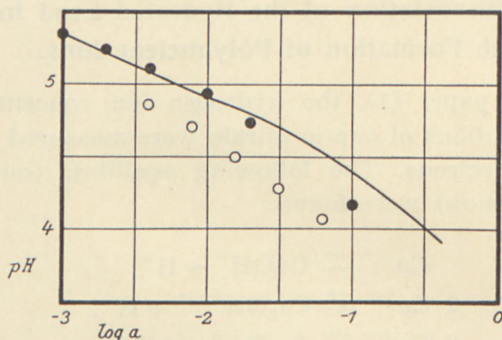
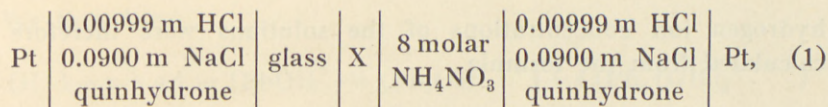


Fig. 1. Measurements of the pH of solutions of lead nitrate (a molar). Open circles: DENHAM and MARRIS, quinhydrone electrode at 25° C. Solid circles: CRANSTON and BROWN, glass electrode at 15° C. The curve represents the measurements of the present paper.

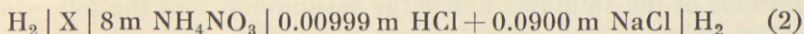
the solutions (see below). In the barium nitrate and in one of the preparations of lead nitrate, no acid or basic impurity could be detected, while two other preparations of lead nitrate contained respectively $3 \cdot 10^{-6}$ and $9 \cdot 10^{-6}$ equivalents of basic impurity per mole. The sodium hydroxide used for the solutions was taken from a 0.01 normal solution, which was stored in a bottle covered inside with a layer of paraffin wax and fitted out with a 5 ml. micro burette and the ordinary device for protecting the contents from the carbon dioxide of the air. It was prepared from a clear, saturated solution of sodium hydroxide *pro analysi* and carbon dioxide free water. Redistilled water was used for all the solutions.

The measurements were carried out as described in the earlier paper on cupric nitrate solutions (1). The cells measured had the composition



where X is the solution under investigation.

Every day, both before and after the measurements, X was replaced by a solution of the composition 0.00999 m HCl + 0.0900 m NaCl, and the e. m. f. (the asymmetry potential) was measured. When this small potential is subtracted from the e. m. f. of the cells (1), the potential E volts of cells of the composition



is obtained.

To a series of measurements at 18° C. in solutions X of constant lead nitrate and barium nitrate concentrations, but varying concentrations of nitric acid or sodium hydroxide, we may apply the formula

$$-\log(\text{H}^+) = A + 17.32 E, \quad (3)$$

where (H^+) is the hydrogen ion concentration of the solution X, and A includes the salt effect and the effect of the liquid-liquid junction of the left half cell (scheme 2), together with the whole effect of the right half cell, the latter having the same composition throughout the measurements. When the concentration of acid or base added is sufficiently small, A attains a constant value A_0 .

In order to determine A_0 for a given concentration of lead and barium nitrate, measurements were carried out on solutions containing in addition so much nitric acid that the hydrogen ion concentration produced by the dissociation of the lead ions was negligible, except, in a few cases, for a small correction. In these solutions, the hydrogen ion concentration was known, and A could be computed by means of equation 3. A_0 was found by extrapolation of A to zero concentration of nitric acid. The results are given in Table 1.

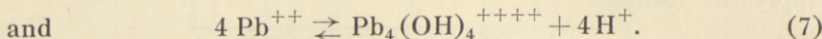
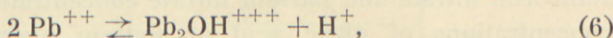
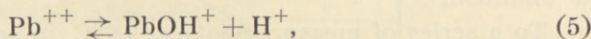
In all the other solutions measured, the concentration of nitric acid or sodium hydroxide was so small compared with that of lead nitrate that we may put $A = A_0$ in formula 3. The

hydrogen ion concentrations of the solutions were therefore calculated from the formula

$$-\log(\text{H}^+) = A_0 + 17.32 E, \quad (4)$$

where A_0 has the values given in Table 1. The results are presented in Table 2, where the second and third column give respectively E and $-\log(\text{H}^+)$. Before analyzing these results, we must consider the theory to be applied.

As we shall see, we may explain the hydrogen ion concentrations of the solutions under the assumption that the following three equilibria occur:



The mass action constants are

$$k_1 = \frac{(\text{PbOH}^+)(\text{H}^+)}{(\text{Pb}^{++})}, \quad (8)$$

$$k_{1,2} = \frac{(\text{Pb}_2\text{OH}^{+++})(\text{H}^+)}{(\text{Pb}^{++})^2}, \quad (9)$$

$$k_{4,4} = \frac{(\text{Pb}_4(\text{OH})_4^{++++})(\text{H}^+)^4}{(\text{Pb}^{++})^4}. \quad (10)$$

When n hydrogen ions and p metal ions take part in the equilibrium, the constant is denoted by $k_{n,p}$. p is left out when it is one.

We consider a series of measurements in solutions where the concentrations of lead and barium nitrate are constant, respectively a and b molar. The lead nitrate contains a small amount of basic impurity, δ equivalents per mole. x is the concentration of sodium hydroxide added (or $-x$ that of nitric acid).

We then have

$$\begin{aligned} (\text{H}^+) + x + a\delta &= (\text{PbOH}^+) + (\text{Pb}_2\text{OH}^{+++}) + 4(\text{Pb}_4(\text{OH})_4^{++++}) \\ &= k_1 \frac{(\text{Pb}^{++})}{(\text{H}^+)} + k_{1,2} \frac{(\text{Pb}^{++})^2}{(\text{H}^+)} + 4k_{4,4} \frac{(\text{Pb}^{++})^4}{(\text{H}^+)^4}, \end{aligned}$$

which may also be written as follows:

$$\frac{(\text{H}^+) [(\text{H}^+) + x]}{(\text{Pb}^{++})} + \frac{(\text{H}^+) a\delta}{(\text{Pb}^{++})} = k_1 + k_{1,2} (\text{Pb}^{++}) + 4k_{4,4} \frac{(\text{Pb}^{++})^3}{(\text{H}^+)^3}. \quad (11)$$

If the decrease in lead ion concentration owing to the reactions 5 to 7 is denoted by \mathcal{A} , we get

$$(\text{Pb}^{++}) = a - \mathcal{A} \quad (12)$$

and

$$\begin{aligned} \mathcal{A} &= (\text{PbOH}^+) + 2(\text{Pb}_2\text{OH}^{+++}) + 4(\text{Pb}_4(\text{OH})_4^{++++}) \\ &= (\text{H}^+) + x + a\delta + (\text{Pb}_2\text{OH}^{+++}) \\ &= (\text{H}^+) + x + a\delta + k_{1,2} \frac{(\text{Pb}^{++})^2}{(\text{H}^+)}. \end{aligned}$$

An approximation leads to

$$\mathcal{A} = (\text{H}^+) + x + k_{1,2} \frac{a^2}{(\text{H}^+)}. \quad (13)$$

From equation 11 and 12 we obtain

$$k = k_1 + k_{1,2} a + 4k_{4,4} \frac{(\text{Pb}^{++})^3}{(\text{H}^+)^3}, \quad (14)$$

where

$$k \equiv \frac{(\text{H}^+) [(\text{H}^+) + x]}{(\text{Pb}^{++})} + (\text{H}^+) \delta + k_{1,2} \mathcal{A}. \quad (15)$$

Here $(\text{H}^+) \delta$ has been used as an approximation for $(\text{H}^+) a\delta / (\text{Pb}^{++})$.

In order to test the theory, we first compute \mathcal{A} from equation 13 and a preliminary value of $k_{1,2}$, and then (Pb^{++}) from equation 12. The values of (Pb^{++}) found in this way are given

in the fourth column of Table 2. k of equation 15 is a sum of three terms of which the first, and by far the most important one, may now be calculated. The third term is a very small correction, which may be estimated from a preliminary value of $k_{1,2}$. The relative importance of the second term, which contains the unknown δ , decreases when x increases within a series of measurements at constant a . We therefore make the preliminary assumption that $\delta = 0$, calculate k from equation 15, and plot it against $(\text{Pb}^{++})^3 (\text{H}^+)^{-3}$. In any of the 20 series of measurements carried out, the points fall close to a straight line, in agreement with equation 14. In some cases, however, there is a small, systematic deviation from the straight line for the points corresponding to the smallest values of x . It is possible to eliminate this deviation by choosing an appropriate value of δ , and adding the correction $(\text{H}^+) \delta$ to the values of k first calculated. In this way, the basic impurity in the preparation of lead nitrate was estimated. The values of k computed from the measurements as explained here, are given in the last column but one of Table 2.

From the straight line obtained when k for a series of measurements is plotted against $(\text{Pb}^{++})^3 (\text{H}^+)^{-3}$, the constants $(k_1 + k_{1,2} a)$ and $4k_{4,4}$ of equation 14 are evaluated. They are presented in the third and fifth columns of Table 3. k , calculated from equation 14 by means of these values of the constants, is given in the last column of Table 2. The agreement between k found from the measurements and k calculated from formula 14 shows that k varies with the hydrogen ion concentration in the way expressed by equation 14. We shall now prove that it also depends upon the lead ion concentration in the way stated in the equation. For this purpose, we compare the results for solutions of different lead nitrate concentration, but constant ionic strength, $\mu = 3(a + b)$. It is seen from Table 3 that, for such solutions, $(k_1 + k_{1,2} a)$ found from the measurements varies practically linearly with a , while $4k_{4,4}$ is practically constant. The values of the three constants k_1 , $k_{1,2}$ and $k_{4,4}$ which best satisfy equation 14 are given in the three last columns of the table. The fourth column presents $(k_1 + k_{1,2} a)$ calculated by means of these constants. The agreement with $(k_1 + k_{1,2} a)$ found for the individual series is always good. For the last two

solutions, $k_{1,2}$ has been calculated from formula 17 (see below), and k_1 has been computed from this value and $(k_1 + k_{1,2}a)$ found from the measurements.

The equilibrium constants found for different ionic strengths may be expressed by means of the following formulae:

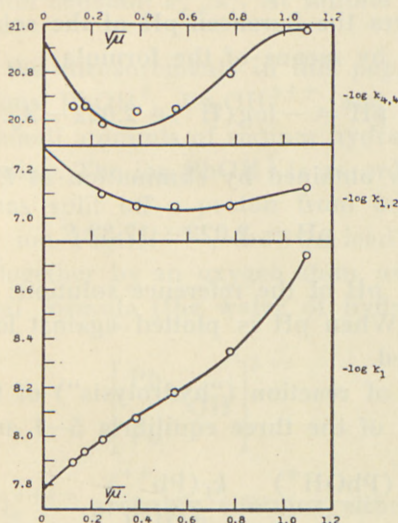


Fig. 2. The mass action constants found from the measurements. The curves represent the formulae 16–18.

$$-\log k_1 = 7.778 + 0.996 \sqrt{\mu} - 0.617 \mu + 0.432 \mu^2 \quad (16)$$

$$-\log k_{1,2} = 7.296 - 0.996 \sqrt{\mu} + 0.993 \mu - 0.189 \mu^2 \quad (17)$$

$$-\log k_{4,4} = 20.93 - 1.992 \sqrt{\mu} + 2.88 \mu - 0.854 \mu^2. \quad (18)$$

The formulae contain three empirical constants each. The fourth constant, the factor before the square root of μ , has been deduced from the Debye-Hückel theory. In Fig. 2, $-\log k_1$, $-\log k_{1,2}$, and $-\log k_{4,4}$, found from the measurements, are plotted against $\sqrt{\mu}$. The curves represent the formulae 16–18.

If we extrapolate to $\mu = 0$ by means of the formulae 16–18, we obtain:

$$k_1^\circ = 1.67 \cdot 10^{-8}, \quad k_{1,2}^\circ = 5.1 \cdot 10^{-8}, \quad \text{and} \quad k_{4,4}^\circ = 1.2 \cdot 10^{-21}.$$

For the cupric ion was found (1):

$$k_1^\circ = 1.07 \cdot 10^{-8}, \quad k_{1,2}^\circ = 15.2 \cdot 10^{-8}, \quad \text{and} \quad k_{2,2}^\circ = 1.29 \cdot 10^{-11}.$$

Thus, k_1° and $k_{1,2}^\circ$ are of the same order of magnitude for the two ions.

Table 4 contains the equilibrium constants k_1 , $k_{1,2}$, and $k_{4,4}$ for lead nitrate solutions, calculated from the formulae 16–18. The fifth column shows $-\log(\text{H}^+)$ for pure lead nitrate solutions, calculated by means of the constants in the table. The next column gives the Sørensen pH of the solutions, calculated from $-\log(\text{H}^+)$ by means of the formula

$$\text{pH} = -\log(\text{H}^+) + 2.022 - A_0.$$

This formula is obtained by elimination of E from formula 4 and

$$\text{pH} = 2.022 + 17.32 E,$$

2.022 being the pH of the reference solution: 0.00999m HCl + 0.0900m NaCl. When pH is plotted against $\log a$, the curve of Fig. 1 is obtained.

The degrees of reaction (“hydrolysis”) of the lead ions according to each of the three equilibria 5–7 are

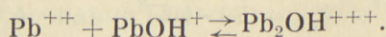
$$\alpha_1 = \frac{(\text{PbOH}^+)}{a} = \frac{k_1(\text{Pb}^{++})}{a(\text{H}^+)},$$

$$\alpha_{1,2} = \frac{2(\text{Pb}_2\text{OH}^{+++})}{a} = \frac{2k_{1,2}(\text{Pb}^{++})^2}{a(\text{H}^+)},$$

$$\alpha_{4,4} = \frac{4(\text{Pb}_4(\text{OH})_4^{++++})}{a} = \frac{4k_{4,4}(\text{Pb}^{++})^4}{a(\text{H}^+)^4},$$

respectively. The total degree of reaction is $\alpha = \alpha_1 + \alpha_{1,2} + \alpha_{4,4}$. The degrees of reaction for pure lead nitrate solutions have been calculated by means of the equilibrium constants and the hydrogen ion concentrations given in Table 4. They are to be found in the last four columns of the table. It is noted that $\alpha_{4,4}$ in pure lead nitrate solutions is extremely small.

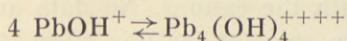
From the equilibria 5 and 6, we derive



The mass action constant of this equilibrium is $k_{1,2}/k_1$. At infinite dilution, it has the value 3.1. For the corresponding

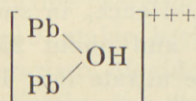
equilibrium with cupric ions instead of lead ions, the constant at infinite dilution was found (1) to be 14.

From the equilibria 5 and 7, we derive

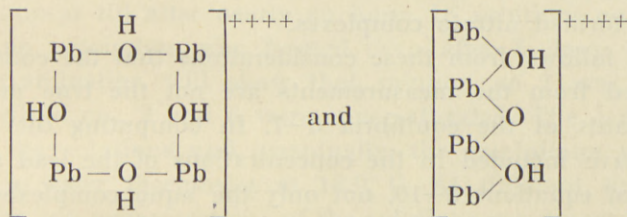


with the equilibrium constant $k_{4,4}/k_1^4$. At infinite dilution, it has the value 1.5×10^{10} .

As a result of the measurements in this paper, it has been shown that the ions PbOH^+ , $\text{Pb}_2\text{OH}^{+++}$, and $\text{Pb}_4(\text{OH})_4^{++++}$ are formed when small amounts of sodium hydroxide are added to lead nitrate solution. The ion PbOH^+ is an ordinary hydrated lead ion which has split off a proton from one of its water molecules. In the ion $\text{Pb}_2\text{OH}^{+++}$, the two lead atoms are undoubtedly bound together by an oxygen atom, as shown in the following structural formula (the water of hydration as usual being left out):



The ion $\text{Pb}_4(\text{OH})_4^{++++}$ probably contains either a ring or a chain of alternating lead and oxygen atoms. The following structural formulae may be suggested:



It speaks in favour of the cyclic structure that a marked tendency to form tetranuclear compounds has been established, while ions containing three atoms have not been found. There is no reason to believe that a chain of four lead atoms is much more stable than one of three, but it is well known that a ring is most stable when containing a definite number of atoms.

All the computations of this paper have been carried out under the assumption that the nitrates present are completely

dissociated. However, there can be no doubt that the nitrate ions, especially in the more concentrated solutions, to a considerable extent have formed coordination compounds and association products with the cations. No data are available which make it possible to account for this effect. Only a rough estimate of the extent of complex formation of the nitrate ions with the lead and barium ions may be ventured. From measurements of the electrical conductivity of solutions of lead and barium nitrate, RIGHELLATO and DAVIES (7) have found the following constants corresponding to infinite dilution:

$$\frac{(\text{Pb}^{++})(\text{NO}_3^-)}{(\text{PbNO}_3^+)} = 0.0647 \quad \text{and} \quad \frac{(\text{Ba}^{++})(\text{NO}_3^-)}{(\text{BaNO}_3^+)} = 0.121.$$

From these values and a rough estimate of the activity coefficients, we find that the constants for 0.2 m solutions are about 0.5 and 1, respectively. Hence, in such solutions about 40 per cent. of the lead ions and about 25 per cent. of the barium ions have taken up one nitrate ion. The percentage of lead and barium ions which have taken up nitrate ions is probably somewhat higher, because complexes with more than one nitrate ion may also be formed. We therefore make the rough estimate that, in the more concentrated of the solutions examined, about one half of the lead ions and one third of the barium ions have formed nitrate complexes.

It follows from these considerations that the constants calculated from the measurements are not the true mass action constants of the equilibria 5-7. In computing the constants, we have included in the concentrations of the lead containing ions of equations 8-10, not only the aquo complexes, but also the complexes in which water molecules have been exchanged with nitrate ions. The apparent equilibrium constants found in this way approach the true constants when the nitrate ion concentration decreases. Therefore, the values found by extrapolation to infinite dilution are true mass action constants for the equilibria 5-7. The formulae 16-18 and Fig. 2 give the apparent constants for solutions of lead nitrate, when μ is calculated under the assumption that the lead nitrate is completely dissociated.

Part 2.

The Precipitates Formed when Solutions of Lead Nitrate and Sodium Hydroxide are Mixed.

A Preliminary Examination.

(X-ray crystal analysis by A. TOVBORG JENSEN).

In each of the experiments summarized in Table 5, 200 ml. of $2x$ molar sodium hydroxide were poured into 200 ml. of ($2a$ molar lead nitrate + $2b$ molar barium nitrate), while a vigorous current of pure, carbon dioxide-free air was passed through the solution. Immediately after the mixtures were made, all the solutions were clear, but, when x was sufficiently great, a crystalline precipitate was formed after some time. In the solution containing most sodium hydroxide (no. 5), the precipitate was observed already after about one minute; in no. 3, it did not appear till after nearly an hour. In solutions nos. 1, 2, and 6, no precipitate was formed even after 5 days. The following examination will show that solution no. 1 was unsaturated, while nos. 2 and 6 were supersaturated. The bottles containing the solutions and, eventually, the precipitates were rotated in a water thermostat at 18.0° C. At different times, the hydrogen ion concentrations of the solutions were measured by means of the glass electrode in the same way as in Part 1. After two days, constant values of $-\log(\text{H}^+)$ were found. They are presented in the fifth column of Table 5. For each of the solutions nos. 2 and 6, two values of $-\log(\text{H}^+)$ are given. The first value refers to the clear, supersaturated solution, the second to a saturated solution obtained when the supersaturated solution was rotated with a small amount of the crystals prepared as described below (preparation A). After some days,

the lower values given in the table were measured. They remained constant on further rotation.

It follows from the analyses given below that the precipitate has the composition $\text{Pb}(\text{OH})\text{NO}_3$. The sodium hydroxide added (x molar) is partly used in forming the three ions PbOH^+ , $\text{Pb}_2\text{OH}^{+++}$, and $\text{Pb}_4(\text{OH})_4^{++++}$, partly in forming the precipitate. If y denotes the part of x which has been consumed by the precipitate, we have (the formation of nitrate complexes being neglected):

$$\begin{aligned} y &= x - (\text{PbOH}^+) - (\text{Pb}_2\text{OH}^{+++}) - 4(\text{Pb}_4(\text{OH})_4^{++++}), \\ (\text{Pb}^{++}) &= a - y - (\text{PbOH}^+) - 2(\text{Pb}_2\text{OH}^{+++}) - 4(\text{Pb}_4(\text{OH})_4^{++++}), \\ \text{and } (\text{NO}_3^-) &= 2a - y. \end{aligned}$$

(PbOH^+) , $(\text{Pb}_2\text{OH}^{+++})$, and $(\text{Pb}_4(\text{OH})_4^{++++})$ are computed from the hydrogen ion concentrations by means of the equations 8–10 and the equilibrium constants given in Table 4. The values are inserted into the above equations, and y , (Pb^{++}) , and (NO_3^-) are calculated. They are to be found in Table 5.

For solutions saturated with the salt $\text{Pb}(\text{OH})\text{NO}_3$,

$$L = \frac{(\text{Pb}^{++})(\text{NO}_3^-)}{(\text{H}^+)}$$

is the ratio between the solubility product $(\text{Pb}^{++})(\text{OH}^-)(\text{NO}_3^-)$ and the ionization constant of water $K_w = (\text{H}^+)(\text{OH}^-)$. $\log L$ is given in the last column of Table 5. For the saturated solutions, $\log L$ is found to be practically constant (mean 3.55). The slight decrease of $\log L$ when the amount of precipitate increases may be due to the decrease of ionic strength accompanying the formation of precipitate. The constancy of L is a confirmation of the formula $\text{Pb}(\text{OH})\text{NO}_3$ found by chemical analysis of the crystals. $\log L$ for solutions where no precipitate was formed is placed in parenthesis. In no. 1 $\log L$ is smaller, in nos. 2 and 6 it is greater than the value found for saturated solutions. This shows that solution no. 1 was unsaturated, while solutions nos. 2 and 6 were supersaturated.

The chemical composition of the precipitate, expressed by the formula $\text{Pb}(\text{OH})\text{NO}_3$, was found in the following way. Solution no. 5 was prepared again, in the same way as before,

only on a larger scale. The crystals (preparation A) were isolated and analyzed. When lead was determined gravimetrically as lead sulphate, the weight 287.6 per atom of lead was found (calculated: 286.2). The equivalent weight of the substance considered as a base was determined as follows. 0.7192 g. was dissolved in 25.01 ml. of 0.1001 m HNO_3 and diluted to 50 ml. If the formula is correct, the solution is identical with a nearly 0.05 m lead nitrate. A glass electrode measurement of the solution was carried out in the usual way. E was found to be 0.1730 volts. According to Table 2, this corresponds to $x = 0.7 \times 10^{-4}$. Hence, 0.7192 g. of the preparation contains $25.01 \times 0.1001 + 50 \times 0.7 \times 10^{-4} = 2.507$ milliequivalents of base, from which we obtain the equivalent weight 286.9 (calculated: 286.2). The equivalent weight was also determined acidimetrically. The substance was dissolved in an excess of nitric acid, and the excess was titrated with sodium hydroxide, methyl red being used as an indicator. Although the endpoint was not quite sharp, the equivalent weight found, 286.8, agrees well with that determined electrometrically.

In order to be able to identify the crystals, X-ray powder diagrams were taken of this preparation and the following ones. The diagram of preparation A contained an immense number of sharp, but rather weak lines. This shows that the preparation consisted of well developed crystals with a large unit cell.

Preparation B. A solution of the same composition as no. 5 in Table 5 was prepared, but instead of mixing equally great volumes of lead nitrate and sodium hydroxide solution, 200 ml. of 1.1 m lead nitrate were poured into 2 litres of 0.0121 m sodium hydroxide, while a current of pure, carbon dioxide-free air was passed through the solution. The mixture immediately turned milky, and soon a deposit was formed. The precipitate was isolated and analyzed. When lead was determined as lead sulphate, the weight 285.7 per atom of lead was found (calculated for $\text{Pb}(\text{OH})\text{NO}_3$: 286.2). The equivalent weight as a base determined electrometrically was 279.8. It follows from these results that the substance contains 1.02 hydroxyl groups per atom of lead, *i. e.* it has nearly the composition $\text{Pb}(\text{OH})\text{NO}_3$. The X-ray diagram showed that its structure was quite different from that of preparation A.

Preparation C. 500 ml. of about 0.125 m sodium hydroxide were added slowly, drop by drop, to 2 litres of 0.0625 m lead nitrate, while a current of pure, carbon dioxide-free air was passed through the solution. A permanent precipitate was not formed till nearly half of the base had been added. The analysis of the preparation gave the following results: When lead was determined as lead sulphate, the weight 286.3 per atom of lead was found. The equivalent weight found by acidimetry was 285.6. Consequently, the substance has the composition $\text{Pb}(\text{OH})\text{NO}_3$. The X-ray analysis showed that its structure was entirely different from that of preparation A. The two diagrams had no line in common. The diagrams of preparations B and C, however, had many lines in common. The diagrams showed that the two preparations were mixtures of the same two phases of different crystal structure. One phase consisted of rather great ($> 2000 \text{ \AA}$.), the other of smaller, possibly colloidal, particles. The first phase was predominant in both preparations. Preparation C, however, contained almost as much of the second phase, while only a small part of preparation B consisted of this phase.

According to Table 5, a 0.1 m lead nitrate containing 6.9×10^{-4} m sodium hydroxide is unsaturated with respect to the salt of the composition $\text{Pb}(\text{OH})\text{NO}_3$ which forms the precipitate in the other solutions of the table. However, in Part 1 (see Table 2), a turbidity was observed in 0.1 m lead nitrate when the sodium hydroxide concentration was only 4.6×10^{-4} m. The solutions were not mixed in the same way in the two cases. In Part 1, a small volume of concentrated lead nitrate solution was pipetted into a great volume of dilute sodium hydroxide solution. When experiment no. 1 was repeated in this way, a turbidity was formed at once. After rotation of the mixture at 18°C ., $-\log(\text{H}^+)$ was found to be 5.16 in one experiment, 5.12 in another. A greater volume of the mixture was made, but the amount of precipitate obtained (preparation D) was still insufficient for a chemical analysis. The X-ray diagram taken of the preparation showed few and rather diffuse lines. The substance, therefore, consists of colloidal particles of a simple crystal structure which is quite different from those of the preparations A, B, og C.

In order to prepare more of the substance, 400 ml. of 1.25 m lead nitrate were added to 4.6 litres of 1.2×10^{-3} m sodium hy-

dioxide, while the solution was stirred by means of a current of carbon dioxide free air. This time the attempt at getting a turbidity failed. The solution was quite clear, even when having been left for a month in a closed flask. In order to test if the turbidity obtained in some cases might be lead carbonate formed from an impurity of carbonate in the sodium hydroxide solution, a little carbon dioxide was added to the clear solution. A precipitate was formed at once (preparation E). Qualitative tests showed that it contained carbonate, but no nitrate. Its equivalent weight was, by acidimetry, found to be 135.7 (calculated for PbCO_3 : 133.6). The X-ray diagram of the preparation was quite different from that of preparation D. A comparison with a diagram of the mineral cerussite (PbCO_3) showed that preparation E has the same crystal structure as this mineral, the only difference being that the particles of the preparation have colloidal size (probably between 500 Å. and 1000 Å.).

It was once more attempted to prepare the substance forming the turbidity. 80 ml. of 1.25 m lead nitrate were added to 8.6 litres of 4×10^{-4} m sodium hydroxide, while the solution was stirred by means of carbon dioxide-free air. A turbidity was formed at once. The flask was closed and left standing for two days. Then the turbidity had deposited, and most of the solution was siphoned off. The precipitate was isolated by means of a centrifuge. It was washed with carbon dioxide-free water and finally dried *in vacuo* over 30 per cent. potassium hydroxide. Yield: 0.16 g. (preparation F). The following analytical data show that the substance is lead carbonate, PbCO_3 . When it was added to a droplet of dilute nitric acid, an effervescence was observed. No nitrate could be detected in the preparation. Lead was determined as lead oxide by heating the substance to 500° C. in an electric furnace. In this way, the weight 265.1 per atom of lead was found (calculated for PbCO_3 : 267.2). The X-ray analysis shows that the preparations D and F have the same structure. Their structure is, however, different from that of the mineral cerussite and preparation E.

We have now identified the turbidity observed in some cases when a concentrated solution of lead nitrate was added to a solution of sodium hydroxide containing insufficient hydroxide for the precipitation of the salt $\text{Pb}(\text{OH})\text{NO}_3$. It was found to

be lead carbonate. It has not, however, been possible to explain why no turbidity is formed when a mixture of the same composition is prepared from the same stock solutions by adding a more dilute lead nitrate solution to its own volume of sodium hydroxide solution.

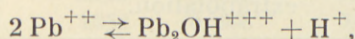
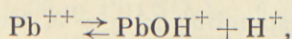
The turbidity observed in some of the solutions of Table 2 (denoted by an asterisk) has, at least in some cases, been lead carbonate. When the solutions were prepared, much care was taken to exclude carbon dioxide, and after the electrode vessel had been filled, a vigorous current of carbon dioxide-free air was passed for 10 minutes through the solution in order to remove any traces of carbon dioxide. In spite of these precautions, it has not been possible to avoid the formation of lead carbonate when a certain amount of sodium hydroxide had been added. Thus, the impurity of carbonate, rather than the solubility of the salt $\text{Pb}(\text{OH})\text{NO}_3$, has set a limit to the concentrations of sodium hydroxide added.

I wish to express my thanks to the head of the laboratory, Professor Dr. NIELS BJERRUM, for advice and kind interest in my work. I am also very grateful to Mr. A. TOVBORG JENSEN for carrying out the X-ray crystallography of this paper.

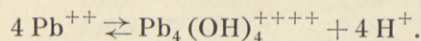
Summary.

In Part 1, the hydrogen ion concentrations of aqueous solutions of lead nitrate, and of solutions containing both lead nitrate and barium nitrate, were measured by means of the glass electrode at 18.0° C. The concentration of lead nitrate varied from 0.4 to 0.005 molar, and the examination included both pure aqueous solutions and solutions containing small concentrations of sodium hydroxide or nitric acid.

The measurements show the presence of the following equilibria:



and



The mass action constants of the equilibria have been computed.

In Part 2, the precipitates formed when more sodium hydroxide was added to solutions of lead nitrate, were examined both by chemical and by X-ray analysis. Different modifications of the salt $\text{Pb}(\text{OH})\text{NO}_3$ were identified. With one of them, solubility measurements were carried out.

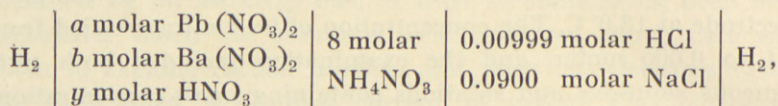
In some cases, when solutions unsaturated with $\text{Pb}(\text{OH})\text{NO}_3$ were prepared by adding lead nitrate to sodium hydroxide, a turbidity was formed. It was shown that the turbidity consisted of lead carbonate. Another modification of lead carbonate, identical with the mineral cerussite, was obtained when carbon dioxide was added to a clear solution of lead nitrate containing a little sodium hydroxide.

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Table 1.

$$A = -17.32 E - \log (H^+),$$

where E is the e. m. f. in volts at 18.0° C. of the cell



measured by means of the glass electrode, and (H^+) is the hydrogen ion concentration of the solution in the left half cell. A_0 , the value of A corresponding to $y = 0$, has been found by extrapolation.

a	b	A when $y =$					A_0
		0.02	0.01	0.005	0.004	0.002	
0.400	0.000	2.038	2.038	..	2.041	2.043	2.045
0.300	0.100	2.045	2.047	2.048
0.200	0.200	2.043	2.042	..	2.045	2.046	2.048
0.200	0.000	2.009	2.015	2.018	..	2.022	2.024
0.150	0.050	2.010	2.013	2.014	..	2.016	2.017
0.100	0.100	2.012	2.016	2.020	..	2.021	2.022
0.050	0.150	2.013	2.016	2.021	..	2.021	2.022
0.100	0.000	2.000	2.007	2.011	..	2.012	2.014
0.075	0.025	1.999	2.005	..	2.009	2.012	2.014
0.050	0.050	1.999	2.005	..	2.008	2.011	2.012
0.025	0.075	2.000	2.006	..	2.011	2.013	2.015

a	b	A when $y =$					A_0
		0.01	0.005	0.002	0.001	0.0005	
0.0500	0.0000	2.009	2.015	2.020	2.024	..	2.027
0.0375	0.0125	..	2.018	2.020	2.024	..	2.027
0.0250	0.0250	2.008	2.017	2.020	2.024	..	2.026
0.0125	0.0375	2.006	2.017	2.019	2.021	..	2.024
0.0200	0.0000	2.011	2.024	2.032	2.036	..	2.039
0.0100	0.0100	2.011	2.026	2.033	2.037	..	2.039
0.0050	0.0150	2.012	2.024	2.032	2.036	..	2.039
0.0100	0.0000	2.013	2.028	2.043	2.049	2.056	2.062
0.0050	0.0000	..	2.030	2.045	2.056	2.063	2.072

Table 2.

The hydrogen ion concentration (H^+) of solutions of lead and barium nitrate containing sodium hydroxide (x molar) or nitric acid ($-x$ molar), measured by means of the glass electrode. Comparison of k found from the measurements with k calculated from formula 14. In the solutions marked with an asterisk, a turbidity was formed either before or during the measurement.

$x \cdot 10^4$	E	$-\log(H^+)$	(Pb^{++})	$\frac{(Pb^{++})^3}{(H^+)^3} 10^{-12}$	$k \cdot 10^8$ found	$k \cdot 10^8$ formula
0.4000 m $Pb(NO_3)_2$. $\delta = 9 \cdot 10^{-6}$.						
-1.014	0.0993	3.765	0.3999	0.013	3.18	3.20
0.000	0.1101	3.952	0.3998	0.046	3.22	3.21
0.419	0.1148	4.033	0.3997	0.080	3.21	3.22
1.123	0.1218	4.155	0.3996	0.186	3.26	3.27
2.144	0.1300	4.297	0.3994	0.496	3.40	3.40
3.516	0.1375 ₅	4.427	0.3993	1.216	3.68	3.69
5.071	0.1427	4.517	0.3991	2.265	4.13	4.13
8.446	0.1490	4.626	0.3986	4.782	5.18	5.17
14.02	0.1540	4.712	0.3980	8.621	(6.96)	6.76
*17.54	0.1542	4.716	0.3976	8.839	(8.61)	6.85
0.3000 m $Pb(NO_3)_2$ + 0.1000 m $Ba(NO_3)_2$. $\delta = 3 \cdot 10^{-6}$.						
0.000	0.1167	4.069	0.2998	0.043	2.45	2.45
0.838	0.1283 ₅	4.271	0.2997	0.175	2.47	2.51
1.961	0.1390	4.455	0.2996	0.623	2.72	2.70
3.262	0.1463	4.582	0.2994	1.496	3.09	3.08
4.924	0.1516	4.674	0.2992	2.819	3.61	3.66
7.020	0.1553 ₅	4.739	0.2989	4.401	4.40	4.34
9.869	0.1587 ₅	4.798	0.2986	6.598	5.36	5.30
14.03	0.1620 ₅	4.855	0.2981	9.737	6.65	6.67
0.2000 m $Pb(NO_3)_2$ + 0.2000 m $Ba(NO_3)_2$. $\delta = 3 \cdot 10^{-6}$.						
0.000	0.1271	4.249	0.1999	0.045	1.61	1.70
0.557	0.1375	4.429	0.1998	0.154	1.74	1.74
1.260	0.1473 ₅	4.600	0.1997	0.502	1.91	1.89
2.245	0.1552	4.736	0.1996	1.283	2.24	2.22
3.369	0.1600	4.819	0.1995	2.274	2.68	2.64
4.930	0.1640 ₅	4.889	0.1993	3.680	3.28	3.23
7.010	0.1675 ₅	4.950	0.1990	5.579	4.02	4.03
9.82	0.1705 ₅	5.002	0.1987	7.953	4.98	5.04
13.47	0.1730	5.044	0.1983	10.57	6.19	6.14

(To be continued)

Table 2 (continued).

$x \cdot 10^4$	E	$-\log(H^+)$	(Pb^{++})	$\frac{(Pb^{++})^3}{(H^+)^3} \cdot 10^{-12}$	$k \cdot 10^8$ found	$k \cdot 10^8$ formula
0.2000 m $Pb(NO_3)_2$. $\delta = 0$.						
-0.514	0.1146	4.009	0.1999	0.009	2.28	2.28
-0.206	0.1202	4.106	0.1999	0.017	2.26	2.28
0.000	0.1237	4.166	0.1999	0.025	2.33	2.29
0.624	0.1350	4.362	0.1998	0.097	2.30	2.33
1.255	0.1434	4.508	0.1997	0.266	2.44	2.44
2.484	0.1536	4.684	0.1996	0.896	2.80	2.84
4.360	0.1604	4.802	0.1993	2.015	3.58	3.56
6.869	0.1653	4.887	0.1990	3.610	4.57	4.58
12.51	0.1707	4.981	0.1984	6.848	6.66	6.66
*22.7
0.1500 m $Pb(NO_3)_2$ + 0.0500 m $Ba(NO_3)_2$. $\delta = 0$.						
-0.514	0.1191	4.080	0.1499	0.006	1.77	1.73
0.000	0.1311	4.288	0.1499	0.025	1.77	1.75
0.384	0.1405 ₅	4.451	0.1499	0.076	1.74	1.78
0.693	0.1465	4.554	0.1498	0.154	1.81	1.83
1.152	0.1532	4.670	0.1498	0.344	1.95	1.95
1.916	0.1602	4.792	0.1497	0.798	2.24	2.24
3.464	0.1672	4.913	0.1495	1.831	2.94	2.91
4.628	0.1702	4.965	0.1493	2.613	3.44	3.41
6.961	0.1740	5.031	0.1491	4.107	4.41	4.37
9.624	0.1770	5.083	0.1488	5.842	5.40	5.48
13.49	0.1798	5.131	0.1484	8.060	6.78	6.90
0.1001 m $Pb(NO_3)_2$ + 0.1000 m $Ba(NO_3)_2$. $\delta = 0$.						
-0.206	0.1315 ₅	4.300	0.1001	0.008	1.48	1.40
0.000	0.1383	4.417	0.1000	0.018	1.47	1.40
0.248	0.1467 ₅	4.564	0.1000	0.049	1.42	1.42
0.624	0.1566 ₅	4.735	0.1000	0.160	1.49	1.49
1.248	0.1663 ₅	4.903	0.0999	0.510	1.72	1.72
2.236	0.1739	5.034	0.0998	1.256	2.16	2.19
4.364	0.1806 ₅	5.151	0.0995	2.797	3.15	3.18
7.481	0.1852 ₅	5.231	0.0992	4.818	4.47	4.47
12.47	0.1891 ₅	5.298	0.0987	7.530	6.40	6.21
*22.4
0.05000 m $Pb(NO_3)_2$ + 0.1500 m $Ba(NO_3)_2$. $\delta = 0$.						
0.000	0.1537	4.684	0.04997	0.014	0.86	0.90
0.280	0.1680	4.932	0.04994	0.078	0.93	0.94
0.560	0.1769 ₅	5.087	0.04991	0.227	1.05	1.04
1.075	0.1854 ₅	5.234	0.04985	0.624	1.33	1.29

(To be continued)

Table 2 (continued).

$x \cdot 10^4$	E	$-\log(H^+)$	(Pb^{++})	$\frac{(Pb^{++})^3}{(H^+)^3} \cdot 10^{-12}$	$k \cdot 10^8$ found	$k \cdot 10^8$ formula
1.750	0.1912	5.334	0.04977	1.239	1.67	1.68
2.809	0.1957	5.412	0.04966	2.107	2.23	2.24
*3.510	0.1975	5.443	0.04958	2.600	2.58	2.55
*4.203	0.1970 ₅	5.435
0.1000 m $Pb(NO_3)_2$. $\delta = 3 \cdot 10^{-6}$.						
0.000	0.1381	4.406	0.0999	0.017	1.56	1.57
0.280	0.1463	4.548	0.0999	0.044	1.60	1.60
0.447	0.1508	4.626	0.0999	0.075	1.63	1.63
0.768	0.1576 ₅	4.744	0.0999	0.170	1.72	1.71
1.312	0.1651 ₅	4.874	0.0998	0.416	1.94	1.93
2.108	0.1712	4.979	0.0997	0.855	2.34	2.33
3.178	0.1757 ₅	5.058	0.0996	1.474	2.88	2.89
*4.583	0.1787	5.109	0.0994	2.087	(3.65)	3.44
0.07500 m $Pb(NO_3)_2$ + 0.0250 m $Ba(NO_3)_2$. $\delta = 3 \cdot 10^{-6}$.						
0.000	0.1435	4.499	0.07495	0.013	1.35	1.35
0.237	0.1524	4.654	0.07493	0.039	1.37	1.37
0.420	0.1579 ₅	4.750	0.07491	0.075	1.42	1.41
0.722	0.1655 ₅	4.881	0.07488	0.185	1.50	1.50
1.122	0.1716 ₅	4.987	0.07483	0.383	1.69	1.68
1.561	0.1760	5.062	0.07478	0.642	1.92	1.91
2.098	0.1794 ₅	5.122	0.07472	0.969	2.20	2.20
2.803	0.1826	5.177	0.07464	1.412	2.56	2.59
3.507	0.1847	5.213	0.07456	1.805	2.94	2.94
0.05000 m $Pb(NO_3)_2$ + 0.0500 m $Ba(NO_3)_2$. $\delta = 3 \cdot 10^{-6}$.						
0.000	0.1517	4.639	0.04997	0.010	1.06	1.12
0.224	0.1623	4.823	0.04995	0.037	1.13	1.14
0.351	0.1671 ₅	4.907	0.04993	0.065	1.18	1.17
0.587	0.1741 ₅	5.028	0.04991	0.151	1.28	1.24
0.873	0.1800 ₅	5.130	0.04987	0.304	1.41	1.38
1.266	0.1850	5.216	0.04983	0.550	1.62	1.61
1.827	0.1892 ₅	5.290	0.04977	0.914	1.94	1.93
2.533	0.1926	5.348	0.04969	1.358	2.33	2.33
3.370	0.1953 ₅	5.395	0.04960	1.868	2.77	2.79
*4.215	0.1975 ₅	5.434	0.04951	2.433	(3.17)	3.30
0.02500 m $Pb(NO_3)_2$ + 0.0750 m $Ba(NO_3)_2$. $\delta = 3 \cdot 10^{-6}$.						
0.000	0.1631 ₅	4.841	0.02498	0.005	0.84	0.87
0.168	0.1757	5.058	0.02497	0.023	0.90	0.89
0.279	0.1828 ₅	5.182	0.02496	0.055	0.91	0.92

(To be continued)

Table 2 (continued).

$x \cdot 10^4$	E	$-\log(H^+)$	(Pb^{++})	$\frac{(Pb^{++})^3}{(H^+)^3} 10^{-12}$	$k 10^8$ found	$k 10^8$ formula
0.475	0.1908 ₅	5.321	0.02494	0.142	1.00	1.00
0.699	0.1963	5.415	0.02491	0.272	1.14	1.12
1.119	0.2022 ₅	5.518	0.02486	0.550	1.40	1.38
1.678	0.2068 ₅	5.598	0.02480	0.950	1.74	1.75
*2.474	0.2085	5.626	0.02473	1.142	(2.39)	1.93
$0.05000 \text{ m Pb}(\text{NO}_3)_2. \quad \delta = 3 \cdot 10^{-6}.$						
0.000	0.1480 ₅	4.591	0.04997	0.007	1.32	1.31
0.210	0.1581	4.765	0.04995	0.025	1.32	1.32
0.419	0.1662 ₅	4.906	0.04993	0.065	1.36	1.36
0.699	0.1738	5.037	0.04990	0.160	1.46	1.45
1.047	0.1799	5.143	0.04986	0.333	1.62	1.62
1.540	0.1850 ₅	5.232	0.04980	0.613	1.89	1.89
2.104	0.1890	5.300	0.04974	0.977	2.17	2.24
*2.816
$0.03750 \text{ m Pb}(\text{NO}_3)_2 + 0.0125 \text{ m Ba}(\text{NO}_3)_2. \quad \delta = 3 \cdot 10^{-6}.$						
0.000	0.1525 ₅	4.669	0.03747	0.005	1.23	1.19
0.168	0.1622 ₅	4.837	0.03746	0.017	1.22	1.21
0.315	0.1697 ₅	4.967	0.03745	0.042	1.22	1.23
0.526	0.1776	5.103	0.03742	0.107	1.28	1.29
0.786	0.1838 ₅	5.211	0.03740	0.225	1.40	1.39
1.155	0.1895	5.309	0.03736	0.461	1.58	1.59
*1.573	0.1933	5.375	0.03731	0.693	1.83	1.82
$0.02500 \text{ m Pb}(\text{NO}_3)_2 + 0.0250 \text{ m Ba}(\text{NO}_3)_2. \quad \delta = 0.$						
0.0000	0.1588	4.776	0.02498	0.003	1.12	1.08
0.1313	0.1689	4.951	0.02497	0.011	1.09	1.09
0.3140	0.1800	5.144	0.02496	0.042	1.11	1.11
0.4734	0.1872 ₅	5.269	0.02494	0.099	1.14	1.16
0.6291	0.1917 ₅	5.347	0.02492	0.170	1.22	1.21
0.8393	0.1965 ₅	5.430	0.02490	0.301	1.31	1.31
1.048	0.1997	5.485	0.02488	0.439	1.42	1.42
$0.01248 \text{ m Pb}(\text{NO}_3)_2 + 0.0375 \text{ m Ba}(\text{NO}_3)_2. \quad \delta = 0.$						
0.0000	0.1695 ₅	4.961	0.01247	0.001	0.96	0.95
0.0944	0.1802 ₅	5.146	0.01246	0.005	0.95	0.96
0.2102	0.1911	5.334	0.01245	0.019	0.96	0.97
0.3146	0.1983	5.459	0.01244	0.046	0.98	1.00
0.4204	0.2028	5.536	0.01243	0.078	1.05	1.03
0.5258	0.2072	5.613	0.01242	0.132	1.08	1.08
0.6317	0.2104 ₅	5.669	0.01241	0.194	1.13	1.14

(To be continued)

Table 2 (continued).

$x \cdot 10^4$	E	$-\log(H^+)$	(Pb^{++})	$\frac{(Pb^{++})^3}{(H^+)^3} \cdot 10^{-12}$	$k \cdot 10^8$ found	$k \cdot 10^8$ formula
0.02000 m $Pb(NO_3)_2$. $\delta = 0$.						
0.0000	0.1598	4.807	0.01998	0.002	1.22	1.20
0.1051	0.1683 ₅	4.955	0.01998	0.006	1.20	1.21
0.2102	0.1760	5.087	0.01997	0.015	1.20	1.21
0.3680	0.1848 ₅	5.241	0.01995	0.042	1.22	1.24
0.5242	0.1907	5.342	0.01994	0.084	1.30	1.28
0.6805	0.1953 ₅	5.422	0.01992	0.146	1.37	1.35
0.8687	0.1996 ₅	5.497	0.01990	0.244	1.44	1.44
*1.064	0.2026 ₅	5.549	0.01988	0.348	1.55	1.55
0.01000 m $Pb(NO_3)_2 + 0.0100$ m $Ba(NO_3)_2$. $\delta = 0$.						
0.0000	0.1697	4.978	0.00999	0.001	1.11	1.12
0.0789	0.1788	5.136	0.00998	0.003	1.11	1.12
0.1831	0.1888	5.309	0.00997	0.008	1.14	1.13
0.2892	0.1972 ₅	5.455	0.00997	0.023	1.14	1.14
0.4192	0.2044 ₅	5.580	0.00995	0.054	1.18	1.17
0.5565	0.2097	5.671	0.00994	0.101	1.24	1.22
0.6904	0.2138 ₅	5.743	0.00993	0.166	1.29	1.29
0.8436	0.2173 ₅	5.804	0.00991	0.251	1.36	1.37
*1.061
0.005000 m $Pb(NO_3)_2 + 0.0150$ m $Ba(NO_3)_2$. $\delta = 0$.						
0.0000	0.1785	5.131	0.004992	0.000	1.10	1.08
0.0627	0.1892 ₅	5.317	0.004989	0.001	1.07	1.08
0.1258	0.1984 ₅	5.476	0.004984	0.003	1.07	1.08
0.2101	0.2076 ₅	5.635	0.004976	0.010	1.09	1.09
0.2936	0.2146 ₅	5.757	0.004968	0.023	1.10	1.11
0.3766	0.2195 ₅	5.842	0.004960	0.041	1.13	1.13
0.4614	0.2241	5.920	0.004951	0.070	1.15	1.16
0.5463	0.2272	5.974	0.004943	0.101	1.20	1.19
0.6297	0.2296 ₅	6.017	0.004934	0.135	1.25	1.23
0.7335	0.2328 ₅	6.072	0.004924	0.196	1.28	1.30
*0.876
0.01000 m $Pb(NO_3)_2$. $\delta = 0$.						
0.0000	0.1673 ₅	4.961	0.00999	0.001	1.20	1.23
0.0786	0.1761	5.112	0.00998	0.002	1.21	1.23
0.1730	0.1850	5.266	0.00998	0.006	1.23	1.24
0.2625	0.1921	5.389	0.00997	0.015	1.24	1.24
0.3920	0.1998	5.523	0.00996	0.037	1.27	1.26
0.5245	0.2057	5.625	0.00994	0.074	1.31	1.30

(To be continued)

Table 2 (continued).

$x \cdot 10^4$	E	$-\log (H^+)$	(Pb^{++})	$\frac{(Pb^{++})^3}{(H^+)^3} 10^{-12}$	$k \cdot 10^8$ found	$k \cdot 10^8$ formula
0.6828	0.2110	5.717	0.00993	0.139	1.36	1.36
0.8332	0.2145	5.777	0.00991	0.209	1.43	1.42
*1.051	0.2177	5.833	0.00989	0.305	(1.58)	1.50
0.005000 m $Pb(NO_3)_2$. $\delta = 0$.						
0.0000	0.1740 ₅	5.087	0.004992	0.000	1.34	1.31
0.0627	0.1841 ₅	5.261	0.004988	0.001	1.29	1.31
0.1258	0.1924	5.404	0.004983	0.002	1.31	1.31
0.2097	0.2015 ₅	5.563	0.004976	0.006	1.30	1.32
0.2848	0.2073 ₅	5.663	0.004969	0.012	1.34	1.32
0.3693	0.2134 ₅	5.769	0.004960	0.025	1.33	1.33
0.4701	0.2186 ₅	5.859	0.004950	0.046	1.35	1.35
0.5469	0.2219 ₅	5.916	0.004943	0.068	1.37	1.37
0.6616	0.2249	5.967	0.004931	0.095	(1.47)	1.40
*0.783

Table 3.

Equilibrium constants found from the measurements in solutions of lead nitrate (a molar) and barium nitrate (b molar).

a	b	$(k_1 + k_{1,2} a) \cdot 10^8$ found	$(k_1 + k_{1,2} a) \cdot 10^8$ calcd.	$4 k_{4,4} 10^{21}$ found	$k_1 10^8$	$k_{1,2} 10^8$	$k_{4,4} 10^{21}$
0.4000	0.0000	3.19	3.18	4.14	0.18	7.50	1.06
0.3000	0.1000	2.43	2.43	4.35			
0.2000	0.2000	1.68	1.68	4.22			
0.2000	0.0000	2.27	2.24	6.41	0.45	8.96	1.60
0.1500	0.0500	1.73	1.79	6.42			
0.1000	0.1000	1.39	1.35	6.40			
0.0500	0.1500	0.89	0.90	6.4			
0.1000	0.0000	1.56	1.56	9.0	0.66	9.0	2.25
0.0750	0.0250	1.34	1.34	8.85			
0.0500	0.0500	1.11	1.11	9.0			
0.0250	0.0750	0.87	0.88	9.3			
0.0500	0.0000	1.30	1.30	9.6	0.85	9.0	2.3
0.0375	0.0125	1.19	1.19	9.1			
0.0250	0.0250	1.08	1.07	7.8			
0.0125	0.0375	0.95	0.96	10			
0.02000	0.0000	1.20	1.20	10	1.04	8	2.6
0.01000	0.0100	1.12	1.12	10			
0.00500	0.0150	1.08	1.08	11			
0.01000	0.0000	1.23	..	9	1.16	(7)	2.2
0.00500	0.0000	1.31	..	9	1.28	(6.5)	2.2

Table 4.

The equilibrium constants, hydrogen ion concentrations, and degrees of "hydrolysis" for pure aqueous solutions of lead nitrate (α molar), calculated by means of the formulae 16—18.

α	$k_1 10^8$	$k_{1,2} 10^8$	$k_{4,4} 10^{21}$	$-\log(H^+)$	pH	$\alpha_1 10^3$	$\alpha_{1,2} 10^3$	$\alpha_{4,4} 10^6$	$\alpha 10^3$
0.4000	0.18	7.50	1.06	3.947	3.92	0.016	0.530	1.6	0.55
0.2000	0.46	8.87	1.56	4.173	4.17	0.069	0.528	2.5	0.60
0.1000	0.66	9.3	2.37	4.397	4.41	0.166	0.464	3.7	0.63
0.0500	0.83	8.8	2.7	4.597	4.59	0.328	0.348	3.2	0.68
0.0200	1.03	7.7	2.4	4.812	4.80	0.668	0.201	1.4	0.87
0.0100	1.17	7.0	2.1	4.953	4.91	1.051	0.126	0.6	1.18
0.0050	1.28	6.5	1.9	5.091	5.04	1.582	0.080	0.2	1.66
0.0020	1.41	6.0	1.6	5.274	5.21	2.640	0.045	0.1	2.69
0.0010	1.48	5.7	1.5	5.414	5.34	3.838	0.015	0.0	3.85
0	1.67	5.1	1.2

Table 5.

Measurements of the hydrogen ion concentrations of lead nitrate solutions saturated with the salt $Pb(OH)NO_3$ at $18.0^\circ C$.

$$L = \frac{(Pb^{++})(NO_3^-)}{(H^+)}$$

No.	α	b	x	$-\log(H^+)$	$y 10^3$	(Pb^{++})	(NO_3^-)	$\log L$
1..	0.1000	0.0000	0.00069	5.196	0	0.09916	0.2000	(3.493) ¹
2..	0.1000	0.0000	0.00138	5.287	0	0.09844	0.2000	(3.581) ²
				5.265	0.07	0.09846	0.1999	3.559
3..	0.1000	0.0000	0.00275	5.268	1.47	0.09709	0.1985	3.553
4..	0.1000	0.0000	0.00551	5.282	4.20	0.09434	0.1958	3.549
5..	0.1000	0.0000	0.01101	5.307	9.70	0.08884	0.1903	3.535
6..	0.0500	0.0500	0.00138	5.595	0	0.04853	0.2000	(3.582) ²
				5.557	0.30	0.04854	0.1997	3.546
7..	0.0500	0.0500	0.00275	5.571	1.65	0.04717	0.1984	3.542
8..	0.0500	0.0500	0.00551	5.601	4.37	0.04441	0.1956	3.540

¹ No precipitate. The solution was unsaturated.

² No precipitate. The solution was supersaturated. When it was seeded, the results in the next line were obtained.

References.

- (1) K. J. PEDERSEN, D. Kgl. Danske Vidensk. Selskab, Mat.-fys. Medd. **XX** 7. (1943)
- (2) J. WALKER and E. ASTON, J. Chem. Soc. **67** (1895) 576, Proc. Chem. Soc. **11** (1895) 112.
- (3) J. H. LONG, J. Amer. Chem. Soc. **18** (1896) 717.
- (4) C. KULLGREN, Z. physik. Chem. **85** (1913) 466.
- (5) H. G. DENHAM and N. A. MARRIS, Trans. Faraday Soc. **24** (1928) 515.
- (6) J. A. CRANSTON and H. F. BROWN, J. Roy. Tech. Coll. (Glasgow) **4** (1937) 54.
- (7) E. C. RIGHELLATO and C. W. DAVIES, Trans. Faraday. Soc. **26** (1930) 592.

