

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 107.]

A STUDY OF SODIUM-LEAD COMPOUNDS IN LIQUID AM-
MONIA SOLUTION.

By F. HASTINGS SMYTH.

Received May 7, 1917.

Introduction.—For some time it has been known that solutions of sodium and potassium in liquid ammonia are capable of dissolving certain other metals such as lead, antimony and bismuth, and since these metals are themselves insoluble in pure ammonia, it follows that their solution is attended with the formation of intermetallic compounds of the sodium or potassium.

Two compounds of lead and sodium have been isolated by Joannis,¹ one having the composition corresponding to the formula NaPb , which is formed by the agitation of a large volume of sodium solution with metallic lead, and in addition another compound having the composition NaPb_4 , formed from the former compound by adding an excess of lead to the ammonia solution. This latter compound separates from its solution according to Joannis, with two molecules of ammonia of crystallization. Both compounds are only sparingly soluble in liquid ammonia.

¹ *Compt. rend.*, **113**, 797 (1890); **119**, 586 (1892).

Mathewson,¹ using Tammann's² method of thermal analysis, has established the existence of the series of compounds Na_4Pb , Na_3Pb , NaPb , Na_2Pb_5 . These compounds were formed by the direct union of the elements and only one of them corresponds to the compound isolated by Joannis.

Kraus³ first showed that solutions of the compounds of lead and sodium formed by the ammonia solution method are electrolytic in nature, and his work indicated that the ions Na^+ and Pb_2^- are present in them.

In an attempt to verify this result, Dr. Posnjak, working in this laboratory, undertook to electrolyze solutions of lead in sodium ammonia solutions. The investigation was of a preliminary nature and the method of procedure and results of his work will be briefly reviewed.

The solutions for the electrolysis were prepared in Dewar tubes, the ammonia being allowed to flow directly from a commercial ammonia cylinder into the tubes. The top of the Dewar flask was closed with a tight-fitting rubber stopper, through which passed three small glass tubes. Through one of the tubes small pieces of freshly cut sodium could be dropped into the ammonia in the flask, and through the other tubes a platinum gauze anode and a lead cathode could be lowered into or withdrawn from the solution. The anode was fitted with a pulley so that it could be rotated by a small motor. The solution was always allowed to stand for several hours in contact with an excess of metallic lead in the bottom of the Dewar tube before adjusting the previously weighed cathode and starting an electrolysis. It was thus hoped to make sure that all lead dissolved from the cathode should be the result of the electrolytic process only. With this arrangement air was probably excluded, since ammonia vapor passed continually out of the container. The concentration of the solution could not, however, be kept constant, neither could sufficient time be allowed before beginning an electrolysis to make certain that the sodium had completely reacted with the lead. Since commercial ammonia was used, dissolved air and water were also present. Even under the most favorable conditions some oxide was always introduced with the sodium and the initial concentration was only roughly estimated. The current used was measured with an ammeter, and the amount of electricity passed determined by taking ammeter readings at short intervals over a definite period of time.

After the completion of an experiment the electrodes were withdrawn from the solution by removing the rubber stopper and then plunged into a previously prepared Dewar tube containing pure ammonia. This method of washing is not altogether satisfactory. As will be seen later, the elec-

¹ *Z. anorg. Chem.*, **50**, 172 (1906).

² *Ibid.*, **37**, 303 (1903).

³ *THIS JOURNAL*, **29**, 1571 (1907).

trodes are difficult to clean under the best conditions. Exposing them to the air even for a moment, moistened with electrolyte at a temperature of -33° , results in the condensation of water and consequent oxidation of sodium and lead. The preliminary results thus obtained are given in Table I.

TABLE I.
Electrolysis of Sodium-Lead Solutions.

Time. Minutes.	Current. Ampere.	Anode gain. G.	Cathode loss. G.	G. atoms lead per faraday.	
				Anode.	Cathode.
40	0.0225	0.2505	0.2533	2.164	2.188
40	0.0255	0.2232	0.2550	1.928	2.203
44	0.0215	0.2750	0.2686	2.260	2.207
41	0.0215	0.2487	0.2465	2.193	2.174
40	0.0215	0.1823	0.2455	1.648 ¹	2.168
40	0.0215	0.2814	0.2444	2.602 ¹	2.214
40	0.0215	0.2383	0.2410	2.154	2.178
				Av., 2.14	2.19

The table is self-explanatory. In the first column is given the time of passing the current through the solutions, and in Col. 2 the value of the current passed as read on an ammeter. The weights of lead deposited at the anode and dissolved at the cathode, respectively, are tabulated in Cols. 3 and 4. Obviously these values should agree. The gram-atoms of lead deposited and dissolved per faraday are given in the last two columns.

Although these results do not permit of more than a qualitative discussion, they point, nevertheless, clearly to the fact that there are not exactly 2 g. atoms of lead deposited per faraday when the sodium-lead solutions are electrolyzed.

It was the purpose of the renewed investigation to electrolyze under carefully regulated conditions the solutions obtained when metallic sodium solutions in liquid ammonia are agitated with an excess of metallic lead. It was hoped to obviate the sources of error in the preliminary work mentioned above, and to establish more accurately the amount of lead transferred from cathode to anode per faraday, and to determine whether this amount is dependent upon such conditions as the concentration of the solution or the magnitude of the current used in the electrolysis. It was proposed also to verify these results by a direct determination of the solubility of lead in sodium-ammonia solutions.

Electrolysis of Sodium-Lead Solutions.

Experimental Details.—The apparatus used is shown diagrammatically in Fig. 1. The container *K* was so arranged that it could be left in a Dewar tube containing a bath of liquid ammonia at atmospheric pressure.

¹ Omitted in taking the average.

The contents could thus always be kept at -33° . The electrodes were introduced through the tubes E and E' of about 1 cm. internal diameter, sealed into the top of the container. The tube E was fitted with a cross tube B which gave a means for introducing a weighed amount of sodium in a manner to be presently described.

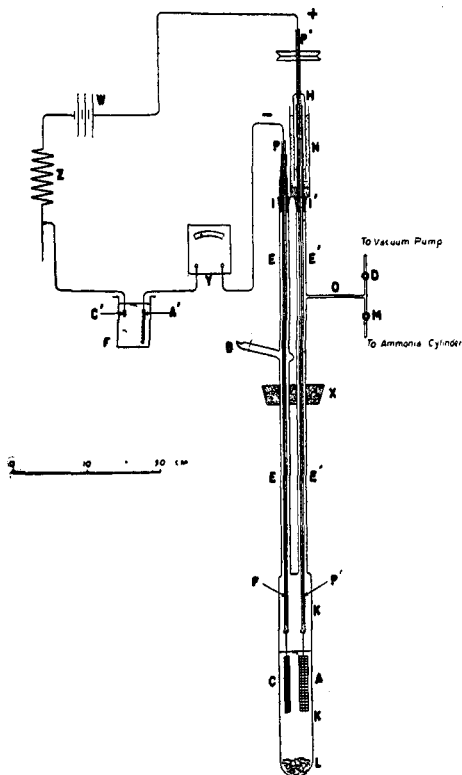


Fig. 1.

The space between P and the small outside tube through I was closed by drawing a piece of rubber pressure tubing over each and wiring it securely. This kind of seal was found entirely adequate. That the anode might be rotated, P' was fitted with a mercury seal as shown in the diagram at N . All the rubber used was previously treated by boiling in caustic potash.

The electrical connections are shown at the left of the diagram. The current was furnished by three Edison-Lalande cells, W , in series with a rheostat, Z . Two copper coulometers in series were used to measure the amount of electricity passed. One of them is shown diagrammatically at F . The cathode C' was of platinum foil, one centimeter square. The coulometers were compared with a silver coulometer and gave results which were concordant to 0.1% of the small current used. They, more-

The anode A consisted of a strip of fine platinum gauze bent into the form of a half cylinder. The cathode C was a cylinder of lead about 6 cm. long and 0.5 cm. in diameter, carefully freed from oxide by scraping with a sharp knife. Both anode and cathode were supported on small platinum hooks, so that they could be easily detached. The hooks were sealed through the supporting tubes P and P' . Electrical connections were made through fine copper wires which passed through P and P' , connecting at the bottom of the latter with the platinum hooks by means of mercury. The tubes P and P' were brought out of the top of the apparatus through tubes inserted in the perforated rubber

over, always gave consistent readings. The ammeter shown at *Y* was used merely to regulate the current.

The apparatus was connected by the tube *O* and the cock *D* to a vacuum pump which gave a vacuum of 0.002 mm. of mercury, and through the cock *M* to the ammonia cylinder shown in Fig. 3 at *Z*. This cylinder, together with the safety device *W* (Fig. 3) have already been described by Kraus.¹ The ammonia is freed from dissolved oxygen and water vapor by the introduction of metallic sodium in the container *Z*. All the glass tubing was cleaned with chromic acid mixture before making into the apparatus forms. The stopcocks were greased with a paraffin-gutta-percha mixture.

Manipulation.—The electrodes were removed from the apparatus together with the tubes *P* and *P'* and from 20 to 30 g. of lead were introduced in the form of freshly prepared turnings shown at *L* (Fig. 1). It was possible by turning the lead in a lathe to prepare a sort of lead wool giving a very large surface and filling the container *K* to a height of 4 or 5 cm. This lead was left in the bottom of each solution during the entire time it was in use. The ends of *E* and *E'* were tightly closed with solid rubber stoppers and sealed with asphaltum paint. This type of seal entirely prevented leakage of air into the apparatus.

The cross tube *B* could be opened at the point shown by the dotted line and a small sealed glass bulb, previously weighed, containing pure metallic sodium introduced in a position as shown at *A* (Fig. 3) lying across the tube *E*.

The form of the bulb *A* and the apparatus for introducing the sodium into it are shown in Fig. 2. The tube *H*, 5 mm. in diameter and several cm. long was drawn down at one end to a very fine capillary *F*, on the end of which was blown the sodium bulb *A*. This bulb had an internal diameter

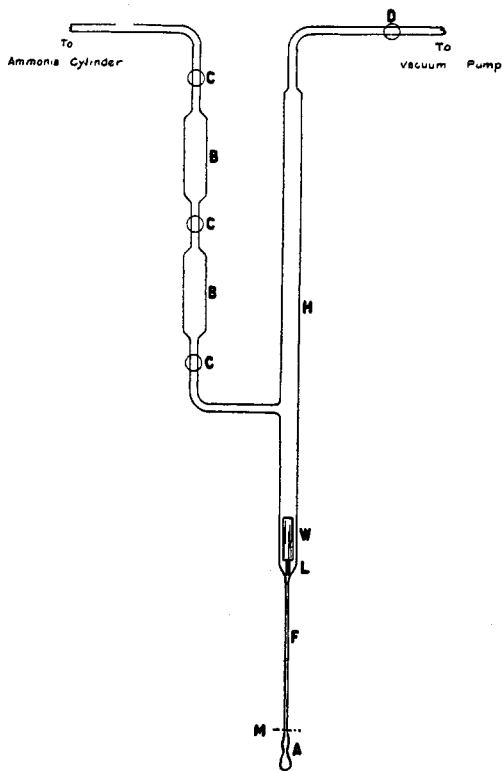


Fig. 2.

¹ THIS JOURNAL, 30, 1205 (1903).

of from 1 to 2 mm. at its central constricted portion. The side tube containing the two small reservoirs B, B , and the cocks C, C , served to connect the tube H with the ammonia cylinder. A piece of the freshly cut sodium of approximately the desired weight was dropped through the tube H into the position shown at L . W is a small glass weight which served later to crush the sodium and thus free the metal from the layer of oxide on the surface. After introducing the sodium, the open end of H was immediately sealed to the vacuum pump connection D , and the whole apparatus exhausted. The cocks D and C were then closed and a paraffin bath was placed around the bulb A , the capillary F and the lower part of H . The temperature of this bath was gradually raised until the sodium was melted and the oxide shell crushed by the weight W . Ammonia gas was now admitted slowly into H . The reservoirs B, B permitted the pressure to increase in H gradually. This pressure forced the molten sodium through the capillary F into the bulb A . The oxide could of course, not pass through the capillary, being filtered out.¹ The sodium was caught as a bright button in the bottom part of A . The bath having been removed, the bulb A was sealed off at the dotted line M . When cool, it was washed with ether, scratched at the constricted portion with a sharp file, weighed to 0.1 mg. and introduced into the tube B of Fig. 1. The end of the tube B was sealed and the entire apparatus thoroughly exhausted through the cock D .

The liquid ammonia bath was now placed around the container K and the lower part of tubes E and E' . The pump was shut off and ammonia allowed to enter under an excess pressure of twenty centimeters of mercury. Condensation on K and the cooled parts of E and E' was rapid and was allowed to continue until sufficient ammonia had distilled over. The solution was always made up to a mark on K which determined its volume.

In the meantime the electrodes had been carefully cleaned and weighed and hung on their respective supports P and P' . The flow of ammonia being partly shut off, the solid stoppers were removed quickly, the electrodes lowered a short way into their respective tubes and the openings closed with the perforated stoppers I and I' . During this part of the operation ammonia gas constantly streamed out of the open ends of E and E' , effectively preventing the inflow of any air and moisture. The anode A was lowered into the position shown in the figure, and the seal at the top adjusted and filled with mercury. The bulb containing sodium in B was broken by lowering P quickly through I , thus striking the bulb with the heavy cathode C . It always broke cleanly into two parts at the point scratched with the file and dropped into the ammonia in K . The opening made in the bulb was large enough to permit a rapid solution of the sodium. When large quantities of sodium were required it was possible

¹ THIS JOURNAL, 30, 1206 (1908).

to have several such bulbs in the tube *B*; as one broke the next one slid into place and could be broken in the manner already described. The cathode was not lowered into the solution until the latter was saturated with lead from the turnings in the bottom of the container. After the pressure tubing, sealing the opening around *I*, had been wired tightly into place, the ammonia was completely shut off at *M*, and the solution stirred over a period of from twenty-four to forty-eight hours by rotating the anode *A*.

When saturation was judged to be complete, the cathode was also lowered into the position shown in the figure, and the electrical connections made. The rate of rotation of the anode could not be raised above 120 r. p. m. with this arrangement and at this rate it was necessary to use very small currents in order to obtain a smooth deposit of lead. Higher current densities invariably produced a sort of "lead tree," which built across, giving direct contact with the cathode. When small crystals formed, as sometimes happened in dilute solutions, they seemed very coherent and no difficulty resulted from loss of material. The time of electrolysis varied from four to ninety hours, according to the current used.

After sufficient lead had been deposited, the current was shut off and the electrodes were drawn out of the solution into the lower parts of the tubes *E* and *E'*. The ammonia pressure was raised again by opening the cock *M* (Fig. 1) and fresh ammonia was allowed to condense on the sides of the tubes and flow over the electrodes. In this manner it was possible to remove adhering solution completely in a few minutes. The method of washing obviously necessitates having the object which is being washed in contact with the wall of the containing vessel, since otherwise no condensing liquid would come in contact with it. For this reason each electrode was provided with a separate tube which just contained it.

When the electrodes were clean and bright they were raised in the tubes and allowed to come to room temperature, after which they were withdrawn with the stoppers *I* and *I'* in the same manner as was used for their introduction. The solid stoppers were replaced and the apparatus was ready for a new electrolysis on the same solution. The electrodes were weighed at once to avoid oxidation. The lead deposited at the anode usually formed a clean coherent coating and remained unoxidized in the air for several hours.

When concordant values had been obtained with any one solution the ammonia was allowed to evaporate and the dry sodium-lead compound which remained in the container was dissolved out in dilute nitric acid. The pieces of the sodium bulb were collected, cleaned, dried and weighed to 0.1 mg. This completed the data needed for calculating the strength of the solution used.

Results.—Table II gives the results of the electrolyses carried out in the above manner. The first column contains a reference letter for each solution. The second column gives the concentration in g. atoms of sodium per liter, and Col. 3 the current used. In Cols. 4 and 5 are given the actual gain and loss of the anode and cathode, respectively, in g. The average of these two values is taken in computing the ratio of the g. atoms of lead transferred from cathode to anode per faraday of electricity. The latter values are found in the last column. Under Col. 7 are given the weights in grams of the copper deposited in the coulometers. Col. 6 contains the percentage difference between anode gain and cathode loss for the lead. Considering the nature of the deposits and the difficulty of washing, the agreement may be considered satisfactory.

TABLE II.

1.	2. Conc.	3. Current. Ampere.	4. Anode gain.	5. Cathode loss.	6. Diff. %.	7. Wt. copper.	8. G. atoms Pb. Faradays
A.....	0.025	0.0011	0.1819	0.1738	4.5	0.0115	2.37
	0.025	0.0011	0.4375	0.4312	1.4	0.0286	2.33
B.....	0.036	0.0050
	0.036	0.0013 ¹	0.7388	0.7236	2.5	0.0489	2.29
	0.036	0.0030 ¹	0.8176	0.8073	1.3	0.0550	2.27
C.....	0.13	0.0020	0.7607	1.0418	...	0.0641
	0.13	0.0020	0.6960	0.7389	5.8	0.0489	2.25
	0.13	0.0030	0.6654	0.6828	2.6	0.0462	2.25
	0.13	0.0035 ¹	0.7436	0.7561	1.7	0.0512	2.25
	0.13	0.010 ¹	0.6431	0.6410	0.3	0.0436	2.26
D.....	0.011	0.005	0.6953	0.6715	3.9	0.0468	2.24
	0.011	0.0025 ¹	0.8041	0.7868	2.5	0.0535	2.28
	0.011	0.0020 ¹	0.6086	0.6097	0.2	0.0409	2.28

Mean, 2.26

Discussion of Results.—It appears certain from the figures in Col. 8 that more lead is deposited per faraday than corresponds to the anion Pb_2^- with a single negative charge. Furthermore, the lead deposited is independent of the concentration throughout the ten-fold range between solutions *C* and *D*, if we discard the high results obtained in *A*. The solution *A* was the first one used, and skill in manipulation had not been acquired. Furthermore, the small amount of the deposit makes the percentage accuracy of the results less. The deposits themselves were not smooth and were difficult to wash. For these reasons no great consideration should be attached to the first two results.

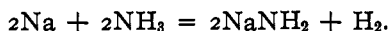
In all the remaining experiments the agreement is good. The large differences between anode and cathode change in the first electrolysis of *C* is due to the fact that the solution was not yet saturated with lead.

¹ Stirred during electrolysis.

Saturation may not have been quite complete in the second electrolysis of this series.

Errors due to the difficulty of cleaning the electrodes tend when averaged to compensate, since this causes the lead dissolved to appear too low and the lead deposited to appear too high by about the same amount. Incomplete saturation of the solution has the opposite effect at each electrode.

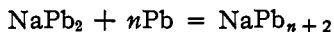
It is doubtless true, as has been mentioned by Kraus,¹ that during the comparatively slow solution of the lead, a still slower reaction between the dissolved sodium and the solvent is proceeding with the formation of sodamide and hydrogen.



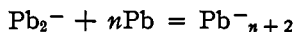
This reaction removes sodium from the solution, for the lead does not react with sodamide at all. When the lead-sodium compound has once formed, however, the formation of the amide ceases entirely. It is difficult to see, however, that small amounts of amide could effect the amount of lead deposited by electrolysis and this possibility has been therefore disregarded.

Large variations of the current used were impossible, owing to the difficulty in obtaining a good deposit with anything other than a low current density. Too low currents, on the other hand, consumed an excessive amount of time. However, the variation between the second run on Solution B and the fifth run on Solution C is nearly ten-fold, and concordant weights of lead were obtained in the two cases. The amount of lead deposited is consequently independent of the current used, and depends only on the amount of electricity passed.

These results may be explained by the assumption of the following equilibrium:



or



If these equations represent a measurable equilibrium, then, in the presence of metallic lead, the ratio of the concentration of the Pb_n^- ion to that of the Pb_2^- ion should be constant, and the amount of lead brought down by electrolysis per faraday should depend solely on this ratio; provided that equilibrium is not destroyed by passing too large a current. That equilibrium conditions here obtained is certain both on account of the small currents used and of the fact that the anode and cathode give check results

The mean amount of lead deposited per faraday is 2.26 g. atoms. In obtaining this result the first values with Solution A are entirely disregarded

¹ THIS JOURNAL, 29, 1571 (1907).

and more weight is given to the final results obtained with each solution in every case. This value corresponds to a mixture of compounds in the solution having the resultant composition of $\text{NaPb}_{2.26}$.

If, in the absence of definite information we put $n = 1$ in the above equilibrium, and if we make the assumption that the compounds NaPb_2 and NaPb_3 are equally dissociated, we can calculate the ratios

$$\frac{(\text{NaPb}_3)}{(\text{NaPb}_2)} = \frac{(\text{Pb}_3^-)}{(\text{Pb}_2^-)} = \text{const.} = \frac{0.26}{0.74} = 0.36,$$

where the brackets denote molal concentration of the substances when one g. atom of sodium is present. Obviously this amounts to assuming about three mols of NaPb_2 to one mol of NaPb_3 .

Solubility Determinations.

If an equilibrium like that assumed really exists, 1 g. atom of sodium should dissolve about 2.26 g. atoms of lead and not four as Joannis indicates. Direct solubility measurements were therefore undertaken.

Experimental Details.—The apparatus employed is shown in Fig. 3. It consisted of a containing vessel for making up the solution in a manner already described, a device for lowering, raising and washing the lead used free from solution without opening the apparatus, together with a means of stirring the solution while the lead was dissolving. A manometer was also attached to detect, if possible, any ammoniation of the compounds formed.

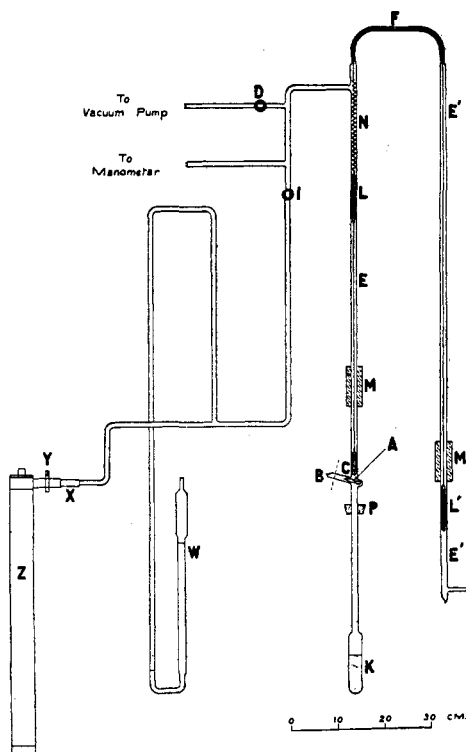


Fig. 3.

As in the electrolysis work, the container K was kept in a bath of liquid ammonia at -33° . The tubes E and E' were large enough to permit two soft iron cores L and L' to slip freely up and down inside of them. L and L' were joined through the spring N and a fine polished wire which

passed through the connecting tube *F*. The lead *C*, for the determination was suspended from *L* by means of a platinum wire. *M* and *M'* were movable solenoids outside the tubes *E, E'*. By means of a current through *M', L'* could be adjusted at any desired height, and the lead could be raised and lowered at will. Friction of the suspension wire in *F* maintained equilibrium. The cross tube *B* served to introduce a weighed quantity of sodium as in the apparatus of Fig. 1. Connections were made as shown to the vacuum pump, the manometer and the ammonia cylinder *Z*.

The manipulation of this apparatus was similar to that of the electrolysis experiments, the main difference being that after the apparatus was once sealed and evacuated it was not reopened for any purpose until work with the solution was finished. The tube *E* was cut midway between the top of the container *K* and the Dewar tube stopper *P*. A piece of lead like that previously used as a cathode was scraped and weighed, attached to the suspension wire and drawn into the position shown in the figure by adjusting *L'*. The container was then sealed back into place.

One or more weighed bulbs filled with pure sodium were introduced into the tube *B*, a few centimeters below the lead *C*, already in position as described. The tube *B* was sealed, the apparatus evacuated and a known volume of ammonia distilled into the container. The core *L* was now given a quick downward pull by means of the solenoid breaking the sodium bulb in the manner described above. The lead was immediately lowered into the sodium solution thus formed, and by means of a make and break circuit through *M*, was moved up and down by means of the suspension spring *N* while solution was taking place. After several hours the lead was withdrawn, washed in fresh ammonia, removed from the apparatus and weighed. The pieces of the sodium bulb were also collected and weighed. No attempt was made to keep or analyze the compounds formed.

Results.—In the following table are given the results of the solubility measurements:

TABLE III.
Solubility of Lead in Sodium Solutions.

No.	Time. Hours.	Wt. sodium. G.	Wt. lead. G.	Conc.	$\frac{\text{G. atoms Pb}}{\text{G. atoms Na}}$
1.....	36	0.0673	1.360	0.11	2.24
2.....	36	0.0988	1.889	0.14	2.12
3.....	24	0.0860	1.680	0.13	2.17
4.....	60	0.0837	1.338	0.12	1.78
5.....	60	0.0895	1.569	0.078	1.95
6.....	72	0.3804	6.305	0.33	1.83
7.....	168	0.3836	5.941	0.34	1.73
8.....	72	0.0746	1.4757	0.093	2.20
9.....	96	0.0755	1.3796	0.094	2.03

In the first column is given the number of the experiment, and in the second the time during which the lead was agitated in the sodium solution. The third and fourth columns contain the weights of lead and sodium determined as described above. The fifth column gives the concentration of the sodium solution in g. atoms per liter, and the last column contains the g. atoms of lead dissolved per g. atom of sodium.

Discussion of Results.—In the more dilute solutions one atom of sodium dissolves at least two and usually considerably more than two atoms of lead, while in the more concentrated solutions and in Solution No. 4 the amount of lead dissolved per atom of sodium is less than this. In no case are results obtained which warrant the selection of any particular value for the amount of lead that one atom of sodium carries into solution with it. We find, however, that the results unmistakably confirm the values obtained in the previous electrolysis work.

The sources of error are: First, the possibility that a sufficient time was not allowed for the action of the lead with the sodium to become complete. This would seem improbable, however, in view of the fact that twenty-four hours' agitation in Expt. 3 gives a very high result, while Expt. 4, with less sodium, gives a low result after sixty hours. Second, it is possible that the lead was not absolutely clean after removal from the solution, though its constancy in weight on exposure to the air and its clean appearance seemed to indicate that it was free from adhering solution. By far the greatest source of error is probably that already mentioned, namely, the loss of sodium by action with the solvent with the formation of sodamide. This reaction is easily catalyzed by platinum or other metals and metallic oxides. It is probable that the lead itself has such an effect, causing the variations in some of the results. In the more concentrated solutions it should be expected that the formation of amide proceeds more rapidly, with a proportionally less amount of action on the lead, which the results confirm. In the dilute solutions probably the larger part of the sodium remains to react with the lead since the results are proportionally higher.

As a means of measuring the amount of the sodamide reaction, the attempt was made to determine the hydrogen evolved during Expt. 9. For this purpose the apparatus of Fig. 3 was fitted with the tube *O*, which could be opened under water through the cock *H*, in such a way that the escaping ammonia could be absorbed and any gaseous residue could be caught in a eudiometer tube. This sample was analyzed by combustion with oxygen and 1.8 cc. of hydrogen were found in it. Blank runs in the same way with gas directly from the cylinder *Z*, showed the entire absence of hydrogen in the ammonia used as solvent in the last experiment. The hydrogen found therefore could have been formed only during the experiment. The quantity of hydrogen collected is equiv-

alent to 0.0035 g. of sodium. If this be subtracted from the total sodium we have available for the lead compound only 0.0720 g. This gives a ratio of g. atoms of lead to g. atoms of sodium of 2.13 instead of 2.03 as given in Table III.

The apparatus was not well designed for the collection of hydrogen after an experiment, as there were too many small side tubes which could not be washed out with fresh ammonia. It is, however, proved that hydrogen is evolved in amounts large enough to make considerable difference in the available sodium and consequently in the ratio thus determined of lead to sodium. Very little doubt is therefore left that all the ratios as shown in Table III are too low. This conclusion is confirmed by the electrolysis data and affords direct evidence that there is formed under the conditions of these experiments a quantity of a compound richer in lead than NaPb_2 . Certainly, however, no large amount of a compound NaPb_4 , such as Joannis appears to have obtained quantitatively, is formed.

The behavior of the solutions during an experiment is of interest. Within thirty minutes after the lowering of the lead into the solution, the latter loses its characteristic blue color, and becomes a very dark green. Shortly after this a metallic looking precipitate collects on the sides of the container. With large amounts of sodium this effect is very marked, and the walls of the tube look as if a silver mirror had been formed on them. This precipitate might be attributed to the formation of the slightly soluble NaPb which Joannis formed by treating lead with an excess of sodium solution. After a prolonged agitation with lead, however, this precipitate always redissolves. The higher compound of lead is therefore much more soluble than that which is formed in the first stages of the reaction.

As ammonia is removed from the solutions by evaporation, the vapor pressure slowly falls, until solid begins to separate, when the pressure remains constant until the last traces of solvent have disappeared. The pressure, then, however, immediately drops to zero, and no evidence of ammoniation of the compound which first separates could be observed.

Summary.—The compounds formed when solutions of metallic sodium in liquid ammonia are agitated with excess of metallic lead at -33° have been investigated. These compounds are very soluble in liquid ammonia and separate without ammonia of crystallization.

It has been found by direct solubility determinations that one atom of sodium carries into solution at least 2.20 atoms of lead, but that the true value is somewhat higher than this, since sodium is lost through interaction with the solvent.

Electrolysis of the sodium lead solutions shows that 2.26 g. atoms of lead are deposited at the anode and dissolved at the cathode for each faraday passed. This value is independent of the concentration of the

solution up to a concentration of 0.1 molal sodium, and also of the electrolyzing current.

This unusual result has been explained by assuming an equilibrium to exist between a Pb_2^- ion and another negative ion of the form Pb_3^- , in the presence of metallic lead. On this basis the equilibrium ratio

$$\frac{(Pb_3^-)}{(Pb_2^-)} = \text{Const.} = \frac{0.26}{0.74} = 0.36,$$

has been calculated.

In conclusion, it is a pleasure to acknowledge the help and encouragement received from Professor C. A. Kraus, formerly of this laboratory, whose active interest has contributed much to the completion of this research.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MANITOBA.]

THE RHYTHMIC PRECIPITATION OF COLLOIDAL MERCURY.

BY HAROLD S. DAVIS.

Received April 20, 1917.

The rhythmic precipitation of solids¹ is a well-known phenomenon. It is obtained in the case of two dissolved substances which interact to form a precipitate when one of the substances is allowed to diffuse into a solution of the other in gelatine. In such a case, the precipitate is not continuous but is formed in distinct layers or rings, separated by clear spaces in which there is no precipitate.

The rhythmic precipitation of a gas, carbon dioxide, has been described by Morse and Pierce.²

In regard to rhythmic precipitation of liquids, Füchtbauer³ states that he obtained a perceptible rhythmic precipitation of chloroform when it was thrown down by potassium hydroxide diffusing into a solution of chloral hydrate.

Experimental Part.

The rhythmic precipitation of mercury was obtained in the following way: A 3% solution of agar-agar was prepared on a steam bath and heated for about half an hour till all the particles had dissolved. To it was added about 5% of solid sodium formate, after which the liquid was sucked up into pieces of small glass tubing, where it set to a jelly. The tubes were then cut into lengths of about 8 cm. and placed in a horizontal position on the bottom of a crystallizing dish containing a 2% solution

¹ Rothmund, "Löslichkeit und Löslichkeitbeeinflussung," 9 (1908); H. J. M. Creighton, *THIS JOURNAL*, 36, 2355 (1914).

² *Proc. Amer. Acad. Sci.*, 38, 625 (1903).

³ *Z. physik. Chem.*, 48, 566 (1904).