HYDROGEN ION CONCENTRATION OF LEAD SOLUTIONS.

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The precipitation method of manufacturing white lead consists in passing carbon dioxide through a solution of basic lead acetate prepared by dissolving lead oxide in acetic acid. The carbonation is continued till the filtrate gives no precipitate with mercuric chloride. In actual practice, the carbonation is continued 45 minutes after the above test is obtained in order to get the right sort of precipitation. Overcarbonation leads to the formation of normal lead carbonate, which has low covering power and to the loss of acetic acid carried away by the excess gases. In order to rationalise the control of the process, it was thought worthwhile to measure pH changes in the manufacture by potentiometric methods.

The measurement of pH solution of lead salts is a matter of some difficulty. The hydrogen electrode does not work owing, perhaps, to the poisoning action of lead on platinum black. Quinhydrone electrode has been tried but it does not work above pH 9. The measurements described in the present paper were done with antimony and bismuth and quinhydrone electrodes, calibrated previously using the valve electrometer potentiometer described in an earlier communication (*Proc. Ind. Acad. Sci.*, 1934, **1A**, 390).

Incidentally, these electrodes were used to measure the pH of distilled water, lead and antimony hydroxide solutions in order to get an idea of their solubility products. Measurements are also reported for the pH of solutions of normal lead acetate and specially prepared, pure basic lead acetate.

EXPERIMENTAL.

Materials used were lead acetate, recrystallised from chemically pure sample, yellow lead oxide and basic lead acetate. The latter was prepared according to the method of Löwe (*J. pract. Chem.*, 1866, **98**, 385) by treating six parts of lead oxide with seven parts of lead acetate in thirty parts of water for about 30 minutes at a temperature of about 25°C. The precipitate containing lead carbonate, excess of lead oxide and the less soluble basic lead acetate were separated from the filtrate designated A.

Basic lead acetate was then separated from the insoluble impurities of lead oxide and lead carbonate contained in the precipitate by treating the precipitate with cold water and then with large quantities of boiling water. The resulting solution containing only basic lead acetate was evaporated with exclusion of air, and basic lead acetate was crystallised out, dried in vacuum on water bath. The amount of lead in the sample as determined by the chromate method was 80.5%. To one part of the filtrate A were added about 10 parts of 90 % alcohol and kept for about five days. Crystalline basic acetate of lead insoluble in alcohol was separated out and dried in vacuum. The amount of lead in this sample was also 80.5 per cent. According to Löwe's formula for dibasic acetate of lead $3PbO,C_4H_6O_3$ (calculated water free), the percentage of lead in the sample amounts to 81.06. According to Jackson (*Bulletin of the Bureau of Standards*, 1915, 11, 331), there is only one basic lead acetate which is capable of existence in the solution of itself. The formula he assigns for the substance is $Pb\ (C_2H_3O_2)_2.2PbO.4H_2O$. The formula assigned by Löwe to his sample of dibasic acetate of lead can also be rewritten as $Pb(C_2H_3O_2)_2.2PbO$, which is the same as that assigned by Jackson to his sample of salt without the water of crystallisation.

The pH values of basic lead acetate and lead acetate solutions were obtained by quinhydrone and antimony electrodes. As solutions of these salts are readily affected by exposure to atmospheric carbon dioxide, a special apparatus (Fig. 1) was designed for the preparation of the solution and the filling up of the solution in the cells without exposing the solutions to air. The water used in making the solutions was freed from carbon dioxide by boiling and allowing to cool in the air which was passed through soda lime tubes. The water was transferred to a measuring cylinder to which a known weight of substance was previously added and the cylinder weighed. The solution was transferred to the electrode vessel which was also previously filled with air free from carbon dioxide. pH values of distilled water and conductivity water were determined by quinhydrone, hydrogen and antimony electrodes.

The pH values of the solutions of yellow lead oxide used in the preparation of basic lead acetate were next determined. The electrodes employed were bismuth and antimony. Quinhydrone electrode was also tried. The saturated solutions of lead oxide were prepared in water carefully freed from carbon dioxide. The vessels used in making the solutions were made of Jena glass. The cell used for the measurement of pH values was made of pyrex glass in some experiments.

DISCUSSION OF RESULTS.

The above results show that the pH values of lead acetate and basic lead acetate as determined by quinhydrone electrode are different from those obtained by the antimony electrode. Britton and Meek (*J. Chem. Soc.*, 1931, 2831), in studying the constitution of acetates, have determined the pH values of solutions made in acetic acid. They

FIG. ①.

APPARATUS FOR PREPARING CO_2 FREE SOLUTIONS.

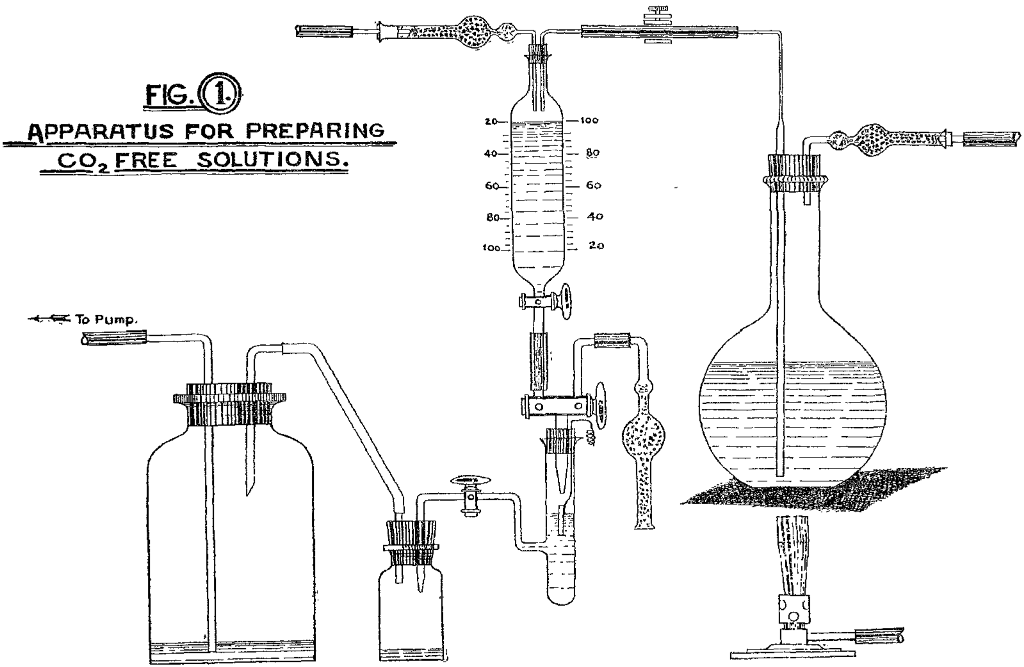

TABLE I.

Results of Experiments carried out with Lead Salts.

Temp. °C.	Solution used for measurement	Electrode used	E.M.F. observed in volt	pH
24.15	Normal lead acetate (0.0852 mol.) in distilled water in pyrex glass ..	Quinhydrone	0.1197	5.70
21.70	Normal lead acetate (0.0852 mol.) in distilled water in pyrex glass ..	do.	0.1197	5.70
24.57	Basic lead acetate (0.001 mol.) ..	do.	0.0377	7.04
25.00	Normal lead acetate (0.0391 mol.) in distilled water in soft glass ..	do.	0.1105	5.78
24.40	Normal lead acetate (0.0391 mol.) in distilled water in soft glass ..	do.	0.1042	5.90
25.00	Normal lead acetate in distilled water in soft glass	Antimony	0.2469	4.66
25.00	Basic lead acetate (0.0119 mol.) in distilled water in soft glass ..	do.	0.3289	6.06
29.53	Basic lead acetate (0.0152) in distilled water in soft glass ..	Quinhydrone	0.0460	6.77
29.77	Basic lead acetate (0.0152 mol.) in distilled water in soft glass ..	Bismuth	0.2320	7.47
29.82	Normal lead acetate (0.0768 mol.) in distilled water in soft glass ..	Quinhydrone	0.1105	5.68
30.40	Normal lead acetate (0.0768 mol.) in distilled water in soft glass ..	Bismuth	0.1161	5.51
25.00	Lead oxide (yellow) in conductivity water	Quinhydrone	0.0565	8.61
25.00	Lead oxide (yellow) in conductivity water in pyrex glass	do.	0.0542	8.51
25.00	Lead oxide (yellow) in conductivity water in soft glass	Antimony	0.4634	8.35
25.00	Lead oxide (yellow) in distilled water in soft glass	Antimony	0.4745	8.52

TABLE I.—(*Contd.*)

Temp. °C.	Solution used for measurement	Electrode used	E.M.F. observed in volt	pH
25.00	Lead oxide (red) in conductivity water in soft glass	Antimony	0.4277	7.73
25.00	Lead oxide (red) in distilled water in soft glass	do.	0.4244	7.68
24.20	Lead oxide (yellow) in conductivity water in pyrex glass	do.	0.4632	8.41
23.95	Lead oxide (yellow) in conductivity water in pyrex glass	Quinhydrone	0.0871	9.18
23.95	Lead oxide (yellow) in conductivity water in pyrex glass	Antimony	0.4733	8.60
29.50	Lead oxide (yellow) in conductivity water in pyrex glass	Quinhydrone	0.0336	8.09
29.50	Lead oxide (yellow) in conductivity water in pyrex glass	Bismuth	0.3057	8.72
26.65	Lead oxide (yellow) in conductivity water in pyrex glass	Quinhydrone	0.0295	8.08
28.80	Lead oxide (yellow) in conductivity water in pyrex glass	Antimony without Sb_2O_3	0.4046	7.01
22.75	Conductivity water in pyrex glass ..	Quinhydrone	0.0463	6.93
22.65	Conductivity water in soft glass ..	do.	0.0471	6.92
25.00	Conductivity water in soft glass ..	Hydrogen	0.6353	6.57
24.95	Distilled water in soft glass ..	do.	0.7073	7.79
25.00	Conductivity water in soft glass ..	Antimony	0.3335	6.13
25.00	Conductivity water in soft glass ..	do.	0.3000	5.57
25.00	Distilled water in soft glass ..	do.	0.3025	5.61
25.00	Antimony trioxide in soft glass ..	Quinhydrone	0.1129	5.74

have also determined the pH values of basic lead acetate solutions prepared by shaking fairly concentrated solutions of lead acetate with varying amounts of lead oxide for several days. The pH values of basic lead acetate increased as the acetate content diminished and tended to exceed the pH value at which lead hydroxide was normally precipitated.

Britton and Meek (*J. Chem. Soc.*, 1932, 183) obtained a value of 5.91 pH for the normal lead acetate which is in rough agreement with the value obtained in Table I. These authors have reported the formation of the compound $3Pb(OH)_2,Pb(C_2H_3O_2)_2$ *from the sudden rise* on addition of 1.5 equivalent of caustic soda. Their study of the mixtures of lead acetate and lead oxide did not include the proportion to form $Pb(C_2H_3O_2)_2,2PbO$, which is the only compound capable of existence in the solution of itself. The solution of this latter salt is nearly neutral according to the authors' measurements.

The pH values determined by the quinhydrone electrode were taken as correct. The pH values obtained with the antimony electrode were regularly less than those obtained by the quinhydrone electrode. These low results are probably due to the reaction of added antimony oxide with the basic lead salt. These results were further checked by making use of the bismuth electrode. The pH values of lead acetate obtained with the bismuth electrode agreed very closely with those obtained with the quinhydrone electrode, thus confirming the view that the lower pH values of lead solutions were probably due to the acidic behaviour of antimony trioxide added. The pH values of basic lead acetate obtained with the bismuth electrode did not agree very closely with those obtained with quinhydrone electrode.

The results obtained with these electrodes in case of water were very different. The value obtained with the hydrogen electrode for distilled water was higher than the one for conductivity water. The pH values of conductivity water were determined by employing three different electrodes. The values are given as under:—

Antimony electrode.

0·3255 volt		
0·3325 ,,	Mean value 0·3335 volt	Mean pH
0·3405 ,,	± 7·5 millivolts	6·13 ± 0·12
0·3355 ,,		

Quinhydrone electrode.

0·0362 volt		
0·0470 ,,	Mean value 0·0471 volt	Mean pH
0·0582 ,,	± 11 millivolts	6·92 ± 0·20
0·0470 ,,		

Hydrogen electrode.

0·6235 volt		
0·6484 ,,	Mean value 0·6353 volt	Mean pH
0·6340 ,,	± 12·5 millivolts	6·57 ± 0·20
0·6353 ,,		

John O. Burton, Harry Matheson and S. F. Acree (*Ind. Eng. Chem. Anal. Edn.*, 1934, **6**, 79) have measured the pH values of tap water, boiler water, and double distilled water. Their values with double distilled water are:—Hydrogen electrode 6.18–7.66; Quinhydrone electrode 6.05–5.71; and Glass electrode 6.57. From the above results it is seen that the smaller drift and variation in the case of the values obtained by us for the conductivity water are due to the use of electrometer triode circuit. The best values, which the three investigators obtained, were those with the glass electrodes. The antimony electrode showed the least drift in our experiments.

The pH values determined by antimony electrode for lead oxide solutions were different from those obtained with the bismuth electrode. For comparison, the pH values were calculated for the yellow form of lead oxide from the solubility product 0.91×10^{-15} obtained by M. P. Applebey and R. D. Reid (*J. Chem. Soc.*, 1922, 2129), and 0.82×10^{-15} obtained by Glasstone (*J. Chem. Soc.*, T., 1921, **119**, 1689, 1914), and are given as under:—

Applebey and Reid: 9.28 pH; Glasstone: 9.27 pH; Authors: 9.34 pH (Bismuth), 8.57 pH (Antimony), and 9.17 pH (Quinhydrone). The above results with bismuth as well as antimony electrodes were calculated by using the values of E_0 obtained from graph by making use of the method of successive approximations. The results lead to the view that the antimony electrode is not as suitable as bismuth electrode for the measurements of lead salts, because of its comparatively more acidic character. Bismuth electrode, if calibrated in the range, gives better results than those obtained with antimony electrode.

The E.M.F. of the cell $Hg|Hg_2Cl_2|KCl$ sat.$||H_2O|Sb_2O_3|Sb$ was 0.3335 at 25°C. The pH calculated by taking the value 0.0293 for E_0, found by calibrating with solutions of known pH, comes out 6.13, almost exactly identical with the value calculated by the solubility product 4×10^{-42}. The quinhydrone electrode, however, gave a value of 5.74 pH. It is obvious that the addition of the antimony trioxide to the electrode for measuring pH values higher than 6.13 is not to be recommended and, as will be shown elsewhere, is not necessary.

TABLE II.

Solution No.	Temp. °C.	Electrode used	E. M. F. observed in volt	pH
I	25·76	Quinhydrone	0·0887	6·13
II	27·83	do.	0·1074	5·77
III	28·22	do.	0·1571	4·93
IV	27·98	do.	0·1685	4·74
V	26·24	do.	0·1739	4·69

The pH values determined by the quinhydrone electrode of the solutions obtained in the process of making white lead (Table II) show that the pH of the starting substance, basic lead acetate is 6.14, which is considerably lower than that of the dibasic acetate of lead investigated by the authors. The initial solution gives precipitate with mercuric chloride. Then the second solution is obtained after bubbling carbon dioxide through the initial solution of basic lead acetate till it gives no longer precipitate with mercuric chloride. The pH determined for solution II is 5.77 as shown in the Table II. The solutions III, IV and V are obtained after bubbling carbon dioxide for 15, 30 and 45 minutes respectively through the solution II. The pH values for III, IV and V are 4.93, 4.74 and 4.69 respectively. The indicators suitable for this range are precipitated by lead salts. Moreover, the pH change is so narrow that electrometric control is highly desirable. Quinhydrone electrode is the only reliable and easily workable electrode for this purpose.

SUMMARY.

1. The pH values of solutions of yellow lead oxide and antimony trioxide have been measured by using antimony, bismuth and quinhydrone electrodes. The results support those calculated from solubility data.

2. The pH values of solutions of normal lead acetate agree approximately with those obtained by Britton. The solutions of basic lead acetate $Pb(C_2H_3O_2)_2,2PbO$ were found to be about pH 7.0.

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