nant until lead hydroxide is exhausted. As a result of this we find at the upper end of CD a slight but unmistakable change of curvature.

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

Summary.

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

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

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

4. The solid phases capable of existence are:

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

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

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

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

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

By Henry Jermain Maude Creighton.

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When a drop of silver nitrate solution is placed on a thin layer of gelatin containing potassium dichromate, silver chromate precipitates out in circles which are concentric to the drop of silver nitrate. Such precipitation of silver chromate has been investigated during the past few years by Liesegang and others.[1] Analogous phenomena have been observed by Liesegang[2] with mercurous chromate, lead chromate and Prussian blue, and by Morse and Pierce[3] with lead sulfate, silver carbonate, phosphate, bromide and thiocyanate, cobalt hydroxide, barium chromate and mercurous bromide. This phenomenon of rhythmical precipitation is explained by Ostwald's theory of supersaturation.[4]

Phenomena similar to the foregoing have recently been observed by the writer with Turnbull's blue and ferrous hydroxide.

The horizontal part of a glass tube 70 cm. long and 2 cm. in diameter, the ends of which were bent up at right angles, was filled with a 10% solution of agar-agar containing small quantities of potassium ferricyanide and sodium chloride. After the jelly had solidified, the vertical arms of the tube were filled with a dilute solution of sodium chloride, and an iron electrode, made from a clean wire nail, was placed in the liquid in each arm. An electric current having a potential gradient of 0.00679 volt per cm. was then passed through the jelly.

Within a short time after the current was started, the end of the jelly near the anode became blue, and for four days the blue color continued to advance through the jelly. During the following twenty-four hours there was no perceptible advance of the color, but at the end of this time a very thin dark blue layer or disc was observed to have formed in the jelly at right angles to the axis of the tube. This blue disc gradually increased in thickness during the next few hours until it attained a width of 1 mm. This disc, which was more intense in color than the blue jelly

Fig. 1.

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[1] R. E. Liesegang, *Z. physik. Chem.*, **23,** 365 (1897); **59,** 444 (1907); **88,** 1 (1914); Morse and Pierce, *Ibid.*, **45,** 589 (1903); Bechhold, H., *Ibid.*, **52,** 185 (1905).

[2] "Chemische Reaktionen in Gallerten," Düsseldorf, 1898.

[3] *Loc. cit.*

[4] "Lehrb. d. allgem. Chemie," 2 Aufl., **2,** 778.

behind it, was separated from the latter by 3 mm. of practically colorless jelly. At the end of another twenty-four hours a second disc had formed which was separated from the first by 4 mm. of colorless jelly. In this experiment a new disc appeared every twenty-four hours, the discs forming in the direction of the flow of the electric current. The time at which each disc appeared, and the distance between each disc and the preceding one is shown in Table I.

TABLE I.

Number of disc.	Turnbull's blue discs.		Ferrous hydroxide discs.	
	Time of appearance of disc. Days.	Distance between consecutive discs. Mm.	Time of appearance of discs. Days.	Distance between consecutive discs. Mm.
1	0	...	0	.
2	1	4.0	1	3
3	2	4.0	2	5
4	3	5.0	3	3
5	4	4.0	4	5
6	5	3.5	5	4
7	.	...	6	4
8	.	...	9	6
9	.	...	11	4
10	.	...	14	6

An experiment similar to the foregoing was carried out, except that the jelly contained small quantities of sodium chloride and phenolphthalein. The ferrous ions diffused into the jelly under the influence of an electric current having a potential gradient of 0.0093 volt per cm. The progress of the hydroxyl ions was followed by means of the phenolphthalein. The ferrous and hydroxyl ions, which were moving in opposite directions, met at the end of one hundred and fifteen days from the beginning of the experiment, and a dark green layer or disc of ferrous hydroxide was precipitated in the jelly at right angles to the axis of the tube. At the end of twenty-four hours, a second disc was observed to have formed. This was separated from the first by 3 mm. of jelly, colored pink by the phenolphthalein. Every day or two a new disc formed, each being separated from the preceding by several millimeters of pink jelly. The discs formed in the opposite direction to the flow of the electric current. The time at which each disc appeared, and the distance between each and the preceding one is shown in Table I. Fig. 1 shows a photograph of the ferrous hydroxide discs. The ferrous hydroxide discs always commenced to form at the bottom of the tube and continued to grow towards the top, always sloping in the opposite direction to the flow of the electric current. Sometimes a new disc started to form before the preceding one was completed. In such cases the old disc ceased growing. The photograph shows several of these partially formed discs.

The cause of the rhythmical precipitation of Turnbull's blue and ferrous hydroxide may doubtless be ascribed to supersaturation phenomena. As the Fe^{++} ions are carried into the jelly by the electric current, a metastable supersaturated solution with respect to Turnbull's blue first forms. Ultimately precipitation occurs and the $FeCy_6^{---}$ ions in the neighborhood are removed; the Fe^{++} ions then advance a few millimeters and form a new supersaturated solution, when the process is repeated. In the case of ferrous hydroxide, the OH^- ions form a supersaturated solution with the Fe^{++} ions. After precipitation has taken place, the OH^- ions must advance a few millimeters before a sufficient number of Fe^{++} ions are encountered to form a new supersaturated solution.

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THE SULFATE METHOD FOR STANDARDIZING A MAGNESIUM SALT SOLUTION.

By C. W. Foulk and O. R. Sweeney.

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For a number of years one of us has had work in progress on the precipitation of magnesium as magnesium ammonium phosphate, the object being to discover, if possible, the causes of the discrepancies among the results by different methods and especially those obtained by various workers with the same method. As the investigation progressed it seemed to fall more and more into a study of the preparation of pure material and of the art of measuring the substances produced, until finally it narrowed to the question of preparing and standardizing a solution of a magnesium salt.

This trend of the work was an evolution rather than a part of the original program. At first a large amount of work was done in the way of comparing methods and of course different results were obtained. Different results were also obtained at times by the use of the same method. These differences were small and might have been due to impure reagents, improper handling or finally to lack of knowledge as to the exact concentration of the solution of magnesium salt used. As the subject was taken up by successive advanced students whose interest prompted them to undertake a share in the experimental work, new sources of error were found and studied. When these corrections were applied, they sometimes had the effect of reducing or eliminating the discrepancies in the results of the magnesium-ammonium-phosphate precipitations and sometimes they had the effect of making these discrepancies larger. The notes on the earlier part of this work were destroyed by the burning of the Chemical Building at the Ohio State University in 1904. A summary of the rest will be presented in a separate paper.