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.

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

THE RHYTHMIC PRECIPITATION OF COLLOIDAL MERCURY.

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The rhythmic precipitation of solids[1] 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, Füchtbauer[3] 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

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[1] Rothmund, "Löslichkeit und Löslichkeitbeinflussing," 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).

of mercurous nitrate, slightly acidified with nitric acid. The dish was put into an air bath at about 53° and left there for twelve hours. At the end of the time, the mercury was found to have precipitated in distinct layers in the tubes.

The tubes were then taken out of the solution of mercurous nitrate, wiped dry and sealed at the ends with paraffin to prevent evaporation. The photograph, shown in natural size in the figure, was made after a couple of days.

The nature of the precipitation in this tube is typical of that in all the other tubes. Starting from the end where precipitation first began, there is a heavy black precipitate, 2.5 mm. in width, then a comparatively clear space of 2.8 mm., in which two, or possibly three, faint bands may be distinguished. The contrast between the clear space and the precipitate is much sharper in the original tube than in the photograph. There follows a well-defined band about 0.4 mm. wide even three more faint ones in a space of about 2.5 mm., and lastly a cloud of precipitate showing no striae.

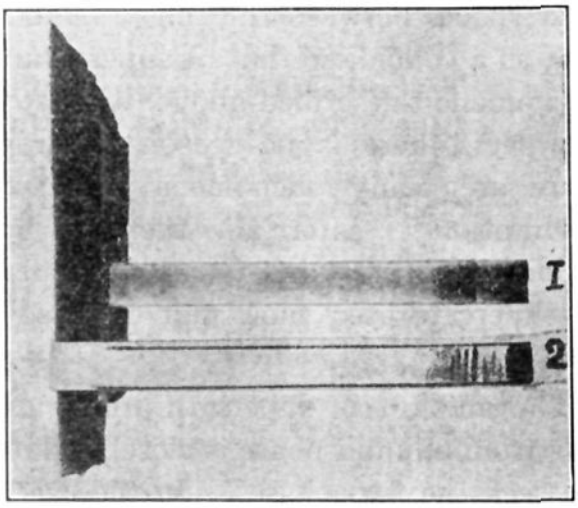

Fig. 1.—Natural size.
1. Photograph of tube.
2. Diagram of tube and rings.

The width of the bands and the distances between excessive bands become less as one moves up the tube. This is exactly the reverse of the phenomenon encountered in the rhythmic precipitation of silver chromate in tubes. However, Stansfield[1] has shown in the case of silver chromate that the width of the bands and the distance between successive bands are dependent on the relative strengths of the interacting reagents.

The reaction depends upon the reduction of mercurous nitrate to metallic mercury by means of the sodium formate. If the temperature is much below 50° the reduction takes place too slowly. When examined under the microscope it was found that the mercury had precipitated in drops and that the smaller the size of the drops, the more frequently they occurred; that is, the smallest drops were the most numerous. These were of fairly constant size, about 0.0001 cm. in diameter. Any drops in the clear spaces between the rings were large ones.

Rhythmic precipitation in the form of concentric rings was obtained by using a watch glass instead of tubes. In this case, a particle of mer-

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[1] *Am. J. Sci.*, **43**, 1–27 (1917).

curous nitrate was placed in the center of a gelatine layer containing sodium formate and covering the glass. This watch glass was tightly covered by another to prevent evaporation.

Discussion of Results.

It is almost generally accepted that rhythmic precipitation is caused by the formation of supersaturated solutions of the precipitate in the clear spaces between the rings. But mercury is not soluble in water except as a colloid, so that, if supersaturation is the true explanation of the phenomenon described above, it must be the supersaturation of a colloid. However, there is no reason to suppose that this is impossible, while there are many phenomena which can only be explained on such an assumption.[1] After all, there is no essential difference between a colloidal solution and a true molecular dispersoid; further the existence of supersaturated molecular dispersoids of liquids in liquids has been established.[2]

The amount of supersaturation possible in the case of a phase separating from a liquid phase is closely related to the interfacial surface tension between the two phases. In the case of most solids this is large; hence, supersaturated solutions of solids in liquids are common, but in the case of most liquids it is comparatively small so that supersaturation of liquids in liquids is usually hard to detect. However, as the following table shows the interfacial surface tension between water and mercury is relatively great; hence supersaturated solutions of colloidal mercury might be expected.

Substances.	Interfacial surface tension.
Calcium sulphate and water	550[3]
Isobutyric acid and water	1.76[3]
Carbon disulphide and water	38[4]
Mercury and water	370[4]

Summary.

(1) The conditions for obtaining a rhythmic precipitation of mercury are described.

(2) It is suggested that this phenomenon is due to the formation of supersaturated solutions of colloidal mercury and the case is advanced as further proof of: (*a*) The existence of supersaturation phenomena in colloidal solutions. (*b*) The existence of supersaturated dispersoids of the type liquid in liquid.

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[1] Wolfgang Ostwald, "Colloid Chemistry," 3rd Ed., translated by Fischer, p. 138.

[2] THIS JOURNAL, **38**, 1166 (1916).

[3] Frank B. Kendrick, *Trans. Am. Electrochem. Soc.*, **23**, 424 (1913).

[4] Landolt, Börnstein, "Tabellen," 1912.