

# Solubility Behavior of Lead Oxide in Perchloric Acid

LELAND W. MARPLE<sup>1</sup> and DAVID N. HUME  
Massachusetts Institute of Technology, Cambridge 39, Mass.

Conflicting reports concerning the solubility of lead oxide in perchloric acid have been resolved by a study over a wide range of ratios of lead oxide to perchloric acid. The maximum solubility corresponds to the formation of the species  $Pb_3(OH)_4^{+2}$ . An excess of lead oxide results in the precipitation of a new compound, the simplest formula for which would be  $Pb_3(OH)_5ClO_4$ , with the almost complete removal of lead from solution.

PATTANAİK AND PANI (3) apparently unaware of prior work (1, 4, 5), reported studies on the solubility of lead oxide in perchloric acid which pointed to the quantitative formation of the soluble species  $PbOH^+$  as the product of the reaction. The disagreement of this result with certain of the earlier investigations, particularly Hayek and Schnell who found good evidence for the formation of  $Pb_3(OH)_4^{+2}$  from the solubility of lead oxide in lead perchlorate solutions, prompted an examination of the solubility behavior in greater detail and over a wide range.

## EXPERIMENTAL

Reagent grade chemicals were used throughout. Yellow lead oxide was heated to 600° C. in an aluminum container to remove carbonate impurities and cooled in vacuo. When treated in this fashion, the oxide that resulted was always bright yellow. Lead oxide prepared by ignition of lead oxalate gave the same results. Sodium perchlorate was prepared from perchloric acid and sodium hydroxide. Carbonate was removed from the sodium perchlorate solutions by addition of a slight excess of perchloric acid and boiling. In order to define the variation of lead content as a function of lead oxide, a series of experiments were performed in which varying amounts of lead oxide were added to 50.0 ml. of a 0.103M perchloric acid—0.320M sodium perchlorate solution. Great care had to be taken to exclude carbon dioxide which reacts avidly with alkaline lead solutions. The mixtures were stirred (magnetically) for 22 hours at 25° C., and then held for two hours at 25.0 ± 0.1° C. Five-ml. samples were then withdrawn by syringe and analyzed gravimetrically for lead by precipitation as the sulfate.

Experiments in which the progress of the dissolution was followed with a glass-calomel electrode pair sealed in the cell showed the reaction to be rapid. With an excess of acid present, solution was complete in a few minutes. With a small excess of oxide, the pH rose to about 8.3 in 2 to 10 min.; if the excess were large, the pH would then climb to about 10.5 and remain constant after two to three hours. The results of these equilibrations are given in Table I.

## DISCUSSION

A plot of the millimoles lead found in solution vs. the total millimoles lead oxide added gives the surprising result shown in Figure 1. From this curve, it is first apparent that a maximum of approximately one and one-half moles of lead oxide can dissolve for each mole of acid added. The peak solubility is found at a ratio of 1.56 moles of lead oxide per mole of perchloric acid. A confirmatory run gave a value of 1.51. This suggests the

predominance in solution of a species of the type  $Pb:OH = 3:4$ , in confirmation of the observations of Hayek and Schnell. This also agrees with the very recent findings of Olin (2) whose careful pH studies indicate that  $Pb_3OH_4^{+2}$  should be the predominant species in solutions of this concentration, and pH range near 8.

The most striking feature of the curve, however, is the complete disappearance of dissolved lead upon the addition of a real excess of lead oxide. That a new solid phase is formed is indicated by the white color of the solid on the descending branch of the curve. When more lead oxide is added than is necessary to precipitate lead from solution completely, the resulting solid is cream to yellow in color

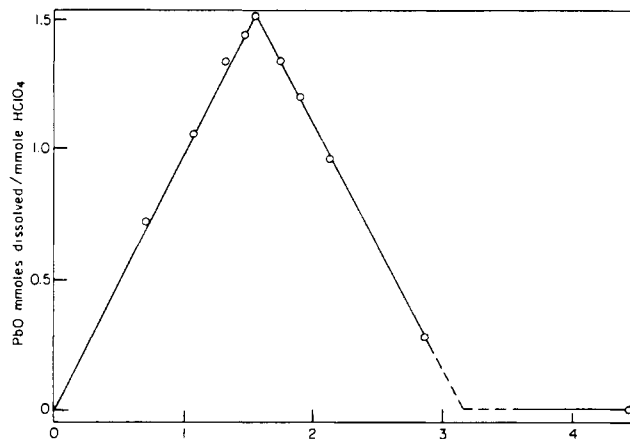


Figure 1. Solubility of lead oxide in perchloric acid as a function of the amount of lead oxide used

Table I. Effect of Added Lead Oxide on the Amount of Lead Dissolved by a Perchloric Acid Solution  
Starting solution is 50.0 ml. 0.103M Perchloric Acid  
(5.15 mmoles) in 0.320M sodium perchlorate

Mmoles PbO Added	Mmoles PbO Dissolved per 0.10 Aliquot	Lead Conc. Moles/Liter
3.70	0.375	0.0751
5.61	0.550	0.1101
6.88	0.696	0.1392
7.65	0.750	0.150
8.08	0.785	0.1571
9.105	0.697	0.1395
9.89	0.624	0.1248
11.04	0.500	0.100
14.85	0.145	0.029
22.88	0.000	0.000
32.89	0.000	0.000

<sup>1</sup> Present address: Iowa State University, Ames, Iowa.

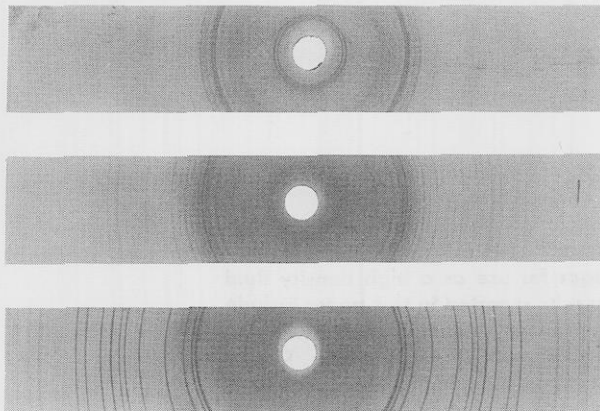


Figure 2. X-ray powder diffraction patterns of solids.

Left to right: white solid from descending branch of solubility curve, yellow solid residue from equilibration with excess oxide, lead oxide.

due to the excess of yellow lead oxide. Examination of the solid phases by x-ray powder diffraction was made using a general Electric XR-D3 instrument employing 1.54A. copper radiation. Figure 2 shows the pattern of the white solid to be distinctly different from the pattern of water-washed lead oxide, and the yellow solid obtained with excess oxide to be a mixture of the two.

From the slope and intercept of the descending branch of the solubility curve, the reaction proportionality would appear to be  $Pb_3(OH)_4(ClO_4)_2 \cdot 3PbO$ . Neglecting hydration, the simplest formula for the product, assuming conversion

of oxide to hydroxide, would then be  $Pb_3(OH)_5ClO_4$ . The white solid was analyzed for lead and perchlorate content, the latter by reduction of the perchlorate to chloride in fused sodium carbonate and subsequent precipitation of the chloride from aqueous solution with silver acetate. The ratio found, 3.2: 1.0, supports the above formula rather than the assertion by Pattanaik and Pani that their white solid phase was free of perchlorate. The fact that their solid phase was always white suggests a possible explanation for both the consistency and the nature of their results. If an experimenter were to assume a priori that  $PbOH^+$  was the product and systematically add two moles lead oxide for each mole of perchloric acid so as to have a 100% excess, the result would always be one mole of lead in solution as  $Pb_3(OH)_4^{+2}$  and one in the solid phase as the basic perchlorate. This could then easily be misinterpreted as indicating a reaction to give only  $PbOH^+$ . The equilibrium pH values of the order of 6.0 to 6.5 are not as readily explained.

This work was supported in part by the United States Atomic Energy Commission under Contract AT(30-1)-905.

#### LITERATURE CITED

- (1) Hayek, E., Schnell, E., *Monatsh.* 85, 472 (1954).
- (2) Olin, A., *Acta Chem. Scand.* 14, 126 (1960).
- (3) Pattanaik, R.K., Pani, S., *J. Indian Chem. Soc.* 34, 709 (1957).
- (4) Reiff, F., Müller, A., *Z. anorg. allgem. Chem.* 229, 285 (1936).
- (5) Weinland, R., Stroh, R., *Ber.* 55, 2706 (1922).

RECEIVED for review September 6, 1963. Accepted March 18, 1963. This work was supported in part by the United States Atomic Energy Commission under contract AT(30-1)-905.