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The Solubility of Red, Yellow, and Black Lead Oxides (2) and Hydrated Lead Oxide in Alkaline Solutions. The Character of the Lead-Bearing Ion

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Lead hydroxide is one of the classical examples of amphoteric hydroxides. A large amount of information has been obtained on the solubility of lead oxide in alkali.[1-6] Notable among the contributors of this information are Mueller,[1] who has obtained data for high concentrations of alkali, and Topleman,[2] who has made a rather comprehensive study of the different forms of lead oxide but has obtained data for only a few concentrations of dilute alkali. The data of Randall and Spencer[3] served the purpose for which they were obtained but they cover only a very limited range of concentration of alkali.

After reviewing this work it was deemed desirable to obtain more comprehensive data on the solubility of lead oxide, particularly at low concentrations of alkali. Such data are necessary to determine the degree of dissociation of lead hydroxide,[7] to investigate the character of the lead bearing ion,[8] to calculate certain free energy values and to afford a further study of the allotropic forms of lead oxide.

Procedure

The general procedure was similar to that described in previous papers.[7-9]

Preparation of Lead Oxide.—Three different preparations of yellow (sometimes called *olive*) lead oxide were used. Preparation Y1 was a Reagent sample of yellow lead oxide supplied by The Merck Chemical Company.[10] This was fine crystalline material with a rich lemon yellow color. Preparation Y2 was obtained by precipitating white lead hydroxide (hydrated lead oxide) from Mallinckrodt Reagent lead nitrate and carbonate free alkali; the method of preparation of the alkali was similar to that described in other papers.[7-9] This material was washed free of salts with conductivity water and the product dissolved in hot 5 *M* sodium hydroxide. On cooling, large flakes of lemon yellow lead oxide precipitated. Preparation Y3 was obtained in a manner similar to that of Preparation Y2 except that an excess of white lead hydroxide was warmed in 5 *M* sodium hydroxide to effect the dehydration. This gave a sample which varied from a yellow to a very definite olive-yellow color.

Two different preparations of red lead oxide were used. Preparation R1 was made by dissolving the white lead hydroxide in hot 10 *M* sodium hydroxide. On cooling, red crystals of lead oxide were formed. Preparation R2 was made by warming an excess of the white lead hydroxide in 10 *M* sodium hydroxide. The solid phase changed through olive-yellow to red after several minutes of stirring.

Black lead oxide was prepared by dissolving the white lead hydroxide in 6 *M* sodium hydroxide heated to about 80°. On slow cooling graphite-like crystals of black lead oxide precipitated. This form of lead oxide must be similar to that described by Topleman[11] in reviewing the work of V. Kohlschütter and P. Scherrer[12] who claim that "Zwei Modifikationen von Blei (2) oxyd existieren: eine sogenannte olivenfarbene, in hellgelben, grünlichgelben, graugrünen und schwärzlichen Farbtönen, über 600° stabile, und eine vermutlich polymere, rote, tetragonale Form, die bei gewöhnlicher Temperatur beständig ist."[12a] Whether this black colored oxide has any other different properties than the lemon-yellow colored oxide in addition to a difference in color remains yet to be determined. Even though it may be assumed from the statement of the above workers that they are the same allotropic modification yet the extreme difference in color would be a suggestion that they may differ in other properties such as density, solubility, etc.

White lead hydroxide was prepared by the method described above in the Preparation Y2 of yellow lead oxide.

All of these preparations were washed at least fifteen times with hot conductivity water previous to use.

Protection against Silica.—Topleman[2] has shown that glass is very readily attacked by a solution of lead oxide and alkali. In order to avoid this difficulty our samples were placed in paraffined flasks which were sealed with a glass-paraffin seal made by filling a 3-inch (8-cm.) glass cap with paraffin and imbedding the neck of the flask in the complete length of this cap so prepared. This gave a very firm seal. It was further sealed and also protected from rupturing in the vigorous stirring process by wrapping the cap-flask joint with several layers of Okonite rubber tape. Several samples, however, were prepared in unparaffined flasks. Comparison of data showed no apparent change in lead content by reaction with dissolved silica. However, it was observed that most of the samples prepared in

(1) Mueller, *Z. physik. Chem.*, **114**, 129 (1925).
(2) Topleman, *J. prakt. Chem.*, **229**, 320 (1929).
(3) Randall and Spencer, THIS JOURNAL, **50**, 1572 (1928).
(4) Wood, *J. Chem. Soc.*, **97**, 887 (1910).
(5) Glasstone, *ibid.*, **119**, 1689 (1921).
(6) Applebey and Reid, *ibid.*, **121**, 2129 (1922).
(7) See paper by Johnston, Cuta and Garrett, THIS JOURNAL, **55**, 2311 (1933), for a discussion of this calculation for AgOH.
(8) See paper by McDowell and Johnston, *ibid.*, **58**, 2009 (1936), for a discussion of this interpretation for copper hydroxide.
(9) Garrett and Hirschler, *ibid.*, **60**, 299 (1938).
(10) We are grateful for the use of this material made available to us by the kindness of The Merck Chemical Company.
(11) Topleman's paper[2] contains an excellent review of information and literature references concerning the different forms of lead oxide.
(12) V. Kohlschütter and P. Scherrer, *Helv. Chim. Acta*, **7**, 337 (1924).
(12a) Two modifications of lead oxide (2) exist: a so-called olive form in bright yellow, greenish-yellow, grey-green and black colors, stable above 600° and a probable polymeric, red, tetragonal form which is stable at ordinary temperatures.

unparaffined flasks gave a variable amount of a white residue which analyzed from $PbO \cdot H_2O$ to $PbO \cdot {}^1/_2H_2O$; little or no silica was found. Only a very few of the samples from the paraffined flasks showed a change in the character of the solid phase throughout the entire range studied. Analysis of each preparation and of the solid phase showed no change in the lead content.

Protection against Contamination.—All water used was conductivity water and all work was carried out in an atmosphere of nitrogen.

Temperature.—The solubilities were measured at 25.00 ± 0.02°.

Analysis.—The alkali content of the samples was determined by titration with standard acid using a mixed indicator. The very dilute samples were made up with a known concentration of alkali. The alkalinity of the very dilute samples was redetermined by titration with standard acid with the aid of a micro buret.

The lead content of the samples was determined by the lead chromate method.[13] This method was tested with standard solutions of lead nitrate throughout the entire range of concentrations studied.

The Equilibrium Period.—Equilibrium was approached from both supersaturation(s) and undersaturation(u). The equilibrium period of twenty-one to thirty days was established on the basis of the agreement of these two values.[14]

The Data

The data are collected in Tables I, II, III, IV, and V, and are shown graphically in Figs. 1, 2, and 3, in which the total concentration of lead oxide is plotted on the ordinates and the concentration of the alkali is plotted on the abscissas. Some samples were made up in pairs and the averages of the (s) and (u) values are given. In many cases it was found convenient to make up individual samples in order to cover more completely the concentration range and to show more graphically any variation in (s) and (u) samples.

Calculation of Data.—The data have been calculated in terms of moles of sodium hydroxide and moles of lead oxide per 1000 g. of water. These calculations were made by the method suggested by Randall and Spencer.[3] The calculations of the alkali were made by assuming that the following reactions occurred on titrating the alkaline samples with acid at the end-point of mixed indicator

$$H^+ + OH^- \rightleftharpoons H_2O \quad (1)$$
$$3H^+ + HPbO_2^- \rightleftharpoons Pb^{++} + 2H_2O \quad (2)$$
$$2H^+ + Pb(OH)_2 \quad Pb^{++} + 2H_2O \quad (3)$$

The following reactions in alkaline solutions above 0.001 *M* have been eliminated as a result of the analysis of the data showing either (a)

TABLE I

WATER SOLUBILITY OF LEAD OXIDE

Moles red lead oxide 1000 g. water	Moles yellow lead oxide 1000 g. water	Moles black lead oxide, 1000 g. water
$2.25^s \times 10^{-4}$	$5.39^s \times 10^{-4}$	$5.55^s \times 10^{-4}$
$2.10^u \times 10^{-4}$	$4.46^u \times 10^{-4}$	$5.24^u \times 10^{-4}$
$2.46^s \times 10^{-4}$	$4.23^u \times 10^{-4}$	$3.90^u \times 10^{-4}$
$2.18^s \times 10^{-4}$	$5.44^u \times 10^{-4}$	
$2.13^u \times 10^{-4}$	$4.76^u \times 10^{-4}$	
Av. 2.26×10^{-4}	$4.10^s \times 10^{-4}$	
	$4.31^s \times 10^{-4}$	
	$5.22^u \times 10^{-4}$	
	$5.02^u \times 10^{-4}$	
	Av. 4.77×10^{-4}	

(13) Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, New York, N. Y., 1927, p. 275.

(14) See refs. 7, 8, and 9, for method of obtaining equilibrium.

TABLE II

THE SOLUBILITY OF RED LEAD OXIDE IN SODIUM HYDROXIDE SOLUTION

Moles of alkali[a] 1000 g. water	Moles of lead 1000 g. water	$K_5 = m_{HPbO_2^-}/m_{OH^-}$
3.00×10^{-4}	1.10×10^{-4}	
4.00×10^{-4}	0.73×10^{-4}	
5.32×10^{-4}	$.67 \times 10^{-4}$	
$9.45^s \times 10^{-4}$	$.82 \times 10^{-4}$	
1.56×10^{-3}	1.18×10^{-4}	4.9×10^{-2}
$3.60^u \times 10^{-3}$	1.77×10^{-4}	3.8×10^{-2}
$4.74^u \times 10^{-3}$	2.19×10^{-4}	4.6×10^{-2}
5.16×10^{-3}	2.91×10^{-4}	5.6×10^{-2}
$7.33^s \times 10^{-3}$	3.49×10^{-4}	4.8×10^{-2}
8.49×10^{-3}	4.57×10^{-4}	5.4×10^{-2}
1.099×10^{-2}	5.30×10^{-4}	4.5×10^{-2}
$1.248^u \times 10^{-2}$	5.87×10^{-4}	4.4×10^{-2}
1.465×10^{-2}	7.29×10^{-4}	4.7×10^{-2}
1.664×10^{-2}	8.06×10^{-4}	5.2×10^{-2}
1.685×10^{-2}	8.56×10^{-4}	4.8×10^{-2}
$2.340^s \times 10^{-2}$	9.21×10^{-4}	3.8×10^{-2}
2.525×10^{-2}	8.95×10^{-4}	3.4×10^{-2}
2.90×10^{-2}	1.20×10^{-3}	4.0×10^{-2}
$4.190^s \times 10^{-2}$	1.68×10^{-3}	4.0×10^{-2}
$4.820^u \times 10^{-2}$	2.09×10^{-3}	4.3×10^{-2}
$8.340^u \times 10^{-2}$	3.35×10^{-3}	4.0×10^{-2}
$9.440^s \times 10^{-2}$	4.47×10^{-3}	4.7×10^{-2}
1.234×10^{-1}	5.59×10^{-3}	4.5×10^{-2}
1.465×10^{-1}	5.74×10^{-3}	4.0×10^{-2}
1.716×10^{-1}	6.86×10^{-3}	3.9×10^{-2}
2.468×10^{-1}	1.20×10^{-2}	4.9×10^{-2}
3.504×10^{-1}	1.80×10^{-2}	5.1×10^{-2}
4.045×10^{-1}	2.04×10^{-2}	5.0×10^{-2}
$5.360^u \times 10^{-1}$	2.85×10^{-2}	5.3×10^{-2}
1.070	5.03×10^{-2}	4.7×10^{-2}
1.324^u	6.00×10^{-2}	
1.316^u	5.31×10^{-2}	
2.750^s	1.201×10^{-1}	
2.911^u	1.022×10^{-1}	
3.281^u	1.363×10^{-1}	
4.070^u	1.177×10^{-1}	
5.040^u	1.154×10^{-1}	

[a] u = equilibrium approached from side of undersaturation. s = equilibrium approached from side of supersaturation. Unmarked values are *average* of pair of u and s values; this is true of Tables II, III, IV and V.

TABLE III

THE SOLUBILITY OF YELLOW LEAD OXIDE IN SODIUM HYDROXIDE SOLUTIONS

Moles of alkali 1000 g. water	Moles of lead 1000 g. water	$K_6^{=}$ $m_{HPbO_2^-}/m_{OH^-}$
$1.50^u \times 10^{-4}$	4.08×10^{-4}	
$3.00^u \times 10^{-4}$	3.47×10^{-4}	
7.02×10^{-4}	2.58×10^{-4}	
$7.48^u \times 10^{-4}$	2.17×10^{-4}	
$7.85^u \times 10^{-4}$	1.63×10^{-4}	
$8.2^s \times 10^{-4}$	2.42×10^{-4}	
$8.2^s \times 10^{-4}$	2.21×10^{-4}	
$1.06^u \times 10^{-3}$	2.55×10^{-4}	
$1.22^s \times 10^{-3}$	2.00×10^{-4}	
1.24×10^{-3}	2.08×10^{-4}	
$1.42^s \times 10^{-3}$	2.25×10^{-4}	
$1.81^u \times 10^{-2}$	2.37×10^{-4}	7.7×10^{-2}
$1.43^s \times 10^{-3}$	2.21×10^{-4}	6.5×10^{-2}
2.58×10^{-3}	2.92×10^{-4}	7.4×10^{-2}
$3.24^s \times 10^{-3}$	3.02×10^{-4}	6.2×10^{-2}
$3.60^u \times 10^{-3}$	3.98×10^{-4}	8.3×10^{-2}
3.79×10^{-3}	3.77×10^{-4}	7.4×10^{-2}
3.99×10^{-3}	3.33×10^{-4}	5.8×10^{-2}
$4.70^u \times 10^{-3}$	4.30×10^{-4}	7.0×10^{-2}
4.92×10^{-3}	4.78×10^{-4}	7.7×10^{-2}
$5.13^u \times 10^{-3}$	4.79×10^{-4}	7.4×10^{-2}
6.41×10^{-3}	5.34×10^{-4}	6.7×10^{-2}
$6.60^u \times 10^{-3}$	6.28×10^{-4}	8.0×10^{-2}
$7.64^u \times 10^{-3}$	7.27×10^{-4}	8.3×10^{-2}
$8.16^s \times 10^{-3}$	6.65×10^{-4}	7.0×10^{-2}
$9.80^u \times 10^{-3}$	7.70×10^{-4}	6.8×10^{-2}
9.95×10^{-3}	7.98×10^{-4}	7.0×10^{-2}
1.16×10^{-2}	1.02×10^{-3}	7.8×10^{-2}
$1.29^u \times 10^{-2}$	1.05×10^{-3}	7.4×10^{-2}
$1.46^u \times 10^{-2}$	1.43×10^{-3}	8.9×10^{-2}
$1.49^u \times 10^{-2}$	1.15×10^{-3}	7.0×10^{-2}
$1.54^s \times 10^{-2}$	1.13×10^{-3}	6.7×10^{-2}
$1.92^u \times 10^{-2}$	1.63×10^{-3}	7.8×10^{-2}
$1.94^s \times 10^{-2}$	1.45×10^{-3}	7.2×10^{-2}
$2.38^u \times 10^{-2}$	1.66×10^{-3}	7.0×10^{-2}
2.43×10^{-2}	1.65×10^{-3}	6.6×10^{-2}
$2.62^u \times 10^{-2}$	1.45×10^{-3}	5.3×10^{-2}
$2.92^s \times 10^{-2}$	1.88×10^{-3}	6.2×10^{-2}
$3.34^s \times 10^{-2}$	2.19×10^{-3}	6.6×10^{-2}
$3.83^s \times 10^{-2}$	2.92×10^{-3}	7.6×10^{-2}
$4.07^u \times 10^{-2}$	3.18×10^{-3}	7.8×10^{-2}
$4.24^u \times 10^{-2}$	2.98×10^{-3}	6.9×10^{-2}
$6.14^u \times 10^{-2}$	4.06×10^{-3}	6.8×10^{-2}
$7.16^s \times 10^{-2}$	4.46×10^{-3}	6.2×10^{-2}
7.58×10^{-2}	5.14×10^{-3}	6.8×10^{-2}
9.80×10^{-2}	7.14×10^{-3}	7.2×10^{-2}
$1.036^s \times 10^{-1}$	7.80×10^{-3}	6.9×10^{-2}
1.216×10^{-1}	8.48×10^{-3}	6.9×10^{-2}
1.449×10^{-1}	1.09×10^{-2}	7.0×10^{-2}
1.885×10^{-1}	1.33×10^{-2}	7.0×10^{-2}
3.018×10^{-1}	2.17×10^{-3}	7.2×10^{-2}
$3.190^u \times 10^{-1}$	2.29×10^{-2}	7.2×10^{-2}
3.51×10^{-1}	2.23×10^{-2}	6.4×10^{-2}
$4.11^s \times 10^{-1}$	3.07×10^{-2}	7.5×10^{-2}
$4.24^s \times 10^{-1}$	3.03×10^{-2}	7.2×10^{-2}
$4.33^s \times 10^{-1}$	3.44×10^{-2}	7.9×10^{-2}
4.60×10^{-1}	3.08×10^{-2}	6.7×10^{-2}
5.94×10^{-1}	3.89×10^{-2}	6.6×10^{-2}
$6.21^s \times 10^{-1}$	4.26×10^{-2}	6.9×10^{-2}
$6.95^u \times 10^{-1}$	4.82×10^{-2}	6.9×10^{-2}
$7.21^u \times 10^{-1}$	4.86×10^{-2}	6.7×10^{-2}
$7.89^s \times 10^{-1}$	5.72×10^{-2}	7.3×10^{-2}
$9.49^s \times 10^{-1}$	7.08×10^{-2}	7.5×10^{-2}
1.141^s	7.27×10^{-2}	
1.393^s	7.98×10^{-2}	
1.540	9.28×10^{-2}	
2.180^u	1.238×10^{-1}	
2.661	1.293×10^{-1}	
3.107^u	1.409×10^{-1}	
3.920^s	1.232×10^{-1}	
3.970^u	1.561×10^{-1}	

TABLE IV

SOLUBILITY OF WHITE LEAD HYDROXIDE IN SODIUM HYDROXIDE SOLUTIONS

Moles of alkali 1000 g. water	Moles of lead 1000 g. water
1.80×10^{-3}	2.85×10^{-4}
2.38×10^{-3}	2.63×10^{-4}
2.29×10^{-3}	2.89×10^{-4}
2.44×10^{-3}	3.11×10^{-4}
$2.95^u \times 10^{-3}$	3.09×10^{-4}
$2.98^u \times 10^{-3}$	3.75×10^{-4}
$4.12^u \times 10^{-3}$	3.75×10^{-4}
$4.16^u \times 10^{-3}$	4.18×10^{-4}
$4.75^u \times 10^{-3}$	4.50×10^{-4}
$5.31^s \times 10^{-3}$	5.02×10^{-4}
$5.65^s \times 10^{-3}$	5.22×10^{-4}
$5.70^s \times 10^{-3}$	6.01×10^{-4}
6.08×10^{-3}	5.47×10^{-4}
$6.12^u \times 10^{-3}$	5.86×10^{-4}
6.46×10^{-3}	5.68×10^{-4}
$1.20^u \times 10^{-2}$	9.06×10^{-4}
$1.41^u \times 10^{-2}$	1.04×10^{-3}
$1.61^u \times 10^{-2}$	1.42×10^{-3}
2.68×10^{-2}	2.29×10^{-3}
4.78×10^{-2}	4.67×10^{-3}
8.12×10^{-2}	7.47×10^{-3}
$9.13^s \times 10^{-2}$	8.46×10^{-3}
12.07×10^{-2}	11.0×10^{-3}

TABLE V

SOLUBILITY OF BLACK LEAD OXIDE IN SODIUM HYDROXIDE SOLUTIONS

Moles of alkali 1000 g. water	Moles of lead 1000 g. water
$1.77^u \times 10^{-3}$	2.67×10^{-4}
$3.88^s \times 10^{-3}$	2.69×10^{-4}
$5.76^u \times 10^{-3}$	5.37×10^{-4}
$1.13^s \times 10^{-2}$	9.55×10^{-4}
$1.35^u \times 10^{-2}$	1.16×10^{-3}
$1.58^s \times 10^{-2}$	1.32×10^{-3}
$2.28^u \times 10^{-2}$	1.77×10^{-3}
$4.71^s \times 10^{-2}$	4.97×10^{-3}
$6.58^u \times 10^{-2}$	5.17×10^{-3}
$1.09^s \times 10^{-1}$	9.37×10^{-3}
$1.21^u \times 10^{-1}$	9.53×10^{-3}
$1.42^s \times 10^{-1}$	1.18×10^{-2}
$1.98^u \times 10^{-1}$	1.71×10^{-2}
$2.16^s \times 10^{-1}$	1.90×10^{-2}

they do not exist or (b) they do not exist to a large enough extent to be considered.

$$4H^+ + PbO_2^= \rightleftharpoons Pb^{++} + 2H_2O \quad (4)$$

$$Pb(OH)^+ + OH^- \rightleftharpoons Pb(OH)_2 \quad (5)$$

In the data tables the concentration of sodium hydroxide per 1000 g. of water refers to equation (1).

The maximum error in the alkali analyses is $\pm 0.5\%$ in the medium and high concentrations but may be as high as $\pm 3\%$ in the very dilute range. The error in the lead analyses is $\pm 0.5\%$ above 0.2 molar sodium hydroxide and $\pm 2\%$ below this value.

Discussion of the Data

The graphs of the data show minima for all forms of lead oxide which are to be expected for such oxides exhibiting a predominating basic dissociation. These data are in accord with

Topleman's findings and serve to establish more definitely the position of the minima.

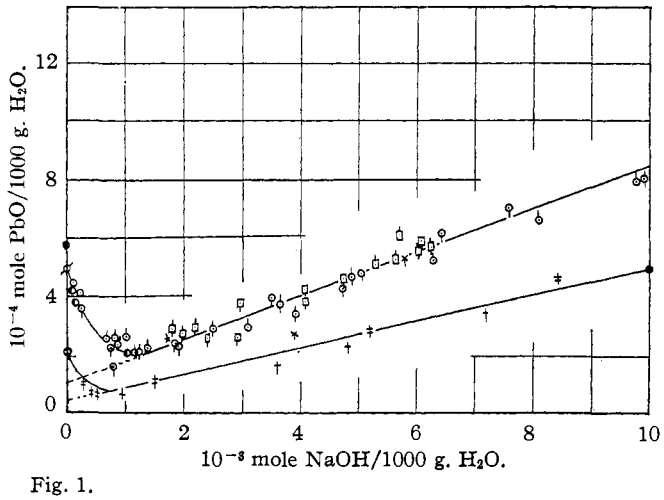

Fig. 1.

	Red	Yellow	White	Black
Average	‡	⊙	⊡	*
Supersaturated	↓	⊙	⊡	*
Undersaturated	†	⊙	⊡	*
Topleman	⊕	⊗	◐	

Furthermore, these graphs show a linear relationship of dissolved lead oxide to alkali above 0.001 M sodium hydroxide which serves to establish the fact that the reaction

$$PbO + OH^- \rightleftharpoons HPbO_2^- \quad (6)$$

is the chief reaction taking place above this concentration of alkali.[15]

If the reaction

$$PbO + 2OH^- \rightleftharpoons PbO_2^= + H_2O \quad (7)$$

does exist it is of very little consequence. This conclusion confirms the opinions of other authors.[2]

The total lead in a sample can be represented by the following equation where m_{Pb} = total lead and $m_{Pb(OH)_2}$ = amount of undissociated lead hydroxide.

$$m_{Pb} = m_{Pb(OH)_2} + m_{Pb(OH)^+} + m_{HPbO_2^-} + m_{PbO_2^=} \quad (8)$$

This and previous work has shown that $m_{Pb(OH)^+}$[3] and $m_{PbO_2^=}$ are not present to any appreciable extent in alkaline solutions above 0.001 M.

These data make it possible to determine $m_{Pb(OH)_2}$ by extrapolating the data to zero concentration of sodium hydroxide (see Fig. 1). With this extrapolated value and the value of the water solubility it is possible to calculate the degree of dissociation of lead hydroxide. The values of $m_{Pb(OH)_2}$ for red and yellow lead oxide as determined graphically are 0.4×10^{-4} and 1.0×10^{-4}, respectively; this indicates that the degree of dissociation of red and yellow lead oxide is approximately 80%.

The value of $m_{HPbO_2^-}$ is determined by subtracting the value of $m_{Pb(OH)_2}$ from the value of m_{Pb} above 0.001 M alkali. The ratio of $m_{HPbO_2^-}/m_{NaOH}$ gives the equilibrium constant (K_6) for the reaction represented by equation (6). The formula for K_6 is $m_{HPbO_2^-}/m_{OH^-} \cdot \frac{\gamma_{HPbO_2^-}}{\gamma_{OH^-}}$; however, the ratio $\gamma_{HPbO_2^-}/\gamma_{OH^-}$ should remain almost unity throughout a wide range of concentration.[16] The constancy of these calculated values of K_6 indicates that reaction (6) is the main reaction taking place.

The free energy of formation of the $HPbO_2$ for the two forms can be calculated from the respective values of K_6 for the red and yellow forms of lead oxide. From (a) the slope of the curves and (b) the average of the individual solubility values of the two forms

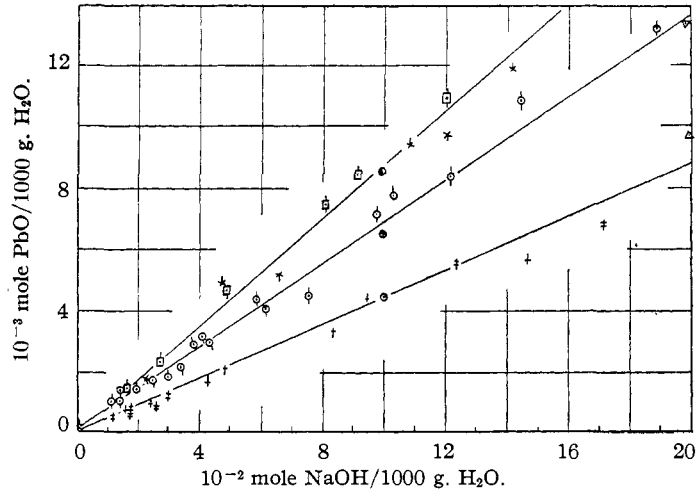

Fig. 2.

	Red	Yellow	White	Black
Average	‡	⊙	⊡	*
Supersaturated	↓	⊙	⊡	*
Undersaturated	†	⊙	⊡	*
Topleman	⊕	⊗	◐	

the following values are obtained for the reaction

(15) For a discussion of this topic see ref. 8.

(16) See refs. 7 and 9 for discussion of this topic as well as for the meaning of any of the symbols used.

$$PbO + OH^- \rightleftharpoons HPbO_2^- \quad (6)$$

$$K_{(6)\,yellow} = \begin{matrix} 7.2 \times 10^{-2} \text{ average} \\ 7.4 \times 10^{-2} \text{ slope} \end{matrix} \quad \Delta F^\circ_{298} = +1550$$

$$K_{(6)\,red} = \begin{matrix} 4.6 \times 10^{-2} \text{ average} \\ 4.6 \times 10^{-2} \text{ slope} \end{matrix} \quad \Delta F^\circ_{298} = +1830$$

The change in free energy for the reaction

$$PbO_{red} = PbO_{yellow}$$

is determined by subtracting the values of ΔF°_{298} obtained above for the reactions indicated by equation (6) giving

$$PbO_{red} = PbO_{yellow} \; \Delta F^\circ_{298} = +280$$

This is in agreement with the value calculated from the data of Applebey and Reid,[6] who have measured the e. m. f. at 18° of the cells

Pb | PbO yellow | NaOH | HgO | Hg
E. m. f. = 0.5594

and

Pb | PbO red | NaOH | HgO | Hg
E. m. f. = 0.5668

in which Δ e. m. f. = 0.0074 and ΔF°_{298} = 340 cal. for the reaction $PbO_{(red)} = PbO_{(yellow)}$.

The dissociation constant for plumbous acid

$$Pb(OH)_2 \rightleftharpoons H^+ + HPbO_2^- \quad (9)$$

can be calculated as follows

$$K_9 = \frac{a_{H^+} \cdot a_{HPbO_2^-}}{a_{Pb(OH)_2}}$$

For a_{H^+} substitute its equivalent Ka_{H_2O}/a_{OH^-} as derived from the dissociation constant for water. Assume $a_{HPbO_2^-}/a_{Pb(OH)_2}$ is equal to $m_{HPbO_2^-}/m_{Pb(OH)_2}$ when m_{OH^-} is 0.01. This research gives values of $m_{HPbO_2^-}$ and $m_{Pb(OH)_2}$ at any value of m_{OH^-}. The value of K is taken as 1.01×10^{-14} at 25°,[17] and the ratio a_{H_2O}/γ_{OH^-} can be assumed to remain unity at low concentrations.

$$K_9 = 1.2 \times 10^{-11} \text{ (red)}; \; \Delta F^\circ_{298} = 14{,}900$$
$$K_9 = 7.4 \times 10^{-12} \text{ (yellow)}; \; \Delta F^\circ_{298} = 15{,}200$$

The value of K_{11} for the reaction

$$Pb(OH)^+ = Pb^{++} + OH^- \quad (11)$$

is calculated from the values

$$Pb + {}^1/_2O_2 = PbO; \; \Delta F^\circ_{298} = -45{,}210^{18} \quad (12)$$
$$H_2O + PbO = Pb(OH)^+ + OH^-; \; \Delta F^\circ_{298} = 10{,}180^{19} \quad (13)$$
$$Pb = Pb^{++} + 2e; \; \Delta F^\circ_{298} = -5830^{20} \quad (14)$$
$$H_2 + {}^1/_2O_2 = H_2O; \; \Delta F^\circ_{298} = -56{,}720^{21} \quad (15)$$
$$2(OH^- = {}^1/_2H_2 + {}^1/_2O_2); \; \Delta F_{298} = 37{,}615^{22} \quad (16)$$

Adding these equations gives

$$Pb(OH)^+ = Pb^{++} + OH^-; \; \Delta F_{298} = 10{,}690$$
$$K_{11} = 1.5 \times 10^{-8} \quad (11)$$

Nature of the Lead-Bearing Ion.—A survey of the results of this research together with other available data indicates that lead hydroxide may have the "formic acid" structure, *i. e.*, one of the hydrogen atoms may be bonded directly to the lead atom as indicated by the structural formula $H—\overset{\overset{\displaystyle O}{\|}}{Pb}—OH$.[23] The monobasicity of lead hydroxide as indicated by the linear slope of m_{PbO}/m_{NaOH} suggests the first clue to this interpretation. The small value of the second dissociation constant of lead hydroxide as a base and the high solubility of lead hydroxide in alkali also support this interpretation. Additional support is found in the fact that lead and carbon atoms have a similar electron configuration, in fact, the chemistry of formic acid which is monobasic and car-

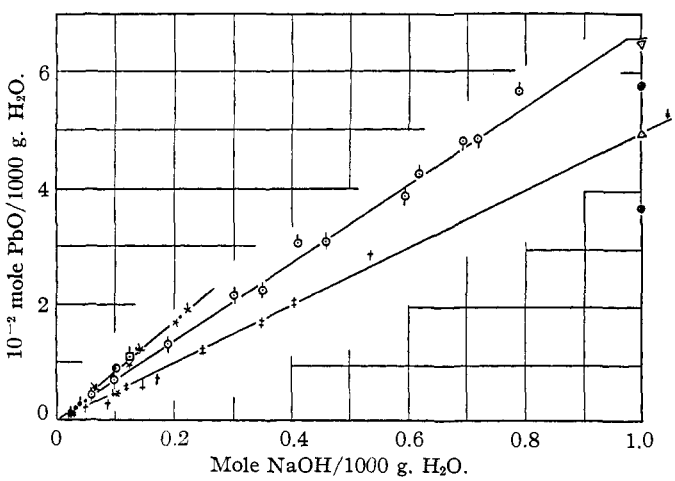

Fig. 3.

	Red	Yellow	White	Black
Average	‡	⊙	⊡	*
Supersaturated	↓	⊙	⊡	*
Undersaturated	†	⊙	⊡	*
Topleman	⊕	⊗	◐	

(17) "International Critical Tables," Vol. VI, p. 152.

(18) Smith and Woods, THIS JOURNAL, **45**, 2632 (1923), corrected for new value of ΔF°_{298} of formation of water = −56,720.

(19) This research. For the red form the water solubility is 2.26×10^{-4} and it is 80% dissociated. In the equation

$$\frac{a_{Pb(OH)^+} \cdot a_{OH^-}}{a_{H_2O} \cdot a_{PbO}} = K_{13}$$

a_{PbO} = unity, a_{H_2O} may be assumed to be unity in such dilute solution, molalities may be substituted for activities, $K_{13} = 3.46 \times 10^{-8}$ and $\Delta F^\circ_{298} = +10{,}180$.

(20) Lingane, THIS JOURNAL, **60**, 724 (1938).

(21) Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933).

(22) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 487, corrected for new value of ΔF of formation of water = −56,720.

(23) We are indebted to Professor H. L. Johnston for suggesting this interpretation of these data. To him also is due our appreciation for his general interest and helpful suggestions during the progress of this work.

bonic acid which is dibasic has a close parallelism in dibasic lead hydroxide and tetravalent lead hydroxide. Formic acid (monobasic) is a much stronger acid than carbonic acid (dibasic) due to the distorted electron shell as a result of the hydrogen–carbon bond. The high solubility of lead hydroxide in alkali may be due to a similar effect. The work of Topleman[2] on tetravalent lead oxide–alkali equilibrium is not extensive enough to draw a definite conclusion about the position of the minimum in the m_{PbO_2}/m_{NaOH} nor is the work of other investigators on the solubility of tetravalent lead oxide in acids.[24] Thus one cannot draw a definite comparison between the relative acid strengths of bivalent and tetravalent lead hydroxide.[25] Mention must be made also of Hantzsch's early suggestion[26] that tin and lead hydroxides both probably have the "formic acid" structure. We are now investigating tin hydroxide. While these data do not prove the type of structure for lead hydroxide, nevertheless it must be concluded that they do suggest that hypothesis in an interesting manner.

The data on black lead oxide are included in this paper because of the interest in this form of the oxide. We failed to check Topleman's[2] values with this form and the yellow form. A criticism of his work does not seem to be justified. We feel, however, that the discrepancy may be due to the fact that different methods of approaching equilibrium were used. On the other hand, Topleman may have succeeded in preparing a more stable form of the olive or yellow oxide. This seems unlikely due to the variety of samples used in the present study. It must be conceded that more information concerning the physical and chemical properties of the black oxide are desirable. The analyses[27] of the lead content of the different lead oxide preparations are as follows

Red	Yellow	Black
92.9	92.5	92.8
92.7	92.7	92.9
92.7	92.7	93.0

theoretical Pb/PbO = 92.8.

A microscopic observation of the black form indicated a homogeneous system; the crystals gave an olive cast when viewed with transmitted light. Furthermore, it was observed that water solutions in which the black oxide was stored showed a white residue which is interpreted as evidence of the formation of the hydrated oxide; some samples showed this same white residue after several weeks of agitation; other samples prepared at the same time showed no white residue, the solid phase remaining black in color and analyzing as PbO.

The agreement in the solubility of the yellow, black, and hydrated forms at low concentrations of alkali may seem rather surprising, especially since Topleman's data indicated a difference in solubility of the white and olive forms. His claim that rapid rotation breaks up the crystals of the yellow lead oxide and tends to produce supersaturation may account for some variation. In spite of evidence that he presents in support of this, we are inclined to believe that this is not sufficient reason to account for the apparent discrepancies in the data of various workers. Evidence that this must be only a minor factor to be considered is the constancy of the values of K_6 of our data for both forms of the oxides; one would not expect this constancy under non-equilibrium conditions over such a wide range of concentration—indeed this is a critical test of equilibrium. Furthermore, Topleman's data for the red and white forms are in agreement with our data except at $m_{OH^-} = 1$. It is well known that the red form is the stable form at ordinary temperatures. The appearance of the white residue (hydrated oxide) in some of our samples—also reported by other workers—leads one to the hypothesis that the yellow oxide and the hydrated oxide may reach the same equilibrium in dilute solutions. Thus one may be confronted with more than one equilibrium in the process of solution—the slower one determining the equilibrium time. If the yellow crystals are severely fractured by vigorous rotation one might reasonably expect the red crystals also to be fractured to an appreciable extent; furthermore, one might hazard the suggestion that if fracturing is an important factor in this work its effect would be more noticeable on that form having the lower solubility, but the red form shows no apparent effect. However, granted that this might be a factor to be considered and granted also that a slow hydration equilibrium might be encountered, then

(24) Dolezalek, *Z. anorg. Chem.*, **51**, 320 (1906); Cumming, *Z. Elektrochem.*, **13**, 19 (1907).

(25) Topleman,[2] however, assumes the data in acid solubility good enough to make this comparison, but it is evident that more work needs to be done on the solubility of tetravalent lead oxide in both dilute acid and dilute alkali to clarify this uncertainty.

(26) Hantzsch, *Z. anorg. Chem.*, **30**, 308 (1902).

(27) We are indebted to Mr. Otis Black for the preparation of the black lead oxide used in this work and for these analyses.

the only apparent solution to the uncertainty seems to lie in the constancy of the equilibrium constants determined over a wide range of concentration of alkali.

The data of Randall and Spencer are all higher than our values as well as those of Topleman. Randall and Spencer admit that their data for the yellow lead oxide show unaccounted-for irregularities.

It can be concluded that in the main the data of this research and those of Topleman are in agreement for the red form which is the stable form at room temperature; and even though there is no agreement in the data of these different researches for the yellow (olive) form, yet the constancy of the value of K_6 for the reaction

$$PbO + OH^- \rightleftharpoons HPbO_2^- \qquad (6)$$

seems to serve as an excellent criterion for the validity of the data of this research, which are extensive, are obtained from several preparations, and are extended over a wide range of concentration of alkali.

Summary

The solubilities of red, yellow, and black lead oxides and hydrated lead oxide were determined in water and in alkaline solutions.

From the data obtained the following calculations were made: (1) the degree of dissociation of lead hydroxide, (2) the ΔF°_{298} of formation of $HPbO_2^-$, (3) the ΔF°_{298} of ionization of $Pb(OH)_2$ as an acid and as a base, (4) the ΔF°_{298} difference between the two forms of lead oxide, and (5) the ionization constant for the second dissociation of $Pb(OH)_2$ as a base.

Evidence for the "formic acid" structure of the lead-bearing ion is submitted.

Some characteristics of black lead oxide are given.

COLUMBUS, OHIO RECEIVED NOVEMBER 17, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WICHITA]

Changes in Volume and Refractometer Readings Attending the Mixing of Cellosolve and Water and of Carbitol and Water at 25°[1]

BY LLOYD MCKINLEY AND AGNES NIBARGER

The observation that pronounced contraction attends the mixing of water with cellosolve (ethylene glycol mono-ethyl ether, mol. wt. 90.09) or with carbitol (diethylene glycol mono-ethyl ether, mol. wt. 134.11) led to a determination of densities and refractive indices of solutions of these ethers[2] at concentrations through 0 to 100% of the organic component in 1% by weight intervals.

The solutions were made in a pair of 100-cc. volumetric flasks which in themselves proved to be satisfactory pycnometers when used in conjunction with a cathetometer. The capacity of such containers above the calibration marks permitted so many additions of water to initial 100-cc. portions of the organic liquid that most of the range was covered before the reverse procedure was employed with water as the sole contents. Following each addition, mixing and wait for the preparation to attain the temperature of the water-bath, the withdrawal of excess solution provided a representative sample for the Abbe refractometer.

Since space is not available for the numerous tabulations arising from this study the results are in general depicted graphically only. Curves AB and AC of Fig. 1 indicate the reciprocal densities of aqueous solutions of cellosolve and of carbitol, respectively, whereas ab and ac show the corresponding refractometer readings.

The analytical rather than the graphical method for arriving at partial specific volumes by the intercept method was chosen. The equations found to fit AB are:

$Y = 0.95169 + 0.001082\,X - 0.0_5 5694\,X^2$; (0 to 18% Cellosolve)

$Y = 1.08155 - 0.002202\,X - 0.0_4 1606\,X^2 - 0.0_7 1233\,X^3$; (18 to 100% Cellosolve)

where Y is the specific volume, and X is % by wt. water. Curve AC is satisfied by the equation, $Y = 0.98938 + 0.02612 \sin(0.174) - 0.01\,X$), where Y is the specific volume, X is % by wt. carbitol, and the angle is in pi radians.

(1) Original manuscript received April 14, 1938.

(2) These ethers were obtained from Carbide and Carbon Chemicals Corporation in a request which specified "high purity." The cellosolve was used as received. The carbitol, however, proved so hygroscopic that use was made only of that fraction which distilled at about 192° into a receiver with a tower of dehydrite.