the ionization constant, K_w, the equation

$$\log K_w = -\frac{4787.3}{T} - 7.1321 \log T - 0.010365T + 22.801 \quad (5)$$

given by Harned and Hamer[1] may be employed. From these values of K_w and the values of γ_w obtained from equation (2), $m_H m_{OH}$ may be computed by equation (1). The limits of validity of these equations are as follows: (1) they may all be applied from 0 to 3 M salt concentration; (2) the temperature ranges of validity of these computations are from 0 to 50° for potassium and sodium chloride solutions, 10 to 40° for lithium chloride solutions, and 0 to 40° for the bromide solutions.

If we had allowed all the parameters of equation (2) to be unrestricted, a more accurate reproduction of the results derived from the experimental data could have been made. The cal-culations are greatly simplified by the use of only two values of a, by using the same value of a at all temperatures, and by expressing B and C by simple linear equations. The average deviations of 2 $\log \gamma_w$, calculated and observed, are given in the last columns of the table. From these, it is clear that γ_w^2 may be computed with an accuracy between ± 0.5 and $\pm 1\%$ depending on which salt solution is under consideration.

Summary

Equations and numerical parameters are given by means of which the ionization constant, the ionic activity coefficient product and ionization of water in potassium, sodium, and lithium chlorides and bromides may be computed throughout wide temperature ranges and at all concentrations up to 3 M.

A New Study of the Preparation and Properties of the Higher Oxides of Lead

BY G. L. CLARK, N. C. SCHIELTZ AND T. T. QUIRKE

Because of its presence in the charged positive plate of the storage battery, the evidences from X-ray examination of highly characteristic distortion in the lattice under certain conditions and the very significant researches of LeBlanc and Erebius,[1] which have demonstrated that the tetragonal PbO_2 lattice persists through a range of compositions from PbO_2 down to $PbO_{1.66}$, unusual interest is attracted to this well-known oxide. It has become evident that a great deal of careful research work upon the structure of lead dioxide is essential in order better to understand the peculiar characteristics of the oxide under various conditions. To this end the preparation of a single crystal of lead dioxide, in order that diffraction patterns may be made, is very desirable. In the estimation of LeBlanc and Erebius, Simon[2] was the first person ever to succeed in preparing large crystals corresponding exactly to the formula PbO_2. Hydrated, crystalline sodium plumbate and water were heated at 250° for three days in an autoclave to produce large crystals supposedly of lead dioxide. Twin crystal clusters (similar to Pb_2O_3 crystals in Fig. 3) were illus-trated in this paper. The crystals were reported as doubly refracting in polarized light with a range of interference colors from dark to light blue, dichroism from red to green or blue, and an X-ray diffraction pattern corresponding to the well-known rutile structure of PbO_2. These crystals were reported to be more resistant to thermal decomposition and the dissolving action of sulfurous acid, nitric acid and other reagents than found for the usual preparations of lead dioxide. Simon re-ported only the presence of these large black crystals, which are illustrated in photomicrographs, and did not mention the granular powder of similar color (Fig. 3), which he kindly submitted upon request to aid investigations in this work.

In the present work, the effort has been made to duplicate the Simon preparation exactly in order to obtain single crystals of lead dioxide for quantitative investigation. The original method of preparation of sodium plumbate due to Fremy[3] consisted in fusing lead dioxide and sodium hydroxide in excess. The mass is taken up with water, filtered, and the filtrate evaporated.

In the course of this investigation serious dif-

(1) LeBlanc and Erebius, Z. physik. Chem., **A160**, 69 (1932).
(2) Simon, Z. anorg. Chem., **185**, 300 (1930).
(3) Fremy, Ann. chim. phys., [3] **12**, 488 (1844), or Z. anorg. Chem., **177**, 109–16 (1928).

ficulties were encountered with this method. In the first place, a considerable excess of sodium hydroxide was required; second, excess of water in taking up the fused mass caused the plumbate to decompose, and in the third place the non-soluble portion has an entirely different structure than the crystals obtained from the filtrate, which later were shown to be mostly sodium carbonate. In a suitable bomb, illustrated in Fig. 1, an attempt was made to prepare these large black crystals from the sodium plumbate. From the
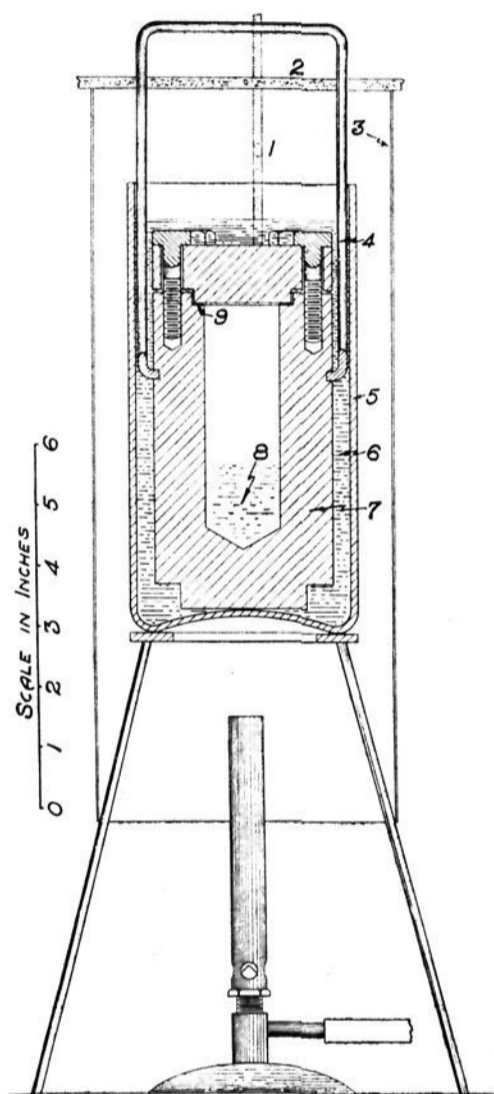

Fig. 1.—Apparatus: 1, thermometer; 2, asbestos cover; 3, steel guard; 4, handle; 5, bath container; 6, solder; 7, steel bomb; 8, reagents; 9, copper gasket.

filtrate of the Fremy method, as used by Simon, there were no results whatever. From the insoluble fraction heated for three days at 250–265° were obtained some rather large crystalline Pb_3O_4, a good crop of the large black crystals and a fine crystalline, dark brown to black substance later shown to be a lead–sodium–oxygen compound. In the next attempt the large black crystals separated on direct heating in the bomb of the constituents of sodium plumbate, namely,

lead dioxide, sodium hydroxide, and water. Three attempts were made using Merck manganese-free lead dioxide with 20, 15 and 10 cc. of water, respectively. With this material no large black crystals were ever obtained over the usual temperature range. A mixture of 15 g. of chemical reagent lead dioxide containing 0.0003% (as maximum) of manganese, 5 g. of sodium hydroxide and 20 cc. of water heated for three days at 260–275° gave an excellent yield of large black crystals. When, therefore, 0.0003% of manganese as manganese dioxide was added to the manganese-free lead dioxide, an exceptionally large crop of well developed, large black crystals was obtained. This illustrates the remarkable catalytic effects, which are observed in the formation of some of these higher oxides of lead.

These large elongated black crystals are definitely of the triclinic system, the axial ratios a to b to c having the values of approximately $1:1:5$, angle $\beta = 46°$, $\gamma = 98°$ and $\alpha = 82°$. Twins are common with b as the twinning axis and 010 as the composition plane. Common crystal forms are the three pinacoids, the prism 110 but not $\bar{1}10$, the dome 011, the dome 101, the dome $\bar{1}01$, and occasionally another prism 130. The crystal has conchoidal fracture and apparently no cleavage, although repeated twinning on the 010 face sometimes similates cleavage. The luster is brilliantly vitreous, the color jet black. Carefully selected crystals gave the following analysis: lead, 89.5, 89.5%; theoretical for Pb_2O_3, 89.62; active oxygen, 3.445, 3.46; theoretical for Pb_2O_3, 3.46. The method for analysis of active oxygen is that used by the U. S. Bureau of Standards. These crystals have a density of 9.925 (while the Simon value, evidently measured for the small granular crystals (Fig. 3) was 9.604). They are very resistant to heat and to the action of sulfurous and nitric acid. Concentrated hydrochloric acid gradually changes the crystals to lead chloride over a period of several days. An X-ray diffraction pattern of these large crystals, shown in Fig. 2c, as compared with the standard pattern for lead dioxide and for the mineral plattnerite (kindly lent by the National Museum) proves conclusively an entirely different crystalline structure, thus positively identifying the existence of Pb_2O_3. The identity of these crystals with those described by Simon, therefore, would seem to indicate that the X-ray pattern, which was described by Simon as corresponding
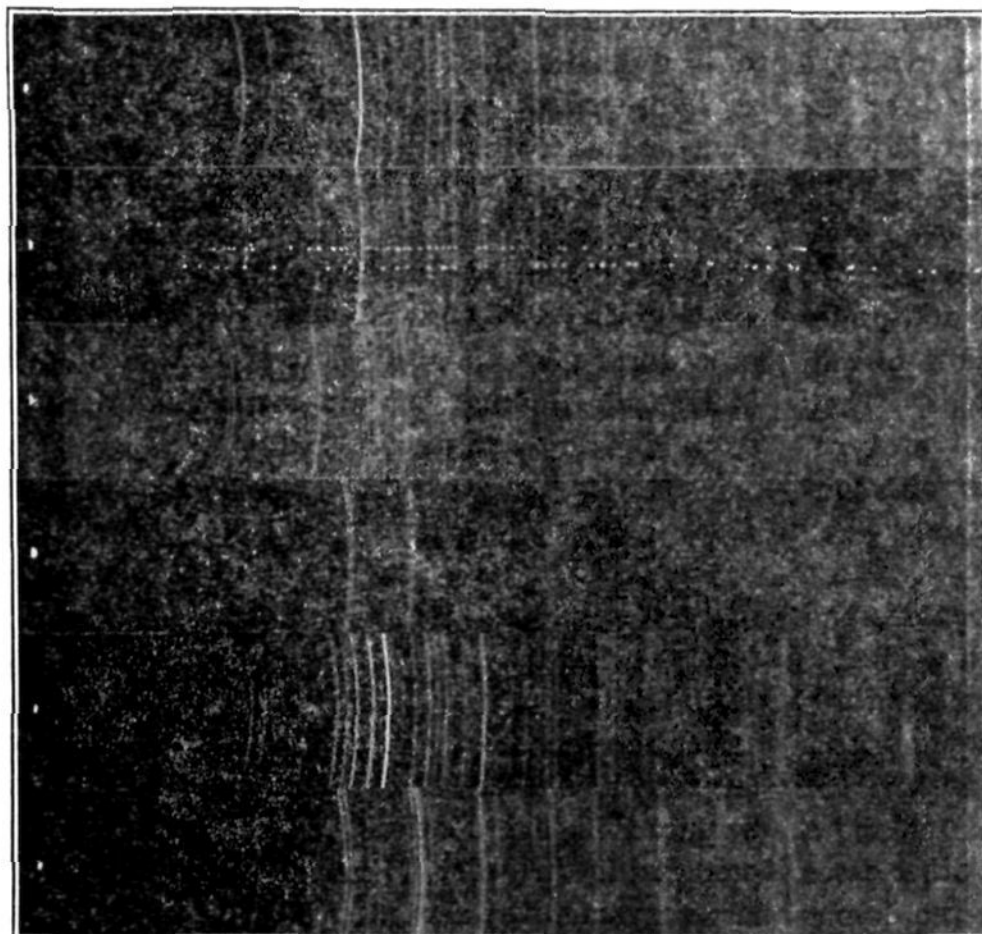
Fig. 2.—Powder diffraction patterns for lead oxides: (a) standard PbO₂—identical with plattnerite; (b) sample submitted by Simon; (c) Pb₂O₃; (d) Pb₅O₈; (e) Pb₃O₄; (f) sodium–lead–oxygen compound.

The density was 9.514, and the stability to temperature and reagents less than that of Pb_2O_3. These small crystals seem to vary in habit between a double pyramid and a short prism terminated with double pyramids apparently of the tetragonal system. The axial ratios make c very nearly equal to one. Lines of some of the pyramid faces parallel to the base indicate the symmetry. The pattern, which is distinctly different from that of PbO_2 or Pb_2O_3, is illustrated in Fig. 2d. Photomicrographs of Pb_2O_3 (large crystals), Pb_5O_8, Pb_3O_4, and the granular material submitted by Simon consisting in a mixture of PbO_2 and Pb_2O_3 are reproduced in Fig. 3.

When the bomb temperatures for mixtures of lead dioxide, sodium hydroxide and water are still higher, namely, 355–375°, exceptionally large and well formed crystals of red lead, Pb_3O_4, are to lead dioxide, must have been made on the granular powder rather than on the large crystals shown in his photomicrographs.

Through the friendly coöperation of Dr. Simon, a sample (Fig. 3) of the original material was sent and an X-ray diffraction pattern prepared under the same conditions as for our own preparations. This pattern shown in Fig. 2b proves the presence of both PbO_2 and Pb_2O_3.

When 15 g. of lead dioxide, 15 g. of sodium hydroxide and 60 cc. of water are heated together for three days at 260–275°, or, better, when 15 g. of lead dioxide, 5 g. of sodium hydroxide and 20 cc. of water are heated for the same time at 295–310°, there is obtained a very good yield of small, black crystals, which upon analysis proved to have the composition Pb_5O_8: lead, found, 88.6%; theoretical, 89.0; active oxygen, 4.03; theoretical, 4.12.

Pb₅O₈
(16 diam.)

Pb₃O₄
(4.6 diam.)

Sample submitted by
Simon (16 diam.)

(5 diam.)   (4.5 diam.)
Pb₂O₃—products from two different preparations.
Fig. 3.

formed. These are as much as one-fourth inch (6.3 mm.) long and one thirty-second inch (0.4 mm.) in cross section and were adapted for the complete X-ray structure analysis heretofore unknown, which will be reported elsewhere.

Preliminary crystallographic examination indicates that these red lead crystals are prismatic in habit. They are entirely transparent and under polarized light show pleochroism, yellow to red. Extinction is inclined 13° to the long axis. They have well-marked cleavage, prismatic in type, making angles of 120° with one another with conchoidal fracture transverse to the long axis. The crystals belong to the monoclinic system, are characterized by almost square cross sections and with great length in proportion to their diameter, terminating in a combination of basal pinacoid and dome with a very high angle beta. Some prisms are terminated by a basal pinacoid with a 101 dome and two faces of the 011 dome, making a four-sided pyramidal termination. In other cases the termination is wedge shaped with the domes 011. Still another termination showed basal pinacoid and the dome 011 terminating the prism 110 and the orthopinacoid 100.

Finally a lead–sodium–oxygen compound was obtained in the bomb at 250–260° by heating 10 g. of lead dioxide, 3.24 g. of sodium peroxide, 10 cc. of hydrogen peroxide and 5 cc. of water. On analysis this compound, heretofore unknown, gave the following composition: lead, 80.9, 80.8%; active oxygen, 5.54, 5.57; sodium, 3.635 and 3.66. This compound is also formed as a by-product when Pb_2O_3 or Pb_5O_8 is prepared according to the procedures given above. The pattern is shown in Fig. 2f. Boiling with water gradually decomposes it giving lead dioxide.

Summary

The oxides Pb_2O_3 and Pb_5O_8 have been prepared by a pressure bomb technique at temperatures of 260–275° and 295–310°, respectively. These have been identified by microscopic examination and X-ray diffraction patterns. The large crystals obtained by Simon and reported to be pure PbO_2 are identical with the Pb_2O_3 crystals prepared in this work. Pb_3O_4 in the form of very large crystals was also prepared in the bomb at 355–375° and identified by its X-ray pattern. A new lead–sodium–oxygen compound is also prepared in the bomb.


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Relative Rates of Decomposition of the Potassium Salts of Certain Meta and Para Substituted Dibenzhydroxamic Acids. A Study of the Lossen Rearrangement[1,2]

BY W. B. RENFROW, JR., AND CHARLES R. HAUSER

The Stieglitz mechanism for the Hofmann and Lossen reactions has been widely accepted for a number of years, but increased knowledge of electrons and valence naturally has introduced modifications in the representation of the process. The following equations are considered to illustrate the best mechanism[3] for these reactions.

The halogen amide or dihydroxamic acid reacts with a base to form a salt. The anion of the salt then releases a negative halogen or carboxylate ion and rearranges to an isocyanate. No evidence has been obtained for the existence of the intermediate
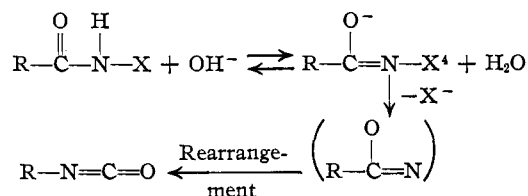
"univalent nitrogen" compound, but such a compound might have a very brief existence. On the other hand, the release of X and the rearrangement might be simultaneous processes.

The factors affecting the ease with which a compound will undergo the Hofmann type of rearrangement were first investigated by Jones and

(1) This paper embodies a part of the material presented by W. B. Renfrow, Jr., to the Graduate School of Duke University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) This paper is considered as the third in the series entitled "The Removal of HX from Organic Compounds by Means of Bases."

(3) In this connection see Waters and Lowry, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, 1936, pp. 363–371.

(4) A resonance form of this ion may be represented by the formula $\left(R-\overset{O}{\underset{\|}{C}}-\overset{-}{N}-X \right)$, but for simplicity it will be represented only in the enolic form. The ion probably has an intermediate structure. See Sidgwick, J. Chem. Soc., 694 (1937).