

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Studies on Lead Oxides.¹ II. Hydrous, Normal and Active Lead MonoxidesBY G. L. CLARK AND W. P. TYLER²

This investigation was undertaken for the purpose of studying the hydrous oxide of lead and the red and yellow modifications of lead monoxide from the standpoint of their preparation from various sources, the X-ray diffraction patterns of products prepared under different conditions, physical-chemical properties such as catalytic activity and heats of reaction of the products, analysis and any other properties of the substances which would contribute to the total knowledge concerning them.

The principal reference works concerning the hydrous oxides and oxides are books by Weiser³ and Fricke and Hüttig.⁴ From these works and cross references found in them most of the information and data for this investigation were obtained. The existing data concerning the lead oxide hydrate include the X-ray diffraction pat-

of several metals other than lead is to be found in the work of Fricke.⁵ Low temperature dehydration products showed distorted X-ray patterns, increased catalytic activity and increased heats of reaction over those found for the normally prepared oxides. It is claimed that this energy difference and the abnormal pattern along with an increase in catalytic activity can be accounted for only on the basis of one or more of four factors. These factors are: (1) colloidal dimensions of the crystallites; (2) lattice stretching; (3) poorly oriented lattice; (4) admixture of amorphous material. In nearly every case the cause has been traced directly to the second or third of these possible phenomena. No work has been reported concerning such properties of the lead monoxides, the yellow orthorhombic form and the red tetragonal modification.

The Hydrous Oxide of Lead.—Preparations of the hydrous oxide of lead were made from lead acetate and ammonium hydroxide, lead acetate and sodium hydroxide and from yellow lead monoxide dissolved in 8 *N* sodium hydroxide, boiled and cooled. The first two products were coarse white powders, while the third consisted of small white crystals about 0.2 mm. in diameter. The analyses for lead and water by usual quantitative procedures of twelve preparations were identical within 0.05%, giving the empirical formula $5\text{PbO}\cdot 2\text{H}_2\text{O}$ or $2\text{Pb}(\text{OH})_2\cdot 3\text{PbO}$ for the product.

The great affinity of these materials for carbon dioxide was noted at once and every precaution taken in all steps of the preparation to exclude it. However, the powders contained small quantities of carbon dioxide (0.17 to 0.30%) shown by X-ray data to be in the form of normal lead carbonate (1.02 to 1.80%). Proper corrections were made in calculations of composition. X-Ray diffraction patterns of these products were taken with a circular, wedge reflection camera, using $\text{Cu-K}\alpha$ radiation. The patterns were identical, a typical example being shown in Fig. 1, and an analysis of the spacings of the lines was made, as listed in Table I. The crystals are monoclinic

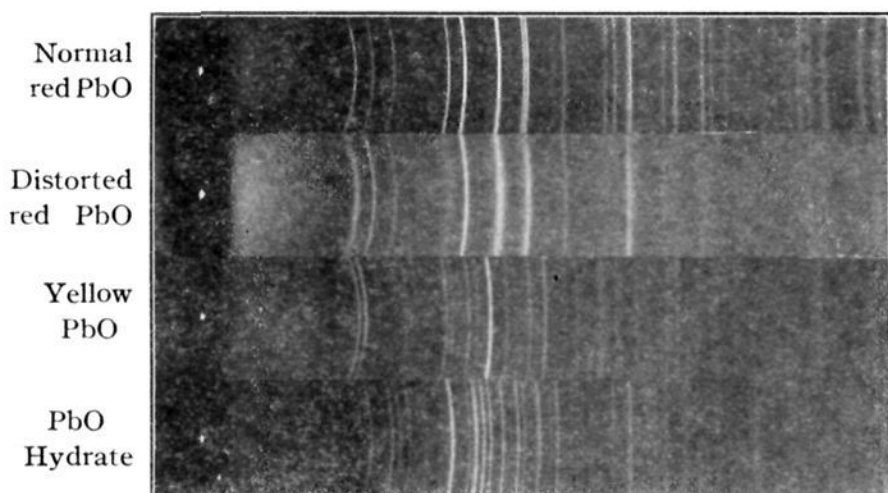


Fig. 1.—Typical X-ray patterns.

tern without any attempt to interpret it, methods of preparation, solubility in alkali, isobaric dehydration curves and analyses. Formulas on record vary from $2\text{PbO}\cdot\text{H}_2\text{O}$ to $3\text{PbO}\cdot\text{H}_2\text{O}$, several investigators having obtained $2.5\text{PbO}\cdot\text{H}_2\text{O}$.

Thorough investigation of the properties of oxides obtained by dehydration of the hydrates

(1) For the first paper in this series see Clark, Schieltz and Quirke, *THIS JOURNAL*, **59**, 2305 (1937).

(2) Portion of thesis submitted in partial fulfillment for the degree of Doctor of Philosophy by W. P. Tyler.

(3) H. B. Weiser, "Inorganic Colloid Chemistry. Vol. II. The Hydrous Oxides and Hydroxides," John Wiley and Sons, Inc., New York, N. Y., 1935.

(4) R. Fricke and G. F. Hüttig, "Handbuch der allgemeinen Chemie. Bd. IX. Hydroxide und Oxyhydrate," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1937.

(5) R. Fricke, *Kolloid Z.*, **69**, 312 (1934).

in all probability. The powder patterns are extremely complex, but by making assumptions concerning the Miller indices of certain observed reflections, it was possible to index nearly all of the lines for which h or l was zero. The nearest approximation gave the following values for the unit cell properties: $a_0 = 5.93 \text{ \AA}$, $b_0 = 4.65 \text{ \AA}$, $c_0 = 6.36 \text{ \AA}$, $\beta = 105^\circ 47'$. The measured average density was 7.73. This results in a rough approximation of one molecule (1.1) of $5\text{PbO}\cdot 2\text{H}_2\text{O}$ in the unit cell. Final solution will depend upon further work with the very minute crystals.

TABLE I

ANALYSIS OF HYDROUS LEAD OXIDE DIFFRACTION PATTERN

Line	Obsd. intensity	Observed spacing \AA .	Possible hkl values	Calcd. spacing, \AA .
1	FF	6.12	001	6.12
2	FF	5.71	100	5.71
3	FF	4.65	010	4.65
4	FF	4.33		
5	F	4.01		
6	F	3.75	011	3.71
7	S	3.60	110	3.605
8	W	3.37		
9	W	3.17		
10	W	3.06	002	3.06
11	FF	2.980		
12	F	2.912		
13	S	2.855	200	2.855
14	FF	2.726		
15	FF	2.669		
16	FF	2.600		
17	S	2.540	012	2.556
18	S	2.438	210	2.433
19	W	2.328	020	2.325
20	W	2.163	120	2.153
21	FF	2.120		
22	W	2.033	003	2.040
23	F	2.003		
24	F	1.988		
25	SS	1.951		
26	F	1.899	300	1.903
27	FF	1.869	013	1.868
28	W	1.838		
29	S	1.798	220	1.800
30	S	1.751	310	1.761
31	S	1.713		
32	S	1.652		
33	FF	1.605		
34	W	1.582		
35	W	1.553	030	1.550
36	FF	1.528	004	1.530
37	W	1.493	130	1.495
38	F	1.449	014	1.453
39	S	1.422	400	1.427
40	FF	1.402		
41	FF	1.388		
42	F	1.377	032	1.382

43	F	1.357	410, 230	1.364, 1.362
44	FF	1.342		
45	F	1.312		
46	FF	1.266		
47	W	1.256		
48	F	1.225	005	1.224
49	W	1.214	420	1.216
50	F	1.200	330	1.200
51	F	1.172		
52	W	1.160	040	1.162
53	W	1.138	500, 041, 140	1.142
54	W	1.100		
55	F	1.075	240	1.081
56	W	1.046		
57	F	1.018	006	1.020
58	W	0.991		
59	F	.948	600	0.951
60	FF	.935	026	.934
61	FF	.924	050	.930
62	W	.913		
63	W	.896	440	.900
64	F	.877		
65	W	.868		
66	FF	.850		
67	W	.835		
68	FF	.810		

SS = Very strong. FF = Very faint.
S = Strong. W = Weak. F = Faint.

The Preparation and Structures of Normal and Active Lead Monoxide.—The starting materials for these preparations were the hydrous oxide of lead, normal lead carbonate and basic lead carbonate, which were decomposed, usually in vacuum, with an Abderhalden drying pistol, at temperatures varying from 100 to 500°. The normal yellow orthorhombic lead monoxide was obtained by heating basic lead carbonate to about 700°. Normal red tetragonal lead monoxide was obtained by heating normal lead carbonate to temperatures between 350 and 500°. X-ray patterns of these two products were sharp-lined normal patterns.

All decompositions of the hydrates at temperatures below 500° showed X-ray patterns of red lead monoxide mixed with small amounts of the yellow form, the amount of yellow increasing with the temperature of preparation. The same was true of basic lead carbonate decomposition at 240–500°, but normal lead carbonate always gave the pure red form below 500°.

On every X-ray pattern of a product resulting from decomposition at minimum temperatures, 100–200° for the hydrate, 240–300° for the carbonates, there appeared a large distortion effect of the lines diffracted by the red form, as illustrated in Fig. 1. This distortion was character-

ized by a broadening and increased diffuseness of reflections from the planes with indices 101, 102, 200, 121, 103 and some smaller spacing planes, while the 110, 002, 112, 113 and 220 reflections remained comparatively sharp. All reflections were considerably less in relative intensity than those on the normal red lead monoxide patterns, the observed intensity decrease varying from 10 to 80%, as determined by integrated darkenings measured from microphotometer curves. The procedure for determining these values was to obtain the photographic darkening from the microphotometer curve at several points on each peak, to plot these values against the horizontal distance from the start of the peak to the point in question and to find the area under this curve by means of a planimeter. This gives the integrated darkening of the line which is proportional to the integrated intensity in the same manner that the peak darkening is proportional to the peak intensity. This is dependent on the properties of the X-ray film used, and it has been shown by other workers in this Laboratory that this is essentially true for the film used here if the darkening is not too great.

Typical values of the percentage decrease in relative intensity of pairs of lines on the distorted patterns compared with the relative intensity of the same pairs of lines on the normal pattern are listed in Table II.

TABLE II

PER CENT. DECREASE IN RELATIVE INTENSITY, DISTORTED COMPARED WITH NORMAL TETRAGONAL PbO

Line ratio	Samples 17-F-J	Sample 28-A
220/110	34	29
004/002	31	12
204/102	21	9
303/101	75	..
200/110	29	14
112/110	41	36
121/110	26	21
002/110	40	58
301/110	76	..
004/110	58	60
204/110	46	39
303/110	80	..

Catalytic Properties.—The method of determining catalytic activity was of necessity a process which would take place at low temperatures to prevent the oxides from changing in nature or structure at higher temperatures. The only suitable method appeared to be by the catalytic decomposition of hydrogen peroxide in neutral

solution. The procedure for these catalysis runs was standardized so that checks could be obtained on different occasions if the temperature remained fairly constant. To ensure comparative results, a check sample was run with each group of samples. The apparatus for measurement of oxygen consisted of an ordinary water jacketed gas measuring buret, one opening of the two-way stopcock leading to the reaction flask. The reaction flask was a 50-ml. Erlenmeyer flask fitted with a two-hole stopper, one opening leading to the gas buret, or to the atmosphere through the two-way stopcock, the other containing a short buret for adding the hydrogen peroxide solution. It was found that shaking of the reaction mixture was necessary if check results were to be obtained. This was accomplished by clamping the flask to the moving table of a motor-driven shaking machine built on the bent eccentric axle principle so that rotation of the table did not occur, but a swirling motion was given to the contents of the flask. This necessitated a flexible connection between the flask and the gas buret.

Each determination of catalytic activity was carried out, usually in duplicate, in the following manner. The samples were well pulverized to avoid lumps; 0.1 g. was weighed into the reaction flask, 7 ml. of water was added, the mixture shaken until the sample was wetted and the flask placed in the shaking machine; the stopper was inserted with the stopcock open to the atmosphere, the liquid level in the gas buret adjusted to zero and the stopcock turned to connect the reaction flask with the gas buret. Exactly 3 ml. of hydrogen peroxide solution, analyzed to be $3 \pm 0.05\%$ and freshly made up, was added from the buret in the reaction flask stopper. At the instant this solution was added, the shaking motor and the interval timer were started simultaneously. This constituted the timed start of the run. In most cases very little error resulted from this procedure since very little more than the 3 ml. of displaced air could be read on the gas buret at the start. During the run the leveling bulb was used to follow the gas evolution in the gas buret and time readings were taken for every few milliliters of evolved oxygen, the interval depending on the speed of evolution and the practicability of making readings.

These data were not exactly as expected for hydrogen peroxide decomposition since most such reactions result in a unimolecular reaction rate.

TABLE III
CATALYTIC ACTIVITIES OF SAMPLES, DESCRIPTION OF PREPARATION AND OF X-RAY PATTERN

Sample	Description of preparation	Description of X-ray pattern	Activity cc. O ₂ evolved per second from H ₂ O ₂ , all on same basis
13-B	Hydrate decomposed, 100°, 4 hr.	Hydrate pattern and trace red PbO, distorted	0.25
13-C	Hydrate decomposed, 100°, 5 hr.	Hydrate pattern and trace red PbO, distorted	.32
13-D	Hydrate decomposed, 100°, 6 hr.	Hydrate pattern and equal red PbO, distorted	.35
13-E	Hydrate decomposed, 100°, 8 hr.	Fainter hydrate pattern and red PbO, distorted	.38
13-G	Hydrate decomposed, 100°, 10 hr.	Fainter hydrate pattern and red PbO, distorted	.50
13-H	Hydrate decomposed, 100°, 12 hr.	Fainter hydrate pattern and red PbO, distorted	.64
15 to 15-E	Hydrate decomposed, 100°; 15, 20, 25, 50, 74, 100 hrs.	Slight trace of hydrate and PbO, distorted; 74, 100 hrs.—no hydrate, PbO, distorted	.90 (all)
17-B	Hydrate decomposed, 200°, air	Red PbO and some yellow PbO, some distortion, active O ₂	.80
17-C	Hydrate decomposed, 300°, air	Red PbO and some yellow PbO, some distortion, active O ₂	.53
17-D	Hydrate decomposed, 400°, air	Red PbO and lot of yellow PbO, slight distortion, active O ₂	.48
17-E	Hydrate decomposed, 400°, vacuum	Red PbO and equal yellow PbO, no distortion	.50
17-K	Hydrate decomposed, 160°, vacuum	Red PbO and some yellow PbO, distorted	.90
17-L	Hydrate decomposed, 200°, vacuum	Red PbO and some yellow PbO, distorted	1.00
17-M	Hydrate decomposed, 250°, vacuum	Red PbO and some yellow PbO, distorted	1.00
17-N	Hydrate decomposed, 300°, vacuum	Red PbO and more yellow PbO, less distorted	0.72
17-O	Hydrate decomposed, 400°, vacuum	Red PbO and equal yellow PbO, less distorted	.50
17-P	Hydrate decomposed, 490°, vacuum	Nearly pure yellow PbO, large particles included	.25
5	Hydrate	Typical hydrate pattern	.29
12	Hydrate	Typical hydrate pattern	.25
14	Hydrate	Typical hydrate pattern	.36
17	Hydrate	Typical hydrate pattern	.50
23	Hydrate	Typical hydrate pattern, smaller particles	.90
11	Hydrate heavily carbonated	Hydrate and lines of PbCO ₃ , perhaps 2PbCO ₃ Pb(OH) ₂	.00
17-F to 17-J	Hydrate decomposed, 130°, vacuum, 5, 10, 20, 40, 91 hrs.	All distorted, red PbO and small amount of yellow PbO, no difference in patterns	.90
23-A	Hydrate decomposed, 150°, vac., 3 hr.	23-A to 23-E are identical with series 17-K to 17-O	.85
23-B	Hydrate decomposed, 250°, vac., 3 hr.		.80
23-C	Hydrate decomposed, 300°, vac., 3 hr.		.61
23-D	Hydrate decomposed, 350°, vac., 3 hr.		.50
23-E	Hydrate decomposed, 400°, vac., 3 hr.		.50
18-A	PbCO ₃ decomposed, 450°, vacuum	Undistorted pure red PbO	.45
18-B	PbCO ₃ decomposed, 250°, vacuum	Distorted red PbO and trace PbCO ₃	2.90
18-C	PbCO ₃ decomposed, 240°, vacuum	Distorted red PbO and trace PbCO ₃	4.00
18-D	PbCO ₃ decomposed, 230°, vacuum	Distorted red PbO and large amount PbCO ₃	1.00
18-E	PbCO ₃ decomposed, 235°, vacuum	Distorted red PbO and moderate amount PbCO ₃	1.80
18-F	PbCO ₃ decomposed, 300°, vacuum	Very slightly distorted pure red PbO	0.64
24-A	Basic PbCO ₃ decomposed, 250°, vac., 3 hr.	Distorted red PbO and yellow PbO and basic PbCO ₃	3.50
24-B	Basic PbCO ₃ decomposed, 240°, vac., 3 hr.	Distorted red PbO and yellow PbO and more basic PbCO ₃	2.40
24-C	Basic PbCO ₃ decomposed, 235°, vac., 3 hr.	Distorted red PbO and yellow PbO and more basic PbCO ₃	2.00
24-D	Basic PbCO ₃ decomposed, 235°, vac., 8 hr.	Distorted red PbO and yellow PbO and less basic PbCO ₃	3.70
24-E	Basic PbCO ₃ decomposed, 300°, vac., 3 hr.	Slightly distorted red PbO and yellow PbO and no basic PbCO ₃	2.00
24-F	Basic PbCO ₃ decomposed, 350°, vac., 3 hr.	Undistorted red PbO and yellow PbO and no basic PbCO ₃	1.25
24-G	Basic PbCO ₃ decomposed, 400°, vac., 3 hr.	Undistorted red PbO and yellow PbO and no basic PbCO ₃	1.00
Separate series of runs at higher temperature, 28°			
18-M	PbCO ₃ decomposed at 450°, vacuum	Pure undistorted red PbO	0.50
18-N	PbCO ₃ decomposed at 450°, vacuum	Pure undistorted red PbO	.53
28	Hydrate	Hydrate	.29
28-A	Hydrate decomposed, 130°, vac., 10 hr.	Distorted red PbO and some yellow PbO	1.20
27	Basic PbCO ₃ decomposed above 650°	Pure yellow PbO, some large particles	0.67

In this case, there appeared to be a short induction period of slow gas evolution followed by a nearly constant rate until about half of the theoretical yield of oxygen (32 cc.) had been evolved. At this point the reaction slowed down and if calculations were made considering 16 cc. as the initial concentration, the remainder of the reaction came closer to following the ordinary law of a first-order reaction. Consequently, both the constant rate in cubic centimeters of oxygen per second and the unimolecular rate constant were calculated.

The data on the various samples are recorded in Table III, together with information concerning the preparation of the sample and the nature of its X-ray pattern.

The only doubt which could be cast on the validity of the catalytic activity tests would be the question of particle size and agglomeration. As far as the X-ray patterns could show, there was very slight difference, if any, between the particle size of the samples compared as to activity with the exception of the extremely coarse hydrates and the yellow oxide which contained a

few large grains. These exceptions tend to prove that even large particle size difference is not a big factor since some of the hydrates have activities nearly as great as the normal red PbO which is very fine and homogeneous in particle size. Physical agglomerations as interferences are ruled out by duplicate runs. A few preliminary runs were made using 0.05-g. samples and, while these were not continued, the results clearly showed a proportional decrease in speed of reaction, thereby further confirming that the phenomenon is surface catalysis.

Heats of Reaction of Lead Oxides with Concentrated Perchloric Acid.—In accordance with the foregoing facts measurements should be made that would give some clue as to whether the more active, distorted oxides actually possess a greater energy content than the normal, less active oxides. If a given reaction is taken as a standard, the difference in the heat of reaction of the distorted and normal oxide should be a measure of the difference in energy content of these two oxides, providing the same final state is reached in every case and calculations are based on a unit quantity of the oxide.

The reaction employed here was the solution of the lead oxide in concentrated perchloric acid. Concentrated acid was necessary since hydrolysis of the product took place if a more dilute solution was used regardless of the large excess of perchloric acid present.

The apparatus consisted of a one-half pint Dewar flask with wide mouth, a Beckmann thermometer, a glass stirrer and a medium speed stirring motor. Since, for all runs, an exact volume of perchloric acid was used, the position of the stirrer and thermometer could be held constant with respect to the liquid level in the flask. The 50-ml. pipet used delivered 82.8 g. of 69.2% perchloric acid at 16°. Although these exact data are of no importance in the calculation, they show the conditions of the runs. Exactly 1 g. of the sample to be dissolved was weighed on glazed paper. This was brought to room temperature before using. The perchloric acid was pre-cooled to 16°, added to the flask and the stirrer was started. The Beckmann thermometer was set so that several minutes would elapse before it would read about 0.3°, the usual starting point for timed readings, in order for equilibrium to be reached between the calorimeter and liquid temperatures. At this point timed readings were

taken every thirty seconds until these readings showed a constant rise. The oxide was then poured into the calorimeter without allowing any of it to touch the calorimeter parts. The last fragments of the sample were carefully brushed into the flask. Readings were continued at thirty-second intervals until the rate of temperature rise again became constant. The true temperature rise was determined by plotting the data, time vs. temperature reading, and extrapolating the lines representing constant rise before and after the reaction to the midpoint between the time of addition of the oxide and the time at which the final constant rate of rise starts. Duplicate runs were made for each sample. The variation between duplicates was such that the maximum error appeared to be $\pm 0.01^\circ$, or, on the basis of a 3° rise, a maximum error of $\pm 0.33\%$. Very few duplicate runs were more than 0.01° apart, or $\pm 0.005^\circ$ deviation from the mean.

For simplicity, the results of these measurements will be given in terms of the rise in degrees, differences in rise and percentage difference in rise which would be proportional to percentage difference in energy content. All rises were calculated on the basis of one gram of the substance concerned. Since the materials are all contaminated with small known quantities of normal or basic lead carbonate or hydrate, the rises per gram for these substances must be known, but since there is a difference in the final state of the solution if one gram is dissolved and if a small fraction of a gram is dissolved, there should be a difference in the heat of reaction of 1 g. of lead carbonate and the heat calculated for 1 g. of lead carbonate when the reaction is carried out with a fraction of a gram. While this difference should not be large in such a great excess of perchloric acid as is used here, the rises per gram on the basis of small quantities of lead carbonate, basic lead carbonate and lead oxide hydrate were found by means of natural and artificial mixtures of known composition with pure red PbO. Once these values were determined the measured rises could be converted to true corrected rises for the red PbO present by means of the analysis of the product and simple algebraic calculations.

Table IV gives for three series of experiments each with a different calorimeter flask and stirrer a list of the measured temperature rises for the normal PbO, the distorted oxides 17-F-J and 28-A, the carbonates, the hydrate, analyses of the nor-

TABLE IV
HEATS OF REACTION WITH CONCENTRATED HClO₄
(Three series each with a different calorimeter flask and stirrer)

Series	Sample	Analysis (%)		Actual rise, °C.	Corrected rise per gram		% increase in heat of reaction, distorted PbO over normal PbO	
		CO ₂	H ₂ O		Max.	Min.	Max.	Min.
1	PbO-18-H Normal	0.04	0.00	3.080	3.085			
	PbO-17-F-J Distorted	.545	.16	3.061	3.145	3.135	1.94	1.62
2	PbO-18-N Normal	.062	.00	2.872	2.880			
	PbO-28-A Distorted	.29	.102	2.863	2.910	2.900	1.04	0.70
3	PbO-18-J Normal	.23	.00	3.133	3.170			
	PbO-28-A	.29	.102	3.162	3.210	3.205	1.26	1.10

Degrees Rise per Gram of Possible Contaminations for the Three Series Used in Corrections

Series	PbCO ₃	2PbCO ₃ ·Pb(OH) ₂	5PbO·2H ₂ O	PbO yellow
1	0.96	1.44	3.11	3.05
2	.90	1.35	2.90	2.896
3	.99	1.48	3.19	3.12

mal and distorted oxides, the corrected rise per gram of the red PbO in the normal and distorted oxides and the maximum and minimum possible percentage differences between them. The question of maximum and minimum differences enters because of the fact that the carbonate impurity in the distorted oxides may be present as normal or basic lead carbonate. If all of the carbon dioxide present is combined as basic lead carbonate, the corrected temperature rise will be a maximum according to the calculations mentioned above. If all of the carbon dioxide present is combined as normal lead carbonate, the corrected rise will be a minimum.

Taking run No. 3, sample 18-J, the corrected rise is 3.170°. The specific heat of 70% perchloric acid is 0.430 cal. per gram. The weight of perchloric acid is 82.84 g. Therefore, the true heat of reaction will be greater than 25,200 cal. per mole of PbO.

Theoretical Considerations and Discussion of Results

In the preceding sections, the preparation of red PbO and mixtures of red and yellow PbO from the hydrate and carbonates at various temperatures has been described in some detail and typical X-ray diffraction pictures have been included. It is evident from the patterns and from the data on the activities of these preparations toward the catalytic decomposition of hydrogen peroxide, that there is a definite difference between the products obtained by the high temperature decomposition of the hydrates and the carbonates and the products obtained by decomposition of the hydrate and carbonates at temperatures only slightly above those at which the dissociation

pressures become great enough to ensure a reasonably rapid decomposition at the existing pressure. The latter type of preparation is typified by increased catalytic activity and by several broad diffuse lines in the X-ray pattern and a readily observable "fading out" or decrease in intensity of lines having large values of sine θ , indicating a definite lattice distortion of some sort.

An attempt to explain the distortion of the active oxides on the basis of directional displacement of the atoms in the lattice was unsuccessful since the indices of reflections which remain sharp on the patterns preclude all such possibilities and no lattice stretching was observed.

Another possible cause of the distorted pattern is based on the theory mentioned by Fricke, Hüttig, *et al.*, that the oxides with higher energy content should show an effect on the X-ray diffraction pattern similar to the so-called Debye-Waller effect of thermal agitation. This effect is described in some detail by Compton and Allison⁶ with nearly sufficient data for calculations. Additional data for this work were obtained from Richtmyer⁷ and from the "International Critical Tables."

This theory states, in brief, that an increase in temperature exerts an influence on the scattering factors for atoms by virtue of the increased thermal energy which presumably increases the amplitude of vibration of the atoms in the crystal, with the result that at high temperatures the scattering factors are decreased according to a characteristic equation.

Recently Zener and Jauncey⁸ and Goetz and

(6) A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment," ed. 2, D. Van Nostrand Co., New York, N. Y., 1935.

(7) F. K. Richtmyer, "Introduction to Modern Physics," ed. 2, McGraw-Hill Book Company, Inc., New York, N. Y., 1934.

(8) C. Zener and G. E. M. Jauncey, *Phys. Rev.*, **49**, 17, 122 (1936)

Jacobs⁹ have demonstrated, the former theoretically, the latter in practice, that the Debye-Waller formulas are applicable to anisotropic solids without change.

Utilizing the available equations under the most favorable assumptions, the results allow a maximum in all experiments of 1.67% decrease in intensity and on the average only 0.1% decrease, obviously far below the carefully measured observed values.

Thus, the distortion of active red PbO is too large to be explained more than in part by applying the principle of increased thermal agitation from increased total energy content. Since the active product has at least twice the catalytic activity of the normal oxide, there must be an increased amount of "active" surface, which is probably due to incomplete formation of the lattice, with the result that the increase in energy may be localized in regions where this distortion has taken place. This is further indicated by the fact that "annealing" of the active samples for some hours, even at 100°, causes a great decrease in activity, accompanied by a sharpening of the X-ray diffraction lines.

It is clear that products of this distorted type may be identified by the X-ray pattern and that an increased catalytic activity, at least for certain reactions, and an increased energy content may be predicted for the compound upon the basis of such a pattern.

The other phenomenon, which requires some explanation, is the formation of the high temperature form of PbO, the yellow orthorhombic modification, at temperatures 450° below the true transition temperature of 585°. The question of crystal polymorphism has been treated historically and theoretically by Buerger and Bloom¹⁰ and practically by Bloom and Buerger¹¹ as applied to antimony trioxide. The data on antimony trioxide show that the cubic low temperature form and orthorhombic high temperature form may both be formed by hydrolysis of antimony trichloride depending on the conditions. The presence of certain foreign ions (specific effect) and possibly the presence of water bound as a hydrate both seem to cause the production of the "unstable" high temperature modification at ordinary temperatures. If the analogy could safely be carried over to the lead monoxides prepared

from hydrates and carbonates, it could be reasoned that either the presence of water or small quantities of acetates might cause stabilization of yellow PbO formed at the low temperatures from the hydrate. The oxide prepared by low temperature decomposition of normal lead carbonate produces no yellow orthorhombic form but that prepared from the basic lead carbonate does contain it. These facts lend support to the theory that hydrate water was responsible for the stabilization, since no tests for acetate were successful.

Since the data show that the distorted red PbO has an energy content greater than yellow PbO, it might be argued that the distorted PbO is a metastable state which should very readily change over to the next lower energy form, the yellow orthorhombic PbO. However, neither long heating of the distorted oxide during the process of preparation at the low temperatures nor aging at room temperature appear to effect this transformation but merely tend to perfect the red tetragonal lattice to the normal condition.

The next paper in this series will present data on the gradual transformation by grinding and by refluxing with water of the orthorhombic to the tetragonal lattice.

Summary

1. The preparation and analysis of powder and small crystals of the hydrous oxide of lead are described. The product always has a composition giving a formula $5\text{PbO}\cdot 2\text{H}_2\text{O}$. X-Ray diffraction studies of this hydrate with wedge reflection camera and Cu-K α radiation give the spacings for the lines of the diffraction pattern. By trial and error methods and a few logical assumptions a very rough estimate of the unit cell dimensions of the hydrate was made considering the crystals to be monoclinic. Density measurements and unit cell dimensions lead to an approximation of one molecule per unit cell.

2. Studies of the preparation of oxides from the hydrate, normal lead carbonate and basic lead carbonate at low and high temperatures are described. The low temperature preparations result in a product which gives a highly distorted X-ray diffraction pattern of the red tetragonal form of PbO usually contaminated with some of the yellow orthorhombic modification. High temperature decompositions of the hydrate and basic lead carbonate give undistorted patterns showing mixtures of red and yellow PbO. High

(9) A. Goetz and R. Jacobs, *Phys. Rev.*, **51**, 151 (1937).

(10) M. J. Buerger and M. C. Bloom, *Z. Krist.*, **96**, 182 (1937).

(11) M. C. Bloom and M. J. Buerger, *ibid.*, **96**, 65 (1937).

temperature decomposition of normal lead carbonate gives an undistorted pure red PbO.

3. Comparisons of the catalytic activity of normal and distorted red PbO, yellow PbO and the hydrate toward hydrogen peroxide decomposition are described. The activity of the distorted product is much greater than that of the other products compared and the difference cannot be attributed to particle size. Activity of the distorted oxide is decreased by "annealing" of the sample, which is accompanied by sharpening of the diffraction lines.

4. Comparisons of the heats of reaction of the normal and distorted red PbO with concentrated perchloric acid are made with the result that the distorted red PbO possesses a 1 to 2% greater energy content than normal red PbO.

5. Relative intensity measurements on the distorted and normal red PbO for comparison

purposes are described and the results are tabulated showing the great decrease in line intensities on the distorted PbO pattern.

6. The discussion of results includes a review of the active properties found for the distorted red PbO and calculations which show that the distortion cannot be accounted for on the basis of atomic displacements by directional stress, or, except to a very slight extent, on the basis of thermal agitation resulting from the increased energy content of the product. Hence, activity must reside in localized, incompletely crystallized surface areas. An explanation of the formation of yellow PbO at temperatures far below the red to yellow transition temperature is postulated on the basis that lattice impurities, such as water, will cause a metastable form to appear in temperature regions in which it is not usually produced.

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RECEIVED SEPTEMBER 19, 1938

[CONTRIBUTION FROM THE COLLEGE OF ST. THOMAS]

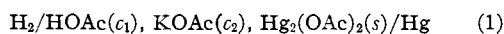
The Activity Coefficients of the Undissociated Part of Weak Acids. I. Acetic Acid in Potassium Acetate Solutions

BY W. D. LARSON AND W. J. TOMSICEK

From measurements of the electromotive forces of the cells

Pt/HOAc(Quinhydrone), HOAc, Hg₂(OAc)₂ (solid)/Hg
Larson and MacDougall¹ found that the mercurous acetate electrode functioned reversibly, and had a standard e. m. f. of -0.5109 ± 0.0002 v. at 25°, when the concentrations were expressed in moles per liter.

We have studied this electrode by means of the cells



in order to obtain a more precise value of its standard e. m. f. In addition, we have measured cells containing potassium acetate at varying concentrations in a solution of acetic acid of constant molality.

The e. m. f. of cell (1) is given by

$$E = E^0 - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{OAc}^-} = E^0 - \frac{RT}{F} \ln K c_1 (1 - \alpha) \gamma_{\text{u}} \quad (2)$$

where K is the thermodynamic ionization constant of the acid, α its degree of ionization, c_1 its

molality, and γ_{u} represents the activity coefficient of the acid molecules.

The purpose of measuring the cells containing potassium acetate was to present a method for determining, from e. m. f. measurements, the effect of salts on the activity coefficient of the undissociated part of weak acids. Data for the effect of potassium acetate on acetic acid are presented to illustrate the method.

Experimental

All materials were prepared as described previously.¹ Potassium acetate was from Mallinckrodt, and was dried at 180° for several hours, and then weighed in a closed, previously weighed bottle.

The acetic acid solutions were analyzed with a standard baryta solution. The solutions containing potassium acetate were made up by diluting a weighed amount of the salt with the stock acid solution to one liter in a calibrated, thermostated flask. The density of the solutions was determined by weighing the solution discharged at 25° from an accurately calibrated 25-ml. pipet. All weighings were corrected for buoyancy. The concentrations were known to within 0.1%.

E. m. f. measurements were made with a potentiometer constructed from four L. and N. dial type resistance boxes whose resistances were correct to within 0.04% as deter-

(1) W. D. Larson and F. H. MacDougall, *J. Phys. Chem.*, **41**, 493 (1937).