X-RAY AND PHYSICAL-CHEMICAL STUDIES OF HYDROUS LEAD OXIDE AND NORMAL AND ACTIVE LEAD MONOXIDES

BY

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THESIS

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I. INTRODUCTION

The general purpose of this investigation is to study the hydrous oxide of lead and the red and yellow modifications of lead monoxide from the standpoint of the preparation of these compounds from various sources, the X-ray diffraction patterns of the compounds, their chemical and catalytic activity, physical-chemical properties such as heats of reaction, analysis, and any other properties of these substances which would be contributions to the total knowledge concerning them.

While there are considerable data in the literature concerning properties of these compounds, there has not been a large amount published concerning the red and yellow forms of PbO as individual compounds other than data to prove the existence and the structures of the two forms. In particular, then, this investigation will consider the red and yellow forms of PbO as individual compounds, whenever possible. X-ray diffraction methods constitute the ideal method of determining the nature of a lead monoxide sample and all samples prepared will be tested by this method. As the historical section of this thesis will point out, no work has been reported concerning the preparation of lead monoxides under conditions such that an "active" or distorted lattice results although this has been done for oxides of several other metals. Another specific purpose of this work is to prepare such products if they exist and to study their properties in an attempt to determine the causes of such phenomena, and to correlate X-ray diffraction data with the physical and chemical properties of the substances.

Another specific purpose of this work is to determine as

much as is possible concerning the preparation, composition and structure of the hydrous oxide of lead about which very little has been reported in the literature.

II. HISTORICAL

The principal reference works concerning recent developments on the hydrous oxides and oxides of metals are Weiser (1) and Fricke and Hüttig (2). A large number of the references used for this work and a fairly complete discussion of many points were obtained from these volumes.

There are very few data reported concerning the hydrous oxide of lead. Since it has been prepared by a variety of methods some of which are listed in the experimental section on the hydrous oxide, and since many formulas have been assigned to this compound depending on the method of drying, it will only be stated here that Weiser (1) lists formulas varying from $2PbO \cdot H_2O$ to $3PbO \cdot H_2O$, several investigators having obtained $2.5PbO \cdot H_2O$. Some slight evidence has been found by means of isobaric dehydration curves for the existence of a definite compound of composition $2PbO \cdot H_2O$. Hüttig and Steiner (3) have probably made the most complete investigation of the dehydration of the hydrate and the various compositions obtained. They also observed that the X-ray pattern was distinctly different from that of red or yellow PbO, but gave no further discussion of the type of crystal structure expected. Natta (4) is said to have deduced that the hydrate was a crystal of low orthorhombic symmetry but no mention of this was found in that article.

The existence of the two forms of PbO, the red tetragonal modification and the yellow orthorhombic form, has been definitely shown by Darbyshire (5). Further work was done on the structures

of these forms by Dickinson and Friauf (6) on the red form and by Halla and Pawlek (7) on the yellow form.

The preparation of oxides by decomposition of the hydrate has been reported by Kohlschütter (8) who found a mixture of yellow and red PbO was formed at low temperatures in air but claimed that pure red PbO was obtained by vacuum decomposition at this temperature. Hüttig and Steiner (3) claimed that this low temperature dehydration gave the yellow form of PbO first, followed by the red form after further dehydration. Observations concerning the validity of this statement will be made in this thesis. Some of the work of Müller (9) on the preparation and properties of the oxides and hydrate will also be considered in the body of this thesis.

The most complete discussion of the preparation of "active" or distorted oxides, their properties and the theory connected with them is given by Fricke and Hüttig (2) and by Fricke (10). In both references Fricke discusses the experimental data on the careful low temperature dehydration of the hydrates of Zn, Be, Mg, Fe, Al and other metals. X-ray examination shows a broadening of lines in some cases, nearly always a decrease in the intensity of high order reflections, and occasionally a stretching of the lattice. Heats of reaction of these oxides with acids revealed an increase of from 0.5 to 5 kilogram calories per mole in the energy content over that of 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 effect has been directly traced to case (2) or (3). It is claimed that in case (3), one can imagine that incomplete lattice formation results from molecules or atoms being missing at random from the lattice, and from the atoms not all being in their proper lattice positions. This would result in an X-ray pattern which showed a decrease in intensity of high order lines, an increase in diffuse scattering, and in some cases, general line broadening.

Some of the papers investigating these phenomena are listed in the bibliography: Mg - Fricke, (11); Be, Al, Zn - Fricke and Wullhorst, (12); Zn - Fricke and Ackermann, (13); Fe - Fricke and Ackermann, (14); Fe - Hüttig, (15). No work whatsoever has been reported on such investigations on PbO as prepared by various methods.

III. THE HYDROUS OXIDE OF LEAD

A. The Preparation of the Hydrous Oxide of Lead

The method which was used for most of this work was that described by Hüttig and Steiner (3). For this preparation, about 80 g. of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ in 400 ml. of water were added in a jet to 400 ml. of NH_4OH solution (sp. gr. = 0.9). Fractions of the above quantities were used for the first preparations. The precipitation was carried out under conditions such that no carbon dioxide could enter during the precipitation, by the use of bulbs of ascarite. The distilled water used for the solution of the lead acetate and for washing the precipitate was boiled and cooled and kept under carbon dioxide free conditions. The precipitate was finally filtered by suction using hardened filter paper. The carbon dioxide which enters the product either was present in the original chemicals or is absorbed by the wet hydrate in the washing and filtering process. Drying the product was accomplished by normal desiccation over anhydrone (anhydrous magnesium perchlorate) in the presence of ascarite to prevent the presence of carbon dioxide in the desiccator. In a few cases, vacuum desiccation (0.1 mm. of Hg) was used with no appreciable difference in the composition of the product from that of the normally desiccated preparation.

It was found by experience that a large portion of the added lead acetate formed no precipitate with the NH_4OH, apparently due to dilution of the solution, and furthermore, that only a fraction of the lead acetate was being utilized in spite of the large excess of NH_4OH present. Consequently, the procedure was revised, so that

400 ml. of ammonium hydroxide were used for 200 ml. of lead acetate solution, with the result that a much increased yield was obtained, although the precipitation was still only about 75 percent efficient. The product obtained in this manner was identical with the original preparation.

The second method of preparation used was undertaken in an effort to ascertain whether another method would yield a product of different composition, or of different properties when dehydrated. This method was used only in the preparation of sample No. 23, and was taken from the method used by Müller (9). 170 g. of 3 M sodium hydroxide which had been treated with barium acetate to remove all carbonate were treated with 60 g. of lead acetate in 500 ml. of water added in a slow stream under carbon dioxide free conditions. Subsequent treatment of the sample was the same as that described above for the previous preparations with ammonium hydroxide.

A third method of preparation was found more or less inadvertently. An attempt was being made to prepare a partially dehydrated hydrous lead oxide according to methods by Müller in investigating the products obtained by boiling plumbite solutions in varying strength sodium hydroxide solutions.

Müller claimed that if a saturated solution of PbO in sodium hydroxide was boiled and cooled, various mixtures of the three products, hydrate, red and yellow lead oxide would be obtained depending on the concentration of the sodium hydroxide. From data in his paper it appeared as though a solution in 8 N sodium hydroxide might yield an active partially dehydrated product. 3 g. of pure yellow lead oxide were dissolved in 30 ml. of 8 N sodium hydroxide and the

solution was boiled for two hours with the flask attached to a condenser with an ascarite bulb at the top. On cooling, a heavy white crystalline precipitate formed which, on washing, filtering and drying could be seen to be composed of crystals about 0.2 mm. in diameter and less. This product of which there was somewhat over 1 g., was sifted through a 250 mesh screen. The fine particles were used for X-ray powder pictures and some of the larger crystals were carefully pulverized also for the purpose of taking powder pictures.

This preparation was attempted again at a later date without success, the usual precipitate being a fine crystalline yellow oxide mixed with lumps of material which appeared to be a mixture of red and yellow lead oxide. Although the concentration of the sodium hydroxide was presumably known by analysis, it is possible that an error in the original or in the later trials may have caused conditions to be sufficiently different to prevent a recurrence of this hydrate formation.

Microscopically, these crystals have the appearance of distorted rhombic dodecahedrons, although they show extinction effects in two directions. Analysis and X-ray patterns as mentioned below show the substance to be very nearly the same in composition as the formerly prepared hydrous lead oxides and identical to those in X-ray pattern. On the basis of the extinction effects and previously published estimates by Kohlschütter (8), it will be assumed that these crystals are of the monoclinic system.

It should be noted that all of the hydrate powders were rather coarse in average particle size but when dried were non-agglomerating. The analysis and the X-ray pattern remained constant

during the whole period of this investigation when the samples were kept over anhydrone, thus indicating a negligible vapor pressure but not necessarily a definite hydrate of invariant composition, since previous work on isobaric dehydration as reported by Fricke and Hüttig (2) gives no indication of definite hydrates within the region of composition covered by these preparations.

B. Analysis of Hydrates

All of the hydrate preparations made by methods 1 and 2 were analyzed quantitatively for carbon dioxide and water by the method to be described below. There could not have been sufficient quantities of adsorbed acetate to affect analysis, since none could be detected qualitatively in the hydrate samples by acidification with sulfuric acid, distillation into water and testing the distillate by odor, taste and litmus paper.

The method of analysis was the usual absorption method. The purification train consisted of a washing tower of concentrated sulfuric acid followed by a U-tube of ascarite and anhydrone. The combustion tube was a pyrex tube, about 3 feet long. The absorption train consisted of a straight drying tube filled with anhydrone for water absorption followed by a bulb for carbon dioxide absorption filled with ascarite followed by anhydrone. A protective tube containing ascarite and anhydrone was used on the end of the train.

The procedure of analysis was as follows: the empty porcelain boat was heated in a stream of air not faster than six bubbles per second for about 10 minutes with all absorption bulbs in the train. After a definite cooling time of 15 minutes the absorption

bulbs were removed with chamois finger stalls and placed beside the balance case for 15 minutes. The boat was kept in the desiccator during this period. The samples were always weighed into the boat from the sample bottle by difference. Before any absorption bulb weighing the bulb was opened to the air for a few seconds. The ignition of the sample was done under conditions identical to the preliminary treatment, ignition being carried out to the point of incipient fusion of the sample, and all water which condensed on the cooler portions of the combustion tube was driven toward the absorption train by heat. The heated tube and flow of air sufficed to carry all moisture into the absorption bulb during the 15 minute cooling period. Duplicate analyses were always run and results on water analysis practically always checked within 0.1 percent, usually within 0.05 percent. Carbon dioxide results checked within from 0.01 to 0.03 percent.

Each of the samples of the hydrates prepared for use in further experiments was analyzed by the above method. The results appeared to be nearly independent of the time of desiccation before analysis. The analysis of six samples gave results in the following range:

Percent CO_2 ranged from 0.17 to 0.3 (not expected to be constant)

Percent H_2O ranged from 2.95 to 3.13 (not expected to be quite constant due to varying CO_2 content)

It will be shown under the X-ray portion of this hydrate study that the probable form of the carbon dioxide in these preparations is normal lead carbonate although it would seem logical to expect a basic lead carbonate under the conditions of preparation. However,

in calculating the empirical formula for the hydrate, it makes a negligible difference on which basis the carbon dioxide content is transformed. The formulas were calculated for all of these preparations on the basis that the requisite amount of lead oxide is united with the carbon dioxide, the remainder of the lead oxide being combined with the water as the hydrate. These formulas vary from $PbO \cdot 0.384H_2O$ to $PbO \cdot 0.407H_2O$, a fair mean of which would give $PbO \cdot 0.4H_2O$. This empirical formula could be stated as $3.5PbO \cdot H_2O$, $5PbO \cdot 2H_2O$, or $2Pb(OH)_2 \cdot 3PbO$.

The analysis of the crystals of hydrate was made by the microanalyst of the chemistry department since the amount of sample was small and it was deemed wise to retain as much as possible of a sample which had not been reproduced by further efforts. This analysis gave values of 3.30 and 3.40 percent water with no carbon dioxide. The smaller of these results was run on a much larger sample than the other, and this gives a formula of $PbO \cdot 0.41H_2O$. The mean value gives $PbO \cdot 0.423H_2O$. This would indicate that there might very possibly be an actual hydrate of this composition, even though others have claimed it is not shown by isobaric dehydration curves.

C. Density of the Hydrate Crystals

The density of the limited supply of lead oxide hydrate crystals was determined using four independent trials. A 5 ml. specific gravity bottle was used. Its volume was determined by means of distilled water at a known temperature. The best non-volatile medium which would exert no solvent effect on the crystals was

kerosene. Its density was determined and the crystal density run followed this immediately at the same temperature. Temperature was constant within 1° during each run. Buoyancy corrections were made whereever necessary. The weighing of the crystals in the kerosene was preceded by evacuation in a vacuum desiccator until no further air bubbles were obtained from the mixture.

Of the four results, only two checked closely enough to report. This difficulty was probably due to microscopic impurities in the sample which were nearly all removed by sorting under a reading glass. The reported values for the density are 7.66 and 7.81 g./ml.

D. X-ray Diffraction Technique and Data Concerning the Hydrate of PbO

In order to substantiate the similarities observed in composition and other properties of the hydrous lead oxide preparations previously discussed, X-ray diffraction photographs for each preparation were obtained.

The X-ray patterns taken for comparison of these products were all taken with one camera of the wedge reflection type in use in this laboratory. It consists of a cylindrical tube with the film holder mounted on the circumference, a collimator defining a cylindrical X-ray beam and an adjustable 30° wedge mounted at the center of the cylinder for holding the sample. Cu-K radiation from a Phillips Metalix tube with a line focus filament was used for all of this work. Some patterns were obtained with the strong beam from this tube from 4 to 6 hour exposures. Others were taken using the weak beam, but for finer work, such as calibration of the camera and calculations of spacings the strong beam was filtered with nickel

foil in order to reduce to a negligible intensity the Cu-K_β lines and lines which are obtained by diffraction of several characteristic tungsten lines originating from tungsten which has sputtered on to the copper target from the filament.

An example of the pattern for all of these hydrate preparations is given in Figure 1. Every preparation gave the same pattern,

Figure 1

and the particle size of all of the samples appeared to be nearly the same, probably in the neighborhood of 10^{-3} to 10^{-4} cm.

In addition to comparing the patterns of these preparations it was desired to determine, if possible, the nature of the carbonate compound which is present in the hydrates. In order to do this, several attempts were made to carbonate the hydrate by means of dry ice, both in the presence and absence of water. The most successful attempt was the result of shaking some of the hydrate for two hours with dry ice in water, filtering and drying. The analysis of the product was: Carbon dioxide, 4.75 percent; water, 2.59 percent. On the basis that the carbon dioxide is combined as lead carbonate, the formula for the hydrate remaining would be $PbO \cdot 0.467H_2O$. On the basis of basic lead carbonate formation, the formula would be $PbO \cdot 0.354H_2O$. These data do not settle the question of what form the carbon dioxide would take, since neither gives the correct formula for the hydrate. Furthermore, analysis alone tells nothing of

changes which might have taken place in the composition of the hydrate. X-ray data, however, give at least a partial solution to this problem. The pattern obtained with this carbonated product contains several lines much stronger than lines in the same position on the hydrate pattern, and even shows some smooth lines which are not visible on the hydrate. On comparison of these lines with the patterns of pure normal lead carbonate and basic lead carbonate, it becomes evident that most of these lines are due to normal lead carbonate, although some could very easily be explained by the basic carbonate. Actually, a mixture of normal and basic lead carbonate as impurity in the hydrate could explain the apparent deviation of the two formulas above from the normal formula, but such an analysis of the situation is not called for and could scarcely be substantiated further.

A more important problem is that of obtaining data on the spacings of the lines of the hydrate pattern. From this it should be possible to estimate the unit cell dimensions, and eventually the number of molecules per unit cell. In order to attempt this, it became necessary to use an accurate method for the determination of the spacings. It was thought that some type of camera other than the wedge reflection type would be of more value since the center of diffraction varies slightly with the position of the wedge and the line positions would not be constant. Furthermore, calibration could only be accomplished by using substances having absorption properties nearly identical to those of the hydrate in order for a calibration curve to be of any value. The only substances fully qualified in this respect would be red PbO, yellow PbO and Pb. Of these, the

lattice constants of Pb and red PbO are the only ones accurately known and this pair of substances do not completely fill out a calibration curve.

Consequently, it was decided to employ a camera of the Seemann-Bolin type as described by Seemann (16), Bohlin (17) and elsewhere, because of the advantages supposedly held by this type of camera. This camera operates on the focusing principle. The defining slit, the sample, and the film must all lie on the circumference of the cylindrical camera. In addition to this, in order to allow the beam to diverge enough to cover the sample well, the focal spot of the X-ray tube target should approximate a point source which also lies on the circumference of the camera. This latter requirement could not be met with the equipment in this laboratory unless a long study was carried out for this specific purpose. However, it was thought that a divergent beam defined by slits such that a large area of the sample was bathed by the beam would prove satisfactory. The advantages of this type of camera are supposed to lie in the facts that the focusing effect increases the speed of taking pictures, that one edge of the line would always be sharp and that depth of penetration of the beam into the sample should have no effect on the position or the sharpness of a line from a given spacing. The latter fact should enable one to calibrate the camera with a variety of substances and obtain a good calibration curve.

Such a camera was designed and was built in the departmental machine shop. Essentially it consisted of a cylindrical brass tube of about 6.3 cm. radius and about 13 cm. in length. The sample holder was an inset in the bottom of the inside circumference, about

1 x 3.5 x 0.1 cm., so that the sample could be rolled down flush with the circumference. The lower slit edge was the inner circumference of the cylinder, the upper slit edge was adjustable and could be moved along the inner circumference of the cylinder.

The film was held flush against the inner surface by spring steel strips, and by brass guides. The opening through the camera wall at the slit was covered with black paper and thin nickel foil. A slit in the top of the camera surmounted by a screw was used for spotting the film with X-rays. Light-tight covers were placed on the ends. A brass shield extended nearly across the camera and from the top to just above the sample to cut out the incident beam and scattering from the slit.

A large number of pictures of NaCl were taken in order to ascertain the optimum slit width and camera position for sharp edged lines. When a setting was found which would give the best results pictures of ZnO, KI, As_2O_3, red PbO, yellow PbO, and the hydrate were taken. On attempting to make calibration curves from these pictures it was found that it was somewhat difficult to make a measurement to the sharp edge of the lines since this edge was hazy. However, a much worse result was discovered when the positions of lines of a given spacing were compared for the different patterns. There appeared to be differences as high as 3 percent in the calibration curves for different substances. This meant that a complete calibration curve was impossible to obtain under the existing conditions and use of this camera was discontinued. It is possible that the camera design or the distance from target to slit was the cause of the trouble although it is difficult to see why absorption effects should enter

to change line positions for different substances, since the theory of the camera shows that penetration depth into the sample can only affect the blurred side of the line and this effect should not depend on the position of the source of X-rays or the degree of perfection of the camera circumference.

As a result of this failure, the spacings for the lead oxide hydrate were calculated from the wedge reflection pattern. Since Pb and red PbO were the only accurately known standards possessing approximately the same absorption characteristics as the hydrate should have, calibrations with these substances were made. There were too many vacant spaces to draw an accurate curve particularly in the region of spacings greater than 2.5 A.U., so the final procedure for determining these unknown spacings was to calculate the effective radius of the camera for various points according to the position and spacing of the red PbO lines. This radius turned out to be nearly constant over large ranges. The unknown spacings were then calculated by use of these radii which were assumed to hold over certain regions of the pattern and which varied from 6.39 to 6.35 cm. The probable accuracy of these spacings, judging from the various calibration curves also employed was $\pm$ 0.015 A.U. at values greater than 3 A.U., about $\pm$ 0.010 A.U. between 2.5 and 3 A.U. and from $\pm$ 0.005 down to $\pm$ 0.002 A.U. as the spacing decreases from 2.5 A.U.

Table I gives the final data for these spacings and includes only those lines caused by diffraction of Cu-K_α radiation, as determined by the use of nickel filters.

An inspection of this table leads to the following data.

Table I

Analysis of Hydrous Lead Oxide Diffraction Pattern

Line	Observed Intensity	Observed Spacing A.U.	Possible hkl Values	Calc. Spacing A.U.
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	300	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	1.403		

Table I (continued)

Line	Observed Intensity	Observed Spacing A.U.	Possible hkl Values	Calc. Spacing A.U.
41	FF	1.388		
42	F	1.377	033	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	0.948	600	0.951
60	FF	0.935	026	0.934
61	FF	0.924	050	0.930
62	W	0.913		
63	W	0.896	440	0.900
64	F	0.877		
65	W	0.868		
66	FF	0.850		
67	W	0.835		
68	FF	0.810		

SS = Very strong

S = Strong

W = Weak

F = Faint

FF = Very faint

Lines 1, 10, 22, 36, 48, and 57 come very close to being a perfect series of integral multiples. Lines 2, 13, 26, 39, 53, 59, lines 3, 19, 35, 52, 60 and lines 7, 29, 50, 63, may be similarly compared. This indicates that these four series of lines are the first and higher orders of diffraction from important planes. It should be kept in mind that in the work of Halla and Pawlek (7) on yellow lead monoxide a suggested structure for the yellow form was given with a statement that the structure could be derived directly from a hypothetical hydrate by removal of water from the lattice. While it is probable that they were under the impression that the hydrate was a low symmetry orthorhombic crystal, the analogy should hold for a monoclinic hydrate crystal and one might expect spacings somewhat larger but following the same general trend of axial ratios for this hydrate. On this basis lines 1, 2 and 3 were chosen to be due to reflections from the 001, 100 and 010 planes, respectively. This corresponds roughly to the orthorhombic yellow lead oxide for which these same spacings would be 5.849, 5.459 and 4.72 A.U. in the same order as above. With this basis assumptions may be made as to the indices of certain lines in order to obtain values for the monoclinic angle, β . Since calculations using the above mentioned three fundamental spacings may be made for all lines for which h or k is zero without the use of the angle, β , the spacings for such lines were calculated. Nearly all of the possibilities fitted observed spacings and these are included in Table I. Calculations were made which proved that the unit cell could not be orthorhombic unless the choice of axes taken here was entirely wrong.

In order to find β , all of the lines between 4 and 10 were

chosen one at a time to represent the $11\bar{1}$, 111, $10\bar{1}$, and 101 reflections and in each case enough calculations were made to show with some certainty that the combination chosen would or would not lead to a check between observed and calculated spacings for the other lines on the pattern. It was obvious from the nature of some of the calculations that no results could be obtained from them. In some cases large gaps existed in which no calculated spacings could fall, although observed spacings were present. In other cases a line for which (hkl) was found gave no line for the plane $(hk\bar{l})$ but both lines should be present. No true fit was found by the calculations.

Since microscopic examination revealed the probability of a β angle in the vicinity of 120° and the assumption that line 8 was the $11\bar{1}$ reflection came somewhere near fitting many observed spacings, a tentative calculation of the unit cell dimensions and the number of molecules in the unit cell was made on that basis. The results follow: $a_0 = 5.93$ A.U., $b_0 = 4.65$ A.U., $c_0 = 6.36$ A.U., $\beta = 105^\circ\ 47'$. Volume of the unit cell = 168.8 cubic A.U., Density = 7.73 g. per ml. These values lead to a unit cell containing, as a very rough approximation, one molecule of $5PbO \cdot 3H_2O$. These results should at best be considered as an approximation until further data on the dimensions and the symmetry of the crystal are made available by work done on the minute single crystals.

IV. THE PREPARATION AND PROPERTIES OF NORMAL AND ACTIVE LEAD MONOXIDE

A. Introduction

The experimental procedure for the preparation and the investigation of the properties of the lead monoxide consisted in preparing oxides from several lead compounds by decomposition at various temperatures, taking X-ray diffraction patterns of each of these preparations, determining the catalytic activity of each of the samples relative to the others and finally choosing certain of the preparations for further tests, in particular, for the determination of energy differences by differences in heats of reaction, and for comparative measurements of X-ray line intensities.

B. X-ray Apparatus

The X-ray pictures were all taken with the same equipment as used for the hydrous lead oxide work; wedge reflection camera, Cu-K_α radiation. Pictures of representative samples were taken with nickel filter. Others, for comparison, were taken without this filtering device. Representative pictures are reproduced in Figure 2. An explanation of these pictures will appear in the description of the samples and in the discussion of results and theory.

C. Catalysis Apparatus

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 insure 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 burette, 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 burette, or to the atmosphere through the two-way stopcock, the other containing a short burette 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 burette.

D. Procedure for the Catalytic Activity Determinations

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 gram was weighed into the reaction flask, 7 ml. of water were added, the mixture was shaken until the sample was wetted and the flask was placed in the shaking machine, the stopper was inserted with the stopcock open to the atmosphere, the liquid level in the gas burette adjusted to zero and the stopcock

turned to connect the reaction flask with the gas burette. Exactly 3 ml. of hydrogen peroxide solution, analyzed to be 3 ± 0.05 percent and freshly made up, were added from the burette 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 burette at the start. During the run the leveling bulb was used to follow the gas evolution in the gas burette 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. 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 close 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.

It seems probable that the constant rate more nearly approaches the conditions of a true catalysis, so these values are the ones reported, although it should be mentioned that the unimolecular rate constants for the various samples follow the same general trend

as the constant rates. The data on the various samples are recorded in Table II together with information concerning the preparation of the sample and the nature of its X-ray pattern. Some of these data are explained more fully below and will be discussed in a later section of this thesis.

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 somewhat proportional decrease in speed of reaction thereby further confirming that the phenomenon is surface catalysis.

E. Preparation of Oxides and Data Concerning Them

The preparations made and studied for their X-ray pattern and catalytic activity will be described in this section. The starting materials for all of these preparations were the lead oxide hydrate prepared as previously described, normal lead carbonate and basic lead carbonate. The normal lead carbonate used was Baker and Adam-

Table II

Catalytic Activities of Samples, Description of Preparation and of X-ray Pattern

Sample No.	Description of Preparation	Description of X-ray Pattern	Activity cc. O_2 Evolved Per Second, from H_2O_2, All on Same Basis.
13-B	Hydrate decomposed, 100°, 4 hr.	Hydrate pattern + trace red PbO, distorted	0.35
13-C	" " " 5 "	Hydrate pattern + trace red PbO, distorted	0.32
13-D	" " " 6 "	Hydrate pattern + equal red PbO, distorted	0.35
13-E	" " " 8 "	Fainter hydrate pattern + red PbO, distorted	0.38
13-G	" " " 10 "	Fainter hydrate pattern + red PbO, distorted	0.50
13-H	" " " 12 "	Fainter hydrate pattern + red PbO, distorted	0.64
15 to 15-E	Hydrate decomposed, 100°; 15, 20, 25, 50, 74, 100 hrs.	Slight trace of hydrate + PbO, distorted; 74, 100 hrs. - no hydrate, PbO, distorted	0.90 (all)
17-B	Hydrate decomposed, 200°, air	Red PbO + some yellow PbO, some distortion, active O_2	0.80
17-C	" " 300° "	Red PbO + some yellow PbO, some distortion, active O_2	0.53
17-D	" " 400° "	Red PbO + lot of yellow PbO, slight distortion, active O_2	0.48
17-E	" " " vacuum	Red PbO + equal yellow PbO, no distortion	0.50
17-K	" " 160° "	Red PbO + some yellow PbO, distorted	0.90
17-L	" " 200° "	Red PbO + some yellow PbO, distorted	1.00
17-M	" " 250° "	Red PbO + some yellow PbO, distorted	1.00

Table II (continued)

Sample No.	Description of Preparation	Description of X-ray Pattern	Activity cc. O_2 Evolved Per Second, from H_2O_2, All on Same Basis.
17-N	Hydrate Decomposed, 300°, vacuum	Red PbO + more yellow PbO, less distorted	0.72
17-O	" " 400° "	Red PbO + equal yellow PbO, less distorted	0.50
17-P	" " 490° "	Nearly pure yellow PbO, large particles included	0.25
5	Hydrate	Typical hydrate pattern	0.29
12	"	" " "	0.25
14	"	" " "	0.36
17	"	" " "	0.50
23	"	Typical hydrate pattern, smaller particles	0.90
11	Hydrate heavily carbonated	Hydrate + lines of $PbCO_3$, perhaps $2PbCO_3 \cdot Pb(OH)_2$	0.00
17-F to 17-J	Hydrate decomposed, 130°, vacuum, 5, 10, 30, 40, 91 hrs.	All distorted, red PbO + small amount of yellow PbO, no difference in patterns	0.90
23-A	Hydrate decomposed, 150°, vac., 3 hr.	23-A to 23-E are identical with series 17-K to 17-O	0.85
23-B	" " 250°, " "		0.80
23-C	" " 300°, " "		0.61
23-D	" " 350°, " "		0.50
23-E	" " 400°, " "		0.50
18-A	$PbCO_3$ decomposed, 450°, vacuum	Undistorted pure red PbO	0.45
18-B	" " 250°, "	Distorted red PbO + trace $PbCO_3$	2.90
18-C	" " 240°, "	" " " + some "	4.00
18-D	" " 230°, "	Distorted red PbO + large amount $PbCO_3$	1.00
18-E	" " 235°, "	Distorted red PbO + moderate amount $PbCO_3$	1.80
18-F	" " 300°, "	Very slightly distorted pure red PbO	0.64
24-A	Basic $PbCO_3$ decomposed, 250°, vac., 3 hr.	Distorted red PbO + yellow PbO + basic $PbCO_3$	3.50

Table II (continued)

Sample No.	Description of Preparation	Description of X-ray Pattern	Activity cc. O_2 evolved Per Second, from H_2O_2, All on Same Basis.
24-B	Basic $PbCO_3$ decomposed, 240°, vac., 3hr.	Distorted red PbO + yellow PbO + more basic $PbCO_3$	2.40
24-C	" " " 255° " "	Distorted red PbO + yellow PbO + more basic $PbCO_3$	3.00
24-D	" " " 235° " 8 "	Distorted red PbO + yellow PbO + less basic $PbCO_3$	3.70
24-E	" " " 300° " 3 "	Slightly distorted red PbO + yellow PbO + no basic $PbCO_3$	3.00
24-F	" " " 350° " 3hr.	Undistorted red PbO + yellow PbO + no basic $PbCO_3$	1.25
24-G	" " " 400° " "	Undistorted red PbO + yellow PbO + 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	" " " " "	" " " "	0.53
28	Hydrate	Hydrate	0.29
28-A	Hydrate decomposed, 130°, vac., 10 hr.	Distorted red PbO + some yellow PbO	1.20
27	Basic $PbCO_3$ decomposed above 650°	Pure yellow PbO, some large particles	0.67

son's C.P. material labeled basic lead carbonate, $2PbCO_3 \cdot 2Pb(OH)_2$, but found by analysis for carbon dioxide and water to be pure normal $PbCO_3$ with a trace of surface moisture. The basic lead carbonate used was Merck's C.P. basic lead carbonate whose composition was confirmed by analysis.

The first series of preparations was made by dehydration of the hydrate at 100° C. The apparatus used was an Abderhalden, or drying pistol, vapor jacketed with steam and evacuated by means of a Cenco Hi-Vac pump to less than 1 mm. of mercury pressure. Anhydrone was used as desiccant in the drying pistol. There were two series of this preparation, series 13 and 15, the first being dehydrations of from 4 to 12 hours, the second being dehydrations from 15 to 100 hours. The X-ray patterns of the products in this series showed a gradual decrease in the quantity of hydrate and an increase in the amount of red PbO present as time of dehydration increased. After 6 hours dehydration the lines were of about equal intensity, and from that time on the red PbO lines were far more intense. At 50 hours there remained only a trace of the hydrate pattern. 74 hours showed complete removal of hydrate lines.

Since the product left in the reaction flask after catalytic decomposition of the hydrogen peroxide by the members of series 15 was considerably darker brown than the original red product it was decided to investigate the possibility of higher lead oxide formation by the hydrogen peroxide reaction. Consequently, some of these residues were allowed to stand until no further decomposition of hydrogen peroxide took place, and were then washed repeatedly and allowed to stand for some time in the wash water and finally filter-

ed and dried. This resulting sample was tested for "active oxygen" by means of a small test tube with side arm into which the sample could be introduced with concentrated hydrochloric acid. The side arm led into a tube of potassium iodide solution. A notable formation of free iodine detectable to the eye and readily confirmed by starch solution resulted. Comparison with the corresponding treatment of normal red PbO prepared at high temperature will be noted later.

The most significant data obtained from the X-ray patterns of series 13 and 15 will be summarized below. Considering the lines of red PbO as indexed and tabulated in Table IV, the reflections from the planes with the following Miller indices appeared practically unchanged in sharpness from those of pure high temperature red lead oxide but weaker: 110, 003, 113, 220, 114, 312. The following lines were definitely broadened and diffuse, in some cases overlapping other neighboring lines: 101, 200, 121, 103, 222, 123. The remainder of the lines appeared to be much reduced in intensity, some notably the 202, 301, 004 having become either so diffuse or faint that they were barely visible. Patterns of this type will be called distorted patterns in the text of this thesis since it will be shown under theoretical discussion that this pattern probably results from a distorted or incomplete lattice formation.

The next series of preparations were decompositions of the hydrate at higher temperatures in air. Samples 17-B, 17-C and 17-D represent dehydrations at approximately 200°, 300° and 400° C., respectively. The temperature was regulated by an electric heater heating a large pyrex tube containing the boat of sample. A chromel-

alumel thermocouple with the hot junction immersed in the sample was used in conjunction with a Leeds and Northrup thermocouple potentiometer with cold junction compensator. The X-ray patterns show with nearly equal intensity the lines of red PbO and yellow PbO, with very little distortion of lines except where a red and yellow lead oxide line are blended to form a wider line. This set of runs is probably of very little value as far as a study of lead oxide is concerned since all of the samples contained some active oxygen. An analysis of 17-D (400° in air) by the Bureau of Standards procedure (18) showed 0.33 percent active oxygen. There was no indication of lattice change or of new lattice formation, but this was to be expected on the basis of the work of Le Blanc and Eberius (19) on the taking up of oxygen by PbO. To eliminate this oxidation, the remainder of the decompositions were carried out in vacuum. Thus, the products obtained contained no trace of active oxygen.

Samples 17-E and 17-K to 17-P were samples prepared by vacuum dehydration at intervals from 160° to 490°. In general, the data recorded in Table II show a decrease in activity with increase in temperature of preparation. The X-ray patterns showed some distortion from 160° to 250°, lessening rapidly above this temperature. At the same time an increase in temperature of preparation appeared to increase the content of yellow PbO gradually, until at 400°, the lines of the two forms were at least of equal intensity. At 490°, the sample prepared was nearly pure yellow PbO of the characteristic large particles in comparison to that of the red PbO in all the pictures. The appearance of the yellow form at low temperatures was not expected since the transition temperature has been set by many

investigators at 587°. At 100° below this temperature nearly pure yellow PbO was obtained. The temperature regulation of this series was inaccurate, since no provision was made to prevent radiation loss from the surface of the heated sample. That this effect was of importance was proved by the fact that above 300° the surface of the sample was of slightly different color from the interior and the surface appeared to contain a little more of the red (lower temperature form) than the interior according to X-ray patterns.

In all subsequent procedures except preparation of series 17-F to 17-J an improved heating furnace was used. The heater was made by wrapping the 1 1/3 inch pyrex tube used for the furnace with 15 feet of No. 26 chromel wire, (20 ohms), electrically and heat insulated by wrappings of asbestos cord. This heater had a 550 watt maximum input, more than sufficient for this work. In fact, the pyrex tube would not stand greater than 500° C. internal temperature under the vacuum employed. The current for the heater was regulated by a parallel lamp circuit bank with "stove-pipe" resistors in series with the bank. The current could be controlled so that the temperature within the furnace was constant to $\pm$ 5°, with only occasional adjustment. The sample boat was placed in the furnace inside of a polished copper cylinder to reduce radiation loss. The pressure was sufficiently low to prevent appreciable oxidation of the copper surface.

To check further on the products obtained by higher temperature dehydration of the hydrates, a series of decompositions was carried out on sample No. 23, a hydrate prepared by the NaOH method described previously. Sample No. 23-A to 23-E were prepared at tem-

peratures from 150° to 400°. The patterns of this series showed the same results as the previous hydrate decompositions at these temperatures; increased quantity of yellow PbO and decreased distortion as the dehydration temperature was raised.

Series 17-F to 17-J was prepared from the same hydrate sample as the other 17 series members. The Abderhalden was again employed for this purpose using amyl alcohol as the heating vapor. This gave a dehydration temperature of approximately 130°. The samples of hydrate were decomposed for 5, 10, 30, 40 and 100 hours. All of these samples gave identical X-ray patterns and were also identical to the long time dehydrations of series 15 except that a few of the strong yellow PbO lines appeared on the patterns at a temperature 350° below the red to yellow transition temperature. The catalytic activities of the preparations in this series were practically identical. After these tests had been made and the X-ray patterns taken, these five samples were combined for further use in heats of reaction experiments and controlled X-ray patterns to be described in a later section. The combined samples were called No. 17-F-J.

In order to prove reproducibility of the results in the preparation of these oxides having distorted patterns a new hydrate sample was dehydrated for 10 hours in the vacuum furnace described above at a temperature of 120° to 130° C. This sample, No. 28-A, was saved for heat of reaction experiments, comparison of catalytic action and special X-ray pictures. The X-ray pattern proved to be identical with that of No. 17-F-J, with the exception of a slightly greater intensity of yellow PbO lines.

Up to this point, no sample of pure undistorted red PbO had

been obtained and it was obvious that it could not be prepared from the hydrate. Since it was essential to have such samples for comparison purposes the next step in the procedure was to prepare such a sample. Müller's methods of preparing the oxides from plumbite solutions (9) were tried but a pure homogeneous product free from lead and barium carbonates was difficult to obtain and the methods yielded comparatively large microscopic crystals which were unsuitable for comparison work with the other preparations. A good preparation of red PbO of any particle size was not prepared even from 16 N NaOH by Müller's method. A fairly good crop of orthorhombic plate crystals of the yellow-green oxide was obtained on boiling yellow PbO powder (prepared by heating hydrate or carbonates well above 800° C.) in 16 N NaOH and cooling slowly.

Series 18-A to 18-N were preparations obtained by heating Baker and Adamson's normal lead carbonate (labeled basic lead carbonate) in vacuum at temperatures ranging from 230°, at which the first noticeable decomposition takes place, to 450°. Every one of these products was nearly pure red PbO except in cases where the time of heating or the temperature was not sufficiently great to completely decompose the carbonate. This fact was proved by X-ray pictures. Again it was noted that there was some of the distortion seen before, on pictures of samples prepared just above the point of decomposition, from 230° to 250°. At 300° and above, the lines on the pattern were sharp. The distorted samples here also showed increased catalytic activity over the normal samples. The normal sample 18-N showed very slight if any darkening in color of the sample after the H_2O_2 catalysis. The washed and dried sample was tested for active oxygen as

the samples of series 15 were treated, with the result that no more than the slightest trace of active oxygen was found. Some of the samples prepared at 400°, 18-H, 18-I, 18-J, 18-L, 18-M, 18-N were carefully analyzed for carbon dioxide and used in some of the heat of reaction studies later. It should be noted that Le Blanc and Eberius (19) claim that yellow PbO only may be prepared by decomposition of lead carbonate (prepared from lead acetate and ammonium carbonate) in vacuum at 250° C. Since this does not appear to be true for normal lead carbonate, either with commercial or with a sample prepared by treating lead acetate with a large excess of ammonium carbonate which analyzed as pure normal $PbCO_3$, it was decided to investigate the decomposition of basic lead carbonate.

Merck's basic lead carbonate (analysis - $2PbCO_3 \cdot Pb(OH)_2$) was used for these trials. Samples 24-A to 24-G are the results of these decompositions from 235° to 400° C. The X-ray pictures show the same distortion of the red PbO lines for samples prepared below 300° C., and large quantities of yellow PbO in these samples. Higher temperatures appeared (from relative line intensities) to give products containing a smaller proportion of yellow PbO. It should be noted, that darker products were obtained at the higher temperatures which might support the indication of less yellow PbO if it were not for the fact that colors appear to be of almost no value in dealing with oxides of lead. The activities of these preparations were high probably because of the distortion and the large amounts of yellow PbO together. As a result of the carbonate and basic carbonate decompositions, the preparation of pure yellow PbO at temperatures below the transition temperature appears to be improbable. The pre-

paration of a pure red PbO can be accomplished. Further support to the theory of the existence of active distorted oxides has been given by the low temperature products of the carbonate decompositions.

F. Heat of Reaction Studies of Lead Oxides with Concentrated $HClO_4$

In accordance with the facts mentioned in the historical sections of this thesis, 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 $HClO_4$ present. The procedure was purely empirical and was designed only to obtain sets of results which could be compared with each other and not with any other series of runs. Since this was the case, exact analysis of new bottles of $HClO_4$ was not necessary, the calorimeter parts, thermometer, temperature of run, temperature of the oxide, etc., were not necessarily the same for different series of runs, but every effort was made to keep conditions constant for one series of runs.

The apparatus consisted of a one-half pint Thermos flask

with wide mouth, a Beckmann thermometer, a glass stirrer and a medium speed stirring motor. Since, for all runs, an exact volume of $HClO_4$ 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. pipette used delivered 82.8 g. of 69.2 percent $HClO_4$ at 16-17°C. Although these exact data are of no importance in the calculations, they show the conditions of the runs. Exactly one gram of the sample to be dissolved was weighed on glazed paper. This was brought to room temperature before using. The $HClO_4$ was pre-cooled to 16°C., 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 30 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°, or, on the basis of a 3° rise, a maximum error of $\pm$ 0.33 percent. Very few duplicate runs were

more than 0.01° apart, or ± 0.005° 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 percent difference in rise which would be proportional to percent 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 $PbCO_3$, basic $PbCO_3$ 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 $PbCO_3$ and the heat calculated for 1 g. of $PbCO_3$ 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 $HClO_4$ as is used here, the rises per gram on the basis of small quantities of $PbCO_3$, basic $PbCO_3$ 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 III gives 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 normal and distorted oxides, the corrected rise per gram of the red PbO in the normal and distorted oxides and the maximum and minimum possible 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

Table III

Heats of Reaction With Concentrated $HClO_4$

Series No.	Sample	Analysis % CO_2	Analysis % H_2O	Actual Rise °C.	Corrected Rise per gram Max.	Corrected Rise per gram Min.	% Increase in Heat of Reaction, Distorted PbO over Normal PbO Max.	% Increase in Heat of Reaction, Distorted PbO over Normal PbO Min.
1	PbO-18-H Normal	0.04	0.00	3.080	3.085			
	PbO-17-F-J Distorted	0.545	0.16	3.061	3.145	3.135	1.94	1.62
2	PbO-18-N Normal	0.062	0.00	2.872	2.880			
	PbO-28-A Distorted	0.29	0.102	2.863	2.910	2.900	1.04	0.70
3	PbO-18-J Normal	0.23	0.00	3.133	3.170			
	PbO-28-A	0.29	0.102	3.162	3.210	3.205	1.26	1.10

Degrees Rise per Gram for the Three Series

Series No.	$PbCO_3$	$2PbCO_3 \cdot Pb(OH)_2$	$PbO \cdot 0.4H_2O$	PbO yellow
1	0.96	1.44	3.11	3.05
2	0.90	1.35	2.90	2.896
3	0.99	1.48	3.19	3.12

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. For normal PbO, the only impurity must be normal lead carbonate. Both values are given although long exposure X-ray patterns of No. 28-A reveal some faint lines which correspond to basic lead carbonate lines, so this combination appears to be most probable. It should be noted that these tabulated data are divided into three separate runs, all with slightly different conditions such as different stirrer or different flask.

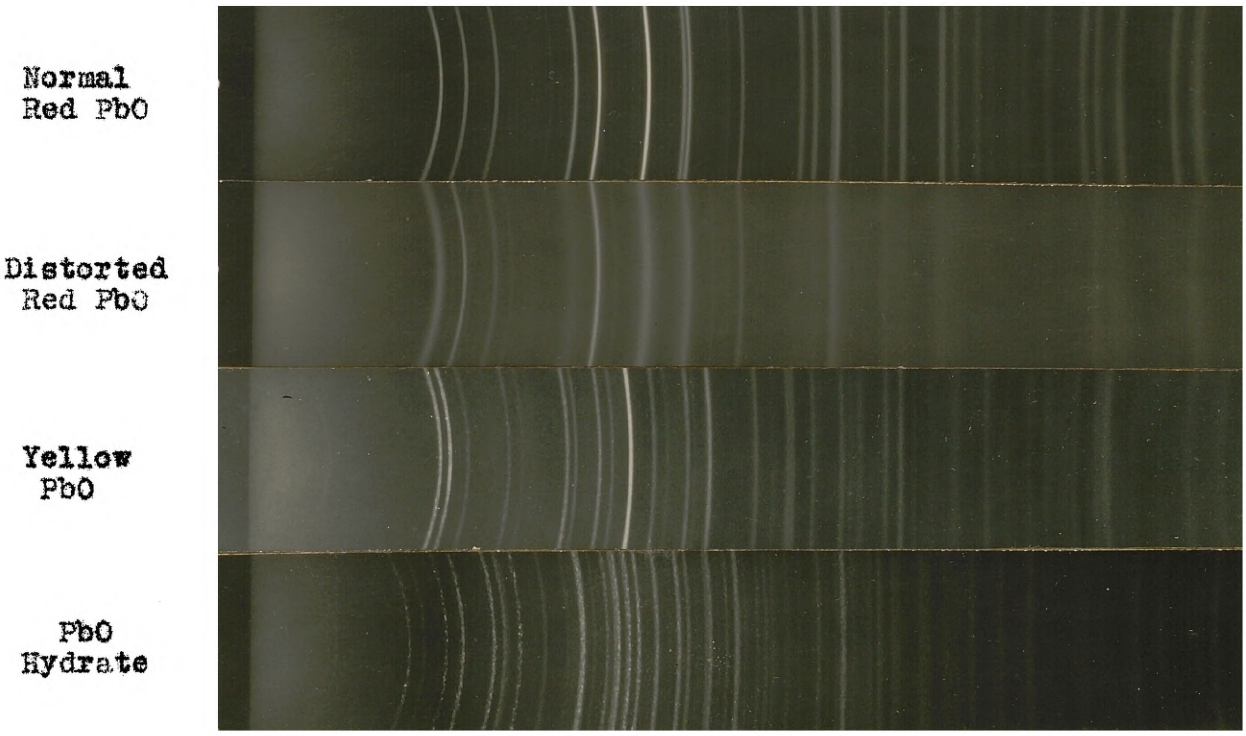
Heats of reaction run on sample of normal yellow PbO give a value of 2.896 with the apparatus of run No. 2, after correcting for the small amount of CO_2 remaining in this preparation made from basic lead carbonate heated well above 600° C. While the distorted patterns showed evidence of the presence of this form of PbO, calculations show that even 10 percent yellow PbO in the distorted PbO would not appreciably affect the corrected values listed in Table III. As a matter of record, a calculation is made here that gives a rough estimate of the value of the heat of reaction of the PbO with $HClO_4$. Since the water equivalent of the calorimater is not used, the true value is larger than that calculated from the greatest observed rise in Table III. Taking run No. 3, sample 18-J, the corrected rise is 3.170°. The specific heat of 70 percent $HClO_4$ is about 0.430 calories per gram (20). The weight of $HClO_4$ is 82.84 g. Therefore, the true heat of reaction will be greater than 25,200 calories per mole

of PbO.

G. Data on Intensity of X-ray Diffraction by Normal and Distorted Red PbO

In Figure 2 are shown typical patterns of the normal red PbO,

Figure 2



distorted red PbO, yellow PbO and the PbO hydrate. It can be seen that the distorted pattern is characterized by a heavy background of scattered radiation and by the aforementioned decrease in line intensity and diffuseness of certain lines.

In spite of the excellent work of Dickinson and Friauf (6) on the structure of red PbO there is still some question as to the oxygen positions. It was thought that there might be a possibility of calibrating the wedge reflection camera such that measured rela-

tive intensities could be read as true relative intensities, providing a basis could be found on which to compare the relative intensities. If such a calibration could be made it would be possible to check to some extent on the intensities predicted for red and yellow PbO on the basis of their structures as determined at the present time. It was also considered necessary to measure the relative intensities of lines on the distorted PbO patterns for comparison with the normal pattern. This could be done nearly as well without knowing the true relative intensity calibration, although further data on the position of the oxygen atoms in the red PbO lattice might help explain the diffusion of the lines on the distorted PbO pattern.

The method used for this attempted calibration was to use two standards whose lattice constants and structure were accurately known, namely, Pb and Bi. These metals were both prepared in the finely divided state by reduction with Na_2SnO_3 solution. The Pb was prepared by adding a dilute plumbite solution to an excess of stannite solution. Extreme care had to be taken to prevent the precipitated wet lead from coming in contact with air more than momentarily, even to the extent of drying under acetone and transfering to vacuum desiccator without removing from the acetone. If these precautions were not taken the product contained large amounts of PbO. The Bi was prepared by adding a large excess of alkaline stannite solution to a $Bi(NO_3)_3$ in HNO_3 solution. Less care was needed in handling the wet Bi precipitate since it was not readily oxidized. Since Pb and Bi have nearly the same mass absorption coefficients for Cu-K_α radiation, the only control on the intensity of the beam was to be sure that for each picture the same amount of radiation went over

the top of the wedge in relation to the intensity of the total incident beam. The Victoreen r-Meter was used for this measurement and control of the height of the wedge was used to vary the amount of radiation passing over the top of it. Lead ends were made for the camera in order to prevent stray radiation and ionized air from fogging the film. The position of the camera, the time of exposure and conditions of developing films were also controlled as carefully as possible with the equipment used.

Each of the patterns so obtained was used to make a microphotometer trace for the calculation of line intensities. In addition, microphotometer curves were run on patterns of normal red PbO and on various distorted patterns; samples No. 17-F-J and 28-A, taken at various exposure times. The microphotometer was adjusted to maximum sensitivity for these runs and the total darkening or zero transmission line was put on each trace for purposes of measurement.

The calculation of relative intensities was made from these traces by measuring the photographic darkening of the peaks of the curves in the case of Pb, Bi and normal PbO, since the lines were of the same type and of about the same thickness. Since the background, which was nearly constant, must be subtracted out to get the true darkening due to the line, the final formula becomes $S = \log \frac{T_B}{T_P}$; where S is darkening, T_B is transmission through the background, T_P is transmission through the peak intensity of the line. These transmissions are measured by the distance between the total darkening base line mentioned above and the point on the curve in question. The relative intensities were then calculated from these measured darkenings.

The theoretical relative intensities were calculated from the crystal structure by the usual method of calculating F, the structure factor for planes of a given set of indices (hkl) for each plane, squaring, multiplying by the number of cooperating planes and comparing these values. Atomic structure factors as a function of $\sin \frac{\theta}{\lambda}$ for Pb, Bi, and O were obtained from the tables of Pauling and Sherman (21).

When an attempt was made to find some relationship between the measured relative intensities and the calculated values at definite positions on the Pb pattern which could be applied to the patterns of PbO and Bi to correlate their theoretical and measured relative intensities, no such relationship could be found. A few isolated pairs of lines gave results which checked as to theoretical and measured relative intensities but no way of calibrating over the whole pattern would work. This attempt was then abandoned but some of the data found for red PbO has been included in Table IV along with further data to be described below.

Since a calibration was unnecessary for the purpose of comparing the patterns of normal and distorted red PbO the following method was adopted for getting this comparison. The lines on the distorted red PbO patterns were in many cases so wide and diffuse that peak intensity measurements would be of no value. Integrated intensity values must be used, so 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

Table IV

Comparison of Intensities of Normal and Distorted Red PbO

Indeces hkl	Spacing A.U.	Calc. Relative Intensity Normal	Integrated Areas Normal-18-N	Int. Areas Distorted 17-F-J	Int. Areas Distorted 28-A	Nature of Line on Distorted Pattern	Yellow PbO Line Which May Interfere hkl	A.U.
101	3.11	74	2.20	7.01	7.04	Broad	111	3.05
110	2.81	39	1.10	4.15	3.06	Sharp	None	
002	2.51	13	1.22	2.75	0.98	Sharp	None	
102	2.12	1	0.055	0.24	0.16	Diffuse	None	
200	1.98	33	1.45	3.88	2.35	Broad	202	2.00
112	1.87	61	3.74	8.36	4.50	Sharp	023	1.84
121	1.67	100	4.57	13.79	6.78	Broad	None	
202	1.56	39	4.34	9.82	5.47	Faint	None	
103	1.54	44				Broad	222	1.53
113	1.44	3	----	----	----	Sharp	None	
220	1.40	34	0.75	1.82	1.01	Sharp	None	
301	1.28	40	1.04	0.91	----	Broad	204	1.29
004	1.25	10	1.13	1.76	0.80	Faint	024	1.24
222	1.23	33	2.62	5.33	3.16	Broad	None	
123	1.21	73						
114	1.14	30	----	----	----	Diffuse	224	1.13
312	1.12	78	----	----	----	Diffuse	115	1.11
321	1.08	69	----	----	----	Broad	None	
204	1.06	36	0.835	2.89	2.21	Faint	None	
303	1.04	33	0.73	0.55	----	Very Faint	None	

Table IV (continued)

Line Ratio	Observed % Decrease in Relative Intensity on Distorted Patterns	
	No. 17-F-J	No. 28-A
$\frac{220}{110}$	34	29
$\frac{004}{002}$	31	12
$\frac{204}{102}$	21	9
$\frac{303}{101}$	75	----
$\frac{102}{110}$	-16	-56
$\frac{300}{110}$	29	14
$\frac{112}{110}$	41	36
$\frac{121}{110}$	26	21
$\frac{002}{110}$	40	58
$\frac{301}{110}$	76	----
$\frac{004}{110}$	58	60
$\frac{204}{110}$	46	-39
$\frac{303}{110}$	80	----

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.

The results of these measurements for some of the lines of normal and distorted red PbO are included in Table IV. Some of the lines were too faint to be measured above the background with any degree of certainty. 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 is also included in Table IV. Since the presence of yellow PbO in these distorted samples has an effect on the measured intensities, note is made in the table of the yellow PbO line and its spacing which might cause interference with each red PbO line measured.

This completes the experimental work of this thesis. Theoretical calculations and discussion concerning the active oxides and their relation to the normal oxide will be considered in the next section.

V. THEORETICAL CONSIDERATIONS AND DISCUSSION OF RESULTS CONCERNING LEAD MONOXIDES

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 H_2O_2, 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 insure 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.

The first comparison to be made of the difference between the normal and distorted oxide was that which has already been noted concerning the catalytic activity, shown in Table II. Here the comparison of distorted sample 28-A with pure red PbO 18-N shows the rate of evolution of O_2 from H_2O_2 to be more than doubled in the case of the "active" No. 28-A. Further examination of the table shows that in every case decomposition of the hydrate from 100° to 300° shows a greater catalytic activity as more of the hydrate is decomposed (as hydrate lines disappear from the X-ray pattern), and also a decrease

in catalytic activity as the temperature of dehydration is raised above 200°. The particle size undoubtedly has an influence on the activity of preparations still containing some hydrate, but for samples prepared above 200° the particle size appears not to differ from that of the lower temperature products and in addition, larger quantities of yellow PbO are found these high temperature preparations, a factor which should, on the basis of the activity of a somewhat coarse pure yellow PbO No. 27, cause an increase in the activity of the products so prepared. The fact that the activity decreases for high temperature preparations indicates that the low temperature products are much more active and that this activity is destroyed by higher temperature. This conclusion has been reached by Fricke, Hüttig, et. al., for other oxides as mentioned in the historical section of this thesis.

The increased catalytic activity of the products obtained by decomposition of $PbCO_3$ — No. 18 and $2PbCO_3 \cdot Pb(OH)_2$ — No. 24 at temperatures where they will just decompose is less easily explained. No. 18-B to D are quite active and do show a definite distortion effect on the pattern which is a mixture of $PbCO_3$ and red PbO. However, this effect is much less marked than in the case of No. 28-A. Since an appreciable quantity of $PbCO_3$ appears to lessen the activity (cf. Table II, sample No. 11) it is to be expected that No. 18-D has lower activity since the pattern shows only partial decomposition. The particle size of these products may be smaller which would cause increased activity although there is no distinct indication of this. It is to be noted again that from 300° on up to 450° the activity decreases (18-A, F, M, N) and the product gives an undistorted pure

red PbO pattern. The series of decompositions of No. 24 — $2PbCO_3 \cdot Pb(OH)_2$, No. 24-A to G, at various temperatures, shows a trend similar to that of the $PbCO_3$ decompositions. Mixtures of the basic lead carbonate, red PbO and yellow PbO appear at temperatures just high enough to start decomposition, the carbonate gradually disappears leaving a distorted pattern even at 300°, and finally above 350° the pattern is that of an undistorted mixture of red and yellow PbO in nearly equal quantities. As a possible explanation of the fact that the distorted patterns from the carbonate decompositions show greater activity than the more highly distorted product obtained from the hydrate, it might be noted that the carbonate content of the decomposed hydrate would probably be present as a coating around some of the oxide particles since the carbonates will not decompose at those temperatures, whereas the residual carbonate content of the decomposed carbonates would be enclosed by the active oxide which resulted from the decomposition. Since carbonate is known to retard the catalysis tremendously, this would indicate that the active oxide from hydrate might still have greater activity than measured, and that there was no reason to doubt the semi-quantitative validity of the activity measurements in the case of this apparent anomoly.

Two outstanding facts remain to be discussed and explained if possible. The first is the cause of the distorted or active properties of the low temperature product red PbO. The second is the formation of yellow PbO at such low temperatures. A forthright explanation of these phenomena does not appear to be easily found, but a theoretical discussion and some calculations will follow, particularly with regard to the first phenomenon.

The first explanation of the distortion which might be considered is that the lattice is changing over to that of yellow PbO and that the differences of certain lines is due to the fact that some planes of each lattice having the same spacing are involved in the observed effect. This, however, can be seen to be a false hypothesis, at least as far as complete explanation is concerned, by examination of Table IV. This shows that many of the red PbO lines, some broad and some sharp, have no yellow PbO line with a spacing close enough to exert any such effect. In addition, it should be noticed that the distorted pattern lines all have a weaker relative intensity (compared either to the 110 intensity or with some other first order line intensity) than the lines on the normal PbO pattern, with one exception.

A second discussion, although not necessarily an explanation, of this distortion might lie in a survey of the atoms lying in the planes which give the strongly distorted lines. The structure factor expressions for red PbO on the basis of the structure given by Dickinson and Friauf (6), lead to the following simplifications. Red PbO has 2 molecules per unit cell. The Pb atoms have been placed at 0 1/2 u, 1/2 0$\bar{u}$ where u = 0.24. The oxygen atoms have been tentatively placed at 000, 1/2 1/2 0 according to the space group of the tetragonal system, D^{7}_{4h}. This results in the expressions:

(1) h, k odd $F_{hkl} = -2F_{Pb}\cos 2\pi l(0.24) + 2f_o$

(2) h, k even $F_{hkl} = 2F_{Pb}\cos 2\pi l(0.24) + 2f_o$

(3) h, k mixed $F_{hkl} = 2f_{Pb}\sin 2\pi l(0.24)$

where f_{Pb} and f_o are the atomic scattering factors for Pb and O.

A consideration of the above structure factor expressions together with the data in Table IV concerning sharpness of lines on the distorted patterns reveals that the lines which are definitely diffuse or broadened are not confined to reflections having any one of the three combinations of the indices h and k given with the structure factor so that no conclusions can be drawn as to the population of the planes that are distorted, nor can the distortion be blamed on a displacement of either oxygen or lead atoms alone. When it is considered that a spacing such as the 001, reflection from which depends almost entirely on the reflecting power of the oxygen, is so faint that it just barely appears on the patterns it seems hardly probable that a displacement of oxygen atoms alone could cause the observed effect.

Further observations of the direction and position of the planes causing sharp reflections on the distorted patterns reveal that there appears to be no direction in which a distortion of lead or oxygen atoms could take place without causing notable distortion of one of these planes. Thus, any attempts at simplifying the distortion effect by predicting the direction of displacement of atoms will not be satisfactory. Furthermore, if a directional distortion of the lattice took place there might be a noticeable stretching of the lattice and this was not observed.

The third discussion concerning the cause of the distorted pattern is based on the theory mentioned by Fricke, Hüttig, et. al., that the higher energy content oxides 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 de-

tail by Compton and Allison (23) with nearly sufficient data for calculations. Additional data for this work were obtained from Richtmyer (23) 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 the equation, $f = f_o\, e^{-M \sin^2\theta}$, where f = scattering factor at temperature T, f_o = scattering factor of the atom at rest, θ is the Bragg angle, and M is defined by:

$$M = \frac{6h^2}{mkT_c\lambda^2}\left[\frac{\phi\left(\frac{T_c}{T}\right)}{\frac{T_c}{T}} + \frac{1}{4}\right]$$

where h is Planck's constant of action, m is the mass of the atom, k is the Boltzmann constant, T_c is the characteristic temperature of the substance defined as the temperature at which $h\nu = kT$ if ν is the characteristic frequency of vibration of the crystal as used in Einstein's relationship between heat capacity, temperature and vibrational frequency (Richtmyer, p. 269),

$$C_v = 3R\left[\frac{e^{\frac{h\nu}{kT}}}{e^{\frac{h\nu}{kT}} - 1}\left(\frac{h\nu}{kT}\right)^2\right], \quad \phi\left(\frac{T_c}{T}\right)$$

is the Debye function values of which may be found in a table in Compton and Allison (23), λ is the wave length of X-rays used.

Unfortunately these equations were originally derived for simpler cases than the diatomic molecule of PbO which crystallizes in the tetragonal system. The Debye-Waller equations were derived for isotropic cubic system crystals, although it is possible to apply it to diatomic solids by calculating f values for both atoms.

The Einstein equation was derived for monatomic solids, but may be applied in some cases to molecules if the heat capacity can be safely assumed to be equal to that of two monatomic solids and if the vibrational frequency is nearly the same for each kind of atom in the molecule. The first assumption is fairly well met by PbO, since $C_{V\ 298^\circ}$ is about 10.64 as calculated from C_p values by means of the approximation $C_p - C_V = A\, C_p^2\, T$, where $A = \frac{0.0214}{T_{melt}}$ (Richtmyer, p. 367). The second assumption is probably not fulfilled even approximately by PbO, but some interesting calculations may be made in spite of this as will be given below.

Recently Zener and Jauncey (34) and Goetz and Jacobs (35) have demonstrated, the former theoretically, the latter in practice, that the Debye-Waller formulas are applicable to anisotropic solids without change. Goetz and Jacobs use the expression $J = J_0\, e^{-M \sin^2\theta}$ where J and J_0 are the relative intensities of a line at temperature T and when the atoms are at rest. This would appear to be slightly incorrect in view of the fact that intensities are proportional to the squares of the structure factor, but there would be a negligible difference if the temperatures used in the calculation do not vary greatly.

A calculation by means of approximations for the exponentials in the Einstein equation was made in order to obtain a value for ν, the characteristic frequency. The value obtained was 7.26×10^{12} sec^{-1} at 298° K. This gives a value of 347° for T_c, the characteristic temperature. Placing this value in the equation for M gives 0.0404 for pure normal PbO at 298° K. In order to determine the change in intensity which would occur if the energy difference ob-

served by heats of reaction were entirely converted into thermal agitation according to the Debye-Waller equations it is necessary to calculate the energy content according to the Einstein equation, $E = \frac{3N_0 h\nu}{e^{\frac{h\nu}{kT}} - 1}$ (Richtmyer, p. 269), add to this the percent increase in measured energy content and calculate the temperature corresponding to this new energy content. This temperature, using the maximum observed energy difference of 1.94 percent, is 305° K. an increase of only 7°. A calculation of the value of M at this temperature gives M = 0.0423.

Since the greatest difference in intensity will be at large values of θ, the 204 spacing is taken for calculations. Using these values of M for the normal and high energy oxides, the decrease in observed intensity for the 204 reflection would be of the order of 0.1 percent. The observed decrease in intensity of this line below the intensity on the normal pattern is about 9 percent when the decrease is calculated by means of intensities relative to those of the 110 reflection, about 21 percent when referred to the 103 reflection. It must be remembered that these observed values are too low, since there is no way of finding what the true J_0 value is on the distorted pattern, and these longer spacing lines undoubtedly are also less intense relatively than on the normal pattern. From this it is apparent that either the Debye-Waller effect furnishes only a small portion of the observed distortion or that the characteristic temperature and frequencies are meaningless for red PbO when calculated on the basis of these formulas.

In order to test this, it was decided to make a calculation on the basis that the characteristic temperature calculations were

invalid but that the characteristic temperature of PbO would be in the neighborhood of that of Pb, 80° K. After carrying through the same type of calculation on this basis, M turns out to be 1 and 1.031 for the normal and high energy oxide at 298° K. and 307° K., respectively. These results would allow a 1.67 percent decrease in intensity, still far below the observed, particularly when relative intensities of other lines are used for comparison which show a greater decrease in intensity than the 304 reflection. If the measured relative intensities of given lines of short spacing are compared with each other on the two types of patterns by means of the first approximation assumption that the lines from 110, 002, and 103 planes are very slightly affected by the distortion and are practically equal to J_0, values of M can be calculated which range from 1.7 to 4 for the various lines. If further steps in this series of approximations are taken the values of M increase to such an extent that no theoretical value for the characteristic temperature could possibly give such large values of M providing the observed energy differences are used to determine the temperature at which M is calculated. Thus it is seen that whether the Einstein equations hold or not for PbO there is little possibility that the Debye-Waller effect as applied to differences in energy content can explain the distorted lattice of the red PbO. It should be noted that while the Debye-Waller equations should strictly be applied only to elements, an attempt to split the equation into two parts, one for oxygen scattering factor and one for lead scattering factor, would scarcely be an improvement on the above calculations, since the oxygen scattering factor has so little effect on the total crystal structure factor, and the value of M for Pb

would be very close to that calculated above on the basis of T_c = 80° K.

In concluding the discussion of the active distorted red PbO it may be said that the distortion 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.

It is clear from the data, X-ray patterns and discussion that such a distortion exists and that products of this 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, although a suitable specific explanation of the phenomenon is lacking.

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° C. The question of crystal polymorphism has been treated historically and theoretically by Buerger and Bloom (36) and practically by Bloom and Buerger (37) as applied to Sb_2O_3. A combination of facts from the data of this thesis with data and theory from the latter references gives a partial explanation of the phenomenon. The data on Sb_2O_3 show that the two polymorphic forms of compound, cubic low temperature stable form and orthorhombic high

temperature stable form may both be formed by hydrolysis of $SbOCl_3$ 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. PbO prepared by low temperature decomposition of normal lead carbonate produces no yellow PbO, but that prepared from the basic lead carbonate does contain yellow PbO. These facts lend support to the theory that hydrate water was responsible for the stabilization, unless the basic lead carbonate contains traces of acetate. The method of preparation of the basic carbonate was not known but no tests for acetate were successful.

Since the data of this thesis show that the distorted 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 PbO. However, neither long heating of the distorted oxide during the process of preparation at the low temperatures nor aging at room temperature appears to affect the composition or degree of distortion of the active red PbO, so the high energy form does not appear to be particularly unstable or metastable.

VI. SUMMARY

1. The preparation and analysis of powder and small crystals of the hydrous oxide of lead is described. The product always has a composition giving a formula $5PbO \cdot 2H_2O$. 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 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 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 can not be attributed to particle size.

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 percent greater energy

content than normal red PbO.

5. An attempt to calibrate the X-ray camera in order to obtain true relative intensities of diffraction lines is described although the attempt was not successful. Relative intensity measurements on the distorted and normal red PbO for comparison purposes are described and the results are tabulated showing the extremely 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 solely on the basis of thermal agitation resulting from the increased energy content of the product. Other possible explanations of the distortion are considered, in particular a discussion of possible directions in which distortion could take place on the basis of the sharpness or diffuseness of lines on the distorted pattern. 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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