28. *An X-Ray Examination of the Oxides of Lead.*

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THERE has been considerable controversy regarding the composition, constitution, and ultimate structure of the oxides of lead. The properties of the various commercial samples differ rather widely according to the methods employed in their preparation.

The ordinary methods of chemical analysis cannot distinguish between the variations in fine structure which are known to exist even in compounds of the same chemical composition. It is this atomic arrangement, however, which determines the behaviour of the substance in its industrial applications. As these are now so extensive, it is necessary to find some explanation, and subsequently, some method of calculation, which can be applied to the study of these variations.

During the present research a number of photographs of lead oxides have been taken, the Debye–Scherrer powder method being used, and by measurement of the spacing of the lines, along with observations of relative intensities, it is possible to come to some conclusion regarding the constitution of the various commercial samples and impure specimens of oxides.

The apparatus employed to take the powder photographs is now so well known that a very brief description will suffice. The oxide in the form of a fine powder is attached to a hair by means of Canada balsam. This hair is mounted in such a manner that it can be completely rotated at the geometrical centre of the surrounding photographic film. The X-rays fall upon the powder and the diffracted beams diverge in various directions and are recorded on the sensitised surface of the film. By comparison of the photographs taken in this way, it is possible to decide whether there is a similarity in the internal atomic arrangement of any two samples, and to detect mixtures of two or more ingredients in any given specimen.

The author has been concerned chiefly with the oxides and some of the compounds of lead, particularly from the point of view of the utilisation of these substances in the manufacture of the lead accumulator. This paper discusses the pure oxides, as well as certain commercial samples of lead monoxide, red lead, etc., and indicates how information regarding the constituents of the commercial oxides can be obtained by examination of the X-ray photographs.

Lead Suboxide.—It is uncertain whether a suboxide of lead exists as a definite chemical compound or whether it is merely a mixture of lead with higher oxides. Winkelblech (*Annalen*, 1837, **21**, 21) regarded the suboxide as a mixture of lead and lead monoxide, and Boussingault (*Ann. Chim. Phys.*, 1833, **54**, 263) said that it contains no metallic lead or lead monoxide, because mercury extracts nothing from it either dry or under water. Later, van Arkel (*Rec. trav. chim.*, 1925, **44**, 652), using X-ray methods, observed that the suboxide was a mixture of tetragonal lead monoxide and metallic lead. More recently, Ferrari (*Gazzetta*, 1926, **56**, 630), also using X-ray methods, found the suboxide to be apparently a true compound of lead with oxygen, possessing a structure of the cuprous oxide type.

The results of this research do not throw any definite light on the problem, but tend to support the view of van Arkel. If the suboxide does exist as a definite compound, it must be of such an unstable nature that few investigators succeed in carrying through the preparation and examination of the substance before it has decomposed. Thus it is possible that a true compound was obtained by Ferrari, although all attempts here to reproduce the same material by the same method of preparation have failed to yield the same structure as indicated by the X-ray analysis.

Material No. 1. Following Ferrari, this sample was prepared by passing carbon dioxide for 15 hours over lead oxalate at 310°. The product was a fine black powder, which gave a slight effervescence when treated with acid, apparently due to a trace of lead carbonate. The photograph did not resemble in any way that obtained by Ferrari, nor did it correspond to any of the other recognised forms or mixtures of the various forms of lead oxide.

Material No. 2. This sample was prepared by heating lead oxalate in a vacuum for 8 hours at 290°. This method also yielded a fine black powder, very similar in appearance to that prepared by Ferrari's method. Whilst this preparation was cooling, air was suddenly admitted when the temperature had fallen to 80°. A pale red flash was seen near the specimen, but no permanent change of colour or other visible alteration in the nature of the material could be observed. The photograph of this preparation is reproduced as No. 2 on the plate, and measurements have indicated definitely that this is merely a mixture of metallic lead and red lead monoxide, thus reproducing the result obtained by van Arkel. For comparison a photograph of metallic lead is given (No. 1).

Material No. 3. This was another attempt to prepare the oxide by the method of Ferrari, but the result was a white powder which on examination by X-rays appeared to consist of a trace of normal lead carbonate and a considerable amount of some other ingredient which did not resemble the original oxalate and has not yet been identified.

Lead Monoxide.—There are many different modes of preparation of lead monoxide, and the products differ widely in colour according to the particular method adopted and the subsequent treatment. These differences have been attributed to differences in the state of aggregation, on the one hand, and in the physical structure, on the other. Although certain features in the behaviour of the monoxide are quite well known and reproducible, nevertheless, in general, these do not account for the variations in physical properties which are so evident.

Samples of lead monoxide can be broadly classed either as red or yellow oxide. It was considered by Ditte (*Compt. rend.*, 1882, **94**, 1311) and others that two enantiotropic forms of lead monoxide were involved, the red form being more stable at the ordinary temperature.

Glasstone (J., 1921, **119**, 1689, 1914) reported that no relation could be observed between specific gravity, colour, and solubility, and therefore concluded that the various forms of monoxide differed only in the state of aggregation of the particles.

On the other hand, Applebey and Reid (J., 1922, **121**, 2129) obtained the oxides in the form of single crystals, and observed very marked differences in properties between the two samples, both from a crystallographic point of view and also in specific gravity, solubility, and electrode potentials. These results suggest that the forms exhibit a true case of dimorphism, and this view is conclusively confirmed by the X-ray examination.

Red variety. This has been examined by Dickinson and Friauf (*J. Amer. Chem. Soc.*, 1924, **46**, 2457), van Arkel (*loc. cit.*), and Levi and Natta (*Nuovo Cim.*, 1926, **3**, 114). The specimen examined here was prepared by boiling a portion of finely powdered yellow monoxide in water until it had been converted into the red variety. The photograph is reproduced as No. 3, and in agreement with

TABLE I.

Lattice Constants (in Å.).

Pb.	Pb_2O(?).		PbO, red.	PbO, yellow.	PbO_2.
4·91 [1]	Mixture [8]		a = 5·55 c = 5·00 [10]	a = 5·50 b = 4·68 c = 5·81 [14]	a = 4·945 c/a = 0·685 [15]
*[2]	Pb	red PbO			
4·98 [3]	4·91	a = 3·87 c = 5·02			
4·91 [4]	5·38 [9]		a = 3·99 c = 5·01 [11]		a = 4·98 c = 3·40 [16]
4·92 [5]					
4·942 [6]			a = 3·87 c = 5·02 [12]		a = 4·97 c = 3·40 [17]
4·935 [7]					
			a = 3·96 c = 5·02 [13]		a = 4·96 c = 3·39 [18]
Present work :					
4·938	Mixture of Pb + red PbO		a = 3·968 c = 5·011	a = 5·459 b = 4·723 c = 5·859	a = 4·931 c = 3·367

Pb_3O_4 Lattice constants not yet determined.
Pb_2O_3 Amorphous.

References.—[1] Vegard, *Phil. Mag.*, 1916, **32**, 65. [2] Kirchner, *Ann. Physik*, 1922, **69**, 59. [3] Owen and Preston, *Proc. Physical Soc.*, 1923, **35**, 101. [4] Kolderup, *Bergens Museums Aarbok*, 1924—25. [5] Davey, *Physical Rev.*, 1924, **23**, 292; 1925, **25**, 753. [6] Phoebus and Blake, *Physical Rev.*, 1925, **25**, 107. [7] Levi, *Nuovo Cim.*, 1924, **2**, 335. [8] van Arkel, *loc. cit.* [9] Ferrari, *loc. cit.* [10] Levi, *Nuovo Cim.*, 1924, **1**, 335. [11] Dickinson and Friauf, *loc. cit.* [12] van Arkel, *loc. cit.* [13] Levi and Natta, *loc. cit.* [14] Halla and Pawlek, *loc. cit.* [15] Davey, *Physical Rev.*, 1924, **23**, 763. [16] Ferrari, *Rend. Accad. Sci. Fis.-Mat. Napoli*, 1925, **2**, 186. [17] van Arkel, *Physica*, 1925, **5**, 162. [18] Goldschmidt, " Geochemische Verteilungsgesetze," VI, 1926.

* Lattice constant not given.

previous investigators the tetragonal type of structure is indicated. In Table I the lattice constants are given for all the oxides examined along with the values obtained by other workers. Although detailed attempts to determine the atomic positions from first principles have not been made here, nevertheless a calculation carried out on the structure proposed by Dickinson and Friauf (oxygen atoms at 000, $\frac{1}{2}\frac{1}{2}0$; lead atoms at $0\frac{1}{2}u$, $\frac{1}{2}0u$) gave good agreement with the observed intensities with $u = 0{\cdot}23$.

Yellow variety. This variety has been previously studied by X-ray methods by Kohlschütter and Scherrer (*Helv. Chim. Acta*, 1924, **7**, 337), and by Halla and Pawlek (*Z. physikal. Chem.*, 1927, **128**, 49). The photograph (No. 4) is clearly very different from that of the red variety, thus supporting the conclusions of Applebey and Reid as opposed to those of Glasstone. As suggested by Halla and Pawlek, the structure appears to be orthorhombic, the dimensions of the unit cell being given in the table. The actual atomic coordinates are not at present known with any certainty.

Other samples of lead monoxide were then examined with the results indicated.

(A) Commercial reddish-brown: mixture of red and yellow oxides, the former apparently in excess.

(B) Commercial yellow: pure yellow oxide, no trace of any other ingredient.

(C) Oxide scraped from surface of oxidised negative plate of a lead accumulator: yellow oxide and metallic lead.

(D) Lead smoke formed by striking an arc between lead electrodes: yellow oxide, no trace of other oxides.

In all the above cases the lattice constants remain in agreement with each other to within at least 0·2%.*

Red Lead.—Red lead, or minium, Pb_3O_4, is perhaps the most variable of all the lead oxides. The commercial material is rarely pure and contains a varying amount of unconverted lead monoxide, referred to as "free" litharge. The various samples differ considerably also in colour, particle size, and various other physical properties, quite apart from the differences to be expected as a consequence of variation in monoxide content. The composition of red lead is expressed in terms of its dioxide content; thus pure Pb_3O_4 would have PbO_2, 34·9%, and any deviation from this value

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* In a recent paper (J., 1931, 2821) Applebey and Powell came to the conclusion that there are only two polymorphic forms of lead monoxide.

The variations in colour appear to be due to the presence of metallic lead, and the amount of lead present could be varied by different degrees of exposure to heat or light. This is in agreement with the fact that only two distinct structures are revealed by the X-ray examination.

indicates an impure sample, the most probable impurity being monoxide.

Diagram No. 5 illustrates a photograph of pure red lead. This evidently has quite a complex structure about which nothing is yet known. It is evident, however, that Pb_3O_4 has a characteristic structure of its own, and is not merely a mixture of other lead oxides. A number of photographs were taken of samples of commercial red lead, and in all cases they resembled that for the pure red lead with the addition of a few lines corresponding to yellow monoxide. Thus, in general, the " free " monoxide content can be attributed largely, if not entirely, to yellow lead monoxide.

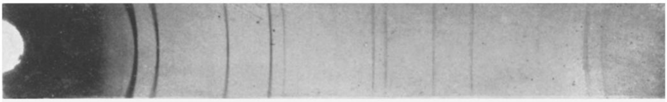
The modification of red lead known as " orange lead " is not an impure form of Pb_3O_4, since its analysis, in general, indicates a dioxide content nearer to 34·9% than that of ordinary red lead itself. Orange lead differs from red lead in bulkiness, size of grain, and in its behaviour towards linseed oil, and considerable speculation has been put forward as to the reason for these differences, which are all the more interesting in view of the closely allied chemical composition.

A photograph of orange lead is reproduced in No. 6, and it is apparent that its structure closely resembles, and probably is identical with, that of ordinary pure red lead : its lines are a little more diffuse, indicating somewhat finer crystalline particles. Thus apparently this is not a case of isomerism but merely a question of variation of state of aggregation or of the size of the ultimate crystalline particles.

Three commercial samples of red lead were then examined : (A), Pb_3O_4, 73·6 ; free PbO, 26·4%. (B), Pb_3O_4, 88·4 ; free PbO, 11·6%. (C), Pb_3O_4, 87·7 ; free PbO, 12·3%. In all these cases the *X*-ray photograph indicated the presence of yellow lead monoxide, and, by mixing pure Pb_3O_4 with yellow oxide in the above proportions, identical photographs could be reproduced. Thus, the free monoxide in commercial red lead is in its yellow form. Also the lattice constants for Pb_3O_4 appear to have the same value in these different commercial samples, just as in monoxide samples.

Lead Sesquioxide.—The preparation of this oxide has been reported by several workers, and although very discordant results have been obtained in the determination of its composition by chemical analysis, nevertheless these results have tended to indicate the existence of a compound of the composition $Pb_2O_3,3H_2O$. Debray (*Compt. rend.*, 1878, **86**, 513) is said to have obtained it by heating lead dioxide to 360° ; this is, however, rather doubtful in view of experiments carried out during the course of this work. Frémy (*Ann. Chim. Phys.*, 1844, **12**, 488) prepared the sesquioxide by mixing alkaline solutions of potassium plumbate and plumbite,

X-Ray Photographs.

1


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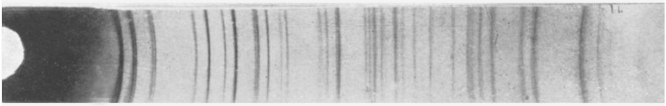

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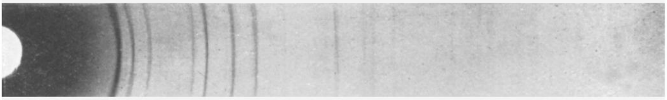

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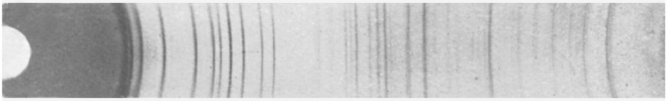

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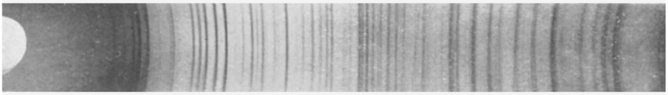

6


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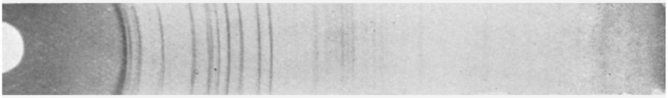
8


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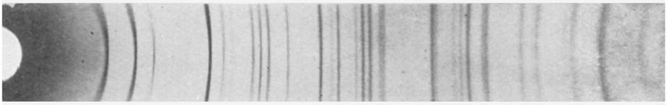

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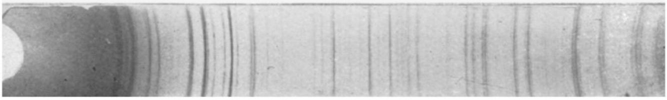

[*To face p.* 216.

and reported that the precipitate, after being washed and dried over sulphuric acid, had the composition of lead trihydroxide, $Pb_2O_3,3H_2O$ or $Pb(OH)_3$. Glasstone (J., 1922, **121**, 1456) discusses the various methods of preparing lead sesquioxide and gives full details of one method which he considers to be the most satisfactory.

Material 1. The first sample investigated was prepared by adding excess of potassium hydroxide to a solution of lead nitrate, redissolving the hydroxide. The sesquioxide was then precipitated by sodium hypochlorite, and dried in a desiccator over sulphuric acid (Found: PbO_2, 57·1. Calc. for $Pb_2O_3,3H_2O$: PbO_2, 57·7%). No lines were visible on the X-ray photograph, indicating that the sample was truly amorphous in accordance with general views.

Material 2. A sample of sesquioxide was then prepared by Glasstone's method (*loc. cit.*). The material was light brown and was very deficient in dioxide (Found: PbO_2, 17%). The X-ray examination again indicated an amorphous substance (No. 7). A portion of this material was heated in air at 140° for 2 hours and again examined by X-rays. Two feeble diffuse lines were now visible. When the material was heated at 300° for the same length of time, four lines became visible, but still diffuse, difficult to measure, and not capable of identification. The material was then heated to 400° and gave a good photograph (No. 8) of yellow monoxide, apparently free from any other oxide. It would appear that dehydration of the sesquioxide is accompanied by decomposition into yellow monoxide.

Carnelley and Walker (J., 1888, **53**, 59) suggested that at 360—415° it forms red lead, but no trace of red lead could be detected during the course of this examination.

Winkelblech (*loc. cit.*) reported the formation of lead monoxide, in agreement with the results obtained here. Our investigation indicates that samples of lead sesquioxide prepared according to two radically different methods are truly amorphous, but are converted into yellow lead monoxide at about 400°.

Lead Dioxide.—The properties of the various samples of lead dioxide appear to be appreciably more constant than those of the other oxides. It can be prepared by a variety of chemical processes, and exhibits little tendency to variable composition. Although there is no doubt as to the existence of PbO_2 as a definite compound, there is some controversy as to whether some of these samples represent polymorphic modifications of dioxide, hydrated dioxides, or contamination with slight traces of a higher oxide, such as Pb_2O_5.

The dioxide was photographed here in order to identify this material in the reactions taking place within the lead accumulator.

This sample was prepared by the action of nitric acid on red lead, analysis indicating PbO_2, 99·8% (see No. 9).

The crystal structure of the dioxide has been studied by Huggins (*Physical Rev.*, 1923, **21**, 719), Davey, van Arkel, Ferrari, and Goldschmidt (*locc. cit.*). The results correspond with a tetragonal space lattice of the rutile type, the lattice constants obtained by the different investigators being given in Table I.

If a loop of fine copper wire is dipped into molten lead and slowly withdrawn, a thin film of metallic lead will appear across the loop containing many fine perforations over its surface. The author has recently shown, by electron diffraction, that these apparent holes are really covered over with a very thin skin of transparent lead dioxide (probably 10^{-5} cm. thick). Thus lead dioxide can be prepared directly by heating metallic lead in air.

In the structure proposed by Ferrari and others, the atoms are arranged as follows :

Pb at $0, 0, 0; \quad \frac{1}{2}, \frac{1}{2}, \frac{1}{2};$
O at $x, -x, 0; \quad -x, x, 0; \quad \frac{1}{2}-x, \frac{1}{2}-x, \frac{1}{2}; \quad \frac{1}{2}+x, \frac{1}{2}+x, \frac{1}{2}.$

Ferrari gives $x = 0{\cdot}35$, and this accords quite well with the intensity measurements from this photograph.

Heating experiments. (1) Pure dioxide was heated at 150° in a continuously evacuated chamber for 2 hours. This caused no observable change in structure, at least in so far as no change appeared in the X-ray photograph. It must be remembered, however, that the presence of another oxide would perhaps not be observable if it were present in a proportion of less than 5%; also that, even if no new constituent had been formed, the dioxide might possibly have lost a considerable number of its oxygen atoms without affecting the X-ray diffraction spectra. In order to settle this point, an extensive quantitative research on lead dioxide alone would be necessary.

(2) Pure dioxide was heated at 300° for 2 hours in a vacuum as above. The photograph (No. 10) indicates, on measurement, that decomposition had occurred into a mixture of red and yellow lead monoxide.

(3) Dioxide containing 15% of red monoxide, when heated in the same manner as (2), yielded a considerable amount of red lead; thus apparently the presence of monoxide is necessary for the formation of red lead. This is of considerable interest because the active material from the positive plate of a lead accumulator (consisting largely of dioxide) behaves similarly when heated to 300°. This suggests the existence of lead monoxide as free PbO in the positive active material, and this can be definitely established by

examination of the positive material directly by *X*-ray methods, the lines of red monoxide being detected in the photograph itself.

Summary.

1. Characteristic samples of the pure oxides of lead have been examined by the Debye–Scherrer *X*-ray powder method of analysis. The lattice constants and parameters are evaluated and a table is given, with references to all former work on the structure of these substances.

2. Attempts to prepare lead suboxide are described, but no definite compound was obtained.

3. Lead sesquioxide was prepared by two different methods, but was found to be amorphous in both cases.

4. Orange lead, apparently a modification of red lead, was found to have a structure identical with that of ordinary red lead.

5. A number of commercial samples of the oxides have been examined. Commercial monoxides are generally mixtures of the red and the yellow variety. Commercial red lead is usually contaminated with yellow lead monoxide, rarely with red monoxide.

6. The changes which take place when lead sesquioxide and lead dioxide are heated have been determined by *X*-ray photographs. The sesquioxide is converted into yellow monoxide when heated in air to 400°. The dioxide decomposes into a mixture of red monoxide and yellow monoxide when heated to 300° in a vacuum. Lead dioxide containing 15% of the red variety of the monoxide, when heated in the same manner, yielded a considerable amount of red lead.

In conclusion I must thank Professor W. L. Bragg in whose laboratory this work has been carried out, also Dr. A. J. Bradley for his valuable advice and general supervision, and Miss R. Boullen for her assistance in a number of the experiments.

THE UNIVERSITY, MANCHESTER. [*Received, November 27th,* 1931.]