145. *The Thermal Decomposition of Lead Dioxide in Air.*

By George Butler and J. L. Copp.

It has been shown that in the decomposition of lead dioxide two oxides, α-PbO_x and β-PbO_x, are formed. The composition of α-PbO_x is close to Pb_7O_{11} and that of β-PbO_x close to Pb_2O_3. The crystal structures of these two oxides are very similar and it is suggested that this is possibly why many earlier workers found only one intermediate oxide.

An extensive literature on the decomposition of lead dioxide and the oxidation of lead monoxide provides definite evidence for the existence of further oxides with structures of the same intermediate type as that of red lead, but fails to define unambiguously their number and composition. Early work [1] indicates that an intermediate oxide, Pb_2O_3, is formed on decomposition of lead dioxide. Moles and Vitoria,[2] Renker,[3] and Baroni [4] assert that this is the only intermediate oxide formed in the composition range PbO_2—$PbO_{1.33}$. Renker considers that the structure of this oxide persists over a range of composition $PbO_{1.50}$—$PbO_{1.34}$, whereas Baroni assigns to a similar oxide a range extending from $PbO_{1.50}$ to $PbO_{1.66}$.

Eberius and Le Blanc [5] conclude that a black modification of red lead, with a composition range $PbO_{1.14}$—$PbO_{1.66}$, is formed on oxidation of lead monoxide, and that an oxide with the same structure, with a composition range $PbO_{1.66}$—$PbO_{1.33}$, is formed by decomposition of lead dioxide. Fischer and Ploetze [6] and Clark and Rowan [7] refer to an intermediate oxide Pb_5O_8. The latter workers also identified a further intermediate structure, PbO_x, in the products of oxidation of lead monoxide. Holtermann and Laffitte [8] have identified an intermediate oxide, formed at high pressures from lead dioxide, as Pb_7O_{11}.

The significance of these conflicting reports has been reduced considerably by the recent work of Byström [9] and of Katz.[10] Byström considers that two intermediate oxides,

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[1] (*a*) Debray, *Compt. rend.*, 1878, **86**, 813; (*b*) Carnelley and Walker, *J.*, 1888, **53**, 59; (*c*) Milbauer, *Chem. Ztg.*, 1909—1914.

[2] Moles and Vitoria, *Anales Fís. Quím.*, 1929, **27**, 52.

[3] Renker, *Bull. Soc. chim. France*, 1936, **3**, 981.

[4] Baroni, *Gazzetta*, 1938, **68**, 387.

[5] Eberius and Le Blanc, *Z. phys. Chem.*, 1932, **160**, *A*, 129.

[6] Fischer and Ploetze, *Z. anorg. Chem.*, 1912, **75**, 10.

[7] Clark and Rowan, *J. Amer. Chem. Soc.*, 1941, **63**, 1305.

[8] (*a*) Holtermann and Laffitte, *Compt. rend.*, 1937, **204**, 1813; (*b*) Holtermann, *Bull. Soc. chim. France*, 1938, **5**, 961; (*c*) *idem*, *Ann. Chim.*, 1940, **14**, 121.

[9] Byström, *Arkiv Kemi, Mineralog. Geol.*, 1945, **20**, *A*, No. 11.

[10] Katz, Thesis, Paris, 1949.

α-PbO_x $(1{\cdot}67 \geqslant x \geqslant 1{\cdot}50)$ and β-PbO_x $(1{\cdot}51 \geqslant x \geqslant 1{\cdot}47)$ exist in the composition range PbO_2—$PbO_{1{\cdot}33}$. Katz reports that a continuous series of solid solutions is formed between the oxides Pb_7O_{11} and Pb_3O_4, and that the solution of composition Pb_2O_3 exhibits the greatest order.

We have attempted to define the number of intermediate lead oxide structures formed on decomposition of lead dioxide, their ranges of composition, and crystal structures. To this end, *X*-ray and chemical analysis have been applied systematically to the products formed on progressive decomposition of lead dioxide in air, (1) at a series of constant temperatures, and (2) at steadily increasing temperatures, *i.e.*, under the conditions of differential thermal analysis.

EXPERIMENTAL

Materials.—Two preparations of lead dioxide were used in these decomposition experiments. The first was a coarse granular material of extreme hardness, prepared electrolytically from lead nitrate by Hamer's method.[11] The product was washed with water, dried at 120°, and stored over phosphoric oxide until required. It contained 84·0% of quadrivalent lead (determined iodometrically) (Calc. for PbO_2 : 86·62%) and was the subject of only a few experiments.

The second preparation used in all later work was a commercial product of A.R. quality; as its content of quadrivalent lead (84·4%) was not changed by successive treatments with nitric acid, it was free from traces of lower lead oxides, and was very pure. This conclusion was confirmed by determining its content of total lead (Found, by means of lead molybdate : Pb, 86·13 ± 0·25%) and by heating a sample of the oxide to constant weight at 600° (Found : PbO, 93·20 ± 0·02. Calc. : 93·31%).

Chemical Analysis.—It has been assumed in all previous work that a determination of the percentage of quadrivalent lead (*P*) in a lead oxide system is sufficient to establish its overall formula PbO_x, where $x = 207{\cdot}21(P + 100)/(207{\cdot}21 \times 100 - 16P)$. We have accepted this convention, and determined *P* by a modification of Bunsen's method described by Eberius and Le Blanc;[12] a known weight of a lead oxide is dissolved and reduced in an excess of hot concentrated hydrochloric acid. The chlorine produced is carried by a stream of carbon dioxide to absorption bulbs filled with potassium iodide solution, the iodine liberated being titrated with standard sodium thiosulphate.

Carefully calibrated volumetric apparatus and weights were used throughout and only reagents of A.R. quality were employed. At first, low and erratic results were obtained by this method, but this was traced to a volatile impurity in the A.R. hydrochloric acid, and was easily eliminated by using constant-boiling acid. The absolute errors inherent in the method were shown to be less than 0·5% by analysing a standard solution of potassium permanganate instead of the lead oxide. Thus we cannot agree with Mrgudich and Clark's statement[13] that the method gives results that are 5% too low.

The O : Pb ratio *x* can be calculated graphically directly from the titre, expressed as ml. of N-thiosulphate per g. of oxide (*V*), from the formula $x - 1 = 223{\cdot}21V/(2000 - 16V)$. A typical set of data from a decomposition experiment is given in Table 1.

TABLE 1. *Analyses of the decomposition products of A.R. lead dioxide at* 343° ± 2°.

Heating time (hr.)	Wt. of oxide taken (g.)	Ml. of N-$Na_2S_2O_3$ per g.	*x*	Heating time (hr.)	Wt. of oxide taken (g.)	Ml. of N-$Na_2S_2O_3$ per g.	*x*	Heating time (hr.)	Wt. of oxide taken (g.)	Ml. of N-$Na_2S_2O_3$ per g.	*x*
0	—	8·152	1·973	22·4	0·1122	6·252	1·734	200·2	0·1490	4·901	1·569
2·1	0·1334	7·812	1·930		0·1328	6·277	1·737	455·2	0·1226	4·914	1·570
	0·1770	7·815	1·930	31·5	0·1254	5·720	1·669		0·1377	4·912	1·570
4·7	0·1370	7·557	1·897		0·1049	5·745	1·672	787·0	0·1611	4·888	1·567
	0·2211	7·557	1·897	50·0	0·0924	5·060	1·586		0·1645	4·884	1·566
8·9	0·0997	7·175	1·850	102·1	0·1303	8·897	1·568	2232	0·2935	4·868	1·565
	0·1263	7·196	1·852		0·2350	4·915	1·570		0·2475	4·867	1·565

X-*Ray Analysis.*—Specimens for *X*-ray analysis were prepared by coating the surface of a glass fibre with a paste of a lead oxide in " Durofix " glue to give a specimen less than 0·5 mm. in diameter. These were exposed for 30 min. in a 9-cm. camera of the back-reflection type to

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[11] Hamer, *J. Amer. Chem. Soc.*, 1935, **57**, 339.

[12] Eberius and Le Blanc, *Z. anal. Chem.*, 1932, **89**, 81.

[13] Mrgudich and Clark, *Ind. Eng. Chem. Anal.*, 1937, **9**, 256.

filtered Co-$K\alpha$ radiation generated at 50 kv and 20 mA. The wavelengths of the incident radiation, which enters the camera through the centre of the film, were taken[14] as $\alpha_1 = 1{\cdot}78890$ Å, $\alpha_2 = 1{\cdot}79279$ Å, $\alpha = 1{\cdot}7902$ Å. The positions of the diffraction lines on the exposed film were measured with a simple scanning instrument designed by Gibson,[15] and the lattice parameters derived therefrom were extrapolated to a Bragg angle of 90° by Nelson and Riley's method.[16]

For lead dioxide a good resolution of the $K\alpha_1$–$K\alpha_2$ doublets was achieved at high Bragg angles, and here the precision of the parameter determinations is probably better than $\pm 0{\cdot}001$ Å. Oxides with an oxygen content lower than about $PbO_{1{\cdot}8}$ gave more diffuse diffraction lines in the high-angle region and in consequence the precision of parameter determinations is reduced to about 0·005 Å.

Differential Thermal Analysis.—We have applied the method of differential thermometry to detect the successive phase changes that occur when lead dioxide is slowly heated from room temperature to 600°, at which temperature red lead is the stable phase.

When the temperature of its surroundings T_e is increased at a constant rate, the temperature T_s of an inert material will also increase steadily. The temperature difference $(T_e - T_s)$ will vary regularly as T_e increases and will be determined by the dimensions and thermal constants of the apparatus. If the material is not inert, then at the onset of, say, an endothermic chemical or physical change in the system the rate of increase of T_s will diminish owing to absorption of heat by the material. When the reaction has progressed to a certain stage the rate of increase of T_s will rise until the original value is regained. Thus the plot of $(T_e - T_s)$ against T_e will show a peak for every endothermic reaction that occurs in the system. By similar reasoning it will be seen that exothermic reactions will give rise to minima in the plot.

This principle was applied as follows. Three silica test-tubes, two containing 2 g. of lead dioxide and one containing 2 g. of alumina (inert in the range 0—600°), were placed in holes drilled symmetrically about the axis of a small cylindrical block furnace (2″ × 2″). The furnace heater was connected to a variable transformer which was activated by a motor geared to change the output voltage from 0 to 270 v in 10 hr. The temperature of the furnace then increased linearly from 20° to about 600° in 10 hr. Throughout the heating chromel–alumel thermocouples (calibrated at the ice-point, the freezing points of tin, lead, and zinc, and at the inversion point of potassium sulphate) were used to measure the temperatures of the inert reference substance and of a sample of lead dioxide, and the difference between these two temperatures. At convenient intervals small samples of the reaction products were withdrawn from the second tube containing lead oxides, and retained for analysis.

Isothermal Decomposition.—Six cylindrical air furnaces (6″ × 1″) were constructed from lengths of brass tubing. The furnace heaters, made by winding each tube with a different length of insulated 30-gauge Nichrome wire, were connected in a series–parallel network and operated from an energy regulator. In this way a set of six different temperatures could be selected by pre-setting the energy regulator and individually controlled to within ±2° of a mean value. Quartz test-tubes, containing about 5 g. of lead dioxide, were placed one in each furnace and heated isothermally for several weeks between 150° and 450°. The products were sampled at intervals by plunging a glass tube of 0·3-mm. diameter in the oxide, and removing a representative plug of the material. These samples were sealed in small test-tubes and retained for analysis. The mean temperature at which each sample decomposed was determined by means of a calibrated chromel–alumel thermocouple. Fluctuations in these temperatures were shown to be less than ±2° by taking frequent readings of a mercury-in-glass thermometer placed with its bulb just above the oxide surface.

Results.

"AnalaR" Lead Dioxide.—(a) *Differential thermometry.* The results of a typical experiment on differential thermal analysis of "AnalaR" lead dioxide are shown in Curve 1, Fig. 1. The ordinate represents the difference between the temperatures of the inert alumina and the reacting lead oxide at any instant; the abscissa represents the temperature of the alumina at the same instant. The three well-defined peaks appearing in this curve indicate that three successive endothermic transitions occur as the temperature of lead dioxide is increased from 20° to above 600° in 10 hr. On repeating the experiment at different rates of heating the

[14] See Bragg, *J. Sci. Instr.*, 1947, **24**, 27.

[15] Gibson, *ibid.*, 1946, **23**, 159.

[16] Nelson and Riley, *Proc. Phys. Soc.*, 1945, **57**, 160.

positions of the maxima and minima on the abscissa were reproduced to within a few degrees, but no better resolution of the three peaks was achieved. In view of the narrow temperature range over which these three transitions occur, this is perhaps not surprising.

The results of a further experiment, which was supplemented by chemical and *X*-ray analysis of the reaction products, are shown in Fig. 2. As the first peak develops, the composition of the lead oxide system changes from $PbO_{1\cdot95}$ to $PbO_{1\cdot6}$, and the characteristic pattern of diffraction lines from lead dioxide is progressively replaced by those characteristic of a new structure. The first peak is undoubtedly due to the conversion of lead dioxide into an intermediate oxide, α-PbO_x, where x is about 1·6. This conclusion was confirmed by preparing, by isothermal decomposition, an oxide of composition $PbO_{1\cdot568}$ and subjecting this material to differential thermal analysis. The results of this experiment are shown in Curve 2, Fig. 1. Only the last two transitions appear.

FIG. 1. *Differential thermometry curves for the decomposition of* (1) *lead dioxide and* (2) α-PbO_x.

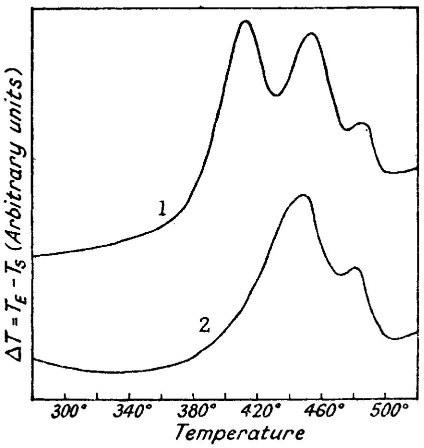
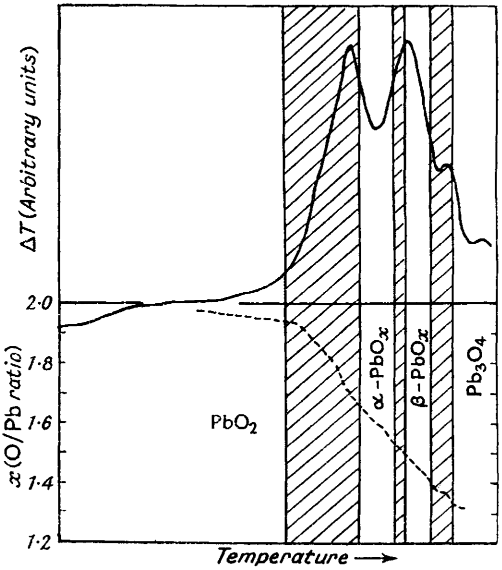


FIG. 2. *Relation between temperature differential and composition of lead oxide.* (*Shaded areas denote regions with two solid phases.*)



The third peak, which develops as the composition of the system changes from about $PbO_{1\cdot4}$ to $PbO_{1\cdot33}$, is associated with the production of red lead from a second intermediate structure.

The origin of the second peak in Curve 1, Fig. 1, is less clear. This peak develops over the composition range from about $PbO_{1\cdot6}$ to about $PbO_{1\cdot4}$, and can be attributed to the formation of a second intermediate oxide β-PbO_x. Its *X*-ray diffraction pattern is, however, so similar to that of α-PbO_x that mixtures of the two structures are difficult to distinguish (see below).

It is probable therefore that the three transitions revealed by differential thermal analysis of lead dioxide are associated with the formation of three intermediate oxides by the successive reactions

$$PbO_2 \longrightarrow \alpha\text{-}PbO_x \text{ where } x \simeq 1\cdot6$$

$$\alpha\text{-}PbO_x \longrightarrow \beta\text{-}PbO_x$$

and

$$\beta\text{-}PbO_x \longrightarrow PbO_{1\cdot33} \text{ where } x \simeq 1\cdot5$$

(b) *Isothermal decomposition.* Those features of our results on the isothermal decomposition of lead dioxide which are relevant to the present discussion are presented in Table 2. This shows how the overall composition of the product PbO_x changes with the heating time at various constant temperatures. The results can be amplified under three headings.

(1) *Decomposition temperatures below* 293° (Fig. 3). At 150° slight decomposition of $PbO_{1\cdot98}$ takes place to an oxide with $x = 1\cdot964 \pm 0\cdot001$ (mean of 4 analyses). (The limits given for x are standard deviations.) At 200° and at 270° the final products have $x = 1\cdot965 \pm 0\cdot002$ and $1\cdot952 \pm 0\cdot003$, respectively. These products are quite stable on prolonged heating (several weeks), and are shown by *X*-ray analysis to contain only lead dioxide.

TABLE 2. *Influence of temperature on the composition of lead oxides.**

	x in products after heating for t hours :				x in products after heating for t hours :		
Temp.	$t = 100$	$t = 1000$	$t = 2200$	Temp.	$t = 100$	$t = 1000$	$t = 2200$
200°	1·965	1·965	—	340°	1·568	1·568	—
270	1·952	1·952	—	343	1·568	1·568	1·565
293	1·92	1·74	—	359	1·560	1·540	—
311	1·79	1·565	—	374	1·52	1·38	1·366
327	1·65	1·570	1·570	384	1·42	1·36	—

* The values of x were interpolated from graphs of x against t.

(2) *Decomposition temperatures between* 293° *and* 359°. Extensive decomposition of lead dioxide sets in at all temperatures above 293°, and between 293° and 359° the composition of the products tends to a limiting value as is shown in Fig. 4. The average value of x for this stable oxide (based on 26 values obtained at temperatures from 311° to 343°) is found to be $1{\cdot}568_5$ with a standard deviation of $0{\cdot}002_5$. This is in excellent agreement with the value of x for Pb_7O_{11}, *i.e.*, 1·571, and is much less than its value for Pb_5O_8. X-Ray analysis of the products formed from lead dioxide in this temperature range and represented in Fig. 4 showed the presence of a single phase α-PbO_x. In the initial products of decomposition of lead dioxide, diffraction lines, characteristic of this oxide, first became visible in a system $PbO_{1\cdot935}$. If it be assumed that 5% of this phase is required to give visible X-ray diffraction lines, then the lower limit of composition for the lead dioxide structure appears to be $PbO_{1\cdot95}$.

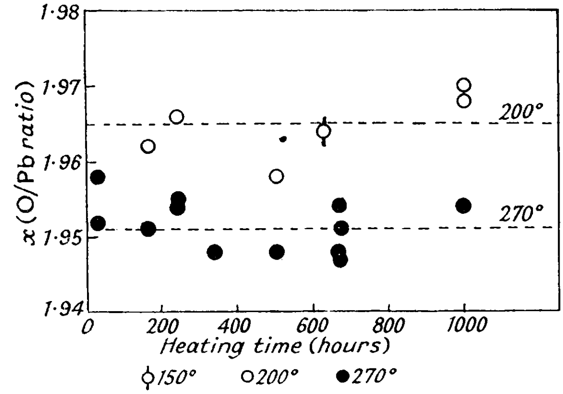


FIG. 3. *Composition of lead dioxide decomposition products at temperatures below* 293°.

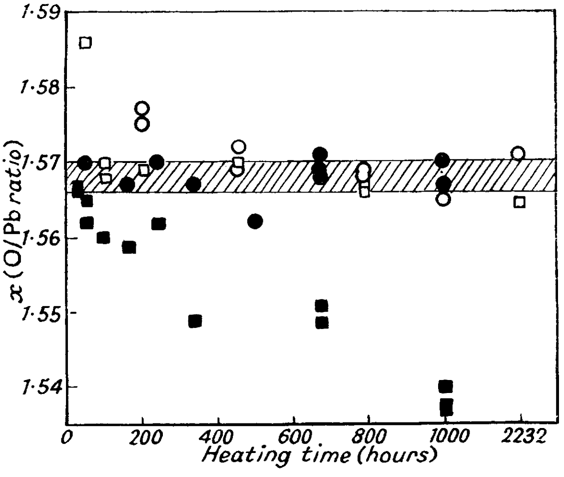


FIG. 4. *Composition of lead dioxide decomposition products at temperatures between* 293° *and* 359°.

As the composition of the products passes from $PbO_{1\cdot935}$ to $PbO_{1\cdot636}$ the diffraction lines of the lead dioxide structure decrease in intensity as the lines of the new phase α-PbO_x become more intense. The system $PbO_{1\cdot636}$ still exhibits very faint lines from the lead dioxide structure; if it be assumed that 5% of lead dioxide is still present in this system, then the upper limit of composition for $\alpha\text{-PbO}_x$ is $\text{PbO}_{1\cdot62}$. The formation of $\alpha\text{-PbO}_x$ from lead dioxide is clearly responsible for the first of the three successive transitions observed in the experiments on differential thermal analysis.

(3) *Decomposition temperatures above* 359° (Fig. 5). The oxide $\alpha\text{-PbO}_x$ is unstable at 359° but even after 1000 hours' heating at this temperature the composition of the product is only $\text{PbO}_{1\cdot538}$ (Fig. 4). At 374° and 384° more extensive decomposition occurs. No arrests in the composition–time curves were noted but the colour of the products changed progressively from black ($\text{PbO}_{1\cdot55}$) through maroon to red ($\text{PbO}_{1\cdot34}$).

Since the second and the third transition shown in Figs. 1 and 2 occur within this composition range, their origins can only be inferred from an interpretation of the *X*-ray diffraction patterns obtained for these coloured systems.

X-*Ray Analysis of Coloured Lead Oxide Systems between* $\text{PbO}_{1\cdot57}$ *and* $\text{PbO}_{1\cdot33}$.—The following qualitative observations are based on a close examination of the *X*-ray diffraction patterns obtained for a large number of these coloured systems. (1) On progressive decomposition of $\alpha\text{-PbO}_x$ no major changes in the *X*-ray diagrams are observed until lines characteristic of red lead appear in a system $\text{PbO}_{1\cdot41}$. (2) The following minor changes which set in at a composition of about $\text{PbO}_{1\cdot50}$ were noted : (*a*) Lines present at high Bragg angles in the *X*-ray diagram of PbO vanish at about $\text{PbO}_{1\cdot50}$; (*b*) a slight shift in line position towards lower angles is observed which indicates an expansion of the unit cell at about $\text{PbO}_{1\cdot50}$ (Table 2); (*c*) the relative intensities of certain diffraction lines change at about $\text{PbO}_{1\cdot50}$. These minor changes occur as the second well-defined transition in Figs. 1 and 2 develops. They suggest that the origin of this transition is the conversion of $\alpha\text{-PbO}_x$ into a further intermediate oxide $\beta\text{-PbO}_x$. These two structures correspond to an almost identical disposition of lead atoms in their respective unit cells. It is therefore difficult to fix an upper limit to the composition range of $\beta\text{-PbO}_x$, the difficulty being further increased by the diffuseness of the diffraction lines. The conversion of $\beta\text{-PbO}_x$ (where x is close to 1·50) into red lead is responsible for the third and last transition recorded in Figs. 1 and 2. Diffraction lines from the red lead structure first appear in an *X*-ray photograph of $\text{PbO}_{1\cdot41}$, so that at this composition the lower limit of the composition range of $\beta\text{-PbO}_x$ has been reached.

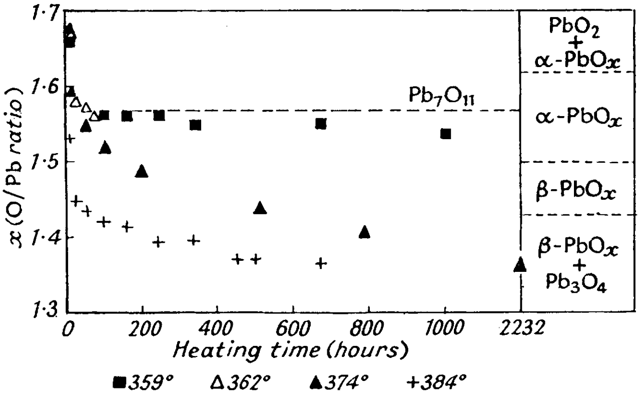


FIG. 5. *Composition of lead dioxide decomposition products at temperatures between* 359° *and* 384°.

Dimensions of the Unit Cells of Lead Dioxide, $\alpha\text{-PbO}_x$, *and* $\beta\text{-PbO}_x$.—The dimensions of the tetragonal unit cell of lead dioxide have been calculated from accurate measurements of the relevant line positions in *X*-ray photographs of systems containing various amounts of its decomposition product, $\alpha\text{-PbO}_x$. With the exception of certain weak lines, the diffraction patterns arising from the intermediate oxides were satisfactorily indexed—$\alpha\text{-PbO}_x$ as a body-centred tetragonal structure, and $\beta\text{-PbO}_x$ as a body-centred cubic structure. The unit cell dimensions of these three oxides are given in Table 3.

In systems where x lies between 1·961 and 1·801, the values of the parameters of the lead dioxide unit cell do not vary by more than 1 part in 5000 (the experimental accuracy) from the mean values $a_0 = 4\cdot957_6$, $c_0 = 3\cdot387_5$, $c/a = 0\cdot6833$. These results support the argument that the lead dioxide structure persists over a very narrow range of compositions. The diffraction lines arising from the lower oxide are more diffuse than the lead dioxide lines and this limits the accuracy of their parameters to less than 1 part in 1000. The diffuseness of these lines is possibly due to comminution of the individual granules in the process of decomposition.

TABLE 3.

x	Phases present	Phase indexed	a_0	c_0	c/a
1·973	PbO_2	PbO_2	$4{\cdot}953_2$	$3{\cdot}386_0$	0·6836
1·961	,,		$4{\cdot}957_1$	$3{\cdot}386_8$	0·6832
1·954	,,		$4{\cdot}957_8$	$3{\cdot}387_5$	0·6833
1·940	,,		$4{\cdot}958_7$	$3{\cdot}388_0$	0·6832
1·935	,, + α-PbO_x		$4{\cdot}957_4$	$3{\cdot}387_4$	0·6833
1·879	,, + α-PbO_x		$4{\cdot}957_5$	$3{\cdot}387_4$	0·6833
1·860	,, + α-PbO_x		$4{\cdot}956_4$	$3{\cdot}386_5$	0·6833
1·801	,, + α-PbO_x		$4{\cdot}958_3$	$3{\cdot}389_0$	0·6835
1·650	,, + α-PbO_x		$4{\cdot}95_7$	$3{\cdot}38_4$	$0{\cdot}682_7$
1·801	PbO_2 + α-PbO_x	α-PbO_x	$5{\cdot}41_8$	$5{\cdot}43_8$	1·004
1·650	,, + α-PbO_x		$5{\cdot}41_6$	$5{\cdot}49_1$	1·014
1·572	α-PbO_x		$5{\cdot}41_6$	$5{\cdot}49_9$	1·015
1·546	α-PbO_x		$5{\cdot}41_5$	$5{\cdot}49_9$	1·016
1·437	β-PbO_x	β-PbO_x	5·491	—	1·000
1·406	β-PbO_x + Pb_3O_4		5·479	—	1·000

Electrolytic Lead Dioxide.—For purposes of comparison the decomposition of an electrolytic preparation of lead dioxide (see p. 726) was carried out. At 150° decomposition takes place to an oxide with $x = 1{\cdot}940 \pm 0{\cdot}001$, and at 250° to an oxide with $x = 1{\cdot}940 \pm 0{\cdot}003$. At 293°, 327°, 343°, and 374° extensive decomposition to a lower oxide is evident.

Distinct heterogeneity was observed when products with an oxygen content less than $PbO_{1{\cdot}70}$ were examined under the microscope. These systems were composed of black grains dotted with tiny patches of a red oxide. If these products are compared with the corresponding systems derived from the A.R. lead dioxide, they should contain dark brown or black lead dioxide and black α-PbO_x. The presence of this red oxide, which can be either Pb_3O_4 or PbO, contributes to the large variability obtained on analysis of these systems, and shows that equilibrium conditions are unattainable with this preparation. This view is emphasised by the absence of any arrest in the composition–time curve obtained at 343° and by the composition $PbO_{1{\cdot}546}$ of the final product. This O/Pb ratio is significantly less than that of α-PbO_x (or $PbO_{1{\cdot}568}$), the stable product of earlier experiments at this temperature.

Although the grain size of this dioxide appeared to be quite large, the *X*-ray diffraction lines were broader than those for the A.R. preparation. This material is therefore either an agglomerate of small crystallites or a mixture of both large and small crystallites. Its physical heterogeneity may account for its non-uniform chemical reactivity.

DISCUSSION

The results of this investigation are consistent with the reaction scheme :

$$\text{Lead dioxide} \longrightarrow \alpha\text{-}PbO_x \longrightarrow \beta\text{-}PbO_x \longrightarrow \text{red lead.}$$

The present discussion is intended : (1) to determine the probable range of composition over which each oxide structure persists, and to summarise their structural parameters; (2) to re-examine the conflicting results of previous work on these systems within the framework of the above reaction scheme; (3) to assess the importance of any evidence that does not conform to this reaction scheme.

(1) *Lead Dioxide.*—(a) *Crystal structure.* The composition of the A.R. lead dioxide used can be represented by $PbO_{1{\cdot}98},0{\cdot}04H_2O$. *X*-Ray analysis confirms that it has a body-centred tetragonal structure. The unit cell dimensions of the unheated dioxide, and of the dioxide present in partly decomposed systems, are compared in Table 4 with values determined by Byström [9] and by Katz.[10]

TABLE 4. *Lattice parameters* (Å) *of lead dioxide*; (a) *unheated specimens*; (b) *partly decomposed systems.*

Authors	x	Pretreatment	a_0	c_0	c/a
Byström	1·988	(*a*)	4·952	3·385	0·6835
	1·96	(*b*)	4·960	3·390	0·6834
Katz	1·99	(*a*)	4·955	—.	0·6827
	1·82	(*b*)	4·958	—	0·6823
This work	1·98	(*a*)	4·953	3·386	0·6836
	1·96—1·78	(*b*)	4·958	3·388	0·6833

Byström's values, originally reported in *k*X units (personal communication), have been transformed into Å units. Our values are in excellent agreement with his, and all three sets of figures suggest that the parameters a_0 and c_0 both increase by about 0·1% when lead dioxide is heated and partly decomposed.

(b) *Decomposition temperature of lead dioxide in air.* Extensive decomposition of lead dioxide in air to a new oxide phase α-PbO_x occurred at temperatures above 293°. Since the dioxide structure was stable at temperatures up to at least 270°, its decomposition temperature in air must be 280° ± 10°. This value agrees well with those reported earlier, *viz.*, 290°,[17] 280°,[1b] 293° for an electrolytic oxide and 314° for a precipitated oxide,[18] and 280°.[2]

At temperatures below 293° a small but definite decrease in the O/Pb ratio of our sample of lead dioxide was recorded. At 150° the ratio changed from 1·973 to 1·964, at 200° to 1·965, at 270° to 1·952, and these values were unchanged by further prolonged heating. In these low-temperature reaction products no other phase than lead dioxide was detected, and high-angle α-doublet lines, which were not resolved in *X*-ray diffraction photographs of the original dioxide, were sharp and perfectly resolved. This suggests that the imperfect structure of the original sample was annealed (with slight loss of oxygen) by prolonged heating at temperatures below 280°. This observation may explain why Reinders and Hamburger [19] could not reproduce the small pressures of oxygen developed when lead dioxide was heated *in vacuo* at these low temperatures. In this connection, we could not measure the dissociation pressure of lead dioxide at 280°. Equilibrium was not achieved even after 400 hr., and after the oxygen evolved had been pumped off, the pressure–time in a second decomposition experiment always lay below the initial curve.

(c) *Composition limits of the lead dioxide structure.* All preparations of lead dioxide have had an O/Pb ratio approximating to but always less than 2, its upper limit, and lines due to second phase, α-PbO_x, were just visible in an *X*-ray diffraction photograph of a decomposition product, $PbO_{1\cdot935}$. This critical value of the O/Pb ratio must be less than that at which the lead dioxide structure becomes unstable, for the first traces of α-PbO_x to be formed will not be detected by *X*-ray methods. If we arbitrarily assume that at least a 5% conversion of the dioxide into α-PbO_x is necessary for the latter phase to be detected, then the lower limit of composition for lead dioxide is close to $PbO_{1\cdot95}$ (if it is assumed that α-PbO_x is Pb_7O_{11}). Further, the lattice parameters of lead dioxide increase slightly in the initial stages of decomposition and then remain constant as an increasing fraction of the dioxide is converted into α-PbO_x. These facts provide supporting evidence for the conclusion that the lead dioxide structure persists over a very narrow range of composition. Byström [9] and Clark and Rowan [7] are of the same opinion. Katz,[10] however, reported the lower limit of composition for lead dioxide to be$PbO_{1\cdot875}$, and Eberius and Le Blanc [12] state that this limit is only reached at $PbO_{1\cdot66}$.

Katz based his value on microphotometer measurements of the intensities of lines due to lead dioxide and α-PbO_x in *X*-ray diffraction photographs of two systems; (1) a system $PbO_{1\cdot82}$, produced by decomposition of lead dioxide, and (2) a synthetic mixture, $PbO_{1\cdot794}$, consisting of 90% by weight of $PbO_{1\cdot82}$ and 10% of α-PbO_x ($x = 1\cdot57$), prepared by complete decomposition of lead dioxide at an appropriate temperature. The ratios of the intensities of selected lines from each phase were calculated for the two systems and plotted against x. A linear extrapolation to zero ratio of line intensities (*i.e.*, no α-PbO_x present) then gave $PbO_{1\cdot875}$ as the lower limit of composition for the dioxide. This procedure is open to criticism, for it assumes that the α-PbO_x formed in the initial stages of reaction is as readily detected in *X*-ray analysis as the products of complete decomposition. Clearly, if the first traces of α-PbO_x arise preferentially from the smallest grains of lead dioxide, or if the phase change proceeds in each grain at an advancing phase boundary, or if sintering of completely decomposed grains occurs, then this assumption is not valid and the derived composition limit must be too low.

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[17] Hempel and Schubert, *Z. Electrochem.*, 1912, **18**, 729.

[18] Krustinsons, *ibid.*, 1934, **40**, 246; 1937, **43**, 65.

[19] Reinders and Hamburger, *Z. anorg. Chem.*, 1914, **89**, 71.

Eberius and Le Blanc's results cannot be reconciled with the view that the lead dioxide structure exists solely in the range of composition extending from PbO_2 down to about $PbO_{1\cdot95}$. It may be possible, however, for the structure to persist in metastable equilibrium at lower O/Pb ratios.

(2) α-PbO_x.—(a) *Composition.* Lead dioxide decomposed in air at temperatures between 293° and 359°, and was converted into a stable black oxide of characteristic structure. Chemical analysis showed that the final product of decomposition (at 293°, 311°, 327°, and 340°) had a constant O/Pb ratio of $1\cdot568_5$. This value is close to that for the empirical formula Pb_7O_{11} (1·571) which was first assigned to α-PbO_x by Holtermann and Laffitte.[8a]

Some authors consider that α-PbO_x is Pb_5O_8 ($x = 1\cdot600$); others support the formula Pb_2O_3. The evidence for these formulæ must be closely examined if a definite composition is to be assigned to α-PbO_x.

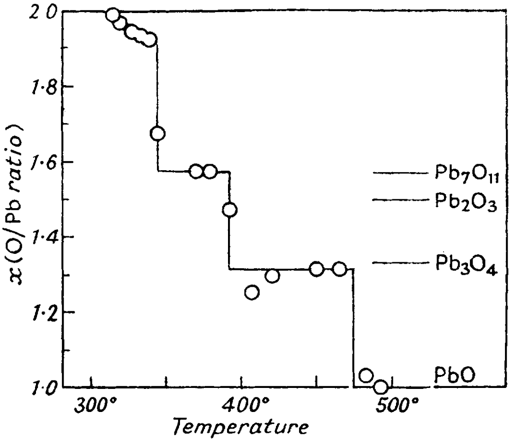

FIG. 6. *Decomposition of lead dioxide from data of Carnelley and Walker.*[1b]

Byström prepared single crystals of α-PbO_x which were shown to have a formula $PbO_{1\cdot586}$. This composition provides no clear proof that α-PbO_x is either Pb_5O_8 or Pb_7O_{11}. Clark and Rowan [7] call this intermediate oxide Pb_5O_8, but again there is little evidence in favour of this particular formula. Thus, when their results for isothermal decompsition of lead dioxide are plotted, the composition–time curves show no portion parallel to the time axis. This is not surprising since only short times of decomposition were used, and no experiments were reported for the temperature range 300—350°. Fischer and Ploetze [6] also favour Pb_5O_8, but again their heating times were too short to verify that an equilibrium composition had been reached. In our experiments equilibrium conditions were achieved and, at several temperatures, the final product had a constant composition, $PbO_{1\cdot568}$. The classical evidence of the composition of α-PbO_x is therefore consistent with this phase's being Pb_7O_{11} ($x = 1\cdot57$) but a final decision must await a complete determination of its structure.

A re-examination of the results quoted by Carnelley and Walker [1b] and by Baroni [4] in support of the formula Pb_2O_3, shows that the evidence suggests more convincingly a composition Pb_7O_{11} for α-PbO_x. This conclusion is immediately obvious from Fig. 6, which is a decomposition curve for lead dioxide, recalculated from the results of Carnelley and Walker by assuming that the final reaction product was PbO. Baroni's evidence for Pb_2O_3 is invalidated by an arithmetical error in calculating the formula of an intermediate oxide formed from PbO and containing 11·35% of active oxygen. Such a system corresponds to $PbO_{1\cdot66}$ and not to $PbO_{1\cdot50}$. Thus the " Pb_2O_3 " of Baroni is a higher oxide, and his results on the decomposition of lead dioxide suggest that it could be Pb_7O_{11} or Pb_5O_8.

(b) *Composition limits of the oxide* α-PbO_x. *X*-Ray diffraction analysis of the products of decomposition of A.R. lead dioxide showed that lines from α-PbO_x gradually replaced those from the lead dioxide structure. The system $PbO_{1\cdot636}$ contained very faint lines due to lead dioxide, *i.e.*, the upper limit of the O/Pb ratio for α-PbO_x is certainly less than

1·636. On the arbitrary assumption that this system still contains 5% of lead dioxide, the upper limit of this ratio for α-PbO_x is 1·62. This figure is lower than that given by Byström ($x = 1{\cdot}66 \pm 0{\cdot}02$) but equal to that calculated from Clark and Rowan's results. Because of the similarity between the structures of α-PbO_x and its first decomposition product β-PbO_x, the lower limit of composition of the former oxide cannot be clearly defined by *X*-ray methods. This limit is probably close to $PbO_{1\cdot5}$, *i.e.*, the value given by Byström. Thus the results of *X*-ray analysis show that α-PbO_x is probably restricted to the range from $PbO_{1\cdot62}$ to $PbO_{1\cdot5}$, and this range may indeed be narrower.

(c) *Decomposition temperature of* α-PbO_x *in air.* α-PbO_x is stable at 343° but loses oxygen on prolonged heating in air at 359°. The decomposition temperature of this oxide is therefore 351° ± 8°, a value that agrees with estimates given by Carnelley and Walker (360°), by Moles and Vitoria (366°), and by Byström (350°).

(3) β-PbO_x.—At temperatures above 359°, α-PbO_x is first converted into β-PbO_x and at 374° this is finally transformed into red lead. The arrangement of lead atoms in β-PbO_x differs but slightly from that in α-PbO_x, and the minor changes in *X*-ray diffraction patterns of systems from $PbO_{1\cdot55}$ to $PbO_{1\cdot41}$ may well have been overlooked by workers who report the existence of only one structure intermediate in composition between PbO_2 and Pb_3O_4. The lower limit of composition of β-PbO_x is close to $PbO_{1\cdot42}$, for this system contained traces of red lead. Byström reports the appearance of red lead in an oxide, $PbO_{1\cdot47}$. The upper limit to the range of β-PbO_x is probably close to $PbO_{1.50}$.

(4) *Crystal Structure of* α- *and* β-PbO_x.—The unit cells for the oxides intermediate in composition between lead and red lead reported in the literature vary from cubic to monoclinic. The fact that the cells of these oxides, as determined by Byström and Katz, may be treated as distorted cubes leads us to believe that a large part of the confusion that exists is due to the varying accuracy of the *X*-ray methods used.

The oxides prepared in this work gave diffraction lines that were quite diffuse. In order to index these lines on a unit cell involving only two parameters it was necessary to neglect several weak lines. In this way the following cells were derived: α-PbO_x, tetragonal, $a_0 = 5{\cdot}41_6$, $c_0 = 5{\cdot}49_6$; β-PbO_x, cubic, $a_0 = 5{\cdot}48_5$. These may be compared with the dimensions of the cubic cells found by Holtermann for Pb_7O_{11}, $a_0 = 5{\cdot}4$, and by Baroni for the oxide " Pb_2O_3 " (see p. 733), $a_0 = 5{\cdot}50$.

Clark and Rowan found the unit cell of Pb_5O_8 to be tetragonal with $a_0 = 5{\cdot}508$, $c_0 = 5{\cdot}460$. This result is inconsistent with our own since a_0/c_0 is greater than unity, whereas our value for α-PbO_x is less than unity. Since these figures must refer to the same oxide, we have re-examined Clark and Rowan's data and find that their *d* spacings may be indexed satisfactorily on the basis of a unit cell with $a_0 = 5{\cdot}441$, $c_0 = 5{\cdot}513$. This is in better agreement with our values.

The most accurate *X*-ray examination of the lead oxides has been carried out by Byström and by Katz. Byström found the following unit cells for the intermediate oxides: α-PbO_x, $1{\cdot}66 > x > 1{\cdot}50$, monoclinic, $a_0 = 3{\cdot}86$, $b_0 = 5{\cdot}41$, $c_0 = 3{\cdot}83$, $\beta = 88{\cdot}68°$; β-PbO_x, $1{\cdot}50 > x > 1{\cdot}47$, orthorhombic, $a_0 = 3{\cdot}89$, $b_0 = 5{\cdot}49$, $c_0 = 3{\cdot}82$. The relationship between these unit cells and those referred to previously may be easily seen by a simple transformation involving rotation about the *b* axis to give a new cell whose sides are the diagonals of the original cell, *viz.*, α-PbO_x, $a' = 5{\cdot}37$, $b' = 5{\cdot}41$, $c' = 5{\cdot}50$, $\beta' \simeq 90°$; β-PbO_x, $a' = 5{\cdot}45$, $b' = 4{\cdot}49$, $c' = 5{\cdot}45$, $\beta' \simeq 90°$.

Katz employed a technique for determining accurately the position of the low-angle lines on the *X*-ray diffraction patterns obtained with oxides prepared both by decomposition of lead dioxide and by oxidation of lead monoxide. He found that between $PbO_{1\cdot33}$ and $PbO_{1\cdot57}$ a large number of solid solutions exist with an orthorhombic, pseudo-cubic structure. These solid solutions can be distinguished only by their deviations from cubic symmetry. At the limits of composition these solutions are disordered but they can become ordered around the composition Pb_2O_3 provided that they are prepared by the slow oxidation of lower oxides. In the range of composition $1{\cdot}33 < x < 1{\cdot}55$ these oxides can be oxidised or reduced in a continuous manner. If, in the course of oxidation, the limit $x = 1{\cdot}55$ is exceeded, on subsequent reduction the composition jumps from $x = 1{\cdot}55$ to $x = 1{\cdot}41$.

It is probable that these treatments are an oversimplification. Thus, the weak lines neglected by us in indexing our diffraction patterns cannot be indexed on either the Katz or the Byström unit cell. To accommodate weak lines, Byström had occasion to double the a_0 axis and to treble the c_0 axis for α-PbO_x, and to double both these axes for β-PbO_x. Again, the lower limit of β-PbO_x in our experiments occurred at about $x = 1{\cdot}42$ and was certainly not as low as 1·33, the value reported by Katz.

The authors thank Prof. G. D. Preston for his interest and for providing facilities for *X*-ray analysis, and Prof. W. F. K. Wynne-Jones and Dr. H. R. Thirsk for helpful discussions. One of them (G. B.) is indebted to the Department of Scientific and Industrial Research for a grant.

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[*Received, September* 1*st*, 1954.]