TABLE II

TESTS ON THE CONVERSION OF MOLYBDENUM SULFIDE TO OXIDE

MoO_3 taken G.	MoO_3 found G.	Difference G.	MoO_3 taken G.	MoO_3 found G.	Difference G.
0.0799	0.0799	0.0000	0.1598	0.1598	0.0000
.0799	.0802	+ .0003	.1598	.1601	+ .0003
.0799	.0798	− .0001	.1598	.1597	− .0001
.0799	.0799	.0000	.1598	.1600	+ .0002
.0799	.0800	+ .0001	.2397	.2393	− .0004
.1598	.1594	− .0004	.2397	.2390	− .0007

In all cases where there was less than 0.1 g. of molybdenum trioxide, constant weight was attained in one hour of heating. For larger amounts as much as two hours was in some cases necessary, but never more. The ignited residues had a very slightly grayish cast. After the filters were once placed in the muffle they required no further attention until they were ready to be cooled and weighed.

An electrically-heated muffle fitted with an armored, high-temperature thermometer, or thermocouple, would of course be ideal; but the arrangement described above can be fitted up in a few minutes with materials to be found in any laboratory.

Summary

The maximum temperature at which molybdenum trioxide can be safely ignited without fear of appreciable loss by volatilization has been established as approximately 600°.

Conditions and apparatus for accurately and conveniently converting molybdenum trisulfide to trioxide have been described.

The use of oxidizing agents to aid the conversion of the sulfide to oxide is unnecessary.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 45]

THE CRYSTAL STRUCTURE OF TETRAGONAL LEAD MONOXIDE

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RECEIVED JULY 28, 1924 PUBLISHED NOVEMBER 5, 1924

Lead monoxide, PbO, may be prepared in two modifications, a yellow, rhombic form and a red, tetragonal form. Of these the former is the more stable[1,2] at higher, and the latter more stable at ordinary temperatures. It has been suggested[3] that the differences between these forms are due simply to a difference in state of subdivision; but this hypothesis

[1] Geuther, *Ann. Chem.*, **219**, 56 (1883).

[2] Ruer, *Z. anorg. Chem.*, **50**, 265 (1906).

[3] Glasstone, *J. Chem. Soc.*, **119**, 1689, 1914 (1921).

is not regarded[4] as tenable in the face of a difference in solubility determined both gravimetrically and electrometrically and in the face of crystallographic evidence. Moreover, the two forms have been found[5] to give quite different X-ray powder diagrams.

Apparently no goniometrical measurements of the red modification have been published, but the fact that it gives optically uni-axial, rectangular plates places it in the tetragonal[6] system. The present paper describes an X-ray investigation of the structure of the tetragonal modification.

Method of Experimentation

One part[1] of lead hydroxide was melted with five parts of potassium hydroxide and the melt allowed to cool slowly in a covered iron crucible. After treatment with water, some very thin red crystals remained. Examination between crossed Nicols showed these to be basal plates.

The angles of reflection of the molybdenum K radiation from the base (001) and from the planes (100) and (110) were measured photographically;[7]

TABLE I

SPECTRAL DATA FROM TETRAGONAL LEAD OXIDE

h k l	Line	Observed angle of reflection	$\frac{d}{n}$	Relative intensities[a]
(001)	Mo K α	4° 2′	($\frac{1}{1} \times 5.050$)	mw
	γ	7 6	$\frac{1}{2} \times 5.014$	w
	β	7 14	$\frac{1}{2} \times 5.013$	m
	α_1	8 7	$\frac{1}{2} \times 5.013$	s
	α_2	8 11	$\frac{1}{2} \times 5.004$	s
	α_1	12 14	$\frac{1}{3} \times 5.011$	vw
	α_2	12 19	$\frac{1}{3} \times 5.008$	vw
	γ	14 20	$\frac{1}{4} \times 5.006$	vw
	β	14 36	$\frac{1}{4} \times 5.007$	mw
	α_1	16 25	$\frac{1}{4} \times 5.009$	ms
	α_2	16 31	$\frac{1}{4} \times 5.010$	m
(100)	γ	8° 57′	$\frac{1}{2} \times 3.983$	w
	β	9 8	$\frac{1}{2} \times 3.976$	ms
	α	10 15	$\frac{1}{2} \times 3.990$	s
(110)	β^b	6° 26′	$\frac{1}{1} \times 2.816$	ms
	α	7 13	$\frac{1}{1} \times 2.826$	s
	γ	12 43	$\frac{1}{2} \times 2.815$	w
	β	12 56	$\frac{1}{2} \times 2.820$	m
	α	14 34	$\frac{1}{2} \times 2.823$	ms

[a] The abbreviations are: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak.

[b] The line γ slightly overlapped β.

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[4] Applebey and Reid, *J. Chem. Soc.*, **121,** 2129 (1922).

[5] Kohlschütter and Scherrer, *Helvetica Chim. Acta*, **7,** 337 (1924).

[6] Groth, "Chemische Krystallographie," Engelmann, Leipzig, **1906**, vol. 1, p. 77.

[7] The X-ray methods used have already been described; Dickinson, THIS JOURNAL, **44,** 276 (1922).

the reflections from the last two planes were obtained by transmission of the beam through a basal plate. The data from these photographs are given in Table I. A number of symmetrical and unsymmetrical Laue photographs were taken through (001). To secure proper coördination of all these photographs in the absence of good face-development, a symmetrical Laue photograph and reflections from (110) and (100) were made with the same crystal.

The Unit of Structure

Application of the equation $n\lambda = 2d \sin\theta$ to the data of Table I shows that $d_{001} = 5.01$ Å. or a multiple of this value. Prior to a structure determination the indices of (100) and (110) may be interchanged. If this is done, then $d_{100} = 2.82$ Å. or a multiple of this value. The smallest possible unit of structure thus has the dimensions 2.82 × 2.82 × 5.01; taking the density[8] as 9.27, the number of PbO in this unit is found to be 1.003. But if Laue photographic spots are assigned indices referred to the axes of this unit, the values of $n\lambda$ calculated for them using the equation $n\lambda = \dfrac{2d_{001}\sin\theta_{hkl}}{\sqrt{(h^2+k^2)\,c^2+l^2}}$ where $c = d_{001}/d_{100}$, are often found much lower than the shortest wave length, 0.23 Å., which could have been present in the spectrum (the peak voltage was about 53 kv.). This unit is therefore impossible. Any larger unit differing from this one only by having d_{001} a multiple of 5.01 Å. is impossible for the same reason. When, however, the directions of the axes are taken in accord with the indices of Table I, d_{100} becomes 3.99 Å. or a multiple of this value. The number of PbO in a unit 3.99 × 3.99 × 5.01 is two, and the Laue photographic data do not conflict with this unit. There is thus no evidence necessitating the assumption of a larger unit.

The Arrangement of the Atoms

On all the Laue photographs examined no plane having $h + k + l$ odd was found to give more than a weak reflection in the first order. Since the reflecting power of the lead atoms must be far greater than that of the oxygen atoms, the weakness of this type of reflection must arise from interference between the lead atoms themselves, rather than from interference between the lead and oxygen atoms. It can readily be shown that the only arrangement of two lead atoms in a unit such that the contribution of the lead atoms to first order reflections from planes having $h + k + l$ odd is zero is the body-centered arrangement; consequently, the lead atoms must have at least approximately this arrangement.

If the lead atoms have precisely the body-centered arrangement, the

[8] Ref. 4, p. 2132.

reflections of odd order from (001) must be due to the oxygen atoms alone. But reference to a tabulation[9] of the coördinates of possible positions[10] in the unit of structure shows that, if the lead atoms are given the non-variant body-centered arrangement, there is no way of placing the oxygen atoms with any tetragonal space-group symmetry in such a way as to give the odd orders from (001). Consequently the lead atoms must have an arrangement which involves one or more parameters and which is capable of approximating the body-centered arrangement when suitable values are given the parameters. There is only one such arrangement: $(0\ \frac{1}{2}\ u)$ $(\frac{1}{2}\ 0\ \bar{u})$, where[11] u is near 0.25. The oxygen atoms may then have any of the arrangements: (a), $(0\ 0\ u)$ $(0\ 0\ \bar{u})$; (b), $(0\ 0\ 0)$ $(\frac{1}{2}\ \frac{1}{2}\ 0)$; (c), $(0\ \frac{1}{2}\ v)$ $(\frac{1}{2}\ 0\ \bar{v})$.

Arrangement (a) is rendered improbable by the absence of the first-order reflection from (100) on the spectral photographs.

The values of the structure factor, S, for first-order reflections from arrangements (b) and (c) are given by

Arrangement (b)	$h + k$ even.	$S = 2(-1)^h \mathrm{Pb} \cos 2\pi l u + 2\,\mathrm{O}$.
	$h + k$ odd.	$S = 2\mathrm{Pb} \sin 2\pi l u$.
Arrangement (c)	$h + k$ even.	$S = 2\mathrm{Pb} \cos 2\pi l u + 2\,\mathrm{O} \cos 2\pi l v$.
	$h + k$ odd.	$S = 2\mathrm{Pb} \sin 2\pi l u + 2\,\mathrm{O} \sin 2\pi l v$.

Planes of the forms {241}, $d = 0.878$, and {041}, $d = 0.980$, were found to reflect more strongly than those of the forms {331}, $d = 0.924$, and {131}, $d = 1.223$. As all of these are planes having $h + k$ even and the same value of l, arrangement (c) gives them all the same structure-factor and is hence ruled out. The structure-factor for these planes for arrangement (a) is shown in Fig. 1 for values of u near 0.25. The above intensity relations evidently necessitate taking u slightly below 0.25. However, the value of u cannot be as low as 0.23 for {075}, $d = 0.496$, reflected considerably more strongly than {546}, $d = 0.500$. The value of u must, therefore, be close to 0.24. It will be noted that this conclusion is not dependent on any quantitative assumption as to the relative reflecting powers of atoms of lead and of oxygen.

In Table II are given representative data from one Laue photograph; in the last column of this table are given values of the structure-factor calculated for arrangement (a) placing u equal to 0.24 and placing the reflecting powers proportional to the atomic numbers. We have found no data in conflict with this arrangement.

[9] Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Washington, *Carnegie Inst. Pub.*, **318,** pp. 73–102.

[10] The assumption is made here that all of the lead atoms are in equivalent positions and likewise all of the oxygen atoms.

[11] The value u = 0.75 also satisfies the conditions but leads to the same possible structures.

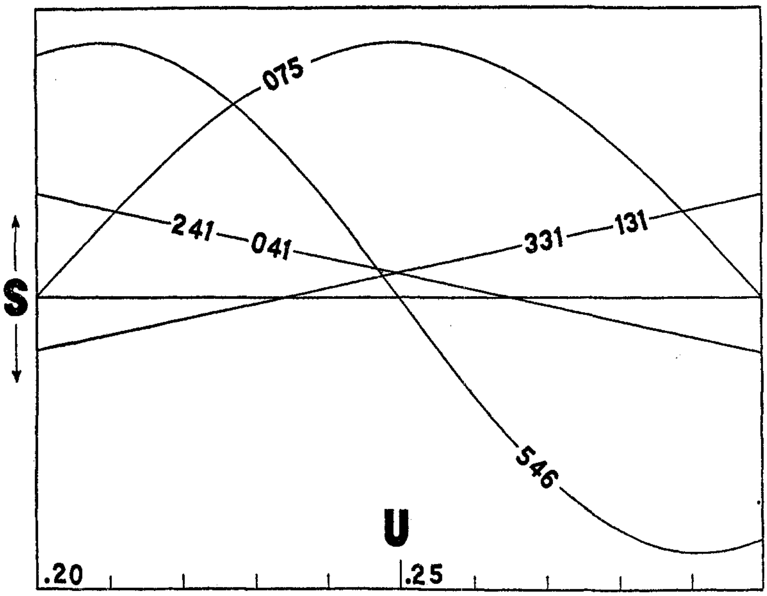

Fig. 1.—Values of the structure factor *S* plotted against *u;* the oxygen atoms have arrangement (*a*).

TABLE II

LAUE PHOTOGRAPHIC DATA; INCIDENT BEAM 18° FROM PERPENDICULAR TO (001)

Plane	Inter-planar distance	Wave length	Esti-mated in-tensity	*S* for u = 0.24	Plane	Inter-planar distance	Wave length	Esti-mated in-tensity	*S* for u = 0.24
$\bar{1}31$	1.222	0.34	faint	6	$\bar{1}54$	0.664	0.40	0.7	143
312	1.128	.33	8	179	$\bar{3}52$	.660	.29	1.0	179
$\bar{4}10$	0.968	.40	0	0	$3\bar{5}2$	.660	.36	1.1	179
$\bar{3}31$	.925	.41	0	6	$1\bar{6}1$	.651	.33	1.1	164
$2\bar{4}1$	.878	.37	0.1	26	$\bar{6}21$	.625	.38	0	26
413	.838	.36	3	161	525	.596	.37	0.4	156
$\bar{4}31$	.788	.38	2.5	164	$\bar{6}31$	.591	.30	.5	164
243	.787	.30	0.1	15	445	.577	.33	.05	67
$\bar{5}10$	.782	.34	2.5	148	$0\bar{7}1$	.567	.32	.5	164
$\bar{1}\bar{5}0$	.782	.36	2.7	148	355	.565	.33	.05	35
$\bar{5}\bar{1}0$	.782	.45	1.2	148	$\bar{7}11$	.561	.37	.00	6
$\bar{2}\bar{5}0$	.742	.39	0	0	605	.555	.34	.05	67
053	.720	.34	1.6	161	165	.550	.36	.2	156
$\bar{1}53$	.709	.39	0.1	47	$1\bar{7}2$	.550	.38	.3	179
$\bar{3}\bar{5}0$	.684	.39	1.2	148	536	.530	.37	.1	169
$\bar{5}31$	.678	.34	0	6	$2\bar{7}3$	.522	.41	.1	161
$5\bar{2}3$	.678	.30	1.0	161	$6\bar{3}5$	.512	.36	.1	156
434	.674	.32	0.1	41	546	.500	.31	faint	60
504	.674	.38	.1	41	075	.497	.30	0.1	156
514	.664	.33	1.0	143					

Discussion of the Structure

The structure obtained for lead oxide is shown in Fig. 2. This structure is derivable from any of the space-groups: V_d^3, C_{4h}^3, D_4^2, D_{4h}^7. In it the shortest distance between lead and oxygen atoms is 2.33 Å. The arrangement of layers of atoms parallel to (001) is shown in Fig. 3. The distance between the nearest lead atoms in layers A and B is 3.84 Å., while the distance between the nearest lead atoms of layers A and C is 3.71 Å.; the lead atoms are thus closer together when there is a layer of oxygen atoms between them than when there is not.

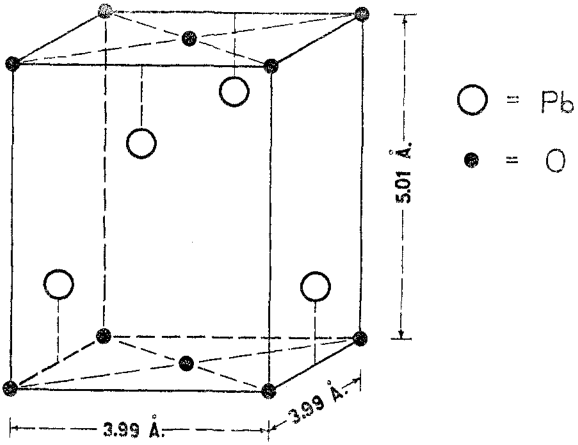

Fig. 2.—Arrangement of the atoms in tetragonal PbO.

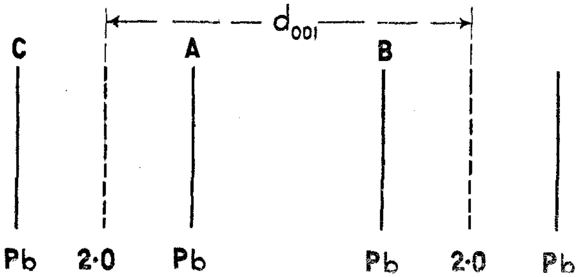

Fig. 3.—Arrangement of atom-planes parallel to (001) in tetragonal PbO.

Summary

The crystal structure of red lead monoxide, PbO, has been determined, using X-ray spectral photographs and Laue photographs. It is found that there are 2 PbO in a tetragonal unit of structure having $d_{100} = 3.99$

and d_{001} = 5.01 Å. The oxygen atoms are at (000) ($\frac{1}{2}$ $\frac{1}{2}$ 0), and the lead atoms at (0 $\frac{1}{2}$ u) ($\frac{1}{2}$ 0 $\bar{u}$) with u = 0.24.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

SCHIFF'S BASES FROM 3,5-DIBROMO-SALICYLALDEHYDE

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RECEIVED JANUARY 15, 1924 PUBLISHED NOVEMBER 5, 1924

An examination of the literature has shown that comparatively few derivatives of dibromo-salicylaldehyde[1] have been prepared, as compared with salicylaldehyde itself, and as the Schiff's bases from the latter compound have in a number of instances shown unusual phototropic and thermotropic properties, the study of aldehydes already under way in this Laboratory has been extended to this field.

Of the fourteen new compounds described in this paper, five appear to exist in two modifications, the properties of which are stated in the experimental section. Some of these may be transformed from one modification to the other by suitable choice of solvents and temperature. None of these Schiff's bases from dibromo-salicylaldehyde shows phototropic properties.

Hantzsch[2] in studying the relation of color to constitution showed that by the introduction of halogen atoms in the molecule of salicylaldehyde, the tendency of the compound to form the yellow quinoid derivative is strengthened. Monobromo- and dibromo-salicylaldehyde give colorless solutions in non-dissociating solvents, but in water they form yellow solutions. In alcohol the color is weak, but distinctly yellow. The salts are bright yellow, not only the sodium and potassium but also the ammonium salts. The ammonium salt is more stable than that of salicylaldehyde, but decomposes on heating. It may be recrystallized from alcohol or ether. Hantzsch also stated that two forms of a salt may be expected only when the tautomeric forms are of nearly equal strength or of equal weakness as to acidity. An example is salicylaldehyde; this aldehyde-phenol is colorless and its ammonium salts are also colorless; therefore it is a true phenol salt, $C_6H_4ONH_4.CHO$. But a slight change in constitution shifts the equilibrium, for the dibromo-salicylaldehyde forms only yellow salts.

In the case of anils prepared in the present study, the influence of the bromine atoms on this equilibrium is very apparent. While in the forma-

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[1] Werner, *Bull. soc. chim.*, 46, 277 (1886). Tummeley, *Ann.*, **251,** 174 (1889). Bradley, *Ber.*, **22,** 1135 (1889). Simonis and Wenzel, *Ber.*, **33,** 1964 (1900). Hantzsch, *Ber.*, **39,** 3080 (1906). Wentworth and Brady, *J. Chem. Soc.*, **117,** 1040 (1920).

[2] Hantzsch, *Ber.*, **34,** 882 (1901); *Ber.*, **39,** 3080 (1906); *Ber.*, **43,** 95 (1910).