342. *Lead Sub-oxide.*

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1. Accurate analyses of the gases evolved when lead oxalate is decomposed in a vacuum at low temperatures (about 300°), and *X*-ray analyses and approximate determinations of the electrical conductivity of the residue, suggest that the grey-black powder obtained by some investigators and reported to be lead sub-oxide is really an intimate mixture of lead and lead monoxide (red tetragonal form).

2. Analyses of the gases evolved on heating lead oxalate as above indicate that the reaction is represented by $3Pb(O{\cdot}OC)_2 \longrightarrow 2PbO + Pb + 4CO_2 + 2CO$.

Much conflicting evidence has been obtained with regard to the existence of lead sub-oxide, Pb_2O. Boussingault (*Ann. Chim. Phys.*, 1833, **54**, 264) and Pelouze (*ibid.*, 1841, **79**, 108) reported having obtained it by carefully heating lead oxalate in a retort from which air was excluded, at a temperature not exceeding 300°. They considered that the resulting fine black powder contained no lead, since mercury extracted none, either dry of under water. Winkleblech (*Annalen*, 1837, **21**, 21; *J. pr. Chem.*, 1837, **10**, 221) regarded this powder as a mixture of lead and lead oxide, but Tanatar (*Z. anorg. Chem.*, 1901, **27**, 305) supported Boussingault's claim; he considered that at higher temperatures the lead sub-oxide decomposes into lead and the monoxide, giving a greyish-green powder, and showed that this powder and the sub-oxide had different heats of solution. On the other hand, Aufenast and Terrey (J., 1926, 1546) found the heat of solution to be very near the value for litharge.

Brislee (J., 1908, **93**, 154) showed that there was a break in the time–reduction curve, obtained when lead monoxide is reduced with carbon monoxide, corresponding to the formation of lead sub-oxide. Denham (J., 1917, **111**, 29) prepared lead sub-oxide by a modification of Tanatar's method, heating lead oxalate in a vacuum below 375°, and confirmed Tanatar's description of its properties. From the *X*-ray spectrum of the supposed lead sub-oxide, van Arkel (*Rec. Trav. chim.*, 1925, **44**, 652) deduced that it is a mixture of lead and lead monoxide; Darbyshire (J., 1932, 211) supported this view, but Ferrari (*Gazzetta*, 1926, **56**, 630) disputed it.

The reaction involved is usually given as $2Pb(OOC)_2 \longrightarrow Pb_2O + CO + 3CO_2$, but an investigation on the kinetics of the thermal decomposition of lead oxalate made it necessary to examine this decomposition accurately.

Experimental.

Preparation and Analysis of Lead Oxalate.—To 2000 c.c. of N/5-lead nitrate solution were added 1600 c.c. of N/5-sodium oxalate solution with constant stirring; both solutions were nearly boiling and had been prepared from "AnalaR" reagents in boiled distilled water. After standing overnight, the precipitated lead oxalate was washed by decantation, and collected on a Buchner funnel; it was well washed again with 1 l. of boiled distilled water, and dried in a vacuum desiccator.

A second sample was similarly prepared except that the volumes of the reagents were interchanged. Both samples were analysed, the lead being estimated as sulphate, and the oxalate by means of standard potassium permanganate solution [Found: (i) Pb, 69·44; C_2O_4'', 29·68; (ii) Pb, 69·45; C_2O_4'', 29·68. Calc.: Pb, 70·1; C_2O_4'', 29·82%].

Three different experimental methods were used: (1) Analysis of the gases evolved when lead oxalate is decomposed by heat; (2) *X*-ray examination of the residue; (3) electrical conductivity of the residue.

(1) *Analysis of Evolved Gases.*—The accuracy of the above equation has been tested by making precise analyses of the gases evolved. The apparatus consisted of a Pyrex reaction tube connected to a McLeod gauge and a Toepler pump. An electric furnace was used to heat the tube, the temperature being measured by means of a thermocouple and potentiometer. The gas evolved was collected over mercury in a gas burette and analysed, the carbon dioxide being absorbed in potassium hydroxide and the carbon monoxide in ammoniacal cuprous chloride solution. The results were as follows, the pressure in the reaction vessel being kept at 0·01 mm. in each case:

Time of heating.	Temp.	CO_2, %.
3½ hrs. with continuous pumping	310°	67·4
3 hrs. with continuous pumping	319	67·6
2½ hrs., no pumping	450	73·4
2½ hrs. with continuous pumping	470	71·9

For the above experiments lead oxalate prepared by the first method was used, but oxalate prepared from excess sodium oxalate solution also gave a carbon dioxide content of approximately 66·6%.

Maumené (*Bull. Soc. chim.*, 1870, **13**, 194) considered that the initial reaction is represented by the equation $3Pb(OOC)_2 \longrightarrow 2PbO + Pb + 4CO_2 + 2CO$, since he obtained a ratio $CO_2 : CO = 2 : 1$. This ratio is considerably modified on further heating, the lead monoxide being reduced by carbon monoxide. If decomposition is performed at a higher temperature, and the gas allowed to remain in the apparatus instead of being pumped off rapidly, we should expect reduction to take place and the carbon dioxide content to be higher than 66·6%. If, however, the gas is pumped off very quickly, this reduction will be negligible, and the resulting gas should contain 66·6% of carbon dioxide.

The above results show that the equation $2Pb(OOC)_2 \longrightarrow 3CO_2 + CO + Pb_2O$, which requires 75% of carbon dioxide, cannot be correct. On the other hand, they support Maumené's views as to the course of the decomposition, the further reaction at higher temperatures, and the reaction if the gases evolved are allowed to remain in the apparatus.

(2) *X-Ray Analysis of Residues.*—The *X*-ray spectra of residues obtained at various temperatures have been photographed by Mr. G. D. Preston, M.A., of the National Physical Laboratory, through the courtesy of Professor C. H. Desch, F.R.S. The residues thus examined were obtained by heating lead oxalate in a vacuum (i) for 3½ hrs. at 310°; (ii) for 3 hrs. at 320°; (iii) for 2 hrs. at 375°; further, (iv) residue (i) was heated at 500° in a vacuum.

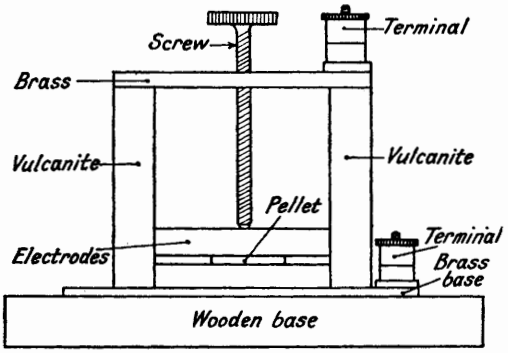
Each of the above residues appeared to be a mixture of lead monoxide (red tetragonal) and metallic lead. The spectra of (i) and (iv) are almost identical. With residues (ii) and (iii) the same spectra are obtained, but (ii) is much finer grained than (iii); both spectra closely resemble those of (i) and (iv).

Conclusions. The residue obtained in (i) and (ii) is the velvet-black powder described by various workers as lead sub-oxide. The above results suggest that this is really a mixture of lead and lead monoxide. The same spectra are obtained at higher temperatures, *e.g.*, (iii) and (iv); here the greyish-green powder described by Tanatar is obtained, which shows that the velvet-black and the greyish-green powder are both mixtures of lead and lead monoxide, and the evidence from (ii) and (iii) suggests that the effect of stronger heating is to coarsen the grain of the residue.

(3) *The Electrical Conductivity of the Residue.*—The composition of the residue must, according to the equation we have established, be either $Pb_2O + PbO$ or $2PbO + Pb$. The electrical conductivity of the latter mixture would be expected to be greater than that of the former owing to the presence of free lead; the conductivity of lead monoxide is known to be almost zero.

The conductivity of pellets of the residue was measured by using the apparatus shown in the figure. The pellet is held between the two thick brass discs by the pressure of the screw. To ensure good contact between the pellet and the metal, the brass discs are covered with

graphite. A potential up to 20 volts was applied, the current being measured with an ammeter. A variable resistance was included in the circuit.



Results. In the following table the thickness of the pellet is denoted by l, and the conductivity by k. The diameter of the pellets was 9 mm.

Potential, volts.	Resistance, ohms.	Current, amps.	l, mm.	$k \times 10^4$, mho/cm.
20	22	0·6	2	2·8
4	0	0·4	2	3·1
4	0	0·72	1	2·9

The above residues were obtained from lead oxalate prepared from excess of lead nitrate; similar values for k were obtained for the residue from oxalate prepared by the other method. No great accuracy is claimed for the value of k, but the marked conductivity indicates that the residue contains metallic lead. The value given for the conductivity of lead monoxide is $3{\cdot}86 \times 10^{-8}$ mho/cm., *i.e.*, about 10,000 times less than that of the residue. These results, like those of the *X*-ray examination, therefore show that the residue is Pb + 2PbO rather than PbO + Pb_2O.

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