CXCIX.—*The Existence of the Suboxides of Lead and Thallium.*

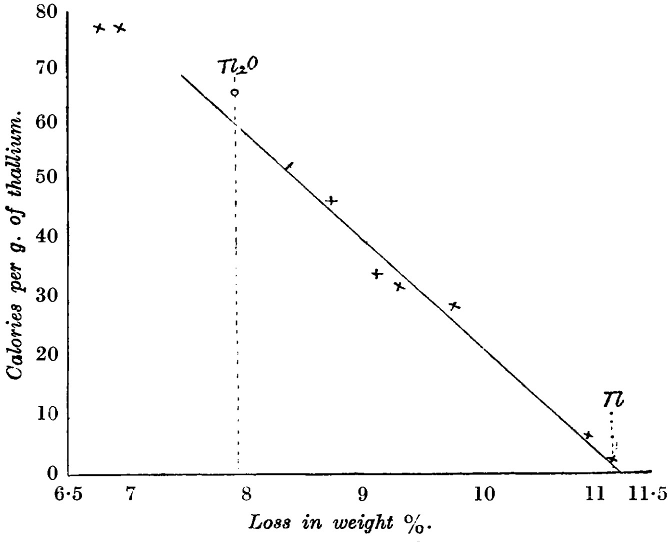
By FREDERICK AUFENAST and HENRY TERREY.

THE black substance obtained by heating lead oxalate has been interpreted as (1) a mixture of litharge and lead, or (2) lead suboxide. The work of Tanatar (*Z. anorg. Chem.*, 1901, **27**, 304) on its heat of reaction with acetic acid pointed to a chemical entity, since he obtained results which indicated a heat of decomposition of lead suboxide into lead and litharge, $Pb_2O \longrightarrow Pb + PbO -$ 5,450 cals. This view is supported by the work of Brislee (J., 1908, **93**, 154) and of Denham (J., 1917, **111**, 29; 1918, **113**, 249; 1919, **115**, 109). Evidence has also been given for the existence of subvalent lead ions by Denham (J., 1908, **93**, 41), Denham and Allmand (*ibid.*, p. 833), and Bell (*Trans. Faraday Soc.*, 1915, **11**, 74).

The similarity of thallium and lead and of many of their salts suggests the possible existence of a thallium suboxide (compare Crookes, *Proc. Roy. Soc.*, 1862, **12**, 150; Lorenz, *Z. anorg. Chem.*, 1896, **12**, 439).

Investigations were first carried out to determine whether breaks could be obtained in the reduction-velocity curves such as were found by Brislee (*loc. cit.*). Thallous oxide was reduced in a stream of hydrogen and the amount of reduction was measured at regular intervals. The results showed in some cases a slight break in the curve corresponding to a compound Tl_4O, but these breaks were not definite enough to be regarded as satisfactory evidence. Experiments were then made on the heat of solution of the products of varying composition obtained by reduction of thallous oxide, and the results are shown in Fig. 1, in which heats of solution per g. of thallium are plotted as ordinates and the extent to which the thallic oxide had lost weight on reduction as abscissæ. If a suboxide had been present, the heat of solution in 3*N*-sulphuric acid would have included a heat of decomposition of the suboxide and the graph would not have been a straight line. Within the limits of experimental error, no evidence was thus obtained for the existence of thallium suboxide. Attempts were also made to measure the oxidation velocity of metallic thallium, but they were abandoned when it was found that the finely-divided metal was never oxidised completely although the initial velocity was very great.

Fig. 1.



○ = *Thomsen's value for* Tl_2O.

Similar calorimetric experiments, in which the products of decomposition of lead oxalate were dissolved in acetic acid, gave results indicating that this supposed suboxide was a mixture of litharge and lead.

EXPERIMENTAL.

For the reduction velocity experiments, thallic oxide was precipitated from a thallic chloride solution by ammonia, washed, and heated to 200° in a current of oxygen to remove the last traces of water. As thallous oxide is very deliquescent, it was decided to measure the reduction by collecting the water evolved rather than by removing the substance and determining the loss in weight. A weighed amount of thallic oxide, spread in a thin layer in a porcelain boat, was gradually heated electrically to 150° in a stream of hydrogen. After a few hours, when scarcely any more water was given off, the temperature was raised to 185° ± 1° and the water produced was collected in calcium chloride tubes which were weighed hourly. The complete reduction to thallous oxide, which took about 30—40 hours, was thus spread over a few days. The product was at first black, changing to a metallic grey colour.

For the heat of solution experiments a known weight of thallic oxide was reduced in a stream of hydrogen to a known composition, and the product was transferred as quickly as possible to the calorimeter, which consisted of a 100 c.c. Dewar vessel fitted with a Beckmann thermometer and a small glass stirrer and containing 25 c.c. of 3*N*-sulphuric acid. The results of these experiments are as follows :

Expt.	Wt. Tl_2O_3 used.	Loss %.	Wt. used for solution.	Rise in temp.	Cals. evolved.	Cals. per g. Tl.
1	0·3926	6·78	0·3657	0·780°	26·86	77·29
2	0·4081	6·96	0·3797	0·809	27·86	77·21
3	0·3669	8·75	0·3242	0·404	13·91	47·36
4	0·4781	8·39	0·4257	0·693	21·44	53·30
5	0·4115	9·14	0·3655	0·400	12·38	34·73
6	0·3494	10·96	0·3029	0·067	2·07	6·81
7	0·3953	11·15	0·3394	0·025	0·77	2·28
8	0·3836	9·33	0·3151	0·325	10·06	32·66
9	0·3693	9·80	0·2848	0·266	8·20	29·51

For Expts. 1—3 and 4—9, the water-equivalent of the calorimeter and its contents was 34·43 g. and 30·94 g. respectively.

These results are shown graphically in Fig. 1, where the figures of column 3 are the abscissæ and those of column 7 the ordinates.

For the preparation of lead suboxide, about 1·5 g. of lead oxalate were heated in a porcelain boat in a vacuum at about 275°; the gas evolved was pumped off periodically, the pressure never being allowed to exceed 1 cm. Evolution of gas ceased after about 24 hours, and the black residue gave off no carbon dioxide when treated with acids. The heat of solution in *N*-acetic acid was determined as with thallium, and after completion of the determination the liquid was filtered from undissolved lead, and the lead in the filtrate and the insoluble lead were determined by conversion into sulphate.

The results of two such experiments are given :

(Water-equivalent of calorimeter and contents = 56·2 g.)

	No. 1.	No. 2.
Weight of suboxide used (g.)	1·332	1·162
Amount of PbO dissolved from suboxide (%)	71·3	68·6
Rise in temperature	1·165°	0·963°
Heat of solution per g.-mol. of PbO (cals.)	15,370	15,140

The mean of these two experiments, *viz.*, 15,250 cals., differs only by about 350 cals. from that obtained with pure litharge, *viz.*, 15,600 cals.

These values are in agreement with those obtained by Sveda (*Chem. Listy*, 1923, **17**, 47, 81, 112), but differ from those of Herschkowitsch (*Z. anorg. Chem.*, 1921, **115**, 159) and Tanatar (*loc. cit.*).

UNIVERSITY COLLEGE, LONDON.

[*Received, March* 18*th*, 1926.]