

## DTA STUDY ON LEAD CHLORIDE

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The hydrolysis of lead chloride by residual water is responsible for the appearance of a second peak in the DTA curve, due to melting of the eutectic  $\text{PbCl}_2\text{--PbO}$  in repeated measurement runs on the same sample. This effect has previously been misinterpreted as a solid–solid transition in pure  $\text{PbCl}_2$ .

Lead chloride has been the subject of many previous investigations [1]. From the literature it is evident that the melting point varies within the temperature range from  $489^\circ$  to  $501^\circ$ . The thermal behaviour of lead chloride has also been studied [2–5]. It has been reported [2–4] that lead chloride exhibits two thermal effects in its DTA curve during heating, one of them corresponding to the structure transition effect at  $422^\circ$ . However, measurements with a Du Pont 990 Thermal Analyzer did not reveal this effect because of the low sample mass [5].

In our measurements with a Du Pont 990 Thermal Analyzer we have found that the DTA curve of lead chloride displays one peak at  $494 \pm 2^\circ$  in the first measurement. A second peak, at  $422 \pm 2^\circ$ , occurs only in repeated measurements on the same sample. Further repetitions of the measurements do not lead to a shift in the lower-temperature peak but, its area increases. The higher-temperature peak, however, shifts towards lower temperature and decreases in area. A plausible explanation of this behaviour is presented in this work.

### Experimental

For the DTA measurements two samples of lead chloride were used: A. R. grade (Lachema) recrystallized from water or from a 2 M solution of hydrochloric acid, and a zone-refined (3 times) material. The recrystallized samples were dried at  $80^\circ$  under a pressure of  $10^{-2}$  torr. Spectral analysis showed the presence of traces of Fe, Al, Si and Ag (in the water-recrystallized sample).

A high-temperature cell ( $1200^\circ$ ) was used with the Du Pont Thermal Analyzer. The measurements were carried out in an argon flow (5 l per hour) dried over a molecular sieve. A Pt – Pt + 13% Rh thermocouple was used for curves in the range from  $300^\circ$  to  $520^\circ$ .

For interpretation of the peak at  $422 \pm 2^\circ$ , some chemical experiments were performed. Since a mass loss was found during the DTA measurements, we were interested in the gaseous phase released during the heating of lead chloride. For this reason the  $\text{PbCl}_2$  samples were heated for 1 hour in the argon atmosphere at 200, 250, 300, 350, 400, 450 or  $500^\circ$  in a glass tube elongated into a capillary (Fig. 1). The volatile

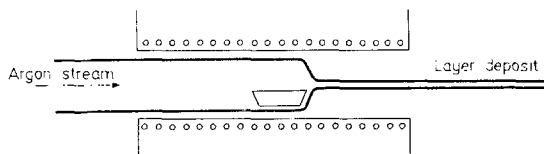


Fig. 1 Equipment in which deposit was obtained

components deposited in the capillary were washed out with hot water, analyzed for lead and chloride ions, and their molar ratios were calculated.

In another experiment a stream of argon was led into an absorption solution to prove the presence of either chlorine or chloride ions. The presence of chlorine was examined by absorption in an aqueous solution of methyl orange at pH 2 [6], but it was not found. To detect chloride ions released during the heating process, an absorption solution containing  $\text{Hg}^{2+}$  ions [7] was used. To follow the amount of chloride ions released at different temperatures, the absorption solution was exchanged at 30-minute intervals in  $50^\circ$  steps from room temperature to the melting point.

Table 1 Ratios of  $\text{Pb}^{2+}:\text{Cl}^-$  found in deposit

a				b			
Temp., $^\circ\text{C}$	Contents of		$\text{Pb}^{2+}:\text{Cl}^-$ ratio in mol	Temp., $^\circ\text{C}$	Contents of		$\text{Pb}^{2+}:\text{Cl}^-$ ratio in mol
	$\text{Pb}^{2+}$ $\mu\text{g}$	$\text{Cl}^-$ , $\mu\text{g}$			$\text{Pb}^{2+}$ , $\mu\text{g}$	$\text{Cl}^-$ , $\mu\text{g}$	
200	0	0	0:0	200	45	5	1:0.65
250	137.5	65	1:2.7	250	10	—	—
300	30	42.5	1:8.28	300	127.5	30	1:1.38
350	21	31.8	1:8.84	350	1400	825	1:3.44
400	470	165.5	1:2.06	400	260	67.5	1:1.52
450 <sub>I</sub>	1100	385.4	1:2.05	450 <sub>I</sub>	625	800	1:7.48
450 <sub>II</sub>	187	93	1:2.90	450 <sub>II</sub>	475	750	1:9.23
500 <sub>I</sub>	13500	4080	1:1.77	500 <sub>I</sub>	8000	6750	1:4.93
500 <sub>II</sub>	5525	1768.3	1:1.87	500 <sub>II</sub>	1875	1150	1:3.58

a) sample recrystallized from water

b) sample recrystallized from hydrochloric acid solution

At 450 and  $500^\circ$  the deposits were divided into two parts (I, II).

## Results and discussion

In the DTA curves of all the samples measured, only one peak was found during the first heating process at  $494 \pm 2^\circ$ . On repeated heating an additional peak occurred at  $422 \pm 2^\circ$ . During further measurement runs this peak did not change its temperature position, but its area increased; at the same time the peak at  $494 \pm 2^\circ$  moved to lower temperatures and decreased in area (Fig. 2, curves *a, b, c*).

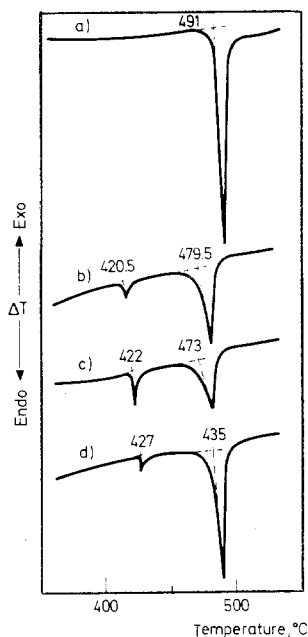


Fig. 2 DTA curves of  $\text{PbCl}_2$ :

- a)* first measurement run
- b)* second measurement run
- c)* third measurement run
- d)* DTA curve of mixture of  $\text{PbCl}_2 + 1.5 \text{ mol\% PbO}$

This behaviour does not correspond to the existence of a phase transition between low- and high-temperature phases of lead chloride, as supposed in the literature. This behaviour and the changes in the DTA curve merely suggest the occurrence of an eutectic and a liquidus effect, the heat of the former increasing and the temperature of the latter decreasing with the number of heating cycles. We consider the reason for this to be the hydrolytic decomposition of  $\text{PbCl}_2$  by water vapour. During this process oxygen-containing compounds are formed.

According to the phase diagram [9] lead chloride and lead oxide form an eutectic compound at 24 mol% lead oxide, with melting point at  $405^\circ$ . We measured DTA curves of mixtures of  $\text{PbCl}_2$  with  $\text{PbO}$  up to 3 mol%  $\text{PbO}$ . Two effects were found in the DTA curves. The upper one corresponds to the liquidus of the lead chloride–lead oxide system and its temperature decreases with increase of the lead oxide content of the mixture, as may be seen in Fig. 3. The lower effect lies at about  $427^\circ$  and

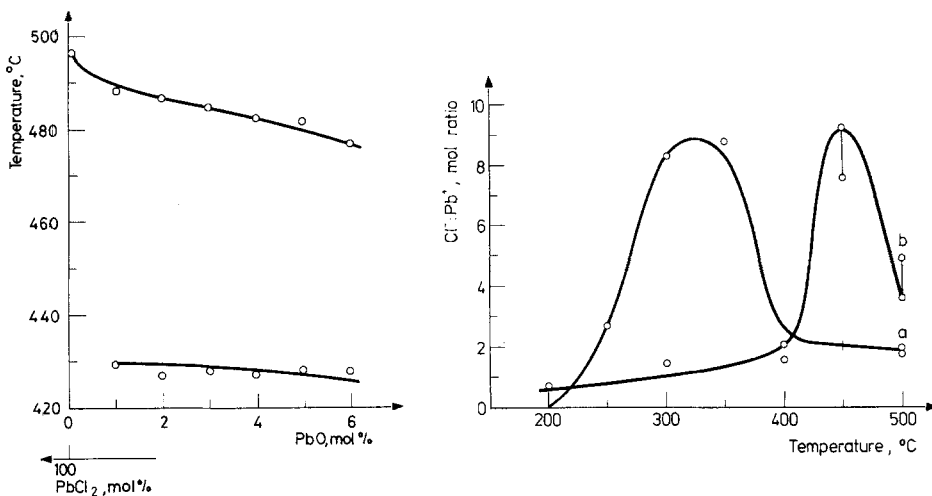


Fig. 3 DTA effects found for mixtures of  $\text{PbCl}_2$  with  $\text{PbO}$  up to 3 mol%  $\text{PbO}$

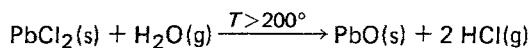
Fig. 4 Molar ratios of  $\text{Cl}^-:\text{Pb}^{2+}$  found in deposit (according to Table 1):  
 curve a):  $\text{PbCl}_2$  sample recrystallized from aqueous solution  
 curve b):  $\text{PbCl}_2$  sample recrystallized from hydrochloric acid solution

shifts very slightly to lower temperature. After repeated measurement runs the DTA behaviours (Fig. 2, curve *d*) of lead chloride and the synthetic mixtures are very similar.

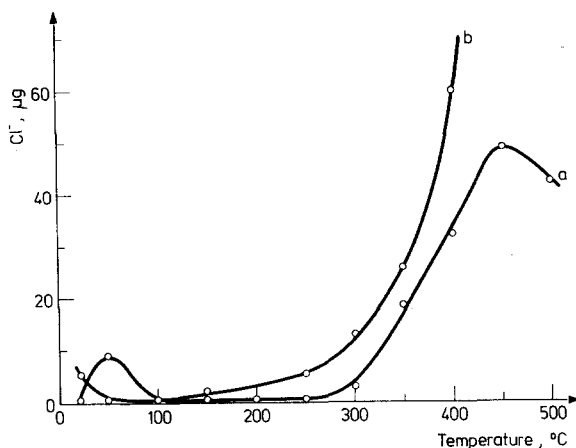
The weight loss of lead chloride in the DTA measurement was found to be 7.37 wt% after the first run and 8.67 wt% after three runs. A chloride ion loss of nearly 1.0 wt% was found in the measured material as compared with the starting material.

The changes in chemical composition of the heated  $\text{PbCl}_2$  are better seen from Table 1 where the results of chemical analyses of deposits in the capillary are given. In Fig. 4 the temperature-dependence of the molar ratios of chloride and lead ions are shown for  $\text{PbCl}_2$  recrystallized from water and from 2 M HCl solution, respectively. The temperature-dependence of the chloride ion loss during heating of the two samples of lead chloride is given in Fig. 5.

Chlorine loss from the heated  $\text{PbCl}_2$  is caused by hydrolysis at elevated temperatures, according to the relation:



The chloride ions released in the form of HCl in this reaction are deposited together with evaporated lead chloride in the capillary of the equipment (see Table 1 and Fig. 4). The amounts of chloride ions sorbed in the absorption solution are shown in Fig. 5.



**Fig. 5** Contents of chloride ions found in gaseous phase released during heating:  
 curve a):  $\text{PbCl}_2$  sample recrystallized from aqueous solution  
 curve b):  $\text{PbCl}_2$  sample recrystallized from hydrochloric acid solution

From the Table and the two Figures it is seen that the hydrolysis starts at about  $200^\circ$ , and reaches its maximum at  $350^\circ$  in the case of  $\text{PbCl}_2$  recrystallized from aqueous solution. At higher temperatures the sublimation of  $\text{PbCl}_2$  predominates, and therefore the ratio  $\text{Pb}^{2+}:\text{Cl}^-$  attains a value of 1:2. In the case of  $\text{PbCl}_2$  recrystallized from hydrochloric acid solution the hydrolysis proceeds more slowly, due to the presence of HCl molecules in the material. At higher temperatures these HCl molecules volatilize.

The water needed for hydrolysis need not originate from the stream of argon; it may be desorbed from the material itself or from the crucibles or tube walls. It is known that the sorption ability of water is extremely high and a very low amount of water is sufficient for the hydrolytic reaction.

After concluding our experiments we learned from a publication of Keller *et al.* [10] that a similar effect had been found with lead bromide. Here too the partial hydrolysis of the halide caused the appearance of an eutectic effect, which had been erroneously interpreted by Modestova [11] as a phase transformation of pure  $\text{PbBr}_2$ . Accordingly, we believe that the phase transformation assumed by Modestova [2–4] and by Blachnik and Alberts [5] is an eutectic effect of  $\text{PbCl}_2$  with  $\text{PbO}$ , the latter generated through hydrolysis by water adhering to the quartz tube. The long annealing time before calorimetric measurement [5] supports this assumption.

However, if samples for DSC measurements were not subjected to such pretreatment they should not show the eutectic effect upon first heating.

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**Zusammenfassung** – Partielle Hydrolyse von Blei(II) chlorid durch Spuren von Wasser führt zum Auftreten eines zusätzlichen DTA-Effekts beim Schmelzen des Eutektikums  $\text{PbCl}_2\text{-PbO}$  nach mehrfachem Aufheizen und Abkühlen. Dieser Effekt war früher fälschlich als Phasenumwandlung des reinen festen  $\text{PbCl}_2$  interpretiert worden.

**Резюме** – Гидролиз хлорида свинца, вызываемый остаточной водой, является ответственным за появление второго пика на ДТА-кривой и обуславливает плавление эвтектики  $\text{PbCl}_2\text{-PbO}$  при повторных измерениях на том же самом образце. Этот эффект ранее ошибочно был интерпретирован как переход типа твердое тело – твердое тело в чистом хлориде свинца.