THE GROWTH OF METAL EXCESS LEAD CHLORIDE FROM THE VAPOUR PHASE*

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During the course of some studies on possible mineral transport processes via the vapour phase, the deposition of lead chloride exhibiting various degrees of blackening was observed. This phenomenon occurs at relatively low temperatures (300–400°) when an atmosphere of hydrogen sulphide is present, and at somewhat higher temperatures in the absence of such an atmosphere. The blackening proved to be due to the presence of appreciable amounts of excess lead in the lead chloride. No sulphur could be detected. Earlier observations by Corbett and von Winbush[1] on this phenomenon refer to the equilibration of lead chloride and molten lead but the product does not appear to have reached the relatively high concentration of excess lead observed in the present experiments. Corbett and von Winbush also carried out transport experiments in which heated lead chloride was sublimed slowly over lead heated to 500–575° in an evacuated system; the condensed lead chloride did not differ from normal.

Pyrosol studies on the system lead/lead chloride reported by Farquhason and Heymann[2] indicated that lead particles of colloidal dimensions could become dispersed in molten lead chloride and that this system solidifies to a grey mass. The black crystals obtained in the present work do not appear to represent a pyrosol as described by Lorenz,[3] although the precise form of the incorporation of the lead has not yet been determined.

Results

In the experiments with an hydrogen sulphide atmosphere, the lead chloride was placed in an alumina boat in an initially evacuated tube subsequently filled with hydrogen sulphide to 3 mm pressure. The boat was heated to 500° using a tube furnace which gave a considerable temperature gradient from the site of the boat to the cooler deposition zone of lead chloride (c. 200°). Over a period of some hours most of the lead chloride was transported, yielding generally the normal white crystals, but with considerable quantities of well-formed black crystals mainly of cubic habit in the hotter part of the deposition zone.

The black crystals contained no detectable sulphur, and in fact were found to contain lead in excess of the stoicheiometric ratio for $PbCl_2$. The mean of four analyses (electrolytic determination) yielded a weight percentage of 76·9 lead compared with 74·5 for stoicheiometric $PbCl_2$. The excess lead corresponds to the

[1] Corbett, J. D., and Winbush, S. J. von, J. Amer. Chem. Soc., 1955, **77**, 3936.

[2] Farquhason, J., and Heymann, E., Trans. Faraday Soc., 1935, **31**, 1004.

[3] Alexander, J. (Ed.), "Colloid Chemistry." Vol. 1, p. 681. (Reinhold: New York 1926.)

formula $Pb_{1.13}Cl_2$ and, as mentioned above, this is considerably greater than the levels previously[1] reported (0.020 mole % at 600°).

It should be noted that crystals, obviously of a wide range of composition (as shown by the varying degrees of blackening), were obtained, and hence the above level of excess lead should not be regarded as the maximum obtainable. No experiments were performed to estimate this latter quantity.

The density of the black crystals was found to be approximately 5.9 g/ml, as compared with the value reported[4] for pure lead chloride of 5.909.

The black crystals were stable to heat to 480°, melting at this temperature to yield a yellow liquid which crystallized again on cooling to form a black compound. It is interesting to note that the melting point of stoicheiometric $PbCl_2$ is 501°, and thus a depression of freezing point of approximately 20° has been achieved by the incorporation of the excess lead.

TABLE 1

RELATIVE INTENSITIES OF PEAKS

Intensities are calculated relative to 111, the strongest reflection, as 100

Index	Black Crystals	Sublimed $PbCl_2$	N.B.S. $PbCl_2$
002	64	21	18
200	77	32	23
101	50	39	34
020	64	52	43
103	64	51	48

X-ray powder diffraction patterns (obtained with CuK_α radiation) were recorded for the black crystals and compared with those for sublimed lead chloride. The patterns were virtually identical in the angles 2θ of reflection of the diffraction peaks. Intensities of diffraction peaks were determined by counting at maximum peak height using a fixed time count. Preferred orientation effects in the sample were eliminated by using a spinning sample holder. Relative intensities of a number of peaks are compared for the black crystals, sublimed lead chloride, and the National Bureau of Standards values[5] (Table 1).

There was no evidence in the X-ray diffraction studies of the existence of a separate lead metal phase. However, studies of the crystal faces with a mineragraphic microscope under polarized light showed the presence of apparent inclusions which had a definite alignment.

Discussion

The general appearance and mode of formation of the lead excess lead chloride suggest that the gaseous lead chloride is undergoing homolytic dissociation either in the gas phase or on the surface of the hot lead chloride crystals, to yield lead in atomic form which is then incorporated in the growing crystal lattice or diffuses into

[4] Fernandez, A. J. I., and Gasco, L., *Chem. Abstr.*, 1955, **49**, 7910*a*.

[5] National Bureau of Standards Circular 539 (1953), Vol. 2.

this lattice. Homolytic dissociation of lead chloride as a gas phase process at 650° seems somewhat surprising in view of the relatively high (78 kcal mole^{-1}) bond dissociation energy of the first Pb–Cl bond in this compound.[6] A surface-catalysed dissociation seems rather more probable and would account for the presence of lead in the crystals exposed to the hottest gases and not elsewhere in the system.

In the case of formation of black crystals in the presence of hydrogen sulphide, a possible reaction for the production of elemental lead is the following:

$$2PbCl_2 + 2H_2S \rightarrow 2Pb + 4HCl + S_2.$$
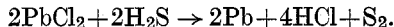
It was observed in the colder portions of the tube that the product was yellow rather than white, although a sulphur phase was not detected by X-ray diffraction techniques.

Again it seems likely that this is a surface reaction on the $PbCl_2$ at elevated temperatures and the elemental lead is incorporated by diffusion.

It should be noted that the PbCl radical has been observed[7] in the gas phase at 692°, and also[8] in the system $PbCl_2$–H_2S at temperatures of the order of 600–650°. This radical might be expected to produce elemental lead by the following disproportionation reaction:

$$PbCl + PbCl \rightarrow Pb + PbCl_2.$$
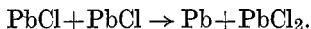
At present no positive comment can be made on the nature of the incorporated lead, although solid solution of lead atoms appears likely. If this is the case, the excess lead atoms do not change the lattice dimensions in any marked degree, although a small expansion may be detectable. It would seem therefore that the lead atoms are located on interstitial sites, the dimensions of which are virtually sufficient to accommodate the neutral atoms without distortion. There are, however, marked increases in the intensity of reflection from certain planes, as shown in Table 1.

[6] Wieland, K., and Herczog, A., *Helv. Chim. Acta*, 1949, **32**, 889.

[7] Wieland, K., and Newburgh, R., *Helv. Phys. Acta*, 1952, **25**, 87.

[8] Walker, A. L., and Buchanan, A. S., unpublished data, 1964.