113. *The System Lead Chloride–Water at 15° to 35°*

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The solubility of lead chloride in water has been redetermined for the temperature range 15—35°; the following average results were obtained (g. per 100 g. of saturated solution): 15°, 0·866; 20°, 0·968; 25°, 1·075; 30°, 1·179; 35°, 1·298. Determinations of lead and chloride in these solutions showed a slight excess of the latter equivalent to about 0·004 g. of lead chloride.

Many determinations of the solubility of lead chloride are on record. Ditte (*Compt. rend.*, 1881, **92**, 718), Lichty (*J. Amer. Chem. Soc.*, 1903, **25**, 474), Demassieux (*Compt. rend.*, 1913, **156**, 892), and Flottmann (*Z. anal. Chem.*, 1928, **73**, 30) each made measurements at a number of temperatures, and numerous single-temperature determinations, mostly at 25°, have been reported. In spite of this mass of data it was difficult to select a series of trustworthy values for the temperature range 15—35°.

A characteristic of aqueous lead chloride solutions which has often been noted, particularly by Ley (*Ber.*, 1897, **30**, 2192) and Benrath (*Z. physikal. Chem.*, 1908, **64**, 693), is the slight hydrolysis which occurs. In our work a careful watch was kept for this by means of determinations of lead and chloride ions, but when it was found that the differences between the ionic concentrations were only slightly outside the limits of experimental error, and were within the limits of accuracy required from our data, the subject of hydrolysis was not pursued further.

EXPERIMENTAL.

The lead chloride was prepared by precipitation from lead acetate solution with hydrochloric acid, followed by recrystallisation from hot aqueous solution containing a little hydrochloric acid. The crystals obtained on cooling were filtered off, washed with methylated spirits, and dried in a partially evacuated desiccator over calcium chloride at room temperature [Found by methods described below: $PbCl_2$, (1) 99·41, 99·70; (2) 99·42; (3) 99·75, 99·98%].

The solubility determinations were carried out in "three-necked" flasks of about 500-ml. capacity, about 400 ml. of distilled water and an excess of lead chloride being used. The flask contents were stirred for about 30 mins. at a temperature some 10° higher than that at which the solubility was to be determined. The temperature was then reduced to the desired value (controlled to $\pm$ 0·02°), and stirring continued for at least 16 hours (overnight) and in some cases for a few days. In one case (15°) samples of solution taken after 7 hours and after 4 days gave the same result: Böttger (*Z. physikal. Chem.*, 1903, **46**, 602) noted the remarkably rapid attainment of equilibrium. Prolonged stirring did not appear to increase hydrolysis in our experiments.

After the solid phase had been allowed to settle, samples of clear saturated solution were withdrawn by a dry pipette fitted with a cotton-wool filter and analysed by two or more of the following methods. *Lead.* (1) As sulphate, after evaporation with sulphuric acid, dilution with water to give about 15% of acid, addition of alcohol, and collection in a sintered-glass crucible. (2) As chloride, after evaporation to dryness on a water-bath with dilute hydrochloric acid, followed by digestion with alcohol, filtration, and rapid drying at 110°. *Chloride.* (3) Volumetrically with 0·1N-silver nitrate, the excess (about 1 ml.) being titrated by Volhard's method after the silver chloride had been filtered off. (4) Weighing the silver chloride filtered off from (3).

The solubilities are shown in Table I according to the analytical method used. From these results the average values already quoted have been derived. That the excess of chloride over lead (see p. 447) is probably due to a slight hydrolysis and not to imperfections in analytical methods is shown in Table II, which is mainly a verification of the chlorine contents of lead chloride obtained in lead determinations by method (2).

TABLE I.

Solubility determinations.

	G. of $PbCl_2$ per 100 g. of solution.		
	Detmn. of Pb.	Determination of Cl.	
Temp.	(2).	(3).	(4).
15°	0·865	0·865	—
15	0·863	0·866	—
15	0·864	0·868	0·869
20	0·961	0·969	0·967
20	0·968	0·971	0·970
25	1·070	1·075	—
25°	1·075	1·081	—
30	1·175	1·178	—
30	1·178	1·181	1·182
35	1·296 *	—	—
35	1·302	1·307	—
35	1·290	1·295	1·296

* 1·300 G. per 100 g. of solution by method (1).

TABLE II.

Verification of methods of analysis.

The $PbCl_2$ shown in col. A was dissolved and its Cl content determined, with the results shown under C and D.

	A.	B.	C.	D.
Temp.	Wt. of $PbCl_2$ obtained by method (2).	Calc. Cl equiv. to A.	Cl calc. from gravimetric AgCl detmn.	Cl calc. from volumetric detmn.
15°	0·4342	0·1108	—	0·1108
	0·4352	0·1111	—	0·1109
	0·4340	0·1108	—	0·1109
	0·4336	0·1107	0·1100	0·1102
	0·4354	0·1112	0·1107	0·1106
25°	0·5384	0·1374	—	0·1374
	0·5382	0·1374	—	0·1374
	0·5406	0·1380	—	0·1379
	0·5416	0·1382	—	0·1381
35°	0·6550	0·1672	—	0·1670
	0·6516	0·1663	—	0·1667

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