XXXVII.—*On the Solubility and Crystallisation of Plumbic Chloride in Water, and in water containing various percentages of Hydrochloric Acid, specific gravity 1.162.*

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ALL the manuals I have consulted give the solubility of plumbic chloride, PbCl_2 , as one part dissolved in 135 parts of water; according to my results, which were conducted with the greatest care, I find it still more soluble than the above states it to be. I used pure crystals of plumbic chloride, which had been recrystallised five or six times from a watery solution, and distilled water which was redistilled specially for this result; the water was allowed (with an occasional shake of the solution) to act upon the crystals for about ten days at a temperature of $15^{\circ}5$ C. (60° F.); some days perhaps it would rise a little more, other days fall, but as near as possible it was kept at the temperature named; it was then taken exactly at $15^{\circ}5$ C., filtered through Swedish filtering paper (the first portion being rejected) into small beakers; the solution was weighed most accurately to the thousandth of the grain in the covered vessel; it was then carefully evaporated in a steam-bath; and the crystals heated to 110° C. (230° F.) cooled down in a desiccator, and then weighed. The four results were:—

No. 1	..	..	·8207
2	..	..	·8256
3	..	..	·8264
4	..	..	·8259

giving a mean of $\cdot 8246$, and showing that one part of plumbic chloride dissolves in 121 parts of water at $15^{\circ}5$ C. (60° F.).

Another fact I have observed in the behaviour of plumbic chloride with water, is, that the salt is partially decomposed, and the solution gives a slight acid reaction to litmus paper, even in the cold, on taking perfectly pure crystals and distilled water, which singly have no acid reaction, but immediately they are brought in contact the acidity is developed, which I can only attribute to the decomposition of the salt; but this acid reaction is much more marked on heating the solution to 100° C. and keeping it at that temperature for several hours; it also has a very striking effect upon the solubility of the salt. 100 parts of distilled water at $17^{\circ}7$ C. (64° F.) dissolve $\cdot 947$ of the pure crystals of plumbic chloride. Another portion of the crystals was boiled in water for three minutes, and the solution was allowed to cool down to $17^{\circ}7$ C.; it then contained, according to two results, $\cdot 927$ per cent. of plumbic chloride. To show what a marked effect boiling the solution of plumbic chloride had upon the solubility, I prepared some crystals of plumbic chloride from an acid solution; they were well washed and dried so as not to leave the slightest trace of acid upon them; then acted upon at the common temperature by 20 ounces of pure water for several days. At the end of that time the water was found to contain $\cdot 942$ per cent. of plumbic chloride at $17^{\circ}7$ C. The twenty ounces were boiled down to six, and the solution cooled to $17^{\circ}7$ C.: it then contained $\cdot 823$ per cent. of plumbic chloride. A second solution of plumbic chloride was boiled for about two hours, and cooled as before; according to the mean of two experiments, it contained $\cdot 741$ per cent. of the salt. From these experiments I think I am justified in saying that plumbic chloride is decomposed by water, with production of free hydrochloric acid: and it is this acid up to a certain point, as we shall see further on, which diminishes the solubility of plumbic chloride. This salt, as regards its solubility in water, behaves in a very peculiar manner. One would have supposed that water at 100° C., poured upon pure crystals, then well shaken, and poured off when clear into a beaker, would have formed a saturated solution at $17^{\circ}7$ C. I have found this not to be the case; when boiling redistilled water was poured upon pure crystals, shaken, poured off into a beaker, and allowed to cool to $17^{\circ}7$ C., it was found from the mean of two experiments to con-

tain only .7668. A second experiment was tried in the same manner, and from the clear solution a very few detached crystals were formed; the mother liquor at $17^{\circ}7$ C. contained .8984 PbCl_2 . A second quantity of boiling water was poured upon the original crystals, and treated as before; the liquor contained .8373. A third quantity of water was poured upon the crystals, and this solution only contained .6854 per cent. of PbCl_2 , at $17^{\circ}7$ C. In these experiments only the small crystals were dissolved, thus forming an almost saturated solution; but the second and third portions of water had only the large crystals to act upon, and could not dissolve a sufficient quantity in the time allotted to them to form a saturated solution. Powdered plumbic chloride was taken, water at the ordinary temperature poured upon it, and allowed to stand for some time; the solution contained at $17^{\circ}7$ C., according to two results, .946 per cent. of PbCl_2 .

Solubility of Plumbic Chloride in dilute Hydrochloric Acid of various strengths.—The solubility of the salt decreases as the quantity of hydrochloric acid increases up to a certain point, but beyond this the solvent power increases step by step as the hydrochloric acid increases. Starting with pure water, which we have already seen dissolves .946 per cent. of PbCl_2 at $17^{\circ}7$ C., then if one-tenth per cent. of hydrochloric acid sp. gr. 1.162 be put into the water, the solubility at once sinks to .838; with two-tenths per cent. of hydrochloric acid, .716, and goes on decreasing till the acid reaches 15 per cent., when the minimum percentage of plumbic chloride is attained; but whether fifteen is the turning point it is difficult to say, because from the tenth to the sixteenth, the difference only varies by the thousandth and ten thousandths per cent., which may be looked upon as errors of experiment; the greatest difference between ten and sixteen is .004; therefore I think I may safely call those numbers the line of no variation. After the sixteenth the percentage steadily ascends, with here and there a break to mar the uniformity, till they culminate in 100 per cent. Theoretically speaking, one would suppose that the differences between the percentages ought to fall and rise with perfect equality; but experiment does not seem to verify this hypothesis, but rather to point to an unequal oscillating movement, for I have found that the differences are great at the two extremes and smaller towards the middle; for instance between 0.1 and 0.9 they vary between tenths and hundredths, and the same again

between 80 and 100; from 10 to 60 the differences are small, ranging only between hundredths and thousandths; from 60 to 80 they ascend considerably, and the differences vary from seven to nine hundredths.

The mode of conducting the experiments was the following:—pure crystals of plumbic chloride, and pure hydrochloric acid of sp. gr. 1.162 were used; the water and acid were weighed out most carefully into stoppered bottles; plumbic chloride was then put in, and the solutions allowed to stand from ten to fourteen days at a range of temperature from 14° to 18° C. (the solutions receiving an occasional shake); they were then taken at 17.7°C., filtered through Swedish filtering paper (the first portion being rejected) into small weighed beakers, which were then covered with a watch-glass and again weighed with the contents; the beakers were then covered with filtering paper to prevent any dust falling into them, put into a steam-bath, and the solutions were gently evaporated to dryness; the crystals were heated to 110° C., cooled over sulphuric acid in a desiccator, and weighed; the results were then calculated.

Crystallisation of Plumbic Chloride.—The works which I have consulted inform me that this compound crystallises in fine brilliant needles. This statement must be taken with some little reserve, as it is only under certain conditions that needle-shaped crystals can be procured. When boiling distilled water is poured upon plumbic chloride in the powdered state, and the clear solution poured off into a beaker and allowed to cool down slowly, white brilliant crystals are not obtained, but cream-coloured cuneiform or arrow-shaped crystals are formed; these crystals cover the bottom and line the sides of the vessels in a peculiar tuft-like manner; when dry, they are very compact and heavy, and under a low power of the microscope appear massive like quartz, but with a distinct pearly lustre; but if the saturated solution is boiled for a few minutes the appearance of the crystals is at once altered; they are now very small needle-shaped crystals. The addition of hydrochloric acid changes the size considerably, and crystals of great beauty may be sometimes obtained; but as the addition of hydrochloric acid increases, the appearance of the crystals also changes, and they pass from needles into hexagonal plates, but it is better seen when the various solutions are evaporated at a gentle heat; for this purpose not more than twenty or thirty grammes should be used. Thus, when the solu-

tion of plumbic chloride, which has been prepared without heat, is evaporated to dryness in the water-bath, beautiful feathery crystals are obtained, not at all like needles, but more like a quill pen with the feathers only on one side; they are not attached to the vessel in which they have been crystallised, as in some cases they are; when the crystals were boiled in water for a short time, the solution allowed to cool down, and then evaporated in the water-bath, a mass of small feathery crystals is obtained, interlaced one with another, so that the vessel can be inverted without detaching the crystals which adhere to the bottom. When the saturated solution is boiled for two or three hours, then cooled, and a portion of the liquor evaporated, no distinct crystals are formed, but a magma of very fine crystalline particles is obtained; when one per cent. of hydrochloric acid is added the solution heated to 100° C., and then cooled, white feathery crystals are formed, and on evaporating the liquid the crystals which form are like feathers compressed, very similar to the crystalline form of antimony; they also adhere tenaciously to the beaker; as the percentage of hydrochloric acid increases, the crystals also undergo a change. On evaporating the solution containing 51 per cent. of hydrochloric acid, the crystals obtained were like fern leaves; on performing the same experiment with 60 per cent. of hydrochloric acid, the crystals appeared to be in a state of transition, passing from the plumose to the lamellar state; with 80 per cent. of hydrochloric acid, the transition was complete, no longer presenting a feathery appearance, the crystals being flat hexagonal plates similar to the drawing; they also glistened like mica; with 100 per cent. the same appearance was presented as with 80. Here again we have a singular phenomenon regarding plumbic chloride; beginning with water, we have cream-coloured arrow-shaped crystals (or perhaps some would call them feathery, as they are wide at the top and pointed at the bottom), then they pass into fern crystals, thence into the transitional state, and lastly become hexagonal plates.

In concluding this paper I am sensible of many defects which perhaps might be removed by repeating the whole of the experiments; I did not think it necessary to do so, as I thought it was possible for all to see that there must be a descending and ascending scale; I therefore preferred leaving the results as I found them.

AND CRYSTALLISATION OF PLUMBIC CHLORIDE, ETC. 355

Table of the Solubility of Plumbic Chloride in Water, and in Water containing various percentages of Hydrochloric Acid (sp. gr. 1.162) at a temperature of 17.7 C.

Pure water dissolves	0.946 p. c.	46 p. c. HCl	0.316 p. c.
Do. containing 0.1 p. c. HCl	0.838 "	47 "	0.327 "
0.2 p. c. HCl	0.716 "	48 "	0.328 "
0.3 "	0.652 "	49 "	0.336 "
0.4 "	0.605 "	50 "	0.356 "
0.5 "	0.502 "	51 "	0.371 "
0.6 "	0.499 "	52 "	0.374 "
0.7 "	0.441 "	53 "	0.395 "
0.8 "	0.426 "	54 "	0.406 "
0.9 "	0.385 "	55 "	0.433 "
1 "	0.347 "	56 "	0.462 "
2 "	0.201 "	57 "	0.469 "
3 "	0.165 "	58 "	0.518 "
4 "	0.145 "	59 "	0.542 "
5 "	0.131 "	60 "	0.559 "
6 "	0.107 "	61 "	0.550 "
7 "	0.100 "	62 "	0.575 "
8 "	0.099 "	63 "	0.600 "
9 "	0.096 "	64 "	0.630 "
10 "	0.093 "	65 "	0.666 "
11 "	0.093 "	66 "	0.721 "
12 "	0.093 "	67 "	0.739 "
13 "	0.093 "	68 "	0.828 "
14 "	0.090 "	69 "	0.854 "
15 "	0.090 "	70 "	0.933 "
16 "	0.094 "	71 "	0.971 "
17 "	0.101 "	72 "	1.040 "
18 "	0.100 "	73 "	1.118 "
19 "	0.100 "	74 "	1.137 "
20 "	0.111 "	75 "	1.208 "
21 "	0.113 "	76 "	1.305 "
22 "	0.112 "	77 "	1.393 "
23 "	0.114 "	78 "	1.347 "
24 "	0.118 "	79 "	1.413 "
25 "	0.129 "	80 "	1.498 "
26 "	0.131 "	81 "	1.475 "
27 "	0.131 "	82 "	1.503 "
28 "	0.134 "	83 "	1.636 "
29 "	0.150 "	84 "	1.677 "
30 "	0.151 "	85 "	1.819 "
31 "	0.157 "	86 "	1.809 "
32 "	0.151 "	87 "	1.898 "
33 "	0.161 "	88 "	1.968 "
34 "	0.165 "	89 "	2.089 "
35 "	0.170 "	90 "	2.117 "
36 "	0.170 "	91 "	2.244 "
37 "	0.181 "	92 "	2.297 "
38 "	0.194 "	93 "	2.407 "
39 "	0.201 "	94 "	2.470 "
40 "	0.216 "	95 "	2.577 "
41 "	0.237 "	96 "	2.611 "
42 "	0.249 "	97 "	2.745 "
43 "	0.258 "	98 "	2.829 "
44 "	0.264 "	99 "	2.851 "
45 "	0.279 "	00 "	2.900 "