VII.—*On the Effect of Heating Sulphate and Sulphide of Lead in Hydrogen and Carbonic Oxide.*

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Sulphate of Lead.

In Hydrogen.—In 1824, Arfvedson reduced sulphate of lead by hydrogen, and found that a mixture of lead and sulphide of lead remained, but I am not aware that the exact nature of the reaction is known.

In order to determine this, sulphate of lead was heated to redness by means of a four-jet Bunsen burner, and a current of pure and dry hydrogen passed over it. The hydrogen was passed through potash and nitrate of silver solution, through concentrated sulphuric acid, a chloride of calcium tube, and a tube filled with anhydrous phosphoric acid; a piece of combustion-tubing, about a foot long, containing the sulphate, followed, and to this was appended a chloride of calcium tube for the water, a potash tube for sulphurous acid and sulphuretted hydrogen, and lastly a chloride of calcium tube to retain any water that might be carried off from the potash-solution.

The error due to the tubing being attacked was found to be much less than might be expected. 1·343 gramme of sulphate of lead was ignited for an hour in a piece of the tubing used; it was then removed, and although the tube was visibly acted on, no difference in weight could be detected. 4·3527 grm. of sulphate ignited for half-an-hour, caused an increase of only ·0015 grm. in the weight of the tube.

At the end of the reduction, the tubes were thoroughly freed from lead by boiling in dilute nitric acid; they were then dried and weighed, and in no instance did the gain exceed a milligramme; so that the error caused by the glass being acted on cannot effect the accuracy of the determinations. Hydrogen was passed through the apparatus until the escaping gas gave no red colour with binoxide of nitrogen; the sulphate was then heated. On first heating, water and sulphurous acid are given off simultaneously, and before the sulphate has attained a red heat, when the sulphide of lead begins to be decomposed. Five minutes' heating completely removes the oxygen and half the sulphur from half a gramme of sulphate, while an hour and half is required to decompose the remaining sulphide, and there is a distinct interval between the end of the evolution of the water and sulphurous acid, and the beginning of that of the sulphuretted hydrogen.

That a mixture of lead and sulphide of lead, and not subsulphide of lead, remains after the first part of the decomposition, was proved by repeatedly stopping the reduction when the oxygen and half the sulphur had been removed, and before any trace of sulphuretted hydrogen was evolved; on examining the residue, numerous globules of metallic lead were always apparent.

The sulphate only must be heated, and the water driven into the chloride of calcium tube by the current of gas; for if the tube in advance of the sulphate is heated, decomposition of sulphurous acid ensues; it is necessary, therefore, to heat the sulphate till the water and sulphurous acid have been eliminated, then to turn out the gas, and continue the current of hydrogen till all the water has been carried into the chloride of calcium tube, when the residual sulphide may be heated. On account of this necessity of allowing the water to be carried slowly into the chloride of calcium tube, the anterior end of the combustion tube was drawn out so as to be connected to the chloride of calcium tube by caoutchouc, and the use of a cork, which would have absorbed water, thus obviated. Towards the end of the reduction, cubes and octohedra of sulphide of lead were found sublimed in the tube.

The mean of a number of determinations gave the following:—

Lead	66·8186
Water	17·3630
Sulphurous acid	10·3416
Sulphuretted hydrogen	5·4712
	99·9944

This agrees with the equation—

$$2(PbO,SO_3) + H_7 = Pb_2 + SO_2 + HS + 6HO,$$

which requires—

Lead	66·8171
Water	17·3969
Sulphurous acid	10·3092
Sulphuretted hydrogen	5·4768
	100·0000

2. *In Carbonic Oxide.*—The same arrangement of apparatus was used for the reduction by carbonic oxide, except that the chloride of calcium tube for collecting water was not required. The carbonic oxide was prepared by Fownes' method, and before drying was passed through potash-solution to remove sulphurous acid; the drying was effected by concentrated sulphuric acid, chloride of calcium, and anhydrous phosphoric acid—and the products were collected in a potash tube.

If it were possible to heat every particle of a mass of sulphate of lead to the same temperature at the same time in carbonic oxide, it would be decomposed according to the equation—

$$2(PbO,SO_3) + 6CO = Pb + PbS + SO_2 + 6CO_2.$$

In this reduction, as also in that by hydrogen, three-fourths of the oxygen are removed by the reducing agent, and the remaining fourth goes off with half the sulphur as sulphurous acid; but there is a difference in the two reductions in one respect: for inasmuch as the affinity of hydrogen for oxygen is greater than that of carbonic oxide for oxygen, it happens in the former case that the oxygen is rapidly removed, and at a comparatively low temperature; while in the latter, five or six times as long a time, and a much higher temperature, are requisite to effect the same result; the consequence of this is that, in the reduction by hydrogen, the temperature does not rise high enough for the first formed portions of sulphide of lead to decompose the sulphate above it, while in that by carbonic oxide, the heat is sufficiently intense, and the reduction sufficiently slow, to allow the sulphide first produced, where the tube is hottest, to act upon the sulphate resting upon it.

Twenty-five determinations were made, but the results were by no means concordant or satisfactory. The best four and their mean are given:—

Residue.	*Products.*
73·3489	50·2045
73·5323	49·4433
73·3160	49·3708
73·5095	50·0306
Mean = 73·4266.	Mean = 49·7623.

Sum = 123·1889.

The determination of the sulphurous acid invariably gave rather less than the theoretical amount; but knowing, as we do, that the products consist of carbonic and sulphurous acids, 100 parts of sulphate of lead and 23·1889 of carbonic oxide, must produce—

Lead	68·3586	Residue = 73·4266
Sulphur . . .	3·8858	
Oxygen . . .	1·1822	
Sulphurous acid . .	13·3226	Products = 49·7623
Carbonic acid . .	36·4397	
	123·1889	

This agrees with the equation, 19 (PbO,SO_3) + $48CO = Pb_8 + 4PbO + 7PbS + 12SO_2 + 48CO_2$, in which 16 equivalents of PbO,SO_3 are decomposed by 48 of CO, according to the equation $2(PbO,SO_3) + 6CO = Pb + PbS + SO_2 + 6CO_2$, and an equivalent of the sulphide produced acts upon 3 eq. of sulphate, according to the well-known equation, $3(PbO,SO_3) + PbS = 4PbO + 4SO_2$.

The full equation given above requires—

Lead	68·3586	Residue	= 73·3545
Sulphur	3·8857		
Oxygen	1·1102		
Sulphurous acid	13·3226	Products	= 49·9600
Carbonic acid	36·6374		
	123·3145		

The oxide of lead seems to form lead-glass as soon as produced, and thus escapes decomposition by the carbonic oxide.

The best results were always obtained when the sulphate was placed in the tube in as much of a mass as possible; when spread out thinly, more oxide of lead appeared to be formed, and the results were exceedingly irregular; but when we remember that sulphide decomposes sulphate of lead according to three distinct equations; that oxide of lead decomposes the sulphide; and lastly, that the manner of placing the sulphate in the tube, the thickness of the glass, and the method of heating, all influence the reduction of the sulphate; it is quite obvious that we can give no definite equation by which in practice sulphate of lead is decomposed by carbonic oxide.

Sulphide of Lead.

The greatest difficulty was experienced in the preparation of sulphide of lead. I do not believe it possible to procure it in a state of purity by precipitating a lead-salt by sulphuretted hydrogen, and drying the precipitate in the air. I invariably found that oxygen had been absorbed.

Two specimens of sulphide of lead prepared by precipitating a solution of the acetate by sulphuretted hydrogen, and drying over a water-bath, were found to gain the following amounts in the air, the time of heating at each different temperature varying from five to nineteen hours.

Oxygen absorbed per hour by 100 parts of sulphide of lead:—

	I.		II.
At 50°C.	·0060	....	·0086
,, 55°C.	·0089	....	·0120
,, 60°C.	·0134	....	·0180
,, 70°C.	·0316	....	·0405
,, 80°C.	·1017	....	·1035
,, 100°C.	·1058	....	·1082
,, 110°C.	·1260	.... at 125°C.	·0295
,, 120°C.	·1319		
,, 130°C.	·1400		
,, 150°C.	·1213		
	When near 150°, sulphurous acid began to be evolved.		When near 125°, sulphurous acid began to be evolved.

The amount of surface had nothing to do with the quantity of oxygen absorbed; for sulphide of lead exposing a surface of four square inches gained no more than when the surface was only one square inch.

As soon as sulphurous acid began to be given off, the heating was discontinued; on gently heating some of each of the above sulphides with very dilute hydrochloric, acetic, or tartaric acid, sulphurous acid was evolved, and lead found in solution, proving that the oxygen absorbed had formed *sulphite of lead,* and not sulphate, as is generally stated.

On one occasion, sulphide of lead, which was exposed to a temperature of 135° C., was found to be glowing, and when blown upon, became red-hot, like ignited charcoal, while large quantities of sulphurous acid were evolved; when removed from the air-bath, the ignition quickly ceased, nor could it be again produced by heating the sulphide to the same temperature.

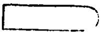
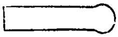
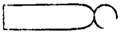
When sulphuretted hydrogen is passed into a solution of acetate of lead, the precipitated sulphide carries down a quantity of acetate with it, so that the supernatant fluid is often entirely free from lead, but on washing the precipitate, a good deal of acetate is found in the washings.

Pure sulphide of lead was prepared in the following manner:—

A rather dilute solution of the acetate or nitrate was precipitated by sulphuretted hydrogen; and the sulphide was thoroughly washed, suspended in cold water through which sulphuretted hydrogen was passed to saturation, then allowed to settle, again washed, and dried at a temperature below 100° C.; when dry, it was heated in a current of dry sulphuretted hydrogen; and finally, in pure and dry hydrogen, to remove any traces of sulphuretted hydrogen, and of sulphur, that might have been carried down during the precipitation.

1. *In Hydrogen.*—When sulphide of lead, which has been dried at 100° C., is heated nearly to redness in hydrogen, carbonic oxide, or carbonic acid, it contracts to about two-thirds its original bulk, changes from black to a light grey colour, and aggregates into a mass, small pieces of which, a centimetre thick, were found to bear a weight of half a kilogramme, and sometimes as much as a kilogramme, without being crushed to powder.

If the heating is continued, the whole mass becomes crystalline throughout. With pure sulphide of lead, this was found to take place when (1), 1·2391 (2), 1·4219 per cent. of sulphur had been lost; but the loss of sulphur has nothing to do with it, for sulphide of lead heated in carbonic acid likewise becomes crystalline.

The crystals were very lustrous and sparkled in the light; they were seen under the microscope to consist of cubes, octohedra, and tabular crystals with flat and rounded ends—the latter were very noticeable. First there were tables with a rounded end simply ; a kind of hemisphere was attached to some ; others had a sphere united by one point only ; and lastly, some of the spheres were seen by themselves . Only one end of the tables was rounded or had the sphere attached, the other was always flat. A number of crystals, similar to those in the mass, were found sublimed in the tube; but the crystals were largest when the reduction was continued till very little sulphide remained, when a few sparkling black crystals were seen floating on the surface of the melted lead.

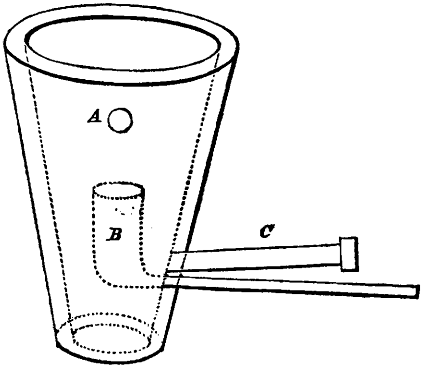
2. *In Carbonic Oxide.*—Sulphide of lead, from which any possible trace of oxygen was removed by previous heating to low redness in hydrogen, was heated in carbonic oxide. Great care was taken to remove the whole of the oxygen from the apparatus before heating; for this purpose, the gas was passed through the apparatus for from half to three-quarters of an hour, a tube containing pyrogallate of potash was then introduced, and the current of gas continued for some minutes. The pure sulphide lost by being heated to redness for an hour in carbonic oxide (1), ·5964 (2), ·4042 per cent. of sulphur; the sulphide was aggregated into a mass, and was crystalline throughout, the crystals being of the same form as those produced by heating the sulphide in hydrogen.

It is stated by Gmelin, that carbonic oxide is decomposed by a red heat; therefore, before submitting sulphide of lead to the action of the gas at a higher temperature than that produced by a four-jet Bunsen burner, it was thought as well to try whether the gas would stand a red heat without suffering decomposition; if it would not, the experiment would of course be fallacious, because we should be acting on the sulphide with a mixture of finely divided carbon and oxygen gas.

In order to determine this, carbonic oxide was passed through a piece of combustion-tubing, which was heated along a foot of its length to bright redness by charcoal. After half an hour's heating, the tube was considerably bent, but no trace of carbon was apparent.

Sulphide of lead was heated to redness by charcoal in carbonic oxide for half an hour; it was found to have lost ·1623 per cent. of sulphur; the mass was very hard; small pieces of it, a centimetre thick, bore a weight of a kilogramme and a half without being crushed; there was no appearance even of the commencement of fusion. It is generally stated, that sulphide of lead fuses at a red heat, but I did not find that fusion ensued before it was heated to whiteness. Sulphide of lead was next submitted to the action of carbonic oxide, at a more intense heat than that produced by ignited charcoal, in a small clay furnace, which, as it allows a piece of porcelain tubing to be heated to whiteness on an ordinary working table, and costs less than a shilling, I may, perhaps, be pardoned for describing somewhat at length.

The furnace was made from a clay crucible 6 inches high, and $3\frac{1}{2}$ internal diameter at the top; two holes, A, were bored at $1\frac{1}{2}$ inches from the top, opposite each other; the internal diameter here was $3\frac{1}{4}$ inches, so that $3\frac{1}{4}$ inches of porcelain tubing can be heated; at $1\frac{1}{2}$ inches from the bottom, a hole of this shape  was bored, into the lower part of which the stem of the pipe B fitted; into the upper part, the nozzle, C, of a pair of bellows; B is one of the



large Dutch pipes, the bowl of which is 2 inches long by 1 inch in diameter; it is easily introduced through the body of the furnace, and placed in the position shown in the figure, which is one-fourth the real size. By means of this pipe, oxygen gas is introduced into the furnace. The furnace is filled with red-hot pieces of charcoal about the size of hazel-nuts, which are brought to intense ignition by the bellows. When the porcelain tubing and the pipe-bowl are at a red heat, a current of oxygen from a gas-holder is turned on; the pipe-bowl, which is 1 inch below the porcelain tube to be heated, is stuffed full of pieces of the pipe stem, of the same length as itself, in order to cause the oxygen to issue from as large a surface as possible, and also to compel it to come in contact with a very large red-hot surface in passing through the pipe-bowl; the consequence of this is, that the oxygen when it issues from the pipe, is at a very high temperature, and the porcelain tube is soon brought to a most intense state of white hot ignition. The surface of the pipe-bowl (= ·7854 square inch) from which the oxygen issued, was found to be fused after once using it, the whole time of passing the oxygen not amounting to a quarter of an hour; the outside of the porcelain tube heated was glazed. This small furnace is easily constructed; a bright white heat may be kept up so long as there is a supply of oxygen, and so long as the materials remain unfused.

Sulphide of lead was placed in a porcelain tube, and heated in carbonic oxide by means of the above furnace; the time of heating was half an hour, at intervals during which the tube was raised to whiteness; at the end of the experiment, the sulphide had lost ·3892 per cent. of sulphur; it was fused, and very brilliant sparkling cubes (some of which had sides of $\frac{1}{16}$th of an inch) were found in the fore part of the tube: had the heating been continued much longer, these would have stopped up the tube. A second experiment in which the sulphide was similarly treated gave a loss of ·4830 per cent. of sulphur.

In each of the above experiments in which sulphide of lead was heated in carbonic oxide, the products were passed into potash-solution, which became yellow, and on treating it with a dilute acid, sulphuretted hydrogen was evolved, proving that *bisulphide of carbon* had been formed.