

XXII.—*On the Occurrence of Prismatic Arsenious Acid.*

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WÖHLER,* in the year 1832, discovered the dimorphism of arsenious acid, and described small crystals produced by sublimation, in a reverberatory furnace in which cobalt ores had been roasted.

These crystals, most of which were only $\frac{1}{12}$ of an inch in length, were thin, colourless, transparent, hexagonal plates having a pearly lustre, and resembling crystals of stilbite. They were flexible like crystallised gypsum, with an easy cleavage parallel to the principal face. They were too small for measurement, but their form was incompatible with the monometric system, and, from the more recent researches of Pasteur, it seems probable that they were derived from the monoclinic.

This peculiar form of arsenious acid has not hitherto, as far as I am aware, been met with in nature. A considerable quantity of thin plates presenting all the characters described by Wöhler, was sent to me for examination by my friend Mr. James Mason, proprietor of the famous San Domingos Mines in Portugal, and they were found to consist of pure arsenious acid.

Some of these plates are over an inch in length; they are colourless, semi-transparent, of a pearly lustre, tough, flexible, and easily cleavable into thin laminæ; there are no perfect crystals, but a few of the plates present a hemitropy similar to that so well known in gypsum, and from this fact it may be fairly inferred that their form belongs to the same system of crystallisation. Their specific gravity at 60° Fah. 3.85; hardness 2.5. Under the microscope they depolarise polarised light.

In the state of crystals, this substance is with difficulty soluble in cold water, but on digesting an excess during four months with the aid of frequent agitation, the water took up 1 per cent. of its weight. When reduced to powder, it dissolved more rapidly, and in a few days the water had taken up 1.75 per cent. It is much more soluble in hot water, and a saturated

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solution, after cooling, retains 2·74 per cent.; a comparative experiment made with ordinary commercial arsenious acid gave 2·76 per cent.

At a low red heat it volatilizes without leaving any appreciable residue. This agrees with the result obtained by Wöhler, who concluded that the crystals did not contain arsenic in a higher degree of oxidation than arsenious acid. I also found, as he did, that it was impossible to reproduce the prismatic form, either by sublimation or by solution; the crystals obtained in these experiments being invariably regular octahedrons tetrahedrons.

The composition was ascertained by oxidising a given quantity, with nitric acid, and subsequently determining the weight of the arsenic acid produced by means of oxide of lead.

10 grains gave (mean of three experiments) 11·59 grains of arsenic acid, the calculated amount being 11·61 (As = 75 : O = 8).

As previously stated this substance was found in the mines of San Domingos, and the circumstances under which it seems to have been formed present peculiar interest.

The mine consists of a huge mass, of several millions of tons, of compact iron pyrites with a certain percentage of copper. It likewise contains small quantities of other minerals, and arsenic is invariably present. The following analysis represents the average composition of the ore:—

Sulphur	48·90
Arsenic	·47
Iron	43·55
Copper	3·10
Zinc	·35
Lead	·93
Lime	·20
Insoluble rock	·73
Moisture	·70
Oxygen and loss	1·07
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* In addition to the above, this pyrites yields traces of thallium, cobalt, nickel, manganese, silver, and gold, and also occasionally bismuth and antimony.

In the eastern part of the mine a considerable increase of temperature gives rise to the inference that spontaneous combustion has been going on for some years. This is attributed to the oxidation of the broken ore left in the old Roman Workings, which had remained full of water, from the time of their abandonment, until drained by the recent operations of Mr. Mason.

On the water being thus drawn off, the action produced by the exposure of the damp pyrites which had accumulated in the old mine, resulted in the chemical changes above referred to.

It is in crevices in the still hot ore that these crystals were found, lining the cavities. They seem therefore to have been produced in the same manner as those examined by Wöhler, but by a far slower process of sublimation, and on a much larger scale, which may account for the large size of the crystals.

With regard to the crystalline form, it may perhaps be ascribed to the influence of an atmosphere charged with sulphurous acid, which pervades that part of the mine. I propose making a series of experiments with a view of determining whether there is any truth in this conjecture, and of ascertaining to what extent the presence of sulphurous acid may modify the crystallisation of arsenious acid.
