

LVII.—*Magnesium Hydrosulphide Solution, and its Use in Chemical Cases as a Source of Hydrogen Sulphide.*

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THE introduction of magnesium hydrosulphide into the arts, as a means of recovery of the sulphur of soda-waste in the form of hydrogen sulphide, led us, in the summer of 1882, to employ it as a source of hydrogen sulphide in the laboratory. Artificially prepared *iron sulphide* yields hydrogen as well as hydrogen sulphide, and we wanted for our experiments hydrogen sulphide in the undiluted state. *Antimony sulphide* and boiling solution of hydrochloric acid form a very unsatisfactory source of the gas when this is wanted in a long-continued, steady stream. *Blende* from its usual admixed minerals is still more unsuitable.

We had tried *pyrrhotite*, probably never before used for this purpose, and found it work satisfactorily in place of artificial iron sulphide, especially with hydrochloric acid slightly warm and not too dilute. But all *pyrrhotite* that we could get from different parts of this country yielded at least small quantities of carbon dioxide from the calcite it contained, and the *pyrrhotite* in powder was too sensitive to dilute acid to allow of the calcite being dissolved out from it. Now there is, so far as we know, no means\* of removing carbon dioxide from hydrogen sulphide, since carbonates, even of the alkaline earths, are decomposed by hydrogen sulphide. It is not always, however, of consequence, even if the hydrogen sulphide is mixed with a little carbon dioxide, and we may recommend *pyrrhotite* as one source of arsenic-free hydrogen sulphide.

The well-known and important observation of J. and R. Otto that artificial iron sulphide when treated with an acid yields hydrogen arsenide along with the hydrogen sulphide, if either acid or iron sulphide contains arsenic, gives a special value to other sources of the gas not liable to this defect. From the experiments of R. Otto, it appears to be the free iron in the artificial iron sulphide which in presence of

\* With one exception, that is. The mixed gases may be separated by passing them through a *hot* solution of calcium or magnesium hydrosulphide, which will retain most, if not all, of the carbon dioxide. This method is useless for analytical purposes, because the hydrosulphides give off much additional hydrogen sulphide; and it is almost useless for getting pure hydrogen sulphide, because these hot washing-solutions are themselves a sufficient source of the gas without the aid of the *pyrrhotite*.

arsenic sulphide and acids generates the hydrogen arsenide. It was, therefore, to be expected that pyrrhotite would yield hydrogen sulphide free from arsenic even if the acid used contained it, and in some experiments we made under these conditions we failed to find the least trace of arsenic volatilised. However, magnesium hydrosulphide solution is not only a more convenient material than pyrrhotite from which to prepare hydrogen sulphide free from arsenic, but it is more unobjectionable, for we need not insist on the importance of having our reagents above suspicion, and accordingly of not going to possibly arseniferous materials, mineral or acid, for pure hydrogen sulphide. It may, perhaps, be the case, too, that pyrrhotite obtained in other countries will not prove such a convenient source as Japanese pyrrhotite. This pyrrhotite is, indeed, remarkable in containing no nickel, and only an infinitesimal amount of cobalt, and may be softer and more sensitive to acids than other pyrrhotites.

R. Otto recommends the use of calcium or barium sulphide with hydrochloric acid as a means of obtaining hydrogen sulphide free from arsenic; from such a source, however, it will of course hardly ever be free from carbon dioxide. He recommends the use of hydrochloric acid free from arsenic, although, as he points out, no hydrogen arsenide can in any case be formed. The sulphide is used in the solid state, and is so sensitive to the action of acids that, in order to get a sufficiently steady stream of gas, the acid must be supplied from a dropping-funnel. Magnesium hydrosulphide solution, however, is easier to procure and easier to use than the above sulphides, and moreover requires no addition of acid. In our opinion, it is very superior to them as a source of hydrogen sulphide.

#### *Preparation of Magnesium Hydrosulphide Solution.*

Hydrogen sulphide obtained from ordinary iron sulphide, and either sulphuric or hydrochloric acid, is passed into a large flask half or two-thirds full of water holding magnesia suspended. If the magnesia happens to be carbonated, as is usual in its commercial forms, this matters little, although freshly calcined magnesia is preferable, as being more easily dissolved. The proportion of magnesia to water must not be too great, one part of commercial impure oxide in ten parts of water being near the limit. An excess of magnesia seems to prevent the formation of such a concentrated solution as can be obtained when the proper quantity is not exceeded. The magnesia slowly dissolves in the stream of gas, much of which, it is hardly necessary to state, passes away unabsorbed. Where, therefore, as in most laboratories, hydrogen sulphide gas is in nearly constant use, the flask of magnesia may conveniently be interposed between the

generator and such solutions as require treatment with the gas. When the solution has been prepared, the flask can be corked to exclude air, or at once used if wanted. It may be preserved unchanged for any time by sealing over the cork with wax or paraffin. Magnesium hydrosulphide solution may also be prepared, of course, as in the magnesia method of sulphur recovery by the reaction between calcium sulphide and magnesium chloride; but for laboratory purposes such a method presents no advantages.

*Some Properties of Magnesium Hydrosulphide Solution.*

A solution found by us to contain 4.35 per cent. of magnesium, equal to 16.31 per cent. of magnesium hydrosulphide,  $\text{MgS}_2\text{H}_2$ , may serve to represent what will usually be obtained by proceeding as above directed. Its sp. gr. was 1.118 at 12°. Such a solution is capable of yielding 12 per cent. of hydrogen sulphide by weight, and readily in practice, 10 per cent., let us say, the amount varying according to circumstances.

The solution, when the impurities of the magnesia have settled down, is nearly colourless, its slight colour being due to polysulphide formed by the action of ferric oxide in the magnesia or of air. Exposed to the air, or heated to about 60° in a flask with delivery-tube, it gives off hydrogen sulphide. But exposure to air also results in oxidation of the hydrosulphide to polysulphide and thiosulphate. However, in a solution left at rest, oxidation is much impeded by the formation of a firm, colourless, transparent, amorphous film on the surface of the liquid, consisting apparently of magnesium hydroxide, but possibly of hydroxyhydrosulphide,  $\text{MgSH.OH}$ . The solution does not readily, if at all, absorb carbon dioxide from the atmosphere in the early stage of its decomposition.

With regard to the effect of heat, already mentioned, a temperature of 60—65° gives a steady evolution of hydrogen sulphide for some time, and this can be maintained for a considerable time longer by raising the temperature to 90—100°. As hydrogen sulphide escapes, magnesium hydroxide separates out in the solid state. These facts are now well known in connection with the process of sulphur-recovery. The poly- (penta- ?) sulphide that may be in solution is only very slightly decomposed even at a boiling heat, but in so far as it is, it yields hydrogen sulphide, solid sulphur, and magnesia. The yellow polysulphide is however readily decomposed by hydrogen sulphide, the products being magnesium hydrosulphide and sulphur. It is hardly necessary to add, that magnesium hydrosulphide will decompose with an acid, and may thus be made if desired to yield its hydrogen sulphide like calcium, barium, iron, and other sulphides.

*Employment of the Solution as a Source of Hydrogen Sulphide free from Arsenic.*

The mode of employing it will be obvious. The flask containing it, provided with a simple delivery-tube, and without washing-bottle, is to be heated, best on a water-bath, to the extent necessary to secure a steady stream of gas. It may often be an advantage to make the following arrangement:—Put the solution to be treated with the gas into a flask or bottle fitted with cork and gas-entry tube, and connect its tube with the delivery-tube of the generator. Keeping the test-flask slightly open, warm the generator until the air is entirely expelled from both flasks, and then close the test-flask tight. The generator being kept warm, the hydrogen sulphide may be sent over into the solution under treatment without waste and without access of air. The level of the liquid in the tube of the test-flask will guide the operator in heating the generator. The gas being unmixed with hydrogen will be absorbed much faster than it is commonly seen to be, and with such an arrangement some little attention is necessary or the solution may be carried over into the generator through the reabsorption of the gas by the magnesia, should this from any cause be allowed to cool a little.

The evolution of hydrogen sulphide from the magnesium salt by heat has advantages over that by the addition of acids to alkaline-earth and other sulphides; firstly, in being steady and under perfect control, and, secondly, in yielding the gas free from any other, active or inactive, except a little water-vapour, free from the spray which effervescence by acids causes, and in no need therefore of any washing.

When the magnesium solution has been used until nearly exhausted, it has only to be placed again, when cold, in a current of ordinary hydrogen sulphide to be restored nearly or fully to its first strength as a source of this gas. Magnesium hydroxide, carbonate, and polysulphide will all thus be reconverted to hydrosulphide, and only the little thiosulphate remain unchanged. After using many times, or after much accidental exposure to the air, the contents can be replaced with fresh magnesia and water with but little cost or trouble.

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