

X.—*The Physical Constitution of some Sulphide Solutions.*

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THE difficulty of ensuring the complete precipitation of certain "insoluble" metallic sulphides has long been known. There has, however, been little or no systematic examination of the solutions of "insoluble" sulphides. In the previous paper, it has been shown that such sulphide solutions, of not inconsiderable strength, may be very easily obtained. I may here briefly recapitulate the methods employed:—

1. The metallic solution is allowed to run into sulphuretted hydrogen water kept saturated by a stream of the gas. It may then be freed from uncombined sulphuretted hydrogen by a current of hydrogen, or dialysed to free it from salts.

2. The metallic hydrates are suspended in water and treated with sulphuretted hydrogen.

3. The metallic sulphides, in a freshly precipitated state, are suspended in water and treated with sulphuretted hydrogen.

These methods are used according as, in the particular case, one or other is most applicable. The solutions obtained have been shown in the previous paper to contain combined sulphuretted hydrogen, to be, in fact, solutions of hydrosulphides.

By the first method we may obtain the solution of any metallic sulphide provided no great excess of acid be present. The second method is not always applicable, but has been used by us in the case of copper and zinc. The third method is applicable to mercury or copper. To give a general idea of the strength of these solutions, the following facts may be mentioned. An arsenide acidified with hydrochloric acid, if allowed to run into sulphuretted hydrogen water, will readily give a solution containing about 5 grams of sulphide in the litre, whilst in the case of mercuric sulphide, a solution containing about 10 grams of sulphide to the litre is readily obtainable. The question naturally suggests itself, Are these apparent solutions actually solutions, or do they merely contain the solid in a very fine state of suspension? When fairly dilute and free from salts, some of the sulphides show no symptoms of settling, even after several months. But the addition of salts or acid will often ensure rapid precipitation. On the other hand, the re-solubility of some of the sulphides after precipitation closely simulates true solution; for instance, on treating mercuric sulphide with sulphuretted hydrogen water, the sulphide redissolves. It is, at first sight, difficult to believe that the sulphuretted hydrogen should have power to cause very fine

division and suspension of the sulphide, but be unable to produce perfect solution.

Questions like these made it seem advisable to undertake a thorough investigation into the physical character of these solutions, which promised results of no little interest.

The solutions chosen for examination were those of mercury, arsenic, and antimony sulphides.

In general terms, the results obtained are as follows :—In the three cases under examination, the fact has been established that they are composed entirely of very minute, solid particles or of very large molecular aggregates. In all cases the particles are large enough to give results with Tyndall's experiment with a beam of light. They are, however, small enough in some cases to simulate the phenomena of liquid diffusion (in the absence of any membrane). They afford a series proceeding from what is more easily proved to be pseudo-solution to matter in a state which more strikingly simulates that of true solution. At one end of the series, we have pseudo-solutions, resolvable under a high power of the microscope into crowds of minute suspended particles in rapid Brownian movement; at the other end, we have solutions which refuse to be analysed by the microscope, which diffuse more or less after the fashion of true solutions, but which, even in exceedingly dilute solutions, reveal the presence of particles not too minute to scatter a beam of light.

These being, broadly, the results obtained, I will now proceed to give the experimental evidence, arranging it in such a way as to pass from more obvious pseudo-solution to what is more nearly allied to true solution as we are accustomed to conceive of it.

Mercury.

Preparation.—The sulphide precipitate may be prepared either in the ordinary way or by allowing an acidified solution of mercuric chloride to flow into sulphuretted hydrogen water. The carefully-washed precipitate is then washed into a Drechsel's bottle provided with stopcocks to prevent access of air, and there treated with sulphuretted hydrogen. In from one to two hours, the sulphide will have completely dissolved. The dissolved sulphuretted hydrogen may then be expelled by a current of pure hydrogen.

General Properties.—Solutions containing about 10 grams of sulphide to the litre may be readily obtained *free from uncombined sulphuretted hydrogen*. Stronger solutions are obtainable in presence of dissolved sulphuretted hydrogen. By transmitted light, the solution has a very clear, brown colour, which in strong solutions becomes so dark as only to be transparent in thin layers. By reflected light, the

solution appears darker and somewhat turbid. When kept in absence of dissolved sulphuretted hydrogen, the upper part of the liquid in the course of five or six days becomes somewhat paler. The lower portions of the liquid grow denser and darker, and after some weeks the whole of the sulphide is slowly deposited as a precipitate. But though, as a final result, we have a precipitate formed, this is no adequate proof that in the freshly prepared solution we are not dealing with a true solution. In presence of sulphuretted hydrogen, the conditions are different; the behaviour of the sulphide under these circumstances is being investigated.

On the addition of salts, the sulphide is more or less rapidly precipitated.

Application of Raoult's Method.—It was thought that if there were true solution, some light might be thrown upon the molecular complexity of the dissolved hydrosulphide by the application of Raoult's method for determining molecular weights. No depression of the freezing point could, however, be detected, and, after freezing, a considerable quantity of the dissolved hydrosulphide remained precipitated. It is obvious that the failure to observe any depression might simply be due to very high molecular weight.

Microscopical Examination.—The most direct evidence on the subject would obviously be that of rendering the suspended particles, if such there be, visible to the eye. The first trials were made with a microscope having a magnifying power of about 600 diameters. From the result, I was at first led to suspect that a true solution was being dealt with. The clear field was not in any way resolvable. It seemed perfectly homogeneous. Owing, however, to some circumstances which once more suggested that the sulphides did not, in the ordinary sense, form perfect solutions, I decided to repeat the microscopical examination, using a higher magnifying power. A microscope, with an immersion lens and capable of magnifying about 1000 diameters, was kindly lent me by Professor E. A. Schäfer. The mercury solution was first examined with a power of about 800 diameters, the lens being immersed in the liquid. Sulphuretted hydrogen was in this case absent. The following is a description of what is seen. At first it is impossible to make out anything beyond a dimly granular appearance; but gradually one becomes aware of exceedingly minute particles in very rapid Brownian movement. The apparently homogeneous solution is really the scene of ceaseless oscillations of innumerable solid particles, crowded together so closely that very little free path is left. Indeed, this last fact is the probable explanation of their being seen at all. In a dilute solution, the motion most likely becomes so rapid as to render the particles invisible.

The presence of minute, vibrating particles in this apparently homogeneous solution is thus placed beyond dispute, but it is still quite conceivable that these particles are suspended in a certain amount of true solution. Other methods for ascertaining whether or not any true solution is present suggested themselves, but were not readily applicable to the case of mercury. Thus, for example, the diffusibility of the solution could not well be tried, owing to the fact that the mercury solution does not keep well in absence of sulphuretted hydrogen. These methods will be described under arsenic and antimony. Meanwhile, the result of two other experiments on the mercury solution may be mentioned.

Filtration through a Porous Cell.—A small porous cell was carefully washed till all traces of impurity had been got rid of. After closing the mouth of the cell by a caoutchouc cork, it was partially immersed in a mercuric sulphide solution and a vacuum created within the cell by means of a filter-pump. The liquid slowly filtered through, but was quite colourless, the sulphide being completely removed.

Spectroscopical Examination.—Observed in thin layers, the solution gave a continuous absorption in the violet and blue, no bands being observable.

Arsenic (α) and (β).

In the case of arsenic, it will be well to divide the subject into two sections, one of which will be discussed before, and the other after, antimony. Under the present heading, Arsenic (α), I shall set down the results obtained with two different arsenic solutions. One solution was obtained by dissolving arsenious acid in a solution of hydrogen potassium tartrate; the other was obtained from an acidified arsenite. When required free from salts, these solutions were subjected to dialysis.

α .—Arsenical Tartrate Solution.

Preparation.—Arsenious acid was dissolved by boiling with acid potassium tartrate. The solution thus obtained was diluted and allowed to run into sulphuretted hydrogen water. The liquid was then freed from uncombined sulphuretted hydrogen by a current of hydrogen.

General Properties.—Solutions containing about 5 grams of sulphide to the litre can be obtained; these, by transmitted light, have a clear yellow colour, becoming darker and slightly reddish in a strong solution. The solutions are strongly fluorescent, and by reflected light, look pale and turbid.

Weak solutions keep well, but the stronger ones deposit a small

amount of precipitate after some months. The presence of sulphuretted hydrogen does not seem to affect this slight precipitation.

The solution may be boiled without producing precipitation. On long-continued boiling, however, the sulphide seems to be partially decomposed, though the solution is not precipitated (see previous paper).

Microscopical Examination.—In the case of this arsenic solution, it was more difficult to discern the presence of particles than with mercury. The full power of 1000 diameters was barely sufficient to resolve the solution into its constituent particles; these were exceedingly minute, but even with this power, it needed practice to discern them. A granular appearance could gradually be made out, and it then became apparent that the granules were endowed with a rapid dancing motion.

Diffusion Experiment.—No exact diffusion experiment was made in this case, but it was observed that the tartrate had the power of carrying out the arsenic particles by its own diffusion. The diffusion of the tartrate being due to its molecular motion, the bombardment of these molecules must have sufficed to move the sulphide particles.

Spectroscopical Examination.—The solution gave a continuous absorption in the violet and blue.

β.—Solution obtained from an Acidified Arsenite.

Preparation.—Arsenious acid was dissolved in caustic soda, and the solution allowed to flow into sulphuretted hydrogen water. The solution was dialysed to free it from salts.

General Properties.—In general appearance, &c., this solution is similar to that just described. A solution containing 5 grams of sulphide to the litre can readily be obtained. The solution, freed from salts, keeps distinctly better than the one described above; a bottle in my possession, closed with an ordinary stopper and thus somewhat liable to oxidation, has been kept for a year; it has deposited some precipitate, but the amount is small, and when last examined, the solution *still remained unresolvable by the microscope*. Salts, as usual, cause precipitation.

Microscopical Examination.—It has at present proved impossible to resolve this solution with the microscope. It presents the appearance of a perfectly homogeneous liquid.

Diffusion Experiments.—The diffusion experiments gave interesting results. The diffusion method is obviously of great use in determining whether the solutions are composed only in part or wholly of suspended solid. It was quite conceivable that the particles discerned in certain cases with the microscope only formed part of the whole

sulphide present, and that the rest was actually in true solution. To attack this question, the following consideration was made use of. It was thought possible that whilst a true solution would be undoubtedly diffusible, suspended particles might very likely not diffuse. In the event of there being no diffusion, it was obviously proved that the *whole* of the sulphide present was in a state of suspension.

Graham's method for liquid diffusion was adopted, the liquid being placed in a small wide-mouthed bottle within a large beaker and covered with water. A solution of arsenic hydrosulphide, obtained by allowing an arsenite acid with hydrochloric acid to run into sulphuretted hydrogen water, was dialysed until free from all chlorides and sulphuretted hydrogen. It remained quite clear by transmitted light. The small bottle was filled with this solution, and closed with a glass plate attached to a glass rod. Water was then poured into the beaker, and siphoned out to remove traces of sulphide which had escaped in closing the bottle. Finally, the beaker was well filled above the level of the small bottle, and the glass plate carefully removed. After 32 days, there was absolutely no sign of diffusion; the outer water remained perfectly colourless, and contained no trace of arsenic. It is evident from this experiment that the *whole* of the sulphide is present in a state of suspension. No tendency to settle was exhibited by the suspended solid. It is noteworthy that these minute solid particles, though in rapid vibratory motion, are incapable of diffusion, and it is difficult to say exactly why they should not diffuse. It might be expected that a particle at the surface, finding its movement less hindered in one direction than the other, would pass beyond the general surface of the other particles. Yet this is not the case.

Antimony.

The only antimony solution obtainable is that resulting from the action of sulphuretted hydrogen on a solution of tartar emetic.

Preparation.—A moderately dilute solution of tartar emetic is allowed to flow into saturated sulphuretted hydrogen water.

General Properties.—The solution has a fine orange-red colour by transmitted light, and is only slightly fluorescent. It keeps well, but has a tendency to deposit small quantities of sulphide. The sulphide is not precipitated by boiling.

Microscopical Examination.—In this case again, it was impossible to ascertain the presence of particles by microscopical examination. The liquid appeared absolutely clear and homogeneous. Some of the tartrate solution was set dialysing on December 1, 1890. As the dialysis proceeded the solution was observed to become more strongly fluorescent. Renewed treatment of a portion of the liquid with

sulphuretted hydrogen did not in any way diminish this fluorescence. On December 11, some of the liquid was examined microscopically, and it was now possible to discern the presence of excessively minute particles of about the same dimensions as those observable with the arsenical tartrate solution. On further dialysis, by which means all the tartrate present was eliminated, the antimony began to precipitate, and in the course of a few weeks was completely thrown down. This is interesting, as showing the progress of a gradual condensation occurring among the minute particles. There was no sudden or irregular change, but, apparently, a regular increase of size among all the particles, forcibly reminding us of molecular condensation. In what way the tartrate prevents this condensation, it is difficult to say.

Diffusion Experiment.—The method of diffusion was again used successfully to answer the question as to how this solution is constituted. But, as in this case the antimony solution cannot be obtained in absence of tartrate, it was necessary to use the device of having the same strength of tartrate both within and without the diffusing bottle. This was accordingly done. Some of the antimony solution was allowed to diffuse into tartrate of the same strength from June 5 to June 29. During this time no diffusion occurred. This settles the question as regards the antimony solution, and proves that it is not a true solution. Subsequently it was thought that perhaps the particles might be smaller and more capable of diffusion when much diluted. A very dilute antimony solution was set diffusing on July 27, 1891. By October, absolutely no diffusion had occurred; indeed the liquid had settled somewhat in the bottle, owing perhaps to the dilution of the acid tartrate present.

When the outer liquid does not contain tartrate, diffusion is at once observed.

Tyndall's Experiment.—Tyndall has shown that light, scattered by finely-divided particles, is completely polarised.

Some of the antimony solution was sealed in a tube, and a beam of light from a lime-light lantern passed through the liquid. The rounded extremity of the tube acts as a concentrating lens, and enables the path of any beam to be very clearly traced. In this case, the track of the beam was marked by a beautiful, soft, red glow, the light of which, on examination with a Nicol's prism, was found to be completely polarised. The solution, therefore, has no true fluorescence, but consists of excessively minute particles in suspension. The most dilute antimony solutions gave similar results.* The distilled water employed showed practically no beam.

Filtration through a Porous Cell.—A porous cell was kept exhausted

* Applied to the mercury sulphide solution above discussed, this experiment, as might be expected, yields similar results.

by a filter-pump and plunged into the freshly-prepared clear, red antimony solution. The liquid filtered through was quite colourless. This experiment tends to support the belief that the whole of the antimony is present in suspension.

Coagulation Experiment.—As another means of testing the condition of the dissolved sulphide, that of its sudden coagulation was used. A true solution so coagulated should develop heat. Careful experiments were made on coagulating a strong antimony solution with a few drops of calcium chloride. Not the smallest change of temperature could be observed, although a change of 0.02° could have been easily seen with the thermometer used.

Spectroscopical Examination.—Like all the other sulphide solutions examined, this liquid gave a continuous absorption in the violet and blue.

Arsenic (γ).

In this case, the solutions were obtained from pure arsenious acid dissolved in water. The acid was dissolved by continuous boiling, and, under these conditions, a strong solution may be obtained.

Preparation.—The arsenious acid was allowed to flow into saturated sulphuretted hydrogen water, through which a current of the gas was continually passing. The uncombined sulphuretted hydrogen was then removed by a current of hydrogen.

General Properties.—In appearance this solution resembles arsenic (α) and (β). It readily forms solutions containing 11 or 12 grams of sulphide to the litre. A strong solution kept for four months in a sealed bulb has deposited a mere trace of precipitate. Weak solutions, kept for the same time, are almost entirely unchanged. But the permanence of the solution is somewhat variable. Though clear by transmitted light, the strong solutions have by reflected light a densely milky appearance.

The solution is not precipitated by boiling, but the addition of certain salts rapidly effects precipitation. Calcium chloride is here again specially potent.

Microscopical Examination.—The microscope, as might be expected from the case of arsenic (β), affords no evidence of the existence of solid particles.

Diffusion Experiments.—On account of the results invariably obtained in other cases, it seemed hardly worth while to submit this solution to the diffusion test. However, I decided to perform the experiment. The same apparatus was used as in the case of arsenic (β). To my surprise, by the following day, distinct diffusion was observed. It seemed just possible that the diffusion might be due to some impurity. Another specimen of resublimed arsenious oxide was therefore used, and, after treatment with sulphuretted

hydrogen, was very carefully freed from uncombined gas by a current of hydrogen. This specimen, however, again diffused markedly in the course of a few days.

It occurred to me that perhaps some small quantity of true solution might be at first formed which would disappear on keeping. To give time for further condensation, some of the sulphide solution prepared as above described was accordingly sealed up in a glass bulb at the end of July. On October 14, the bulb was opened and some of the liquid placed in the small diffusion bottle. This was then closed with a glass plate in the usual way, covered with distilled water, and left covered till next day to acquire the temperature of the room. On October 15, the diffusion bottle was uncovered at 1 o'clock, the outer liquid being left quite colourless. By the next day, marked diffusion had occurred, which day by day increased. It had been previously observed that on prolonged diffusion with exposure to air, the sulphide solution becomes altered, arsenious acid being found in the outer liquid. In the present case, therefore, the diffusion was stopped on October 26, by which time the outer liquid was deeply coloured. The diffusion is of course slow, but to give some rough idea of its rate the following numbers are given. The diffusion in this case occupied 11 days. The main object of the experiment was to ascertain whether a weighable quantity would diffuse.

Capacity of small bottle.	As_2S_3 in bottle.	Volume of outer liquid.	As_2S_3 in outer liquid.	Diameter of bottle.
77 c.c.	0.8210 gram.	350 c.c.	0.1185 gram.	30 mm.

The diffusion of a dichromate solution of similar strength would be completed in five or six days.

We have here the rather remarkable fact of particles so small as to diffuse after the fashion of the molecules of a liquid, yet revealing themselves as solid particles under the scrutiny of other tests. That the diffusion is due to the motion of the particles themselves, and not to that of the water molecules, is made quite clear from the previous diffusion experiments. For instance, with antimony it was found that diffusible substance (acid potassium tartrate) could carry out the sulphide when present in the little bottle alone, but not when present in equal strength throughout both liquids.

Tyndall's Experiment.—On sending a beam of lime-light through the diffusible arsenic solution, the track of the beam was marked by a soft, yellow glow, the light of which, when examined by a Nicol's prism, was found to be completely polarised. This is proof positive of the existence of solid particles, but how is the presence of any true solution to be disproved? Analogy forcibly suggests that this solu-

tion will resemble the others in being homogeneous rather than partly solution and partly suspended solid. But something more than this is needed.

Obviously, if there be any true solution, it is this which will be *first* formed on allowing the arsenious acid to flow slowly into sulphur-*et*ted hydrogen water. Hence, if a very dilute solution be thus carefully prepared, there should be no particles present capable of revealing themselves in a beam of light. Accordingly, some dilute arsenious acid solution was allowed to flow very slowly into sulphur-*et*ted hydrogen water. An exceedingly dilute sulphide solution of a faint yellow colour was thus obtained.* When examined with a beam, the track of the light was, however, still marked by a soft glow of polarised light. This seems to leave little room for doubt that the diffusible sulphide solution is entirely composed of particles sufficiently large to scatter light. The fact that after long keeping the sulphide still retains its diffusibility also forcibly suggests that the diffusibility is not due to the presence of a little true solution at first formed. It is inconceivable that a solution so unstable as to be partially precipitated even in exceedingly dilute solutions when first formed could remain unchanged for months in the presence of a comparatively vast amount of solid.

Coagulation Experiment.—It was thought that perhaps some evidence as to the state of the sulphide might be obtained from sudden coagulation of the liquid. Careful experiments were made by coagulation with a few drops of calcium chloride, but not the slightest change of temperature was discernible.

Application of Raoult's Method.—No perceptible depression of the freezing point was obtained.

Some General Properties of the Sulphide Solutions.

It has already been observed that these solutions are precipitated by salts or acids. But these bodies are by no means equally active in producing precipitation. The following substances were added to an arsenic solution [arsenic (β)] with the results stated.

Precipitate (but sometimes only when strong).	Do not precipitate.
Calcium chloride (at once).	Sodium borate.
Sodium chloride.	Sodium acetate.
Ammonium chloride	Ammonium succinate.
Chrome alum.	Gallic acid.
Sodium phosphomolybdate.	Alcohol.
Sodium phosphate.	

* These dilute arsenious sulphide solutions are beautifully clear and transparent, and by their appearance suggest that they are perfect solutions.

On freezing the solutions completely, almost the whole of the sulphide is precipitated. The similarity of the absorption spectra has been already noted.

On evaporation in a vacuum, mercury and arsenic sulphides yield a colloidal mass.

Summary.

The sulphide solutions examined have been shown to consist entirely of very minute solid particles in each case revealed by Tyndall's experiment.

In two cases, mercury and arsenic (α), these particles have been found to be visible with a powerful microscope, and have been observed to be, as nearly as could be determined, of the same size and all in rapid vibratory motion. In one case, that of antimony, the gradual condensation of the particles from those quite invisible under the microscope to those just visible, but of uniform size, and finally to larger aggregations ultimately settling as precipitate, has been followed.

In the case of arsenic (γ), these particles are so fine'y divided, or vibrate so rapidly as to simulate the behaviour of molecules composing a liquid. They are capable of diffusion, and retain this power even after prolonged keeping.

The obvious theoretical suggestions of these experiments I propose to deal with in the next paper, in which a number of observations on colloid solutions will be recorded. In closing, however, it may be pointed out that while sulphuretted hydrogen can split up mercuric sulphide into minute vibrated particles in a state of very perfect suspension, and arsenic sulphide is capable of existing in a state of suspension so perfect as to simulate the phenomena of liquid diffusion, but yet revealing solid particles by Tyndall's experiment, it is easy to conceive of a case in which the process of subdivision has gone still further, and Tyndall's experiment is no longer adequate to discover the suspended particles. Passing on from this, there seems no satisfactory reason for imagining the existence of any sharp boundary between solution and pseudo-solution. It is quite possible that the one merges by imperceptible gradations into the other. In this event, the vibratory motion of these minute particles, which so forcibly reminds one of molecular motion, becomes a phenomenon of special interest. This subject will be more conveniently dealt with in the following paper.

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