

- Hagen. Berl. Akad., 78, 1845.  
 Hannay, J. B. Proc. Roy. Soc. Edin., 437, 1905.  
 Kohlrausch, F. Ann. phys., 20, 798 (1906); 22, 191 (1907).  
 Lebaigue. J. pharm. chim., 7, 87 (1868).  
 Leduc and Larcodote. J. phys., 1, 364 and 716 (1902).  
 C. r., 134, 589; 135, 95 and 732 (1902).  
 Lohnstein, F. Ann. phys., 20, 237 and 606; 21, 1030 (1906); 22, 737 (1907).  
 Mathieu. J. phys. [2], 3, 203 (1884).  
 Ollivier. Ann. chim. phys., 8th ser., 10, 229 (1907).  
 Rayleigh. Phil. Mag., 5th ser., 20, 321 (1899).  
 Rosset. Bull. soc. chim., 23, 245 (1900).  
 Tate, T. Phil. Mag., 27, 176 (1864).  
 Traube. J. pr. Chem. [2], 34, 292 and 515 (1886).  
 Ber., 19, 874 (1886).  
 Volkman, P. Ann. physik. (2), 11, 206.  
 Worthington. Proc. Roy. Soc., 32, 362 (1881).  
 Phil. Mag., 5th ser., 18, 461 (1884); 19, 46 (1885); 20, 51 (1885).

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## THE ACTION OF HYDROGEN SULPHIDE ON ALKALINE SOLUTIONS OF ZINC SALTS.

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The fact that the zinc sulphide, or the zinc hydrosulphide, precipitated from alkaline solutions of zinc salts by sodium or potassium hydrosulphide is soluble in an excess of these reagents, and that the zinc sulphide, or zinc hydrosulphide, precipitated from alkaline solutions of the metal by hydrogen sulphide dissolves when the gas is permitted to act on the solutions for some time, appears to have escaped the notice of the analytical chemists.<sup>1</sup> At all events, in no work on analytical chemistry to which I have access is this remarkable behavior of zinc sulphide referred to. The solution of the zinc sulphide is a colloidal one, for the zinc in it will not pass through parchment paper. The zinc sulphide, or zinc hydrosulphide, acts towards sodium and potassium hydrosulphides in much the same way that zinc oxide, or zinc hydroxide, acts towards sodium and potassium hydroxides. The analogy between the two reactions almost compels one to conclude that the change takes place in the sense of the equation:



If, however, an alkali sulphozincate is actually formed, it must be very unstable, for concentrated solutions of mineral salts, when added to its solution, precipitate only zinc sulphide, or possibly zinc hydrosulphide:

<sup>1</sup> I noticed this peculiar behavior of zinc sulphide some three or four years ago and supposed that my observation was a new one. I found, however, that the reaction was first observed by Julius Thomsen in 1878 (Ber., 11, 2044) and subsequently examined by A. Villiers (Compt. rend., 120, 97). Lottermoser (Saulung chem. u. tech. Vorträge, VI) und Winsinger (Bull. de l'Acad. des Sciences de Bruxelles, [2], 14, 321) also refer to it.

and then too the zinc sulphide separates out gradually, and in a slimy condition, when the solution is allowed to stand.

In many books on qualitative analysis the student is directed to separate manganese from zinc by adding to the solution of their chlorides an excess of sodium or potassium hydroxide. Now if the alkaline solution of the zinc, after its separation from the manganous hydroxide, be treated for 15–20 minutes with a rapid current of hydrogen sulphide the zinc sulphide which is first precipitated may dissolve. The smaller the amounts of zinc and sodium chloride present in the solution, and the more rapid the current of gas, the more readily does the zinc sulphide formed pass into solution. Should a student pass a rapid current of hydrogen sulphide into such a solution, and then leave the spot and not return until after the lapse of some 15–20 minutes, the chances are he will find the solution clear, or nearly so, and report no zinc. I have convinced myself by a number of experiments that there is, in a case of this sort, considerable danger of overlooking the zinc. It is a significant fact that Fresenius<sup>1</sup> uses hydrogen sulphide water in order to test for the zinc in the alkaline solution. He is also careful to state that an excess of the reagent is to be avoided. However, in describing the special reactions of zinc<sup>2</sup> he states that hydrogen sulphide precipitates from alkaline solutions all the zinc in the form of the hydrated sulphide. Nothing is said about an excess of the reagent, although he does mention the fact that ammonium chloride greatly promotes the separation of the precipitate.

In the following experiments I used a sodium hydroxide solution of zinc oxide containing 8 grams of the oxide in a liter:

1. Ten cc. of the solution were diluted to 150 cc. and treated with a rapid current of hydrogen sulphide. The zinc sulphide was precipitated almost immediately, but at the end of 15 minutes it had passed into solution.

2. To 10 cc. of the solution, made faintly acid with hydrochloric acid, a few drops of a concentrated solution of manganous sulphate were added and the metals precipitated as sulphides with yellow ammonium sulphide. After filtering, dissolving the precipitate in a small amount of very dilute hydrochloric acid, and separating the manganese with excess of sodium hydroxide the alkaline filtrate was diluted to about 150 cc. and treated with a rapid current of hydrogen sulphide. In 15 minutes the zinc sulphide had dissolved and the solution was clear.

3. The experiment was repeated with a solution containing the same amount of zinc oxide along with considerable amounts of manganese, cobalt and nickel. The alkaline solution of the zinc oxide, however, behaved toward the sulphuretted hydrogen gas exactly as it did in 1 and 2.

<sup>1</sup> Anleitung z. qualit. chem. Analyse, 1874, 291.

<sup>2</sup> *Loc. cit.*, p. 137.

On standing, all three solutions became turbid, owing to a gradual separation of the zinc sulphide.

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## THE DETERMINATION OF ANTIMONY AND ARSENIC IN LEAD-ANTIMONY ALLOYS.

BY GEORGE M. HOWARD.

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The separation and determination of antimony and arsenic in alloys with anything like commercial rapidity, and at the same time with a fair degree of accuracy, is by no means a simple matter. The apparent lack of satisfactory published methods led to the development several years ago of the method here described, which, while involving nothing radically new, has proved very serviceable in the author's laboratory.

One great advantage of this method is that tin does not interfere and does not have to be removed, which makes it available for type metal, etc. Iron and copper in small amounts are also without effect, and in fact there seems to be nothing at all likely to be present which interferes. The method is applicable also to many other cases besides lead-antimony alloys—as for instance to the mixed sulphides of antimony and arsenic obtained in many analyses. Some operators object seriously to any method involving the use of hydrogen sulphide, but if the details of manipulation here given are followed there will be no inconvenience whatever from that source.

The procedure is as follows:

The sample in fine filings, 0.5 to 2 grams according to circumstances, is weighed into a 125 cc. Erlenmeyer flask, 60–70 cc. of strong hydrochloric acid added, and two or three drops (not more) of nitric acid (1.4). The flask is then placed on a hot plate where it will be just short of boiling until solution is complete. Frequent agitation considerably hastens the action. It is sometimes necessary to make further additions of nitric acid, but this should be done carefully and an excess avoided. When the metal is all dissolved (10–20 minutes) the flask should be moved where it will boil vigorously for a few minutes until the color changes from reddish yellow to colorless—or, if iron or copper is present, to straw yellow. Now, while still hot, hydrogen sulphide is passed into the solution until it is completely saturated—15 minutes is usually sufficient. If insufficient hydrochloric acid has been used, or the solution has been boiled so long on the plate that much has been lost, antimony sulphide will be precipitated as the solution cools. The hydrogen sulphide treatment is most conveniently handled by fitting the flasks with two-hole