Experiments upon the decomposition of Sulphide of Arsenic by water

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The method of precipitating arsenious acid with sulphydric acid which is described in Johnsons edition of Fresenius p 253 may lead to incorrect results when a temperature higher than 45° Centigrade is attained during the expulsion of the excess of sulphydric acid by means of carbonic acid in consequence of the ready decomposition of the sulphide of arsenic when heated with water and the statement made by Fresenius p 138 that the sulphide of arsenic boiled with water undergoes a very trifling decomposition is scarcely correct as will be seen from the following experiments

Three grammes of pure arsenious acid As_2O_3 were dissolved in a solution containing 12 grammes of pure Carbonate of Sodium $NaCO_3$ the solution made acid with HCL and diluted to the bulk of a litre

This solution was then divided into 20 parts of 50 CC each each containing 0.150 gramme of arsenious acid. Two of these 50 C.C. solutions were taken and Sulphydric acid gas H_2S was passed through them for 40 minutes at the end of which time complete saturation had ensued During the process of saturation the solutions were warmed as in all the succeeding experiments on a steam chest to a temperature of 55°C the conditions which seemed most favorable to the prevention of the separation of free sulphur. The solutions were allowed to stand thus for four hours some of the clear solution was then poured off into a test tube and H_2S. passed through it in order to demonstrate the complete precipitation of the tersulphide As_2S_3. The solutions A and B were then boiled to expel the H_2S. no further trace of H_2S being obtained with lead paper after two and a half hours Solution A was then filtered and the As_2S_3 determined by drying at 100° and weighing upon a tared filter

Of the arsenious acid was recovered 55.80 per cent

The filtrate was then resaturated with H_2S as before the reprecipitated As_2S_3 washed by decantation caught upon a weighed filter and determined per cent obtained = 44.49 which added to the previous per cent gives 100.29 per cent In order to ascertain the effect of long continued boiling solution B was boiled an additional two and a half hours making in all five hours the As_2S_3 filtered off and determined as before amount obtained = 19.057 per cent

The As_2S_3 was then determined in the filtrate and found to be 80.94 per cent the sum of which is 99.997 per cent

To ascertain whether the sulphide by long standing in the water is at all acted upon and also whether it dissolves as sulphide or is decomposed ~~as~~ into sulphydric acid and arsenious acid two distinct experiments were made

Two solutions containing one part by weight of arsenious acid to 1500 parts of water were treated with H_2S and after complete saturation were left for three weeks at a temperature of 20 °C at the end of which time the As_2S_3 was filtered off and H_2S passed through the filtrate

As_2S_3 was recovered in the one case to the extent of 2.07 per cent in the other 2.28

The clear liquid standing above the precipitated sulphide was tested after four hours and again after three days but it gave no precipitate with sulphydric acid

To decide the second question As_2S_3 was precipitated from a solution and the H_2S removed by passing carbonic acid through it the solution being in a boiling condition at the time This was continued for one hour after all trace of the H_2S had disappeared

The precipitate was then allowed to settle and thoroughly washed by decantation with hot water

It was then transferred to a flask from whence a delivery tube was carried to a second flask containing a very dilute solution of Acetate of lead and immersed in a basin of cold water

The contents of the first flask were then heated to boiling the vapors escaping by the delivery tube into flask no 2

In 35 minutes a black coloration of the liquid which in a short time showed a visible precipitate of sulphide of lead clearly demonstrated the presence of H_2S resulting from the decomposition of the As_2S_3

The extent of the decomposition of As_2S_3 in water depends upon three things

1st the relative proportion of As_2S_3 to the water

2nd the temperature at which the H_2S is driven off

and 3rd the length of time the As_2S_3 is exposed to the action of the water at this temperature

In the following experiments the ratio of As_2S_3 to H_2O was 1:1500

Various temperatures were taken between 20°C and 100°C and it will be seen how the solubility varies accordingly

The temperature was in every case maintained until the H_2S was entirely expelled which time varies of course with the temperature being shorter for higher temperatures

The solution itself and not its vapours was always tested with acetate of lead to ascertain when the expulsion of the H_2S was complete

The expulsion was expedited in every instance by the passage through the solution of a rapid current of Carbonic acid gas

In each case after precipitation the solution was left standing for several hours then tested in order to make certain that the precipitation was complete

After the expulsion of the H_2S by CO_2 the $As S_3$ was filtered off immediately and washed The arsenic which had passed into the filtrate was precipitated ~~A~~ & by a further passage of H_2S the excess of which was removed by CO_2 at the normal temperature of the laboratory This As_2S_3 was dried at 100° and weighed on a tared filter the second filtrate was tested to render certain that no As_2S_3

had been decomposed and gone into solution during the second precipitation The following table shows the temperature at which the As_2S_3 was treated the amount decomposed and the length of time required to get rid of the H_2S

Temperature	per cent of As_2S_3 decomposed	Time required for expulsion of H_2S
20°C	none decomposed	5½ hours
25°C	" "	5 "
30°C	" "	4¾ "
35°C	the merest trace	4½ "
40°C	0.32 0.25 per cent	4 "
45°C	~~5.42~~ 2.09 2.46	3¾ "
58°C	5.42 6.01	3¾ "
65°C	8.47 8.85	3¾
73°C	11.98 11 83	3½ "
87°C	17.49 17.09	3¼ "
94°C	21.66 21.36	3 "
105°C	23.49 24.07	2½ "

Two analyses were made in each case for the sake of comparison

The above table shows that temperatures above 35-0C the As_2S_3 is decomposed and loss occurs unless the As_2S_3 be recovered from the filtrate while at and below 35^{0}C the As_2S_3 is practically insoluble and undecomposable during the limited period required for the expulsion of the H_2S

The effect of the CO_2 on the As_2S_3 seems to be favorable that is to say more of the As_2S_3 is decomposed in a hot solution free from CO_2 than in one through which CO_2 is being passed

In several experiments this difference varies from 5-8 per cent according to temperature duration etc. There seems to be another method for getting rid of the excess of H_2S which commends itself namely washing by decantation. It has much advantage as regards time over the carbonic acid method and seems to insure equally accurate results. A number of analyses conducted by this method ranged from 99.92 ~~to~~ to 100.01. Care should be taken that the solution be warmed to about 60^{c} when the precipitate settles down leaving a clear solution above and admits of being easily washed by decantation. The wash water should only be slightly warmed