

(2 g.) allows a detection of 1 mg. of HCN; while 50 cc. of a 4% solution of $K_4Fe(CN)_6$, (*i. e.*, 2 g.) will likewise permit a detection of 0.5 mg. of HCN. In the presence of small quantities of the above cyanogen compounds the test is reliable to 0.1 mg. of HCN.

In the presence of smaller amounts of ferro- or ferricyanides the test becomes correspondingly more delicate. When the test is applied to solutions containing much ferricyanide, one should add as much copper solution to a blank, containing approximately the same amount of ferricyanide, as to the solution being tested for cyanide and the difference in shade should be noted, or the quantities of copper solution necessary to give a certain depth of color should be compared.

For the average requirements of qualitative analysis, tenth-normal copper sulfate solution will suffice.

Inasmuch as the test gives a decided reaction for relatively small amounts of cyanides, and also furnishes an indication of the relative amount present in the solution examined, as well as being applicable in presence of other cyanides, this test is proposed for general qualitative purposes.

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A NEW PROCEDURE FOR THE SEPARATION OF THE COPPER AND TIN GROUPS.

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Despite the many shortcomings of the ammonium polysulfide method for the separation of the copper and tin groups, no procedure has ever been devised whereby a sharp separation of these groups from each other might be obtained. The objections to the ammonium polysulfide method, as shown by the work of A. A. Noyes,¹ are as follows:

1. Ammonium polysulfide dissolves some copper sulfide² and mercuric sulfide,³ thus making the separation of these metals incomplete, and at the same time causing confusion by their precipitating with the metals of the tin group.

2. Under certain conditions a large quantity of tin⁴ remains undissolved by the ammonium polysulfide.

¹ THIS JOURNAL, 29, 170.

² 5 to 10 mg. of copper may dissolve in the ammonium polysulfide when a large amount of copper is present.

³ 0.5 to 1 mg. of mercury may dissolve in ammonium polysulfide when a large amount of mercury is present.

⁴ When large quantities of elements of the copper group and only 3 to 5 mg. of tin are present, the whole of the tin may remain undissolved and when much cadmium is present, together with tin in the stannous state, as much as 15 mg. of the latter may be left in the residue.

3. When the ammonium polysulfide filtrate is acidified with hydrochloric acid, a heavy precipitate of sulfur usually comes down, thus obscuring the presence of sulfides of the tin group.

There are three other reagents which are in use, or have been suggested for use to effect the separation of the divisions of the hydrogen sulfide group. They are sodium carbonate, sodium hydroxide, and potassium hydroxide.

The Sodium Carbonate Method.—This method, we are informed, was devised by H. T. Beans and is in use at the present time at Columbia University. A brief outline of this method is also given by Hinds.¹ The method as given in the unpublished notes of H. T. Beans may be briefly summarized as follows:

The precipitated sulfides of the hydrogen sulfide group are treated with a mixture of 25 cc. of 3 *N* sodium carbonate and 20 cc. of 3% hydrogen peroxide solutions. The mixture is then diluted to 200 or 300 cc. and warmed gently (not over 50°). A few bubbles of hydrogen sulfide are now passed into the solution, and, if a black precipitate appears, more hydrogen sulfide is passed in until precipitation is complete. The residue now contains the metals of the copper group, and the filtrate, those of the tin group.

The notes from which the authors got the method showed that it had not been sufficiently worked out to determine its efficiency. It was therefore thought worth while to investigate the possibilities of this method as a substitute for the ammonium polysulfide separation.

A great number of experiments and test analyses were carried out according to the procedure as given in the notes referred to above. Lack of space does not permit us to give the results of these experiments in full, but suffice it to say that the sodium carbonate and hydrogen peroxide method was found to be thoroughly inadequate in effecting the separation of the two groups from each other, because whenever antimony was present, it was found that, on adding the sodium carbonate and hydrogen peroxide to the precipitated antimony sulfide, about one-half of the antimony came down from the solution in the form of a heavy white flocculent precipitate.² The complication which such a state of affairs would cause in an analysis is quite evident. Not only would the test for antimony in the tin group be rendered considerably less delicate, but in

¹ "Qualitative Analysis," page 91.

² To determine the amount of antimony which remained undissolved by the sodium carbonate and hydrogen peroxide treatment, separate solutions containing 50 mg. and 250 mg., respectively, of antimony as antimony trichloride were completely precipitated as sulfide, and treated with a mixture of sodium carbonate and hydrogen peroxide, in accordance with the directions given in the notes of Beans. The white residues, which remained unacted upon by this treatment, after having been washed to acid reaction with hot water slightly acid with hydrochloric acid, were then dissolved in strong

addition, the antimony remaining undissolved would give rise to complications in the analysis of the copper group. There are, moreover, some minor objections to this method, but it was not thought worth while to go into them, inasmuch as the incomplete separation of the antimony was sufficient to condemn the method.

The Separation by Means of the Caustic Alkalies.—The action of the caustic alkalies in dissolving the sulfides of the tin group and leaving the sulfides of the copper group unacted upon is mentioned in nearly all the texts on qualitative analysis. However, a search of the literature revealed only one instance where any attempt was made to work up a scheme of separation by means of the hydroxides of sodium and potassium.¹ A brief outline of the method of J. Walker² is as follows:

The precipitated sulfides of the hydrogen sulfide group are treated with caustic soda, a few drops of ammonium polysulfide being added to oxidize any stannous tin that may be present. Sodium peroxide is also added to the boiling sodium hydroxide solution in order to reprecipitate any mercuric sulfide present.³ By this method the sulfides of arsenic antimony and tin are taken into solution, while the sulfides of the remaining metals are left in the residue.

The method is, however, open to objection for the reason that when antimony sulfide is treated with a mixture of sodium hydroxide⁴ and sodium peroxide, a large proportion of the antimony always remains undissolved as a white precipitate.

It is thus apparent that none of the methods mentioned have anything to recommend them for use in the separation of the divisions of Group 2 in place of the ammonium polysulfide separation.

After much experimentation, the authors have devised a procedure for the separation of the copper and tin groups, which is free from the objections to the ammonium polysulfide separation, as mentioned above. Further, the method possesses the merit of adequately providing for the systematic detection of pentavalent arsenic.

hydrochloric acid and analyzed for antimony by Weller's volumetric method. The solution containing 50 mg. showed approximately 30 mg. of antimony in the residue from the sodium carbonate treatment. The solution containing 250 mg., showed 125 mg. antimony in the residue.

¹ In Clowe's "Qualitative Analysis," the caustic alkalies are suggested as a reagent for the separation of the divisions of the hydrogen sulfide group, but no provision is made for the complications which the use of this reagent involves. The use of the caustic alkalies is also suggested in F. M. Perkin's "Qualitative Analysis."

² J. Walker, *J. Chem. Soc.*, 83 (1903).

³ According to Walker the solution of HgS is due to K₂S formed by the action of an excess of NaOH on a tin group sulfide. But no experimental evidence is offered (See Test Experiment 6.)

⁴ When potassium hydroxide is used in place of sodium hydroxide, the antimony sulfide dissolves completely.

Procedure for the Analysis of the Filtrate from the Silver Group.

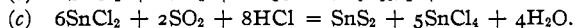
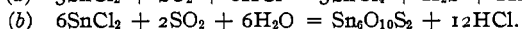
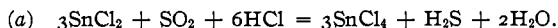
1. *Precipitation of the Alkaline Earth metals and Part of the Lead.*—Neutralize the filtrate¹ from Group 1 with NH_4OH and reacidify with 5 cc. HCl (1.19); add 8 cc. 20% H_2SO_4 and boil; cool and treat with an equal volume 95% alcohol. The precipitate is allowed to settle and the clear liquid decanted off through an ashless filter. Wash the precipitate once by decantation, keeping as much of it as possible in the beaker. The residue may consist of the sulfates of Ba, Sr, Ca and Pb. It is analyzed for these metals in accordance with the method given by Curtman and Frankel.²

NOTES.—1. The H_2SO_4 precipitates all the Ba and Sr and most of the Ca and Pb—about 10 mg. Ca and 15 mg. Pb pass into the filtrate. The Pb is subsequently detected in the H_2S precipitation, and the Ca by treating the filtrate from Group 3 with $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

2. *Precipitation of Group 2.*—Boil down the filtrate from the H_2SO_4 treatment with constant stirring to one-half its volume.² Add 3 to 4 cc. HCl (1.19) and 75 cc. saturated SO_2 solution. Heat for 20 to 25 minutes. Boil down to one-half its volume, cool, render slightly alkaline with concentrated NH_4OH and just acidify with dilute HCl . Add exactly 2.5 cc. HCl (1.19) heat the solution to boiling and pass in H_2S for a few minutes. Without filtering dilute the solution to 120 cc. with cold water and treat again with H_2S till precipitation is complete. Filter. The filtrate is set aside for the analysis of Groups 3 and 5. The residue may contain the sulfides of Hg, Pb, Bi, Cu, Cd, As, Sb and Sn.

NOTES.—1. 3 to 4 cc. concentrated HCl are added to the filtrate from the H_2SO_4 and alcohol treatment in order to prevent the Sb from precipitating on dilution with SO_2 solution next added.

2. The function of the H_2SO_3 is two-fold: (a) To reduce pentavalent As to the more easily precipitated form; (b) to oxidize stannous salts to the stannic condition, in which higher valence the sulfide is soluble in KOH . The reactions which take place, according to Prescott and Johnson³ are represented by the following equations:



3. The solution after treatment with SO_2 is boiled down to one-half its volume to drive off the excess of SO_2 , which, if present, would yield a precipitate of sulfur with H_2S .

4. When SnCl_2 is oxidized to SnCl_4 by SO_2 , more or less H_2S is formed as shown in the equations above. Thus a little SnS_2 is frequently precipitated in the solution. Likewise, if any As or Sb is present, a little of the sulfides of these metals may form. With the exception of the As_2S_3 , these precipitates are dissolved when the solution is concentrated to expel the excess of SO_2 .

3. *Separation of the Copper and Tin Groups.*—Wash the precipitated

¹ The volume should not exceed 30 cc.

² THIS JOURNAL, 34, 1493.

³ "Qualitative Analysis," 5th edition, p. 86.

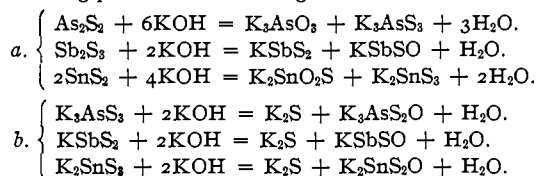
sulfides three times with a saturated solution of NaCl containing H_2S . Transfer the precipitate to a beaker and boil for one and one-half minutes with 25 cc. 25% KOH solution.¹ Dilute with 35 cc. of cold water and pass in a few bubbles of H_2S .² Filter through a double filter. The residue, after washing with hot water is analyzed for Hg, Pb, Bi, Cu and Cd. To the clear filtrate, add 30 cc. 3% H_2O_2 and boil gently for one minute with constant stirring. If a black precipitate appears, filter on a separate filter and test for Hg by dissolving the precipitate in aqua regia and adding SnCl_2 .

NOTES.—1. In washing the precipitated sulfides, NaCl is preferred to an ammonium salt, because the latter would tend to precipitate some Sn from the KOH solution of the potassium stannate formed on the addition of H_2O_2 .

2. KOH dissolves the sulfides of As, Sb and Sn(ic), leaving the sulfides of Hg, Bi, Cu and Cd completely undissolved. PbS is dissolved to a slight extent, but is reprecipitated by a few bubbles of H_2S . More than a few bubbles of H_2S should be avoided, for reasons stated below in Note 4.

3. Some of the sulfides have a tendency to pass through the filter, notably CdS. By passing the mixture through a double filter, a clear filtrate is obtained.

4. When a Sn group sulfide is dissolved in KOH, K_2S is always formed due to the action of the excess of KOH on the thio salt (see Test Exp. 6). The reactions may be looked upon as taking place in the following manner:



Some K_2S is also formed in consequence of the treatment of the KOH solution with H_2S .

5. If any HgS is present, it will be partly dissolved by the K_2S formed, as shown above, and consequently will appear in the filtrate along with the Sn group metals. The addition of H_2O_2 to the alkaline filtrate oxidizes the K_2S to the sulfate, thus causing the HgS to reprecipitate.³

4. *Treatment of the Filtrate for the Tin Group Metals.*—Boil down the filtrate from the H_2O_2 treatment to 50 cc. with stirring. While hot, quickly neutralize with concentrated HCl and add 10 cc. in excess. Heat the solution to boiling till clear. Add 50 cc. of a saturated SO_2 solution and heat for 20 to 25 minutes. Boil down to about 70 cc. Make slightly alkaline with concentrated NH_4OH and then just acid with dilute HCl. Add exactly 2.5 cc. HCl (1.19), heat to boiling and pass in H_2S for a few minutes. Dilute the mixture to 120 cc. with cold water and again saturate

¹ 100 cc. of the KOH solution contains 25 g. of solid KOH.

² See Test Experiment 6.

³ Walker, *J. Chem. Soc.*, 83 (1903), makes use of Na_2O_2 to reprecipitate the dissolved HgS . The authors use H_2O_2 first, to avoid the introduction of sodium which has a tendency to precipitate antimony; second because Na_2O_2 increases the concentration of the alkali.

with H_2S until precipitation is complete. The precipitate consisting of the sulfides of As, Sb and Sn, is treated in the usual manner.

NOTES.—1. The action of H_2O_2 on the As, Sb and Sn sulfides in KOH solution is to oxidize the arsenic sulfide to arsenic acid and the Sb and Sn sulfides to the higher oxides. Therefore, when the alkaline solution is acidified with HCl, the Sb and the Sn, for the most part, come down in the form of white amorphous precipitates. The longer these precipitates are allowed to stand, the more insoluble they become. The hot alkaline solution is therefore quickly neutralized with strong HCl and the precipitate formed immediately dissolved by an excess of this reagent.

2. The filtrate from the H_2O_2 treatment is boiled to destroy the excess of H_2O_2 , which, if present, would oxidize the SO_2 next added.

3. The H_2SO_3 is added in order to reduce the arsenic acid to the arsenious condition, whereby precipitation with H_2S is more easily and completely accomplished.

4. In order to insure complete precipitation of the As, Sb and Sn, the acidity of the solution must be carefully adjusted before the treatment with H_2S .

Test Experiments.

I.

The Action of Sodium Hydroxide¹ on the Sulfides of Group 2.—In order to determine whether NaOH could be used to separate the sulfides of the divisions of Group 2, the following experiments were carried out:

Separate solutions, each containing 500 mg. of one of the metals of Group 2, were completely precipitated with hydrogen sulfide, filtered, washed and boiled with stirring for 2 minutes with 25 cc. of a 20% NaOH solution.²

The sulfides of Hg, Cu, Bi and Cd were found to be completely insoluble.³ PbS dissolved to a small extent (about 1 mg.), but was completely reprecipitated on passing a few bubbles of H_2S into the alkaline solution. As_2S_3 , As_2S_5 , Sb_2S_3 , and SnS_2 were practically completely soluble⁴ in the caustic soda. SnS, at times, dissolved almost completely, leaving behind only a very small black residue, which was most likely some form of metallic tin, as shown by the solvent action of HCl upon it with the evolution of hydrogen. At other times, nearly all of the SnS remained undissolved by the sodium hydroxide.

Of interest are a few experiments which were performed with mixtures of SnS with As_2S_3 and Sb_2S_3 , respectively:

1. A mixture of 300 mg. As, as a HCl solution of As_2O_3 , and 200 mg. Sn, as $SnCl_2$, was completely precipitated with H_2S , filtered, washed, and treated with 25 cc. of a 20% NaOH solution. After boiling the mixture from 2 to 5 minutes, a heavy brownish black precipitate remained undissolved. The filtrate from this precipitate gave good tests for both As and Sn. The residue, after washing with hot water slightly acidified with HCl, was boiled with strong HCl, diluted and filtered; the filtrate gave a good test for Sn. The residue which remained from this treatment was treated with concentrated HNO_3 in which it readily dissolved with the evolution of oxides of nitrogen. The resulting solution, after reduction with SO_2 , was treated with H_2S . A heavy precipitate of As_2S_3 came down.

Conclusion.—When As_2S_3 is boiled in the presence of SnS with a NaOH solution, part of the As is reduced to the metallic condition (brownish black residue, above) which remains after treatment with strong HCl, but is readily soluble in strong HNO_3 ,

¹ Similar results were obtained with potassium hydroxide.

² 100 cc. of the caustic soda solution contained 20 g. solid NaOH.

³ The complete insolubility of the sulfides was proved in every case by the negative tests obtained in the concentrated filtrates.

⁴ See note under Test Experiment V. Similar residues were obtained here.

2. 300 mg. Sb, as SbCl_3 , and 200 mg. Sn, as SnCl_2 , were precipitated with H_2S ; after boiling the precipitated sulfides with NaOH , as above, a large black residue remained. The filtrate was tested for Sb and Sn with decided positive results. The residue, after washing with dilute HCl , was boiled with concentrated HCl and filtered. The filtrate gave a good test for Sn. The residue immediately dissolved in strong HNO_3 with the evolution of oxides of nitrogen. On long boiling a white precipitate came down, which on dissolving in tartaric acid, and treating with H_2S gave a heavy orange-colored precipitate of Sb_2S_5 .

Conclusion.—When a mixture of Sb_2S_3 and SnS is boiled with a solution of NaOH , part of the Sb_2S_3 is reduced to black metallic Sb.

3. In order to ascertain whether the reduction of the As_2S_3 and Sb_2S_3 was due to the action of the Na_2SnO_2 , which is one of the substances formed when SnS dissolves in NaOH ($2\text{SnS} + 4\text{NaOH} = \text{Na}_2\text{SnO}_2 + \text{Na}_2\text{SnS}_2 + 2\text{H}_2\text{O}$), some precipitated As_2S_3 was dissolved in NaOH solution. To the clear solution was added a freshly prepared solution of Na_2SnO_2 and the mixture was heated. A brownish flocculent precipitate and metallic mirror soon formed. The solution was filtered; the residue was boiled with strong HCl and then filtered. The residue from this treatment was dissolved in HNO_3 , reduced with SO_2 , and treated with H_2S . A heavy lemon colored precipitate was As_2S_3 .

4. Likewise, when a solution of Sb_2S_3 in NaOH was treated with a solution of Na_2SnO_2 , a black flocculent precipitate and metallic mirror formed. This precipitate was shown to be Sb.

Thus the objections to the use of NaOH , as a reagent for separating the copper and tin groups, are:

a. SnS is not regularly dissolved by NaOH .

b. In the presence of SnS , the sulfides of As and Sb when treated with a solution of NaOH are partly reduced and metallic As and Sb are precipitated. Experiments performed with KOH gave similar results.

II.

The Action of a Mixture of NaOH and H_2O_2 on the Sulfides of Group 2.—Since the above experiments showed that the separation of the divisions of Group 2 by means of NaOH is rendered incomplete by the insolubility of SnS therein, the following experiments were carried out in order to determine the effect of using a solution of H_2O_2 in conjunction with the NaOH , the purpose of the H_2O_2 being to oxidize the SnS . Separate solutions, each containing 500 mg. of one of the metals of Group 2, were completely precipitated with H_2S , washed, filtered, and boiled for 2 minutes with a mixture of 25 cc. of a 20% solution of NaOH and 20 cc. of a 3% H_2O_2 solution. The sulfides of Hg and Cd were completely insoluble. PbS , CuS , Bi_2S_3 , were partly soluble. As_2S_3 , SnS and SnS_2 were practically completely soluble¹, while Sb_2S_3 was found to be only partly soluble.

Sb_2S_3 .—When 500 mg. of Sb, precipitated as Sb_2S_3 , were treated with NaOH and H_2O_2 a large white precipitate immediately came down.

PbS .—When 50 mg. of Pb precipitated as PbS , were treated as above, the black precipitate became white and then dissolved completely. (H_2O_2 oxidizes the PbS to PbSO_4 which dissolves in NaOH .) However, when a few bubbles of H_2S were passed into the solution, the Pb was completely precipitated.

CuS .—On adding NaOH and H_2O_2 to 500 mg. Cu, as freshly precipitated CuS , the latter was converted to a beautiful blue granular substance.² The mixture was boiled for 2 minutes, diluted and filtered. The filtrate possessed a light blue color;

¹ See note under Test Experiment V. Similar residues were obtained here.

² The composition of these precipitates is being investigated.

on treating it with a little H_2S , a black precipitate of CuS was thrown down. The filtrate from this treatment was no longer blue and gave a negative test for Cu .

Bi_2S_3 .—On the addition of $NaOH$ and H_2O_2 to 500 mg. Bi as Bi_2S_3 , the latter, a dark brown flocky precipitate, was converted into a very light brown granular substance.¹ The mixture was boiled for 2 minutes, diluted, and filtered. A little H_2S was then passed into the clear filtrate; a dark brown precipitate of Bi_2S_3 came down. The filtrate from this second precipitation gave a negative test for Bi .

Conclusion.— $NaOH$ and H_2O_2 cannot be used for separating the divisions of Group 2, because the sulfide of Sb is only partly dissolved, the remainder coming down as a white precipitate (probably the metantimonate of Na).

III.

The Action of a Mixture of KOH and H_2O_2 on the Sulfides of Group 2.—Since the partial insolubility of the Sb_2S_3 in $NaOH$ and H_2O_2 was due most likely to the formation of the metantimonate of Na , which is not very soluble, it occurred to the authors to substitute KOH for $NaOH$, inasmuch as the corresponding potassium compound is known to be soluble.

Separate solutions, each containing 500 mg. of one of the metals of Group 2, were completely precipitated with H_2S , washed, filtered, and boiled for 2 minutes with 25 cc. 25% KOH and 20 cc. 3% H_2O_2 solutions. HgS and CdS were completely insoluble. The sulfides of Pb , Cu and Bi were partly soluble. As_2S_3 , Sb_2S_3 , SnS , SnS_2 were practically² completely soluble.

The sulfides of Pb , Cu and Bi were acted upon by KOH and H_2O_2 in the same manner as by $NaOH$ and H_2O_2 . When H_2S was led into the alkaline solution, the PbS was completely reprecipitated by a few bubbles of H_2S ; but the CuS and Bi_2S_3 required much more H_2S for their reprecipitation.

When H_2S was led into the KOH solution containing H_2O_2 , and the solution was then acidified, a heavy precipitate of sulfur came down (the acid liberating H_2S from reaction with the K_2S , and the H_2S being oxidized to S by the H_2O_2).

Conclusions.—(a) A mixture of KOH and H_2O_2 ³ when used to separate the sulfides of Group 2 possesses the disadvantage in requiring the prolonged treatment of the alkaline solution with H_2S for the purpose of rendering the CuS and Bi_2S_3 completely insoluble.

(b) The method has the further objection in yielding a precipitate of S when the alkaline solution, after treatment with H_2S for the reasons stated above, is acidified with HCl .

IV.

Oxidation of the Solution Containing the Metals of Group 2 by Means of H_2O_2 , before Precipitating with H_2S , and Treatment of the Precipitated Sulfides with KOH .—Since the preceding experiments showed that it is not feasible to oxidize stannous tin, when it is in the form of SnS , the following experiments were performed in order to determine whether oxidizing the stannous tin while in solution (before precipitation with H_2S) would be more desirable:

Separate 25 cc. solutions, each containing 500 mg. of one of the metals of Group 2, were neutralized with NH_4OH and reacidified with 10 cc. HCl (1.19). 10 cc. of 3% H_2O_2 were then added and the mixture boiled down with stirring, to one-half this volume.⁴ The solutions thus freed of the excess H_2O_2 were then neutralized with NH_4OH ,

¹ The composition of these precipitates is being investigated.

² See note under Test Experiment V. Similar residues were obtained here.

³ No better results could be obtained by substituting Br water for H_2O_2 .

⁴ When 500 mg. of Sb , as $SbCl_3$, are oxidized by H_2O_2 , the concentration of acid necessary to hold the Sb in solution is 9 cc. HCl (1.19) in a volume of 50 cc. The

reacidified with 2.5 cc. concentrated HCl and H₂S passed in until precipitation was complete. The precipitated sulfides were then boiled for 2 minutes with 25 cc. of a 25% KOH solution. The sulfides of As, Sb, stannic and stannous Sn were practically¹ completely soluble. The sulfides of Hg, Cu, Bi and Cd were completely insoluble. PbS dissolved to a very small extent, but was completely reprecipitated on treating the alkaline solution with a little H₂S.

As₂S₅.—The action of H₂O₂ on the As in solution is to oxidize it to the pentavalent condition with the result that its subsequent complete precipitation with H₂S, as is well known, is rendered very difficult.

500 mg. As, as a HCl solution of As₂O₃ were treated with H₂O₂ as given above, and then treated with a stream of H₂S for one-half hour in a hot solution containing 2.5 cc. HCl (1.19) in a volume of 40 cc.; it was found that a relatively large proportion of the arsenic had not been precipitated.

Conclusion.—While the preliminary oxidation of the solution containing the metals of Group 2 by H₂O₂ is advantageous, inasmuch as the stannous tin is thereby oxidized, it is undesirable because the As is oxidized at the same time to the pentavalent condition, in which state its subsequent precipitation with H₂S becomes a long and tedious process.

V.

Treatment of the Solution Containing the Metals of Group 2 with SO₂, Followed by the Addition of KOH to the Precipitated Sulfides.—The following experiments were performed in order to determine whether SO₂ could be used to oxidize stannous tin while in solution (before precipitation with H₂S):

Separate 25 cc. portions, each containing 500 mg. of one of the metals of Group 2, were neutralized with NH₄OH and reacidified with 5 cc. HCl (1.19). 75 cc. of a saturated solution of SO₂ were added and the resulting solution warmed for 25 minutes. After boiling down to one-half its volume to drive off the excess of SO₂, the solution was neutralized with NH₄OH and 2.5 cc. HCl (1.19) were added. H₂S was then passed into the solution for several minutes and again after dilution to 120 cc. until precipitation was complete. The precipitated sulfide, after filtering, was in each case boiled for 2 minutes with 25 cc. 25% KOH. The result of this treatment showed that the sulfides of Hg, Cu, Bi and Cd were completely undissolved. PbS dissolved to a small extent but was completely precipitated with a little H₂S. The sulfides of As, Sb and Sn were practically completely dissolved.²

Conclusion.—From the above experiments it is evident that by using SO₂ to oxidize stannous tin, KOH may be used to separate the sulfides of the divisions of Group 2. The use of SO₂ has the added advantage of reducing pentavalent As at the same time.

VI.

Formation of K₂S when a Tin Group Sulfide is Treated with KOH.—A mixture of 500 mg. Sb, as SbCl₃, and 10 mg. Pb, as Pb(NO₃)₂, was completely precipitated with H₂S, filtered, washed and then boiled for 1 minute with 25 cc. 25% KOH. The mixture was boiled down to half its volume in order to decompose the excess H₂O₂ which would otherwise have given a precipitate of S with the H₂S subsequently added

¹ See note under Test Experiment V. Similar residues were obtained here.

² A very slight residue remained on the filter when 500 mg. of As, Sb or Sn in the form of sulfides were dissolved by the KOH and the resulting solution filtered. The residues from the As and Sn(ic) solutions were no more than a smudge on the filter. The residues from the Sb and Sn(ous) solutions were more noticeable than these; but still could leave no doubt as to the absence of a significant amount of a metal of the Cu group. When diminishing amounts of the metals (400, 300 mg., etc.) were taken, the residues became more and more unnoticeable.

ture was diluted with 35 cc. water and filtered; a black residue was obtained. The perfectly clear filtrate was then treated with H_2S . No precipitation or coloration formed, showing that the PbS was completely undissolved by the KOH because of the presence of K_2S derived from the solution of Sb_2S_3 in the excess of KOH .¹ The experiment was repeated with mixtures of 500 mg. As, as an HCl solution of As_2O_3 , and 5 mg. Pb , as $Pb(NO_3)_2$, and with 500 mg. Sn , as $SnCl_4$, and 50 mg. Pb , respectively. The same results were obtained. Therefore, in the presence of a relatively large amount of a Sn group sulfide, the treatment of the KOH solution with H_2S in the procedure may be dispensed with. Further evidence of the formation of K_2S is supplied in Test Experiment 7.

VII.

The Action of H_2O_2 in Reprecipitating HgS from the KOH Solution.—It was found that more or less HgS always passed into the alkaline filtrate with the sulfides of the tin group because of the presence of K_2S in the solution. In the following experiments a method has been adopted for completely reprecipitating the HgS without bringing down any of the Sn group metals:

A mixture of 25 mg. Hg , as $Hg(NO_3)_2$, and 500 mg. As , as a HCl solution of As_2O_3 was completely precipitated with H_2S . The mixed sulfides, after washing, were boiled for 2 minutes in 25 cc. of a 25% KOH solution; the precipitate completely dissolved to a clear solution. The solution was diluted with 35 cc. of water and treated with a few bubbles of H_2S ; it still remained clear. 30 cc. 3% H_2O_2 were then added and the mixture was boiled for one minute. A black precipitate came down. The mixture was boiled for one minute longer and filtered. The residue gave a positive test for Hg . The filtrate was concentrated to one-half its volume in order to oxidize the As_2S_3 to arsenic acid and to decompose the excess H_2O_2 ; it was then acidified with HCl . No precipitate of any kind came down, thus showing the HgS to have been completely precipitated by the H_2O_2 .

When 1 mg. Hg , as $Hg(NO_3)_2$, was treated with 500 mg. Sn , as $SnCl_4$, as above, on the addition of the H_2O_2 to the alkaline solution, the HgS was completely reprecipitated and a good confirmatory test with $SnCl_2$ was obtained.

To test the method the following test analyses were used:

TEST ANALYSES.										
Solution.	Hg.	Pb.	Cu.	Bi.	Cd.	As(ous).	As(ic).	Sb(ous).	Sn(ous).	Sn(ic).
1.....	I	I	...	500	I	...
2.....	I	...	I	500	...
3.....	...	I	...	I	2	500
4.....	500	I	...
5.....	I	...	I	500	...
6.....	500	2	I
7.....	I	.	250	250
8.....	I	2	500	I
9.....	I	...	500	...	2
10.....	2	...	2	500	...
11.....	I	.	500
12.....	I	500	...	I
13.....	I	500

The results of the above analyses were all successful. 1 mg. of arsenic was always detected by using the $(NH_4)_2MoO_4$ confirmatory test.

¹ See Test Experiments 1 and 5, showing the solubility of PbS in KOH .

In analyses Nos. 2, 5, 9 and 10, very slight residues¹ were left on the filter after treatment of the precipitated sulfides with KOH, but in no case was the size of the residue such as to indicate the presence of significant amounts of metals of the Cu groups.

Summary.

1. The well-known objectionable features of the ammonium polysulfide method for the separation of the copper and tin groups have led to many attempts to replace it by a more suitable process; of these the sodium carbonate, sodium hydroxide, and potassium hydroxide methods taken alone or in conjunction with hydrogen peroxide are the best known. These have been examined and their shortcomings pointed out.

2. A scheme of analysis has been devised which overcomes the chief difficulties in the analysis of the filtrate of Group 1. The chief features of the method are:

(a) The preliminary precipitation of the alkaline earth metals together with some of the lead before precipitation of Group 2 with hydrogen sulfide.

(b) Treatment of the filtrate from the precipitation of the alkaline earth metals with sulfur dioxide before passing in hydrogen sulfide, in order to oxidize stannous tin and to reduce pentavalent arsenic.

(c) The complete separation of the sulfides of the divisions of Group 2 by means of potassium hydroxide.

3. The results of a number of test analyses show the method to be trustworthy.

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EQUILIBRIA IN THE SYSTEMS, WATER, ACETONE AND INORGANIC SALTS.

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Introduction.

The dehydration of acetone is very similar to that of alcohol and ether. In most cases where dehydration of organic liquids takes place, the phenomenon of the formation of two definite layers also takes place. The salts most commonly used for dehydration purposes are CaO, CuSO₄, CaCl₂, K₂CO₃, Na₂SO₄, MgSO₄, CaSO₄, and KCl. CaCl₂ offers disadvantages inasmuch as it frequently forms compounds with the liquids and cannot be used in drying them. The only experiments of value on the efficiency of these drying agents were made by Siebenrock² in the

¹ See note under Test Experiment 5.

² *Monatsh.*, 30, 759-66.