

the residue and solution analyzed separately: the residue after the evaporation to dryness with HCl was shown by P. 5 to contain several milligrams of SiO_2 ; the solution was found to contain several milligrams of aluminum and of calcium and a trace of iron.

The experiment was repeated, using a nickel crucible: the aqueous extract acidified with HCl gave no precipitate with H_2S nor with NH_4OH and $(\text{NH}_4)_2\text{S}$. A slight black residue of a nickel oxide insoluble in water remained: this dissolved in HCl and gave a precipitate with NH_4OH and $(\text{NH}_4)_2\text{S}$, which was estimated to contain 1 mg. Ni.—This experiment was repeated, except that 0.3 mg. KNO_3 was added to the fusion: 4.5 mg. Ni as nickel oxide were obtained.

PART II. ANALYSIS OF THE SILVER, COPPER, AND TIN GROUPS

GENERAL DISCUSSION

A survey of the main features of the method adopted for the analysis of the hydrochloric acid and hydrogen sulphide precipitates may be obtained by referring to the "Tabular Outline" following this chapter. Here only the modifications introduced into the process ordinarily followed will be discussed.

In the precipitation and analysis of the silver group the usual process has been adhered to, the only addition being a provision for the detection of thallium by removing the lead with sulphuric acid and then adding potassium iodide.

In the direction for the precipitation of the copper and tin groups by hydrogen sulphide, especial attention is given to securing the proper conditions as to acid concentration and temperature for a satisfactory separation of these elements from those of the iron group; for indefiniteness in this respect is one of the most common sources of difficulty to the inexperienced analyst. In our process, as will be seen by reference to P. 21, it is directed to precipitate first from a hot, moderately acid solution. The fairly large acid concentration has the advantage of preventing the precipitation by hydrolysis of basic salts of titanium, bismuth and antimonous antimony, and of hastening the precipitation of the arsenic. The high temperature promotes the precipitation of arsenic, molybdenum, and platinum, and causes all the sulphides to separate in a more readily filterable form. The solution is, however, finally diluted so as to contain 4 cc. of hydrochloric acid of specific gravity 1.12 in 100 cc., and is saturated with hydrogen sulphide in the cold: for only with an acid as dilute as this and then in the cold is it possible to precipitate as little as 1 or 2 mg. of cadmium or lead. Attention may be called to our experiments described in the chapter on "Confirmatory Experiments and References," which show that under these conditions the separation is a remarkably satisfactory one—at any rate from a qualitative analysis point of view, since not

only is the precipitation of the copper and tin groups complete, but one milligram of zinc, iron, or nickel is found in the filtrate, even when 500 milligrams of cadmium, copper, or tin are present.

In the case of substances originally dissolved without the use of nitric acid, which may therefore contain tin or antimony in the stannous or antimonous state, the hydrogen sulphide precipitate is, as usual, treated with ammonium polysulphide. The separation of certain elements by this reagent is, however, far from complete. Thus copper and mercury dissolve in not insignificant quantity in the polysulphide; and tin may remain entirely undissolved, even when several milligrams are present, if cadmium, copper, or mercury is also present in large quantity; moreover, gold, platinum, and the elements allied to them divide themselves between the residue and solution to so large an extent and to so different an extent in different combinations, as to make this reagent entirely unsatisfactory for separating these elements; and with molybdenum the solution is seldom complete, though a large proportion of it always dissolves. New experiments confirmatory of these already known facts will be found described below in the chapter on "Confirmatory Experiments." Yet in a scheme devoted primarily to the common elements there seems to be no alternative process of separation which, on the whole, is nearly so satisfactory; especially since it is not difficult to separate tin from the elements of the copper group in the course of the analysis of the latter, and since enough copper and mercury always remain undissolved by the ammonium polysulphide to enable as little as two milligrams to be detected.

In the case of substances not completely soluble in water, the treatment with nitric acid, recommended in Part I, converts tin and antimony into the higher state of oxidation; and this makes it practicable, as our experiments have shown, to substitute ammonium monosulphide for the polysulphide in the case of such substances, which constitute by far the larger proportion of those ordinarily submitted to analysis. This has the advantage of not dissolving cupric and mercuric sulphides appreciably, thereby not only making the tests for copper and mercury more delicate, but also making it possible to decide with certainty from the appearance of the precipitate produced by acid in the ammonium sulphide solution whether or not any element of the tin group is present. The monosulphide has, of course, the same defects as the polysulphide in not completely extracting tin and the rarer elements, but not in any more marked degree when these elements are in the higher state of oxidation. This will be evident by reference to the "Test Analyses of the Tin Group."

In the process of analysis of the copper group (see Table IV) the important modifications introduced have reference to the extraction of the tin, which may, as just stated, remain wholly in the residue undissolved by ammonium sulphide, and to provision for the presence of barium of

which, when an oxidizing agent, like a ferric salt, is present, small quantities may be completely precipitated as barium sulphate in the hydrogen sulphide treatment. The residue undissolved by nitric acid, which may consist of mercuric sulphide and metastannic acid, is treated with bromine water instead of with an acid-oxidizing mixture, in order to dissolve out the mercury and leave behind the tin, which can then be dissolved in ammonium sulphide and united with the main solution of the tin group. Barium sulphate, if present in the H_2S precipitate, is not dissolved by the treatment with ammonium sulphide, but passes into solution in considerable quantity in the hot, moderately concentrated nitric acid, and separates out, together with lead sulphate, upon evaporation with sulphuric acid and subsequent dilution. Provision is made for the separation of these two sulphates by treatment with ammonium acetate solution and for the detection of barium in the residue.

TABULAR OUTLINE

TABLE III.

ANALYSIS OF THE SILVER GROUP

Precipitate : $AgCl, Hg_2Cl_2, PbCl_2, *TiCl_3$. *Treat with hot water (P. 12).*

Solution : $PbCl_2, *TiCl_3$. <i>Add H_2SO_4 (P. 13).</i>		Residue : $AgCl, Hg_2Cl_2$. <i>Pour NH_4OH through the filter (P. 15).</i>	
Filtrate : $*Ti_2SO_4$. <i>Add KI (*P. 13a).</i>	Precipitate : $PbSO_4$. <i>Dissolve in $NH_4C_2H_3O_2$, $Add K_2CrO_4$ (P. 14).</i>	Black Residue : $HgNH_2Cl + Hg$.	Solution : $Ag(NH_3)_2Cl$. <i>Add HNO_3 (P. 15).</i>
Yellow precipitate : $*TiI_3$.	Yellow precipitate : $PbCrO_4$.	White precipitate ; $AgCl$.	

For the analysis of the tin group various processes have been proposed and are in general use. As will be seen from Table V the method of separation here adopted is based entirely on the different solubilities of the three sulphides of arsenic, antimony, and tin in hydrochloric acid of varying concentration. This process, which seems to have been first suggested for the separation of antimony and tin by Loviton,¹ and which has been utilized in part by Bailey and Cady in their text-book on qualitative analysis, we have somewhat developed by a detailed study of the best conditions for making it a good qualitative method. We believe this method is the one best adapted to the purposes of ordinary qualitative analysis, because of its great simplicity, and because of the fact that the tests, while being of sufficient delicacy to detect one milligram of any of these ele-

¹ J. Chem. Soc. 54, 992 (1888)

TABLE IV

ANALYSIS OF THE COPPER GROUP.

H₂S PRECIPITATE : HgS, PbS, Bi₂S₃, CuS, CdS, As₂S₃, As₂S₅, (with As₂S₃ and S₂), Sb₂S₃, Sb₂S₅, SnS, SnS₂, *PtS₂, *Au and *Au₂S_{1.3}, *Se, *Te (and TeS₂?), *MoS_{2.3}, [BaSO₄].

Digest with ammonium sulphide (P. 22).

Residue: HgS, PbS, Bi₂S₃, CuS, CdS, [*PtS₂], [*Au and Au₂S_{1.3}], [*MoS_{2.3}], [SnS], [SnS₂], BaSO₄.

Boil with HNO₃ (P. 23).

Residue : HgS, SnO₂, *Au and Au₂S_{1.3}, *PtS₂

Add Br₂ solution* (P. 24).

Solution : Pb, Ba, Bi, Cu, Cd as nitrates.

Add H₂SO₄, evaporate, add water (P. 26).

Residue: SnO ₂ . Dissolve in (NH ₄) ₂ S (P. 25). Unite with tin group (P. 41).	Solution. Add KCl, evaporate to a small volume (*P. 24a).		White precipitate : PbSO ₄ , BaSO ₄ . Add ammonium acetate (P. 27).		Filtrate. Add NH ₄ OH (P. 28).		Solution (NH ₄) ₃ AsS ₄ , (NH ₄) ₃ SbS ₄ , (NH ₄) ₂ SnS ₃ , [* (NH ₄) ₂ PtS ₃ (?)], [* (NH ₄) ₃ AuS ₃ (?)], *(NH ₄) ₂ SeS ₃ (?), *(NH ₄) ₂ TeS ₃ (?), *(NH ₄) ₂ MoS ₄ . Add HCl (P. 41).					
	Yellow precipitate: *K ₂ PtCl ₆ .	Filtrate. Add NaOH and H ₂ C ₂ O ₄ and heat (*P. 24a).		Solution : Pb(C ₂ H ₃ O ₂) ₂ . Add K ₂ CrO ₄ (P. 27).	Residue: BaSO ₄ .	Precipitate : Bi(OH) ₃ . Dissolve in HCl, evaporate, add to water (P. 29).		Filtrate : Cu(NH ₃) ₄ SO ₄ (blue), Cd(NH ₃) ₄ SO ₄ .				
		Purple precipitate: *Au.	Solution. Add SnCl ₂ (P. 24).						Yellow precipitate: PbCrO ₄	To a small part add CH ₃ COOH and H ₂ S (P. 30).	To the remainder add KCN and H ₂ S (P. 31).	
			White or gray precipitate: Hg ₂ Cl ₂ or Hg.									Black residue : Bi.
Precipitate: See Table V.												

TABLE V
ANALYSIS OF THE TIN GROUP

PRECIPITATE FROM AMMONIUM SULPHIDE SOLUTION : As_2S_5 , Sb_2S_3 , SnS_2 , $*PtS_2$, $*Au_2S_3-6$, $*SeS_2(?)$, $*TeS_2(?)$, $*MoS_3$.
Heat with 10 cc. HCl (1.20) (P. 42).

Solution : $SbCl_3$, $SnCl_4$. Dilute to 50 cc., heat and pass in H_2S (P. 45).		Residue : As_2S_5 , $*PtS_2$, $*Au$, $*Se$, $*Te$, $*MoS_3$. Dissolve in HCl and $KClO_3$, evaporate to a small volume (P. 43).		
Orange precipitate : Sb_2S_3 . Dissolve in HCl , add Zn and Pt (P. 46).	Solution : $SnCl_4$. Cool, dilute, pass in H_2S (P. 47).	Yellow precipitate : $*K_2PtCl_6$. Dissolve in hot water, add KI (*P. 43a).	Filtrate : II_3AsO_4 , $*AuCl_3$, $*H_2SeO_3$, $*H_2TeO_3$, $*H_2MoO_4$. Add NH_4OH , NH_4Cl and $MgCl_2$ (P. 44).	
	Black deposit : Sb . Treat with $NaOCl$.		Dark red color : $*K_2PtI_6$.	White precipitate : $MgNH_4AsO_4$. Dissolve in HCl , add H_2S (P. 44).
Black deposit : Sb .	Gray deposit : Sn . Dissolve in HCl , add $HgCl_2$ (P. 47). White precipitate : Hg_2Cl_2 .	Yellow precipitate : As_2S_5 , As_2S_3 , and S .	Purple or dark yellow precipitate : $*Au$.	Filtrate. Evaporate, add strong HCl and Na_2SO_3 (*P. 43c).
				Red precipitate : $*Se$.
				Black precipitate : $*Te$.
				Filtrate. Boil off SO_2 , add $KCNS$ and Zn (*P. 43e).
				Deep red color : $*Mo(CNS)_4$.

ments, do not have in the case of arsenic and antimony the extreme sensitiveness of the reduction tests based on the decomposition by heat of hydrogen arsenide and antimonide.

Of the rarer elements precipitated by hydrogen sulphide, provision has been incidentally made for the detection of all the more important ones, namely for that of molybdenum, selenium, tellurium, gold, and platinum. The treatment with hot concentrated hydrochloric acid employed for separating the sulphides of antimony and tin from that of arsenic makes such provision comparatively simple; for the sulphides of all these rarer elements are left, with that of arsenic, together at one place in the scheme (except that gold and platinum may also remain in the copper group residue, and have to be tested for also in the analysis of that group). No attempt has been made to include the other so-called platinum elements, since the reliable detection of these can be effected only by a special and complicated process. These elements will be treated in the "System of Analysis Including Nearly All the Metallic Elements," previously referred to.

PROCEDURES AND NOTES

Analysis of the Silver Group

Procedure 11.—To the cold aqueous solution of the substance (P. 3) add 4 cc. HCl (1.12) from a small graduate. (White precipitate, presence of SILVER GROUP). Filter, and wash the precipitate with a small quantity of cold water, adding the washings to the filtrate. Finally dilute the filtrate to a volume of about 40 cc. (Precipitate, P. 12; filtrate, P. 21).

Notes.—Nonformation of a precipitate proves absence of silver and mercurous mercury, but not of lead (or thallos thallium), since PbCl_2 (and TlCl) are fairly soluble in water. Owing to the common-ion effect, the solubility of the chlorides is greatly decreased by the addition of HCl; but 20-40 mg. Pb (and 5-15 mg. Tl) may remain in solution, and thus escape detection in this group.

Since the subsequent precipitation of the copper and tin groups by H_2S must be made in a dilute HCl solution of known strength, a definite amount of HCl is added at this point and the solution is diluted to a known volume.

Procedure 12.—Pour repeatedly through the filter containing the HCl precipitate (P. 11) a portion of 10-20 cc. boiling water. Wash the residue thoroughly with hot water. (Residue, P. 15; solution, P. 13).

Procedure 13.—Add to the aqueous extract from the HCl precipitate (P. 12) one-fifth its volume of concentrated H_2SO_4 ; cool, shake the mixture, and allow it to stand for 5 minutes. (White precipitate, presence of LEAD). Filter, wash the precipitate with H_2SO_4 (1.20) and then with a little water. (Precipitate, P. 14; filtrate, reject or test for thallium by * P. 13a.)

***Procedure 13a.**—To test for thallium add to the filtrate from the H_2SO_4 precipitate (P. 13) 2-3 cc. KI solution. (Yellow precipitate, presence of THALLIUM). If the solution becomes brown, owing to the liberation of free iodine, add a little H_2SO_3 solution.

***Notes.**—Thalious iodide is much less soluble than the corresponding chloride, and its solubility is greatly decreased by KI, owing to the common-ion effect. PbI_2 is also difficultly soluble, but cannot be precipitated here, since lead has been removed by H_2SO_4 in P. 13. The presence of even 0.5 mg. thalious thallium in 15 cc. of solution may easily be detected in the cold by means of KI. Free iodine oxidizes thalious to thallic salts, but these, as well as the iodine itself, are reduced by H_2SO_3 .

Thalious salts are oxidized to thallic salts rapidly by halogens and *aqua regia*, and slowly by hot concentrated HNO_3 . Upon evaporating a thallic chloride (TlCl_3) solution and heating the residue at 120° , more or less complete reduction takes place by decomposition into TlCl and Cl_2 . Pure thallic salts give no precipitate with HCl , thalious salts a white one; while mixtures of them give yellow precipitates ($\text{TlCl}_3 \cdot x\text{TlCl}$). For these reasons, even when the substance has been dissolved in HNO_3 and the solution has been evaporated as described in P. 4, thallium will be precipitated with this group by HCl if much of it is present.

Procedure 14.—Pour repeatedly through the filter containing the H_2SO_4 precipitate (P. 13) a 10-20 cc. portion of a 10% ammonium acetate solution; add to the filtrate a few drops K_2CrO_4 solution and 2-5 cc. dilute acetic acid. (Yellow precipitate, presence of LEAD).

Notes.—The solubility of PbSO_4 in solution of ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) depends on the formation by metathesis of undissociated lead acetate, which is much less ionized than most other salts of the same type. On the addition of a chromate to this solution the much more difficultly soluble PbCrO_4 is precipitated, and is not dissolved by dilute acetic acid.

Procedure 15.—Pour repeatedly through the filter containing the residue insoluble in hot water (P. 12) a 10-20 cc. portion of NH_4OH (0.96). (Black residue on the filter, presence of MERCUROUS MERCURY). Acidify the filtrate with HNO_3 . (White precipitate, presence of SILVER).

Notes.—The black residue produced by the action of NH_4OH on Hg_2Cl_2 is a mixture of finely divided mercury with the white mercuric compound HgCl_2NH_2 , which may be considered to be a derivative of HgCl_2 , formed by replacing an equivalent of chlorine by the univalent radical NH_2 .

AgCl dissolves readily in NH_4OH , owing to the formation of a soluble complex salt, $\text{Ag}(\text{NH}_3)_2\text{Cl}$, which in solution is largely dissociated into $\text{Ag}(\text{NH}_3)_2^+$ and Cl^- ions. This complete cation has so slight a tendency to dissociate that in a normal

solution of NH_4OH the ratio of its concentration to that of the simple Ag^+ ion is about 10'. HNO_3 reprecipitates the AgCl from its solution in NH_4OH , owing to the facts that the complex cation is slightly dissociated according to the equation $\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$, and that the NH_3 combines with the added acid, forming NH_4NO_3 , thus causing the complex cation to dissociate further, until the Ag^+ concentration increases to such an extent as to make the product of it into the Cl^- concentration greater than the solubility product for AgCl . The test is less delicate when the NH_4OH is neutralized with HCl , owing to the solubility of AgCl in strong chloride solutions, which arises, probably, from the formation of a salt with a complex anion, like $\text{NH}_4^+\text{AgCl}_2^-$.

Precipitation and Separation of the Copper and Tin Groups

Procedure 21.—Treat separately as follows the various acid solutions previously obtained (P. 11, 4, 2, 5, 6, 7, 8), each of which should contain 4 cc. HCl (1.12) or 1.5 cc. H₂SO₄ (1.84) and have a volume of about 40 cc. Heat the solution in a conical flask nearly to boiling, and pass into it H₂S gas until it is saturated, and then for 10-15 minutes longer, keeping the solution at 70-90°. [*If the rarer elements are likely to be present, continue the precipitation in a pressure bottle as described in N. 2]. Cool the mixture; without filtering add to it 60 cc. water, completely saturate it in the cold with H₂S gas, cork the flask, shake it, and allow it to stand 15 minutes. Filter, and wash the precipitate with hot water. Precipitate, P. 22; filtrate, P. 61).

Notes.—The effect of acid on the precipitation of the sulphides is explained by the Mass Action Law and Ionic Theory as follows: When a dilute solution, whether aqueous or acid, is saturated at a definite temperature with H₂S gas under the atmospheric (or any definite) pressure the H₂S as such always has the same concentration. This ionizes, however, to a slight extent into H⁺ and HS⁻, and to a still less extent into 2H⁺ and S⁼. It is only the latter form of ionization that needs to be considered here. Now between the H₂S and its ions must be maintained the equilibrium expressed by the equation $(C_H)^2 \times C_S = \text{const.} \times C_{H_2S}$; or, since in this case $C_{H_2S} = \text{const.}$, as just stated, it follows that also $(C_H)^2 \times C_S = \text{const.}$ From this it is evident that when C_H is increased by the addition of acid to the solution, C_S must be decreased in the proportion in which the square of C_H is increased; thus, if C_H is doubled, C_S will be reduced to one-fourth. But in order that a sulphide—for example, of the formula M⁺⁺S⁼—may precipitate the concentration product C_M × C_S must attain a value equal to the solubility product, which is the value of this concentration product which prevails in pure water in contact with the solid sulphide. The solubility product varies, however, with the nature of the sulphide and with the temperature; and therefore the acid concentration that will barely permit of precipitation when C_M has a definite value (for example, 1 mg. in 100 cc.) will be different for different sulphides and for the same sulphide at different temperatures. Thus if the elements are arranged in the order in which they are precipitated from cold HCl solutions of decreasing concentration, the series is approximately as follows: arsenic, mercury and copper, antimony, bismuth and stannic tin, cadmium, lead and stannous tin, zinc, iron, nickel and cobalt, manganese. The acid concentration which permits precipitation also varies with the nature of the acid, since the various acids are ionized to a different extent; thus zinc is precipitated from a fairly concentrated solution of acetic acid, since, owing to the slight ionization of this acid, the H⁻ concentration is less than in a far more dilute solution of hydrochloric acid.

The solution is first saturated with H₂S at nearly the boiling temperature, because certain elements, especially arsenic in the higher state of oxidation (and the rarer elements, platinum and molybdenum), are slowly and incompletely precipitated in the cold, and because the precipitates of almost all sulphides separate from hot solutions in a form better suited for filtration. In case precipitation seems to continue after the solution has become fully saturated with H₂S, it indicates that one of the elements just named may be present; and, to insure complete precipitation of the arsenic, the heating and passage of the gas must sometimes be continued for an hour longer. [*In case of molybdenum and the platinum elements, it is necessary,

after most of the sulphide has separated, to cool the solution, to saturate it in the cold with H_2S in a stout bottle, to stopper the bottle with a cork securely held in place by wire, and to heat the bottle in a vessel of boiling water for an hour.] The solution is at first diluted to only about 40 cc., because arsenic is more rapidly thrown out from rather strongly acid solutions, and because antimony would be precipitated as hydroxide if the solution were further diluted and were kept near the boiling temperature; moreover, bismuth and a moderate quantity of antimony do not precipitate as oxychloride at this dilution, but might do so if the solution were at once further diluted. The solution is finally diluted to 100 cc. completely saturated in the cold, and allowed to stand, in order to cause the precipitation of even 1 mg. of cadmium, lead, or stannous tin. Zinc, iron, nickel, and cobalt, on the other hand, do not precipitate at all under these conditions, even when 500 mg. are present alone; and even 1 or 2 mg. of any of them can be detected in the filtrate when large quantities of elements of the copper and tin groups are also present.

If at first a white or yellowish precipitate forms which immediately turns black with more H_2S , it indicates mercury. The white compound is $HgCl_2 \cdot 2HgS$, and this is converted into HgS by the excess of H_2S . An orange precipitate separating from the hot, more concentrated solution shows antimony or much cadmium (or selenium); a yellow one, arsenic or stannic tin. A yellow precipitate separating from the cold, more dilute solution shows cadmium. All the other sulphides are black or brownish black. For the composition of the H_2S precipitates, see Table IV. The quantity of sulphur combined with the metallic element, however, varies with the conditions of precipitation, owing to partial reduction, in the cases of arsenic, arsenic and antimonious antimony [*and of gold, selenium, tellurium, and probably molybdenum]. The extent to which the sulphides are combined with water and with hydrogen sulphide is also variable and in general unknown.

When oxidizing substances, like ferric salts, are present, H_2S is oxidized to sulphur and to some extent to H_2SO_4 . Barium, if present, is thereby precipitated as $BaSO_4$; and all but one or two milligrams of it may be completely precipitated even when 20 milligrams are present.

Procedure 22.—Transfer the H_2S precipitate (P. 21) to a small casserole, add to it 10-25 cc. ammonium monosulphide (if the original substance was treated with HNO_3 in P. 3), or 5-10 cc. ammonium polysulphide (if it was dissolved in water alone), cover the dish, and warm the mixture slightly (to 40-60°) for about 10 minutes with frequent stirring. Add 10 cc. water, filter, and wash once with hot water. [If the residue is considerable in amount and much has been extracted from it by this treatment, as indicated by its appearance, or as determined in P. 41, warm it again with ammonium monosulphide or polysulphide, and filter, collecting the filtrate separate from the first one]. Wash the residue thoroughly with hot water, to which, in case the precipitate tends to pass through the filter, about 5% solid NH_4NO_3 should be added. (Residue, P. 23; solutions, P. 41).

Notes.—In separating the copper and tin groups it is better to use (colorless) ammonium monosulphide rather than (yellow) polysulphide whenever the H_2S precipitate must contain any tin and most of any antimony present in the state of the higher sulphide (SnS_2 or Sb_2S_3). This is the case when hot concentrated nitric acid was used originally in dissolving the substance, but may not be so when water

alone (or HCl) was used; hence the directions as to the choice between the two solvents. The polysulphide has the disadvantage that it dissolves a not inconsiderable quantity of CuS and HgS, thus making the tests for copper and mercury less delicate, and making it more difficult to determine from the color of the HCl precipitate obtained from the ammonium sulphide solution in P. 41 whether or not elements of the tin group are present. The polysulphide must, nevertheless, be used if tin may be present as SnS, or much antimony as Sb₂S₃; for in the monosulphide SnS is almost insoluble and Sb₂S₃ is only moderately soluble (50-100 mg. Sb in 10 cc. of the reagent).

In order that the separation of the copper and tin groups by ammonium sulphide may be as complete as possible, it is necessary to employ a concentrated reagent highly charged with hydrogen sulphide, and containing, in the case of the polysulphide an appropriate excess of sulphur. Suitable reagents are prepared by completely saturating a measured volume of NH₄OH of specific gravity 0.90 with H₂S in the cold, adding a fresh portion of NH₄OH (0.90) equal to two-thirds of the original volume, and diluting a measured volume of the mixture with an equal volume of water. From this solution, which constitutes "ammonium monosulphide," the "ammonium polysulphide" is prepared by dissolving in 1 liter of it 25 grams of flowers of sulphur. These reagents, especially the monosulphide, should be kept as far as possible out of contact with the air, which is conveniently done by storing them in small, completely filled, glass-stoppered bottles; for the oxygen of the air destroys the sulphide with liberation of sulphur, which at first combines with the still unchanged sulphide, but precipitates later when the oxidation becomes more complete. The monosulphide reagent is a solution of (NH₄)₂S and of the products of its hydrolysis, NH₄SH, NH₄OH, and a little H₂S. The polysulphide contains in addition various polysulphides of the forms (NH₄)₂S₂₋₅ and (NH₄)HS₂₋₅ in unknown proportions.

The action of ammonium sulphide in dissolving the sulphides of the tin group depends on the formation of soluble salts of sulpho acids with complex anions, such as (NH₄)₃AsS₃, (NH₄)₃SbS₃, (NH₄)₂AsS₄, (NH₄)₃SbS₄, and (NH₄)₂SnS₃.

When ammonium monosulphide is used, 500 mg. of any of the common tin-group elements, in the form of higher sulphide, dissolve in 25 cc. of the reagent, provided this has been prepared as described. When the polysulphide is used, 500 mg. of any of the common tin-group elements, whether present as the higher or lower sulphide, dissolve in 10 cc. of the reagent. The quantity of SnS and Sb₂S₃ dissolved by the polysulphide increases with its concentration and the excess of sulphur which it contains. A reagent containing a greater excess of sulphur is not used, however, since this would dissolve more CuS and HgS.

*Of the rarer elements, gold and platinum divide themselves in the ammonium sulphide treatment between the solution and the residue in a proportion which depends in large measure on the other elements which are present with them. They may, therefore, be found mainly either with the copper or with the tin group, and should be tested for in the course of the analysis of each group. Molybdenum dissolves in moderate quantity in either ammonium monosulphide or polysulphide, but when a quantity as large as 50 mg. is present much of it remains with the copper group; yet there is no danger of not finding a considerable part of it in the tin-group solution, and its presence in the copper-group residue does not interfere with the detection of any of the elements, since it is not precipitated by any of the reagents used. When molybdenum is present, even in as small a quantity as 1 mg. the ammonium sulphide solution has an orange-red color; and this becomes very deep when a moderate quantity is present. Selenium and tellurium pass completely, or almost completely, into the ammonium sulphide solution.

Even when a quantity of only 1 or 2 mg. of arsenic or antimony is present with a large quantity (even 500 mg.) of an element of the copper group, enough is extracted by either the monosulphide or polysulphide to be detected in the subsequent tests. With tin, however, the separation is imperfect; for, when a large quantity of elements of the copper group and only 3.5 mg. of tin are present, the whole of this may remain undissolved; indeed, when much cadmium is present and the tin is in the stannous state, as much as 15 mg. of the latter may be wholly left in the residue, even when the polysulphide is used. On this account it is necessary to test for tin in the course of the analysis of the copper group.

Of the sulphides of the copper group none dissolve to a significant extent in the monosulphide. Considerable CuS (5-10 mg.) and a little HgS (0.5-1.0 mg.) may, however, dissolve in the polysulphide when the substance contains a large quantity of these elements. Yet when 2 mg. of either of these elements are present it can be detected in the analysis of the copper group, even when the polysulphide is used, provided only one treatment with it has been made.

Analysis of the Copper Group

Procedure 23.—To the residue from the ammonium sulphide treatment (P. 22) in a casserole add 10-20 cc. of a mixture of one volume HNO_3 (1.20) and two volumes water, heat to boiling, and boil gently for a minute or two. (Black residue, possible presence of MERCURY). Filter and wash. (Residue, P. 24; solution, P. 26.)

Notes.—Boiling HNO_3 of this concentration dissolves the sulphides of lead, bismuth, copper, and cadmium almost immediately, and is therefore preferable to a more dilute acid, with which the reaction would require for its completion several minutes' boiling. Scarcely any HgS is dissolved by the above treatment, unless the boiling is long continued. If, however, more concentrated HNO_3 be used, or if the acid become concentrated by long boiling, the black HgS is dissolved in part, and the remainder is converted into a heavy, white, difficultly soluble compound ($\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgS}$).

Any SnS or SnS_2 not extracted by the ammonium sulphide treatment will be converted by HNO_3 into metastannic acid, most of which remains undissolved. Therefore, even a light-colored residue must be carefully collected if tin is to be tested for in this group.

Procedure 24.—Transfer the residue undissolved by HNO_3 (P. 23), with the filter if necessary, to a casserole, add 10-40 cc. saturated Br_2 solution, cover the dish, and warm slightly for 5-10 minutes, with frequent stirring. Boil the mixture until the bromine is expelled, and filter. (Residue, P. 25). [*If the solution is yellow, indicating that gold or platinum may be present, treat it by *P. 24a, and then proceed as follows]. Cool the solution, and add to it a few drops of HCl (1.12) and a 2% SnCl_2 solution, at first drop by drop; then add several cubic centimeters of a 10% SnCl_2 solution. (White precipitate turning gray, or gray precipitate, presence of MERCURY). (Residue and solution, reject).

Notes.—Bromine water dissolves the sulphides of mercury, platinum, and gold, but leaves in the residue any metastannic acid. In case tin need not be tested for at this point, the residue may be more quickly dissolved by warming it with HCl

(1.12) and adding gradually a little solid KClO_3 ; since metastannic acid is soluble in HCl , this then passes into solution with the mercuric salt.

In the final test for mercury HCl is added to prevent the precipitation of a basic tin salt when the SnCl_2 reagent is diluted, and to cause the formation at first of white Hg_2Br_2 or Hg_2Cl_2 . For the latter reason, also, dilute SnCl_2 solution is added drop by drop to the cold solution. By the excess of SnCl_2 the white precipitate is reduced to gray, finely divided mercury.

*Platinum and gold compounds, if not removed, are reduced by SnCl_2 , the former giving a reddish brown solution and the latter a dark-colored or purple precipitate of metallic gold. The presence of these elements would thus interfere with, or prevent the detection of, mercury, and it is therefore directed to remove them.

***Procedure 24a.**—To the solution of the sulphides in bromine water (P. 24) add about 0.5 gram solid KCl and 1-2 cc. HCl (1.12), evaporate until KCl crystallizes out, cool, and add water drop by drop until almost all the KCl has dissolved. (Yellow precipitate, presence of PLATINUM). Filter and wash with a little saturated KCl solution. Confirm the presence of platinum in the precipitate by *P. 43a. To the filtrate add 10% NaOH solution till alkaline, and then about 1 cc. more. Then add saturated oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) solution until the solution becomes distinctly acid, dilute to about 15 cc., and digest on a steam bath for 10-15 minutes. (Purplish black or dark yellow precipitate, presence of GOLD). Filter. Reject the precipitate. Test the filtrate for mercury with SnCl_2 solution by the last part of P. 24.

Notes.—For notes upon this process, see *P. 43a and 43b. By means of it can be detected 1 mg. of gold or platinum in the presence of much mercury (at least 200 mg.), or 1 mg. of mercury in the presence of much gold or platinum.

Procedure 25.—If it is necessary to extract tin (see Note below) from the residue undissolved by HNO_3 and bromine water (P. 24), digest it, if it is still dark-colored, with another portion of bromine water to extract the rest of the mercury, filter, reject the filtrate, and warm the residue slightly with 2-5 cc. ammonium monosulphide, filter, and unite the solution with the main ammonium sulphide solution obtained in P. 22.

Notes.—If it is desired to detect with certainty the presence in the substance of a quantity of tin smaller than 5 mg., and if elements of the copper group are present in large quantity (100-500 mg.), it is necessary to recover the tin that remained with the copper group; for as previously stated, a quantity of tin as large as 5 mg. (or even larger when stannous tin and cadmium are both present) may remain entirely in the residue undissolved by ammonium sulphide when this residue is large. By extracting the tin as described in this procedure and uniting it with the main solution of the tin group 2 mg. of tin can be detected.

Procedure 26.—To the HNO_3 solution (P. 23) add 2-3 cc. concentrated H_2SO_4 , and evaporate in a casserole until fumes of H_2SO_4 begin to come off. Cool and pour into 10-15 cc. cold water, rinsing out the casserole with the same solution. Cool again, shake, and allow the mixture to stand 5 minutes, but not much longer. (Finely divided white precipitate, pres-

ence of LEAD or BARIUM; but a coarsely crystalline precipitate may be due to bismuth). Filter and wash the precipitate with H_2SO_4 (1.20), and finally with a little water. (Precipitate, P. 27; filtrate, P. 28).

Notes.— PbSO_4 is somewhat soluble both in water and in concentrated H_2SO_4 , but much less so in moderately dilute H_2SO_4 , its solubility being scarcely appreciable in mixtures containing one volume of H_2SO_4 (1.84) and two to six volumes of water. That the solubility in dilute H_2SO_4 is less than that in water is due mainly to the common-ion effect. Concentrated H_2SO_4 is, of course, an entirely different solvent. PbSO_4 dissolves fairly readily in dilute HNO_3 (or in dilute HCl), owing to metathesis arising mainly from the tendency to form hydrosulphate ion (HSO_4^-); hence, although this effect of HNO_3 is partly counteracted by the presence of much H_2SO_4 , yet, to ensure complete precipitation of PbSO_4 , the HNO_3 must be removed by evaporation.

When much bismuth is present it ordinarily is dissolved at first when the water is added to the concentrated H_2SO_4 , provided the mixture is kept cold; but from this solution a coarsely crystalline precipitate of an oxysulphate, such as $(\text{BiO})_2\text{SO}_4$, separates slowly upon standing in the cold but almost immediately upon heating, and to such an extent that there may remain in solution not more than 50 mg. of bismuth. If such a precipitate has separated with the PbSO_4 , filter, treat the filtrate by P. 28, and dissolve the precipitate by pouring repeatedly through the filter a 5-10 cc. portion of HCl (1.12), and test the solution so obtained for lead by following P. 26 and P. 27.

Procedure 27.—Pour repeatedly through the filter containing the H_2SO_4 precipitate (P. 26) a 10-20 cc. portion of a 10% ammonium acetate solution. To the filtrate add a few drops of K_2CrO_4 solution and 2-5 cc. 30% acetic acid solution. (Yellow precipitate, presence of LEAD).

Note.—This confirmatory test for lead should not be omitted; for the H_2SO_4 precipitate may consist not only of PbSO_4 but of $(\text{BiO})_2\text{SO}_4$ or of BaSO_4 , which last closely resembles PbSO_4 in appearance. $(\text{BiO})_2\text{SO}_4$ dissolves in ammonium acetate solution and gives a yellow precipitate on adding K_2CrO_4 ; but this precipitate, unlike PbCrO_4 , dissolves readily in acetic acid. BaSO_4 is not dissolved by ammonium acetate solution, owing to its very slight solubility in water and the fact that barium acetate, unlike lead acetate, is a largely ionized salt. If a white residue remains, this should be tested for barium, since under some circumstances substantially the whole of this element present in the substance may be found at this point. This test may be made by boiling the residue with strong Na_2CO_3 solution (whereby BaSO_4 is changed to BaCO_3), filtering out and washing the residue, dissolving it by pouring a small portion of dilute HCl through the filter, diluting sufficiently, and passing in H_2S to make sure that no lead is present or to remove it if present, boiling to expel H_2S , and adding 1-2 cc. H_2SO_4 (1.20). A white precipitate so obtained shows the presence of barium.

Procedure 28.—To the H_2SO_4 solution (P. 26) add NH_4OH slowly until a strong odor of it persists after shaking. (White precipitate, possible presence of BISMUTH; blue solution, presence of COPPER). Shake to cause coagulation, filter, and wash the precipitate. (Precipitate, P. 29; filtrate, P. 30 and 31).

Notes.—The precipitate produced by NH_4OH may also consist of $\text{Fe}(\text{OH})_3$, or of other hydroxides of the iron group, if these elements were carried down in the H_2S precipitate or were not completely removed from it by washing. The formation of a small precipitate is, therefore, not a sufficient proof of the presence of bismuth, and the confirmatory tests must be applied. Antimony which, like bismuth, gives with water a precipitate of an oxychloride cannot be present in sufficient quantity to be precipitated by NH_4OH .

That $\text{Cd}(\text{OH})_2$ or $\text{Cu}(\text{OH})_2$, though only very slightly soluble in water, dissolves in NH_4OH is due to the conversion of the Cd^{++} or Cu^{++} ion in the saturated solutions into the complex cathion $\text{Cd}(\text{NH}_3)_4^{++}$ or $\text{Cu}(\text{NH}_3)_4^{++}$, which is formed by the combination of the simple ion with un-ionized ammonia. These complex cathions have an extremely small ionization tendency; thus for cadmium in a normal NH_4OH solution the ratio of the concentration of the complex to the simple ion is about 10⁷. The solubility of these hydroxides in NH_4OH is greatly increased by the presence of ammonium salts, since these salts, owing to the common-ion effect, greatly reduce the ionization of the NH_4OH , and therefore the OH^- concentration in the solution, thus enabling the Cd^{++} or Cu^{++} concentration, and therefore also the corresponding complex ion concentration, to attain a much larger value than in the saturated solutions of $\text{Cd}(\text{OH})_2$ or $\text{Cu}(\text{OH})_2$ in NH_4OH alone. It will be noticed that four distinct equilibria are involved—that between solid $\text{Cd}(\text{OH})_2$ or $\text{Cu}(\text{OH})_2$ and its ions; that between Cd^{++} or Cu^{++} , NH_3 , and $\text{Cd}(\text{NH}_3)_4^{++}$ or $\text{Cu}(\text{NH}_3)_4^{++}$; that between NH_4OH , NH_3 , and H_2O ; and that between NH_4OH , NH_4^+ , and OH^- . It may be further mentioned that, since in any dilute solution the concentration of the water is substantially the same, the concentration of any hydrate (like NH_4OH) is proportional to that of the anhydrous substance (NH_3).

Procedure 29.—Dissolve the NH_4OH precipitate (P. 28) by pouring a little HCl (1.12) through the filter, evaporate off the acid almost completely, leaving the residue only barely moist with it, add 1-2 cc. water, pour the solution into a flask containing 100 cc. water heated to 50-70°, and allow the mixture to stand 2 or 3 minutes. (White precipitate, presence of BISMUTH). Filter, wash once, and pour through the filter a freshly prepared solution of sodium stannite. (Black residue, presence of BISMUTH).

Notes.—The white precipitate of BiOCl formed in the first confirmatory test for bismuth is produced by the hydrolysis of BiCl_3 . If HCl , the other product of the hydrolysis, is present in the solution, the reaction will not be complete, and a greater or less quantity of bismuth will remain in solution. This quantity increases rapidly with the acid concentration in accordance with the Law of Mass-Action. For this reason, if the presence of half a milligram of bismuth in the precipitate is to be detected, the HCl must be removed by evaporation so completely that not more than 0.2 cc. remain, and the solution must be added to a large volume of water. Warm water is used, because the precipitation of BiOCl takes place more rapidly at the higher temperature.

The solution of sodium stannite (Na_2SnO_2) is prepared when needed by adding a 10% NaOH solution to a 10% SnCl_2 solution until the $\text{Sn}(\text{OH})_2$ first formed is dissolved. The solution must be freshly prepared, because it decomposes spontaneously into sodium stannate (Na_2SnO_3) and metallic tin, and because it oxidizes in contact with air to sodium stannate. $\text{SnO}_2\cdot\text{H}_2$ is an example of a so-called amphoteric substance—one which acts either as a base or an acid, as is shown by its solubility in both acids and alkalis.

The final test with sodium stannite depends on the reduction of BiOCl to black metallic bismuth. The test is an extremely delicate one, and by it may be detected a quantity of bismuth so small as to produce only a scarcely visible turbidity of BiOCl ; for, when the precipitate in such a solution is collected on a filter and treated with stannite, the black color of the bismuth is very apparent. Antimony oxychloride, even if present, is not blackened by the stannite. The NH_4OH precipitate itself might be directly tested with this reagent; for the other reducible substances, like $\text{Fe}(\text{OH})_3$, $\text{Pb}(\text{OH})_2$, or $\text{Cu}(\text{OH})_2$, that might possibly be present in that precipitate are not reduced by short contact with stannite solution in the cold. It is, however, often desirable to get the double indication of the presence of bismuth, as furnished by the precipitation of the oxychloride by water and by its blackening with the sodium stannite.

Procedure 30.—Acidify one-fourth of the NH_4OH solution (P. 28) with acetic acid, add 2-3 drops 3% $\text{K}_4\text{Fe}(\text{CN})_6$ solution, and allow the mixture to stand for several minutes. (Red precipitate, presence of COPPER). If it is uncertain whether there is a precipitate, pour the solution through a filter and wash with a little water. (Pink color on the filter, presence of COPPER).

Notes.—Cadmium is precipitated by $\text{K}_4\text{Fe}(\text{CN})_6$, as well as copper; but the cadmium precipitate is white, and does not prevent the pink color of the copper compound from being detected, provided only a small quantity of $\text{K}_4\text{Fe}(\text{CN})_6$ is added; for the copper salt, owing to its smaller solubility, is first precipitated. Nickel, if present, would, like copper, give a blue solution with excess of NH_4OH ; but it would give a greenish white, not a red precipitate, with $\text{K}_4\text{Fe}(\text{CN})_6$. Aside from copper, only the rarer elements, uranium and molybdenum, give red precipitates with this reagent; and they do not do so in an acetic acid solution, such as is obtained in the procedure.

Procedure 31.—To the remainder of the NH_4OH solution (P. 28 and 30) add solid KCN till the blue color disappears, and pass in H_2S gas for about half a minute. (Flocculent yellow precipitate, presence of CADMIUM). (Precipitate and solution, reject).

Notes.—By the addition of KCN the copper salt is reduced from the cupric to the cuprous state and then combines with the excess of KCN to form the complex salt $\text{K}^+ \text{Cu}(\text{CN})_2^-$ (potassium cuprocyanide). This result is due to the fact that cupric cyanide tends to decompose spontaneously into cuprous cyanide and cyanogen, and that this reaction takes place completely in KCN solution, owing to removal of the cuprous cyanide by combination with the excess of KCN . In the presence of NH_4OH the cyanogen is not evolved as a gas, but reacts with it, forming cyanate (NH_4CNO) and cyanide and other more complex products. The fact that neither CuS nor Cu_2S is precipitated from this solution by an alkaline sulphide shows that neither the Cu^{++} nor Cu^+ concentration is sufficient to cause the value of the solubility product to be attained. The extremely small Cu^+ concentration is due to the very slight ionization tendency of the complex anion $\text{Cu}(\text{CN})_2^-$; thus it has been estimated that in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple Cu^+ ion is about 10^{20} .

The cadmium ammonia salt is also converted by KCN into a complex cyanide, namely, $\text{K}^+ \text{Cd}(\text{CN})_4^-$ (potassium cadmicyanide), since its complex anion has a much smaller ionization tendency than the cation $\text{Cd}(\text{NH}_3)_4^{++}$; thus in a normal KCN

solution the ratio of the concentration of the complex anion to that of the simple Cd^{++} ion is about 10^{17} . Yet this complex anion is sufficiently dissociated into Cd^{++} ion to cause the solution to become saturated with CdS when an alkaline sulphide is added.

A very small black precipitate (which may be due to HgS or PbS) may sometimes be produced in the final test for cadmium with H_2S ; but, provided the analysis has been properly conducted, not in sufficient quantity to prevent the yellow color of 1 or 2 mg. of CdS from being seen. In case a black precipitate is produced, and thus prevents a positive conclusion as to the entire absence of cadmium, the precipitate may be treated, in order to eliminate the black sulphide, as follows: Boil the precipitate for about 5 minutes with about 15 cc. of a mixture of one volume of H_2SO_4 (1.20) with four volumes of water, filter, cool the filtrate, add to it three times its volume of water, and pass H_2S into it for 5-10 minutes. A yellow precipitate of CdS should then be obtained, if cadmium is present.

Analysis of the Tin Group

Procedure 41.—Dilute in a small flask the first portion of the ammonium sulphide solution (P. 22) with about 20 cc. water, make it distinctly acid with HCl , and warm it slightly for 5 minutes with frequent shaking to coagulate the precipitate. (Fine, not flocculent, white or pale yellow precipitate, absence of TIN GROUP; deep yellow or orange flocculent precipitate, presence of TIN GROUP). Treat the second portion of the ammonium sulphide solution (P. 22) in the same way, and unite the precipitate, if considerable in amount, with the first one. Filter out and wash the precipitate, using suction, finally sucking it as dry as possible. (Precipitate, P. 42; filtrates, reject).

Notes.—Much time is saved by determining at this point whether or not any element of the tin group is present. When ammonium monosulphide has been used, there is usually no difficulty in drawing a definite conclusion in regard to this from the size and appearance of the HCl precipitate; for in the absence of the tin group only a very small, nearly white precipitate of finely divided sulphur separates. When, however, ammonium polysulphide has been used, it may not be possible to decide as to the presence or absence of a small quantity (1-5 mg.) of arsenic, antimony, or tin; for not only is a fairly large precipitate of sulphur then obtained, but it may be darkened in color by the presence of CuS or HgS : yet when the precipitate is nearly white, and finely divided or granular, the conclusion can be drawn at once that no element of the tin group is present in quantity as large as 1 mg.; and when it has a pronounced yellow color (indicating arsenic or tin) or an orange-red color (indicating antimony) the conclusion can be drawn that one of these elements is present. In this connection it may be mentioned that a mixture of SnS_2 and Sb_2S_3 does not always have a color intermediate between those just mentioned, but may be brown or dark gray.

When, however, the HCl precipitate from a polysulphide solution is fairly small and is dark brown (indicating copper) or dark gray or black (indicating mercury or one of the rarer elements) or of unpronounced yellow or orange color, so as to make any conclusion as to the tin group doubtful, the precipitate is best treated as follows: Heat it with 15-20 cc. NH_4OH (0.96) almost to boiling for 5 minutes and filter; test the precipitate for copper by P. 23, 28 and 30 if it has not already been found present; add to the filtrate a few drops of ammonium monosulphide,

filter out any precipitate, heat the filtrate to boiling, make it acid with HCl, shake, filter out the precipitate, and treat it by P. 42 as usual. The character of the HCl precipitate thus obtained will clearly indicate the presence or absence of the tin group; for by the treatment with NH_4OH the excess of sulphur originally present and any CuS is left undissolved, and by the $(\text{NH}_4)_2\text{S}$ added to the solution any mercury present is precipitated, so that the HCl precipitate can contain only sulphides of the tin group and a very little sulphur. As_2S_5 , Sb_2S_5 , and SnS_2 all dissolve in NH_4OH (though in the cases of Sb_2S_5 and SnS_2 less abundantly than in ammonium sulphide), owing to the formation of a mixture of salts of the intermediate sulpho acids, such as $\text{H}_3\text{AsO}_3\text{S}$ and $\text{H}_3\text{AsO}_2\text{S}_2$. The addition of $(\text{NH}_4)_2\text{S}$ to the NH_4OH solution and the heating serve to convert these into more highly sulphurated acids, from which HCl will then precipitate the simple sulphides completely.—The incidental removal of the small amounts of CuS and HgS by the NH_4OH treatment is not necessary as far as the analysis of the tin group is concerned, since their presence does not interfere with the detection of even 1 mg. of arsenic, antimony, or tin; but it does enable 1 or 2 mg. of copper to be detected which might otherwise be lost.

When the HCl is added to the solution of the sulpho salts, the corresponding sulpho acids which are liberated decompose immediately into H_2S and the solid sulphides, which are now necessarily in the higher state of oxidation, since the lower sulphides, if originally present, have been oxidized by the polysulphide. The fact that the sulpho acids decompose while the sulpho salts are stable is a consequence of the Mass-Action Law, which, when applied to the dissociation of the complex anions taking place, for example, according to the equation, $\text{SnS}_3 = \text{SnS}_2 + \text{S} =$ evidently requires that these decompose to a greater extent into the un-ionized sulphides (SnS_2 , etc.) the smaller the concentration of the $\text{S} =$ ion in the solution. Now in the solution of the largely ionized $(\text{NH}_4^+)_2\text{S} =$ there is a fairly large concentration of $\text{S} =$ ion; but when the solution is made acid with HCl, the $\text{S} =$ ion is, for the most part, converted by the relatively large concentration of the H^+ ion into the slightly ionized substances HS^- and H_2S ; and consequently the concentration of the un-ionized sulphides in the solution becomes great enough to exceed the solubility value, and the solid sulphides separate out.

Procedure 42.—Transfer the precipitated sulphides dried by suction (P. 41) to a wide test tube, add from a small graduate exactly 10 cc. HCl (1.20), and heat nearly but not quite to boiling (preferably by immersing the test tube in hot water or on a steam bath) for about 10 minutes with frequent stirring. Add 5 cc. water from a graduate containing 40 cc. water, filter, wash once with about 5 cc. water from the graduate, collecting this wash water with the filtrate; remove the filtrate, and add to it the water remaining in the graduate; wash the residue with HCl (1.12). (Residue, P. 43; filtrate, P. 45).

Notes.—If a much weaker HCl solution than the acid of specific gravity 1.20 is used, or if the acid becomes diluted by an unnecessary quantity of water left in the precipitate, much Sb_2S_5 will be left undissolved. Even with the strong acid some Sb_2S_5 may remain undissolved, especially when a large quantity is present, in which case the residue, if small in amount, will have an orange color. This small quantity of Sb_2S_5 would be only very slowly removed by further treatments with HCl; it does not, however, interfere with the subsequent tests for arsenic. Moreover, when only a small quantity of Sb_2S_5 is originally present, a large propor-

tion of it is extracted, so that it will not escape detection. Sb_2S_3 dissolves with formation of $SbCl_3$ and liberation of sulphur; SnS_2 with formation of $SnCl_4$.

If the solution be kept just below the boiling point during the treatment with HCl, the amount of As_2S_3 which dissolves in 10 minutes is insignificant; but this is no longer true if the solution be allowed to boil, for the boiling rapidly expels from the solution the H_2S liberated from the other sulphides or by slight decomposition of the As_2S_3 itself, and thus enables the decomposition of the latter to proceed further.

As_2S_3 is more rapidly dissolved by HCl than is As_2S_5 . If the former can be present in the precipitate, which can occur only when HNO_3 or *aqua regia* was not used in dissolving the original substance and if ammonium monosulphide was employed for separating the copper and tin groups, the procedure should be modified as follows: After the addition of HCl to the sulphides saturate with H_2S in the cold, and then heat nearly but not quite to boiling for 10 minutes, passing a slow current of H_2S gas through the mixture. Under these conditions scarcely any As_2S_3 dissolves.

About 5 cc. water are added to the HCl solution to enable it to be filtered. If more be added, and the H_2S has not been completely expelled from the solution, a precipitate of Sb_2S_3 may separate. If this happens after the filtration, it does, of course, no harm. Care must be taken to follow closely the directions in regard to the quantities of HCl and water used; for the subsequent separation of antimony and tin (P. 45) depends upon a proper concentration of the acid.

The greater part of any CuS and HgS present will be dissolved by the HCl, and will be precipitated later with the Sb_2S_3 (P. 45). A little remains with the As_2S_3 , but this does not interfere with the tests for arsenic. *Of the precipitates of the rarer elements, PtS_2 , Au_2S_3 , Se, and MoS_3 are dissolved by the HCl scarcely at all, and TeS_2 only to a small extent. The dissolving of the last, like that of As_2S_3 , can be entirely prevented by passing a slow current of H_2S through the hot HCl solution.

Procedure 43.—Warm the residue from the HCl treatment (P. 42) with 5-10 cc. HCl (1.12), adding solid $KClO_3$ in small portions until the reaction is complete; filter off the sulphur, and evaporate the solution to about 2 cc. [If the solution is still distinctly yellow, or if a yellow precipitate has separated, test for and remove platinum by *P. 43a, and treat the filtrate as follows]. Add NH_4OH gradually until the solution after shaking smells of it; cool filter off and reject any precipitate. Add to the filtrate about one-third its volume of NH_4OH (0.90) and several drops of magnesium ammonium chloride reagent, and shake. If no precipitate appears, rub the walls of the test tube gently with a glass rod for a minute or two. (White crystalline precipitate, presence of ARSENIC). Collect the precipitate on a filter and wash it once with NH_4OH (0.96). (Precipitate, P. 44; filtrate reject, or test for gold, selenium, tellurium, and molybdenum, by *P. 43b).

Notes.—The main reaction between $KClO_3$ and concentrated HCl is the formation of Cl_2 ; the yellow color results from the formation of a small proportion of chlorine dioxide, ClO_2 .

As_2S_5 , though only very slowly dissolved by HCl alone, is dissolved rapidly by it in the presence of Cl_2 , because of the destruction of the H_2S , one of the reaction products, by oxidation. It is dissolved with formation of H_3AsO_4 ; $AsCl_3$ has not

been shown to exist. When, as here, arsenic is present in the higher state of oxidation, solutions of it may be boiled without loss of an amount of arsenic significant in qualitative analysis.

A white precipitate, obtained on adding NH_4OH , may arise from the presence of mercury. The NH_4OH solution may contain not only arsenic, but also certain rare metals and the small quantities of copper (if ammonium polysulphide was used), antimony, and stannic tin that were not dissolved out of the sulphide precipitate by HCl .

The test for arsenic depends on the formation of magnesium ammonium arsenate, $\text{Mg}(\text{NH}_4)_2\text{AsO}_4$. This salt is somewhat soluble in water, and therefore the solution tested should be fairly concentrated. Owing to hydrolysis (into NH_4OH and $\text{Mg}^{++}\text{HAsO}_4^-$), the precipitate is much more soluble in water than in a strong NH_4OH solution; hence the addition of a large quantity of the latter. Like other crystalline precipitates, it tends to form a supersaturated solution. Precipitation is promoted by agitation, by rubbing the walls of the tube with a glass rod, and by increasing the degree of supersaturation, which is done by concentrating and adding NH_4OH . Provided these precautions are taken and the total volume of the final solution does not exceed 5 cc., the presence of even half a milligram of arsenic can be detected. Care must be taken not to scratch the glass by violent rubbing, since the powdered glass may be mistaken for the $\text{MgNH}_4\text{AsO}_4$ precipitate. The magnesium ammonium chloride reagent contains MgCl_2 and NH_4Cl . The presence of the latter salt prevents the precipitation of $\text{Mg}(\text{OH})_2$ by NH_4OH , by reducing the OH^- concentration.

***Procedure 43a.**—Evaporate the solution of the sulphides in HCl and KClO_3 (P. 43) until KCl crystallizes out, cool, and add water drop by drop until the KCl just redissolves. (Yellow precipitate, presence of PLATINUM). Filter, wash the precipitate with a little cold saturated KCl solution, and treat the filtrate by P. 43 to detect and remove arsenic. Dissolve the precipitate by pouring repeatedly a 5-10 cc. portion of hot water through the filter, and add to the solution a few drops of KI solution. (Deep red color, presence of PLATINUM).

Notes.—Potassium chlorplatinate, $\text{K}^+\text{PtCl}_6^-$, is fairly soluble in water, but much less so in a saturated KCl solution, owing to the common-ion effect. The deep red color formed on the addition of KI to K_2PtCl_6 is due to the formation of K_2PtI_6 in solution. When the K_2PtCl_6 is present in excess a black precipitate of PtI_4 separates, but this dissolves readily on further addition of KI .

***Procedure 43b.**—To the filtrate from the MgCl_2 precipitate (P. 43) add 2-3 cc. saturated oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) solution, and evaporate in a casserole to 3-4 cc. to expel the excess of ammonia. Make the solution slightly acid with $\text{H}_2\text{C}_2\text{O}_4$, if it is not already so, add about 10 cc. water, and digest on a steam bath for several minutes. (Purple precipitate, presence of GOLD). To the mixture add 2-3 cc. HCl (1.12) to dissolve any tellurium hydroxide, and filter. (Precipitate, reject; filtrate, *P. 43c).

Notes.—Metallic gold is precipitated readily from a solution of ammonium oxalate only when the solution is hot and slightly acid; but even under these conditions the precipitation is complete only after several minutes. If these conditions are not realized, several milligrams of gold may escape detection. The more powerful

reducing agents, H_2SO_3 and SnCl_2 , also precipitate gold, but they reduce selenium and tellurium (and mercury) compounds as well.

***Procedure 43c.**—Evaporate the filtrate from the $\text{H}_2\text{C}_2\text{O}_4$ precipitate (*P. 43*b*) almost to dryness, add 10 cc. HCl (1.12), and filter off any KCl that has separated. Collect the filtrate in a test tube, add about 0.2 gram solid Na_2SO_3 , and allow the mixture to stand for at least 5 minutes, adding more Na_2SO_3 if the SO_2 odor disappears. (Red precipitate, presence of SELENIUM). Filter. (Precipitate, reject; filtrate, *P. 43*d*).

Notes.—By the action of H_2SO_3 on selenious acid (H_2SeO_3) in the cold a voluminous red precipitate of selenium is quickly formed; but the reaction is complete only after several minutes. When the solution is hot the more compact black modification of selenium is obtained; but the test is then less delicate and less characteristic.

Tellurium is reduced by H_2SO_3 in moderately dilute HCl solutions, but not at all when the concentration of the acid is as great as that of specific gravity 1.12. Selenium, however, separates completely from a more concentrated acid, as well as from a more dilute one. For these reasons, though a greater concentration of HCl is unobjectionable, a lesser concentration would cause the precipitation of tellurium and obscure the selenium test.

***Procedure 43d.**—Dilute the filtrate from the H_2SO_3 precipitate (P. 43*c*) with an equal volume of water, and add a few drops of KI solution and a little solid Na_2SO_3 . (Black precipitate, presence of TELLURIUM). Filter after a few minutes. (Precipitate, reject; filtrate, *P. 43*e*).

Notes.—As already stated, tellurium is precipitated by H_2SO_3 alone when the HCl solution of specific gravity 1.12 is diluted somewhat with water, especially if the mixture is kept hot. The precipitation, however, is much more rapid and is complete after a few minutes even in the cold if KI is also present. KI alone does not reduce tellurium compounds, but precipitates black TeI_4 , which dissolves somewhat in excess of KI , forming a deep red solution of K_2TeI_6 . The advantage of adding KI is that the iodine compound of tellurium is more rapidly reduced by H_2SO_3 than is the chlorine compound or tellurous acid itself.

Selenious acid is immediately reduced to selenium by KI in HCl solution; but this element is completely precipitated by H_2SO_3 in *P. 43*c* if the directions there given are followed; even if not so removed, it would give a red precipitate, not a black one.

Molybdic acid by this treatment is also slowly reduced to a lower compound, which remains in solution. Iodine may thereby be liberated and even precipitated after all the H_2SO_3 has been oxidized. For this reason the solution should not be allowed to stand for more than half an hour before filtering.

***Procedure 43e.**—Boil the filtrate from the KI precipitate (*P. 43*d*) until the SO_2 is expelled, cool the solution, add 3 or 4 cc. 10% KCNS solution and some granulated zinc. (Red color, presence of MOLYBDENUM). [If it is desired to form a better estimate of the quantity of molybdenum present, treat the solution as described in the Note below].

Notes.—The H_2SO_3 is boiled out, since otherwise sulphur would be precipitated by the action of zinc. The red color is due to the formation of $\text{Mo}(\text{SCN})_4$, corresponding to MoO_3 , an intermediate stage in the reduction of molybdic acid (H_2MoO_4) by the zinc. The color may appear before the addition of zinc, since the

H_2MoO_4 may already have been partially reduced by H_2SO_3 and HI. Long-continued action of zinc causes the red color to disappear; for the chloride MoCl_3 , corresponding to the oxide Mo_2O_3 , to which H_2MoO_4 is finally reduced, gives a colorless solution with KCNS. Ferric salts also give a red color with KCNS; but a coloration arising from the presence of iron as an impurity disappears almost immediately on the addition of zinc, owing to reduction to the ferrous state. It is difficult from the depth of the red coloration to form an estimate of the quantity of molybdenum present. The molybdenum may be obtained in the form of a precipitated sulphide by treating the solution to which KCNS and zinc have been added as follows: Add a little solid KClO_3 and boil to reoxidize the molybdenum, and finally to expel the chlorine, adding more HCl (1.20), if necessary; pass H_2S into the solution for 10 minutes, keeping it near the boiling point.

Procedure 44.—Dissolve the $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl}$ precipitate (P. 43) by pouring a little HCl (1.12) through the filter, heat the solution obtained nearly to boiling, and pass in H_2S for at least 5 minutes, keeping the solution hot. (White precipitate turning yellow, presence of ARSENIC). (Precipitate and solution, reject).

Notes.—The slow formation in a dilute acid solution of a pale yellow precipitate with H_2S is a characteristic test for H_3AsO_4 . The precipitate is a mixture of As_2S_3 , As_2S_5 , and sulphur, but the amount of As_2S_3 is comparatively small in the presence of strong HCl and at high temperatures.

A considerable amount of H_2S may be absorbed by a dilute H_3AsO_4 solution before any precipitate appears. This is due to the formation of $\text{H}_3\text{AsO}_3\text{S}$, which then decomposes slowly, giving H_2AsO_3 and sulphur. This last decomposition may be accelerated by increasing the H^+ concentration and by raising the temperature. The H_2AsO_3 formed reacts at once with H_2S , and As_2S_3 is precipitated. The rate of this reaction depends upon the rate of the slowest of the single reactions—the decomposition of $\text{H}_3\text{AsO}_3\text{S}$. As_2S_5 is produced directly by an independent reaction, which takes place very slowly.

Procedure 45.—Heat the solution of the sulphides (P. 42), which should contain 10 cc. HCl (1.20) in a total volume of 50 cc., to about 90° , and pass in H_2S gas for about 5 minutes, keeping the solution at about 90° . If no precipitate appears, add about 5 cc. water, and again saturate with H_2S at the same temperature as before. (Orange red precipitate, presence of ANTIMONY). Filter while hot, add 5 cc. water, heat the filtrate nearly to boiling, again saturate with H_2S to ensure complete precipitation of antimony, and filter if any precipitate forms. Wash the precipitates with hot water. (Precipitate, P. 46; filtrate, P. 47).

Notes.—By following carefully the directions given in P. 42 and this procedure, a good separation of antimony and tin may be obtained; when only 1 mg. of antimony is present it is precipitated as Sb_2S_3 , while even 500 mg. of (stannic) tin give no precipitate. If, however, the HCl solution be too concentrated, a small quantity of antimony will escape detection; hence the precaution of adding a little water to the solution and repeating the treatment with H_2S . If the HCl solution be too dilute, or if it be not kept hot, some SnS_2 may precipitate when a large amount of tin is present. When mixed with a little Sb_2S_3 a brown precipitate results.

If mercury or copper be present in the substance and ammonium polysulphide has been used, HgS or CuS may be precipitated at this point as a gray or black precipitate.

Procedure 46.—Dissolve the H_2S precipitate (P. 45) in a little strong HCl in a small casserole and evaporate the solution to about 1 cc. Introduce beneath the solution a piece of platinum foil and place upon it a piece of pure tin. After several minutes wash carefully with water, and cover the platinum foil with (alkaline) NaOCl solution. (Black deposit on the platinum undissolved by NaOCl , presence of **ANTIMONY**). (Precipitate and solution, reject).

Notes.—Mercury and copper, if present, will also be precipitated in the metallic condition upon the platinum, but the antimony may be easily distinguished from them by its black color. Tin is used rather than zinc in precipitating the antimony, since zinc would also precipitate tin from the solution.

The treatment with NaOCl serves to prove that the black precipitate does not consist of arsenic or tellurium; for these elements are readily dissolved by it, while antimony is not. Since, however, several milligrams of arsenic must be present before the treatment with tin would give a deposit on the platinum, an arsenic deposit will probably never be obtained in an actual analysis.

Procedure 47.—Cool the filtrate from the H_2S precipitate (P. 45), dilute with 20 cc. water, and pass in H_2S for 10 minutes. (Yellow precipitate, presence of **TIN**). If there is a precipitate, evaporate the mixture without filtering to 5-10 cc., add about 1 gram of granulated zinc, and allow the action to continue for several minutes, but not until all the zinc is dissolved. (Gray; spongy precipitate, presence of **TIN**). Decant the solution into a test tube, allow any particles suspended in it to settle out, decant again, and unite the two residues. Heat the residues with 2-5 cc. HCl (1.20) until everything (except any particles of carbon) is dissolved. Dilute the solution with one-half its volume of water, and pour it at once through a small filter into 5 cc. HgCl_2 solution. (White precipitate, presence of **TIN**).

Notes.—The solution is precipitated with H_2S in the cold, because a small quantity of SnS_2 would not separate from a hot solution unless the acid were more diluted. The addition of much water is avoided, since it has to be evaporated off in the confirmatory test.

In the confirmatory test the precipitate of SnS_2 is not filtered off, but is dissolved by concentrating the acid by evaporation, since it clogs the filter and tends to pass through it. The zinc must not be allowed to dissolve entirely, since the tin might then also dissolve. Care must also be taken not to lose it in the process of decantation or by failing to dissolve it completely. Finally, since SnCl_2 oxidizes rapidly in the air, the solution in HCl must be immediately added to the HgCl_2 solution. If these precautions are observed, the presence of half a milligram of tin in the HCl solution of the sulphides (P. 42) may be detected after some practice. The confirmatory test is, however, less delicate than the precipitation by H_2S . but it is more characteristic, since SbCl_3 , even if present, does not reduce HgCl_2 .

TEST ANALYSES

Numerous analyses were made to test the efficiency of the process above described. Nearly all of those which were made after the procedure assumed final form are reproduced in the tables below. In these tables the numbers in each vertical column show the weights in milligrams of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S; that is, when the element was present, that the test for it, however small, was unmistakable, and therefore conclusive; and when the element was absent, that a good blank test was obtained. When the test was very small, especially in comparison to the quantity of the element present, though still unmistakable, this is sometimes indicated by the symbol S—. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing to the appearance or small size of the precipitate, this is indicated by the letter D. When the test was not tried, if the element was present, a dash is used in place of a letter; or, if the element was not present, dots are inserted.

Silver Group

All these analyses (Nos. 1-9) were begun at P. 11 and carried through P. 15.

T.A. No.	1	2	3	4	5, 6	7	8	9
Pb	500 S	500
Ag	o S	1 S	500 S	500 S	o S	1 F	1 S—	2 S
Hg.....	o S	1 S	o S	1 S	500 S	500 S	500 S	500 S

Copper Group

The following analyses (Nos. 10-20) were begun at P. 21 and were carried through P. 23-31, P. 22 being omitted. In addition, tin was tested for by P. 25, 41, 42, 45, and 47.

T.A. No.	10	11	12	13	14	15
Hg.....	500 S	500 S	500 S	500 S	1 S—	o S
Sn (ous).....	o S	2 F	4 S	2 S, F ¹	2 S, F ¹	o S
Pb	o S	1 S—	1 F	2 S	1 S	o S
Bi.....	o S	1 S	1 S	o S	500 S	500 S
Cu	o S	1 S	1 S	o S	1 S	o S
Cd	o S	1 S	1 S	o D ²	1 S	o S

T.A. No.	16	17	18	19	20
Hg.....	o S	1 S	o S	1 S	2 S
Sn (ous).....	o S	2 S	o S	2 S	o ₂ S
Pb	o S	1 S	o S	1 F	1 S
Bi	o S	1 S	o S	1 S	1 S
Cu	500 S	500 S	o S	1 S	1 S
Cd	o D ²	1 S	500 S	500 S	500 S

The following analyses (Nos. 21-28) were begun at P. 21, the H_2S precipitate was digested once with 10 cc. ammonium polysulphide (P. 22), and the residue analyzed by P. 23-31.

T.A. No.	21	22	23	24	25	26	27	28
Hg (ic)	2 S	I D
Cu	2 S— ³	5 S	3 S	2 S ⁴	2 S ⁵	3 S
Bi	500 S
Sn (ous)	300 S	300	300	50 S
Sb (ous)	300 S	300 S	200 S

The following analyses (Nos. 29-30) were made in the same way, except that 25 cc. ammonium monosulphide were used.

T.A. No.	29	30
Hg (ic)	I S	I S
Cu	I S ⁶	I F
Sb (ic)	300—
As	250—
Sn (ic)	250—

Tin Group

In the following analyses (Nos. 31-56) the substances were dissolved directly in ammonium polysulphide and the solution treated by P. 41-47.

T.A. No.	31	32, 33	34, 35, 36	37, 38	39, 40	41, 42, 43	44, 45	46	47
As	0 S	2 S	I S	500 S
Sb	500 S	500 S	500 S	0 S	0 S	I S	500 S	500 S	500 S
Sn	0 S	500 S	500 S	0 S	I S— ⁶	I S

T.A. No.	48	49	50	51	52	53, 54	55	56
As	0 S	I S	2 S	I S	500 S	500 S	500 S
Sb	0 S	I S	I S	2 S	200 S	I S	I S	0 S
Sn	500 S	500 S	I S	2 S	500 S	I S	I S—, F ¹	I S

In the following experiments (Nos. 57-90), in which a large quantity of an element of the copper group was present with the tin group, the analysis was begun at P. 21, the H_2S precipitate was treated once with 10 cc. ammonium polysulphide, and the solution analyzed by P. 41-47. The copper-group residue was not treated by P. 23-25 to recover tin.

T.A. No.	57	58	59	60	61	62
Bi	500—	500—	500—	500—	500—	500
As	0 S ⁷	I F	2 S	I S
Sb (ous)	0 S	I S	2 S	0 S
Sn (ous)	0 S	I F	2 S	0 S	2 S	I S ⁸

T.A. No.	63	64	65	66	67	68
Hg	500—	500—	500—	500—	500—	500—
As	0 S ²	I S	2 S	0—
Sb (ous)	0 S	I S	2 S	0 S
Sn (ic)	0 S	I F	2 F	5 F	5 F	10 S ⁹

T. A. No.	69	70	71	72	73	74	75
Cu	500—	500—	500—	500—	500—	500—	500—
As	0 S ⁷	1 S	2 S	0 S
Sb (ous)	0 S	1 S	2 S	0 S
Sn (ous)	0 S	1 F	2 F	2 F	4 S—, F ¹	5 S ⁹	3 S—, F ¹
						(stannic)	
T. A. No.	76	77	78	79, 80	81	82	83
Cd	500—	500—	500—	500—	500—	500—	500—
As	0 S ⁷	2 S	1 S	1 S	0 S
Sb (ous)	0 S	2 S	1 S	1 S	0 S
Sn (ous)	0 S	2 F	0 S	2 F	10 F	10 S—, F ¹	15 S ⁸
Sn (ic)	0 S
T. A. No.	84	85	86	87, 88	89	90	
Cd	500—	500—	500—	500—	500—	500—	
As	
Sb (ous)	
Sn (ous)	15 S—, F ^{1,10}	20 S ⁹	25 S—, F ^{1,10}	25 S	
Sn (ic)	3 F	5 S ⁹	

The following analyses (Nos. 91-97) were made by Mr. A. L. Smith in the same way as the preceding ones, except that 25 cc. ammonium monosulphide, instead of 10 cc. polysulphide, were used in digesting the H₂S precipitate.

T. A. No.	91	92	93	94	95	96	97
Hg (ic)	500—
Bi	500—	500—	500—
Cd	500—	..	250—	..
Cu	500—	250—	..
As (ic)	1 S
Sb (ic)	2 S	4 S	2 S	2 S	1 S	1 S	1 S
Sn (ic)	5 F ¹²	10 F ¹²	5 S	5 S	5 F ¹²	5 F ¹²	5 F ^{12,13}

In the following analyses (Nos. 98-100), also made by Mr. A. L. Smith, the solution in ammonium monosulphide and the residue were treated separately in order to detect tin. It was not detected in any case in the analysis of the solution. The results shown in the table were obtained in the analysis of the residue.

T. A. No.	98	99	100
Hg (ic)	250—	250—	..
Bi	250—	250—	..
Cd	250—
Cu	250—
Sn (ic)	2 F	5 S	3 S—, F ¹

Mixtures Containing the Rarer Elements

The following analyses were made, starting at P. 41, with an ammonium polysulphide solution, and following P. 42, 43, and *P. 43a-43e.

T. A. No.	101	102	103	104	105
As.....	300 S	200 S	200 S
Sb.....	200 —
Sn.....	200 —	200 —	200 —
Se.....	0 S	1 S	1 S	1 S	0.5 S
Te.....	0 S	1 S	1 —	2 S	1 S
Mo.....	100 S	50 S	1 S	0 S	0.5 S

The following analyses were begun at P. 21, the H₂S precipitate was extracted with ammonium polysulphide (P. 22), the solution was analyzed by P. 41-43 and *P. 43a-43e, and the residue treated by P. 23, 24, and *P. 24a.

T. A. No.	106	107	108
Cu.....	300—	200—	100—
Hg.....	0 S	0 S	0 S
Pt.....	5 S ¹¹	3 S ¹¹	2 S ¹¹
Au.....	5 S ¹¹	3 S ¹¹	1 S ¹¹
Te.....	10 S

The following analyses (Nos. 109-111) were made by Mr. A. L. Smith, beginning with P. 21 and following through the whole process as described in P. 21-47. Ammonium monosulphide was used in separating the copper and tin groups.

T. A. No.	109	110	111	112 ¹⁸	113
Hg (ic).....	1 D ¹⁴	1 —	1 F ¹⁴	..	2 D ¹⁴
Pb.....	1 F	1 S	1 S—	..	1 S
Bi.....	0 S	1 S ¹⁹	1 S ¹⁹	..	1 S
Cd.....	1 D	1	1 F ¹⁶	1 S	2 S
Cu.....	1 S	1 S	1 S	..	1 S
As (ic).....	1 F	1 S	1 S	..	1 S
Sb (ic).....	0 S	1 S	1 S—	1 S	1 S
Sn (ic).....	2 S	1 S—, F ¹	1 S—, F ¹	..	2 S
Pt.....	1 S ¹⁵	1 S ²⁰	1 S	..	1 S ¹⁵
Au.....	1 S ¹⁵	1 S ²⁰	1 S ¹⁵	..	1 S ¹⁵
Se.....	1 F	1 F ²¹	1 S—	1 S	2 F ²¹
Te.....	1 F	1 F	1 S— ¹⁷	1 S	2 F ²²
Mo.....	1 D.	1 D	1 S— ¹⁷	1 S	2 S

¹The confirmatory test with HgCl₂ failed, but a distinct precipitate of SnS₂ was obtained.

²A very small, dark precipitate was obtained.

³No blue color was produced with NH₄OH, but a slight pink precipitate with K₄Fe(CN)₆ was visible on the filter.

⁴A good blue color was obtained with NH₄OH, showing that a small quantity of copper is not dissolved out of a large copper-group precipitate by the polysulphide.

⁵No blue color could be seen, but a very distinct pink precipitate formed with K₄Fe(CN)₆.

⁶In this analysis the confirmatory tin test failed, but this was doubtless due to the fact that the SnS₂ precipitate was filtered off and dissolved in HCl, instead of evaporating the mixture as usual.

¹⁷The HCl precipitate from the polysulphide solution was very light-colored, or, if not, when it was extracted with NH_4OH the solution gave no precipitate with HCl; so the analysis was not carried further.

*A fair SnS_2 precipitate was produced, but owing to an accident the confirmatory test was not tried.

¹⁸The SnS_2 precipitate produced in P. 47 was estimated to contain only 1.3 mg. Sn.

¹⁹In these analyses the moist H_2S precipitate was left on the filter for several hours before treating with ammonium polysulphide.

²¹Satisfactory tests were obtained for gold and for platinum both in the copper and tin groups; and the final precipitates were not far from equal in size.

²²No precipitate of SnS_2 was produced in P. 47.

²³The residue undissolved by ammonium sulphide was treated by P. 23, 24, 25, 41, and 42, and the HCl solution so obtained reduced directly with Zn, the residue dissolved, and HgCl_2 added; but no test for tin was obtained.

*A black precipitate was produced in the test with SnCl_2 , probably due to the presence of gold. It was treated with hot HNO_3 (1.20), and it did not dissolve, showing it was not wholly mercury; the solution after evaporation with HCl was tested with SnCl_2 , but only an inconclusive turbidity was obtained.

²⁵Tests for these elements were obtained in the analyses of both the copper and tin groups.

²⁶All or nearly all the cadmium failed to be precipitated by H_2S from the 100 cc. of solution containing 4 cc. HCl (1.12), even though the gas was passed in for 10 minutes; for it was recovered from the filtrate by adding 50 cc. more water and passing in H_2S for 10 minutes, and then confirmed by P. 23, 28 and 31.

²⁷Nearly all the tellurium and molybdenum failed to be precipitated by H_2S ; for they were recovered from the filtrate by adding NH_4OH and NH_4SH and acidifying, and were detected by treating the precipitate by P. 43, *43a, *43c, *43d, and *43e.

²⁸In T. A. No. 112 the last part of P. 43b was omitted.

²⁹No distinct turbidity was visible, but upon filtering and treating with sodium stannite the filter was much darkened.

³⁰Tests for these elements were obtained only in the analysis of the tin group.

³¹A red precipitate separated in the lead test upon evaporation with H_2SO_4 , which was probably selenium, and indicated that it had not been dissolved out by $(\text{NH}_4)_2\text{S}$.

³²In testing for arsenic with MgCl_2 a flocculent precipitate accompanied the crystalline one of the $\text{MgNH}_4\text{AsO}_4$, and on dissolving this in HCl and adding H_2S a black precipitate resulted. This was dissolved in HCl and KClO_3 and treated by *P. 24d: a black precipitate resulted, showing that tellurium was precipitated with the arsenic.

The test analyses of the silver group (Nos. 1-9) show that 1 mg. of mercurous mercury is detected in the presence of 500 mg. of either lead or silver; and that 1 mg. of silver is detected without difficulty in the presence of 500 mg. of lead, but that in the presence of 500 mg. of mercury 1 mg. of silver lies at about the limit of detectability.

The test analyses of the copper group (Nos. 10-20) show (at any rate when the ammonium sulphide treatment is omitted) that even 1 mg. of mercury, bismuth, copper, or cadmium is detected in the presence of 500 mg. of any other one of these elements; that with lead in presence of 500 mg. of any one of these elements 1 mg. is near the limit, probably owing

to the difficulty of securing complete precipitation with H_2S ; and that with stannous tin the limit of detectability is at 2 mg. The blank tests were satisfactory in all cases, except that a very small, dark precipitate was sometimes obtained in the cadmium test with H_2S . Even when the H_2S precipitate was treated with ammonium polysulphide (T. A. Nos. 21-28), which dissolves some copper and mercury, these elements were detected in all cases where 2 mg. were present; and when monosulphide was used (as in T. A. Nos. 29-30) 1 mg. of mercury was twice detected, while with copper it was found in one analysis and lost in the other.

The test analyses of the tin group in which the copper group was not present, which were begun with an ammonium polysulphide solution of the elements (Nos. 31-56), show that 1 mg. of arsenic, antimony, or tin is invariably detected, even in the presence of 500 mg. of any other one of these elements.

The test analyses in which the elements of the tin group were associated with 500 mg. of an element of the copper group and in which the H_2S precipitate was treated with ammonium polysulphide (Nos. 57-90) show that 1 mg. of arsenic or antimony is almost always detected; but that a much larger quantity of tin in some combinations is not detected, if only the ammonium sulphide solution is analyzed for it. Thus, while in the presence of bismuth 1 to 2 mg. of stannous tin were found, yet in the presence of copper 4 to 5 mg., and in that of cadmium 10-15 mg. of it were lost; and 3 to 5 mg. of stannic tin were lost in the presence of mercury or cadmium.

In the analyses in which ammonium monosulphide was used (Nos. 91-97), the detection of antimony in the higher state of oxidation and of arsenic is nearly as satisfactory, 1 or 2 mg. having been always found; but a larger quantity of stannic tin remains with the copper group than when the polysulphide is used, 5 mg. being retained even by bismuth.

These results clearly show the necessity of testing for tin in the analysis of the copper as well as of the tin group, and T. A. Nos. 98-100 show that it can be detected in the copper group analyses when 3 mg. are present.

In the test analyses with mixtures containing the rarer elements (Nos. 101-113) 1 mg. of platinum or gold was always detected; and the same was true of 1 mg. of selenium, tellurium, and molybdenum in the analyses that started at the beginning of the tin group, but not in those where elements of the copper group were present and the analysis was begun with the H_2S precipitation.

CONFIRMATORY EXPERIMENTS AND REFERENCES

Analysis of the Silver Group

P. 11: *Solubility of $PbCl_2$ and $TlCl$ in Water and in HCl .*—See Noyes, *Z. phys. Chem.*, **9**, 614, 623 (1892); Engel, *Ann. chim. phys.*, (6) **17**, 359 (1889); Ditte, *Compt. rend.*, **92**, 718 (1881).

**P. 13a: Test for Thallium with KI.*—To 50 mg. Pb as $PbCl_2$, dissolved in 20 cc. water, 5 cc. H_2SO_4 (1.84) were added; the mixture was cooled and filtered; and to the filtrate a few drops KI solution were added: no precipitate appeared.—The experiment was repeated, except that 1 mg. Tl as Tl_2SO_4 was also present: a pale yellow precipitate of TII resulted.

To solutions containing 0.5 mg. Tl as Tl_2SO_4 and 4 cc. HCl (1.12) and 10 cc. or 20 cc. water, respectively, a few drops of a normal KI solution were added: a yellow precipitate separated in the first experiment, but only a faint yellow turbidity appeared in the second.

Oxidation of Thallous Salts.—100 mg. Tl as Tl_2SO_4 were dissolved in 10 cc. HNO_3 (1.42) and evaporated to about 2 cc.; the solution was diluted to 20 cc. and 1-2 cc. HCl (1.12) added: a large light yellow precipitate separated, thus showing that some, but not much, of the thallium had been oxidized.

100 mg. Tl as Tl_2SO_4 were dissolved in 2 cc. HNO_3 (1.42) and about 5 cc. HCl (1.20) were added: a white precipitate separated at first, but dissolved on warming. The mixture was evaporated to about 2 cc., cooled, and diluted to 20 cc.: no precipitate separated, even when a little HCl was added, thus showing that the thallium was in the thallic state.—The experiment was repeated, except that the *aqua regia* solution was evaporated to dryness and the residue dried by heating slightly; to it 4 cc. HCl (1.12) and 20 cc. water were added: a large light yellow precipitate separated, showing that the thallic salt had been largely but not completely reduced.

P. 14: Explanation of the Solubility of $PbSO_4$ in Ammonium Acetate Solution.—See Noyes and Whitcomb, *J. Am. Chem. Soc.*, **27**, 747 (1905).

P. 15: Molecular Formula of Gaseous Mercurous Chloride.—Baker (*J. Chem. Soc.* **77**, 646., 1900) has shown that absolutely dry mercurous chloride vapor has a density corresponding to the formula Hg_2Cl_2 .

Conditions of Mercurous Salts in Solution.—See Ogg, *Z. phys. Chem.*, **27**, 290-299 (1898); Abel, *Z. anorg. Chem.*, **26**, 377 (1901).

Action of NH_4OH on Hg_2Cl_2 .—For the evidence that the black residue is a mixture of Hg and $HgClNH_2$, see Barefoed, *J. prakt. Chem.*, **39**, 201 (1889); Pesci, *Gazz. chim. ital.*, **21**, 569 (1901); and Sen, *Z. anorg. Chem.*, **33**, 197 (1903).

Complex Silver-Ammonia Anions.—See Bodländer and Fittig, *Z. phys. Chem.*, **39**, 597 (1902); Whitney and Melcher, *J. Am. Chem. Soc.*, **25**, 69 (1903); Bodländer and Eberlein, *Z. anorg. Chem.*, **39**, 197 (1904); Lucas, *Z. anorg. Chem.*, **41**, 193 (1904).

Solubility of $AgCl$ in Chloride Solutions.—See Comey, *Dictionary of Solubilities*, p. 373.

1 mg. Ag as $AgCl$ was dissolved in 5 cc. NH_4OH (0.96), the solution obtained was made acid with HCl: no precipitate separated.—The experiment was repeated, using HNO_3 instead of HCl: a precipitate formed.—5 mg. Ag as $AgCl$ were dissolved in 15 cc. NH_4OH (0.96), and the solution made acid with HCl: no precipitate separated. An equal volume of water was added: $AgCl$ precipitated.

Precipitation and Separation of the Copper and Tin Groups

P. 21: Order of Precipitation of the Sulphides of the Copper and Tin Groups from Cold HCl Solution.—2 mg. As as As_2O_3 , 2 mg. Hg, and 2 mg. Cu, each as chloride, were in separate experiments dissolved in 2 cc. HCl (1.20), and 2 mg. of each of the elements of the copper and tin groups were in separate experiments dissolved in 4 cc. HCl (1.12); each solution was put into a small bottle, saturated completely with H_2S at room temperature, the bottle corked, and allowed to stand 15 minutes. In cases where no precipitate formed the solution was successively diluted

with measured quantities of water, being again saturated with H_2S and allowed to stand after each addition: the most strongly acid solution from which each element separated is shown by the following table:

cc. HCl (1.20).....	2
cc. HCl (1.12).....	..	4	4	4	4	4
cc. Water	0	0	4	12	44	96
Elements precipitated	As	Hg, Cu	Sb	Bi, Sn (ic)	Cd	Pb, Sn (ous)

The cadmium, lead, and stannous sulphides precipitated slightly and only after several minutes; the others almost at once.

Order of Precipitation of the Sulphides of the Iron Group from Weakly Acid Solutions.—50 mg. Zn and 500 mg. Zn as nitrate, 500 mg. Fe (ous), 500 mg. Ni, 500 mg. Co, and 500 mg. Mn as sulphate were in separate experiments dissolved in 1 cc. HCl (1.12) and 100 cc. water, saturated with H_2S at room temperature, and allowed to stand 10 minutes: zinc was precipitated from both its solutions, but none of the other elements.—The experiments with 50 mg. Zn and 500 mg. Zn were repeated, except that 2 cc. HCl (1.12) was used: ZnS precipitated after several minutes in the 500 mg. portion, but not in the 50 mg. one.

500 mg. each of ferrous Fe, Co, Ni, and Mn as sulphate were dissolved in 100 cc. water and saturated at room temperature with H_2S for 10 minutes: FeS slowly precipitated in considerable quantity, but none of the other sulphides.—The experiment was repeated, except that the substances were dissolved in 10 cc. 10% acetic acid solution, 1 cc. 10% $NaC_2H_3O_2$ solution, and 90 cc. water: the result was the same. The last experiment was repeated, except that 10 cc. instead of 1 cc. $NaC_2H_3O_2$ solution were used: large quantities of NiS and CoS as well as of FeS precipitated, but no MnS.—In another experiment 500 mg. Mn as $MnSO_4$ were dissolved in 1 cc. 10% $HC_2H_3O_2$ solution, 10 cc. 10% $NaC_2H_3O_2$ solution, and 90 cc. water, and saturated with H_2S : no MnS precipitated.

Precipitation of Arsenic, Platinum, and Molybdenum by H_2S .—100 mg. As as H_3AsO_4 , 100 mg. Mo as H_2MoO_4 , and 25 mg. Pt as H_2PtCl_6 were dissolved in separate 100 cc. portions of dilute HCl (one volume HCl (1.12) to twenty-five volumes water) and were saturated with H_2S in the cold: less than 1 mg. of As and of Pt, but considerable Mo, precipitated as sulphides in 10 minutes. The three solutions were then filtered, heated to boiling, and saturated with H_2S at that temperature for about 15 minutes: a large precipitate resulted in each case. The solutions were filtered, saturated in the cold with H_2S , and heated in pressure bottles in the steam bath for 1 hour: a considerable precipitate separated from each solution, estimated to contain about 5 mg. As in the arsenic solution and 10 mg. Mo in the molybdenum solution.

100 mg. As as H_3AsO_4 were added to 100 cc. HCl (1.20) and saturated in the cold with H_2S : a large yellow precipitate separated. After 5 minutes the mixture was diluted with half its volume of water and filtered; the filtrate was heated to 100° and H_2S passed in for 10 minutes: a small precipitate estimated to contain only 3.5 mg. As resulted. These two experiments with arsenic acid show that the precipitation takes place much more rapidly in the presence of concentrated HCl.

Precipitation of Cadmium and Lead by H_2S .—Separate solutions containing 5 mg. Cd, 5 mg. Pb, 10 mg. Cd, and 10 mg. Pb, respectively, in 100 cc. of a mixture of one volume HCl (1.12) and fifteen volumes water were saturated in the cold with H_2S for 15 minutes: precipitates began to form only after 10 or 15 minutes in each of the solutions.

Separate solutions containing 1 mg. Cd and 1 mg. Pb in 100 cc. of a mixture of

one volume HCl (1.12) and twenty-five volumes water were saturated in the cold with H₂S: both solutions showed precipitates, but that in the case of lead was scarcely visible until it was collected on a filter. The PbS was filtered out and NH₄OH and (NH₄)₂S added to the filtrate: a brown color corresponding to 0.1-0.2 mg. Pb resulted, showing that substantially all the lead was precipitated.

Precipitation of Zinc by H₂S.—Solutions containing 500 mg. Zn in three 100 cc. portions of dilute HCl, containing one volume HCl (1.12) to twenty-five volumes water, to forty volumes water, and to fifty volumes water, respectively, were saturated in the cold with H₂S, then heated to boiling, and again saturated with H₂S: in the cold, H₂S failed to produce a precipitate in any of the solutions in 5 minutes; but on heating, a slight precipitate formed in the 1 : 40, and a heavy one in the 1 : 50, but none in the 1 : 25 mixture.

Precipitation of Titanium Hydroxide by Hydrolysis.—Separate 100 mg. portions of Ti in 100 cc. dilute HCl, containing one volume HCl (1.12) to twenty volumes water, to ten volumes water, and to eight volumes water, respectively, were saturated in the cold with H₂S and then heated in pressure bottles in a steam bath for 2 hours: in the 1 : 20 volume solution a very large white precipitate had formed in 30 minutes; the 1 : 10 solution remained clear for 45 minutes, and then showed only a turbidity; and the 1 : 8 solution remained unchanged during the 2 hours.

Precipitation of Bismuth and Antimony Oxychlorides by Water.—Separate solutions containing 500 mg. Bi as nitrate, 400 mg. Sb as SbCl₃, and 300 mg. Sb as Sb₂O₃ (obtained by evaporating an SbCl₃ solution with *aqua regia*) were evaporated with HCl almost to dryness; 4 cc. HCl (1.12) and 36 cc. water were added, and the mixture was heated: from the bismuth solution no precipitate separated either in the cold or upon heating; in the antimonous solution a large white precipitate formed in the cold, but dissolved almost completely upon heating; and in the antimonic solution a large precipitate separated in the cold and did not appear to dissolve upon heating. To the bismuth solution 20 cc. more water were added: a white precipitate then began to form.

Separation of the Copper and Tin Groups from the Iron Group by H₂S.—Mixtures of elements as shown below were dissolved in 4 cc. HCl (1.12) and 36 cc. water and treated exactly as described in P. 21, except that the solutions containing cadmium were diluted at once to 100 cc. and saturated at room temperature with H₂S; the solutions were filtered after 10-30 minutes, the filtrate boiled to expel H₂S, HNO₃ added the mixture again boiled, NH₄OH added to detect iron, any precipitate filtered off, and H₂S was passed into the filtrate or (NH₄)₂S was added to it to detect zinc, nickel, or cobalt: the results are recorded below as in the test Analyses:

Cd	500—	500—	500—	500—	500—
Zn	0 S	2 S	1 S ¹
Fe	0 S	2 S	1 S
Ni	0 S	1 S
Cu	500—	500—
Bi	200—	200—
As (ous)	100—	100—
Sb (ous)	100—	100—
Sn (ic)	200—	200—
Zn	1 S ¹
Fe	1 S	0 S
Ni	1 S	1 S
Co	1 S ²

¹A nearly white precipitate was obtained with (NH₄)₂S.

²The black (NH₄)₂S precipitate was dissolved in *aqua regia* and the solution evaporated just to dryness: the residue had a slight pink color.

Composition of the H₂S Precipitates.—From solution of HgCl₂ in excess, see Rose, *Pogg. Ann.*, **13**, 64 (1828). From arsenic acid solutions, see C. E., P. 44. From antimonious solutions, see Klenker, *J. prakt. Chem.*, **59**, 150 (1899). From chloroplatinic acid, see Antony and Lucchesi, *Gazz. chim. ital.*, **26**, 211 (1896). From gold chloride, see Hoffmann and Krüss, *Ber. d. chem. Ges.*, **20**, 2369, 2704 (1887). From selenous acid, see Ditte, *Compt. rend.*, **73**, 625, 660 (1871); Divers and Shimidzu, *J. Chem. Soc.*, **47**, 441 (1885). From tellurous acid, see Becker, *Liebig's Ann. Chem.*, **180**, 260 (1875).

Action of HNO₃ on H₂S.—Separate 50 cc. portions of mixtures of one volume of HNO₃ (1.20) in 2.5, 5, 10, and 20 volumes of solution were heated to boiling and saturated with H₂S at that temperature: in the first solution a precipitate of sulphur soon appeared, in the second a slight precipitate formed after 10 minutes, and in the last two no precipitates formed in 20 minutes.

Precipitation of BaSO₄ in the H₂S Treatment.—Separate solutions of 500 mg. Fe as FeCl₃ and 2, 5, 10, and 20 mg. Ba as BaCl₂ in 4 cc. HCl (1.12) and 36 cc. water were treated with H₂S according to P. 21. The filtrate in the experiment with 20 mg. Ba was evaporated to 20 cc. cooled, and allowed to stand: 1 to 2 mg. Ba separated as BaSO₄. This was filtered off, the filtrate was divided into two parts. To one part H₂SO₄ was added: no precipitate separated. To the other part BaCl₂ was added: a precipitate of BaSO₄ corresponding to several milligrams Ba separated, thus proving that the H₂S filtrate contained sulphuric acid but very little Ba, and that therefore the amount of H₂SO₄ formed during the H₂S precipitation was more than sufficient to combine with 20 mg. Ba. Each of the remaining three filtrates was evaporated with about 2 cc. H₂SO₄ (1.84) to fuming, cooled, and diluted to 15 cc.: 1-2 mg. Ba as BaSO₄ separated in each case. Thus in no case did the filtrate contain more than 2 mg. Ba.—All four of the H₂S precipitates were boiled with HNO₃, as in P. 23 and the filtrates treated with H₂SO₄ as described in P. 26: precipitates of BaSO₄ were obtained in each case, but that in the experiment with 2 mg. Ba was very small. The residues undissolved by HNO₃ were boiled with Na₂CO₃ solution, filtered, and the precipitate tested for barium: in the experiment with 20 mg. were found several milligrams barium, but in that with 10 mg. only a small quantity, and in the remaining two experiments no barium at all.

P. 22: Hydrolysis of the Alkaline Sulphides and Composition of the Polysulphides.—It has been shown by C. F. Sammet (*Thesis, M. I. T.*, 1903) that a solution of the empirical composition (NH₄)₂S containing 0.1 formula weight per liter is practically completely hydrolyzed into NH₄OH and NH₄SH, and that in the same solution the latter is only slightly (roughly, 0.3%) hydrolyzed into H₂S and a second equivalent of NH₄OH. But in a solution containing only half as much NH₄OH, *i. e.*, in a solution containing 0.1 formula weight NH₄SH per liter, the degree of the hydrolysis increases to several per cent.

Küster and Heberlein (*Z. anorg. Chem.*, **43**, 71, 1905) have found Na₂S in a solution containing 0.05 formula weights per liter to be 86% hydrolyzed into NaOH and NaSH, and NaSH in 0.01 normal solution to be only 0.15% hydrolyzed into NaOH and H₂S. For the degree of hydrolysis of NaSH, Walker (*Z. phys. Chem.*, **32**, 137, 1900) found practically the same value by an independent method.

Küster and Heberlein also investigated the hydrolysis of the polysulphides of sodium, and showed that the degree of hydrolysis decreases with increasing sulphur-content; thus a solution of the composition Na₂S₂ was 65%, a solution of Na₂S₄, only 12% hydrolyzed. They found further that Na₂S solutions when saturated with

sulphur at 24° have the empirical composition Na_2S_x where x has values varying from 4.48 to 5.24 when the concentration varies from 2.0 to $\frac{1}{2}$ formula weights Na_2S per liter. It was found that x varied only slightly with the temperature. According to these authors, Na_2S_4 and less readily Na_2S_5 , have been obtained in the solid form by evaporating aqueous solutions; but Na_2S_3 have not been so obtained. All of these have, however, been crystallized from alcoholic solutions (H. Böttger, *Liebig's Ann. Chem.*, **223**, 335, 1884; H. Rebs, *Liebig's Ann. Chem.*, **246**, 358, 1888).

Bloxam (*J. Chem. Soc.*, **67**, 300, 1894; **77**, 753, 1900) found that a very concentrated ammonium sulphide solution prepared from NH_4OH (0.88) so as to have exactly the composition $(\text{NH}_4)_2\text{S}$ dissolved sulphur until the composition became approximately $(\text{NH}_4)_2\text{S}_{4.5}$. He has obtained under various special conditions the following solid salts: $(\text{NH}_4)_2\text{S}_4$, $(\text{NH}_4)_2\text{S}_5$, $(\text{NH}_4)_2\text{S}_6$, $(\text{NH}_4)_2\text{S}_7$, $(\text{NH}_4)_2\text{S}_8$, and $(\text{NH}_4)_2\text{S}_9$; Na_2S , NaSH , Na_2S_3 , and Na_4S_6 ; K_2S , KSH , K_2S_3 , K_2S_4 , K_2S_5 , K_4S_8 , and K_4S_9 .

Ammonium Salts of the Sulpho Acids.—The following ammonium sulpho salts have all been prepared in the crystalline form by adding alcohol to concentrated solutions of the sulphides in ammonium sulphide: $(\text{NH}_4)_3\text{AsS}_3$ and $(\text{NH}_4)_3\text{AsS}_4$ (Berzelius, *Pogg. Ann.*, **7**, 141 and 18, 1826); $(\text{NH}_4)_3\text{SbS}_3$ (Pouget, *Ann. chim. phys.* (7), **18**, 532, 1899); $(\text{NH}_4)_3\text{SbS}_4$, $(\text{NH}_4)_3\text{SbS}_{4.4}\text{H}_2\text{O}$ (Stanek, *Z. anorg. Chem.*, **17**, 121, 1898); $(\text{NH}_4)_2\text{SnS}_3 \cdot 3\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SnS}_3 \cdot 7\text{H}_2\text{O}$ (Stanek, *loc. cit.*, p. 213). certain other arsenous salts, including NH_4AsS_3 , have also been prepared in the solid state. On evaporating a solution of Sb_2S_3 in $(\text{NH}_4)_2\text{S}$ in a vacuum at a low temperature, the meta salt NH_4SbS_2 is usually obtained; on evaporating at a high temperature, or on treating NH_4SbS_2 with water, solid $(\text{NH}_4)_2\text{Sb}_2\text{S}_7$ is formed. Berzelius states that a solution of the empirical composition $(\text{NH}_4)_2\text{S}$ saturated with As_2S_3 or As_2S_5 contains these substances in the proportion $\text{As}_2\text{S}_3 : 2(\text{NH}_4)_2\text{S}$ or $\text{As}_2\text{S}_5 : 2(\text{NH}_4)_2\text{S}$. Pouget finds that a solution of $(\text{NH}_4)_2\text{S}$ saturated with Sb_2S_3 contains less antimony than corresponds to the ratio $\text{Sb}_2\text{S}_3 : 3(\text{NH}_4)_2\text{S}$. A K_2S or Na_2S solution dissolves sufficient Sb_2S_3 to give a solution of the composition $\text{Sb}_2\text{S}_3 : 2\text{K}_2\text{S}$ or $\text{Sb}_2\text{S}_3 : 2\text{Na}_2\text{S}$. There does not appear to be any direct evidence as to the nature of these salts in solution.

*Solid sulpho salts of the rare elements have been obtained from alkaline sulphide solutions as follows: K_3AuS_3 (Antony and Lucchesi, *Gazz. chim. ital.*, **26**, 359, 1896); $3\text{K}_2\text{S} \cdot \text{TeS}_2$, $3\text{Na}_2\text{S} \cdot \text{TeS}_2$, and $3(\text{NH}_4)_2\text{S} \cdot \text{TeS}_2$ (Berzelius); K_2MoS_4 , $(\text{NH}_4)_2\text{MoS}_4$ (Berzelius, *Pogg. Ann.*, **7**, 429, 1826); Krüss, *Liebig's Ann. Chem.*, **225**, 29, 1884).

Solubility of the Sulphides of the Tin and Copper Groups in Ammonium Hydroxide, Monosulphide, and Polysulphide.—500 mg. As as As_2S_3 , Sb as Sb_2S_3 , Sn as SnS , Cu as CuS , Hg as HgS , Cd as CdS , Bi as Bi_2S_3 , and 100 mg. Pb as PbS , all freshly precipitated by H_2S , and 500 mg. As as As_2S_5 , 100 or 500 mg. Sb as Sb_2S_5 , and 100 or 500 mg. Sn as SnS_2 , all precipitated from ammonium polysulphide, were warmed (but not enough to cause boiling through escape of gas) in a covered casserole for about 5 minutes with (a) 15-20 cc. NH_4OH (0.96); (b) 10 cc. of the ammonium monosulphide reagent; and (c) 10 cc. of the ammonium polysulphide reagent. The solutions were then filtered and the filtrates acidified with HCl . The amount dissolved was estimated from the size and color of the precipitate or from the amount of the undissolved residue. The results are given below: the numbers represent roughly the number of milligrams of the element dissolved, a + sign indicating that this amount dissolved readily and that probably much more would have dissolved.

	(a) NH_4OH (0.96)	(b) Monosulphide	(c) Polysulphide
As_2S_3	500 +	500 +	500 +
As_2S_5	500 +	500 +	500 +
Sb_2S_3	0.5-1	50-100	500
Sb_2S_5	100 ¹	300	500 +
SnS	0 ²	0-3 ³	500
SnS_2	100 ¹	300	500 +
CuS	0-0.3	0	5-10
HgS	3-10	0	1
PbS	0	0	0.1-0.3
CdS	0	0	0
Bi_2S_3	0	0	0

The orange Sb_2S_3 was found to be changed into the black variety, stibnite, by continued treatment with ammonium monosulphide, and black HgS was changed into the red modification by continued treatment with the polysulphide. It was also noted that the HgS which dissolves in NH_4OH may be precipitated by adding a few drops of monosulphide.

500 mg. Cu and 500 mg. Hg as freshly precipitated sulphides were in separate experiments warmed to 50° or 60° in covered casseroles with 25 cc. ammonium monosulphide for 15 minutes; the residues were filtered off, and the filtrates made acid with HCl : a slight precipitate of sulphur separated, which was only very slightly darkened, thus showing that only an insignificant quantity of CuS or HgS had dissolved.

An ammonium monosulphide solution was prepared from NH_4OH (0.90) as described in the Note, except that the solution was not diluted with the equal volume of water. From this solution several different ammonium polysulphide solutions were prepared, containing, respectively, 20, 10, 5, 3, and 1 grams dissolved sulphur in 200 cc., and their solvent power for SnS and CuS tested as follows:

500 mg. Sn as freshly precipitated SnS were warmed gently in a covered casserole with (a) 10 cc. of these undiluted solutions; (b) 5 cc. of them + 5 cc. water; and (c) 5 cc. of them + 10 cc. water. The mixture was stirred frequently with a glass rod. The amount of tin in milligrams dissolved in a solution containing x grams of dissolved sulphur in 200 cc. and the time required to dissolve it are given below.

	$x = 10$ g.	$x = 5$ g.	$x = 3$ g.	$x = 1$ g.
(a) 10 cc. undiluted	500 4 minutes	500 5 minutes	500 15 minutes	100 5 minutes
(b) 5 cc. + 5 cc. H_2O	500 ¹ 5 minutes	500 10 minutes	..	100 10 minutes
(c) 5 cc. + 10 cc. H_2O	500 8-10 minutes

500 mg. Cu as CuS were similarly treated for 5 minutes: the following table shows roughly the number of milligrams Cu as CuS that dissolved in a solution containing x grams dissolved sulphur in 200 cc. where x has the stated values.

	$x = 20$ g.	$x = 10$ g.	$x = 5$ g.	$x = 3$ g.	$x = 1$ g.	$x = 0$ g.
(a) 10 cc. of solution	25 +	..	12	6	0.5	..
(b) 5 cc. + 5 cc. H_2O	8 ³	4	3	0.2	0
(c) 5 cc. + 15 cc. H_2O	6-8

¹Only about 100 mg. of the element as sulphide were taken in these experiments.

²A few milligrams (5-15) of a yellow precipitate (SnS_2), containing little or no SnS were precipitated on acidifying the filtrate.

³The regular reagent described in the Note has this composition.

Solubility of the Sulphides of the Rarer Elements in Ammonium Sulphide.*—Ribau (*Bull. soc. chim.*, **28, 241. 1877) has shown that pure, freshly precipitated PtS_2 is nearly insoluble in ammonium sulphide, but dissolves in large quantity when mixed with sulphides of either the tin or copper groups.—Under "Test Analyses of the Tin Group" it is shown that small quantities of platinum and gold divide almost equally between the copper and tin groups when copper is also present.

50 mg. Mo as freshly precipitated sulphide were digested in a covered casserole at 40-60° with 25 cc. ammonium monosulphide for 15 minutes; the deep red solution was filtered and acidified with HCl: a precipitate estimated to contain about 35 mg. Mo separated. The residue was digested a second time with 25 cc. ammonium monosulphide: only about half the residue dissolved.—The experiment was repeated, using 10 cc. portions of ammonium polysulphide: the result was the same, about two-thirds dissolving in the first treatment and about half the residue in the second.

200 mg. Te were freshly precipitated with H_2S from a hot HCl solution containing 4 cc. HCl (1.12) and 36 cc. water; the black precipitate was digested with 25 cc. ammonium monosulphide: the precipitate dissolved completely in 3 or 4 minutes. The solution was acidified with HCl: a black precipitate separated. This was digested with 10 cc. ammonium polysulphide; it dissolved immediately. To the solution HCl was added: a black precipitate separated.

200 mg. Se as H_2SeO_3 were precipitated by Na_2SO_3 in an HCl (1.12) solution, as in *P. 43c. The red precipitate was filtered off and washed with HCl (1.12). It was then dissolved in hot HNO_3 (1.20); the solution was evaporated just to dryness and the residue dissolved in 4 cc. of HCl (1.12) and 36 cc. of water. The solution was heated to boiling and saturated with H_2S . A yellow precipitate which partly changed to red during the precipitation was produced. The solution was diluted to 100 cc. and again saturated with H_2S in the cold; the precipitate was filtered off and digested with 25 cc. ammonium monosulphide: the finely divided portion of the precipitate dissolved in a few minutes, forming a deep red solution, but the larger particles turned black on the surface and dissolved very slowly. After a few minutes the solution was filtered and the black residue digested successively three times with a fresh 25 cc. portion of ammonium monosulphide: finally it all dissolved. The successive sulphide solutions were acidified with HCl (1.12): a bright yellow precipitate formed at first in every case, but that in the first solution gradually became orange within a few hours.

Extraction by Ammonium Monosulphide and Polysulphide of Arsenic, Antimony, and Tin Sulphides from those of the Copper Group.—See "Test Analyses of Tin Group."

Mixtures of 5, 10, 15, and 20 mg. Sn as SnS with 500 mg. Cd as CdS were digested at 80-90° with the ammonium polysulphide reagent in a pressure bottle for half an hour, and the solutions were analyzed by P. 41-47: no test for tin was obtained with the mixtures containing 5 or 10 mg. Sn; a precipitate of SnS_2 was obtained in the experiment with 15 mg., but the confirmatory test (P. 47) failed. In that with 20 mg. both tests for tin gave conclusive results.—The experiment was repeated with a mixture of 5 mg. Sn as SnS_2 and 500 mg. Cd as CdS: small but satisfactory tests for tin were obtained.

Analysis of the Copper Group

P. 23: *Solubility of the Copper Group Sulphides in HNO_3 .*—500 mg. of Pb, Bi, Cu, and Cd as sulphides were treated in separate experiments according to P. 23: the sulphides dissolved almost completely when the solution began to boil, but the

sulphur residue remained dark-colored (except in the case of cadmium) even after several minutes' boiling.

500 mg. Pb, Bi, Cu, and Cd as sulphides were in separate experiments boiled in an open casserole with about 30 cc. of a mixture of one volume HNO_3 (1.20) and three volumes of water: Bi_2S_3 and CuS dissolved in 5 minutes or less, PbS dissolved less readily, and CdS only after 10-15 minutes.—The experiment was repeated, except that 50 cc. of a still more dilute acid was used: the result was the same, except that solution took place somewhat less rapidly.

500 mg. Hg as HgS were treated according to P. 23; and the filtrate was evaporated with excess of HCl to a small volume, diluted, and saturated with H_2S : a precipitate of HgS estimated to contain less than 1 mg. Hg resulted.—The experiment was repeated, except that 30 cc. HNO_3 (1.20) were used and the boiling continued for 10 minutes: a precipitate of HgS estimated to contain 2 mg. Hg resulted.—The experiment was repeated, except that 30 cc. of a mixture of one volume of HNO_3 (1.20) and three volumes of water were used and the boiling continued for 10 minutes: a precipitate of HgS containing about 0.5 mg. Hg was formed.—1 mg. Hg as HgS was boiled with HNO_3 (1.20) for 10 minutes: no change in the amount of the sulphide was apparent.

Action of Strong HNO_3 on HgS .—500 mg. Hg as HgS were boiled for 10 minutes with 30 cc. HNO_3 (1.42): the black precipitate had then become pure white. The filtrate was freed from HNO_3 and saturated with H_2S : a precipitate containing several milligrams Hg was formed.—The experiment was repeated, replacing the HNO_3 (1.42) by the strength used in P. 23: no change in the appearance of the precipitate took place.

Action of Dilute HNO_3 on Au and PtS_2 .—That small quantities of gold and platinum are not dissolved in P. 23 is shown by the results of Test Analyses, Nos. 106-113.

Oxidation of PbS to PbSO_4 .—500 mg. Pb as freshly precipitated PbS were treated according to P. 23, and to the filtrate BaCl_2 was added in large quantity: a precipitate of BaSO_4 estimated to correspond to 20-30 mg. Pb was formed.—The experiment was repeated, except that the sulphide was boiled for 10 minutes with a more dilute acid, containing one volume HNO_3 (1.20) and three volumes water: the result was the same.—The experiment was repeated, except that HNO_3 (1.20) was used and the mixture boiled for 10 minutes: there was left with the sulphur a small white residue of PbSO_4 , estimated to contain 5 mg. Pb, showing that the amount of H_2SO_4 formed increases with the HNO_3 concentration.

Solubility of PbSO_4 in Dilute HNO_3 .—To 50 and 100 mg. Pb as PbSO_4 in separate experiments 30 cc. of a mixture of one volume HNO_3 (1.20) and three volumes of water were added and the mixtures heated: the 50 mg. dissolved in the cold, the 100 mg. upon boiling.

Action of HNO_3 on SnS , SnS_2 and Sb_2S_3 .—10 mg. Sn as SnS and 10 mg. Sn as SnS_2 were in separate experiments treated by P. 23: there was a white residue in each case. The filtrate was evaporated with H_2SO_4 to slight fuming, diluted, and saturated with H_2S : a yellow precipitate of SnS_2 estimated to contain 0.5 mg. Sn was formed.

10 mg. Sb as freshly precipitated Sb_2S_3 were treated by P. 23: the orange color of the sulphides disappeared at once, and a small white precipitate separated, which was estimated to contain 3-4 mg. Sb.—The experiment was repeated with 5 mg. Sb: no white residue was left.—The filtrates in these two experiments were made alkaline with NH_4OH : no precipitate of antimony hydroxide separated, even on standing.

P. 24: Behavior of HgS, PtS₂, Au, and Metastannic Acid towards Bromine Solution.—100 mg. Hg and 500 mg. Hg as precipitated HgS were warmed slightly in a covered casserole with 30-40 cc. saturated Br₂ solution: the 100 mg. dissolved completely, and about three-fourths of the 500 mg. dissolved. The latter was treated with another portion of bromine water: the residue became nearly white, but blackened slightly when treated with ammonium sulphide.

The experiment was repeated with 10 mg. Sn as metastannic acid, obtained by treating SnS with dilute HNO₃ by P. 23, the solution was boiled, filtered, and saturated with H₂S: scarcely any precipitate of SnS₂ was formed.—That even small quantities of Au and PtS₂ dissolve in bromine solution is shown by the results of Test Analyses, Nos. 106-113.

Reduction of Hg₂Cl₂ by SnCl₂.—To 1 mg. Hg as HgCl₂ in 20 cc. water one drop SnCl₂ solution (1% Sn) was added: a nearly white precipitate formed at once. One or two drops more SnCl₂ were added: the precipitate darkened rapidly.—The experiment was repeated, except that 0.3 to 0.5 cc. HCl (1.12) was added to the HgCl₂ solution before the SnCl₂: a precipitate formed, which remained white for some minutes, even after the addition of several drops of SnCl₂ solution.

Color of Dilute Solutions of Gold and Platinum.—1 mg. Au as AuCl₃ and 1 mg. Pt. as H₂PtCl₆ were added in separate experiments to 20 cc. water and boiled: the solutions had a very pale yellow color, but this color was distinct. A few drops of bromine water were added, and the solutions were boiled to expel the bromine: the yellow color was more pronounced than before.

**P. 24a: Detection of Gold, Platinum, and Mercury in the Presence of Each Other.*—Mixtures of elements as shown below dissolved in a little dilute HCl were treated by *P. 24a; and the tests, recorded as in the Test Analyses, resulted as follows:

Pt	o—	o—	1 S	50 S
Au	10 S	1 S	1 S	o—
Hg	1 S	200 S	200—	1 S

P. 25: Separation of Metastannic Acid from HgS.—See Test Analyses, Nos. 10-20.

P. 26: Solubility of PbSO₄ in Water and H₂SO₄.—According to Böttger (*Z. phys. Chem.*, **46**, 604. 1903), 10 cc. of the saturated solution in water at 25° contain about 0.3 mg. Pb.

To determine at what concentration of H₂SO₄ the precipitation was nearly complete, several 2 mg. portions of Pb as Pb(NO₃)₂ were evaporated to fuming with 5 cc. H₂SO (1.84), and the clear solutions obtained were poured into varying amounts of water; the mixtures were cooled, shaken, allowed to stand for a few minutes, filtered, made alkaline with NH₄OH, and treated with H₂S: with 10, 15 and 20 cc. water, the final alkaline solution remained almost colorless when treated with H₂S, thus showing that the amount of lead remaining in the filtrate was scarcely appreciable; when as much water as 50 cc. was used, the liquid was much darkened by H₂S and a small precipitate of PbS separated on standing.

Influence of HNO₃ on the Solubility of PbSO₄.—To each of several solutions containing 1 mg. Pb as Pb(NO₃)₂ in 5 cc. HNO₃ (1.20) and 15 cc. water were added 2 cc. of H₂SO₄ (1.84); the mixture was shaken violently and allowed to stand: only in one or two cases did a precipitate of PbSO₄ separate within 10 minutes. 3 cc. more H₂SO₄ were then added to the solutions that remained clear: PbSO₄ precipitated in every case.—The experiment was repeated, except that 2 mg. Pb were taken: a precipitate of PbSO₄ separated when the 2 cc. H₂SO₄ were added.—To 1 or 2 mg. Pb in 10 cc. HNO₃ (1.20) and 10 cc. water 2 cc. H₂SO₄ were

added: no precipitate resulted. 3 cc. H_2SO_4 more were added: when 2 mg. Pb were present, a precipitate formed.—The last experiment was repeated with 4 mg. Pb, using 2 cc. H_2SO_4 (1.84): a precipitate of $PbSO_4$ separated.

P. 26: Precipitation of Bismuth from H_2SO_4 Solutions.—500 mg. Bi as nitrate were evaporated to fuming with 5 cc. H_2SO_4 (1.84) and cooled: a large quantity of a white solid separated. The mixture was added to 20 cc. cold water and cooled: almost all dissolved, only a very small white residue (2-3 mg.) being left, which was proved by P. 14 not to be $PbSO_4$; but on standing overnight a large, coarsely crystalline white precipitate (probably bismuth oxysulphate) separated. This was filtered off and the filtrate made alkaline with NH_4OH : a precipitate estimated to contain 40-80 mg. Bi separated. In another experiment the filtrate, instead of being treated with NH_4OH , was diluted with two volumes of water and allowed to stand: more of the precipitate separated slowly.—The experiment was repeated, except that the clear solution obtained on dilution with cold water was heated to boiling: a large white precipitate separated at once, which was similar in appearance to that obtained in the former experiment; this did not dissolve when the solution was cooled and shaken.—Separate portions of the white precipitates which had separated in the preceding experiments from the dilute H_2SO_4 solution on standing, and on heating, were treated with 30-40 cc. cold H_2SO_4 (1.20): the precipitates dissolved only slightly, even on standing. The undissolved precipitates still containing about 300 mg. Bi were collected on filters and about 10 cc. HCl (1.12) poured over each: clear solutions were quickly obtained.

P. 27: Behavior of Bismuth Compounds and of $BaSO_4$ towards Ammonium Acetate and K_2CrO_4 .—5 mg. Bi as solid bismuth oxysulphate, (see P. 26, Note) were treated by P. 28, 20 cc. normal ammonium acetate and 5 cc. 5-normal acetic acid being used: a yellow precipitate very similar in appearance to $PbCrO_4$ was formed on the addition of K_2CrO_4 , but this dissolved quickly in the acetic acid.—The experiment was repeated with 1 mg. Bi as nitrate: the result was the same.

1 and 10 mg. Ba as $BaCl_2$ were treated with H_2SO_4 by P. 26, and the precipitates of $BaSO_4$ obtained were treated with ammonium acetate and K_2CrO_4 by P. 27: no yellow precipitate was obtained on adding the K_2CrO_4 .—The white residues (of $BaSO_4$) together with the filters, were boiled with 20 cc. saturated Na_2CO_3 solution, filtered out, and washed; the residues were dissolved in a little HCl (1.12), 1 cc. H_2SO_4 (1.84) was added, and the mixture was evaporated to fuming, cooled, and diluted: a white precipitate of $BaSO_4$ separated in each experiment.

P. 28: Nonprecipitation of Small Quantities of Antimony by NH_4OH .—10 mg. Sb as $SbCl_3$ and 2 cc. H_2SO_4 (1.84) were added to 10 cc. water; the mixture was evaporated to fuming, cooled, diluted to 15 cc., made just alkaline with NH_4OH , and allowed to stand for 30 minutes: no precipitate separated; but when 10 cc. more NH_4OH (0.96) were added, a very slight white precipitate separated.—The experiment was repeated, except that the $SbCl_3$ solution was first warmed with $HCl + HNO_3$ to convert it into the antimonic state: no precipitate separated from the NH_4OH solution, even on standing. Compare C. E. P. 23, last experiment.

Complex Copper-Ammonia and Cadmium-Ammonia Cations.—See Dawson and McCrae, *J. Chem. Soc.*, **77**, 1239 (1900); Euler, *Ber. d. chem. Ges.*, **36**, 3400 (1903); Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904); Locke and Forssell, *Am. Chem. J.*, **31**, 268 (1904).

P. 29: Precipitation of $BiOCl$.—To 0.25 cc. HCl (1.20) was added 1 mg. Bi as chloride, and the solution poured into 100 cc. water at 60° : a precipitate of $BiOCl$ appeared in about a minute. After 5 minutes the solution was filtered, made alkaline with NH_4OH , and treated with H_2S : no precipitate formed.—The experiment was repeated, using 0.5 cc. HCl (1.20) instead of 0.25 cc.: no precipitate of

BiOCl formed in 5 minutes.—It was again repeated, using 0.5 cc. HCl and 2 mg. Bi : a precipitate of Bi had formed after 5 minutes, but the filtrate also gave a precipitate with H_2S .—It was again repeated, using 1 cc. HCl (1.20) and 6 and 8 mg. Bi : with 8 mg. Bi a precipitate formed, but not with 6 mg.

In a number of experiments 1 mg. Bi dissolved in 0.25 cc. HCl (1.20) was poured into 100 cc. water at various temperatures: a precipitate of BiOCl appeared in less than 1 minute when the temperature was 55° , 70° , 80° , or 90° , in about 2 minutes at 45° , in about 5 minutes at 25° , and only after 10-15 minutes at 15° .

Decomposition of Sodium Stannite Solution.—A sodium stannite solution was prepared as directed and kept in a stoppered bottle for a week: a black, crystalline deposit appeared at the bottom of the bottle.

Action of Sodium Stannite on BiOCl.—Vanino and Treubert (*Ber. d. chem. Ges.*, **31**, 1113, 1898) have shown that the black precipitate formed by the action of a stannite solution is metallic bismuth, and not BiO , as was formerly supposed to be the case.

0.5 mg. Bi as BiCl_3 was added in one experiment to 100 cc. water, and in a second one to 500 cc. water; the precipitate formed (which was scarcely visible in the second case) was collected on a filter, washed with water, and then treated with Na_2SnO_2 : the greater part of the filter was at once blackened.

10 mg. Pb as Pb(OH)_2 were treated on a filter first with a cold Na_2SnO_2 solution and then with a solution at about 60° : in the first case no blackening occurred in several minutes, while in the second it occurred almost immediately.—The experiment was repeated with 20 mg. Sb as antimonous and with 20 mg. Sb as antimonous hydroxide: no blackening was observed in either case.—The experiment was repeated with 2 mg. Fe as Fe(OH)_3 : the red precipitate did not change color in the cold in 10 minutes; but, when the hot Na_2SnO_2 was poured over it, it slowly became darker.

P. 30: Precipitation of Copper Ferrocyanide in the Presence of a Cadmium Salt.—A solution containing 1 mg. Cu as CuSO_4 , 500 mg. Cd as $\text{Cd(NO}_3)_2$, and 2 cc. H_2SO_4 (1.84) was made alkaline with NH_4OH : the solution remained colorless. One-fourth of the solution (about 10 cc.) was acidified with acetic and two drops of a 4% $\text{K}_4\text{Fe(CN)}_6$ solution added: a white precipitate separated, which had at first only a slight pink tinge, but this color deepened and was very apparent after 10 minutes. Excess of $\text{K}_4\text{Fe(CN)}_6$ was then added: much more of the white precipitate separated, and the pink color of the copper salt was almost obscured.—The experiment was repeated, except that only 0.5 mg. Cu was taken: the result was exactly the same, thus showing that this test is a very delicate one, provided only two to three drops of $\text{K}_4\text{Fe(CN)}_6$ solution are first added.

**Precipitation of Molybdenum and Uranium by Potassium Ferrocyanide.*—1 and 100 mg. Mo as MoO_3 , and 1 and 10 mg. U as $\text{UO}_2(\text{C}_2\text{H}_5\text{O}_2)_2$, in separate experiments were dissolved in 2 cc. NH_4OH (0.96), the solutions made acid with acetic acid, and several drops of $\text{K}_4\text{Fe(CN)}_6$ solution added: no change was observed.—The experiments were repeated, except that the NH_4OH solution was acidified with HCl instead of with acetic acid: with the 100 mg. Mo and the 10 mg. U a large dark red precipitate separated at once: with the 1 mg. portions a deep red solution was obtained, from which a dark red precipitate separated after a minute or two.

P. 31: Complex Cuprocyanide and Cadmiocyanide Anions.—See Euler, *Ber. d. chem. Ges.*, **36**, 3404 (1903); Bodländer, *Ber. d. chem. Ges.*, **36**, 3933 (1903).

Behavior of Mercury, Lead, and Bismuth in the Cadmium Test with H_2S .—1 mg. Hg , 1 mg. Pb , and 1 mg. Bi were treated in separate experiments by P. 26, 28, and 31, filtering immediately after the addition of H_2SO_4 and of NH_4OH : there resulted a precipitate with H_2SO_4 in the case of lead and with NH_4OH in the case

of bismuth, but none in the case of mercury with these reagents. With H_2S in the KCN solution small dark brown precipitates formed in the lead solution and in the mercury solution, and a very small black one in the bismuth solution.—The experiment was repeated with 150 mg. Pb and with 150 mg. Bi, the precipitates of $PbSO_4$ and of $(BiO)_2SO_4$ and $Bi(OH)_3$ being filtered after cooling and standing a few minutes: even less precipitate resulted in each case than when only 1 mg. was used.

Separation of CdS from Black Sulphides by Dilute H_2SO_4 .—1 mg. Cd as CdS, freshly precipitated by H_2S from an NH_4OH solution, was boiled gently for about 5 minutes with 20 cc. of a mixture of one volume of H_2SO_4 (1.20) with four volumes of water; the solution was filtered, diluted with two or three times its volume of water, and saturated with H_2S in the cold: a yellow precipitate of CdS separated.

The experiment was repeated, except that in separate experiments 1 mg. Cu, 1 mg. Pb, and 1 mg. Hg were mixed with 1 mg. Cd: a distinctly yellow precipitate was obtained in each experiment.

About 50 mg. Cd as CdS were boiled for 5 minutes with 20 cc. of a mixture of one volume H_2SO_4 (1.20) and four volumes of water: the sulphide did not dissolve completely.

Analysis of the Tin Group

P. 41: Detection of the Tin Group by the Appearance of the HCl Precipitate from the Ammonium Polysulphide Solution.—Separate 10 cc. portions of the ammonium polysulphide reagent (see P. 22, Note) were diluted to known volumes in some experiments with hot water, and in others with cold water; the solutions were then made acid by adding HCl slowly, and the mixtures were shaken and allowed to stand: from cold solutions of a total volume of 30 to 50 cc. the sulphur separated as a pure white, finely divided precipitate, which coagulated slowly on shaking, and had then only a faint yellow tinge which did not change on warming. From more concentrated solutions, and especially from hot solutions, the yellow color after coagulation was more pronounced. Separate 10 cc. portions of the ammonium polysulphide reagent containing 1 mg. As were diluted with 20 cc. and with 40 cc. water; HCl was slowly added until the solutions were acid; the mixtures were shaken and allowed to stand: the precipitate had at first the appearance of pure sulphur, but it coagulated more quickly, became flocculent, and turned brilliant yellow. Further experiments showed that the coagulation and change of color took place more quickly when the mixture was slightly warmed after coagulation.—The experiment was repeated, using 1 mg. Sb instead of As: the HCl precipitate remained white as long as the solution remained alkaline, but on further addition of HCl the orange color of the Sb_2S_3 became very apparent; the precipitate quickly coagulated and became flocculent.—The experiment was repeated with 1 mg. Sn: the HCl precipitate had a very faint yellow tinge; it coagulated only slowly, and appeared like the pure sulphur precipitate, except that it had a much darker yellow color. The experiment was repeated with 1 mg. Cu as $CuSO_4$: a dark orange-yellow (liver-colored) precipitate was obtained.—The experiment was repeated with 1 mg. Hg as $HgCl_2$: the HCl precipitate was nearly white, but when warmed slightly it became dark gray in color.

Color of a Mixture of Tin and Antimony Sulphides.—500 mg. Sn as $SnCl_2$ and 200 mg. Sb as $SbCl_3$ were slowly added to 10 cc. of a warm ammonium polysulphide solution, and the clear solution obtained was at once acidified with HCl: a brown precipitate separated, which slowly became dark gray in color.—The experiment was repeated, except that the ammonium polysulphide solution was cooled and diluted to about 40 cc. and HCl was slowly added: the precipitate was at first

yellow with an orange tint, but on standing it slowly became darker, assuming first a brown and finally a dark gray color.—These precipitates were treated by P. 42-47: the antimony and tin dissolved completely in HCl (1.20) (P. 42), and the antimony was completely precipitated in P. 45 as an orange precipitate.

Composition of the Substances Formed by Dissolving As₂S₃ and Sb₂S₃ in Alkalies.—For evidence that salts of intermediate sulpho-oxyacids of arsenic are formed when As₂S₃ is dissolved in an alkali, see McCay, *Ber. d. chem. Ges.*, **32**, 2471 (1899); *Z. anorg. Chem.*, **25**, 459 (1901); McLauchlan, *Ber. d. chem. Ges.*, **34**, 2166 (1901); Weinland and Lehman, *Z. anorg. Chem.*, **26**, 322 (1901). Treadwell, (*Qual. Anal.*, p. 188, 1902) concludes that K₃SbO₃ is not formed by the action of KOH on Sb₂O₃ according to the equation $Sb_2S_3 + 6KOH = K_3SbO_3 + K_3SbS_3 + 3H_2O$, because this solution is stable when diluted, while a solution of K₃SbO₃ is not.

For evidence that the precipitation of arsenic is incomplete when a solution of As₂S₃ in an alkali is made acid, see Weinland and Lehman, *loc. cit.*, and Vanino and Griebel, *Z. anal. Chem.*, **40**, 589 (1901).

Presence of Copper and Mercury in the Tin Group.—For the solubility of CuS and HgS in NH₄OH and in ammonium mono- and polysulphide, see C. E., P. 22. For the fact that copper and mercury will divide in the heating with HCl (1.20), see below.—That the presence of even 2 mg. Cu or of Hg does not interfere with the detection of arsenic is shown in C. E., P. 43.—That the same amount of copper or mercury does not prevent the detection of antimony is shown in C. E., P. 46.

P. 42: Solubility of Sb₂S₃ in HCl (1.20).—500 mg. Sb as sulphide, freshly precipitated from an ammonium polysulphide solution, and therefore consisting mainly of Sb₂S₅, were treated according to the procedure: nearly all the antimony dissolved, but the sulphur residue had an orange-red color. The residue was treated a second time in the same way, and the HCl solution diluted and saturated with H₂S: a small precipitate of Sb₂S₃ estimated to contain 1 or 2 mg. Sb formed. The sulphur residue was again treated with HCl: scarcely any Sb dissolved, although the residue still had a distinct orange color.

A mixture of 1 mg. Sb as Sb₂S₃ with 500 mg. As as As₂S₃ (freshly precipitated from an ammonium polysulphide solution and carefully dried by suction) was treated by the procedure, and the residue subjected to a second and then to a third treatment; the separate HCl solutions were diluted and treated with H₂S by P. 45: the first solution contained about 0.6 mg. Sb, the second about half this amount, and the third only a trace.—This experiment was repeated, except that the sulphides were not carefully dried before adding HCl (1.20): the second HCl solution contained more Sb than the first, thus showing that the presence of water interferes with the action of the HCl.

Formation of SbCl₃ by Dissolving Sb₂S₃ in HCl.—See Classen and Bauer, *Ber. d. chem. Ges.*, **16**, 1067 (1883).

Solubility of As₂S₃ in HCl (1.20).—Seven different 500 mg. portions of As as As₂S₃, freshly precipitated from an ammonium polysulphide solution, were treated by the procedure; and the filtrates were warmed and saturated completely with H₂S: only a faint precipitate resulted, in no case corresponding to more than a small fraction of a milligram of arsenic.—The experiment was repeated, except that the HCl (1.20) was boiled gently for 5 minutes: the filtrate was found to contain 5-10 mg. As. The vapors given off blackened lead acetate paper held above the flask.

Solubility of As₂S₃ in HCl (1.20).—Six separate 500 mg. portions of As as As₂S₃, freshly precipitated from H₂AsO₃ solution by H₂S in five of the experiments and by

acidifying a solution of As_2S_3 in NH_4OH in the remaining one, were treated by the procedure and the filtrate saturated with H_2S : in each experiment distinct precipitates of As_2S_3 were obtained, which were estimated to contain between 1 and 5 mg. As.—The experiments were repeated, except that a slow current of H_2S was passed through the HCl during the experiment: the filtrates then gave with H_2S scarcely any precipitate.—A solution of 100 mg. As as As_2O_3 in 20 cc. HCl (1.20) was saturated with H_2S for 5 minutes at about 90° , the solution decanted off, water added, and H_2S again passed in: no more precipitate separated.

Solubility of CuS and HgS in HCl.—10 mg. Cu as CuS and 10 mg. Hg as HgS , freshly precipitated, were treated in separate experiments by P. 42: the greater part but not all of each of the precipitates was dissolved.

**Solubility of TeS_2 in HCl (1.20).*—50 mg. Te as TeO_2 dissolved in HCl were added to 10 cc. ammonium polysulphide; the solution was treated by P. 41, the black HCl precipitate was heated with HCl (1.20) by P. 42, and the filtrate was saturated with H_2S : a precipitate formed estimated to contain about 1 to 2 mg. Te.—The experiment was repeated, except that the HCl solution was kept saturated with H_2S : in this case no tellurium dissolved.

**Insolubility of Sulphides of Pt, Au, Se, and Mo in HCl (1.20).*—20 mg. Pt. 10 mg. Au, 50 mg. Se, and 50 mg. Mo, all as sulphides precipitated by acidifying an ammonium polysulphide solution, were in separate experiments digested at about 90° for 10 minutes with 10 cc. HCl (1.20), diluted, and filtered, as described in P. 42; the filtrates were saturated with H_2S at 100° , diluted to 50 cc. again heated and saturated with H_2S : no precipitate separated in any case, not even after several minutes, thus showing that nothing had dissolved in the HCl .

P. 43: Reactions between $HClO_3$ and HCl .—See Schacherl, *Liebig's Ann. Chem.* **182**, 193 (1876); Bray, *Z. anorg. Chem.*, **48**, 242 (1906).

Non-existence of $AsCl_3$.—See Smith and Hora, *J. Am. Chem. Soc.*, **26**, 632 (1904). For earlier references, see Baskerville and Bennet, *J. Am. Chem. Soc.*, **24**, 1070 (1902).

Non-volatility of Arsenic Acid from HCl Solution.—2.0 grams As as As_2O_3 , containing a small amount of As_2O_5 , were dissolved in 20 cc. HCl (1.20) and distilled until only half the volume remained in the flask; 10 cc. more of HCl (1.20) were added and the solution distilled as before; and this operation was repeated several times; the distillates were collected in separate portions of cold water and saturated with H_2S : in the first distillates yellow precipitates appeared at once, which decreased in amount from about 15 mg. As in the first distillate to about 0.5 mg. As in the fifth. (This was evidently due to the As_2O_5 present as impurity). These solutions were filtered and the filtrates treated at 90° with H_2S for several minutes: very little, if any, precipitate was obtained, showing that arsenic in the higher state of oxidation was practically absent. From later distillates precipitates containing about 0.5 mg. As separated quickly with H_2S in the cold, and no further precipitate separated when the solutions were heated and treated with H_2S . Thus even from this concentrated solution of arsenic acid in the presence of concentrated HCl only a trifling amount of arsenic volatilized. Since the higher halogen compound of an element is in general more volatile than the lower, it is therefore highly probable, from the above result, that $AsCl_3$ is not present even in concentrated HCl solution.

Non-influence of Mercury, Antimony, or Tin on the Test for Arsenic with $MgCl_2$.—2 mg. Hg as $HgCl_2$, 2 mg. Sn as $SnCl_2$, 2 mg. Sb as Sb_2S_3 were treated in separate experiments according to the procedure: with mercury a precipitate was obtained with NH_4OH , and the filtrate when acidified with HCl and treated with H_2S gave no precipitate; with tin and antimony no permanent precipitate formed in the NH_4OH solution, nor was one formed with $MgCl_2$ and NH_4Cl .

Delicacy of Test for Arsenic.—0.5, 1, and 2 mg. As as H_2AsO_4 were treated in

separate experiments according to P. 43, the final volume being in each case about 5 cc.: with 2 mg. the $MgNH_4AsO_4$ precipitate appeared immediately upon shaking; with 1 mg. after gentle stirring; and with 0.5 mg., slowly after rubbing with a glass rod for a minute or two.

*P. 43a: *Action of KI on K_2PtCl_6 .*—To 5 mg. Pt as H_2PtCl_6 were added 10 cc. water and a few drops KI solution: a deep red solution resulted. 5 cc. CS_2 were added and the mixture shaken: the water layer remained dark red, and the CS_2 solution was colored slightly, owing to the presence of a trace of iodine. The water layer was shaken with a fresh portion of CS_2 : this time the CS_2 layer was colorless, thus proving that only an insignificant quantity of iodine was present, and therefore that the platinum compound is not reduced. To the solution some H_2SO_4 solution was added: the color of the solution changed at once to a pale yellow.

*P. 43b: *Action of Oxalic Acid on Solutions of Chlorauric, Selenous, Tellurous, and Molybdic Acids.*—2 mg. Au as $AuCl_3$ were dissolved in one experiment in a dilute HCl solution containing about 0.5 gram $H_2C_2O_4$, in a second one in a dilute solution of NH_4OH and $(NH_4)_2C_2O_4$, and the solutions were evaporated to 3-4 cc.: no precipitate separated in either case. The solutions were then evaporated almost to dryness to expel the excess of HCl and of NH_4OH , were diluted to about 15 cc., and again boiled: a purple precipitate of gold quickly appeared in both cases.—In another experiment 0.5 mg. Au as $AuCl_3$ was added to 10 cc. of a dilute $(NH_4)_2C_2O_4$ solution which had been made slightly acid with $H_2C_2O_4$, and the solution was heated to boiling: a purple precipitate of gold separated.

5 mg. Au as $AuCl_3$ were treated according to the procedure: a precipitate of gold appeared quickly and continued to separate for 2 or 3 minutes. After about 5 minutes the gold was filtered off and the filtrate again digested for several minutes on the steam bath: no further precipitate of gold separated.

50 mg. Se as H_2SeO_3 , 50 mg. Te as H_2TeO_3 , and 50 mg. Mo as $(NH_4)_2MoO_4$ were treated in separate experiments by *P. 43b: in the case of tellurium a white precipitate separated from the $H_2C_2O_4$ solution on evaporation, but it dissolved readily on adding HCl; in the other two experiments no precipitate formed and no color change was noticed.

*P. 43c: *Action of H_2SO_3 on H_2SeO_3 .*—1 mg. Se as SeO_2 in 10 cc. HCl (1.15) was saturated with SO_2 gas at room temperature: a red precipitate appeared at once and continued to increase slowly. After 5 minutes the solution was filtered and the filtrate allowed to stand: it remained clear.—The experiment was repeated, except that the solution was saturated at 90° : a reddish precipitate appeared at once, but it changed rapidly to a very compact, nearly black precipitate that collected at the bottom of the test tube.—The first experiment was repeated with 0.5 mg. Se: a considerable red precipitate separated within 5 minutes.

Action of H_2SO_3 on H_2TeO_3 .—100 mg. Te as TeO_2 were dissolved in separate experiments in 10 cc. HCl (1.20), in 10 cc. HCl (1.20) and 5 cc. water, and in 20 cc. HCl (1.12). Each solution in a test tube was saturated with SO_2 gas, was allowed to stand 5 minutes, and then placed in a steam bath at 100° for 15 minutes: no precipitate of tellurium was formed in any case. Enough water was added to make the volume 30 to 40 cc.: a black precipitate of tellurium appeared at once.

In each of eight test tubes were placed 0.5 mg. Te as TeO_2 and 25 cc. saturated H_2SO_3 solution. To the first of these were added 3 cc. 40% HCl, to the second 4 cc., to the third 5 cc., and so on up to the eighth, which contained 10 cc.; the tubes were then all heated in a steam bath: those with 3 and 4 cc. HCl gave scarcely any precipitate; in the others the quantity of precipitate increased with the increase of acid up to 7 cc., and then decreased steadily with further increase in the amount of HCl.

*P. 43d: *Action of KI and of KI + H₂SO₄ on Tellurium Solutions.*—For the formation of TeI₄ in the reaction between H₂TeO₃ and KI, see Gooch and Morgan, *Am. J. Sci.*, (4), **2**, 271 (1896). For the formation of K₂TeI₆, see Wheeler, *Am. J. Sci.*, (3), **45**, 267 (1893). As to its deep red color, see Norris and Fay, *Am. Chem. J.*, **23**, 109 (1900).

To prove that tellurium itself and not an iodide of it is precipitated by H₂SO₄ and HI, 20 mg. Te as TeO₂ were dissolved in 10 cc. HCl (1.12) and 1 mg. I as KI and a little solid Na₂SO₃ were added: a large black precipitate formed slowly. This was filtered off after half an hour, the filtrate was diluted to 20 cc., and to it were added a few drops KI solution and a little solid Na₂SO₃: a black precipitate estimated to contain only 1 to 2 mg. Te resulted.—The experiment was repeated, except that the mixture was allowed to stand overnight before filtering; only about 0.2 mg. Te remained in solution. Thus a large quantity of tellurium may be completely precipitated when only a very small quantity of iodine is present.

To determine the proper concentration of HCl for the complete precipitation of the tellurium, a few drops of KI solution were added to solutions containing 0.5 mg. Te as TeO₂ dissolved in 10 cc. HCl (1.20), in 15 cc. HCl (1.15), in 20 cc. HCl (1.12), and in 30 cc. HCl (1.06), respectively: a deep red color resulted in each case, but was less intense in the most concentrated and in the most dilute HCl than in the other two solutions. A crystal of Na₂SO₃ was added to each solution: no change was observed in the three more concentrated HCl solutions, but a black precipitate of tellurium formed in the most dilute solution.—In another experiment 0.1 mg. Te was dissolved in 20 cc. HCl (1.06), and a drop of KI and a crystal of Na₂SO₃ added; a black precipitate resulted.

50 mg. Te as TeO₂ were treated according to the procedure, and the precipitated tellurium filtered off after 5 minutes: the filtrate had a strong odor of SO₂, but no more tellurium separated in half an hour, even when a little KI was added.

Action of HI on H₂SeO₃.—See Norris and Fay, *Am. Chem. J.*, **23**, 109 (1900).

Action of HI on H₂MoO₄.—To separate solutions of 50 mg. Mo as MoO₃ in 10 cc. HCl (1.20) and in 20 cc. HCl (1.12) a few drops of KI solution were added: iodine was slowly liberated in both cases, but more rapidly in the more strongly acid solution.

*P. 43e: *Action of Zinc and KCNS on H₂MoO₄.*—To 1 mg. Mo as MoO₃ dissolved in 20 cc. HCl (1.06) in a test tube were added a crystal of KCNS and some granules of zinc: a brilliant red color appeared very quickly and remained unchanged for about 5 minutes: the color slowly changed to yellow, and then faded until after about half an hour the solution was nearly colorless.—The experiment was repeated, except that the KCNS was not added until after the action of the zinc had continued for 15 minutes: a yellow color resulted.—The experiment was repeated, except that the KCNS was added after about an hour: the solution remained colorless.

For the composition of the red compound produced with KSCN and zinc, see Sand and Burger, *Ber. d. chem. Ges.*, **38**, 3384 (1905); **39**, 1761 (1906).

P. 44: *Action of H₂S on H₃AsO₄ Solutions.*—See McCay, *Am. Chem. J.*, **10**, 459 (1888). Brauner and Tomicek, *J. Chem. Soc.*, **53**, 145 (1888). Usher and Travers, *J. Chem. Soc.*, **87**, 1370 (1905).

P. 45: *Separation of Antimony and Tin by H₂S.*—Known amounts of Sb and Sn as chlorides were added to an ammonium polysulphide solution and precipitated as Sb₂S₃ and SnS₂ with HCl; the precipitates were dried by suction and digested with 10 cc. HCl (1.20) at 90° for 10 minutes in a 50 cc. conical flask. Each solution so obtained was diluted to a known volume and treated with H₂S

just below the boiling point. The volume of the diluted solution at which the precipitation of Sb_2S_3 was nearly or quite complete and that at which the precipitation of SnS_2 began and became considerable are given in the following table:

Experiment No.	Sn mg.	Sb mg.	Volume of solution at which precipitation of antimony was nearly complete.		Volume of solution at which precipitation of tin began. was considerable.	
		
1.....	500	0	50	60
2.....	500	0	60	70
3.....	400	1	40	50	60	70
4.....	500	1	..	50	60	70
5.....	500	1	..	55	60	70
6, 7	500	200	40	50	60	70
8.....	10	500	40	50
9.....	200	200	..	50
10.....	0	1	..	55

In Experiment No. 1 a slight yellow precipitate of SnS_2 appeared in testing for antimony, but a good blank was obtained in No. 2. In Experiment 4 an orange-red precipitate of Sb_2S_3 was obtained; in Experiment 5 a dark-colored precipitate, which gave a good confirmatory test for antimony. In Experiment 10 the Sb_2S_3 precipitate did not separate until the last 5 cc. of water were added.

Precipitation of CuS and HgS from HCl Solution.—1 mg. Cu and 0.5 mg. and 4.5 mg. Hg as chlorides were added in separate experiments to 10 cc. HCl (1.20) and 40 cc. H_2O , and the solutions were heated to boiling and saturated with H_2S at 90° : in the first two cases light gray precipitates formed slowly, which on the filter appeared to be black; in the last case a black precipitate. The precipitates were filtered out, the solutions diluted and treated with H_2S : in the mercury experiments they gave no precipitates, but in the case of Cu a very slight precipitate formed.

P. 46: Influence of Copper and Mercury on the Reduction Test for Antimony.—1 and 2 mg. Hg as HgS and 1 and 2 mg. Cu as CuS were treated in separate experiments according to P. 46: the mercury separated on the platinum as a gray, loosely adhering film, the copper as a red, metallic, firmly adhering deposit, which could not be mistaken for antimony.—The experiments were repeated in the presence of 0.5 and 1 mg. Sb: characteristic black deposits of Sb were obtained.

Behavior of Arsenic and Tellurium in the Reduction Test for Antimony.—1, 4, and 10 mg. As as H_2AsO_4 and 0.5 mg. Te as H_2TeO_3 were treated in separate experiments according to P. 46: with the 10 mg. As and with the tellurium black deposits on the platinum were obtained, which dissolved readily in a normal, cold alkaline solution of $NaOCl$; no deposit of arsenic was obtained with the 1 or 4 mg. As. It is therefore improbable that a black deposit of arsenic will ever be obtained in an actual analysis, since only very small amounts will be dissolved in the HCl treatment (P. 42).

Insolubility of Sb in NaOCl.—1 mg. Sb precipitated on platinum foil by the action of HCl and Sn was treated in the cold for 5-10 minutes with a normal, alkaline $NaOCl$ solution: no change took place.

P. 47: Effect of Temperature on the Precipitation of SnS_2 .—A solution of 1 mg. Sn as $SnCl_4$ in 10 cc. HCl (1.20) was successively diluted with portions of water and saturated with H_2S at 90° after each dilution: a precipitate formed only when the volume of the solution had become 110-120 cc.—The experiment was re-

peated several times, except that the solutions were saturated for 5-10 minutes with H_2S at 20° : a precipitate formed when the volume became 60-70 cc.

Delicacy of Confirmatory Test for Tin.—0.5 Sn as $SnCl_4$ was treated in several experiments according to P. 47: in all cases a precipitate of SnS_2 , and in most cases one of Hg_2Cl_2 , was obtained.

A STUDY OF THE FERROCYANIDE METHOD FOR THE DETERMINATION OF ZINC

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The Committee on Uniformity of Analysis for the Society of Western Chemists and Metallurgists in their provisional method recommended the employment of granulated lead to remove copper, previous to titration. Low in his "Technical Methods," says—"The use of granulated lead as a precipitant of copper is not recommended."

This disagreement of opinion between authorities of their weight persuaded me to settle the question for myself and led to a fuller study of the conditions influencing the determination, the results of which follow. In all instances the burette was kept covered until end point was determined in order to avoid any possible tendency to reach checks by knowing the burette reading.

Effect of Acid.—Bulk at starting 150 cc.; weight of zinc used 0.18546 gram. Ammonium chloride 5 grams.

Excess of acid in CC.	CC. of Ferrocyanide consumed	
	$85^\circ - 40^\circ$	$95^\circ - 70^\circ$
0	38.2	38.2
1	37.1	37.1
3	37.0	37.0
5	37.0	37.0
7.5	37.0	37.1
10	37.15	37.4
15	37.3	38.1
20	38.0	38.6

A certain amount of free hydrochloric acid is necessary to sharpen the end reaction. An excess of from one to ten cc. does not affect the results sensibly. Beyond these limits increase of acid increases consumption of ferrocyanide, particularly when the titration is conducted at a high temperature.

Effect of Potassium Chlorate.—Conditions as before with constant use of an excess of 5 cc. of concentrated hydrochloric acid.