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An Investigation into the Chemistry of the Reinsch Test for Arsenic and Antimony, and its Extension to Bismuth.*

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PART I.

THE initial work for this research was carried out with a view to finding a method for the separation of small amounts of arsenic from antimony when separating of the latter element from copper (Completed method, ANALYST, 1922, 47, 1). In view of the rather perplexing results obtained in the qualitative examination, it seemed desirable to investigate further the reactions involved.

SUMMARY OF PREVIOUS WORK.—The literature of the Reinsch test does not appear to be extensive; the following are the principal papers, that could be traced, dealing with the chemistry of it:—

Reinsch's original memoir was published in 1841 in the J. prakt. Chem. (24, 244)and another in the Neuer Jahresbericht der Pharmacie (16, 135). The first-named is entitled "On the behaviour of solutions of arsenic and antimony and the metals towards copper"; in it he states the method of using the test, attempts to determine the limits, and goes into the question of the identification of the arsenic obtained in the film. One feature of the paper is an outline of the tests carried out in the cold over a period of several weeks, under which conditions he found that the reaction in dilute hydrochloric acid was much more rapid than in strong, which difference disappeared on heating; he states also that, under these conditions, access of air causes acceleration—a surprising result which is certainly not borne out at higher temperatures. He explicitly states that hydrochloric acid is necessary to the test, and that the reaction will not take place in sulphuric or

* Communication from the Research Department, Woolwich.

acetic acids; this statement appears to have been lost sight of latterly. He was also familiar with the fact that bismuth as well as antimony gives the test. Throughout he appears to have been under the impression that the arsenic is deposited as element; it is possible that this may have been the case with his films deposited in the cold, as these seem to have differed in appearance from the ordinary film. A somewhat curious assertion occurs in this paper to the effect that tin and lead in hydrochloric acid solution of certain concentrations and in the presence of air, but not otherwise, will deposit on copper in a powdery form when allowed to stand for some days. No confirmation of this statement, which on the face of it seems improbable, could be obtained.

Bettendorf states (Zeitsch. für Chem. (2), 5, 492) that the hydrochloric acid used for the test must not be weaker than sp. gr. $1 \cdot 1$. This is not borne out by experience.

Fresenius, in a paper before the Chemical Society (April 15, 1844), mentions the Reinsch test, drawing attention to its difficulties, but only as an introduction to a test of his own.

Lippert's paper (J. prakt. Chem., 81, 168) deals solely with the composition and properties of the deposit formed by arsenic in the Reinsch test, to which deposit he ascribes the composition Cu_5As_2 .

Drinkwater states (ANALYST, 1883, 8, 241) that selenium deposits on copper from hydrochloric acid solution in the same manner as arsenic.

Macallan points out that a deposit of copper sulphide might be obtained in testing decomposing organic matter for arsenic (ANALYST, 1883, 8, 46).

J. L. Howe and P. S. Mertius published "Notes on Reinsch's test" (J. Amer. Chem. Soc., 1896, 18, 953), in which the following statements were made:—(1) All arsenic compounds soluble in hydrochloric acid give a deposit immediately on heating. (2) Commercial "metallic" arsenic readily gives the deposit. (3) Bright crystals of freshly sublimed "metallic" arsenic give no deposit. (4) Arsenates deposit only after several minutes heating. (5) In the presence of nitric acid or chlorates there is no deposit owing to the copper dissolving. (6) Presence of organic matter does not affect the result.

J. St. G. Gray (*Chem. News*, 1871, 73) recognised four metals: arsenic, antimony, bismuth and mercury, as answering to the test, and stated that mercury could be distinguished from the other three, because it could be removed from the copper by rubbing the latter with gold.

John Clark read a paper on improvements in Reinsch's process before the Chemical Society, May, 1893. This deals with minor details only.

In the first confusion caused by the arsenic scare of 1900, the Reinsch test was recommended by the Expert Committee of the Manchester brewers as a rapid method of sorting large numbers of samples of beer, sugar, etc.

QUALITATIVE TESTS.—In searching for a method of separating small quantities of arsenic from small quantities of antimony it seemed desirable to investigate thoroughly the conditions (*e.g.* as to reaction, presence of other reagents, etc.) under which these two elements are deposited on copper. This qualitative trial was carried out as follows:—Slips of copper foil were cleaned with nitric acid (sp. gr. 1.2) and placed in small beakers, about 10 c.c. of dilute solution of arsenious oxide or tartar emetic added, and the whole heated on a plate.

The following results were obtained: \rightarrow

Reagent tried	Antimony	Arsenic
Sodium hydroxide	No deposit	No deposit
Ammonia solution	No deposit	No deposit
Tartaric acid	No deposit	No deposit
Tartaric acid with sodium hypo- phosphite	No deposit	No deposit
Phosphoric acid	No deposit	No deposit
Phosphoric acid with sodium hypo- phosphite	No deposit	No deposit
Sulphuric acid	No deposit	No deposit
Sulphuric acid with sodium hypo- phosphite	No deposit	No deposit
Sulphuric acid + sodium chloride	Immediate deposit	Immediate deposit
Phosphoric acid + sodium chloride	Slight delay	Immediate deposit
Tartaric acid + sodium chloride	Slight delay	Slight delay
Oxalic acid + ammonium chloride	Very considerable delay	Considerable delay
Ammonia + ammonium chloride	No deposit	No deposit
Acetic acid + ammonium chloride	Slight delay	Considerable delay
Ammonium chloride made acid with one drop of acetic acid	Slight delay	No appreciable deposit; after 30 mins. the addition of a few drops of acetic acid brought the arsenic down in two or three minutes
Ammonium chloride + ammonium nitrate made strongly acid with acetic acid	Prompt deposit	Prompt deposit
Copper nitrate pptd. with am- monia acidified with acetic acid	No deposit	No deposit
Acetic acid + potassium iodide cold	Deposit slowly formed	No deposit
Acetic acid + potassium iodide warmed	Prompt deposit	Deposit slowly formed
Acetic acid + potassium iodide warmed with a little iodine	Fairly prompt deposit	Very slight deposit after some time
Potassium cyanide (strong solution) boiled	1mmediate deposit	Very slight deposit very slowly formed
Potassium cyanide + cuprous chloride	Deposit rather slower	

It may be mentioned in passing that the reactions with potassium iodide and acetic acid and with potassium cyanide were tried somewhat exhaustively with a view to getting a quantitative separation of antimony and arsenic, but without result, as they did not appear to go to completion.

It will be noticed from the above reactions that there appear to be two essentials to the Reinsch test:—(a) Halides; (b) a certain amount of hydrogen ion.

With a view to determining the influence of the various factors, it was decided to attempt a set of measurements of the reaction velocity with varying amounts of sodium chloride, sulphuric acid, and arsenic, antimony, or bismuth, as the case might be. The method adopted was as follows:—

APPARATUS.—A 300 c.c. beaker was fitted with a cover made from a cork plate; through two holes in the cover, about an inch apart, passed two glass rods, and at the bottom end of each rod was a fork formed by fusing on two thinner rods, the fork being at about 30° to the axis of the main rod; the end of



each prong of the forks was bent upwards to form a hook. One of these hooked forks dipped into the 300 c.c. beaker, the other into a small 20 c.c. beaker standing on the bottom of the larger one. The outer beaker contained the solution to be tested, the inner one distilled water; the hook dipping into the outer beaker supported a slab of cleaned and prepared electrolytic copper, that dipping into the inner beaker a slab of an alloy used as a standard and varying according to the element being investigated. (See diagram.)

PROCEDURE.—The solution to be tested (as a rule 100 c.c.) is placed in the larger beaker, with a fragment of porcelain to ensure steady boiling, the small

beaker containing water is lowered into position excentrically, and the whole covered with a glass and set to boil on the plate. The slab of electrolytic copper is prepared by cleaning it thoroughly with nitric acid (sp. gr. 1.2), rinsing, drying and polishing it on fine emery paper, and finally again rinsing it to remove any adherent particles. The standard to be used is then placed in one glass holder and the electrolytic copper in the other, and both are lowered into a beaker containing boiling water acidified with a few drops of sulphuric acid and left there till the solution in the test beaker is boiling; the glass holders, together with the cork plate and the two slabs, are then lifted from their containing beaker and plunged into the beaker containing the test solution in such a way that the holder containing the standard rests on the bottom of the inner beaker, while that containing the copper slab rests on the bottom of the outer beaker, and is therefore immersed in the test solution. The number of seconds which elapse before the colours of the two slabs match is carefully noted. With regard to the preparation of the copper slab the polishing, though not essential, seems to result in far more concordant results and far better colours; apparently the better the polishing the more certain the reading; this point will be referred to again later.

The following were found to be the best standards for this method, and were used throughout:—

Bismuth 90:10 Cu As alloy, polished, but not etched; this standard required frequent repolishing.

The comparison was often a matter of some difficulty, and required considerable experience; it was very rarely possible to get an exact match of colours, and it was often necessary to reject experiments owing to the colour or texture of the film being quite different from that of the standard; this was almost unknown in the case of antimony, and seldom occurred in that of bismuth, but arsenic gave a good deal of trouble owing to black or velvety grey films. The aim, of course, throughout was to obtain, not an exact match of the standard, but a point in the course of the reaction which could be identified and noted.

No very definite rules can be laid down on the subject of angle of lighting or angle of observation; the procedure adopted was to arrange the slabs at an angle of 45° to the main direction of the light and observe from a point immediately opposite to them, *i.e.* normal to their surface. It is, however, desirable constantly to shift one's point of observation, looking sometimes at an angle of 45° , or even less, to the surfaces; this is due to the wide variations in the brilliancy and reflecting power of the deposited film. With these precautions, however, and given deposits of the proper colour, concordant readings are easily obtained, at any rate where the time of reaction is small (say under 200 seconds). In dealing with longer times the method is as a rule considerably less accurate, but these longer times occur, generally, on portions of the curves where a very large error in the time makes very little difference to the direction of the curve. The actual matching of the Bi experiments was more difficult than that of arsenic and antimony owing to the paleness of the deposit.

The following results were obtained by this method and plotted as curves:-

INFLUENCE OF VARYING CHLORIDE.—Acid strength kept constant throughout each set of curves; strength of element under examination (*i.e.* As. Sb. Bi) kept constant through each single curve.

Arsenic.

Standard used. 70: 30 Cu-As alloy polished and etched with 1.2 sp. gr. nitric acid.

In all cases 25 c.c. 1:3 sulphuric acid and the necessary amounts of arsenic and sodium chloride made up to 100 c.c.

0.16 grm. As		0.08 gr	0.08 grm. As		0.04 grm. As		m. As	0·01 gr	0.01 grm. As	
NaCl (Grms.)	Time (Secs.)									
0.10	720	0.20	400	••	••	0.40	470	0.60	430	
0.20	260	0.40	270	0.40	340	0.60	370	1.00	360	
0.40	185	0.60	200	0.60	240	0.80	230	1.50	290	
0.60	120	0.80	160	0.80	180	1.00	190	2.00	230	
0.80	90	1.00	135	1.00	160	$2 \cdot 00$	120	3.00	170	
1.00	75	1.50	80	2.00	85	3.00	85	4 ·00	140	
1.50	50	$2 \cdot 00$	65	3.00	60	4 ⋅00	70	5.00	120	
2.00	40	3.00	45	4 ·00	50	5.00	60	6.00	110	
3 .00	25	4.00	40	5.00	45	6.00	55	••	••	
4 ·00	20	5.98	35	••	••	••	••	••		

Antimony.

Standard used 50: 50 Cu-Sb alloy, polished and etched with 1.2 sp. gr. nitric acid.
In all cases 25 c.c. 1: 3 sulphuric acid and the necessary amount of antimony and sodium chloride made up to 60 c.c.

0.10 grm. Sb 0.05 grm. Sb		0•02 grm. Sb		0·01 gr	0-01 grm. Sb		0·005 grm. Sb		
NaCl (Grm s.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)
0.15 0.20 0.25 0.40 0.60	80 32 21 13 10	$\begin{array}{c} 0.15 \\ 0.20 \\ 0.40 \\ 0.60 \\ 0.80 \\ 0.00 \end{array}$	$130 \\ 55 \\ 28 \\ 17 \\ 12$	$\begin{array}{c} 0.15 \\ 0.20 \\ 0.25 \\ 0.40 \\ 0.60 \\ 0.00 \end{array}$	$160 \\ 70 \\ 60 \\ 35 \\ 25 \\ 22 \\ 32 \\ 32 \\ 35 \\ 35 \\ 35$	$\begin{array}{c} 0.15 \\ 0.20 \\ 0.25 \\ 0.40 \\ 0.60 \\ 0.00 \end{array}$	$ 195 \\ 90 \\ 80 \\ 50 \\ 37 \\ 30 $	$\begin{array}{c} 0.20 \\ 0.25 \\ 0.30 \\ 0.35 \\ 0.60 \\ 0.00 \end{array}$	140 90 75 70 50
$\begin{array}{c} 0{\cdot}80 \\ 1{\cdot}50 \end{array}$	$\frac{7}{3}$	$2 \cdot 00$	5 	$\begin{array}{c} 0\cdot 80 \\ 1\cdot 50 \end{array}$	$\frac{22}{17}$	$0.80 \\ 2.00$	$\begin{array}{c} 30 \\ 25 \end{array}$	$0.80 \\ 2.00$	40 35

Bismuth.

Standard used 90: 10 Cu-As alloy, polished, not etched.

In all cases 10 c.c. 1:3 sulphuric acid and the desired quantities of bismuth and sodium chloride made up to 100 c.c.

0.01 grm. Bi		m. Bi	0·005 g	rm. Bi
Time	NaCl	Time	NaCl	Time
(Secs.)	(Grms.)	(Secs.)	(Grms.)	(Secs.)
200	••	••	••	
128	0.05	120	0.20	160
80	0.10	50	0.25	120
70	0.20	40	0.40	90
60	0.40	35	0.60	80
55		••	••	
55	••	••	0.80	75
55	1.00	33	1.00	75
55	6.00	25	••	• •
	rm. Bi Time (Secs.) 200 128 80 70 60 55 55 55 55 55 55	$\begin{array}{ccccccc} {\rm rm.~Bi} & 0 \cdot 02~{\rm gr} \\ {\rm Time} & {\rm NaCl} \\ ({\rm Secs.}) & ({\rm Grms.}) \\ 200 & & & \\ 128 & 0 \cdot 05 \\ 80 & 0 \cdot 10 \\ 70 & 0 \cdot 20 \\ 60 & 0 \cdot 40 \\ 555 & & \\ 555 & & \\ 555 & 1 \cdot 00 \\ 555 & 6 \cdot 00 \\ \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

INFLUENCE OF VARYING ARSENIC OR ANTIMONY.—Curves for these were plotted from the figures obtained for the preceding set of curves.

In the case of arsenic a few additional points were determined to complete the curves. In all cases 25 c.c. of 1:3 sulphuric acid was used, and the bulk made up to 100 c.c.

Grms.	Sec	conds	Grms.		Seconds
0·025 As 2·00 NaCl	}	90	0·044 As 0·40 NaCl	}	320
0·024 As 1·00 NaCl	} 1	180	0·024 As 3·00 NaCl	}	70

In the above sets of curves the acid strength, though constant throughout each set, varies from one element to another; it will be shown in the following set that at a certain concentration of acid a maximum effect is obtained, and that further addition of acid is without influence. This concentration was well exceeded in all the sets.

INFLUENCE OF VARYING ACID STRENGTH.—In all cases 1.0 c.c. of 1:3 sulphuric acid contained 0.456 grm. of H_2SO_4 . In this series three curves were plotted for each element; in the second of these the amount of the element was the same as in the first, and the sodium chloride altered, and in the third the sodium chloride was the same as in the first, and the amount of element altered.

Arsenic.

Standard used 70: 30 Cu-As alloy, polished and etched with 1.2 nitric acid. In all cases the bulk made up to 100 c.c.

Arsenic	0.16 grm.	Arsenic	0.08 grm.	Arsenic	0·16 grm.
Sodium chlorid	le 2.00 grms.	Sodium chlorid	le 2·00 grms.	Sodium chloride	1.00 grms.
1:3 H ₂ SO ₄	Seconds	1:3 H ₂ SO ₄	Seconds	1:3 H ₂ SO ₄	Seconds
1.0 c.c.	450	2.0 c.c.	260	2.0 c.c.	530
$2 \cdot 0$	240	$3 \cdot 0$	160	3.0	270
3.0	130	$4 \cdot 0$	130	4.0	180
4 ·0	110	5.0	105	$5 \cdot 0$	145
5.0	90	6.0	85	6.0	120
6.0	65	7.0	70	7.0	105
7.0	55	8.0	65	8.0	95
8.0	50	9.0	55	9.0	90
9.0	45	10.0	55	10.0	88
10.0	40	13.0	50	13.0	85
13.0	40				

Antimony.

Standard used 50: 50 Cu-Sb alloy, polished and etched with 1.2 sp. gr. nitric acid. In all cases the bulk made up to 100 c.c.

Antimony Sodium chlorid	0.005 grm. e 0.50 grm.	Antimony Sodium chlorid	0.005 grm. le 1.00 grms.	Antimony Sodium chloride	0.01 grm. 1.00 grms.
$1:3$ H_2SO_4	Seconds	$1:3$ H_2SO_4	Seconds	1:3 H ₂ SO ₄	Seconds
1.0 c.c.	360	0.5 c.c.	470	0.5 c.c.	420
$2 \cdot 0$	230	1.0	270	1.0	200
$3 \cdot 0$	200	$2 \cdot 0$	140	2.0	110
4.0	180	4 ·0	100	4.0	80
6.0	160	6.0	85	6.0	65
8.0	155	7.0	90	8.0	65
10.0	155	8.0	85	10.0	65
		9.0	90		
		10.0	85		

Bismuth.

Standard used 90:10 Cu-As alloy, polished, not etched. In all cases the bulk made up to 100 c.c. In stating the amounts of acid, allowance is made for that contained in the bismuth solution.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	grm.) grm.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	conds
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	60
5.9 40 3.8 65 8.3	45
	45
25.0 40 4.8 50	
5.8 50	

The bismuth curves were obtained with great difficulty owing to the acid strength being barely great enough to keep the bismuth in solution. In all three of these sets at a certain concentration of acid, which remains constant for any one element, but varies from one element to another, the curves become horizontal, and further addition of acid is without effect on the rate of reaction. This point is

For	$\operatorname{arsenic}$	Approx.	12 [.] 0 c.c.	1:3	$H_2SO_4 = 5.47$	per	cent.	H ₂ SO ₄ .
,,	antimony	,,	6·0 c.c.	1:3	$H_2SO_4 = 2.74$	per	cent.	H ₂ SO ₄ .
,,	bismuth	,,	5.0 c.c.	1:3	$H_2SO_4 = 2.28$	per	cent.	H ₂ SO ₄ .

As this point appears to be constant, whether the amount of sodium chloride, or of the element under examination, is varied, it is presumably connected with a change induced in the surface of the copper by the acid. This will be discussed later.

It had been observed in the course of the qualitative work that the presence of soluble copper salts inhibited the Reinsch reaction; it was thought desirable to investigate this action quantitatively. The method used was the same as before; the amounts of element, sodium chloride, and acid, were kept constant, and varying amounts of copper sulphate added.

With the higher amounts of copper the colour of the slabs was considerably masked by the blue colour of the solution, and this necessitated withdrawing them momentarily to make comparison; this method appeared to give accurate results.

Arsenic.		Antin	nony.	Bismuth.		
Standard 70:3	0 Cu-As alloy	Standard 50:5	60 Cu-Sb alloy	Standard 10:90 As-Cu alloy		
As, 0.08 NaCl, 2.00 1 : 3 H₂SO₄, 25 c.c. Bulk, 100 c.c.		Sb, (NaCl, $1:3 H_2SC$ Bulk, 1	0.01 1.00 $0_4, 25$ c.c. 00 c.c.	Bi, 0.01 NaCl, 1.00 1:3 H ₂ SO ₄ , 10 c.c. Bulk, 100 c.c.		
Cu (Grm.)	Time (Secs.)	Cu (Grm.)	Time (Secs.)	Cu (Grm.)	Time (Secs.)	
Nil 0.005 0.03 0.05 0.06 0.07 0.08	$35 \\ 45 \\ 60 \\ 80 \\ 90 \\ 110 \\ 160$	Nil 0·01 0·02 0·03 0·04 0·05	47 65 110 200 320 530	Nil 0·01 0·02 0·03 0·04 0·045	60 70 100 150 270 630	
0.09 0.10	260 400	0·10 N	o trace after 20	minutes		

The most noticeable thing about these curves is the fact that quite a small proportion of copper, as a cupric salt, will stop the reaction altogether; and this limiting proportion for arsenic is quite different from that for antimony; it would seem probable that one could separate arsenic from antimony by having a small percentage of cupric sulphate present. Another aspect of the case presents itself; it will be shown later that cuprous chloride is one of the principal products of the Reinsch reaction, and it became necessary to find out whether the inhibiting property belonged to soluble copper salts generally, or whether it was confined to cupric salts; obviously, if the former were the case, the Reinsch reaction could never go to completion. Cuprous sulphate not being readily obtained, it seemed better to produce cuprous chloride from the sodium chloride already in the test solution than to complicate calculations by adding cuprous chloride itself; in addition to this, it was very necessary to avoid adding any copper in the higher state of oxidation, as the inhibiting effect of quite small amounts of this has already been shown. The following procedure was adopted:---A mixture of 6.0 grms. of sodium chloride, 25 c.c. 1:3 sulphuric acid, and 59 c.c. of water was set to boil in the test beaker, and to this, when boiling, was added the weighed amount of cuprous oxide; when this had practically dissolved (but without more

loss of time than could be helped on account of danger of oxidation) 16 c.c. (=0.08 grm. As) of the arsenic solution was added, and, as soon as this boiled, the test was carried out in the ordinary way. The following results were obtained:—

Cu ₂ O	Time
Nil	35 seconds
0·2 grm.	55 "
0.3 "	55 ,,

The solution always contained a trace of cupric copper amply sufficient to explain the 20 seconds lag. Apparently, although most of the cuprous oxide was attacked by the hydrochloric acid to form cuprous chloride, some of it was attacked by the excess sulphuric acid, giving cupric sulphate and metallic copper in the usual way; the evidence for this, apart from the faint bluish colour of the solution, lay in the fact that the trace of copper formed, though resembling cuprous oxide in appearance, was speedily blackened by the arsenic depositing on it when the arsenic solution was added.

When it is borne in mind that a similar amount of copper in the cupic state would (as is seen by reference to the curve) have probably stopped the reaction altogether, or have, at any rate, slowed it down to hours instead of seconds; and also that the increase from 0.2 grm. to 0.3 grm. of cuprous oxide is attended by no measurable increase in the time of reaction, it seems fair to draw the conclusion that cuprous salts have no inhibiting action on the Reinsch reaction. The following results were obtained for antimony and bismuth by the use of a similar method:—

Bismuth. A trial was made with 0.02 grm. Bi, 2.0 NaCl, 25 c.c. 1:3 H₂SO₄ and 0.2 grm. of Cu₂O per 100 c.c.

This gave a reading of 90 secs. (30 secs. without cuprous oxide). There was, however, considerable difficulty in dissolving the cuprous oxide, an appreciable amount of metallic copper being left on the bottom, corresponding, of course, to a similar amount of cupric salt in solution. A second test was accordingly made with 0.02 grm. of bismuth, 6.0 grms. of sodium chloride, 20 c.c. of 1:3 sulphuric acid, and 0.3 grm. of cuprous oxide, which gave the following results:—

		Cu ₂ O Grm.	Seconds				
		0·30 Nil	30 25				
Antimony.	0.02 grm.	Sb, 6.0 grms.	NaCl, 20 c.c. 1:3	H ₂ SO ₄ ,	made up	to I	100 c.c.

Grm.	Seconds	
0·30 Cu ₂ O	30	
Nil	25	

A necessary precaution to be taken in all use of the Reinsch reaction, either qualitatively or quantitatively, at once suggests itself. Since cuprous chloride is necessarily present in the solution as a product of reaction, and since cupric salts are fatal to the reaction, it is very necessary to ensure that the cuprous chloride does not get oxidised in any way, even slightly. So far as the author is aware, this precaution, up to the present, has been neglected and the matter left to chance. PRODUCTS OF REACTION.—Deposits were obtained in a form that easily flaked off the copper. This is the normal state of things with arsenic and bismuth; the case of antimony will be dealt with later. The deposits were washed thoroughly with water, then with alcohol, and dried rapidly in an electric oven. Details of the analyses are as follows:—

Arsenic.—The sample (0.5000 grm.) was dissolved in dilute sulphuric acid and hydrogen peroxide. Solution boiled, excess of tartaric acid added, liquid made strongly alkaline with caustic soda, sulphuretted hydrogen passed. Copper separated as sulphide, ultimately titrated with sodium thiosulphate. Arsenic in filtrate separated as sulphide in solution acidified with sulphuric acid, ultimately titrated with iodine.

	Grm. Per cent.	Percentage composition of $Cu_{\delta}As_{2}$
Copper Arsenic	$\begin{array}{rcrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{c} 67 \boldsymbol{\cdot 74} \\ 32 \boldsymbol{\cdot 26} \end{array}$
	99.46	100.00

This analysis seems to indicate that a certain amount of the element arsenic is deposited electrolytically, in addition to the compound Cu_5As_2 .

Bismuth.—The sample (0.3728 grm.) was dissolved in dilute sulphuric acid and hydrogen peroxide, solution boiled, neutralised, and bismuth thrown down as basic carbonate with ammonium carbonate, according to the usual procedure, and weighed as Bi₂O₃. *Result*: Weight of Bi₂O₃, 0.4140 grm.; bismuth, 99.50 per cent. Only a trace of copper was found in the filtrate from the bismuth carbonate.

Antimony.—The case of this element is much more complicated than the foregoing. If copper is boiled with a mineral acid solution of antimony containing chlorides, the first effect observable is the formation of a purple film on the copper, the colour of which corresponds with that of the compound Cu₂Sb. On continuing the boiling, bluish-white flecks appear on the purple and these spread until the entire surface is coated with a uniform white film; after this no further colour change takes place. If the white film has been produced in not too strongly acid a solution, it will be found, on removal from the liquid, that it is strongly adherent, and will take a brilliant polish; if, however, strong hydrochloric acid has been used the film flakes off readily, leaving a clean surface of copper underneath. If the white film is heated with trichloracetic acid solution it turns purple; this is apparently due merely to the solution of the white constituent. Conversely, if the film is deposited in a solution of trichloracetic acid and sodium chloride, it remains purple, but deposition in this case is slow, the film is, as a rule, fairly closely adherent, and the copper dissolves away somewhat rapidly.

Many attempts to get a pure detached sample of either the white, or the purple, films uniformly resulted in failure. The following analysis was carried out on a sample which was quite obviously a mixture of the two varieties:—A weighed quantity (0.3045 grm.) was dissolved in hydrochloric acid and potassium chlorate,

chlorine boiled off, sulphurous acid added and the excess boiled off; excess of Rochelle salt added, the whole made strongly alkaline with sodium hydroxide, and hydrogen sulphide passed through the liquid for a considerable time. The copper sulphide precipitate was filtered off, ignited and redissolved in nitric acid, and the copper estimated by titration with thiosulphate solution. The filtrate was acidified, the antimony separated as sulphide with the usual precautions, the sulphide dissolved in sodium peroxide solution, the solution boiled and acidified with hydrochloric acid, and the antimony estimated by Rowell's method. Results.— Antimony, 75.8; copper, 24.6 per cent.; (total, 100.4 per cent.).

There appear to be only two compounds of copper and antimony known— Cu_3Sb and Cu_2Sb . The percentage compositions of these two compounds are as follows:—

			Cu₃Sb	Cu ₂ Sb
Antimony	••	••	38·83	48.78
Copper	••	••	61.17	51.22

It will be noted that the percentage of antimony in the film is considerably higher than either of these, and therefore it would seem that the deposition of the purple film is followed by that of pure antimony, probably electrolytically. There seems no reason to doubt, in view of its appearance, that the purple film is the compound Cu₂Sb; there is no evidence whether or no Cu₃Sb also comes down.

In all three cases a considerable amount of copper goes into solution as cuprous chloride, but the solution remains colourless unless oxidation takes place.

In the case of arsenic no evolution of hydrogen arsenide appears to occur.

(To be continued.)