

# ANTIMONY:

ITS HISTORY, CHEMISTRY, MINERALOGY, GEOLOGY,  
METALLURGY, USES, PREPARATIONS, ANALYSIS,  
PRODUCTION, AND VALUATION; WITH  
COMPLETE BIBLIOGRAPHIES.

*FOR STUDENTS, MANUFACTURERS, AND  
USERS OF ANTIMONY.*

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To

PROFESSOR JAMES FURMAN KEMP  
(COLUMBIA UNIVERSITY)

UNDER WHOSE GUIDANCE THE AUTHOR HAS LEARNED  
THE VALUE AND METHODS OF SCIENTIFIC  
RESEARCH

This Book is Dedicated,  
AS A TOKEN OF GRATITUDE.

## PREFACE.

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A METALLURGICAL work in English by a Chinese author is unusual ; but long residence in America, and in England and other parts of Europe, and much study of English literature, have familiarised me with the language, and have encouraged me to make it the medium for presenting my work to the English-speaking public ; and I desire to express my thanks to Messrs Charles Griffin & Co. for the opportunity they have afforded me of doing so.

My researches concerning Antimony have extended over several years, and I would express my thanks to Professor Kemp, of Columbia University, for his valuable guidance.

References to Antimony are scattered through the technical literature of many languages, and the subject is dealt with in general treatises on metallurgy. There does not, however, appear to be any English text-book devoted to its special consideration, and foreign works on this subject are not readily accessible to English readers, who have had to content themselves with the necessarily condensed notes in the standard work on metallurgy by Phillips and Bauerman, and Professor Louis' translation of Carl Schuabel's work. These, although valuable, do not claim to be exhaustive, and the modern volatilisation process naturally finds but little mention. It seems likely, however, to become the sole process by which the poorer classes of antimony ores can be economically treated ; and as these ores are of rapidly growing importance, possibly as a result of the exhaustion of the richer grades of ore, a description of the process is of importance.

It has been my privilege to carry out practical tests of the volatilisation process patented by Mons. H. Herrenschildt, and the results are incorporated in this book. I am also greatly indebted to that gentleman for kindly reading through the greater part of my MS., especially the chapter on the Metallurgy of Antimony.

Invaluable suggestions resulting from his many years' experience in antimony smelting were freely given and gladly received.

I also desire gratefully to acknowledge the assistance derived from the consideration of articles which have appeared in the technical press, and especially from the study of the following works:—Friedheim's *Handbuch der anorganischen Chemie*, Abegg's *Handbuch der anorganischen Chemie*, Moissan's *Traité de Chimie Minérale*, and Frémy's *Encyclopédie Chimique*. The chapter on the Chemistry of Antimony is based on these studies. Beringer's *Text-book of Assaying* and Parry's *Assay of Tin and Antimony* have likewise proved serviceable in dealing with the Analysis of Antimony.

My brother, Dr C. H. Wang, has kindly seen this work through the press, as my duties in Hunan necessitated my return to China.

In conclusion, I venture to hope that the arrangement and coordination of the very scattered records of the results of other people's work embodied in the present volume may prove of service to metallurgical students, to manufacturers, and to users of antimony.

C. Y. WANG.

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# THE METALLURGY OF ANTIMONY.

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## CHAPTER I.

### THE HISTORY OF ANTIMONY.

THE natural sulphide of antimony was known to the people of ancient times.\* It was used by them as medicine, and as an article of toilet by women to paint their eyebrows with.

In St Jerome's translation of the Hebrew of Ezekiel xxiii. 40 we read, "circumlinisti stibio oculos tuos," and in the second book of Kings ix. 30 we find, "Porro Jezebel introiter eius audite depixit oculos suos stibio." The latter passage, as translated by Cheyne and Driver, runs thus, "set her eyes in paint (literally, antimony)."

The Hebrew and Arabic word for antimony is "kohl," which was altered to "alcool" or "alkohol" in other languages; thus the Spanish translation of the above passage from Ezekiel is, "alcoholaste tus ojos." As a matter of fact, the word "alcohol" was, in the Middle Ages, used to designate anything in the form of fine powder; and it was only at later periods that it was used to mean spirit of wine.

Dioscorides called this metal *στίμμυ*, and mentioned that it was known also by *πλατυόφθαλμον* (meaning "eye-expander"), *γυναικείον* (meaning "womankind"), etc. He also mentioned that the roasting of crude antimony could be done in a current of air under moderate heat until it burnt, and that if it were heated more strongly it would melt like lead. This statement might suggest the idea that he was acquainted with the metal itself.

The term "stibium" was given to the metal by Pliny, and the term "antimonium" by the Latin author Geber; but both these

\* M. Berthelot has made a curious observation in regard to a vase found at Tello Chaldea by M. de Saizec, which was cast in metallic antimony (*Rev. Archéol.*, 1887, 3<sup>e</sup>, t. ix.).

terms had been used to stand for the sulphide of antimony up to the time of Lavoisier.

In the beginning of the fifteenth century \* or thereabouts there lived in Germany a monk by the name "Basil Valentine," who has been supposed to be the author of many books on antimony and its allied subjects. As an historical figure he was shrouded with mystery. Doubts had been entertained as to the genuineness of the writings attributed to him. Consequently Emperor Maximilian I. commanded that this question should be examined into. The conclusion was that he was a Benedictine monk of Southern Germany, and that nearly all the works attributed to him had undergone many changes and alterations, introduced by later authors.† City Chamberlain Thölde, of Frankenhansen, Thuringia, published a list of his works in the early part of the seventeenth century: *Triumph-Wagen des Antimonii* ("Triumph Car of Antimony"); *Von dem grossen Stein der uralten Weisen* ("On the Great Stone of the Ancient Philosophers"); *Offenbarung der verborgenen Handgriffe* ("Revelation of the Hidden Key"); *Letztes Testament* ("Last Testament"); *Schlussreden* ("Concluding Words"). The language he uses is frequently obscured by mystical pictures and alchemistic ideas; yet he deserves the credit of having made many careful and conscientious observations.

The most important of his writings is the *Triumph-Wagen des Antimonii*.‡ Professor Schorlemmer has, however, shown that this was a forgery, dating from about the year 1600. The nature of this book can be seen from the following passage, as translated in Roscoe and Schorlemmer's *Chemistry*: "In order, as is most proper, that I may say something about the name of the material, it should be understood that this material was long known to the Arabians, and from ancient time was termed by them 'asinat.' The Chaldeans entitled it 'stibium,' and in the Latin tongue it has been called 'antimonium' up to the latest times, and in our own German mother-tongue the same material has been foolishly called 'Spicssglas,' for this reason, that this material can be fluxed and a glass made from it." The operation of producing metallic antimony, as described by

\* Probably Basil Valentine was born in the year 1460, at Peterskloster, in Erfurt.

† Consequently Basil Valentine is sometimes known as the pseudo-Basil Valentine.

‡ This book has been translated into English: *The Triumphal Chariot of Antimony*, by Basilius Valentini, translated by Theo. Kerckringius: James Elliot & Co., London, 1893. It has also been translated into Latin by an unknown author under the title *Currus triumphalis antimonii*.



Basil Valentine, is as follows (taken from Roscoe and Schorlemmer's *Chemistry*): "Antimonium is a master in medicine, and from it, by means of cream of tartar and salt, a king (regulus) is made, steel-iron being added to the spießglas during fusion. Thus by an artifice a wonderful star is obtained which the learned before my time have termed the 'philosophical signet star.' . . . Take good Hungarian spießglas, and with the same quantity of crude tartar and half as much saltpetre rub these small and let them fuse well in a wind furnace; afterwards pour out into a mould and allow to cool, when a regulus is found."

Basil Valentine was well acquainted with the starred surface of pure metallic antimony, and remarked that the starred and the unstarred antimony had exactly the same composition, and that the starred one was due to the use of iron in its preparation; while, in opposition to this idea, other chemists of the period traced the cause of the starred one to the favourable conjunction of stars. He also knew that antimony did not possess the full character of a metal, and for this reason he called it lead of antimony. Furthermore, he noticed that spießglas contained sulphur, and he was acquainted with sulphur auratum (a mixture of  $Sb_2S_3$  and  $Sb_2S_5$ ). He gave distinct recipes for the preparation of antimony trichloride (butter of antimony), powder of algaroth (basic chloride of antimony), antimony trioxide, potassic antimoniate. In his time antimony was used for the preparation of printers' type, mirrors, and bells, and was also used as medicine.

The story of the accidental poisoning of certain monks by spießglas administered to them by someone who had observed that pigs could be fattened if they were fed with a little spießglas, thus originating the word "anti-moine,"\* has been proved by Kopp to be without any foundation, as Basil Valentine wrote his book in German; and hence the story must have been invented by a Frenchman. It has been suggested that the word "antimony" might be derived from "antimonos," meaning, opposed to solitude, as it was supposed that it could only be found in combination with other elements in nature.

Paracelsus was the first one to use antimony as a medicine to be taken internally. His emetic was a solution of antimony in wine. In the year 1564, not long after the death of Paracelsus, a work on antimony by Louis de Launay appeared. In 1566 the Parliament forbade its use as medicine; but this law was, upon the decision of the Faculty of Paris, repealed in 1650.

\* The term "antimonium" is found in the writings of Constantin, a doctor, who lived towards the end of the twelfth century, long before Basil Valentine.

Boyle, in his book *On the Unsuccessfulness of Experiments (Opera*, ed. 1772, i. 325), says: "And it may perhaps also be from some diversity either in antimonies or irons, that eminent chemists have (as we have observed) often failed in their endeavours to make the starry regulus of Mars and antimony. Insomuch that divers artists fondly believe and teach (what our experience will not permit us to allow) that there is a certain respect to times and constellations requisite to the producing of this (I confess admirable) body. Upon this subject I must not omit to tell you that a while since an industrious acquaintance of ours was working on an antimony, which, unawares to him, was, as we then supposed, of so peculiar a nature, that making a regulus \* of it alone without iron, the common way (for this manner of operation I inquired of him), he found, to his wonder, and showed me his regulus adorned with a more conspicuous star than I have seen in several stellate reguluses of both antimony and Mars." Lemery, in his *Cours de Chymie*, 1675, argued against the idea that the planet Mars had anything to do with the appearance of the stars in antimony.

With regard to the metallurgy of antimony, Agricola, in his *Mining*, book xii., 1557, wrote:—"The liqutation is done in pots. The pot, with holes in the bottom, is belly-like shaped, that is, narrow at the top, and is placed over an empty vessel, supported on a bed, upon which and around the pots are thrown earth and coal-dust, which is heated with logs of wood from above." After this impractical method came the method of Balthasar Rössler, who in 1650 wrote *Speculum metallurgicæ politissimum*. His experiment runs thus:—20-30 centner (quintal=100 lbs. in weight) of the sulphide of antimony are allowed to melt in an oven. The liquid is mixed with 10 per cent. of its quantity, 3 parts of saltpetre and 1 part of ashes of wood. This mixture is allowed to stand until a slag is formed. In order to extract the silver or gold contained in the metal, it is mixed with an equal quantity of iron, or half as much copper or lead. This is put into a refining furnace and is allowed to remain there until all the "Spicss" is volatilised. Still later than Rössler, Lazarus Ercker recommended the following method:—The sulphide of antimony, together with iron needles, was melted before a blast or in an oven, with the use of saltpetre to cover the liquid, which, after solidification, must be remelted three or four times, until the beautiful stars appeared upon the surface of the metal. The

\* One part of antimony in one thousand parts of gold is sufficient to destroy the working properties of it. From this peculiar action the ancients gave it the name "regulus" or "little king."

precipitation method came after this. In the eighteenth century the roast-reduction method commenced to be used; in the thirties of the nineteenth century, the reverberatory furnace; and in 1896 electrolytic antimony first appeared in the market.\*

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\* For the historical development of the volatilisation process, *vide* the chapter on the Metallurgy of Antimony.

## CHAPTER II.

### THE CHEMISTRY OF ANTIMONY.

#### SECTION I.—THE ATOMIC WEIGHT OF ANTIMONY.

(a) **Selection of Atomic Weights.**—Berzelius in 1852 already knew that the ratio of the oxygen contents of the three oxides of antimony is 3 : 4 : 5, but he wrote their formulæ as  $\text{SbO}_3$ ,  $\text{SbO}_4$ ,  $\text{SbO}_5$ , and considered the double of 129 as the atomic weight of antimony. When he, however, found out in 1826 the existence of the sesqui-oxide, he changed the above formulæ to  $\text{Sb}_2\text{O}_3$ ,  $\text{SbO}_2$ ,  $\text{Sb}_2\text{O}_5$ , whereby  $\text{Sb} = 129$ . Gmelin at first gave the same formulæ, and put 64·5 as the atomic weight; but they were subsequently changed back to  $\text{SbO}_3$ ,  $\text{SbO}_4$ ,  $\text{SbO}_5$ .

It is now admitted that antimony has three H-equivalents, which are related to one another as 5 : 4 : 3, that is,  $\text{Sb}_{x_5}$ ,  $\text{Sb}_{x_4}$ ,  $\text{Sb}_{x_3}$ .

Now, we consider 120 as the true atomic weight of antimony, for the reason that this number is in harmony with the following laws and rules:—

1. With *Avogadro's Law*, since the number 120 denotes the smallest quantity of antimony which, in a vaporous condition, can be present in combination in a double normal volume. Also the content of combination of antimony in solution, according to the theory of van't Hoff, is in harmony with this number, in so far that the phenomenon of its being a cathode through hydrolysis is not entirely absent, this being due to the weak basic character of antimony.

2. With *Dulong-Petit's Rule*, since the atomic heat, as calculated with this number, amounts to between 6·0–6·3, which hardly deviates from the normal value.

3. With the *Theory of Isomorphism*. We know only so much about it that the element Sb is isomorphous with the elements arsenic and bismuth, and also with its next atom-analogies from the same natural group.

4. With the *Periodic Law*. The properties of antimony and its compounds are the functions of its atomic weight, 120.

(b) **Determination of the Atomic Weight.**—1. Berzelius in 1812 devoted much time and energy to determine the atomic weight of

antimony, but expressed himself with great dissatisfaction as to the results obtained, in the following words: "*Ich habe niemals mit einer Materie, wo es so ausserordentlich schwer gewesen ist, konstante Resultate zu erhalten, gearbeitet.*" He oxidised metallic antimony with the aid of nitric acid, and then heated the residue, whereby from 100 parts of antimony he obtained 124·8 parts of  $\text{Sb}_2\text{O}_3$ . Hence

$$\begin{aligned} 124\cdot8 : 100 &= \text{Sb}_2 + 64 : \text{Sb}_2, \\ \therefore 100\text{Sb}_2 + 6400 &= 121\cdot8\text{Sb}_2, \\ 24\cdot8\text{Sb}_2 &= 6400, \\ \therefore \text{Sb} &= 129, \text{ approximately.} \end{aligned}$$

This number 129 was considered by Berzelius as the true atomic weight, and had been taken so until the 'fifties of the nineteenth century.

2. Kessler, 1855-60. The work of Kessler does not show any particular exactness; the interest of his work lies in the fact that he, for the first time since Berzelius, obtained results which approach more closely to the true value 120. The following are his results:—

a.	Through oxidation of $\text{Sb}_2\text{O}_3$ from 100 parts Sb	= 123·84.
b.	" " of Sb with $\text{K}_2\text{Cr}_2\text{O}_7$	= 123·61.
c.	" " of Sb with $\text{KClO}_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$	= 123·72.
d.	" " of $\text{Sb}_2\text{O}_3$ with $\text{KClO}_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$	= 123·80.*
e.	" " of $\text{Sb}_2\text{O}_3$ with $\text{K}_2\text{Cr}_2\text{O}_7$	= 123·85.
f.	" " of emetic tartar	= 119·80.

3. Schneider in 1856 reduced a natural sulphide of antimony from Arnsberg to its metallic form in a current of hydrogen. From 100 parts of  $\text{Sb}_2\text{S}_3$  he obtained 28·52 as an average value of sulphur evolved. Hence the proportion:

$$\begin{aligned} 2\text{Sb} : 3\text{S} &= 100 : 28\cdot52 : 28\cdot52, \\ \therefore \text{Sb} &= 120\cdot53. \end{aligned}$$

4. Rose in 1856 published the results of the analysis of antimony chloride by Weber, in which he gave 120·63, the mean value of 120·2, 121·1, 120·6.

5. Dexter in 1857 carried out some valuable work in Bunsen's laboratory to determine the atomic weight of antimony. He carefully weighed out a small quantity of antimony and oxidised it with nitric acid, and finally heated the residue until it was converted into  $\text{Sb}_2\text{O}_4$ . From 100 parts of  $\text{Sb}_2\text{O}_4$  there were 79·283 (average value) parts of Sb. Hence the proportion:

$$\begin{aligned} 2\text{Sb} : 64 &= 79\cdot283 : 20\cdot717, \\ \therefore \text{Sb} &= 122\cdot46. \end{aligned}$$

6. Dumas in 1859 caused chlorine to act upon metallic antimony;

\* In 1861 Kessler corrected this value and changed it to 122·35.

and, to be sure that there was no free chlorine present, he distilled it many times through pulverised antimony. A suitable quantity of the trichloride thus obtained was taken and was decomposed by means of a solution of tartaric acid. The chlorine thus set free was determined by the quantity of silver chloride that could be deposited in a bath of silver solution of known strength. Hence the following proportion :

$$\text{SbCl}_3 : 3\text{Ag} = 70.512 : 100$$

(the atomic weight of Ag taken to be 107.92).

$$\therefore \text{Sb} = 121.88.$$

This value is a little too high, due to the fact that the trichloride used contained some oxychloride, as was proved by Cooke later.

7. Unger in 1871 made an analysis of Schlippe's salt,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ , and found that the result was best in harmony with the given formula when 120 was taken as the atomic weight of antimony. From 7.347 grms. of Schlippe's salt he obtained 3.291 grms. of sodium sulphate and 3.0864 grms. of pure antimony pentasulphide. Hence, from the relationship

$$3\text{Na}_2\text{SO}_4 : \text{Sb}_2\text{S}_5 = 3.291 : 3.0864, \\ \text{Sb} = 119.71.$$

8. Cooke, 1877. The analytical work of J. P. Cooke, in regard to the atomic weight of antimony, started a new epoch in the history of the determination of atomic weights. Cooke followed in the footsteps of Stas with particular regard to his methods of working and to his exactitude in chemical manipulations, but worked always with small quantities of substances, thus reducing the source of error to a minimum, this being in opposition to Stas' practice, who was known always to use large quantities of substances, even sometimes up to several hundred grams.

The following independent methods for the determination of the atomic weight of antimony are given by Cooke:—

a. *Synthesis of Antimony Trisulphide*.—Balls of antimony were dissolved in part in hydrochloric acid in the presence of some nitric acid. The solution was boiled until it became colourless and only trivalent antimony was present. The loss in weight of the balls of antimony gave the quantity of antimony dissolved. The solution was then diluted with a solution containing acetic acid. Water impregnated with hydrogen sulphide was added by means of a syphon, and the antimony trisulphide thus formed was washed six times with hot water. After this it was dried at a temperature of  $130^\circ$ ;\* and at  $210^\circ$  the red trisulphide was changed to its black modification. In

\* The scale used in this book is Centigrade.

the red modification Cooke found the average sulphur content to be 28·5731; hence the ratio  $2\text{Sb} : 3\text{S} = 71\cdot4269 : 28\cdot5731$ , whereby  $\text{Sb} = 120\cdot22$ . In the black modification he found the average sulphur content to be 28·5182; hence the proportion  $2\text{Sb} : 3\text{S} = 71\cdot4818 : 28\cdot5182$ , whereby  $\text{Sb} = 120\cdot54$ .

*β.* With antimony trichloride the analysis gave  $\text{Sb} = 121\cdot86$ , while with antimony tribromide  $\text{Sb} = 119\cdot882$ , and with antimony iodide  $\text{Sb} = 119\cdot86$ .

In the years 1880–81 Cooke made his final determination of the atomic weight of antimony. This time he used antimony trichloride and made the determination by the gravimetric method. The result obtained was  $\text{Sb} = 119\cdot88$ .

*Summary.*—The following is a summary of the different values assigned for the atomic weight of antimony as obtained by different workers and investigators employing different methods:—

Authority.	Years.	Proportions.	Atomic Weight.
Berzelius . . . . .	1812	$2\text{Sb} : \text{Sb}_2\text{O}_4$	129·0
" . . . . .	"	$2\text{Sb} : \text{Sb}_2\text{S}_3$	128·9
Kessler . . . . .	1855–60	$\text{Sb}_2\text{O}_3 : \text{O}_2$	120·86
" . . . . .	"	$2\text{Sb} : \text{O}_2$	121·31
" . . . . .	"	$2\text{SbCl}_3 : \text{O}_2$	121·21
" . . . . .	"	$\text{SbCl}_3 : 3\text{AgCl}$	124·26
" . . . . .	"	$3[\text{C}_4\text{H}_4\text{K}\text{SbO}_7 \cdot \frac{1}{2}\text{H}_2\text{O}] : \text{K}_2\text{Cr}_2\text{O}_7$	119·59
Schneider . . . . .	1856	$\text{Sb}_2\text{S}_3 : 2\text{Sb}$	120·53
Rose (Weber) . . . . .	"	Analysis of $\text{SbCl}_3$	120·63
Dexter . . . . .	1857	$2\text{Sb} : \text{Sb}_2\text{O}_4$	122·46
Dumas . . . . .	1859	$\text{SbCl}_3 : 3\text{Ag}$	121·88
Unger . . . . .	1871	$3\text{Na}_2\text{SO}_4 : \text{Sb}_2\text{S}_3$ in Schlippe's salt	119·71
Cooke . . . . .	1877	$2\text{Sb} : \text{Sb}_2\text{S}_3$ (red modification)	120·22
" . . . . .	"	$2\text{Sb} : \text{Sb}_2\text{S}_3$ (black modification)	120·54
" . . . . .	"	$\text{SbCl}_3 : 3\text{AgCl}$ ( $\text{Ag} = 107\cdot92$ )	121·86
" . . . . .	"	( $\text{Ag} = 107\cdot90$ )	121·84
" . . . . .	"	$\text{SbBr}_3 : 3\text{AgBr}$ ( $\text{Ag} = 107\cdot92$ )	119·91
" . . . . .	"	( $\text{Ag} = 107\cdot90$ )	119·88
" . . . . .	"	$\text{SbI}_3 : 3\text{AgI}$ ( $\text{Ag} = 107\cdot92$ )	119·86
" . . . . .	1880–81	$\text{SbBr}_3 : 3\text{AgBr}$ ( $\text{Ag} = 107\cdot92$ )	119·90
" . . . . .	"	( $\text{Ag} = 107\cdot90$ )	119·88
" . . . . .	"	$\text{SbBr}_3 : 3\text{Ag}$ ( $\text{Ag} = 107\cdot92$ )	119·90
Schneider . . . . .	1880	$\text{Sb}_2\text{S}_3 : 2\text{Sb}$	120·41
Pfeifer . . . . .	1881	$3\text{Cu}^{\text{II}} : 2\text{Sb}^{\text{III}}$	122·36
" . . . . .	"	$3\text{Ag} : \text{Sb}^{\text{III}}$	121·86
Bongartz . . . . .	1883	$2\text{Sb}^{\text{III}} : 3\text{BaSO}_4$	120·64
Popper . . . . .	1886	$3\text{Ag} : \text{Sb}^{\text{III}}$	121·20
Friend and Smith . . . . .	1902	$\text{C}_4\text{H}_4\text{K}\text{SbO}_7 : \text{KCl}$	120·43

The International Commission for the Determination of Atomic Weights took 120 as the true atomic weight of antimony, but since 1902 it has been changed to 120·2.

## SECTION 2.—THE ELEMENT ANTIMONY.

Antimony, like phosphorus and arsenic, has several allotropic modifications. Besides the gray form of antimony, the most common and the best known, there is another form which is an explosive. This latter is very unstable and changes easily to the stable metallic form. The most unstable modification is yellow antimony, which does not possess any metallic property, corresponding thus to white phosphorus and yellow arsenic.

**Metallic Antimony.**—Pure antimony is a silver-white,\* shining, brittle metal. By slow cooling it crystallises in the hexagonal system, isomorphic with the gray form of arsenic, while rapid cooling makes it granular and crystalline. Moreover, when molten antimony is allowed to solidify slowly without any disturbance, and when it is covered by a layer of slag, a fern-like appearance is seen on the solidified surface. This is the so-called “antimony star” or regulus *antimonii stellatus*. The specific gravity is 6.5178, according to Kahlbaum, Siedler, and Rot.

The coefficient of cubical expansion, between 0° and 100°, is 0.003161. The coefficient of linear expansion depends upon the direction taken, being 0.00001692 at 40° along the axis of the hemidodecahedron, and 0.00000882 at the same temperature along a direction perpendicular to it (*Landolt, Börnstein, Meyerhoff*).

The metal is a conductor of heat and electricity. The electrical conductivity, in reciprocal ohms, is  $2.71^{10^4}$  at 0°,  $2.47^{10^4}$  between 0° and 37°,  $0.62^{10^4}$  during melting,  $0.88^{10^4}$  when it changes entirely into a liquid state, and  $0.82^{10^4}$  at 860°. The absolute conductivity for heat is 0.042 between 0° and 30°, 0.0442 at 0°, and 0.0396 at 100° (*Landolt, Börnstein, Meyerhoff*).

The specific heat is as follows:—

Temperature Interval.	Specific Heat.	Observer.
- 186° to - 79°	0.0462	Behn.
- 79° to + 18°	0.0484	„
- 75° to - 20°	0.0499	Pöbel and Jahn.
- 20° to 0°	0.0486	„
0° to + 33°	0.0495	„
0° to + 100°	0.0495	Bunsen.
17° to 92°	0.05079	Gaede.
15°	0.04890	Naccari.
100°	0.05031	„
200°	0.05198	„
300°	0.05366	„

\* With a slight tinge of blue, which may be intensified by the presence of impurities in the metal.



The metal melts at  $630.6^{\circ}$  (*Holborn and Day*). In this liquid state it can dissolve not only the solid metal itself, but also the sulphide of the metal.

The boiling-point of the metal under atmospheric pressure is  $1300^{\circ}$ ; it is  $290^{\circ}$  in the vacuum of cathode light (*Krafft, Bergfeld*). The colour of the fume of antimony is green (*Linck*).

**Explosive Antimony.**—In a bath of hydrochloric acid and antimony proto-chloride, with antimony metal as anode and platinum-foil as cathode, metallic antimony is deposited upon the cathode. This antimony is quite different from the ordinary kind. Its hardness is less, being 5.78, and it explodes, when it is scratched with a sharp point, with the development of heat and the setting free of white fume. When it is rubbed with a pestle in a mortar, strong detonation occurs, with a simultaneous development of light and heat. The same phenomenon can be produced when the dried substance is heated to  $200^{\circ}$ , the resulting reaction product being the ordinary antimony.

Recently E. Cohen and his students have made researches into this remarkable explosive form of antimony. It can be obtained through electrolysis from a solution in chlorine and bromine; while, on the other hand, from a solution in fluorine alone only the ordinary antimony can be obtained, without any admixture of halogens.

The important factors for the production of this particular explosive form of antimony are a particular temperature and a particular halogen concentration, the concentration of H being unimportant. The following table shows the fact that the temperature to render the explosive modification unexplosive varies directly as the concentration:—

Concentration.

10%	SbCl <sub>3</sub> ,	at $16^{\circ}$ - $17^{\circ}$ ,	shining and explosive;	$23^{\circ}$ ,	not shining and not explosive.
15.6%	"	at $0^{\circ}$ ,	"	$30^{\circ}$ ,	"
21.2%	"	at $10^{\circ}$ ,	"	$50^{\circ}$ ,	"

As a rule, the higher the concentration of the electrolyte is, the larger the quantity of the halogens taken up by the metal.

Its heat of solution is higher than that of the ordinary kind. Hence the heat of transformation is the difference between the two, which is calculated to be 20 to 21 calories.

The sensitiveness of the explosive modification decreases with an increase of the amount of halogens in solution. The stability increases as the temperature decreases. Comparatively, the explosive modification is meta-stable. It is still uncertain whether it is crystalline or amorphous.

**Black Antimony.**—Another meta-stable form of antimony is black antimony. It is produced when metallic antimony vapour is

suddenly cooled. For its production a vacuum is used, such as that employed for the production of yellow arsenic, heated inside by electricity and cooled externally by liquid air. It can also be produced by leading a current of oxygen into liquid antimony hydride at  $-40^{\circ}$ , or by heating the yellow modification of antimony at  $-90^{\circ}$ .

This black modification is amorphous, has a specific gravity of 5.3, and is easier liquefied and is more active chemically than the ordinary metallic form. It oxidises easily in the air under ordinary temperature, and is sometimes spontaneously combustible. At  $100^{\circ}$  it changes gradually to the ordinary metal, but suddenly at  $400^{\circ}$ .

**Yellow Antimony.**—It is the most unstable of all the modifications of antimony. It was discovered by Stock, Guttmann, and Siebert, and corresponds to white phosphorus and yellow arsenic. It cannot be produced by a sudden cooling of antimony vapour, but only by introducing oxygen into antimony hydride at  $-90^{\circ}$ . The reaction can be accelerated by ozonising. It can also be produced by the action of chlorine upon antimony hydride.

As stated, it is very unstable and changes into the black modification above  $-90^{\circ}$  under ordinary light.

**Chemical Properties.**—Pure antimony oxidises very little at the ordinary temperature. By being heated it is converted into the trioxide, which rises in the form of smoke from the upper surface of the metal. It can also be oxidised by any oxides that can easily give up their oxygen component, *e.g.* manganese peroxide, quicksilver, lead oxides, etc. It can also be oxidised in the presence of steam. Hydrogen reduces the trioxide.

In concentrated nitric acid the metal can be converted into the trioxide or the pentoxide through the agency of nitrous oxide. Which oxide is produced depends entirely upon the temperature and the concentration. Powdered antimony, particularly if previously heated, is powerfully acted upon by chlorine and bromine, resulting in the production of pentachlorides or pentabromides, with evolution of light.

Antimony is attacked by hydrochloric acid only when it is in the state of very fine powder. Dilute sulphuric acid does not attack it, while with hot concentrated acid it forms antimonious sulphate. Aqua regia in the cold dissolves it easily, forming the pentachloride.

When ignited with a mixture of nitre and soda it explodes, forming an alkaline antimoniate. With alkaline nitrate and chlorate the metal decrepitates, resulting in the formation of an antimoniate.

The metalloids, with the exception of boron, carbon, and silicon form compounds with antimony.

## SECTION 3.—THE COMPOUNDS OF ANTIMONY.

Antimony has three valences, 3, 4, and 5.\* Its chemical properties are very similar to those of arsenic. In other ways it stands close to the zinc group, particularly to the elements germanium and zinc. The likeness between antimony and germanium is so close that the discoverer of the latter at first called it Eka-antimony of Olendelejeff. Analytically, antimony presents some difficulty in its separation from zinc.

A. *The Compounds of Antimony of 3 Valences.*

In this condition antimony is a weak base and possesses an electro-positive character. Its ion concentration is not great.

**Antimony Hydride,  $SbH_3$ .**—It corresponds to phosphorus hydride ( $PH_3$ ) and arsenic hydride ( $AsH_3$ ). It was discovered by Lewis Thompson in 1837, and about the same time independently by Pfaff. However, the production of pure antimony hydride and the determination of its physical constants are matters of recent times.

It is formed when hydrogen is generated in the presence of a soluble antimony compound, or when the compounds of antimony and the alkali metals are decomposed by water, or when an antimony-zinc alloy is treated with sulphuric acid or hydrochloric acid.

It can also be formed when metallic zinc is treated with a weak solution of hydrochloric acid or of sulphuric acid on the addition of a solution of antimony salt.

According to Stock and Doht, 1 gram of the alloy of zinc and antimony ( $Zn : Sb = 4 : 1$ ) in a mixed solution of tartaric acid and hydrochloric acid can produce 0.1 to 0.15 gram of pure antimony hydride. But according to Stock and Guttman a better result could be obtained by putting finely powdered magnesium antimonide ( $Sb : Mg = 1 : 2$ ) into a cold weak solution of hydrochloric acid.

Antimony hydride is a colourless, inflammable gas with a characteristic damp and weak hydrogen sulphide smell. It burns with a greenish flame, producing a white smoke of steam and antimony trioxide. 1 c.c.<sup>3</sup> weighs 5.302 mgrms. at 0° and 754 mm. pressure. On an average it is 4360 times heavier than air and 3994 times heavier than oxygen. The observed density, on account of molecular association or of molecular attraction, is 2.95 per cent. more than the theoretical one.

The boiling-point of the liquid is  $-18^\circ$  (*Olszewski*). The specific

\* May be called tri-, quadri-, quinqui-.

density is 2.26 at  $-25^{\circ}$  and 2.34 at  $-50^{\circ}$  (*Stock and Guttman*). At  $-91.5^{\circ}$  it becomes solid (*Olszewski*).

1 vol. of water can dissolve  $\frac{1}{2}$  vol. of antimony hydride; 1 vol. alcohol, 15 vols.; 1 vol. carbon bisulphide, 250 vols. at  $0^{\circ}$ . The inhaling of even a small quantity of  $\text{SbH}_3$  will produce giddiness and headache.

Antimony hydride is endothermic. Berthelot and Petit have determined that 84.5 calories of heat will be set free from the decomposition of one of its molecules. From this it can be deduced that its decomposition may be accompanied by explosion.

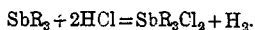
At ordinary temperatures the rapidity of its decomposition depends upon the nature of the vessel containing it. In antimony hydride we have an instance of what is known as "auto-katalysis." The decomposition of liquefied  $\text{SbH}_3$  at room temperature is very rapid; while in a gaseous state its decomposition at such temperature is slow.

Antimony hydride is very sensitive towards oxygen. At ordinary temperature these two gases react on each other with the formation of water and antimony. Even at  $-90^{\circ}$  (the melting-point of  $\text{SbH}_3$ ) this reaction is still possible, with the production of yellow antimony, while at the temperature of liquid air there is no such reaction.

The oxides of nitrogen can easily be reduced by  $\text{SbH}_3$ . With chlorine it reacts with a simultaneous development of light and a loud noise; with bromine it reacts with less energy; and with iodine the action is slower still. Alkalies decompose it. When it is acted upon by powdered sulphur, the resulting products are sulphuric acid and orange sulphide of antimony.

**Alkyl-combination.**—Antimony hydride ( $\text{SbH}_3$ ), like arsenic hydride ( $\text{AsH}_3$ ) and phosphorus hydride ( $\text{PH}_3$ ), can give rise to organic compounds in which the H-component is replaced by an alkyl. It is then called *stibine*. It can be produced by allowing iodine-alkyls to act upon potassium antimonide or upon sodium antimonide, or by the reaction between antimony chloride and zinc-alkyls.

It is self-inflammable and is not soluble in water. It reacts upon oxygen, sulphur, and chlorine with the formation of  $\text{SbR}_3\text{O}$ ,  $\text{SbR}_3\text{S}$ ,  $\text{SbR}_3\text{Cl}_2$ . It behaves like a metal thus:—



Some of the constants of the compounds are:—

	Boiling-point.	Sp. Gr. ( $15^{\circ}$ ).
Trimethylstibine, $\text{Sb}(\text{CH}_3)_3$ . . . . .	81°	1.523
Triethylstibine, $\text{Sb}(\text{C}_2\text{H}_5)_3$ . . . . .	159°	...

Like phosphine and arsine, the tertiary stibine has the power of combining with iodine-alkyls, forming a salt which is called the

compound of stibonium. In a solution it can be ionised into  $\text{SbR}_4$  and I.

Some other compounds are: Tetramethylstibonium chloride,  $\text{Sb}(\text{CH}_3)_4\text{Cl}$ ; tetraethylstibonium chloride,  $\text{Sb}(\text{C}_2\text{H}_5)_4\text{Cl}$ ; tetramethylstibonium hydroxide,  $\text{Sb}(\text{CH}_3)_4\text{OH}$ .

**Antimony Trihaloids.**—Antimony combines with the halogens to form a series of characteristic compounds. For fluorine, chlorine, and iodine there occur the tri- and pentahaloids; and for bromine only the trihaloid is known. The characteristic of the trihaloids is the capability of being hydrolysed; and in water they form insoluble oxyhaloids.

**Antimony Trifluorides.**—When metallic antimony is brought into an atmosphere of fluorine, it burns, with the production of a white solid fluoride, probably the trifluoride (*Moissan*). When antimony trioxide is put into hydrofluoric acid and the solution is gradually diluted, crystals of fluoride are deposited. As an amorphous mass, it can be produced by dry distillation of antimony powder with quicksilver fluoride.

The trifluoride is dimorphous, and it crystallises generally in rhombic octahedra, but sometimes also in prisms. According to Ruff and Plato, its specific gravity is 4.379 at 20.9°, and its molecular volume 40.3.

By mixing antimony trioxide and the carbonate of alkalies in hydrofluoric acid, the following complex alkali-antimony fluorides are obtained:—

Chemical Formulae.	Crystalline Forms.	Solubility in Water.	Remarks.	Observers.
$\text{LiSbF}_4, \text{LiF}$	Crystallises with difficulty.	1 : >20	...	Flückiger.
$\text{NaSbF}_4, 2\text{NaF}$	Small prisms.	1 : 14	...	„
$\text{KSbF}_4$	Large rhombic octahedra or prisms.	1 : 2.8	Becomes dull in air.	„
$\text{KSbF}_4, \text{KF}$	Leaf-like or in plates.	1 : 9 (at 13°) 1 : <2 (boiling-point)	Melts at 120°.	„
$\text{NH}_4\text{SbF}_4, \text{NH}_4\text{F}$	Rhombic plates or prisms.	1 : 0.9 (cold)	...	„
$\text{CsSbF}_4$	Prisms.	...	...	Wells and Metzger.
$\text{C}_2\text{SbF}_4, \text{CsF}$	Rhombic prisms.	...	...	...
$4\text{C}_2\text{SbF}_4, 3\text{SbF}_3$	Generally in plates.	...	...	...
$\text{CsSbF}_4, \text{SbF}_3$	Needles.	...	...	...
$\text{CsSbF}_4, 2\text{SbF}_3$	Prisms.	...	...	...

A solution of this kind of salt has an acid reaction, thus showing that the salt in solution is at least partially dissociated into an alkali fluoride and an antimony fluoride.

**Antimony Trichloride.**—This compound has been known since the time of Basil Valentine, who knew a method of producing it by distilling chloride of mercury with antimony trisulphide, and named it “butyrum antimonii.”

When antimony sulphide, taken in excess, is heated in a current of chlorine, the resulting product is a mixture of two chlorides, chloride of sulphur and chloride of antimony, which can be separated by fractional distillation.

The best way to produce chloride of antimony is thus:—1 part of crude antimony is added to 4 to 5 parts of concentrated hydrochloric acid in a retort, in which, from time to time, a small quantity of potassium chlorate is placed in order to oxidise any accompanying sulphides that might be present in the crude material used. The distilling of the solution is commenced as soon as the sulphide is completely dissolved. If the material contains much lead, the latter will be separated out as lead chloride with a violent pressure on the wall of the vessel. When this happens, it is best to allow the solution to cool down and to pour off the liquid from the deposited residue. The concentration of the liquid is continued until a drop from it becomes solid. On redistilling it the chlorides of foreign metals remain behind, while the chloride of antimony, together with a little iron chloride, is distilled over. In order to obtain an iron-free chloride, it is then put into water, when the iron chloride is dissolved and the antimony chloride is changed into an insoluble oxychloride. This is washed, redissolved in concentrated hydrochloric acid, boiled, and then distilled as before. The distillate will give rise to transparent, white crystals of the rhombic system. At 26° the solid chloride has a specific gravity of 3·064 (*Landolt, Börnstein, Meyerhoff*). The melting-point is 73·2°, and the specific density of this colourless liquid is 2·676. The molecular volume is 100·7 (*Kopp*). The boiling-point is 223° under atmospheric pressure, 113·5° under a pressure of 23 mm. (*Anschütz and Evans*), and 103° under 14 mm. The specific density of the vapour is 7·96, or a little more than 7·85, the theoretical value.

The chloride is soluble in bisulphide of carbon and ether. The heat of combination is 91·4 cal.

The following is a list of the complex salts of antimony chloride in combination with other elements:—

## COMPLEX SALTS (COLOURLESS).

Chemical Formulæ.	Crystalline Forms.	Observers.
$K_3SbCl_5$	Crystalline leaves.	Fehling's Dict.
$Na_3SbCl_5$		...
$(NH_4)_3SbCl_5$	Right-angled prisms	...
$SbCl_3 \cdot 2KCl$	Triclinic columns.	...
$SbCl_3 \cdot 2NH_4Cl \cdot H_2O$	Cubes.	...
$2SbCl_3 \cdot 3CsCl$	...	Saunders.
$SbCl_3 \cdot RbCl$	...	Saunders & Wheeler.
$2SbCl_3 \cdot RbCl \cdot H_2O$	...	Wheeler.
$10SbCl_3 \cdot 23RbCl$	...	Saunders.
$7SbCl_3 \cdot 16RbCl$	...	"
$SbCl_3 \cdot BaCl_2 \cdot 2\frac{1}{2}H_2O$	Star-like needles.	...
$2SbCl_3 \cdot HCl \cdot 2H_2O$	Crystalline leaves.	Engel.

Besides these products of addition, there occur a great number of products of displacement. With concentrated sulphuric acid the chloride is changed to the sulphate, with the production of hydrochloric acid.

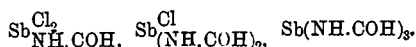
The solubility of the trichloride is as follows (after *Bemmellen, Meerburg, and Noodt*):—

Temperature	0°	15°	20°	25°	30°	35°	40°	50°	60°	72°
Mol. $SbCl_3$ in	} 47.9	64.9	73.0	78.6	84.9	91.6	108.8	152.5	360.4	$\infty$
100 mol. $H_2O$										

An excess of water will give rise to a strong hydrolysis and the separating out of basic antimony chloride, the composition of which depends upon the temperature and the quantity of water.

If heated with antimony sulphide, the chloride is changed to the sulphochloride, which is used as a medicine and as a corrosive or macerating agent for wool.

When antimony chlorine is dissolved in formamide, a peculiar phenomenon is observed. The chlorine atoms of the chlorine gradually change places with the  $NH.CO.H$  as dilution increases, with the formation of a series of ever-changing compounds, thus:—



This kind of reaction is called *amidolysis* (*Bruni and Mannelli*).

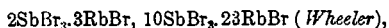
**Antimony Tribromide.**—When powdered antimony is put into a solution of bromine, the intensity of the heat evolved is so great that the bromine is vaporised and the metal is melted. In order to

counteract this effect, bisulphide of carbon is used. The solution is then distilled, producing the tribromide, which can be purified by sublimation. Obtained in this way, it is a colourless crystalline mass, though crystals belonging to the rhombic system can be formed from a solution of bisulphide of carbon. The specific gravity of the solid mass is 4.148 at 23°. It melts at from 90° to 94°, forming a liquid having a specific gravity of 3.641. Its molecular volume is 116.8 (*Kopp*). The boiling-point is 275.4°, and the specific density of its vapour is 12.57 (*Worcester*).

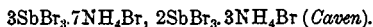
Its chemical properties are analogous to those of the trichloride.

It absorbs water from the moisture of the air, and in water it changes into an oxybromide.

The complex salts are :—



and the yellow ammonium salts are :—



**Antimony Tri-iodide** can be best obtained by putting the pulverised metal in a solution of iodine in bisulphide of carbon with a slight excess of the metal. The medium used is then distilled off, and the product thus obtained is purified by sublimation (*Nicklès*). The reaction will be very energetic and violent if bisulphide of carbon is not used. The powder must also be added in small quantity at a time.

The solid tri-iodide has been observed to possess three allotropic modifications, the relationship of which, one to another, is not yet known. The stable form, crystallising in the hexagonal system, is obtained by sublimation at a temperature over 114°. It can also be obtained from a diluted solution. It is red, and its specific gravity is 4.848 at 26°. It is isomorphic with bismuth iodide. The metastable form, crystallising in the monoclinic system, is obtained by allowing the carbon bisulphide solution to be evaporated in sunshine. It is red, and its specific gravity is 4.768 at 220°. The most unstable of the three is the greenish-yellow rhombic form, which is obtained through sublimation at a low temperature. At higher temperatures the two unstable forms change to the stable modification.

The melting-point of the stable form is 167°. The liquid is garnet red and boils at 401°, forming a red vapour, the specific density of which is 17.59, the theoretical one being 17.33.

The tri-iodide is soluble in carbon bisulphide, alcohol, and benzol. It is changed to the sulphate in sulphuric acid.



The other properties of the tri-iodide are analogous to those of the trichloride and the tribromide.

The following are some of the complex salts:—

Chemical Formulæ.	Colour.	Crystallisation.	Observers.
$\text{NH}_4\text{SbI}_4 \cdot \text{SbI}_3 \cdot 9\text{H}_2\text{O}$	Red.	Prisms.	...
$2\text{NH}_4\text{SbI}_4 \cdot \text{NH}_4\text{I} \cdot 3\text{H}_2\text{O}$	Dark-brownish black.	Small leaves.	...
$2\text{NH}_4\text{SbI}_4 \cdot \text{NH}_4\text{I}$	Red.	Prisms.	Caven.
$\text{NH}_4\text{SbI}_4 \cdot 3\text{NH}_4\text{I}$	"	"	...
$\text{NH}_4\text{SbI}_4 \cdot 3\text{NH}_4\text{I} \cdot 3\text{H}_2\text{O}$	Almost black.	"	...
$\text{BaSbI}_4 \cdot 9\text{H}_2\text{O}$	Orange-red.	Rhombic prisms.	...
$2\text{KbSbI}_4 \cdot \text{RbI}$	...	...	Wheeler.

**Antimony Trioxide,  $\text{Sb}_2\text{O}_3$ .**—In nature it appears under two forms: as rhombic oxide and as senarmonite belonging to the octahedron form of crystallisation. It can be artificially produced by roasting pure antimony in a crucible with a current of air. The oxide thus obtained might contain some tetroxide. It can also be obtained by heating the metal to red heat in a current of vapour (*Regnault*). The two crystalline forms of trioxide found in nature can be artificially produced (*Bonsdorff, Mitscherlich, Wöhler, H. Rose, Des Cloiseaux*).

The rhombic form has a specific gravity of 5.6, while the octahedral form has 5.22 to 5.33. The octahedral form can be transformed into the rhombic form by rapid heating. The specific heat of the trioxide is 0.0927 between 18° and 100° (*Neumann*). When it is in the form of a white powder it becomes yellow when heated, regaining its whiteness on cooling. It melts at a dark-red heat, forming a yellow liquid which, on being suddenly cooled, solidifies to a gray mass resembling asbestos. It is volatile and can be sublimed at higher temperatures. The specific density of its vapour is 19.60 at 15.60°, as opposed to 19.19, the theoretical value (*V. Meyer and C. Meyer*). The trioxide is neither soluble in water, nor in dilute sulphuric acid, nor in dilute nitric acid. With hydrochloric acid it is changed into the chloride, with tartaric acid to the complex salts of antimony tartrate, and with the hydroxides of the alkalis to antimonates. All these are soluble in water. If the vaporised trioxide and air be passed over ignited, finely divided oxides of those metals which form compounds with antimonic acid, antimonates are formed from the reaction between the oxides and the antimonic acid.

The trioxide can be reduced by hydrogen to metallic antimony. When the trioxide is heated in the air, it is oxidised to the tetroxide,

$Sb_2O_3$ . Sulphur reacts upon the trioxide with the formation of antimony sulphide and sulphur dioxide. With antimony sulphide the trioxide melts without decomposition, forming the so-called antimony-glass. The trioxide, especially in the form of vapour, is poisonous.

The equilibrium existing between the trioxide, the tetroxide, and oxygen, and also the partial pressure exercised by the oxygen, when the metal is heated in the air, are still unknown.

**Antimony Hydroxides or Hydrates.**—The three possible hydrates of antimony, as derived from antimony trioxide, are:—

$HSbO_2 = (Sb_2O_3 + H_2O)$  or  $(SbO)OH$ , metantimonious acid or monohydrate or metahydrate.

$H_4Sb_2O_5 = (Sb_2O_3 + 2H_2O)$ , pyro-antimonious acid.

$Sb(OH)_3 = (Sb_2O_3 + 3H_2O)$ , ortho-antimonious acid.

$HSbO_2$  is obtained by decomposing tartrate of antimony and potassium with acetate or alkaline carbonate (*Long*). This hydrate presents the character rather of a base than of an acid. Nevertheless it can give rise to the formation of antimonites.

$H_4Sb_2O_5$  is obtained by dissolving antimony trisulphide in an alkaline liquor, which is subsequently sulphurised by the addition of copper sulphate (*Fresenius* and *Schaffner*) until a portion of the liquid, filtered off, gives, with an acid, a white precipitate. Aided by heat, it changes gradually to the anhydride form, even in the presence of water. The dissociation tension (*Dissoziationsspannung*) of this hydrate is greater than the vapour-pressure of water. Sereno doubts the existence of this hydrate.

$SbO_3H_3$  (*Clarke* and *Stallo*) is obtained by decomposing tartrate of antimony and barium with an equivalent quantity of cold dilute sulphuric acid. After filtration, the liquid gradually gives rise to a deposit of white powder, which is then carefully washed and dried at  $110^\circ$ .

These hydrates are not known as crystals. They are amphoteric in character; on the one hand they behave like acids, forming antimonites with the alkalis, and on the other hand like bases, forming salts of the acids used.

**Antimonites.**—They are salts formed from the acids derived from  $Sb_2O_3$ , and are obtained from a solution of antimony hydroxides in alkaline liquor. The sodium salts derived from  $HSbO_2$  are:—

		Sp. Gr.	
$NaSbO_2 \cdot 3H_2O$	Octahedron.	2·86	Very hard to dissolve in hot water.
$NaSbO_2 \cdot 2HSbO_2$	Large crystals.	5·05	Almost insoluble in water.

A solution of sodium metantimonite gives a precipitate from the salts of heavy metals. Cupric antimonite is precipitated when

a copper sulphate solution is added to a solution of tartar emetic. A solution of alkaline antimonite has a reducing character; for example, chromates can be thus reduced to chromites, etc.

**Antimonious Oxyhaloids.**—When water is allowed to act upon the halogen combinations of antimony, it is observed that there results a deposit of a white crystalline material. By hydrolysis, a basic salt of antimony produces:—

(1a) *Antimonious oxyfluoride*,  $Sb_4O_3F_6$ . This is obtained by evaporating a solution of antimony trifluoride.  $FCl$  is evaporated off, and a white oxyfluoride is left behind.

(1b)  $Sb_8O_7F_{10}$  was obtained by Flückigen from the action of humidity upon the trifluoride.

(2) *Antimonious oxychloride*. This has long been known as the product of the action of water upon antimony trichloride. Paracelsus (1493–1541), Glauber, and Basil Valentine wrote about the methods to obtain it. They described it as a white powder and called it *mercurius vitæ*. Later, Victor Algarothus, a physician, used it as a medicine, and hence it came to be called Algaroth powder. In 1871 Sabanejew first succeeded in unravelling its chemical composition. According to him, the first product of water acting upon the trichloride is  $SbOCl$ , which, when again acted upon, changes to  $Sb_4O_5Cl_2$ . Still later, van Bremmelen, Meerburg, and Noodt found another oxychloride whose probable composition is  $2SbOCl.SbCl_3 = Sb_3O_2Cl_5$ .

(2a)  $SbOCl$  is the normal oxychloride, giving rise to beautiful crystals. It is soluble in bicarbide of sulphur, benzol, and chloroform, but not in water, alcohol, or ether.

(2b)  $Sb_4O_5Cl_2$  is not soluble in alcohol, but is soluble in hydrochloric acid and tartaric acid. It is the principal constituent of Algaroth powder.

(2c)  $Sb_4O_4Cl_5$  is decomposed by water, with the formation of  $SbOCl$ .

(2d)  $Sb_8OCl_{22}$  or  $SbOCl + 7SbCl_3$  (*Schneider and Sabanejew*).

(2e)  $SbOCl_3$ .

(2f)  $Sb_3OCl_{13}$  or  $SbOCl_3 + 2SbCl_3$  (*Williams*).

(2g)  $Sb_4O_4Cl_7$  or  $3SbOCl_3 + SbO_2Cl$  (*Williams*).

(2h)  $Sb_3O_{11}Cl_4$  (*Cooke, Sabanejew, Krenzel*).

(2i)  $10Sb_4O_4Cl_2$ .

(3a) *Antimonious oxybromide*,  $Sb_4Br_2O_5$  (*Cooke, Servillus, and Mac-Ynov*).

(3b)  $SbOBr$  (*Cooke*).

(4a) *Antimonious oxyiodide*,  $SbI_3O_5$ , yellowish in colour.

(4b)  $SbOI$ .

(4c)  $Sb_4O_5I_2$ .

**Antimony Trisulphide,  $\text{Sb}_2\text{S}_3$ .**—It can exist in two forms: (1) crystals, (2) amorphous.

1. *Crystals.*—They can be obtained by fusing antimony and sulphur together in proper proportion and then compressing the fusion product (*Spring*). They can also be obtained by the following methods:—

(1a) Reduction by the use of sulphur in excess upon oxide of antimony (*Jannash* and *Remmler*) or antimonate (*Unger*).

(1b) Action of hydrogen sulphide upon the vapour of the trichloride (*Durocher*, *Arctowsky*) or any other compound of antimony (*Carnot*).

(1c) Action of a solution of sulphur anhydride upon antimony in closed tubes (*Geitner*).

(1d) Reaction between chloride of sulphur and antimony (*Herrmann* and *Köchlin*).

(1e) Reduction of oxide of antimony by sulphocyanide of potassium at high temperatures (*Warren*). Action between tartar emetic and a solution of sulphocyanide of ammonium in closed tubes heated to  $230^\circ$ – $250^\circ$  (*Weinschenk*).

(1f) Decomposition of the pentasulphide, heated to  $200^\circ$ – $230^\circ$  in a current of carbonic anhydride (*Rose*, *Paul*).

(1g) Crystallisation of the amorphous sulphide under the action of heat in a current of inert gas or hydrogen sulphide (*Mourlot*, *Mitchell*); or by the action of vapour in closed tubes heated to  $200^\circ$  (*Schumann*, *De Séurmont*).

System of crystallisation, rhombic. Hardness, 2 to 2.5.

Specific density is as follows:—

D = 4.603 ( <i>Neumann</i> )	} Natural sulphide.
D = 4.624 ( <i>Schröder</i> )	
D <sub>16</sub> = 4.890 „	} Sulphide produced by combining the elements.
= 4.614 to 4.641 ( <i>Rose</i> )	
D = 4.752 ( <i>Karsten</i> )	} Sulphide produced by fusing the amorphous sulphide.
D <sub>16</sub> = 4.756 to 4.806 ( <i>Rose</i> )	
D <sub>27</sub> = 4.29 ( <i>Cooke</i> )	
D <sub>16</sub> = 4.640 ( <i>Rose</i> )	} Transformation of the amorphous sulphide by dilute acid.
D = 5.01 „	
D = 4.57 „	} Reduction of the pentasulphide.

It is a conductor of electricity. Its specific heat is 0.0907 (*Neumann*) or 0.0840 (*Regnault*).

2. *Amorphous.*—There are three modifications of the amorphous sulphide:—

(2a) The ordinary metallic black sulphide. It is easily powdered, giving a streak like that of graphite. Its specific gravity is between 4.6 and 4.7.

(2b) The red modification is generally obtained in the presence of water. Hence it may be considered as a hydrate of the trisulphide, *i.e.*  $\text{Sb}_2\text{S}_3 \cdot 2\text{H}_2\text{O}$ . But both Rose and Fuchs have been able to obtain this red variety, by quickly cooling the liquefied sulphide, with the specific gravity 4.15. It can be obtained thus:—

*a. Dry Method (Guinchant and Chrétien).*—A small boat, filled with the sulphide, is heated in a porcelain tube traversed by a current of nitric acid. In the vicinity of the boat the porcelain tube is cooled by a current of running water, upon which the sulphide deposits. The boat must be heated to  $850^\circ$ . The product thus obtained contains a little sulphur, which can be washed off. Its specific density is 4.278.

*β. Wet Method.*—The product obtained by passing  $\text{H}_2\text{S}$  into a solution of antimony salts or tartar emetic has an orange-red colour.

(2c) The dark violet modification is obtained by pouring the liquefied sulphide into cold water. In transmitted light a thin section appears red. The streak is also red.

When heated to high temperatures, the red modification changes to the ordinary black sulphide.

The density and the heat of formation of these three modifications are:—

	Density.	Heat of Formation.
Red . . . . .	4.120	Wet = 34.0 cal., dry = 32.6
Violet . . . . .	4.278	33.9
Black (melted) . . . . .	4.652	38.2
Black (synthetic) . . . . .	4.659	...

From the above, the heat of transformation can be calculated:—

Violet $\rightarrow$ black	= + 4.3 cal.
Red (dry) $\rightarrow$ black	= + 5.6 ,,
Red (wet) $\rightarrow$ black	= + 4.2 ,,

Specific heat = 0.0816 between  $20^\circ$  and  $500^\circ$ ; 0.220 at  $500^\circ$ .

Melting-point =  $555^\circ$  (*Pélabon*); the heat of melting = 17.5 cal. (*Guinchant and Chrétien*). The specific heat above the melting-point = 0.263.

The liquefied sulphide is capable of dissolving  $\text{Cu}_2\text{S}$ ,  $\text{HgS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{PbS}$ , and  $\text{BiS}$ . The melting-point of the sulphide is lowered in a regular manner when any of them is being dissolved. This fact enables one to determine the molecular weights of these sulphides by using antimony sulphide as the solvent (*Guinchant and Chrétien*, and *Pélabon*). The molecular depression constant of the sulphide is  $k = 790$  (determined from  $\text{Ag}_2\text{S}$  and  $\text{PbS}$ );  $k = 797$  (from  $\text{Cu}_2\text{S}$ ); and  $k = 788$  (from  $\text{HgS}$ ) (*Pélabon*).

The sulphide readily dissolves metallic antimony. In fact, antimony and antimony trisulphide are soluble in each other. This solution gives rise to two layers, which have been studied by Chrétien and Guinchant, and Pélabon.

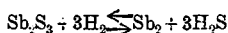
The specific density of a solution of antimony and antimony trisulphide is :—

Temperature.	Specific Density.	
	The Sb Layer.	The Sb <sub>2</sub> S <sub>3</sub> Layer.
13	6.75	4.63
643	...	3.85
698	6.55	...
1116	...	3.82
1156	6.45	...

The composition of the Sb phase :—

Temperature.	Per cent. Metal.	Temperature.	Per cent. Metal.	Temperature.	Per cent. Metal.
539	11.28	702	16.8	1036	21.0
595	13.2	750	17.96	1108	21.8
640	14.34	800	...	1130	21.3
660	15.7	825	20.0	1167	21.2
698	16.5	960	20.6	1180	21.1

Above 360° the reaction between Sb<sub>2</sub>S<sub>3</sub> and H is thus :—



(*Berthier, Schneider, Rose*). The relative importance of this reaction has been studied by Pélabon.

Fluorine decomposes it in the cold, with the production of a blue flame and fluoride of antimony (*Moissan*).

Chlorine reacts upon the crystallised surface in the cold ; if heat is applied, the trichloride and chloride of sulphur are formed (*Rose*).

Bromine attacks it when heated (*Jannash and Remmler*). With iodine it gives rise to iodine sulphide and the tri-iodide (*Schneider*).

Air and oxygen oxidise it easily to Sb<sub>2</sub>O<sub>3</sub> when heated. Büchner says, however, that the very finely pulverised powder can be acted upon by oxygen at ordinary temperatures.

With ozone it forms the sulphate (*Mailfert*).

Boiling water oxidises it slowly. According to De Clermont and Frommel, hydrogen sulphide is evolved at 89°. Oxidation is only accelerated in the presence of the vapour (*Regnault*). Hydrogen peroxide, according to Thenard, gives rise to the sulphate. If water is in excess, antimonious acid is produced (*Zambelli* and *Luzzato*), and in the presence of the alkalies antimonates are formed (*Hampe*, *Raschig*).

Hydrogen sulphide combines with it to form salts of sulphantimonites with the metals.

Phosphorus hydride attacks it, with the formation of hydrogen sulphide and antimony phosphoride (*H. Rose*).

With chloride of phosphorus it forms chloride of antimony and sulphide of phosphorus, and also sulphophosphoride of antimony (*Brandimont*).

Carbon monoxide reduces it only partially, while carbon reduces it completely to the metallic state.

The sulphide is desulphurised by potassium, sodium, copper, iron, and zinc.

By heating the sulphide in a solution of ammonium chloride there is produced the chloride together with ammonium sulphide, which passes off with the aqueous vapour (*Ph. de Clermont*).

A boiling alkaline solution decomposes it into the oxide, while sulphide of the alkalies is formed; by a secondary reaction antimonites and sulphantimonites are formed. The same result can be obtained by fusion.

Sulpho-salts and sulphantimonites are formed by the reaction between the sulphide and alkaline sulphide.

Carbonates of the alkalies act like the alkaline hydrate; they give rise to the formation of the oxide and sulphides of the alkalies, with evolution of carbonic acid; secondary actions produce sulphantimonites, antimonites, and antimony sulphide. The solution of the sulphide is never complete, even when it is heated; and, according to *Terreil*, carbonate of potassium does not help it. This has been demonstrated by *Weppen* and affirmed by *Terreil*. When a solution of sodium carbonate, to which the sulphide has been added, is being cooled, there are formed the sulphide, neutral and acid antimonites of sodium, and antimonious acid, constituting what is called "Kermes mineral."

A solution of sulphurous gas has no action upon it (*Berthier*); but, according to *Goverant*, a small quantity of the sulphide is attacked, with the production of hydrogen sulphide and sulphur. Dilute sulphuric acid has no action upon the sulphide crystals, but attacks

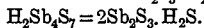
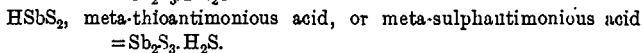
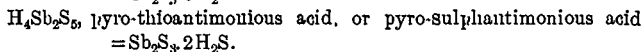
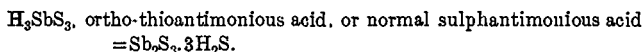
the amorphous sulphide slowly, perhaps giving rise to crystals of the sulphide. Strong sulphuric acid changes it to the sulphate (*Rose, Websky, Heusgen*). Fuming nitric acid attacks it, with the formation of sulphuric acid and antimonious acid, while ordinary nitric acid attacks it to form the nitrate and the sulphate, with the separation of sulphur (*Bunsen*).

Oxidisers, such as chlorate and nitrate of potassium, decompose it with explosion. It is also decomposed by a mixture of ammonium chloride and ammonium nitrate.

The sulphide is sensibly dissociated at about 600° (*Guinchant and Chrétien*), and is completely so in the electric furnace of Moissan (*Mourlat*).

**Thio-antimonious Acids or Sulphantimonious Acids.**—These acids are not known in the free state. In fact, they decompose immediately after their formation into hydrogen sulphide and sulphide of antimony. The complex anions of the acids are only stable in the presence of a neutral solution or in that of hydroxyl ions. The thio-antimonious acids are in part dissociated into the neutral and  $S''$  ions.

The important thio-antimonious acids or sulph-antimonious acids are:—



The following are some of the important salts formed from the thio-antimonious acids, according to Pouget and Stauck:—

Chemical Composition.	Colour.	Crystal Form.	Solubility.
$K_3SbS_3$	Colourless.	Crystalline.	Very easily soluble.
$K_4Sb_2S_6$	...	Octahedron.	...
$KSbS_2$	Red.	Prismatic.	Not soluble in cold water.
$K_2Sb_2S_7$	Red.	Octahedron.	...
$Na_3SbS_3 \cdot 9H_2O$	...	...	Easily soluble in water.
$NaSbS_3$	Black.	Powder.	Not soluble in water.
$Na_2Sb_2S_7 \cdot 2H_2O$	Red.	Crystalline.	...
$(NH_4)_3SbS_3$	White.	Powder.	Soluble in water; not soluble in alcohol.
$NH_4SbS_2 \cdot 2H_2O$	Yellow.	Needles or leaves.	Not soluble in water.

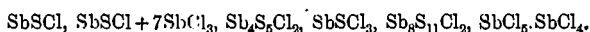


Chemical Composition.	Colour.	Crystal Form.	Solubility.
$(\text{NH}_4)_2\text{Sb}_4\text{S}_7$	Red.	Microscopic needles.	...
$\text{Ba}_9\text{Sb}_9\text{S}_8\text{H}_2\text{O}$	Golden yellow.	Crystalline.	...
$\text{Ba}_2\text{Sb}_2\text{S}_8\text{H}_2\text{O}$	Grayish green.	...	...
$\text{Ba}_2\text{Sb}_4\text{S}_9\text{H}_2\text{O}$	...	...	...
$\text{Sr}_3\text{Sb}_3\text{S}_8\text{H}_2\text{O}$	White.	Crystalline.	...
$\text{Sr}_2\text{Sb}_2\text{S}_5\text{H}_2\text{O}$	Yellow.	Crystalline.	...
$\text{Ca}_2\text{Sb}_2\text{S}_5\text{H}_2\text{O}$	...	...	...
$\text{Ag}_3\text{SbS}_3$	Brown.	...	Not soluble in water.
$\text{KAg}_2\text{SbS}_3$	Brown.	Crystalline.	..
$\text{Zn}_3\text{Sb}_2\text{S}_5$	Orange.	Amorphous.	..
$\text{KZnSbS}_3$	White.	Crystalline.	..
$\text{Mn}_3\text{Sb}_2\text{S}_5$	...	Amorphous.	..
$\text{KMnSbS}_3$	Rose.	Crystalline.	..
$\text{Pb}_3\text{Sb}_2\text{S}_5$	Brown.	Amorphous.	..
$\text{K}^+\text{PbSbS}_3$	Brown.	Crystalline.	..
$\text{Fe}_3\text{Sb}_2\text{S}_5$	...	} Amorphous.	..
$\text{Ni}_3\text{Sb}_2\text{S}_5$	...		..
$\text{Co}_3\text{Sb}_2\text{S}_5$	...		..
$\text{Cu}_3\text{Sb}_2\text{S}_5$	Black.	Amorphous.	..
$\text{Cu}_3\text{SbS}_3$	Reddish brown.	Crystalline.	..
$\text{KCu}_2\text{SbS}_3$	Yellow.	Crystalline.	..

The native minerals corresponding to some of these salts or to some other of the salts of thio-antimonious acids, are:—

Ortho-thioantimonites	{	Boulangerite, $(\text{SbS}_3)_2\text{Pb}_3$ ".
		Pyrargyrite, $(\text{SbS}_3)\text{Ag}_3$ .
		Bournonite, $(\text{SbS}_3)_2\text{Pb}_2$ "Cu".
Meta-thioantimonites	{	Zinkenite, $(\text{SbS}_2)_2\text{Pb}$ ".
		Miargyrite, $(\text{SbS}_2)\text{Ag}$ .
		Wolfsbergite, $(\text{SbS}_2)_2\text{Cu}$ ".
		Berthierite, $(\text{SbS}_2)_2\text{Fe}$ ".
Pyro-thioantimonites	{	Plumosite, $\text{Sb}_2\text{S}_5\text{Pb}_2$ .
		Panabase, $\text{Sb}_2\text{S}_5(\text{CuFe})_2$ .

**Antimony Sulph-haloids.**—When the trisulphide is dissolved in a solution of chloride of antimony, the sulphochloride is formed; but it has not been possible to isolate it (*Schneider*). The brown mass is crystalline and is strongly hygroscopic. The important sulphochlorides are:—



The sulphiodide,  $\text{SbSI}$ , is obtained by fusing the trisulphide and the tri-iodide together.  $\text{Sb}_2\text{S}_3\text{I}_6$  may also be mentioned.  $\text{SbSbI}$  exemplifies the sulphobromides.

**Antimony Oxysulphide**,  $\text{Sb}_2\text{S}_2\text{O}$  or  $\text{Sb}_2\text{O}_3 \cdot 2\text{Sb}_2\text{S}_3$ .—This can be obtained by imperfectly roasting the sulphide. The substance thus obtained, on being melted in a crucible, gives upon cooling a vitreous mass called "antimony glass."

**Antimony, Triselenide**,  $\text{Sb}_2\text{Se}_3$ .—This is obtained by melting antimony and selenium together in proper proportion. It is gray, metallic, and crystalline. The amorphous variety is in the form of a black powder, which is obtained by passing the selenium hydride gas into a solution of tartar emetic. At  $145^\circ$  the black powder cakes into a gray mass (*Chelsmann*); at  $605^\circ$  this melts, and on cooling crystallises out (*Pélabon*). When in the liquid state it can dissolve the sulphide; and when heated in air it changes to the trioxide, with the formation of selenium dioxide.

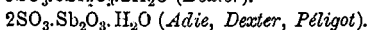
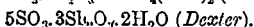
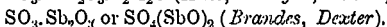
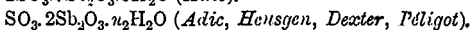
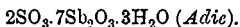
The other less important compounds of antimony and selenium are  $\text{Sb}_2\text{S}_3\text{Se}_2$ , sulphoselenide of antimony;  $2\text{SeO}_2\text{Sb}_2\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , the basic selenite of antimony; and  $4\text{SeO}_2\text{Sb}_2\text{O}_3$ , the acid selenite of antimony (*Nelson*).

**Antimony Telluride**,  $\text{Sb}_2\text{Te}_3$ .—This is obtained by fusing antimony and tellurium together in proper proportion. It melts at  $595^\circ$  and is a solvent for metallic antimony.

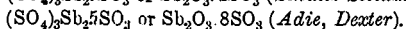
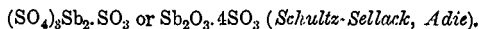
**Antimony Sulphate**.—This is obtained by dissolving the metal or the oxide in concentrated sulphuric acid. On cooling, the sulphate crystallises out in long needles. Its specific gravity = 3.6246; and it is very hygroscopic (*Schultz-Sellack, Metz*). When water is added to it, the hydrate,  $\text{Sb}_2(\text{SO}_4)_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , is formed. When heated in air, it changes to the trioxide and the tetroxide, with the evolution of  $\text{SO}_3$ .

The neutral salt =  $(\text{SO}_4)_3\text{Sb}_2$  (*Dexter, Adie*).

The basic salt is obtained by putting the neutral salt into a more or less dilute solution of sulphuric acid. The most important basic salts are:—



The important acid salts are:—



The complex salts of antimony sulphate, which may then be regarded as the salt of the complex acid  $\text{H} \cdot [\text{Sb}(\text{SO}_4)_2]$ , can be obtained

by dissolving the alkali sulphates and the oxide in concentrated sulphuric acid. They are:—

	Specific Density.
Na[Sb(SO <sub>4</sub> ) <sub>2</sub> ] . . . . .	3.2598
K[Sb(SO <sub>4</sub> ) <sub>2</sub> ] . . . . .	3.3296
NH <sub>4</sub> [Sb(SO <sub>4</sub> ) <sub>2</sub> ] . . . . .	3.0948

**Antimony Nitrate.**—It is obtained by dissolving the oxide in cold fuming nitric acid. On moderate heating it changes to the pentoxide, which is again converted into the tetroxide on further heating. Finally the trioxide is produced (*Peligo*).

Antimony in combination with nitric acid and oxygen gives rise to two salts: 2Sb<sub>2</sub>O<sub>5</sub>.N<sub>2</sub>O<sub>5</sub> and 2Sb<sub>2</sub>O<sub>5</sub>.N<sub>2</sub>O<sub>3</sub>.

Normal Antimony Acetate, Sb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>3</sub>, is slightly soluble in benzol, and is not soluble at all in ether; etc.

**Antimony with Phosphorus** forms the following combinations:—

(a) SbP, antimony phosphide, is white and metallic, obtained from the reaction between phosphorus and liquefied antimony.

(b) Phosphite of antimony.

(c) Sulphophosphate, PS<sub>4</sub>Sb.

**Antimony with Arsenic** gives rise to the following:—

(a) Arsenides: SbAs, Sb<sub>2</sub>As, and SbAs<sub>3</sub>.

(b) Arsenite.

**Complex Salts of Sb<sup>III</sup> with Organic Acids.**—There is a large number of these salts. The best known are the salts formed with tartaric acid and tartar emetic, 2C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.SbOK.3H<sub>2</sub>O.

Some of the complex antimony oxalates are:—

Composition.	Form.
NaSb(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> .2½H <sub>2</sub> O	Large monoclinic prisms.
KSb(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> .H <sub>2</sub> O	Cry-stalline needles.
NH <sub>4</sub> Sb(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O	Beautiful prismatic crystals.
K <sub>3</sub> Sb(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> .4H <sub>2</sub> O	Star-grouped needles.
Na <sub>3</sub> Sb(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> .5H <sub>2</sub> O	Small rhombic crystals.
(NH <sub>4</sub> ) <sub>3</sub> Sb(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> .1½H <sub>2</sub> O	White needles.
K <sub>10</sub> Sb <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>11</sub> .28H <sub>2</sub> O	Monoclinic prisms.
K <sub>10</sub> Sb <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>11</sub> .7H <sub>2</sub> O	" "

### B. The Compounds of Antimony of 4 Valences.

The number of these compounds is very small. The important ones are:—

**Antimony Tetroxide, Sb<sub>2</sub>O<sub>4</sub>.**—In nature it is known as antimon-

ochre, cervantite, and stiblich. It is obtained by heating the metal or the trioxide or the trisulphide for a long time in air. The same result is obtained when nitrate of antimony is heated to red heat.

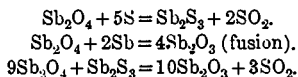
Pure antimony tetroxide is a white powder, which changes to yellow on being heated, and changes back to the original colour when it becomes cold again. Its specific density = 6.69 at moderate temperatures. It cannot be melted and is not volatile. It is not soluble in acids, with the exception of concentrated hydrochloric acid. It can be reduced by carbon, potassium cyanide, potassium, and sodium.

At the temperature of the melting of silver, the dissociation pressure of the oxygen is so great that the trioxide is formed.

When the tetroxide is heated with antimony the trioxide is formed. The tetroxide is reduced by sulphur, with the formation of  $\text{SO}_2$ .

Under certain circumstances the tetroxide behaves as if it were a mixture of the trioxide and the pentoxide.

Some of the important chemical reactions are :—



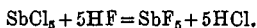
$\text{Sb}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , the hydrate, was first prepared by Berzelius.

**Antimony Tetrasulphide,  $\text{Sb}_2\text{S}_4$ .**—This was obtained by Berzelius by passing hydrogen sulphide gas into a solution of the tetroxide. Rose was able to obtain it from the decomposition of an aqueous solution of the fusion-product of the trisulphide and bisulphate of potassium by tartaric acid. It is a reddish-yellow powder.

**Antimony Tetrahaloids.**—The tetrachloride and the tetrabromide are not known in the free state, but only in solution.

### C. *The Compounds of Antimony of 5 Valences.*

**Antimony Pentafluoride,  $\text{SbF}_5$ .**—Berzelius first indicated its existence in the action between hydrofluoric acid and antimonious acid. It was obtained by Marignac, Moissan, Q. Ruff, and W. Plats. According to Ruff and Plats, the pure pentafluoride can be obtained by allowing the pentachloride to be acted upon by hydrofluoric acid for three days at  $25^\circ$ – $30^\circ$ .



It is a heavy liquid, having a consistency like that of oil, and solidifying into a substance resembling paraffin. Specific density at

$22.7^\circ = 2.993$  ; mol. vol. = 72 ; boiling-point =  $149^\circ - 150^\circ$ . It is soluble in water, and in moist air it gives rise to  $\text{SbF}_5 \cdot 2\text{H}_2\text{O}$ .

Some of the complex salts of meta-fluo-antimonic acid [ $\text{H}(\text{SbF}_6)$ ] are :—

Composition.	Crystal Form.	Solubility.	Remarks.
$\text{KSbF}_6$	Thin rhombic plates.	Easily soluble.	Unchanged in air.
$\text{KSiF}_6 \cdot \text{KF} \cdot 2\text{H}_2\text{O}$	Monoclinic.	" "	Melts at $90^\circ$ .
$\text{NaSbF}_6$	...	" "	...
$\text{NH}_4\text{SbF}_6$	Small needles.	" "	...
$\text{NH}_4\text{SbF}_6 \cdot \text{NH}_4\text{F} \cdot \frac{1}{2}\text{H}_2\text{O}$	Rhombic prisms.	" "	...
$\text{CsSb}_5\text{F}_9 \cdot \text{OH}$	...	" "	...

**Antimony Pentachloride,  $\text{SbCl}_5$ .**—If powdered metallic antimony is added to a chlorate, it burns, forming  $\text{SbCl}_5$ . It is colourless, and boils at  $140^\circ$  under the ordinary atmospheric pressure. Its specific density at  $20^\circ = 2.346$ .

We may mention the following derived compounds :—

$\text{SbCl}_5 \cdot \text{SbCl}_4$	$\text{SbCl}_5 \cdot \text{SeCl}_4$	$\text{SbCl}_5 \cdot \text{PCl}_5$
$2\text{SbCl}_5 \cdot \text{SbCl}_4$	$\text{SbCl}_5 \cdot \text{SeOCl}_2$	$\text{SbCl}_5 \cdot \text{POCl}_3$
$\text{SbCl}_5 \cdot \text{CNCl}$	$2\text{SbCl}_5 \cdot 5\text{NOCl}$	

With organic acids it forms the following compounds :—

$2\text{SbCl}_5 \cdot 3\text{C}_6\text{H}_5\text{NO}_2$	$\text{SbCl}_5 \cdot \text{C}_6\text{H}_5\text{O}_2$
$\text{SbCl}_5 \cdot (\text{C}_2\text{H}_5)_2\text{O}$	$\text{SbCl}_5 \cdot \text{C}_{10}\text{H}_{10}\text{O}_2$

A few of the chlor-antimonates are :—

$\text{KSbCl}_6 \cdot \text{H}_2\text{O}$	$\text{FeSbCl}_6 \cdot 8\text{H}_2\text{O}$
$\text{NH}_4\text{SbCl}_6 \cdot \text{H}_2\text{O}$	$\text{Ag}(\text{SbCl}_6) \cdot 2\text{NH}_3$
$\text{Ca}(\text{SbCl}_6)_2 \cdot 9\text{H}_2\text{O}$	$\text{Ni}(\text{SbCl}_6)_2 \cdot 6\text{NH}_3$
$\text{MgSbCl}_7 \cdot 9\text{H}_2\text{O}$	$\text{Zn}(\text{SbCl}_6)_2 \cdot 4\text{NH}_3$

**Antimony Pentabromide,  $\text{SbBr}_5$ .**—This cannot be produced in a pure form. The following are some of its compounds :—

$\text{KSbBr}_6 \cdot \text{H}_2\text{O}$	$2\text{CsSbBr}_6 \cdot \text{CsBr}_6 \cdot 2\text{H}_2\text{O}$
$\text{NH}_4\text{SbBr}_6 \cdot \text{H}_2\text{O}$	$\text{LiSbBr}_6 \cdot 4\text{H}_2\text{O}$

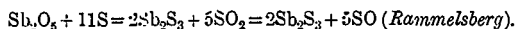
**Antimony Penta-iodide,  $\text{Sb}_2\text{I}_5$ .**—This is obtained by heating antimony at  $130^\circ$  with an excess of iodine. It is dark brown, and melts at  $78^\circ - 79^\circ$ .

**Antimony Pentoxide,  $\text{Sb}_2\text{O}_5$ .**—When metallic antimony is treated with nitric acid, the pentoxide is formed. In a dry way it can be obtained thus :—

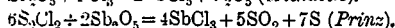
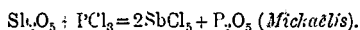
- (a) Pulverised antimony with oxide of mercury.  
 (b) Oxidisers, such as potassium permanganate, with the inferior oxides or sulphides.

It can also be obtained by treating the metal or the pentasulphide with hydrogen peroxide or peroxide of sodium. It is a yellowish powder, which changes to black when heated. Its specific density = 5.6. It does not melt and has no taste.

It dissociates into oxygen and the tetroxide at 300°. It is not soluble in water, but soluble in hydrochloric acid. Sulphur reduces it :



Carbon reduces it partially. Iodic acid decomposes it in part, liberating iodine (*Bunsen*). With a current of hydrogen sulphide it forms  $\text{Sb}_4\text{S}_5\text{O}$ . Sulphide of carbon reduces it (*Müller*). We have also:—



*The Hydrates or Acids derived from the Pentoxide.*—Berzelius was able to obtain  $\text{SbO}_3\text{H}$  by treating the product of reaction between antimony and dilute nitric acid with water. Fremy, by boiling antimonate of potash with nitric acid, obtained  $\text{Sb}_2\text{O}_5\text{H}_6$ . Geuther obtained  $\text{SbO}_4\text{H}_2$  from  $\text{Sb}_2\text{O}_5\text{H}_6$ , and  $\text{HSbO}_3$  from  $\text{SbO}_4\text{H}_2$  heated to 175°.

Senderens' conclusion is as follows:—The hydrates of the pentoxide can be obtained by precipitating the red liquid obtained from the action of nitric acid upon the trichloride with water.

(a)  $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , soluble in water.

(b)  $\text{Sb}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ , obtained from (a) by being dried in the open air.

(c)  $\text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  obtained from (b) by desiccation in the presence of sulphuric acid.

(d)  $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , obtained by heating (c) to 200°.

(e)  $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , obtained from  $\text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , heated to 300°. At 400°,  $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$  loses its water component and becomes  $\text{Sb}_2\text{O}_5$ , which finally breaks down to  $\text{Sb}_2\text{O}_4$  at a still higher temperature.

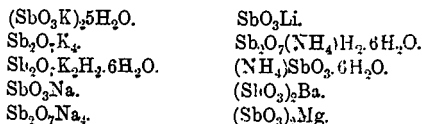
Delacroix was able to obtain  $\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ . At any rate the most important of these are:—

$\text{H}_2\text{SbO}_4$  = Ortho-antimonic acid.

$\text{H}_4\text{SbO}_7$  = Pyro-     "     "

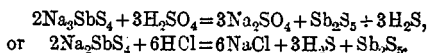
$\text{HSbO}_3$  = Meta-     "     "

Some of the important salts of these acids are :—

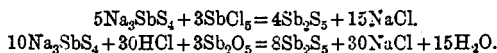


Besides these there are the antimonates of strontium, calcium, aluminium, manganese, iron, nickel, cobalt, and tin.

**Antimony Pentasulphide,  $\text{Sb}_2\text{S}_5$ .**—It is obtained by decomposing the sulpho-salts with acids. It is called *soufre doré d'antimoine* in French, and *Goldschweifel* in German. It is generally obtained in a pure condition from Schlippe's salt :—



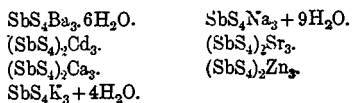
According to Bertsch and Harmsen we have :—



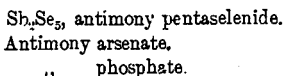
According to L. Prunier, the process is :—Fuse the trisulphide and sulphur together. The product of fusion is boiled with a solution of monosulphide of sodium. After filtration, the liquid is concentrated for crystallisation. This salt is redissolved in a solution with excess of acid. The pentasulphide is then precipitated.

The pentasulphide is easily dissociated: it loses its sulphur component partially at  $120^\circ$ , and changes to the trisulphide if the temperature is raised higher. Hydrogen reduces it (*Hüffter*). When heated in air, it oxidises with a flame. It alters in humid air (*Otto* and *Jahn*). Alkaline solutions change it to a mixture of sulph-antimonate and antimonate.

The most important salts of sulph-antimonic acid ( $\text{H}_3\text{SbS}_4$ ) are :—



With other elements we have :—



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## CHAPTER III.

### THE MINERALOGY OF ANTIMONY.

#### Native Antimony.

*Composition.*—Sb.

*Properties.*—Rhombohedral. Usually massive, with a very distinct lamellar structure; sometimes granular. Colour and streak tin-white. Brittle. H. = 3·3-5. G. = 6·6-6·75.

*Occurrence.*—Antimony has been found native in ferruginous mineral water (*Will*), in coal, and in the sands of rivers (*Campbell*). The impurities found associated with it are generally silver, iron, and arsenic. It occurs in veins of silver and other ores in Dauphiny, Bohemia, Sweden, the Harz, Mexico, and New Brunswick.

#### Allemontite.

*Composition.*—SbAs<sub>3</sub>.

*Properties.*—Rhombohedral. Reniform masses and amorphous; structure curved lamellar, sometimes granular. H. = 3·5. G. = 6·13-6·203. Lustre metallic, sometimes dull. Colour tin-white or roddish gray, sometimes tarnished to brownish black. It emits fumes of As and Sb before the blowpipe.

*Occurrence.*—It occurs at Allemont, Příbram in Bohemia, Schladming in Styria, and Andreasberg in the Harz.

#### Ammiolite.

*Composition.*—Rivot's analysis of similar mineral from Chili gave:

Antimony . . . . .	86·5	per cent.
Mercury . . . . .	22·2	„
Telluride . . . . .	14·8	„
Copper . . . . .	12·2	„
Quartz . . . . .	2·5	„

*Properties.*—Earthy powder. Colour deep red.

*Occurrence.*—Filling cavities in the quartzose or argilla-ferruginous gangue of mercurial tetrahedrite.

**Arequipite.**

*Composition.*—Silico-antimonate of lead.

*Properties.*—Compact, wax-like. Fracture conchoidal. H. = nearly 6. Colour honey yellow. Fuses with difficulty before blowpipe on charcoal, resulting in antimonial vapours and buttons of lead.

*Occurrence.*—In quartzose gangue with argentiferous lead carbonate and chrysocolla at the Victoria mine, Tibaya, Peru.

**Arsenstibnite.**

It is an arsenical hydrate of antimony.

**Atopite.**

*Composition.*—Perhaps a calcium pyro-antimonate,  $\text{Ca}_2\text{Sb}_2\text{O}_7$  or  $2\text{CaO}\cdot\text{Sb}_2\text{O}_5$ . Iron, manganese, and the alkali metals are also present.

*Properties.*—Isometric; in octahedrons. Under reducing flame on charcoal, sublimes in part and leaves a dark infusible slag.

*Occurrence.*—At Långbau, in Wermland, Sweden.

**Barcenite.**

*Composition.*—Santos gave the following analysis:—

Antimony . . . . .	50·11 per cent.
Sulphur . . . . .	2·82 „
Mercury . . . . .	20·75 „
Calcium . . . . .	3·88 „
Oxygen . . . . .	17·61 „
Water . . . . .	4·73 „

Hence it is an antimonate of mercury.

*Properties.*—Massive; structure finely granular. Brittle. H. = 5·5. G. = 5·343. Lustre dull. Colour dark gray. Streak ash-gray with slight greenish tint.

*Occurrence.*—Huitzuco, state of Guerrero, Mexico.

**Berthierite.**

*Composition.*—Probably  $\text{FeSb}_2\text{S}_4$  or  $\text{FeS}\cdot\text{Sb}_2\text{S}_3$ .

*Properties.*—In elongated prisms; also fibrous, massive and granular. H. = 2–3. G. = 4–4·3. Lustre metallic. Colour dark steel-gray. Before blowpipe on charcoal gives off sulphurous and antimonial fumes, leaving behind a black magnetic slag.

*Occurrence.*—Associated with quartz, calcite, and pyrite in Anvergne, in the Vosges, at Anglar and La Creuse.

### Bindheimite.

*Composition.*—Hydrated antimonate of lead,  $Pb_3Sb_2O_8 + 4H_2O$  or  $2PbO.Sb_2O_5.3H_2O$  or  $PbO.Sb_2O_5.H_2O$ .

*Properties.*—Amorphous, reniform or spheroidal. H. = 4. G. = 4.60–4.76. Lustre resinous, dull or earthy. Colour white, gray, brownish, yellowish. Streak white to grayish or yellowish.

*Occurrence.*—A product of the decomposition of other antimonial ores. At Nerchinsk, Siberia; Horhausen; in Cornwall; in Sevier Co., Arkansas.

### Boulangerite.

*Composition.*— $Pb_2Sb_2S_3$  or  $3PbS.Sb_2S_3$ .

*Properties.*—In plumose masses, showing on the fracture a crystalline structure; also granular and compact. H. = 2.5–3. G. = 5.75–6.0. Lustre metallic. Colour bluish lead-gray. Behaves before the blow-pipe like zinkenite.

*Occurrence.*—Abundant at Molières, Franco; in Lapland; at Nerchinsk; Ober-Lahr in Sayn-Altenkirchen; Silbersand, near Mayence, in the Eifel; Wolfsberg in the Harz; Příbram in Bohemia; and near Bottino in Tuscany.

### Bournonite.

*Composition.*— $(Pb : Cu_2)_3Sb_2S_6$  or  $(Pb : Cu_2)S.Sb_2S_3 :: 14Cu.Sb_2S_3$  (if  $Pb : Cu_2 = 2 : 1$ ).

*Properties.*—Orthorhombic. Twins, often repeated, forming cruciform and wheel-shaped crystals. Crystals short prismatic to tabular; often in parallel juxtaposition; prismatic faces often vortically striated. Also massive, granular, compact. Rather brittle. H. = 2.5–3. G. = 5.7–5.9. Lustre metallic. Colour and streak steel-gray. Opaque.

*Occurrence.*—At Noudorf, Wolfsberg, Clausthal, and Andreasberg, in the Harz; at Příbram in Bohemia; at Kapnik, Hungary; at Sorveo in Piedmont; and in Cornwall.

### Breithauptite.

*Composition.*—NiSb; arsenic is sometimes present.

*Properties.*—Hexagonal; crystals thin, tabular. Arborescent and

disseminated, massive. Brittle.  $H. = 5.5$ .  $G. = 7.541$ . Lustre metallic. Colour bright copper-red. Streak reddish brown. Opaque.

*Occurrence.*—In the Harz.

### Cervantite.

*Composition.*— $Sb_2O_4$  or  $Sb_2O_3 \cdot Sb_2O_5$ .

*Properties.*—Orthorhombic. In acicular crystals. Also massive.  $H. = 4-5$ .  $G. = 4.084$ . Lustre greasy or pearly, bright or earthy. Colour yellow or nearly white. Streak yellowish white to white. Before blowpipe, infusible and unaltered.

*Occurrence.*—A product of alteration of other antimonial ores. At Cervantes in Galicia, Spain; Chazelles in Auvergne; Felsőbánya, Kremnitz in Hungary; Pereta in Tuscany; also in Cornwall, Borneo, Mexico, Quebec, and California.

### Chalcostibite.

*Composition.*— $CuSbS_2$  or  $Cu_2S \cdot Sb_2S_3$ .

*Properties.*—Orthorhombic.  $H. = 3-4$ .  $G. = 4.75-5.0$ . Lustre metallic. Colour between lead-gray and iron-gray.

### Chanarcillite.

Named from Chanarcillo. A silver-white ore for which Domeyko gives the formula  $Ag_2(As, Sb)_3$ .

### Corongnite.

*Composition.*—An antimonate of lead and silver. An analysis gives :—

$Sb_2O_5$	. . . . .	58.97	per cent.
PbO	. . . . .	21.48	„
$Ag_2O$	. . . . .	7.82	„
$Fe_2O_3$	. . . . .	0.52	„
$H_2O$	. . . . .	11.21	„

*Properties.*—Amorphous.  $H. = 2.5-3$ .  $G. = 5.05$ . Colour, exterior grayish yellow, interior blackish.

*Occurrence.*—At the mines of Mogollon, Huancavelica, etc., Peru.

### Dyscrasite.

*Composition.*—A silver antimonide including  $Ag_3Sb$  and  $Ag_5Sb$ .

*Properties.*—Orthorhombic. Twins producing stellate forms.  $H. = 3.5-4$ .  $G. = 9.44-9.85$ . Lustre metallic. Colour and streak silver-white. Opaque.

*Occurrence.*—In the Wenzelgang, Baden; at Wittichen in Suabia and at Andreasberg in the Harz, associated with ores of silver, native arsenic, galena, etc.; at Allemont, France; Casalla, Spain; and in Bolivia, South America.

### Dürfeldtite.

*Composition.*—Analysis gives:—

S	. . . . .	24.15 per cent.
Sb	. . . . .	30.52 ,,
Pb	. . . . .	25.81 ,,
Ag	. . . . .	7.34 ,,
Cu	. . . . .	1.86 ,,
Fe	. . . . .	2.24 ,,
Mn	. . . . .	8.08 ,,

*Properties.*—In masses of fibrous structure, and also in fine needles. H. = 2.5. G. = 5.4. Colour light gray. Lustre metallic.

*Occurrence.*—Anquimarca, Peru.

### Famatinitite.

*Composition.*— $\text{Cu}_3\text{SbS}_4$  or  $\text{Cu}_2\text{S.Sb}_2\text{S}_5$ .

*Properties.*—Orthorhombic. Also massive. Rather brittle. H. = 3.5. G. = 4.57. Colour gray with a tinge of copper-red. Streak black. Opaque.

*Occurrence.*—With emargite, chalcopyrite, pyrite, etc., in the Sierra de Famatina, Argentine Republic; also at Cerro de Pasco, Peru.

### Freieslebenite.

*Composition.*— $(\text{Pb}, \text{Ag})_8\text{Sb}_4\text{S}_{11}$  or  $5(\text{Pb}, \text{Ag})_2\text{S.2Sb}_2\text{S}_5$  or  $\text{Pb}_6\text{Sb}_4\text{S}_{11}$ .

*Properties.*—Monoclinic. Habit prismatic; prismatic planes vertically striated. Rather brittle. H. = 2-2.5. G. = 6.2-6.4. Lustre metallic. Colour and streak light steel-gray. Fuses easily before blowpipe.

*Occurrence.*—At Freiberg, Saxony; at Kapnik, Hungary; at Felsőbánya, Hungary; and at Hiondelencina, Spain.

### Guejarite.

*Composition.*— $\text{Cu}_2\text{Sb}_3\text{S}_7$  or  $(\text{Cu}_2\text{S.2Sb}_2\text{S}_5)$ .

*Properties.*—Orthorhombic. In prismatic crystals. Gives off antimony fumes before blowpipe; yields metallic copper when treated with soda.

*Occurrence.*—At the copper mines at foot of Muley-Itacu, Andalusia.

**Jamesonite.**

*Composition.*— $\text{Pb}_2\text{Sb}_2\text{S}_5$  or  $2\text{PbS}\cdot\text{Sb}_2\text{S}_3$ .

*Properties.*—Orthorhombic. Usually in acicular crystals; but common in capillary, cobweb-like forms. Brittle.  $H. = 2-3$ .  $G. = 5.5-6.0$ . Lustre metallic. Colour steel-gray to dark lead-gray. Opaque.

*Occurrence.*—Principally in Cornwall, associated with quartz and crystals of bournonite; also in Siberia; in Hungary; at Valencia d'Alcántara in Spain; Sevier Co., Arkansas; at the Montezuma mine, Nevada.

**Kermesite.**

*Composition.*—Antimony oxysulphide,  $\text{Sb}_2\text{S}_2\text{O}$  or  $2\text{Sb}_2\text{S}_3\cdot\text{Sb}_2\text{O}_3$ .

*Properties.*—Usually in tufts of capillary crystals; prismatic; orthodiagonal.  $H. = 1-1.5$ .  $G. = 4.5-4.6$ . Lustre adamantine. Colour cherry-red. Streak brownish red. Feebly translucent.

*Occurrence.*—Results from the alteration of stibnite. At Malaczka, near Posing, in Hungary; at Braunsdorf, near Freiberg.

**Kobellite.**

*Composition.*— $\text{Pb}_2(\text{Bi}\cdot\text{Sb})\text{S}_5$  or  $2\text{PbS}\cdot(\text{Bi}\cdot\text{Sb})_2\text{S}_3$  (if  $\text{Bi} : \text{Sb} = 2 : 1$ ).

*Properties.*—Massive, sometimes fibrous and radiated like stibnite; also finely granular. Before the blowpipe, on charcoal, a yellow coating of  $\text{Bi}_2\text{O}_3$  near the assay, and, beyond, white  $\text{Sb}_2\text{O}_3$ .

*Occurrence.*—In the cobalt mine of Hvena in Sweden.

**Livingstonite.**

*Composition.*— $\text{HgSb}_4\text{S}_7$  or  $\text{HgS}\cdot 2\text{Sb}_2\text{S}_3$ .

*Properties.*—In groups of slender prismatic crystals; also columnar, massive, resembling stibnite.  $H. = 2.0$ .  $G. = 4.81$ . Lustre metallic. Colour bright lead-gray. Streak red.

*Occurrence.*—Huitzuco, Mexico.

**Meneghinite.**

*Composition.*— $\text{Pb}_4\text{Sb}_2\text{S}_7$  or  $4\text{PbS}\cdot\text{Sb}_2\text{S}_3$ .

*Properties.*—Orthorhombic; crystals slender prismatic, vertically striated. Also massive.  $H. = 2.5$ .  $G. = 6.34-6.43$ . Lustre metallic, bright. Colour blackish lead-gray. Streak black and shining.

*Occurrence.*—At Bottino in Tuscany; Ochsenkoff, Saxony; and at Goldkronach,

**Miargyrite.**

*Composition.*— $\text{AgSbS}_2$  or  $\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ .

*Properties.*—Monoclinic; crystals normally thick tabular. Brittle.  $H. = 2\cdot25$ .  $G. = 5\cdot1-5\cdot3$ . Lustre metallic-adamantine. Colour iron-black to steel-gray, but thin splinters are deep blood-red.

*Occurrence.*—Braunsdorf, Saxony; Příbram in Bohemia; and Clausthal.

**Monimolite.**

*Composition.*—An antimonate of lead, iron, and sometimes calcium; in part,  $\text{R}_3\text{Sb}_2\text{O}_8$ , with  $\text{R} = \text{Pb}, \text{Fe} = 3 : 1$ .

*Properties.*—Usually octahedral, also cubic. Also massive and incrusting.  $H. = 5\cdot6$ .  $G. = 6\cdot58$ . Lustre greasy to submetallic. Colour yellowish or brownish green, dark brown to black. Streak straw-yellow, cinnamon-brown. Translucent to nearly opaque.

*Occurrence.*—Harstig mine, Wermland, Sweden.

**Nadorite.**

*Composition.*— $\text{PbClSbO}_2$  or  $\text{PbSb}_2\text{O}_4\cdot\text{PbCl}_2$ .

*Properties.*—Orthorhombic.  $H. = 3\cdot5-4$ .  $G. = 7\cdot02$ . Lustre resinous to adamantine. Colour smoky brown to brownish yellow. Streak yellow.

*Occurrence.*—Constantine, Algiers.

**Plagionite.**

*Composition.*—Perhaps  $5\text{PbS}\cdot4\text{Sb}_2\text{S}_3$ .

*Properties.*—Monoclinic. Crystals thick tabular.  $H. = 2\cdot5$ .  $G. = 5\cdot4$ . Lustre metallic.

*Occurrence.*—At Wolfsberg, Arnsberg.

**Plumbostannite.**

*Composition.*—Sulphantimonate of lead, tin, and iron.

*Properties.*—Amorphous, granular.  $H. = 2$ . Feel greasy, like graphite.

*Occurrence.*—Peru.

**Polybasite.**

*Composition.*— $\text{Ag}_7\text{SbS}_6$  or  $9\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ .

*Properties.*—Orthorhombic.  $H. = 2-3$ .  $G. = 6\cdot0-6\cdot2$ . Lustre metallic. Colour iron-black. Streak black.

*Occurrence.*—Mexico; Chili; Příbram.

**Pyrargyrite.**

*Composition.*— $\text{Ag}_3\text{SbS}_3$  or  $3\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ .

*Properties.*—Rhombohedral. H. = 2.5. G. = 5.77–5.86. Lustre metallic-adamantine. Colour black to grayish black; by transmitted light deep-red. Streak purplish red.

*Occurrence.*—At Andreasberg in the Harz; Freiberg, Saxony; Bohemia; and Kremnitz, Hungary.

**Rivotite.**

*Composition.*— $\text{Sb}_2\text{O}_3$ ,  $\text{As}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{CaO}$ ,  $\text{CO}_2$ .

*Properties.*—Amorphous, compact. H. = 3.5–4. G. = 3.55–3.62. Colour yellowish green to grayish green. Streak grayish green.

*Occurrence.*—Sierra del Cadi.

**Romeite.**

*Composition.*—Antimonite of calcium, perhaps  $\text{CaSb}_2\text{O}_4$ .

*Properties.*—Tetragonal. H. = above 5.5. G. = 4.713. Colour honey-yellow.

*Occurrence.*—Piedmont.

**Sarawakite.**

*Composition.*—May be antimony chloride.

*Properties.*—Minute crystals, probably tetragonal. Soft. Lustre adamantine. Colourless or greenish yellow. Transparent.

*Occurrence.*—Found in native antimony in Borneo.

**Schneebergite.**

*Composition.*—Calcium and antimony with a little iron and traces of copper, bismuth, zinc, magnesia, and sulphuric acid.

*Properties.*—Isometric. H. = 6.5. G. = 4.1. Lustre vitreous to adamantine. Colour honey-yellow.

*Occurrence.*—At Schneeberg.

**Senarmonite.**

*Composition.*— $\text{Sb}_2\text{O}_3$ . O = 16.7; Sb = 83.3.

*Properties.*—Isometric, in octahedrons. Also granular; in crusts. H. = 2–2.5. G. = 5.22–5.30. Lustre resinous, inclining to sub-adamantine. Transparent to translucent. Colourless or grayish. Streak white.



*Occurrence.*—A result of the decomposition of stibnite and other ores of antimony. Algeria; Malaczka, Hungary; Quebec.

### Stephanite.

*Composition.*— $\text{Ag}_2\text{SbS}_4$  or  $5\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ .

*Properties.*—Orthorhombic; crystals usually short prismatic. Massive. H. = 2–2.5. G. = 6.2–6.3. Lustre metallic. Colour and streak iron-black.

*Occurrence.*—Freiberg, Bohemia, Hungary, Harz.

### Stibnite.

*Composition.*— $\text{Sb}_2\text{S}_3$ ; S = 28.6, Sb = 71.4. Sometimes auriferous, also argentiferous.

*Properties.*—Orthorhombic; crystals prismatic, often acutely terminated; vertical planes striated or deeply furrowed longitudinally; crystals often curved, bent in knee-shaped forms or twisted. Commonly occurs in confused aggregates of acicular crystals, also in radiating groups; massive, coarse or fine, columnar. H. = 2. G. = 4.52–4.62. Lustre metallic, highly splendid. Colour and streak lead-gray.

*Occurrence.*—See chapters on Geology.

### Tanzite.

*Composition.*—Arsenio-antimonate of bismuth, analogous to bindheimite.

*Properties.*—Amorphous, earthy. Colour yellow.

### Tetrahedrite.

*Composition.*— $\text{Cu}_3\text{Sb}_2\text{S}_7$  or  $4(\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3)$ .

*Properties.*—Isometric. H. = 3–4.5. G. = 4.4–5.1. Lustre metallic. Colour steel-gray to dark gray.

*Occurrence.*—Garnish mines; Harz.

### Ullmannite.

*Composition.*—Sulphantimonide of nickel,  $\text{NiSbS}$  or  $\text{NiS}_2\cdot\text{NiSb}_2$ .

*Properties.*—Isometric. H. = 5–5.5. G. = 6.2–6.7. Lustre metallic. Colour steel-gray. Streak grayish black.

*Occurrence.*—Duchy of Nassau, etc.

**Valentinite.**

*Composition.*— $\text{Sb}_2\text{O}_3$ ;  $\text{O} = 16.7$ ,  $\text{Sb} = 83.3$ .

*Properties.*—Orthorhombic; crystals often aggregated in fan-shaped or stellar groups; also massive.  $\text{H.} = 2.5\text{--}3$ .  $\text{G.} = 5.566$ . Lustre adamantine. Colour snow-white, occasionally peach-blossom red and ash-gray to brownish. Streak white. Translucent to subtransparent.

*Occurrence.*—Results from decomposition of antimony ores. *Vide* chapter on Geology.

**Zinkenite.**

*Composition.*— $\text{PbSb}_2\text{S}_4$  or  $\text{PbS.Sb}_2\text{S}_3$ .

*Properties.*—Orthorhombic.  $\text{H.} = 3\text{--}5$ .  $\text{G.} = 5.3\text{--}5.35$ . Lustre metallic. Colour and streak steel-gray.

*Other less important antimony minerals are:—*

Brongniardite,  $\text{Pb}_2\text{S}_5$  or  $\text{PbS.Ag}_2\text{S.Sb}_2\text{S}_3$ .

Diaphorite,  $(\text{Pb,Ag}_2)_5\text{Sb}_4\text{S}_{11}$  or  $5(\text{Pb,Ag}_2)\text{S.2Sb}_2\text{S}_3$ .

Epiboulangerite,  $\text{Pb}_3\text{Sb}_2\text{S}_3$  or  $3\text{PbS.Sb}_2\text{S}_3$ .

Geokronite,  $\text{Pb}_7\text{Sb}_2\text{S}_8$  or  $5\text{PbS.Sb}_2\text{S}_3$ .

Hematostibnite,  $8\text{MnO.Sb}_2\text{O}_5$ .

Horsfordite,  $\text{Cu}_4\text{Sb}$ .

Kilbrickenite,  $\text{Pb}_6\text{Sb}_2\text{S}_9$  or  $6\text{PbS.Sb}_2\text{S}_3$ .

Manganostibnite,  $10\text{MnO.Sb}_2\text{O}_5$ .

Ochroite,  $\text{Pb}_7\text{Sb}_3\text{O}_7$ ,  $2\text{PbCl}_2$ .

Partzite, hydrated oxide of Sb, mixed with various metallic oxides

Polyargyrite,  $\text{Ag}_{24}\text{Sb}_{16}\text{S}_{15}$  or  $12\text{Ag}_2\text{S.Sb}_2\text{S}_3$ .

Pyrostilpnite,  $\text{Ag}_3\text{SbS}_3$  or  $3\text{Ag}_2\text{S.Sb}_2\text{S}_3$ .

Semseyite,  $\text{Pb}_7\text{Sb}_6\text{S}_{16}$  or  $7\text{PbS.3Sb}_2\text{S}_3$ .

Steinmannite, antimonial galena.

Stetefeldtite, contains  $\text{Sb}_2\text{O}_5$ , S, Ag, Cu, FeO, CuO,  $\text{H}_2\text{O}$ .

Stromeyerite,  $(\text{Ag,Cu}_2)\text{S}$  or  $\text{Ag}_2\text{S.Cu}_2\text{S}$ .

Stylytopite,  $3(\text{Cu}_2\text{.Ag}_2\text{.Fe})\text{S.Sb}_2\text{S}_3$ .

Tennantite,  $\text{Cu}_8\text{As}_4\text{S}_7$  or  $4\text{Cu}_2\text{S.A}_3\text{S}_3$ .

Volgerite, hydrous antimonious acid.

Warrenite,  $\text{Pb}_3\text{Sb}_4\text{S}_9$  or  $3\text{PbS.2Sb}_2\text{S}_3$ .

Wolfachite,  $\text{Ni(As,Sb)S}$ .

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## CHAPTER IV.

### THE GEOLOGICAL OCCURRENCE OF ANTIMONY ORES.

THE principal ores of antimony that have any commercial value are:—

1. *Antimony glance*,  $Sb_4S_3$ ; also known by the names "gray antimony ore," "stibnite," or "antimonite." It contains 71·4 per cent. of antimony and 28·6 per cent. of sulphur.

2. *Native antimony*. It occurs too rarely to be of any commercial importance.

3. *Valentinite*,  $Sb_2O_3$ ; the rhombic form of the oxide of antimony, which is also known as "white antimony" or "antimony bloom." It contains 83·4 per cent. of antimony, and 16·6 of oxygen.

4. *Senarmontite*,  $Sb_2O_3$ ; the cubic form of the oxide of antimony.

5. *Kermesite*,  $2Sb_2S_3 \cdot Sb_2O_3$ ; also known as "antimony oxysulphide," "red antimony ore," "antimony blende," or "pyrostilbite."

6. *Cervantite*,  $Sb_2O_4$ ; also known as "antimony ochre."

When antimony ores, specially antimonite, undergo decomposition, the resulting alteration-products generally are: valentinite, senarmontite, kermesite, and cervantite. According to Foullon, there is a case at Rozslan in Macedonia where the southern part of the vein carries antimony ore, while its northern part carries auripigment and some realgar. The antimonite has been oxidised to antimony ochre, valentinite, and red antimony ore, all accompanied by gypsum and sulphur.

The principal types of antimony deposits are:—\*

1. *Veins*.—The ore is generally found disseminated irregularly in veins of quartz; sometimes, though rarely, it occurs in lenticular masses. The other gangue materials, besides quartz, are brown spar, calc-spar, and heavy spar. The products of decomposition of stibnite are stilbite, antimony-ochre, valentinite, and senarmontite; more rarely, also pyrostilbite, pyrite, bournonite, berthierite, galena, zinc-

\* "Stilbite was one of the minerals formerly cited as having been originated in veins by volatilisation from lower sources. But it has probably, in all cases, been derived from solutions of alkaline sulphides" (*Kemp*).

blende, steinmannite, zinkenite, and cumular-ochre, rarely native gold. Antimony salts of other metallic sulphides may also be found. Antimony sulphide occurs in laminar crystals or in granular forms, often massive, generally intermingled with quartz, thus forming a compact mass occupying the whole vein. Stibnite-quartz ore might be considered as an extreme development of silver or lead ore.

In 1851 Sénarmont, in order to explain the formation of stibnite in veins, made an experiment to obtain it by heating in a closed vase a mixture of antimony and sulphur in the presence of pure water up to 300°, or in the presence of bicarbonate of soda at 250°. The contact rocks are occasionally similar to those of veins containing lead ore, rocks having white mica and green minerals. Hereafter this type is denoted by A.

(a) *Sub-Type: Antimonial Gold-Quartz Veins.* The stibnite is itself gold-bearing, and accompanies other free gold-bearing gangues. Hereafter this sub-type is denoted by B.

2. Beds of epi-minerals, *i.e.* impregnated non-calcareous rocks. In this case the antimony ore is impregnated in the rocks. Hereafter this is denoted by C.

3. *Epigenetic Stocks.* The type is a metasomatic antimonial deposit. Hereafter this type is denoted by D.

4. *Bedded Deposits* of antimony ore. The deposits are of sedimentary origin. Some of the so-called bedded deposits may be due to the impregnation of the country, *i.e.* of the neighbouring rocks. Hereafter this is denoted by E.

In the following we shall take up the antimonial deposits of each country in turn.

#### GERMANY.

Ores of antimony sometimes occur in the Devonian rocks of Rhenish Prussia between Wintrop and Mentrop, four miles from Arnsberg, where are found bands of bituminous limestone from 6 inches to 18 inches in thickness, interstratified between clay slates and siliceous shales. Stibnite penetrates all these strata, which are overlain by Millstone Grit. It is also noticed that the stibnite accumulates more plentifully towards the middle part of the various beds, but gradually thins out near the bedding planes of deposition. Sometimes fragments of the "country" are included in the more massive portions. (D.)

At the Hoffnung mine, near Brück, on the Ahr, the Devonian graywacke slates have a N.-S. strike, with a dip of 45° towards the west, cut through by N.-E. veins, dipping from 40° to 50° S. The

stibnite, sometimes associated with iron pyrites and brown spar, is found in true veins, or between the planes of stratification, or in cleavage fissures. This is a good example of the lateral immigration of antimony ore from fissures into and along beds of shaly rocks. (C.)\*

At Böhmsdorf and Wolfsgalgen, near Schleiz, stibnite is found in quartz veins traversing palæozoic schists. The subsidiary minerals are zinc-blende, plumose stibnite, pyrophyllite, and iron spar. (A.)

At Mobendorf, antimony ore occurs in veins, cutting the gneiss formation, with fillings of stibnite and some berthierite, bournonite, striated kaolin, steinmannite, zincite, kermesite, stibiconite, pyrite, quartz, and brown spar. At Braunsdorf, a few kilometres off, the same ore is found intimately associated with rich silver ores. In the vicinity of Freiberg, the quartz-stibnite vein is simply the continuation of a true quartz formation. For this reason Freiesleben called it the "Mobendorf formation" (A).

#### Summary.

Mobendorf	} Crystalline Schist.	
Haynichen (Niedersteigis)		
Ennersdorf		
Seiferdorf		
Rochlitz		
Schöneck		
Brandholz		
Wolfsberg		Silurian.
Goesdorf		Lower Devonian.
Arnsberg		Culm.

#### HUNGARY.

At Magurka, according to von Cotta, the granite is traversed by many quartz veins, varying from a few centimetres to 4 m. in thickness. They carry stibnite and free gold, enclosing sometimes some of the country. The accessory minerals found in these veins are galena, zinc-blende, pyrite, copper pyrite, brown spar, and calc-spar. Ordinarily the quartz occurs along the walls of the veins, while the stibnite occupies the central part. (B.)

At Pricov, near Selcan, stibnite is found, according to A. Hoffmann, in veins of hornstone, generally accompanied by kersantite dykes, cutting through the granite. At a depth of 18 m. (59 ft.) the stibnite is decomposed to stibiconite. (A.)

Some of the veins carrying antimony ores in the Rechnitz

\* By some authors this is classified under E.

Mountains have been followed for a distance of 3 km. (2 miles), cutting crystalline schists. According to A. Schmidt, the veins are especially rich when the country is a chloritic or graphitic schist. The principal vein-fillings are quartz, calc-spar, stibnite, stibiconite, and pyrite. The country, that is, the graphitic schists, is sometimes so impregnated with stibnite, that it may be profitably worked for a distance of 3 to 4 metres away from the walls of the veins. (A and C.)

Between Arany Idka and Rosenau, in Upper Hungary, stibnite veins are found, containing quartz and carbonates, together with small amounts of jamesonite, berthierite, blende, and auriferous pyrite. (A.)

At Felsőbánya, along the boundary of an amphibole trachyte and of a recent one, there is found a conglomerate which contains quartz with pyrite, often realgar and stibnite, with galena, blende, etc. This is classified by De Launay under Tertiary antimony, that is, its origin is sedimentary. (E.)

Antimony ores are also found at Kremnitz, Toplitzka, Schemnitz, Felsőbánya, Nagybánya, Dobschau, Gisno, Gross-Göllnitz.

#### BOHEMIA.

A typical example of antimonial gold-quartz veins, as described by Posepny, is found at Krásnáhora (or Schönberg) and Milesov (or Milleschau) in Central Bohemia. Most of the veins are accompanied by dykes—mostly lamprophyre dykes, but some are of porphyry—cutting through an intrusive stock of granite intercalated between schists. The stibnite often constitutes the larger part of the filling, with a gold content of 100–133 g. (\$66–\$87·88) per ton. (B.)

Antimony ore is also found at Hata, Brodkowic, Příbram, and Michaelsberg.

#### SERVIA.\*

*The Antimony Deposits of Kostainik.*—The main mass of the rocks in this locality consists of light-gray to ash-gray limestones, probably of Triassic age, upon which gray and blackish soft clay slates, and in part also clastic graywacke slates, rest. These limestones and slates are cut through at many localities by biotite trachytes, and less often by hornblende andesites of trachytic habit. These eruptive rocks appear as dykes, sheets, and stocks within the strata, and also

\* From "Lehre von den Erzlagerstätten," von Beck: Berlin, Gebrüder Borntraeger, 1903; translated by Weed, "The Nature of Ore Deposits," *N. Y. Eng. and Min. Journ.*, 1905.

perhaps from effusive lava flows. The origin of the antimony deposits is traceable to the igneous rocks.

The ores appear in three different forms :—

(1) Tufts and stringers of stibnite, quartz, and calcite in decomposed trachyte, as found in the mines of Kik and Stolitza. (C.)

(2) Antimony veins in the slates. At Rovind there occurs a compound vein, dipping at 30°. Transverse stringers containing stibnite are enclosed between two parallel bounding fissures, of which the foot-wall is always the richest, while the hanging wall is mostly barren. (A.)

(3) Interbedded ore masses. The deposits of this kind consist mainly of a dark, very finely crystalline ground-mass of quartz, intimately intergrown with tufts of stibnite. They lie between an

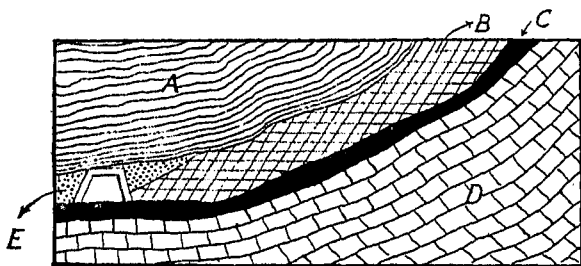


FIG. 1.—Bed-like deposit of antimony ore near Kostaiuik.

- |                                    |               |
|------------------------------------|---------------|
| A, Clay slate.                     | C, Clay.      |
| B, Quartz layer with antimony ore. | D, Limestone. |
|                                    | E, Trachyte.  |

overlying slate and an underlying limestone, and are always accompanied by a trachyte intrusion near by, which sends out narrow apophyses, forming sometimes the walls of the deposits, or cutting through them in a parallel direction or at an acute angle. This is shown in fig. 1. (D.) The stibnite has mostly been superficially altered into antimony-ochre, stiblite, or valentinite, and in many cases it has been entirely leached out, leaving a skeleton of gray quartz behind. At times the quartzose ore has been crushed and recemented together by quartz or calc-spar.

At other places—as, for instance, in the Zavoric III. mine (fig. 2)—the ore-bearing quartz mass cuts into the underlying limestones with very irregular borders, thus suggesting the idea that considerable portions of calcium carbonate have been leached out and replaced by the quartzose ore. (D.)



All the phenomena observed indicate the plausibility of the theory that the ores were deposited from solutions due to uprising waters dissolving out the antimony content from the eruptive rocks, and that these solutions deposited their burdens not only in clefts and fissures, but also penetrated laterally into the joints between the

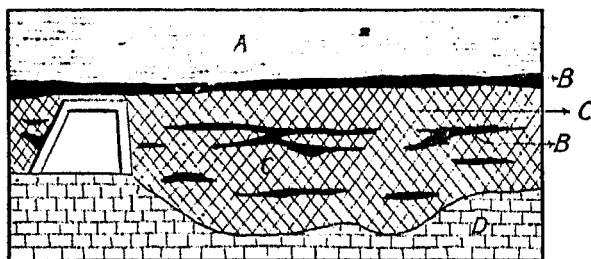


FIG. 2.—Cross-section of a heddled antimony deposit in limestone at the Zavarja III. mine.

- |                  |                                |
|------------------|--------------------------------|
| A, Clay slate.   | C, Quartz layer with antimony. |
| B, Antimony ore. | D, Limestone.                  |

strata whenever there occurred an impervious stratum checking the downward flow of the solutions, and that also sometimes having become stagnant, they dissolved the underlying limestone and replaced it by the mineral burdens they carried.

Antimony ore is also found at Lošnica.

#### FRANCE.

The greater part of the antimony deposits of France is found in the Central Plateau.\* They generally occur in the form of veins, most of which have more or less been exploited. At the Nudes mine, in Bourbonnais, the gangue is mainly quartz. At Bresmy, canton Savigny, the deposit is formed of two veins, contained in the granite. Here the minerals are accompanied by a sort of white micaceous granulite, analogous to that found at Magurka in Hungary, and consist of quartz and stibnite, the latter being thinly covered over with the oxide. (A.)

At Villerange, in La Creuse, the antimony veins present an interesting phase, in that they cut the graywacke of the Culm formation, and in consequence their age can be very easily determined. South of Saint-Gireix (Haute-Vienne) the micaceous or amphibolic schists

\* The largest antimony mine is La Lucette, in Mayenne, discovered by Herrenschildt. The antimony contains gold.

are cut by numerous veins of granulite, along the axis of which one often finds veins of quartz charged with antimony sulphide. (A.)

At Bresnay, east of Allier, and at Montignat, west of Mouluçon, there is observed, in addition to metamorphism, a common origin for the stibnite and the rock containing white mica, as if the antimony had been leached out of the rock by underground water. (C.)

The most important of the deposits in the Central Plateau are those which have been worked at Freycenet, Licoune, etc., in Puy-de-Dôme, Cantal, and Haute-Loire. These deposits are enveloped in the fundamental or primitive formations of gneiss, mica-schist, and granite. The veins, being generally vertical, contain lenses of stibnite, separated at intervals by quartzose gangues. Sometimes the stibnite is intimately mixed with the quartzose gangue, and nearly always it is accompanied by iron sulphide. (A.)

Mention may be made of the antimony deposit at Ardèche, which has been spoken of as sedimentary in origin (E). But it may be an impregnation or a metasomatic alteration of the Triassic dolomite in which the deposit is found (C or D).

In Corsica the veins occur in sericite schist, the gangue minerals being quartz, calcite, blende, and, rarely, pyrite, cinnabar, and bournonite.

Besides the above-described localities, the following may be mentioned: Auvergne, Gard, Aude, Vendée, Lyonnais, Bouc, Septèmes near Marseilles.

#### ITALY.

The principal deposits are found in the province of Tuscany and in the island of Sardinia. The Pereta mine in Tuscany is opened in a mass of chalcedonic quartz, in which stibnite is sparsely and irregularly disseminated, thus rendering its winning difficult and costly, especially since the quartz is very hard. According to Coquand and Toso, the mass of crushed white quartz exists in the form of a great ellipsoid, of which neither the hanging wall nor the foot wall can be exactly determined, intercalating Eocene calcareous shales in the north and cutting Miocene limestones in the south. Hydrogen sulphide (*putizze*) has been detected to the north of the outcrop. The stibnite is found in the form of stringers and pockets enclosed in the sulphur-bearing quartz, which is sometimes encrusted with stibnite, enclosing in turn small crystals and aggregates of sulphur. Undoubtedly the enclosing rocks have been subjected to metamorphism and have been impregnated with sulphurous emanations.

tions, which have transformed the alberese (a variety of Eocene calcareous rock found in Tuscany) in part to gypsum and anhydrite. It is not quite certain whether the antimony deposit has any genetic relation with the sulphurous vapour. (Probably C.)

At San Martino, Tuscany, cinnabar is found accompanying the stibnite.

At Monte Auto there is a peculiar occurrence of antimony ore, which is found in great blocks distributed in a black clay containing no other kind of rock except occasionally masses of dolomite, impregnated with stibnite. (D.)

At Siena, the Cettine di Cotorniano mine is opened in a vein of blackish quartz-like rock, in which, near the surface, oxide of antimony is found, changing, however, to the sulphide at some depth. (A.)

At Rosia, the stibnite is accompanied partly by calcite and partly by quartz.

At Su Suergin, in Sardinia, the deposits occur at the contact of the Rhætic limestone with Permian slate. Antimony glance, accompanied by pyrites, is also found in the mica schist. Traverso gave the opinion that these deposits are of sedimentary origin rather than of vein formation. (E.)

#### ENGLAND.

Antimouy ore is found very sparingly in Cornwall.

#### SPAIN.

Veinlets of quartz, carrying stibnite, occur generally in a belt of metamorphic schists and shales, their strikes being between W. 10° S. E. 10° N. and S.W.-N.E. The shale, for a breadth of about three feet, seems to be mineralised by veinlets of quartz with stibnite, by pockets and impregnations of that mineral, whose walls are generally not well defined. (A and C.)

Near Vinuela, in Malaga, native antimony is found to be impregnated in the clayey shales, the size of the impregnated masses vary ing from that of an egg down to minute spangles.

Other localities that may be mentioned are Estremadura and Badajoz, Caurel, Brollou, Orense.

#### PORTUGAL.

In the district of Evora, antimony ore occurs in quartz lodcs at the contact of Palæozoic beds and granite. (A.)

The principal antimony veins, in the neighbourhoods of Valongo, Paredes, and Gondomar, in the district of Oporto, may be roughly divided into two systems, according to the directions of their strikes. The one system has a strike, N.  $10^{\circ}$  to  $20^{\circ}$  W., coinciding with that of the country, and hence the deposits may be described as bed-like lodes ; and the system has a course N.  $30^{\circ}$  to  $60^{\circ}$  E. Both of these occur in Silurian rocks. Near the town of Alcontim, in the district of Faro, there occur two distinct lodes : one running E.-W. and the other N.W., the latter of which has the same strike as the country. These occur in the slates of the Culm formation. Besides these localities may be mentioned Braganza.

#### ALGIERS.

The antimony deposits of Sidi-Rgheis are situated in the southwestern part of the province of Constantine, and have been mined at Sempsa and Djebel-Hamimat. They occur in the clays and limestones of the Lower Neocomian. The ore, according to Coquand, is in part a compact antimony oxide, and in part a granular crystalline variety containing senarmontite. At times the oxide deposits may be superimposed by bundles of stibnite needles. The deposits possess little gangue and are generally in the form of very irregular masses, parallel to the plane of stratification. According to Beck, they are impregnations (C), while de Launay classifies them under sedimentary deposits, and Coquand considers them to be contemporaneous with the enclosing rocks. (E.)

At Djebel-Taia, stibnite is associated with cinnabar.

#### TURKEY.

At Allchar, in Macedonia, the antimony deposit is found associated with a great quantity of realgar, together with orpiment. The sulphur is undoubtedly derived from the decomposition of stibnite, and is the principal agent in changing many of the oxides into sulphides ; while, together with oxygen, it transforms the neighbouring chalk into gypsum. This deposit is a good example of paragenesis.

Other antimony ore localities are Adrianopolis, Monastir, Rozdan, Mytilene, Chios, Aidin, Eudemisch.

#### SWEDEN.

At Sala, in Westmannland, a small quantity of native antimony is found associated with the argentiferous lead ore. It occurs in the primitive formations.

## RUSSIA.

Small quantities of antimony ore have been found.

## NORTH AMERICA.\*

Kern County, California.—Veins containing stibnite occur; the gangue is usually quartz. (A.)

Humboldt County, Nevada.—Antimony deposits have been worked for many years in veins with quartz gangue. The most important of the American mines are the Beulah and the Genesee, at Big Creek, near Austin. Pure stibnite, attaining to a width of three feet, has been found in some of the richest veins. (A.)

Sevier County, Arkansas.—The veins, with quartz gangue, appear to be generally interbedded in Trenton Shales and to lie along anticlinal axes. (A.)

Iron County, Utah.—Disseminations of stibnite are found in sandstone and conglomerate, following the planes of stratification. They are generally masses of radiating needles, occurring in sandstone and between the boulders of conglomerate. Blake thinks that the ore has been crystallised out from descending solutions. Above the sandstone eruptive rocks are found. (C.)

In Sonora, senarmontite ore has been worked, but it was soon exhausted.

York County, New Brunswick, Canada.—Veins of quartz or of quartz and calcite carrying stibnite occur over several square miles. The wall rocks are clay slates and sandstones of Cambro-Silurian age.

Besides those described above, the following localities may be mentioned: California (Havilah, Bousby, Erskine Creek, Grace Darling, Padre, San Emidio, Crowell); Utah (Garfield County); Idaho (Kingston); South Dakota; Mexico; Canada (Rawdon, Nova Scotia).

## SOUTH AMERICA.

Antimony ore has been found in the following places:—Nicaragua, Chili, Peru (district Yauli and Huancavelica),† Bolivia (at S. Pablo, near Lipez, and in the vicinity of Tasna), Argentine Confederation (at Charillos, in dept. S. Antonio de los Cobres, in prov. Salta).

\* Taken from *The Ore Deposits of the United States and Canada*, by Professor Kemp, 1900.

† Stibnite is here found associated with quicksilver deposits—a case of paragenesis.

## CHINA.\*

From private information received by the author, the ore seems to occur in veins of quartz. The low-grade ore carries more or less gold and silver. (A and B.) The principal localities are Nanning, Ssucheng, Taiping, and Hsilin districts, in Hunan province.

## JAPAN.

According to K. Yamada, stibnite veins are found in the island of Shikoku. They are, as a rule, thin, and occur in schists and other palæozoic rocks. The gangue is generally composed of quartz, and sometimes of quartz and pyrite. (A.)

At Itshinokawa, the veins occur in sericite schist, having as gangue materials quartz and a little calc-spar, banded with druses which contain very large beautiful crystals. (A.) At the Nakase mine, the stibnite is gold-bearing. (B.)

At Kano, in the southernmost part of the Hondo peninsula, the veins are 2 to 9 feet in width, and continue for a distance of 6000 feet, cutting through the crystalline schist mountains. (A.)

At Totsugawa, south of Kyoto, the vein cuts through a quartzitic and graphitic schist. (A.)

The remaining localities are Nara, Ehrme, Yamaguchi.

## BORNEO.

In the northern part of Borneo (Sarawak) the antimony ore, sometimes accompanied by pure arsenic and arsenic sulphide, occurs in quartz veins, cutting through the limestone and the slate formations.

## COCHIN-CHINA.

Stibnite has been found between Quan-Yuen and Moucai in Tonkin. It has also been found in rounded stones or boulders of varying size, which have a peculiarly smooth yellowish-brown surface, accumulated in the beds of torrents.

## ASIA MINOR.

Stibnite, with quartz as gangue, is found in the vicinity of Smyrna.

\*The author will soon make a geological excursion in the province of Hunan.

## INDIA.

Antimony ore has been found in the following localities:—  
Tenasserim, Shigri, Jhelum district.

## AUSTRALIA.

*New South Wales.*—At a mine near Armidale, the vein varies in width from 10 inches to 15 inches. The ore has also been found at Hargrave's Falls and in the vicinity of Aberfoil. In the Macleay district the veins have been successfully worked. In the Bathurst district the ore occurs in blocks without any well-defined lode. On the Munga Creek, the ore is found to be enclosed in a quartzose matrix. (A.) East of Broken Hill, in the Barrier Range, the ore is argentiferous. A vein occurring in the crystalline schists of this region carries, wherever it cuts amphibolitic intrusions, rich silver-antimony ores, dyscrasite ( $Ag_2Sb_2$ ), stromeyerite ( $CuAgS$ ), and antimonious silver chloride, the gangue being calcite and iron-spar. (B.)

*Victoria.*—At Costerfield, antimonial reef is found. At Whroo, concretions of antimony ore are found in many veins. In this remarkable instance the sulphide is enclosed in successive concentric layers of oxide, with here and there scattered grains of gold. Stibnite is also found at Munster Gully, Dunolly, and at Donovan's Creek; the lode of the latter locality consists of nearly pure stibnite, attaining to a width varying from 1 foot 6 inches to 2 feet. At Sunbury, there occurs a vein having an irregular course approaching to the strike of the Silurian strata. This vein, 3 inches to 8 inches in thickness, carries about 2 oz. of gold per ton. (B.) Auriferous antimonial veins are said to occur 17 miles from Melbourne.

*Australasia.*—Antimony ores are also found in Queensland, New Zealand, and New Caledonia.

## SOUTH AFRICA.

Antimony ore is said to have been found in the Murchison Range in the Transvaal.

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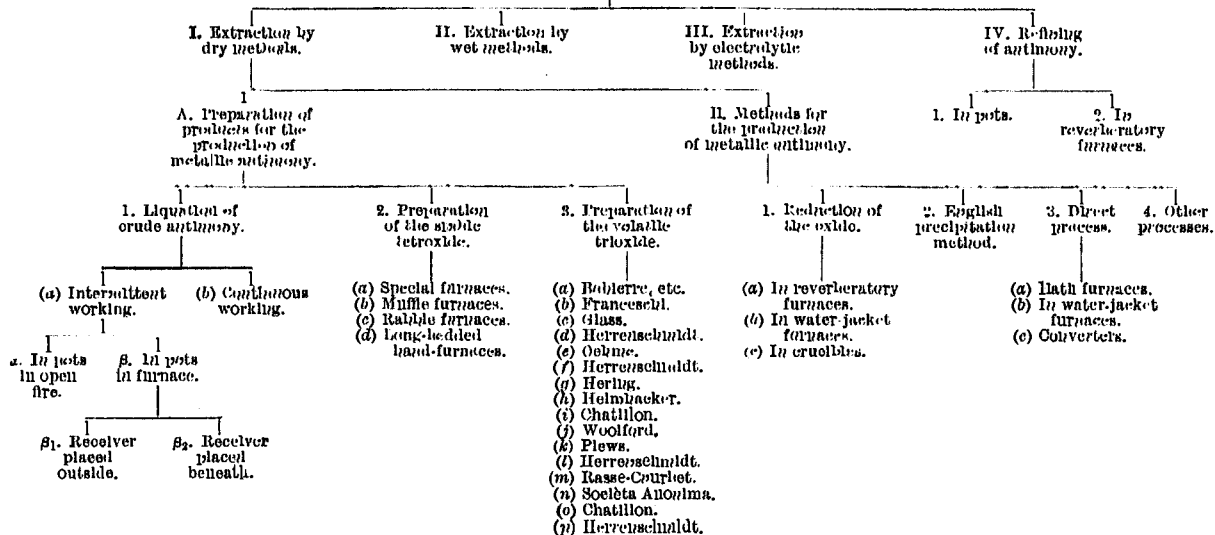
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## METALLURGY OF ANTIMONY.





## GENERAL SCHEME OF THE METALLURGY OF ANTIMONY.

### I. Extraction by dry methods.

#### A. Preparation of products for the production of metallic antimony.

1. Liquration of crude antimony.
  - (a) Intermittent working.
    - a.* In pots in open fire.
    - β.* In pots in furnace.
      - β*<sub>1</sub>. Receiver placed outside the furnace.
      - β*<sub>2</sub>. Receiver placed below the pot in the furnace.
  - (b) Continuous working.
    - a.* In tubes.
    - β.* In reverberatory furnaces.
2. Preparation of the stable tetroxide.
  - (a) Special furnace for ore dust.
  - (b) Muffle furnaces.
  - (c) Rabble furnaces.
  - (d) Long-bedded hand-furnaces (*Fortschaujelungsofen*).
3. Preparation of the volatile trioxide.
  - (a) Bobierre, Ruolz, Rousseau's process.
  - (b) M. de Franceschi's process.
  - (c) Glass' process.
  - (d) Herrenschildt and Borthwick's process.
  - (e) Oehme's process.
  - (f) Herrenschildt's process.
  - (g) Hering's                    "
  - (h) Helmhacker's            "
  - (i) Chatillon's               "
  - (j) Woolford's               "
  - (k) Plews'                    "

- (l) Herreschmidt's process.
- (m) Rasse-Courbet's     "
- (n) Miniere e Fonderie d'antimonio Società  
Anonima's process.
- (o) Chatillon's     "
- (p) Herreschmidt's process

#### B. Methods for the production of metallic antimony.

1. Reduction of the oxide (either tetroxide or trioxide).
  - (a) In reverberatory furnaces.
  - (b) In water-jacket or blast furnaces.
  - (c) In crucibles.
2. Extraction of metallic antimony from antimonium crudum.
  - (a) The so-called English precipitation method of reduction.
3. Direct processes, *i.e.* extraction of metallic antimony direct from the ore.
  - (a) Bath furnaces.
  - (b) Water-jacket furnaces or blast furnaces.
  - (c) Converters (Mannesse or Bessemer.)
4. Other processes.

#### II. Extraction by wet methods.

#### III. Extraction by electrolytic methods.

#### IV. Refining of antimony.

1. In pots.
2. In reverberatory furnaces.

## CHAPTER V.\*

### THE METALLURGY OF ANTIMONY.

THE principal ore for the extraction of antimony is sulphide of antimony or stibnite, commonly known as antimony-glance. The other ores—cervantite or antimony-ochre, kermesite, valentinite, senarmontite, which occur only in small quantities in nature— together with the fumes and slags from the previous smelting of antimony, are generally mixed up with antimony-glance preparatory to smelting. Dry methods are generally adopted for the extraction of the metal, or of the metal in different combinations, while the proposals for the use of wet processes or of electro-metallurgical methods have not yet found practical application. The more or less pure sulphide of antimony is called “crude antimony,” and the refined metal itself is called “antimony regulus.”

#### I. EXTRACTION BY DRY METHODS.

##### A. Preparation of Products for the Extraction of Metallic Antimony.

1. **Liquation of Crude Antimony.**—Ores containing more than 90 per cent. of the sulphide do not require any further treatment, and are considered to be crude antimony. Ores containing less than 90 per cent. and more than 40 or 50 per cent. are subjected to the liquation process for the production of crude antimony. The best size of the pieces of ore for this treatment is walnut size. Smaller-sized ore or ores of poorer quality are generally worked up for the production of the metal.

The maintenance of the proper temperature in the liquation process is very important, in order to obtain the best result. If the temperature is above a red heat the sulphide is volatilised, and if the tem-

\* In the compilation of this chapter, use has been made of the information contained in the standard metallurgical works of Phillips and Bauerman, of Bruno Kerl, and of Carl Schnabel in drawing up the descriptions of the older methods.

perature is too low the residue will contain too large a proportion of antimony, part of which at least should go to the liquated product as crude antimony. It has already been mentioned that the best size of the pieces of ore is that of walnuts; for, if the size is in any way smaller, the liquation process is less complete, and hence the residues are too rich in the sulphide; furthermore, fine ores lie so close together as to render the escape of the fused sulphide difficult.

(a) *Intermittent Working.*

As a rule, closed furnaces use more fuel and cost more for labour than open ones (reverberatory), which, on the other hand, lose more antimony through volatilisation and oxidation than closed ones. This loss can, however, be eliminated by the use of the condensation apparatus of Herrenschildt, to be mentioned later.

The smelting is done in pots, which are either heated directly by the burning fuel or by the flame coming from a fireplace. In the liquation in pots, the working is carried on intermittently, while continuous working is permitted in that of tubes or reverberatory furnaces, thus economising the consumption of fuel.

a. *Intermittent Liquation in Pots in Open Fire.*—Pots, being in direct contact with the fuel, are used at Wolfsberg in the Harz, at Magurka, Rosenau, and Gross-Göllnitz in Hungary, at Milleschau in Bohemia, and at Malbosc in France. The only merit

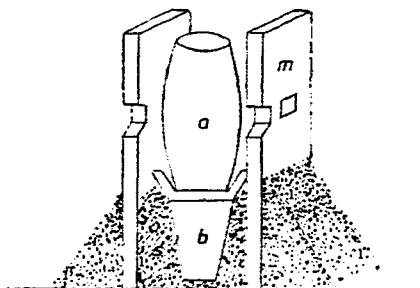


FIG. 3.

of this method is its simplicity, and for this reason it can be carried on without much difficulty at the mines. If the ores are rich and fuel (wood or coal) is cheap at the mine, this method can be used with advantage.

The pots are made of fire-clay, and are able to hold from 11 to 36 lbs. There are in the bottom of each pot four or five holes, each varying from 0.4 to 0.6 inch in diameter, through which the molten sulphide escapes. Below these pots rest receivers, made of burnt clay, for the collection of the liquefied crude antimony. These receivers are embedded in sand, ashes, or breeze, thus ensuring the slow cooling of their contents. The pots are arranged in several

rows at regular distances apart, each having from twenty to thirty pots. The rows of pots are separated from one another by walls of dry masonry, and fuel (coal or wood) is used to fill the spaces between the pots, and between the pots and the walls. The time required for one shift of the pots varies according to the amount of the charge,

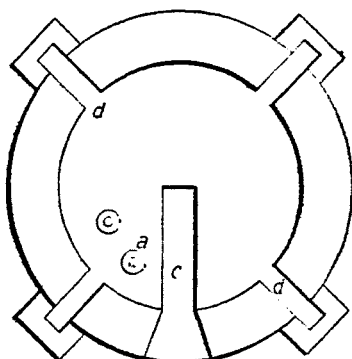
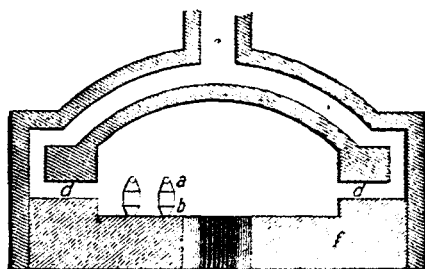


FIG. 4.

- a*, 0.5 m. high, 0.99 m. broad above, 0.26 m. wide at belly, 0.21 m. 0.24 m. below, with five holes, each above and below.  
 13 mm. wide. *c*, Fireplace.  
*b*, Belly-shaped vessel, 0.24 m. high, *d*, Leading to flue, *e*.

generally from two to twelve hours. At the conclusion of each shift the pots are lifted off from the receivers, emptied of their residues, again charged, and finally placed in position. The receivers may be emptied after each charge or when they are full. The residues contain, generally, not less than 12 per cent. of the sulphide.

Fig. 3 shows the arrangement of this method as used at Wolfsberg in the Harz. *a* is the pot; *b*, the receiver; *e*, the non-conducting

material; *m*, the masonry wall, provided with draught-holes. The pot is 12 inches in height, 8 inches in diameter, and holds 22 lbs.

At Malbosc (Ardèche), in France, the charge is 33 lbs. per pot. The receiver is emptied every forty hours, after four charges. During this period, twenty pots produce 1020 lbs. of the sulphide, with consumption of 3330 lbs. of coal and 448 lbs. of brushwood.

*β. Intermittent Liqutation in Pots in Furnace.*—Pots in a furnace give greater economy of fuel and render the working of poorer ores easier. The pots are placed on each side of the fire-grate in the furnace, or are arranged in a circle around it. The receivers are either placed directly below the bed of the furnace—in this case they are surrounded by sand to prevent their coming into contact with the flame—or they

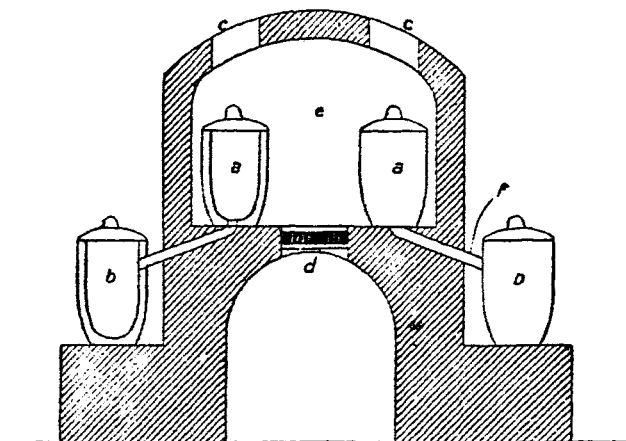


FIG. 5.

*e*, Heating chamber.  
*d*, The grate.  
*f*, Clay pipes.

*b*, Receiving vessels.  
*a*, Pots.  
*c*, Openings in the roof.

are placed entirely outside and are connected by clay pipes to the bottom of the pots. The latter arrangement is more satisfactory, as it does not necessitate the interruption of the working of the furnace when the receivers have to be emptied. A good example of the former can be seen from the works at La Lincoule in France. This is shown in fig. 4.

It can also be seen at Milleschau in Bohemia and at Banya in Hungary.

Each vessel carries 20 kgs. 1500 kgs. of 50 per cent. sulphide ore requires the consumption of 0.46 to 0.49 cb.m. of wood.

A good example showing the receiving vessels placed outside can be seen from fig. 5, as used in Hungary.

An intermediate form is shown in fig. 6.

(b) *Continuous Working.*

a. *In Tubes.*—Liquation in tube furnaces gives better results than those obtained with pot furnaces, the consumption of fuel being less and the production higher. Fig. 7 shows the construction of the furnaces used at Malbosc.\* while fig. 8 shows another type of tube furnaces.

The tubes are arranged in groups of four, placed over four receivers, *b*, which are carried on carriages, *c*, with wheels. There are three

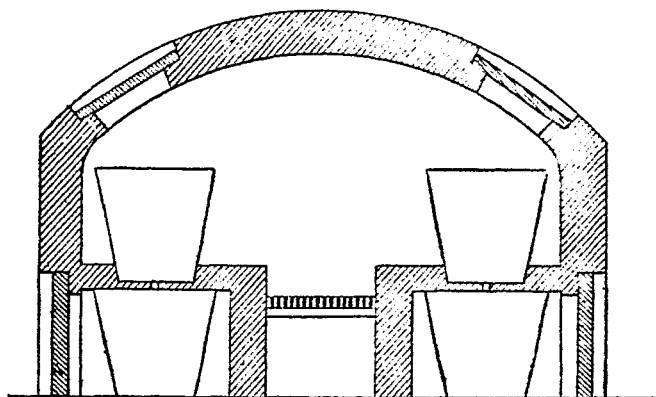


FIG. 6.

grates, *d*, from which the flame, after playing around the tubes, *a*, escapes into the chimney. *e* is a hole in the side of the tube, by means of which the residue is drawn out, the size being 2.7 ins. wide and 4.7 ins. high. The hole is closed with a clay plug or with a luted plate. The size of the tubes is 3 ft. 3 ins. high, 10 ins. in diameter at the upper end, and 7½ ins. in diameter at the bottom, their walls being 0.6 to 0.8 inch thick.

It must be noted that a newly built furnace must be heated to a bright red heat for forty-eight hours before a charge can be started. The regulation of the temperature is an important factor, and is adjusted according to the colour of the product, which should be of a bluish tint, while a red colour is an indication that the heat has been too great.

\* This has been replaced by the apparatus patented by Herrenschmidt.

The charge for each tube is 5 cwts. of ore; three hours are required for complete liquation; the yield is only 50 per cent. of the sulphide

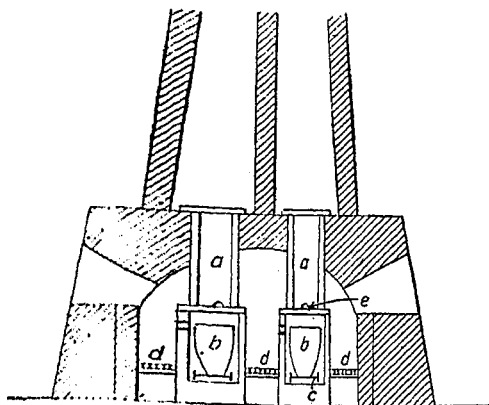


FIG. 7.

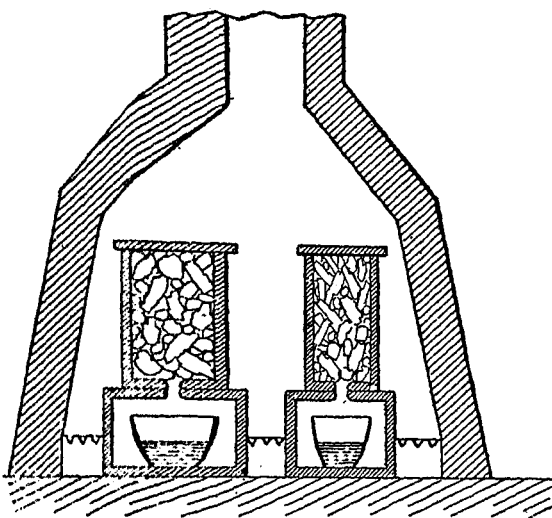


FIG. 8.

content; 64 cwts. of coal are used for the production of 100 cwts. of the sulphide; the tubes last twenty days each.

The cost of producing 100 kilos. of sulphide in tube furnaces is:—

Labour	. . . . .	1.53 fr. (=7.4d. per cwt.)
Fuel	. . . . .	1.28 fr. (=6d. ,, )



The cost of producing the same in pot furnaces is:—

Labour . . . . .	2.21 fr. (=10½d. per cwt.)
Fuel . . . . .	6.34 fr. (=2s. 8d. ,, )

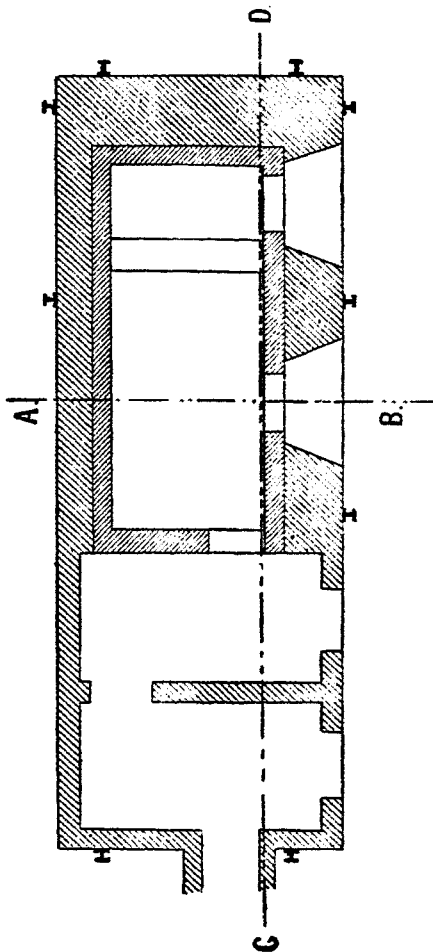


FIG. 2. — 1' diam. Scale = 10'.

*β. Continuous Liqation in Reverberatory Furnaces.*—This method of liqation possesses the merit of being the least expensive in fuel, labour, and repairs; but necessitates a great loss of the sulphide through volatilisation during the operation.

It can thus be seen that its adoption is only recommended where

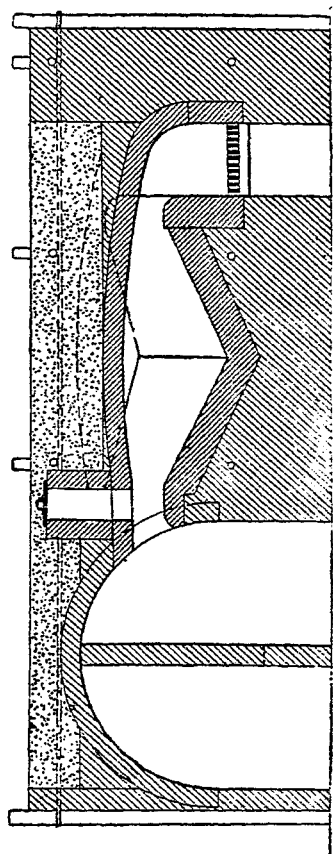


Fig. 10.—Section on C.D. Scale =  $\frac{1}{4}$  in.

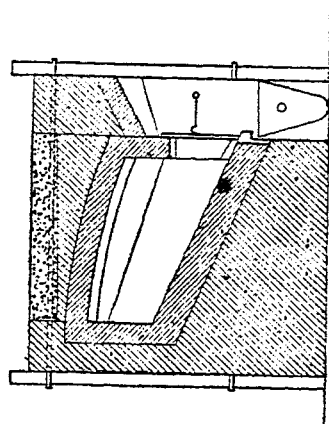


Fig. 12.—Section on A B. Scale =  $\frac{1}{4}$  in.

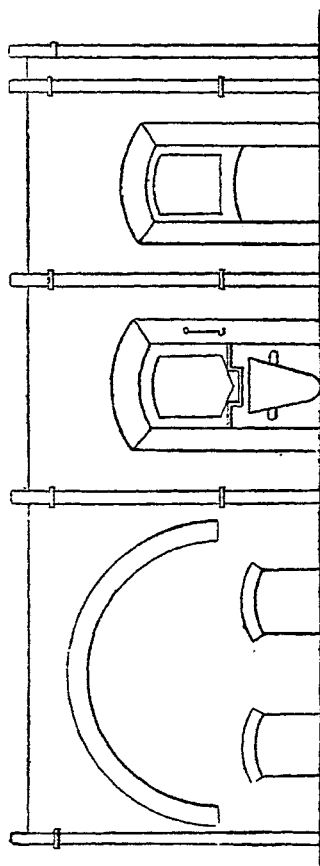


Fig. 11.—Perspective view. Scale =  $\frac{1}{4}$  in.

fuel is dear and the cost of mining is low, and where it is a question of producing large quantities of crude antimony with great rapidity. Thus, under these special conditions the loss of the sulphide may be practically neglected.

The construction of such a reverberatory furnace is that of the ordinary type, with the exception that there must be present a tap-hole at the deepest point of the bed for the removal of the liquated sulphide.

Figs. 9, 10, 11, 12 show the construction of a liquation reverberatory furnace.

The inevitable loss in tubes and in reverberatory furnaces can be prevented by using the condensation apparatus of Herrenschildt.

*Products of Liquation.*—The crude antimony thus produced generally contains some impurities (1 to 4 per cent. of iron sulphide and 0.2 to 3.4 per cent. of arsenic sulphide).

The following is an analysis of a liquation residue given by Bruno Kerl:—

$Sb_2S_3^*$	56.40
FeS	2.87
FeS <sub>2</sub>	1.23
SiO <sub>2</sub>	59.84
Al <sub>2</sub> O <sub>3</sub>	4.65
CaO	5.22
CO <sub>2</sub>	4.10
Alkali and carbonaceous matter	1.69

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The liquation residues, if sufficiently rich, are worked up for antimony regulus.

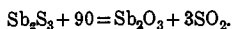
2. **Preparation of the Stable Tetroxide.**—Since the sulphide and the oxide of antimony ore are not mutually decomposed on heating, as are the sulphide, oxide, and sulphate of lead in the preparation of the metal from galena, a roasting and reaction process cannot, therefore, be used for the winning of antimony from its ores. When sulphide and oxide of antimony are melted together, a glass of oxy-sulphide is formed. Antimony tetroxide can only be reduced to the trioxide in the presence of the sulphide, while at the same time antimony glass is formed.

An oxidised ore is generally mixed up with the roasted sulphide for the reduction process; and any ore, when sulphuretted, is worked together with antimony glance.

\*The  $Sb_2S_3$  is not only found in the interior of the pieces, but covers them with a film of thin glaze.

The product of oxidising roasting may be either the stable tetroxide ( $\text{Sb}_2\text{O}_4$ ) or the volatile trioxide ( $\text{Sb}_2\text{O}_3$ ). The latter method is called "volatilising roasting" (Germ. *verflüchtigende Röistung*), and will be treated under the next heading.

The chemical changes which take place for the production of the stable tetroxide are as follows:—When antimony glance is heated not much above  $350^\circ\text{C}$ ., the trioxide is formed, with the evolution of sulphur dioxide:



A part of the trioxide is further oxidised to the pentoxide,  $\text{Sb}_2\text{O}_5$ , which, combining with some of the trioxide, forms the tetroxide,  $\text{Sb}_2\text{O}_4$ . When oxides of metals are present, antimonates are formed. If the ore contains a large quantity of sulphides of foreign metals, which would, under ordinary circumstances, form sulphates, if they alone were calcined, antimonates of the foreign metals are formed.

The roasted mass should contain the tetroxide principally, if the ore is comparatively pure and if the correct temperature and proper quantity of air have been maintained throughout the process of roasting. But ideal conditions are very seldom met with; hence the product may contain antimony glass, undecomposed sulphide, and antimonates, arseniates, and sulphates of foreign metals, if the ore contains these foreign sulphides and arsenic compounds.

According to Bidou, the proper temperature for roasting antimony glance is about  $350^\circ\text{C}$ .; if the temperature is too low, the sulphide is not decomposed, and consequently antimony glass is formed from the mechanically melting together of the sulphide and the trioxide at a dark red-heat; and if the temperature is too high, the mass begins to frit together, thereby preventing the penetration of air to the interior of the mass, and both the sulphide and the oxide are volatilised.

The fritting of the mass during roasting can be prevented by constant and regular rabbling. The presence of gangue has a good effect in obviating, partially at least, this difficulty. This accounts for the fact that, the richer the ore is, the more difficult it is to roast. But, with rich ores, it is impossible to prevent to some extent the loss due to the liquation of the sulphide and the formation of flue dust, which mainly consists of the trioxide, the tetroxide, the sulphide, arsenic compounds, and carbonaceous matter. Towards the end of roasting the temperature can be raised a little, in order

to further roast any remaining unoxidised sulphide. An ore properly roasted should have an ashy-gray colour on cooling, and should appear reddish in colour while in the furnace. Furthermore, it should give a soft feeling under the rabble and should be free from any fritting together of the mass. An excess of air is necessarily required for the formation of the stable tetroxide instead of the volatile trioxide.

The roasting of antimony glance for the production of the tetroxide is now carried out in reverberatory furnaces, provided with arrange-

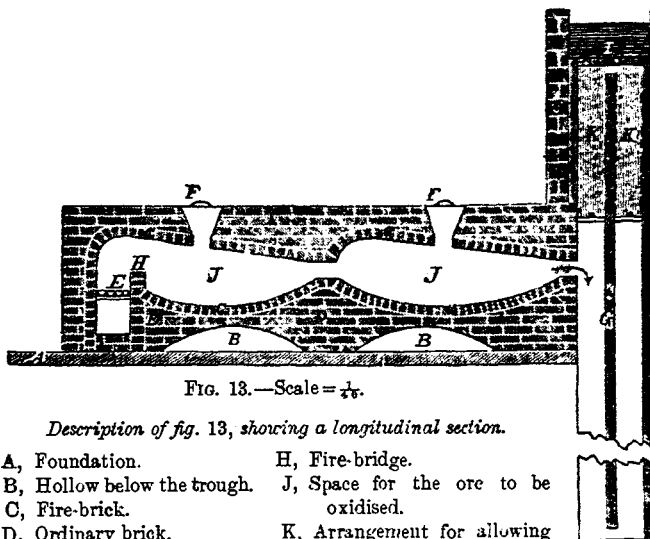


FIG. 13.—Scale =  $\frac{1}{4}$ ".

*Description of fig. 13, showing a longitudinal section.*

- |  |  |
|--|--|
| A, Foundation.                         | H, Fire-bridge.                                |
| B, Hollow below the trough.            | J, Space for the ore to be oxidised.           |
| C, Fire-brick.                         | K, Arrangement for allowing the water to drip. |
| D, Ordinary brick.                     | L, Water reservoir.                            |
| E, Grate.                              | M, Chimney.                                    |
| F, Funnel-shaped opening for charging. |  |
| G, Condensation chamber for the oxide. |  |

ments for condensation. In Hungary muffle furnaces and special furnaces for the roasting of ore dust were used in 1862; these will be described first.

The *special furnace* for ore dust is shown in figs. 13 and 14.

The stirring of the charge in this furnace must be attended to as frequently as possible, to prevent any fritting together of the mass.

The *muffle furnace* is shown in figs. 15 and 16. Its use is to make possible the production of more or less pure tetroxide, together

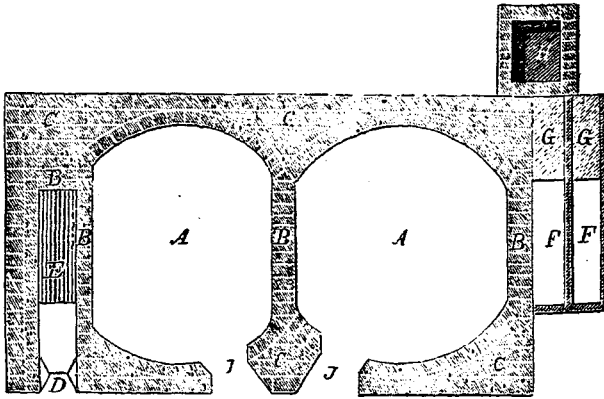


FIG 14.—Scale =  $\frac{1}{16}$ .

*Description of fig. 14, showing a plan-view.*

- |                       |                                       |
|-----------------------|---------------------------------------|
| A, Oxidation chamber. | F, Condensation chamber.              |
| B, Fire-brick.        | G, Arrangement for the water to drip. |
| C, Ordinary brick.    | H, Chimney.                           |
| D, Door.              | J, Working door.                      |
| E, Grate.             |                                       |

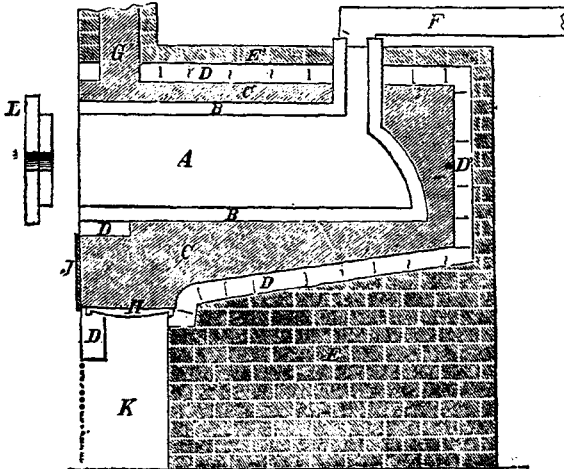


FIG. 15.—Scale =  $\frac{1}{3}$ .

*Description of fig. 15, showing a cross-section.*

- |                                    |  |
|------------------------------------|--|
| A, Muffle inside.                  | G, Outlet for smoke.   |
| B, The fire-clay muffle.           | H, Grate.  |
| C, Heating space.                  | J, Door.   |
| D, Fire-brick.                     | K, For ashes.  |
| E, Ordinary brick.                 | L, Profile of the cover, with hole for the admission of air. |
| F, Outlet for sublimation product. |  |

with a better control of the oxide and of the smoke coming from the fireplace.

The two kinds of reverberatory furnaces now in actual use for roasting are rabble furnaces and long-bedded hand-furnaces (*Germ. Fortschauelfungsofen*).

The *rabble furnaces* were used formerly at Bouc and Septaunes in France. Fig. 17 shows a plan view, while fig. 18 shows a section across A B. *a* is an egg-shaped horizontal bed, 8 ft. 3 ins. long, 4 ft. 7 ins. wide at its greatest width; *r r* are fireplaces, 5 ft. 3 ins.

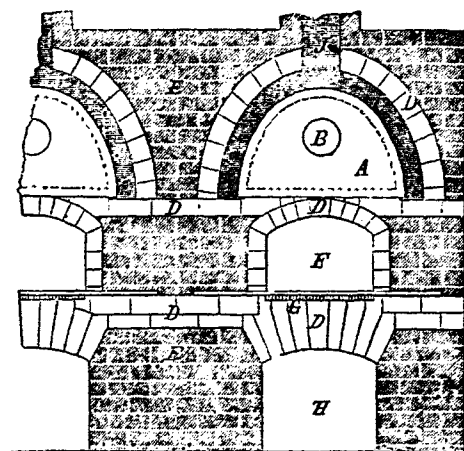


FIG. 16.—Front view. Scale =  $\frac{1}{4}$ .

- |                                   |                    |
|-----------------------------------|--------------------|
| A, Cover for the muffle.          | E, Ordinary brick. |
| B, Hole for the admission of air. | F, Door for fuel.  |
| C, Heating space.                 | G, Grate.          |
| D, Fire-brick.                    | H, Ash-pit.        |
|                                   | J, Exit for smoke. |

long and 1 ft. 2 ins. wide; *b*, door for working; *d*, flue leading to the main chimney; *f*, hood for the removal of antimonial fumes from the furnace-men. In six hours 5 to 6 cwts. of ground and sifted ore can be roasted in such a furnace; the door must be closed during the first two hours, but toward the end it is opened so that the workmen can stir and rabble the charge well. The loss of antimony in well-executed roasting is about 2 per cent.

At Siena the method of working is thus:—4 cwts. of fine ore charged at one time. Time of roasting = 3 to 12 hours, according to

the richness of the ore. Consumption of lignite per charge = 77 lbs.  
Loss of antimony = 5 per cent.

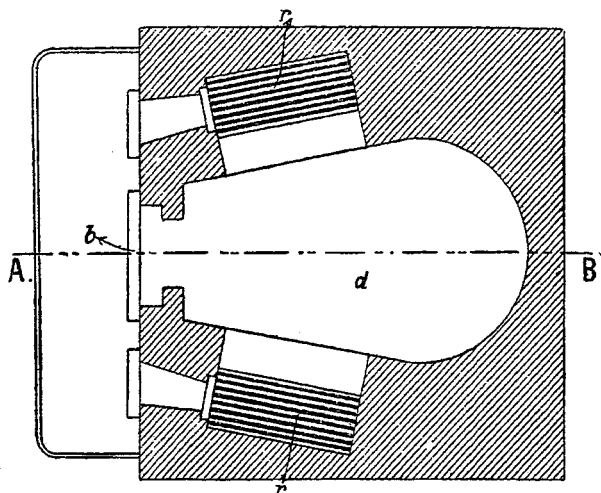


FIG. 17.—Scale =  $\frac{1}{4}$  in.

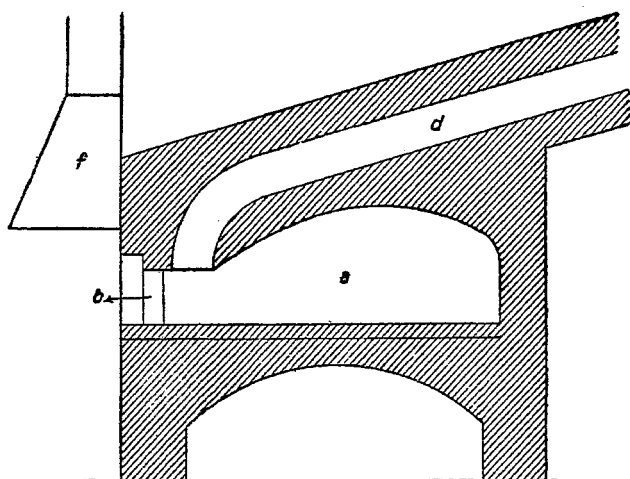


FIG. 18.—Section across A B. Scale =  $\frac{1}{4}$  in.

It must be noted that, the richer the ore is, the slower the roasting will be.

*Fortschaufelungsofen.*—The dimensions of this furnace (practically



a reverberatory furnace), as used in New Brunswick, are as follows:—

Length . . . . .	42' 6"
Width . . . . .	7' 6"
Working doors on each side . . . . .	10
Height from bed to roof . . . . .	2' 1"
Width of fire-grate . . . . .	2' 1"
Height of fire-bridge . . . . .	5' 2"
Breadth of fire-bridge . . . . .	1"

The method of working is as follows:—

Capacity of furnace . . . . .	30 cwts.
Charges . . . . .	5 to 6 cwts. at one time.
Shift . . . . .	} 3 charges (18 cwts.) during 24 hours, so that each charge remains in the furnace for 40 hours.
Consumption of wood . . . . .	
Loss of Sb . . . . .	7.5 per cent.

The ore must be strongly heated and thoroughly rabbled every five minutes during the last two hours before being drawn. Properly roasted ore must have a dull grayish-yellow colour.

The furnaces, as used at Banya, have the following dimensions:—

Length . . . . .	26' 3"
Width . . . . .	6' 6"
Working doors on each side . . . . .	5
Ores roasted in 24 hours . . . . .	24 cwts.

Charges of 4 cwts. each are introduced at the colder end of the furnace, and are then finally drawn after twenty hours at the opposite end. Stepped grate is used, and the fuel is lignite.

The following operation for roasting the ore is carried out in Tuscany, Italy:—200 kilos. are charged into a reverberatory furnace, heated up a little previously. The temperature is then raised to not more than 350°. Rabbling is carried on for from three to twelve hours. Rich ores require a longer time. Each operation requires 35 kilos. of lignite, and the loss due to volatilisation is not more than from 5 to 8.5 per cent.

Another type of the same kind of furnace is shown in figs. 19, 20, 21, 22.

Furnaces with a trough-shaped bed sloping towards one of the longer sides of the furnace have been proposed for the performance of both reduction and roasting at the same time. The use of having the slope is for the tapping off of any portion of the sulphide that is unavoidably liquated during the roasting.

3. Preparation of the Volatile Trioxide.—The so-called volatilising roasting is for the production of the volatile trioxide when the admis-

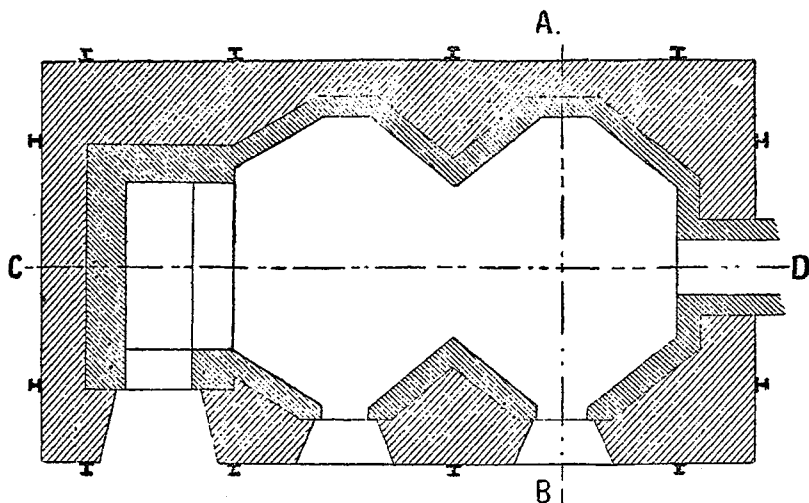


FIG. 19.—Plan. Scale =  $\frac{1}{8}$  inch.

sion of air is restricted and higher temperatures are maintained. Steam at a high temperature can effect the formation of the trioxide, with the simultaneous evolution of hydrogen sulphide.

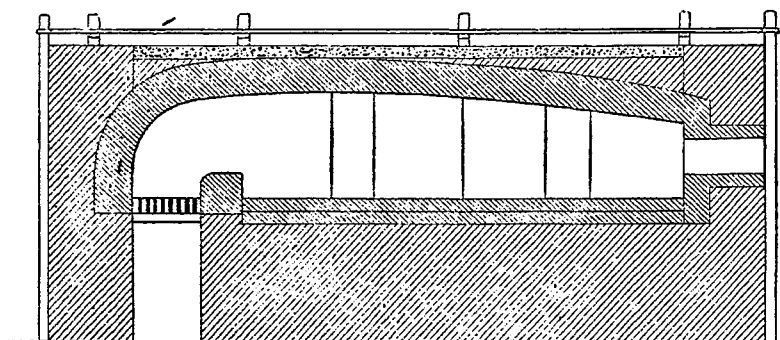


FIG. 20.—Section on C D. Scale =  $\frac{1}{8}$  inch.

The advantages of this method for treating antimony ore are:—

(1) The separation of arsenic from antimony, due to the fact that arsenic oxide is more volatile than antimony trioxide.

(2) If the ore contains gold or silver, the latter is generally found in the residues after volatilisation.

(3) This method makes it possible to treat low-grade ores, *e.g.* 7 per cent. to 20 per cent., with profit.

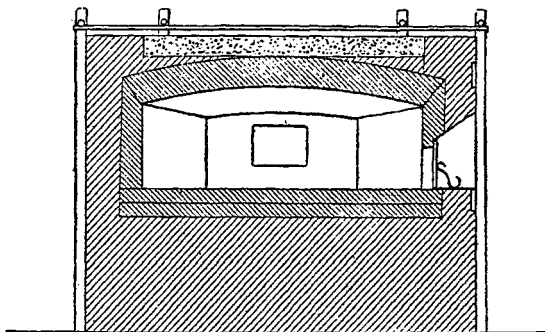


FIG. 21.—Section A B. Scale =  $\frac{1}{8}$  in.

(4) With different devices for condensation, the loss of antimony is practically nil.

(5) The economising of fuel.

(6) The trioxide, thus condensed, can be reduced to metallic antimony, or it can be used for other industrial purposes—for instance, to make paints.

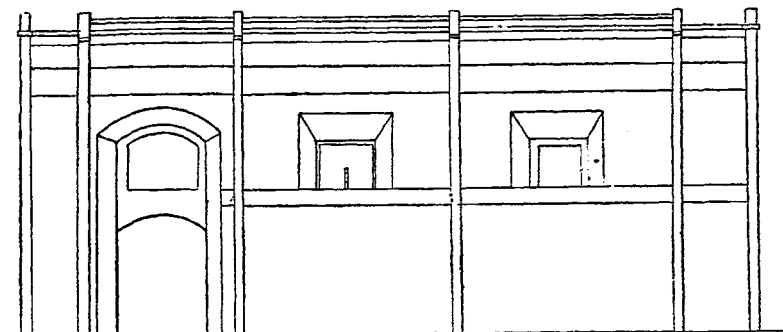


FIG. 22.—Perspective. Scale =  $\frac{1}{8}$  in.

From these we might be led to believe that this method forms the proper line of development of the metallurgy of antimony in the future, judging from the most favourable results that have already been attained in France, in which country this method has reached its highest perfection.

The historical development of the many processes based upon the volatilisation method that have been brought forward, is shown by the following list and descriptions :—

- 1844. Bobierre, Ruolz, Rousseau.
- 1858. M. de Franceschi.
- 1862. Glass.
- 1876. Herrenschmidt, Borthwick.
- 1880 (?). Oehme.
- 1881. Herrenschmidt.
- 1883. Hering.
- 1883. Helmhaecker.
- 1888. Chatillon.
- 1889. Woolford.
- 1902. Plews.
- 1903. Herrenschmidt.
- 1906. Rasse-Courbet.
- 1907. Miniere e Fonderie d'antimonio Società Anonima, Italy.
- 1907. Chatillon.
- 1908. Herrenschmidt.

These will be taken up in their proper order.

Bobierre, Ruolz, and Rousseau were the first persons to put forward the idea of producing antimony trioxide by the volatilisation method, in 1844. For a brief description of their process, see under Chapter VI.

M. de Franceschi followed in 1858 by using air only, and admitting it in limited quantities.

In 1862 Glass proposed to draw air through a bath of melted sulphide in order to obtain the volatile oxide and produce an impure regulus.

The next important step was taken by M. Herrenschmidt and Borthwick, who in 1876, in Australia, patented the process shown in fig. 23, especially applied to ores containing gold. This process consisted of a rotating roasting furnace, having the section of an elongated horizontal truncated cone, with a ventilator and a chamber for the deposit of the volatile oxide formed.

In 1880 (?) Oehme described the following process for producing very pure antimony oxide :—

In twenty-four hours 600 kilos. of ore can be treated. The charge must remain about twenty-four hours in the retort or muffle. The working of this process is not so easy as it appears, as some dexterity is required in admitting the proper quantity of air and water. The formation of more hydrogen sulphide than sulphurous acid indicates a deficiency of water added; if the air is in excess, the tetroxide is formed instead of the volatile trioxide. A dark-red heat is best for obtaining a satisfactory result. The residue of a well-

roasted ore should have a grayish appearance. Ore containing less than 30 per cent. of antimony is not suitable for this kind of furnace.

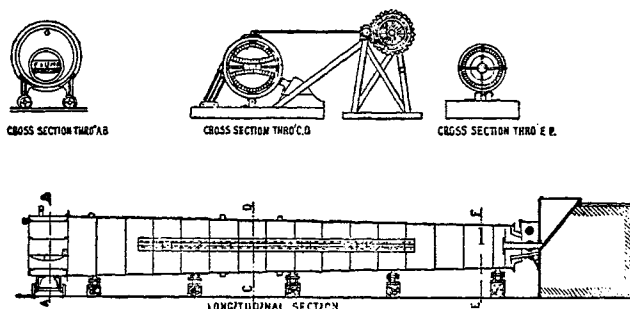


FIG. 23.—Herrenschmidt's revolving furnace.

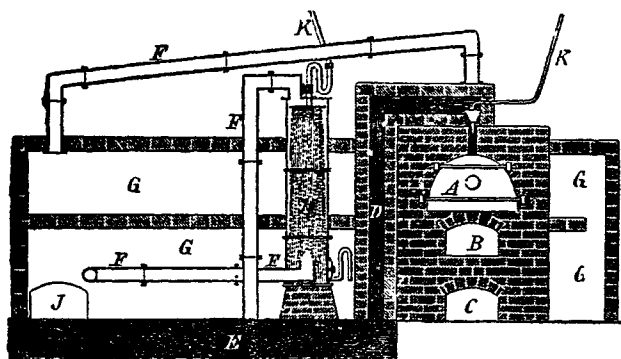


FIG. 24.—Scale =  $\frac{1}{4}$ .

- |  |   |
|--|---|
| A, The muffle in which the ore is to be volatilised.             | G, Condensing chamber.  |
| B, The fireplace.  | H, The last chamber in which any remaining gas is to be condensed by a stream of water running through K. |
| C, The ash-pit.  | J, Door for emptying the contents of the chamber.   |
| D, Iron flue, through which any uncondensable gases pass out.    | K, Small pipe to lead water into the muffle.  |
| E, Channel under the ground.                                     |   |
| F, Iron pipe leading the trioxide into the condensing chamber G. |   |

In 1881 M. Herrenschmidt patented a process,\* of which the following is a brief description :—

The natural sulphide ore, containing, say, 25 per cent. of antimony,

\* New South Wales patent No. 991, Oct. 10, 1881.

is introduced into a blast furnace or a cupola with 10 per cent. of coal. If the mineral is an oxide, then 25 per cent. of coal is required. In immediate connection with the furnace or cupola is a chamber for the condensation of the volatile oxide thus produced, and beyond it a reservoir containing water for the condensation of the last trace of the volatile trioxide. The practical working of this process may thus be summarised:—200 lbs. of coal are burned in the furnace or cupola; on it is put one ton of sulphide ore or 800 lbs. of oxide ore;

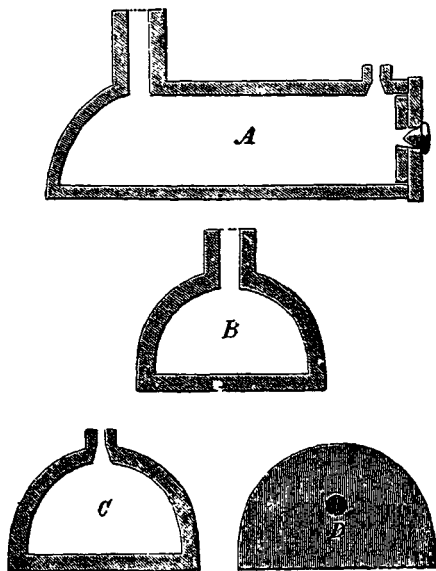


FIG. 25.—Scale =  $\frac{1}{4}$ .

A, Profile of the muffle.  
B, A section on the back.

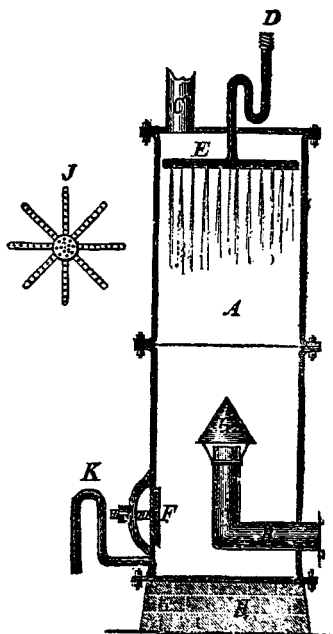
C, A section on the front.  
D, The cover, with an air-hole.

air is then drawn in by means of a ventilator; the oxygen of the air thus introduced combines in part with the antimony, forming the volatile oxide, and in part with the sulphur, forming sulphurous acid.

The process of Hering (1883) was analogous to that of Herrenschildt, the principal difference being that the roasting was effected in a reverberatory furnace.

In 1883 Helmhacker first mentioned the use of cloth or sack for the condensation of the fine volatile oxide, in place of water, which is so destructive to the metallic lining of the reservoir.

Chatillon, who is now the owner of several large antimony smelting works in Haute-Loire (France), patented a process\* in 1888, which is briefly thus:—Coke and ore are charged alternately into an ordinary roasting furnace, from which the volatile oxide thus developed is aspirated by a series of ventilators—generally three—into which boiling water is introduced for catching the volatile oxide in the currents passing through them; the last trace of the oxide is absorbed by the water contained in a series of basins.



- A, The inside of the chamber.
- B, Pipe for supplying antimony oxide.
- C, Outlet.
- D, Water-pipe.
- E, Star-shaped piece for sprinkling.
- F, Manhole.
- G, Protector-piece against the shower for the pipe.
- H, Brick foundation.
- J, Plan view of E.
- K, Water overflow.

FIG. 26.

Woolford's process (1889) is very similar to those described above.

M. Plews' patent† is as follows (1902):—The sulphide mineral is first broken into pieces not larger than 1 cubic centimetre, and is then charged into a furnace already heated to dark red by means of any kind of smokeless combustible material. An oxidising flame is then produced in the furnace, and the temperature is raised to light red and is so maintained until all the volatile oxide is given off. With certain minerals, the antimony is not easily volatilised by an

\* French patent No. 189,974, April 16, 1888.

† French patent No. 318,658, Feb. 13, 1902.

oxidising flame; in this case periodic alternations of an oxidising flame and of a reducing flame are maintained so long as necessary. Ventilators are used to produce a draught carrying the volatile oxide from the furnace into the chambers for condensation. The last trace of the oxide not yet condensed is finally absorbed in a basin of water. A rotative furnace of the ordinary type is preferred to any other kind. Coal gas or oil gas may be used. (Fig. 27.)

In 1903 M. Herrenschildt patented\* a process which is a great improvement upon his former patents. In order to thoroughly condense the oxide produced, the apparatus must possess a large cooling surface, have a large volume for facilitating the deposition of

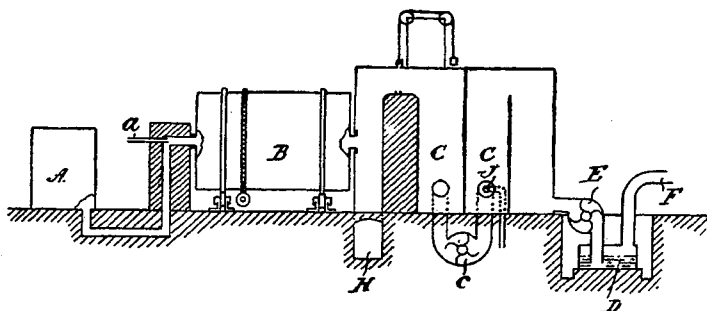


FIG. 27.

- |                                |                              |
|--------------------------------|------------------------------|
| A, Gas-producer.               | H, Flue in connection with a |
| a, Air inlet.                  | chimney, to be used when     |
| B, Rotative roasting furnace.  | an intense heat is required. |
| C C, Condensation chambers.    | The water vapour used may    |
| c, Ventilator.                 | be introduced at J.          |
| D, Reservoir containing water. |                              |

the oxide, and be able to subdivide the current of volatile oxide. The apparatus described below possesses these three principal factors. Fig. 28 is a longitudinal view, and fig. 29 is a transverse section.

Rasse-Courbet's process is as follows†:—Fig. 30 shows a longitudinal view and a section across A A of fig. 31, which is itself a section across B B of fig. 30. Fig. 32 shows the subsidiary parts of the apparatus. The furnace is composed of several muffles, *a*, and of a hearth. The muffles are so arranged that the flame may play around them through the canals, *c*, and then passes into the chimney, *d*.

\* French patent No. 333,306, June 23, 1903.

† French patent No. 362,453, Jan. 16, 1906.



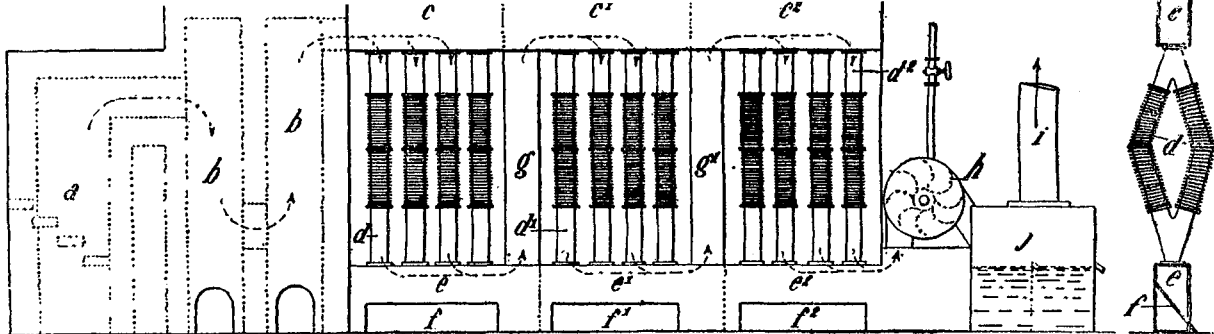


FIG. 28.

FIG. 29.

*a*, Roasting furnace for the production of the volatile oxide.  
*b b*, Flues placed immediately after the furnace.

*c c'*, Sheet-iron case.  
*d d'*, *Tuyaux à allettes*, i.e. tubes with outside linings.  
*e*, Another case at the base.

*f*, An inclined wall for the discharging of oxide deposited.  
*h*, Ventilator for aspirating the oxide.

*j*, Tub in which the uncondensable oxide is absorbed.  
*i*, Final outlet.

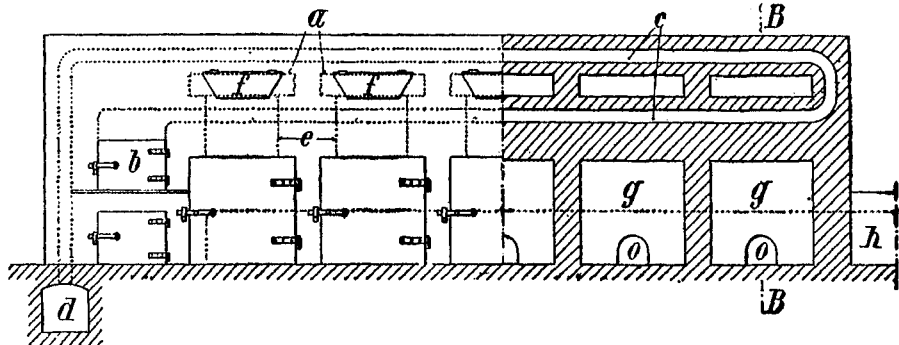


FIG. 30.

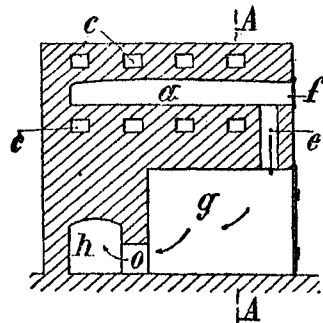


FIG. 31.

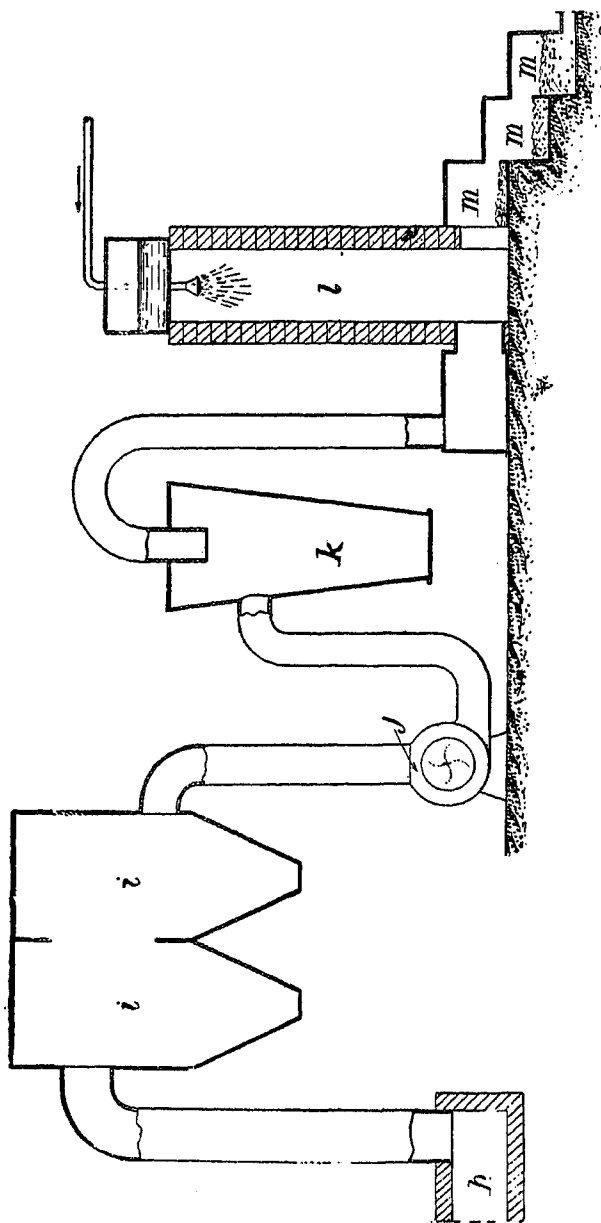


FIG. 82.

The mineral is introduced into the muffles through doors, *f*, which are closed during the roasting.

The muffles are not in communication with one another; each muffle has an opening through, *e*, into a chamber, *g*, which communicates, through an opening, *o*, with a channel, *h*, connected with the condensing chambers, *i*. The circulation of the vapour is obtained by means of a ventilator, *j*, placed immediately after the last chamber of condensation. The remaining gas, after passing through *h*, is washed by a water-shower in *l*, and then passes into the basins, *m*.

The *Miniere e Fonderie d'antimonio Società Anonima*, Genoa, Italy, one of the principal antimony smelters, patented in 1907 the following process\* :—

In other processes the oxide produced is generally condensed either in long flues, or on baffles, or in large condensation chambers. In many cases the volatile matter is mixed with water in the ventilators, after which the oxide is separated out by decantation. The condensation in these cases is not always complete, and the object of the present invention is to prevent any loss of the oxide by filtering through cotton, linen, or any other fabric that will arrest the oxide contained in the smoke.

In order to prevent the carbonisation of the tissues used, it is necessary to cool them to about 100°. If the oxide-containing fumes have too high a temperature, they must be cooled by passing them through chambers or metallic tubes more or less surrounded by water. Care must be taken not to allow the oxide at its early stage to come into contact with any water, as the presence of water would destroy the permeability of the tissue and lead to the formation of sulphurous acid. In order to overcome the resistance to the draught, offered by the tissues used, it is necessary to use ventilators.

Figs. 33, 34, 35, 36 represent cooling and condensing chambers; figs. 37, 38, 39, 40, filtering chambers.

Fig. 33 is a cross-section of fig. 34. The walls and foundations of these chambers are of masonry, stone-concrete, or sheet-iron. The roof is always bordered lengthwise by L-shaped plates, 2, so as to serve as evaporating basins for the water flowing over the roof. The condensed oxide falls into the sacks, 3, from which it can be discharged. Figs. 35, 36 show another form of condensing chambers, fig. 35 being a cross-section; the channels are arranged in chicanes, 5, with openings, 4, for the discharge of the condensed oxide.

Fig. 37 represents a cross-section, and fig. 38 a longitudinal section,

\* French patent No. 381,517, Sept. 4, 1907.

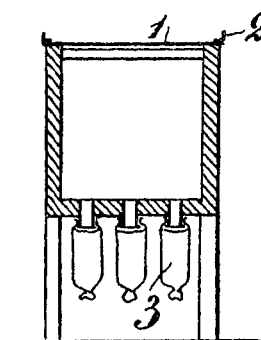


FIG. 33.

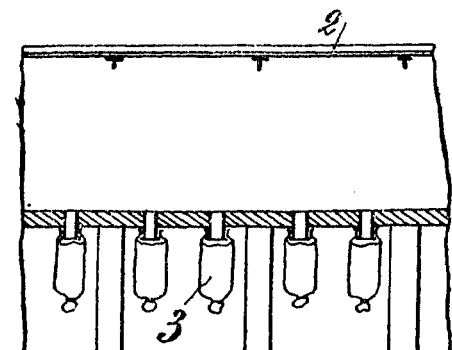


FIG. 34.

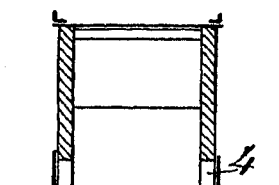


FIG. 35.

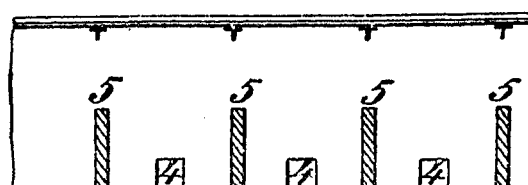


FIG. 36.

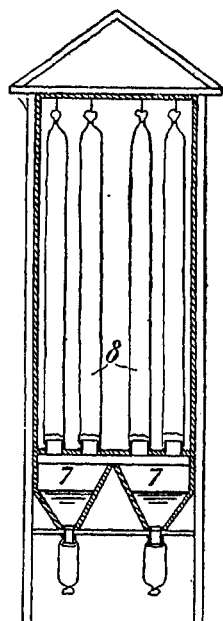


FIG. 37.

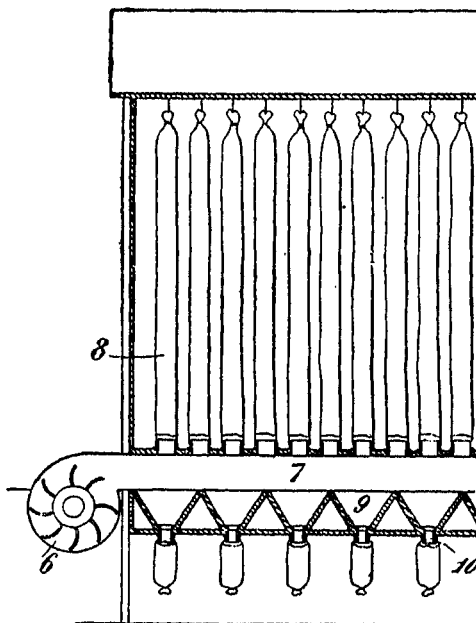


FIG. 38.

of the filtering chambers. The smoke from the condensing chamber is aspirated by a closed ventilator, 6, through the passage, 7, over which are hung a series of sacks, 8. The oxide, filtered off by means of these sacks, falls down into hoppers, 9, and is then discharged through 10. The remaining gas may then be taken to an ordinary chimney.

Figs. 39 and 40 represent another form of filtering chambers. The fume from the condensing chambers is aspirated by a ventilator (not represented) through tubes, 11, made of sheet-iron. Below these tubes are suspended the sacks, 12, by means of which the

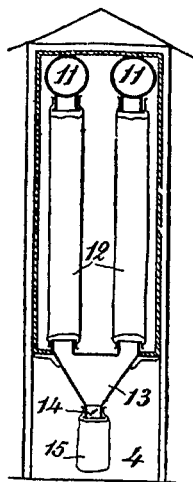


FIG. 39.

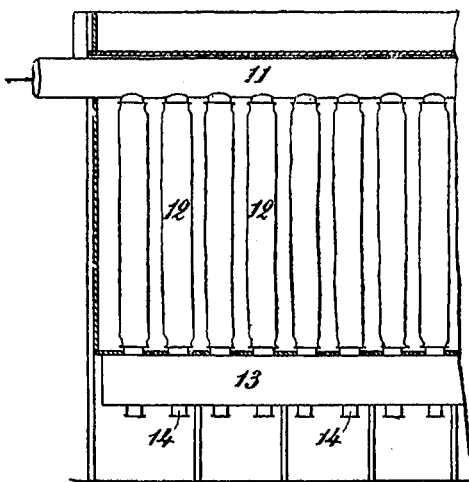


FIG. 40.

oxide is filtered off, falls into hoppers, 13, and is then discharged into 15, through 14.

M. Emmanuel Chatillon patented \* in 1907 another process which will be described later on. The main advantages of this process are :—

- (a) The possibility of treating ore dust.
- (b) The saving of the heat evolved, in the furnace as well as in the chamber of condensation. In the latter the heat is used to raise the temperature of the air before passing into the furnace.
- (c) The complete filtration of the oxide by means of sacks.

Fig. 41 shows a vertical section across A A of fig. 42 and B B of fig. 43. Figs. 42 and 43 are horizontal sections through C C and D D of figs. 41 and 44 respectively.

\* French patent No. 382 504, Oct. 3, 1907.

The roasting furnace is composed of two cupolas, *ab* and *cd* rectangular in section and communicating with the superior part, *e*,

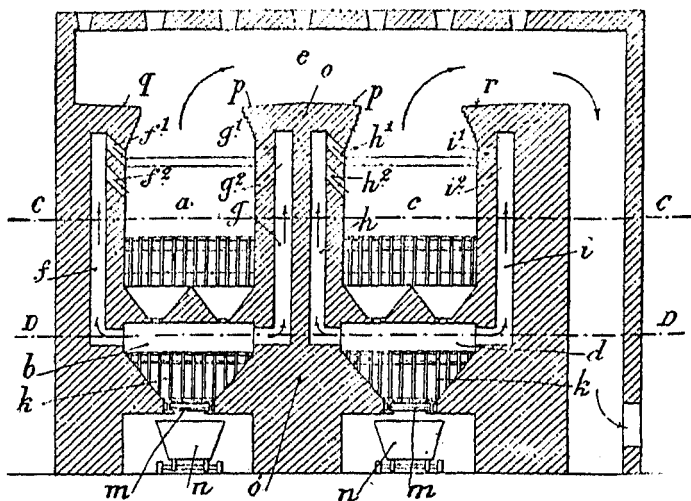


FIG. 41.

common to both; each cupola is charged, as usual, with alternate layers of combustible material and ore; each cupola, *a, c*, communicates with an inferior cupola, *b, d*, where the last traces of the oxide are

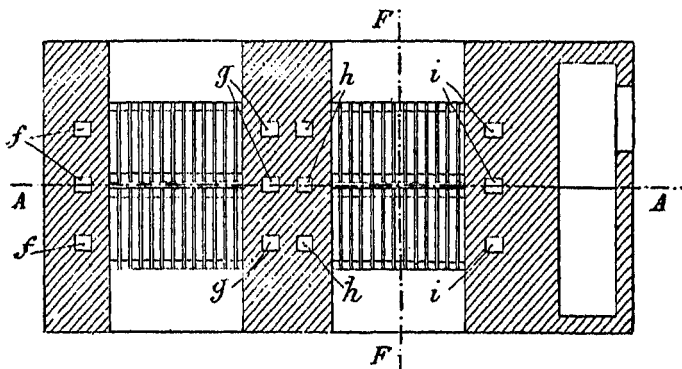


FIG. 42.

removed from the scoria, and where hot air is produced, which, together with the metallic gas, returns into the superior cupola through little channels in the masonry, *f, g, h, i*, and through *j<sup>1</sup>, j<sup>2</sup>, g<sup>1</sup>, g<sup>2</sup>, h<sup>1</sup>, h<sup>2</sup>, i<sup>1</sup>, i<sup>2</sup>*.

The inferior cupola also communicates with a kind of grated hopper, K, two surfaces of which consist of inclined bars and two

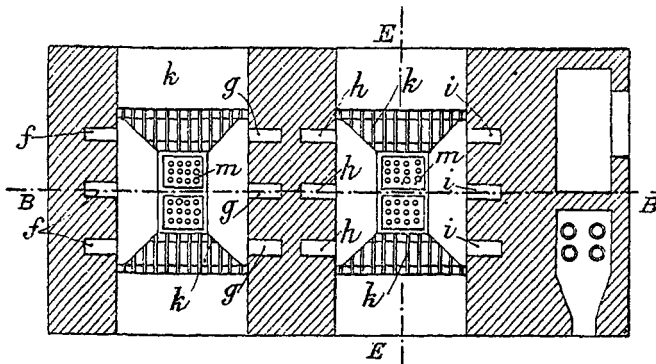


FIG. 43.

of inclined masonry. The finished scoria passes into this, and then through the movable register, *m*, into the waggon, *n*.

The parts *p*, *q*, *r* are enlarged by the corbelling out of the bricks,

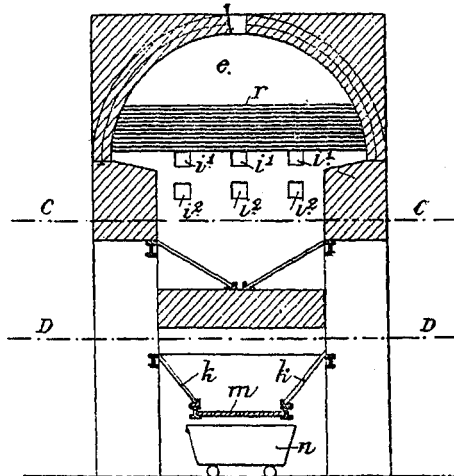


FIG. 44.

and are more or less inclined inward towards each cupola; they form a surface of about 4 metres square, and are destined to receive the dust ore, which is melted by the heat, falls into the cupolas drop by drop, and, on meeting the hot air coming into the cupola through

$f^1$ ,  $f^2$ ,  $g^1$ ,  $g^2$ , and  $c$ , is changed into volatile oxide. The filtering and condensing chambers may be connected with  $k$ .

The latest improvement in the volatilising process is embodied in a patent \* obtained by M. Herrenschmidt, with which the author is personally familiar. The fundamental principle is the same as that of his earlier patent, 1903; the only difference being in the details, which are clearly shown in fig. 45, and Plate opposite p. 100.

*The Herrenschmidt Process of Antimony Smelting.* (1) *Introduction.*—The present account is based upon a personal study of the new process, and contains the results of a few experiments carried out in the *Laboratoire de recherches industrielles pour tous minerais* of M. Herrenschmidt, at Le Genest (Mayenne), France, to whom all the credit is due. The experiments on the volatilisation process, given in the patent No. 386,107 taken out by M. Herrenschmidt April 5, 1908, in France, were carried out by that gentleman and myself on the 24th, 25th, and 26th of May 1908.

(2) *Description of the Apparatus.*—Fig. 1 of fig. 45 is a longitudinal section. Fig. 2 is a cross-section along  $a b$ . Fig. 3 is a cross-section along  $c d e f$ . Fig. 4 is a horizontal section along  $J Y$ .

The broken mineral is charged, together with a certain percentage of fuel, into the roasting furnace,  $a$ , the bottom of which is formed by horizontal iron bars,  $b$ , arranged symmetrically at even distances apart.

The volatile antimony trioxide is deposited on condensation pipes,  $c$  (Fr. *tuyaux à ailettes*), in the condensing chambers,  $d$ , by the aid of the two ventilators,  $h$ .

The last trace of the uncondensed oxide is laid down by the water coming from the coke-tower,  $i$ , at the top of which are the water-pipe,  $j$ , and the see-saw water-distributor,  $k$ . The roasting furnace is built partly of bricks and partly of cast metal; the condensing chambers are all of cast-iron; and the coke-tower is formed of wood. Each condensing chamber is 1 metre long.

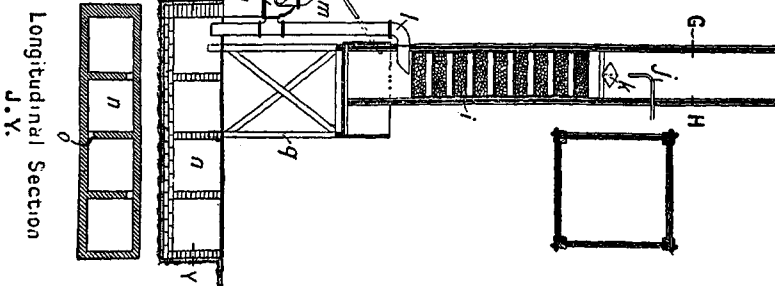
(3) *Description of the Process.*—(a) The guaranteed results of the apparatus just described are:—

The yield in oxide is never less than 90 per cent. of the metal contained in the ore.

With ores direct from the mine, containing 10 to 15 per cent. of antimony, 6 tons can be treated every twenty-four hours, with a consumption of 4 to 5 per cent. gas coke or 6 to 7 per cent. of charcoal.

\* French patent granted April 5, 1908, No. 386,107.





Longitudinal Section.

Fig. 1.

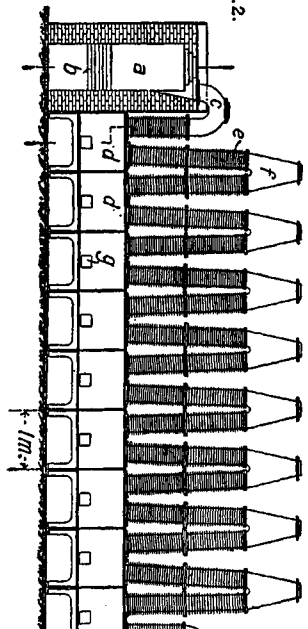


Fig. 2.

Cross Section  
C.D.E.F

Cross Section  
A.B.

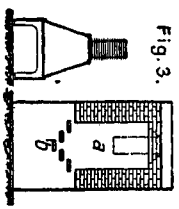


FIG. 45

With ores containing 18 to 20 per cent. of antimony,  $4\frac{1}{2}$  tons per twenty-four hours can be treated, with a consumption of 5 to 6 per cent. gas coke or 7 to 8 per cent. charcoal.

The gold, if present in the quartz of the ore, is almost all recoverable from the scoria.

For each apparatus four workmen are employed in the twenty-four hours, and 3 H.P. is used for the ventilators and pump.

(b) The working conditions.—The best size of ore to be treated is from 1 to 4 centimetres. The ore dust must be separated out and, if in large quantity, can be moulded with 7 to 8 per cent. of clay into balls of the proper size and charged along with the ore.

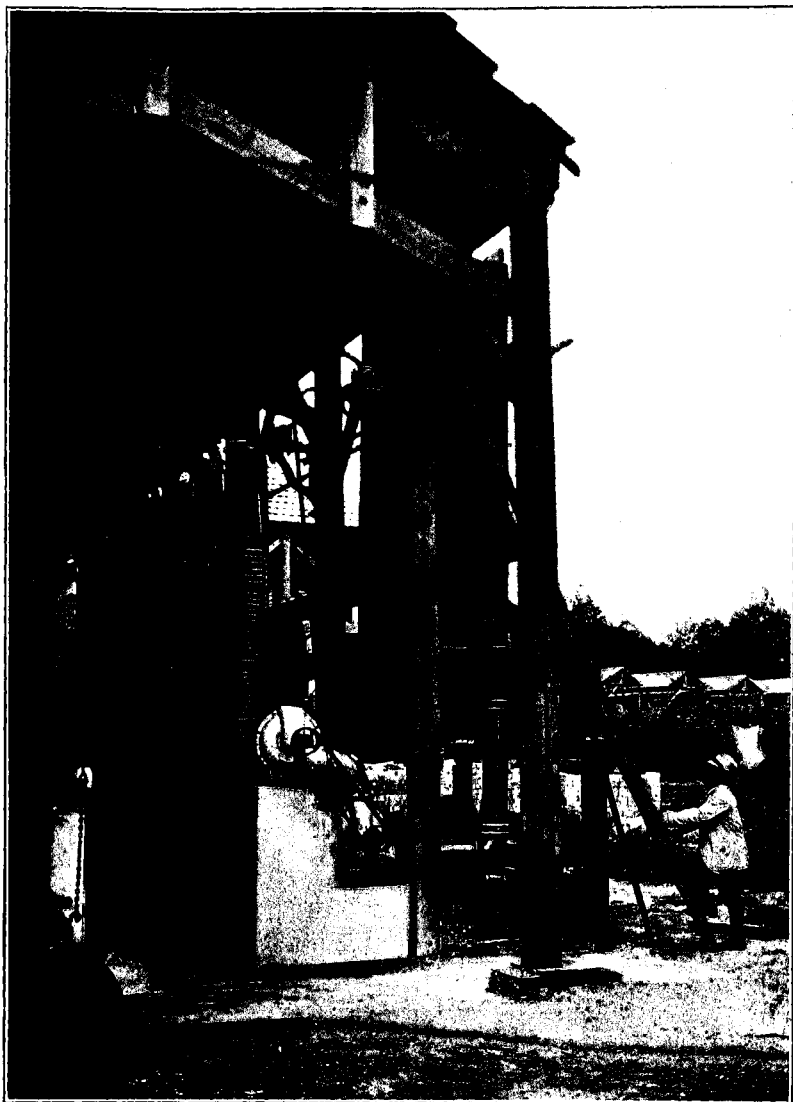
(c) The actual working is thus:—The roasting furnace is at first charged with old scoria up to a height of about 10 centimetres above the uppermost iron bar forming the bottom; then enough wood and charcoal are put in to a height of another 10 centimetres; as soon as they are lighted and burn freely, another charge of 300 kgs. of old scoria, mixed with 6 per cent. of charcoal, is put in; and, finally, when the burning is thorough and the furnace is hot, a charge of 50 kgs. of ore (containing about 15 to 20 per cent. Sb) mixed with 2 kgs. of charcoal is put in, and this is continued until the furnace is full to within 30 centimetres from the mouth. The same charge is continued every 12 to 14 minutes, according to the rate of revolution of the ventilators—which is from 1200 to 1400 revolutions per minute—and the scoria is discharged accordingly.

Gas coke gives better results, if it is obtainable; and, if it is used, only 2 to 6 per cent., or 1 to 3 kgs. for every 50 kgs. of the same class of ore, are necessary, according to the richness of the ore roasted.

The temperature of roasting should not be more than 400° C.

Water used per day for one apparatus is 30 cubic metres.

(4) *Results of the Experiments.* (a) *First Experiment.*—The furnace was lighted at 8.30 a.m. on the 24th of April, and it was not until 10.5 a.m. that the furnace was hot enough to admit the first charge. The working was continued regularly until 11 p.m. of the same day; the total working time was therefore 12 hours 55 minutes. The charging was as follows:—Each charge consisted of 50 kgs. of ore, minus the ore dust, which had previously been sieved off. The first three charges were mixed with 10 per cent. of charcoal, the fourth to the tenth charges with 4 per cent., the eleventh to the nineteenth with 2 per cent., and from the nineteenth to the last with 4 per cent. The total charges amounted to 2850 kgs. of ore.



HERRENSCHMIDT ANTIMONY FURNACES.



The products of roasting ( $\text{Sb}_2\text{O}_3$ ) are:—

1st condensing chamber . . . . .	76 kgs.
2nd „ „ . . . . .	65 „
3rd „ „ . . . . .	65 „
4th „ „ . . . . .	48 „
5th „ „ . . . . .	49 „
6th „ „ . . . . .	44 „
7th „ „ . . . . .	34 „
8th „ „ . . . . .	2½ „
9th „ „ . . . . .	19 „

Total = 424 kgs.

It should be noted that the cleaning of the chambers and pipes for the removal of all the oxide was carried out in the next experiment.

(b) *Second Experiment.*—The first charge in the second experiment commenced at 11.5 a.m. on the 25th of April, and the last charge stopped at 10.30 p.m. of the same day, thus giving a total of 11 hours 25 minutes working time. Each charge consisted of 50 kgs. of ore mixed with 4 per cent. of charcoal. The total charges amounted to 2725 kgs. of ore.

The products of roasting ( $\text{Sb}_2\text{O}_3$ ) are:—

1st condensing chamber . . . . .	176 kgs.
2nd „ „ . . . . .	103 „
3rd „ „ . . . . .	96 „
4th „ „ . . . . .	61 „
5th „ „ . . . . .	45 „
6th „ „ . . . . .	38 „
7th „ „ . . . . .	32 „
8th „ „ . . . . .	28 „
9th „ „ . . . . .	23 „

Total = 602 kgs.

These numbers represent the actual amount of oxide extracted from the ore, *plus* the cleanings of oxide, due in part to the first experiment

Further cleaning of the pipes and chambers gave 32 kgs. The condensing tanks, *n*, in fig. 4 of fig. 45, gave 178 kgs. of dried oxide. Now, if all had been thoroughly cleaned up—the pipes, the condensing chambers of the coke-tower, and the precipitating tanks—there would have resulted at least 5 kgs. of oxide more.

(c) *Conclusion.*—The ore treated contained 19.5 per cent. of antimony.

The oxide found in the first chamber contained 23 per cent. of impurities.

An analysis of an average sample of the oxide from the other chambers gave .5 per cent. of impurity.

Total quantity of oxide obtained :—

1st experiment . . . . .	424 kgs.
2nd „ . . . . .	602 „
Dried oxide (from tanks) . . . . .	178 „
Cleanings . . . . .	32 „
Estimated cleanings . . . . .	5 „
	<hr/>
	1241 kgs.

The amount of ore treated was :—

1st experiment . . . . .	2850 kgs.
2nd „ . . . . .	2725 „
	<hr/>
	5575 kgs.

The actual quantity of pure oxide obtainable was :—

$$\begin{aligned}
 & 1241 \cdot [(76 + 176) \times .23 + (989 \times .005)] \\
 & = 1241 - (58 + 5) \\
 & = 1178 \text{ kgs. of pure oxide, which is equivalent to about 981 kgs. of pure Sb.}
 \end{aligned}$$

Now, since the ore analyses recorded 19.5 per cent. Sb, then in 5575 kgs. of ore there are 1087 kgs. of Sb.

Hence the percentage loss is :—

$$\frac{1087 - 981}{1087} \times 100 = \text{a little less than 10 per cent.}$$

Again, the scoria, when analysed, was found to contain only 1.3 per cent. of Sb, which is equivalent to 52 kgs. of Sb considered as loss in the scoria ( $52 = 1.3 \text{ per cent.} \times 4000 \text{ kgs. of scoria}$ ). Most probably, if the different parts of the apparatus were thoroughly cleaned of their oxide, the loss would not be more than 5 per cent.

Practically, in twenty-four hours  $5\frac{1}{2}$  tons of such ore can be treated, with a consumption of 4 per cent. charcoal. It is most probable that at least 7 tons could be treated per day, if the rate of revolution of the ventilators were increased from 1200 to 1400 per minute.

The reason why charcoal was used in these experiments is that, although gas coke gives better results from an economical point of view, it is not easily obtainable in some of the out-of-the-way places, where perhaps the price of charcoal is not very far above that of gas coke, if not actually less.

Generally speaking, it costs about 70 francs to produce one ton of oxide by this process in France.

The complete apparatus described above costs 10,000 francs.

## B. Methods for the Production of Metallic Antimony.

1. **Reduction of the Oxide.**—The object of this is to reduce the oxide (trioxide or tetroxide) to metallic antimony, commonly called antimony regulus. Now, if coal were the only agent used for the reduction, there would be a great loss due to volatilisation, and, in addition, some unaltered sulphide of antimony in the roasted ore. Therefore alkaline substances like potash, soda, Glauber salt, etc., are added in order to form a fusible slag, which, being lighter than the metal produced, would form a cover over the metallic bath, thus preventing any possible volatilisation, and would dissolve any sulphide of antimony present. This slag also serves as a refining medium, removing any impurities present from the final metallic product.

The working expenses of the roasting and reduction process are less than those of the precipitation method, and hence it is suitable for the working of poorer ores and liquation residues, while the latter can only be adopted—and even then very rarely—when ore is rich, but coal and labour cheap.

(a) *Reduction in Reverberatory Furnaces.*—In the ordinary way, this process is simple and can easily be controlled, but there is a considerable loss of antimony; hence it is adopted when ores are rich and fuel is cheap. The loss of metal amounts to at least 12 per cent., and sometimes, according to Helmhacker, to as much as 30 or 40 per cent. This kind of furnace has been in use at Bouc, at Septèmes, at Siena, and in New Brunswick.

At Bouc and Septèmes, the roasted ores are generally worked up together with oxide ores from Algiers, and with antimonial flue dust.

The furnace-beds are egg-shaped, 7 feet 10 inches long, 5 feet 3 inches wide in the centre, and 3 feet 4 inches at the fire-bridge. The fire-bridge is 1 foot 4 inches above the fire-bars and 1 foot below the roof. The bed is a deep and hollow one, built of fire-brick, and slopes from every part to a tap-hole through which the metal flows into a tapping-pot placed below it. The maximum height of the roof above the bed is 3 feet 3 inches. The opening by which the charge is introduced is 1 foot 4 inches wide. The flue, about 8 inches in diameter, generally leads into condensing chambers 400 feet long, for the deposition of the antimonial vapour. At the end of the system of condensing chambers is the main chimney.

Figs. 46 and 47 show the type of reverberatory furnace used at Spetèmes.

Figs. 48, 49, 50, and 51 show another type of the same furnace.

The dust obtained from the condensing chambers contains up to 50 per cent. of antimony. The charge for this furnace consists of 400 to 500 lbs. of roasted ore, oxidised ores, and flue dust, 90 to 110

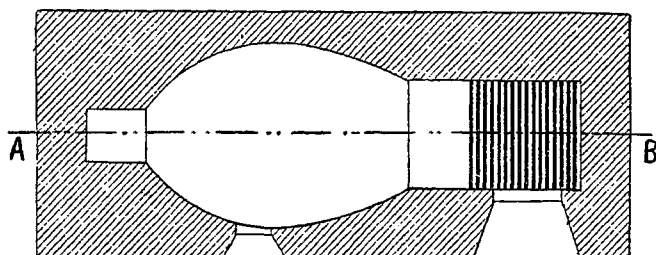


FIG. 46.—Scale =  $\frac{1}{4}$  in.

lbs. of a flux consisting of salt, smaller quantities of soda, and sometimes a small quantity of Glauber salt, 65 to 75 lbs. of ground charcoal, and 220 to 330 lbs. of slag from previous charges, the slag containing principally common salt.

The furnace is first charged with the fluxes and is then fired ; about

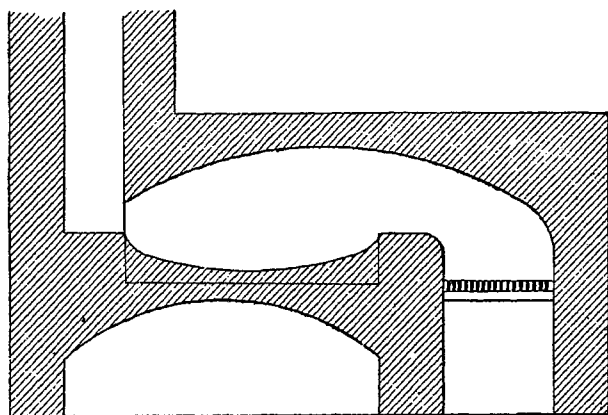


FIG. 47.—Section A B. Scale =  $\frac{1}{4}$  in.

an hour after their charging the liquefied fluxes will remain in a state of tranquil fusion. The other ingredients are then charged in portions of about 44 lbs. at intervals of fifteen minutes, and are well stirred. The scum produced after each charge is drawn off through the working door. The furnace is strongly fired after the last charge.



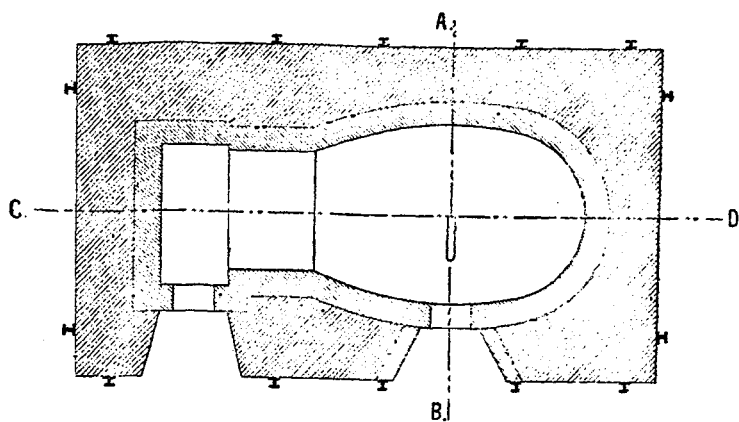


FIG. 48.

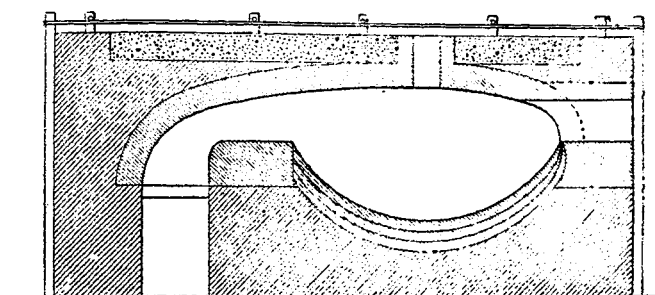


FIG. 49.—Section C D.

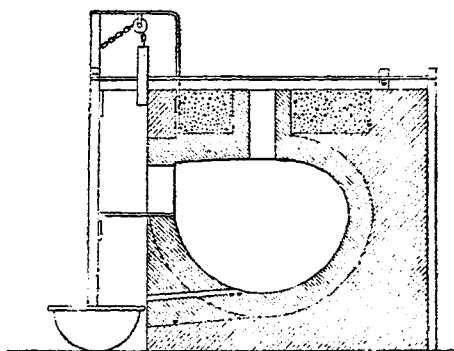


FIG. 50.—Section A B.

Altogether, the process occupies from four to six hours. The combined action of the charcoal and soda is to separate the antimony from its oxygen and sulphur compounds, while the gangue is slagged by the soda, and the foreign metals, if present, are carried into the slag as sulphides by the action of the sulphide of soda resulting from the reduction of the Glauber salt by the charcoal. The influence of the salt added is like that of the Glauber salt and soda, acting as a flux and as a cover, and in addition carrying the foreign metals present into the slag as chlorides.

The fuel consumption is 5-6 cwts. per charge, and the loss amounts to 14 or 15 per cent.

It must be borne in mind that the metal drawn off from the tapping-hole must be covered over with the slag during its cooling in

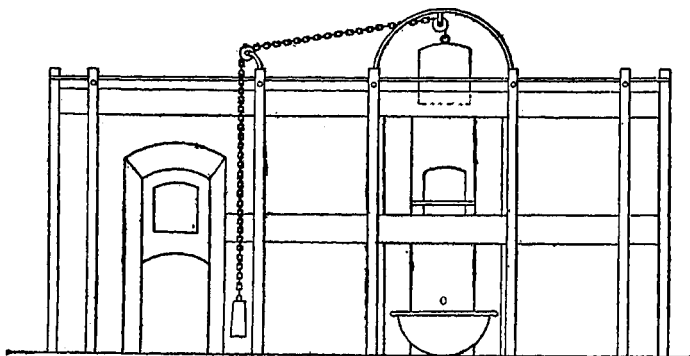


FIG. 51.—Front view.

the tapping-pot. When solid, the regulus is freed from its slag by hammering.

The following figures were obtained from the working of 830 charges as practised at Siena :—

368,838	lbs. of roasted ore.
268,918	,, sea salt.
12,641	,, soda ash.
88,628	,, Glauber salt.
38,205	,, slag from previous charges.
4,409	,, iron slag.

The antimony obtained weighed 113,573 lbs.

In New Brunswick the reduction and the refining are carried out consecutively in the same operation. The furnace dimensions are: diameter, 8 feet 6 inches; the depth in the centre is 1 foot 6 inches; the beds are built of fire-clay and are concave,

The operation is thus :—

Roasted ore charged at a time . . . . .	5 cwts.
Cover of Glauber salt . . . . .	1 cwt.
Coarse, hard wood-charcoal, powdered . . . . .	82 lbs.

Before the first charge is made the bed of the furnace must be heated to redness. The charge generally melts in about four hours, when it begins to effervesce, with the evolution of carbonic oxide, which escapes through the layer of slag and burns. The charge is rabbled until boiling ceases, when it is allowed to settle for half an hour. After this the charge is allowed to cool by leaving the fire-door open. This is continued until the slag attains a low red heat and, being in a pasty condition, is drawn off. Refining materials—27·5 lbs. of Glauber salt and 11 lbs. of wood-charcoal—are immediately added, and the furnace is strongly heated. After an hour and a half, when boiling ceases, the metal and the slag are drawn off together into an iron mould. Care must be taken to leave at least half an inch of slag as a cover for the metal, thus preventing the possibility of the metal solidifying before the mould is filled. As soon as the ingot becomes solidified, the slag—essentially a sulpho-salt of antimony mixed with sodium carbonate, containing about 15 per cent. of antimony—is removed and is again smelted with one-fifth of its weight of iron for subsequent use.

At one of the works in Hungary the refining is said to be combined with the reduction. In a reverberatory furnace 5 cwts. of roasted ore are smelted with 10 per cent. of small coal, together with 3 to 6 per cent. of Glauber salt, for twenty hours ; after the removal of the slags thus formed, 22 to 25 lbs. of slag from a previous refining of antimony are added. The lading of the metal is commenced as soon as this is fused.

According to M. Herrenschmidt, the trioxide produced by the volatilisation method can be reduced in the following way :—An ordinary reverberatory furnace furnished with condensing apparatus, as shown in fig. 52, is previously heated before the following charge is commenced :—

10 parts of the trioxide.
6 parts of crude antimony.
1 part of carbon (charcoal or anthracite).

After six hours the charge must be thoroughly rabbled, with the result that antimony metal is formed.

The following proportions may be employed :—

80 parts of trioxide.
20 parts of sulphide (crude).
12 to 15 parts of carbon.

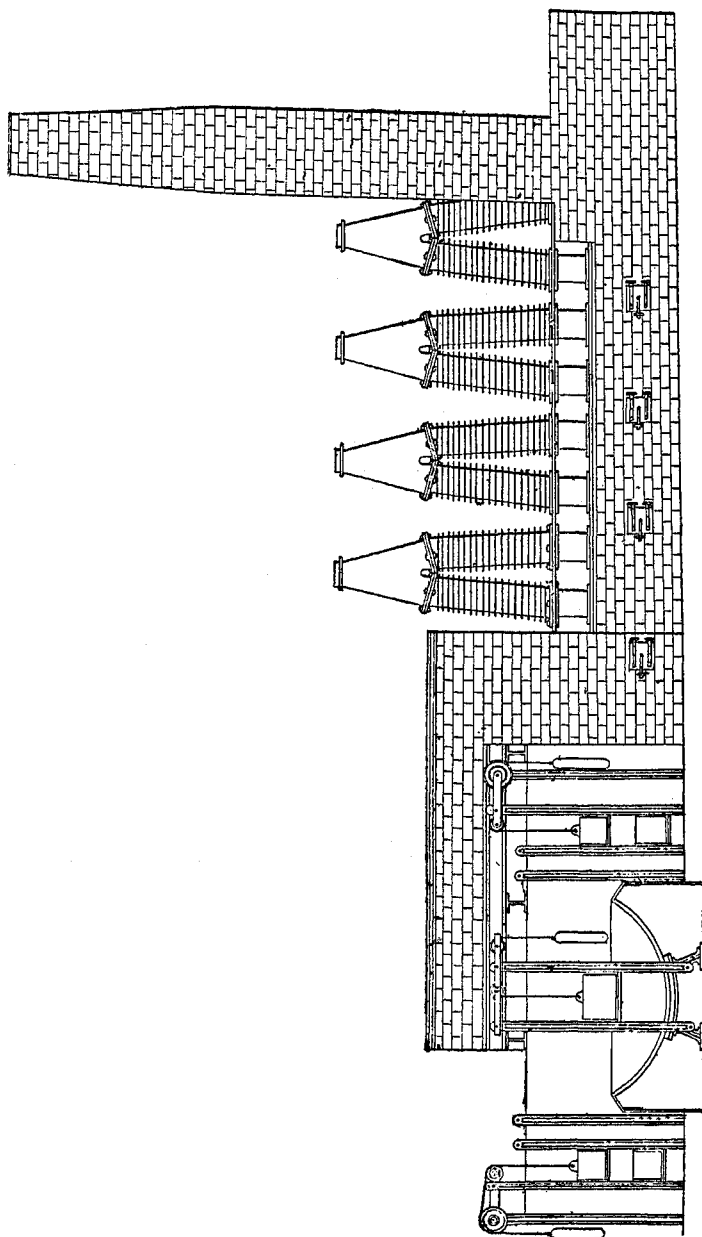


FIG. 52.

The starring of the metal can be brought about by using a purifying mixture of 6 parts of carbonate of soda and 4 parts of antimony trioxide, which has previously been melted in a small chamber at one end of the reverberatory furnace. This mixture should be poured out as soon as the metal is allowed to run into moulds.

(b) *Reduction in Water-jacket or Blast Furnaces.*—At Bouc and Septèmes, ores containing 30 to 40 per cent. of antimony were at first roasted in reverberatory furnaces, and the roasted product was reduced in three tuyered shaft furnaces which were worked on the “spur” principle with covered “eye.” Their dimensions were: height, 10 feet 10 inches; depth, 2 feet 7 inches to 3 feet; width, 1 foot 11 inches. In twenty-four hours 2 to 2½ tons of ore were worked, with the consumption of one-half the weight of ore of coke. The crude metal produced contained 92 to 95 per cent. of antimony, and was refined.

Hering proposed to work the liquation products, with the composition shown on previous page, in a circular shaft furnace of the following dimensions:—

- Height, 19 feet 8 inches.
- Diameter at the tuyere level, 3 feet 4 inches.
- Blast, 530 cubic feet per minute, at a pressure of 7·8 inches of water.
- Residues melted, 7 tons.
- Tap cinder added, 150 per cent.
- Limestone used, 40 per cent.
- Gypsum or Glauber salt, 5 per cent.
- Coke consumption, 14 per cent.

At Bányá, near Schläining, in Bohemia, antimony ores, consisting of sulphides and oxides, mixed with a considerable proportion of siliceous waste, are smelted in a blast furnace for crude antimony, which is then refined in a reverberatory furnace.\*

The average percentage composition of the materials charged into the blast furnace is given in the table on page 110.

The furnace has a round stack 6 m. high, 1·4 m. in diameter at the throat, and 1 m. at the hearth, which is provided with five water-tuyeres and three outlets for the molten product—an upper one for slag, and two at the bottom. One of these has a slight rise for tapping, while the other, which is horizontal, is used for blowing out the furnace.

Blast, supplied by a screw-blower, gives 15 cb.m. per minute at 30 cm. water-pressure. The gases are collected by a tube leading from the side of the furnace a short distance below the throat. The

\* This is taken from *Berg. u. hütt. Ztg.*, 1886, p. 102, as translated by Bauerman in his *Elements of Metallurgy*, p. 494.

furnace is kept continuously in blast for three weeks, and smelts about 19 tons of material daily.

	Dressed Ores.		Oxidised Ores.	Liquation Residues.		Flue Dust.	Refining Slag.
	Raw.	Calcined.		Raw.	Calcined.		
Sb	43.3	48.9	46.4	21.4	23.1	56.1	25.7
Fe	14.4	...	...	12.9	...	...	...
S	25.3	0.7	3.6	15.1	2.4	...	...
Fe <sub>2</sub> O <sub>3</sub>	...	23.4	2.4	...	17.3	6.9	...
SiO <sub>2</sub>	11.7	23.3	26.6	41.6	49.2	10.8	5.9
Al <sub>2</sub> O <sub>3</sub>	0.3	4.0	...	0.5	2.4	...	...
CaCO <sub>3</sub>	3.3	...	7.0	4.0	...	...	...
CaO	...	1.0	...	4.0	0.7	...	...
Sb <sub>2</sub> S <sub>3</sub>	...	...	...	...	...	...	...
FeS	...	...	...	...	...	...	2.4
Na <sub>2</sub> S	...	...	...	...	...	...	53.4
C	...	...	...	...	...	5.0	9.0

The smelting mixtures are of two kinds:—

	Kilos.	
	A.	B.
Calcined dressed ores	550	600
Calcined liquation-residues	750	600
Ores balled with lime	200	...
Flue dust balled with lime	100	...
Raw ore	...	100
Oxidised ore	...	100
Raw liquation-residues	...	100
Limestone	600	800
Foul furnace-slugs	400	400
Refining slugs	...	200
Crude Sb, Metal No. III.	...	100

The most favourable result is obtained when these mixtures are used alternately, two charges of A being followed by one of B.

Lime, about 10 per cent., is used to ball up part of the washed ore to a compact mass, and 7 per cent. lime is used for the same purpose for the flue dust. This is only necessary at the beginning, for it is found that after eight days' blowing these stuffs can be charged as powders without interfering with the working of the furnace.

The products are unrefined metallic antimony, slag, and flue dust. The antimony is divided into three classes:—

	I.	II.	III.
Sb	90.02	73.80	65.04
Fe	6.23	16.66	23.80
S	2.85	8.42	10.46

The first two are sent to be refined, and the last is taken back to the blast furnace.

The relative proportions of the total production of the furnace:—

No. I is	.	.	.	.	.	82.5
„ II. is	.	.	.	.	.	9.0
„ III. is	.	.	.	.	.	8.5

The slags vary in composition:—

		I.	II.
SiO <sub>2</sub>	.	46.9	45.9
CaO	.	34.6	31.4
FeO	.	15.1	19.9
Sb	.	0.5	0.9

No. I. is obtained from mixture A, and No. II. from mixture B.

Calcination is effected in a reverberatory furnace. Length, 8 m.; breadth, 2 m. Five working doors on each side. Heated with brown coal upon a step-grate furnace. The production is 1200 kilos. per day.

The ore, charged in 200-kilo. lots, clots and softens, giving off a large quantity of sulphurous acid as soon as it attains red heat, but subsequently becomes dry and in the state of powder. The average time for a charge to remain in the furnace is twenty hours.

The refining of the metal is conducted in a reverberatory furnace, with an iron bed 4 m. long by 2.5 m. broad, covered with a layer of fire-clay 0.28 m. thick. Brown coal is used upon an ordinary grate. The furnace is provided with working doors on one side and tapping-hole at the end of the bed. The gases evolved are used to warm the moulds before they are used. The charge is as follows:—

450	kilos.	No. I. (coarsely broken).
50	„	„ II. (in powder).
42	„	sulphate of soda.
5	„	charcoal dust.
150	„	unroasted ore.

Operation lasts ten hours; and a final slag is obtained by the addition of 3.40 kilos. of carbonate of potash, 2.60 kilos. of carbonate of soda, 1 kilo. of raw and 6 kilos. calcined crude regulus (liquated sulphide of antimony), 12 kilos. of the same slag from previous operations. The impurities of refined antimony are:—

As	.	.	.	.	.	0.330	per cent.
Fe	.	.	.	.	.	0.052	„
Ag	.	.	.	.	.	0.006	„
S	.	.	.	.	.	0.720	„

According to Herrenschildt, the following process is possible with the use of a water-jacket furnace.

Balls, about the size of an egg, are made of the following composition :—

The trioxide . . . . .	82 per cent.
Carbon (anthracite or powdered charcoal) . . . . .	12 „
Carbonate of soda . . . . .	6 to 7 „

These balls are charged into the furnace with 5 to 20 per cent. coke. The loss of oxide is about 33 per cent., which can be recovered from the condensing chambers, as shown in fig. 45.

The metal thus obtained has to be remelted, either in a crucible or in a reverberatory furnace, for the purpose of “starring.”

(c) *Reduction in Crucibles.*—This method, on account of its high cost, is only adopted when the ores are rich or when crude antimony or the volatile oxide is available. The use of crucibles and pot furnaces precludes the possibility of working large quantities.

The roasted ore is fused with 10 per cent. of its weight of crude argol, or with charcoal or anthracite and potash or soda, in crucibles made of fire-clay, heated in a wind furnace or in a galley furnace. The mould in which the melted metal is cast must be coated with tallow or with a thin layer of fire-clay cream.

According to Knab, we have the following :—

One crucible contains 26·5 lbs. of roasted ore, with 10 per cent. of charcoal and 7·15 per cent. of salt or soda.

Pots are arranged 10 or 12 in each furnace.

Each pot turns out 4 or 5 charges in 24 hours.

Consumption of coal, 70 to 80 per cent. of weight of ore.

Life of each pot, 7 or 8 charges.

A new process\* just discovered by Herrenschmidt consists of melting, in a crucible, balls of the following composition :—

Antimony oxide.
Powdered anthracite.
Carbonate of soda.
Water.

The decided advantage of this process is that the “starring” of the metal can be effected in a single operation.

The furnace used is shown in fig. 53.

2. **Extraction of Metallic Antimony from Antimonium Crudum.**—This method is only applicable to rich ores and crude antimony. The following process to be described involves the use of rich ore; if crude antimony is under consideration, the composition of the charge

\* The author is under obligation not to give the details until the patent is taken.



should be adjusted accordingly. The fundamental principle involved in this method is that, when iron is added, the sulphur of the stibnite ore has more affinity for the iron, and consequently iron sulphide is formed, even at a comparatively low temperature, the antimony being separated out in the metallic state. Owing to the high specific gravity of the iron sulphide, it is difficult to completely separate it from the metallic antimony; and, for this reason, sodium sulphate and carbon are added in order to produce sodium sulphide, which, combining with the iron sulphide, forms a fusible slag of low specific gravity.

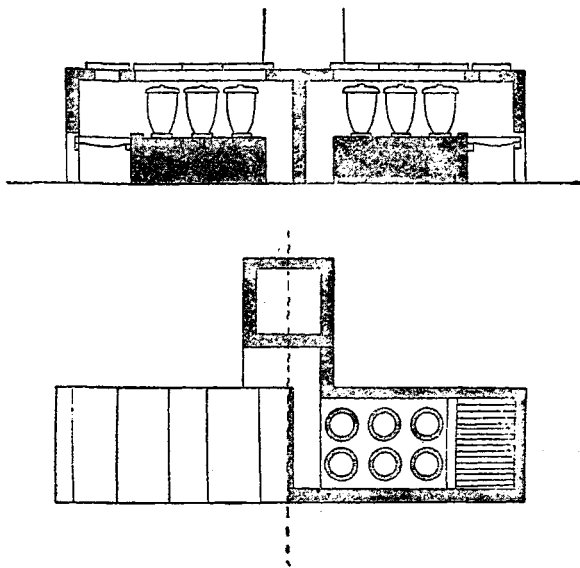


FIG. 53.

In England, instead of sodium sulphate and carbon, common salt is used. As a rule, iron, in the form of turnings, shavings, or tin-plate cuttings, is used. The proportion of iron used must not be in any way too high, as, if sulphides of lead and arsenic are present in the ores, they will then be reduced by the excess of iron, and enter into the antimony as impurities.

In most cases the theoretical proportion of iron required to desulphurise the antimony sulphide is not sufficient, because, when sodium sulphate and carbon are used, part of the iron is used in decomposing the sodium sulphate. According to Karsten, it has

been found by experiment that, with 10 per cent. of Glauber salt and 2 to 3 per cent. of coal, 44 per cent. of iron is required; whereas Liebig states that 42 per cent. is sufficient, while Hering uses only 40 per cent. The following proportions are given by Berthier:—Antimony sulphide, 100; forge scale, 60; soda, 45 to 50; coal dust, 10. Iron separates out as  $\text{FeS}$ , or as  $\text{Fe}_8\text{S}_7$ , according to Schweder.

In England, where the ores used are free from the impurities of lead and arsenic, iron is generally used in excess, part being afterwards eliminated by a subsequent fusion with more sulphide of antimony.

The loss of antimony occasioned during the process is due to volatilisation and slagging: 64 per cent. is the yield, as given by Karsten, when crucibles are used; but Berthier gives 65 to 67 per cent.; whereas, theoretically, the yield should be 71.5 per cent.

This process is generally carried out in crucible furnaces, as adopted in England, Hungary, and other places; but shaft furnaces have been used experimentally; reverberatory furnaces are sometimes used, in spite of the great loss of antimony.

The English process\* of smelting is as follows:—

The ores for smelting must be free from lead and arsenic. The ore is ground under edge runners and passed through a coarse screen, the largest to pass through being the size of a hazel-nut. After grinding, a sample is taken to be assayed for the amount of iron. The process consists in reducing the sulphide by metallic iron in crucibles in a long reverberatory furnace. The dimensions of the furnace are: 54 feet long, including the fireplaces, 7 feet 4 inches broad (inside size), covered by a low arch which springs almost from the surface of the ground, the bed itself being below the ground level. It is heated by a fireplace at each end, communicating into a common flue in the middle of the floor of the furnace. The crucibles are lowered into their places through circular holes (14 inches in diameter) in the arch. There are forty-two holes, twenty-one on each side. There are two 4-inch holes in the furnace roof at each end of the bed, used for the removal of clinkers, etc. The sides and roof of the furnace are covered with cast-iron plates. The pair of crucibles nearest the fireplaces at each end is kept for "starring" or refining the crude metal. The charge for each crucible is: 42 lbs. of ground ore, containing about 50 per cent. of antimony, 16 lbs. of iron, 4 lbs. of common salt, and 1 lb. of skinmings from the next operation, or else the same weight of impure slag from a previous melting. The iron usually consists of

\* Taken from "Antimony," by Professor Kemp, *The Mineral Industry*, 1892, p. 23.

13 lbs. of wrought iron, but not cast iron. Tinned scrap is preferred; and, if it is used, it is beaten up into a round ball, large enough to fit the top of the crucible. The remaining iron is in the form of turnings or borings, mixed with the ore together with the salt. The mixture is dropped into the crucible through a funnel; the furnace hole is then closed for about half an hour, when the crucible is again examined. The salt used assists the separation of the slag, and tends to promote the fusion of the siliceous matters of the ore. On an average four meltings can be made in each crucible per twelve hours; the richer the ore is, the shorter is the time required.

The crucibles used are generally 20 inches high and 11 inches outside across the mouth. They are made of a mixture of good fire-clay and plumbago, which latter must be free from iron. The clay used has the following compositions:—

	Stourbridge.	Hexham.
Water, H <sub>2</sub> O . . . . .	7·00	7·44
Silica, SiO <sub>2</sub> . . . . .	69·00	59·05
Alumina, Al <sub>2</sub> O <sub>3</sub> . . . . .	22·00	25·61
Protoxide of iron, FeO . . . . .	1·50	2·20
Lime, CaO . . . . .	0·49	0·88
Magnesia, MgO . . . . .	0·54	0·75
Potash, K <sub>2</sub> O . . . . .	0·41	1·97
Soda, Na <sub>2</sub> O . . . . .	0·18	0·28
Titanic acid, TiO <sub>3</sub> . . . . .	...	1·53
	101·12	99·71

On the whole, the Stourbridge quality is the better of the two.

The crucible, when dry, weighs 42 lbs., of which 35½ lbs. are dry clay, and the remaining 6½ lbs. plumbago.

The mould, conical in shape, with a ¾-inch circular hole at the bottom, is placed opposite to each crucible. The metal thus obtained is known as "singles," and contains 91·63 per cent. antimony, 7·23 per cent. iron, 0·82 per cent. sulphur, and 0·32 per cent. insoluble matter.

The next operation is to purify the "singles" with a small quantity of liquated sulphide of antimony. The charge for this second process is: 84 lbs. of singles broken small, 7 to 8 lbs. of liquated sulphide of antimony, and 4 lbs. of salt. The fusion is closely watched, and great care must be taken that the metal and the sulphide mix together thoroughly. The fused mass is stirred now and then with an iron rod, the time required for a charge being about 1½ hours. When fusion is complete, the slag and matte are ladled off with an iron spoon, and the contents of the crucible poured into the

moulds used in the previous fusion; the matte and skimmings are added to subsequent smeltings of ore.

The metal thus obtained is known as "star bowls," and contains 99.53 per cent. antimony, 0.18 per cent. iron, 0.16 per cent. sulphur. The presence of sulphur, due to the excess of sulphide used, is indicated by the crystalline pattern being covered over with small glistening patches; this appearance is known as "flouring."

In order to remove this sulphur another fusion is necessary. The custom of the trade is to sell antimony as "starred" or crystallised on the upper surface, and therefore it is necessary to obtain this star on the surface. These two results are achieved by melting the metal with a peculiar flux known as the "antimony flux," a substance not easily prepared, and one which is often difficult to obtain at first; but once obtained, its subsequent production is easy. The process of making this flux is a rule-of-thumb one, and is carried out thus:—Three parts of ordinary American potash are melted in a crucible, and two parts of ground liquated sulphide of antimony are mixed in. When the mixture is complete and the fusion has become quiet, the mass is poured out and tried on a small scale in order to find out whether it yields a good "star"; if it does, the ingot of metal obtained is broken and the metal then examined, in order to judge whether it is free from sulphur. But if not, the flux is remelted and more of one ingredient or the other is added, as experience dictates.

The consumption of coal per week is 22 tons, or  $1\frac{1}{2}$  tons per shift of twelve hours. About eleven crucibles are used per ton of antimony produced. The loss amounts to 10 per cent., due to volatilisation. The yield of such furnace, for ore containing 52 per cent. antimony, is  $14\frac{1}{2}$  tons per week.

The fume given off is collected in condensing chambers. It is whitish in colour, heavy and crystalline, appearing like arsenic, and contains 70 to  $72\frac{1}{2}$  per cent. of metallic antimony.

The smelting of this fume is thus carried out:—A test experiment is made in order to ascertain the amount of carbon, in the form of coke or anthracite, necessary to reduce all the antimony present in the fume. This having been found, the fume is mixed by grinding it under edge-runners with the proper quantity of carbonaceous matter; a few pounds of the mixture so produced are added to each charge of ore and iron required in smelting for singles. As the gases given off in the process are apt to cause the mixture in the pots to overflow, the "boiling ore" is looked upon with disfavour

by the workmen. The flues generally require cleaning four times a year.

In the process described above, the first operation of smelting the ore with iron is called "*singling*," the second operation, or resmelting the singles for the production of the bowl metal, is called "*doubling*," and the last operation is called "*refining*" or "*frenching*."

On an average, one man can smelt 10 to 11 cwts. of ore in twelve hours. It has been observed that a small quantity of the oxide mixed with the sulphide improves the appearance of the metal.

The following table shows the number of men required to work a furnace :—

	Per Side of the Furnace per Shift, 12 Hours.	For the Whole Furnace per Shift, 12 Hours.	Per Day of 24 Hours.
Firemen . . . . .	1	...	4
Furnacemen . . . . .	4	...	16
Refiners . . . . .	...	2	4
Metal-breakers . . . . .	...	2	4
Charge-mixer . . . . .	...	1	2
Workers on day-shift only, viz. one smith, one boiler and engine- man, and three labourers	...	...	5
		Total	35

At Magurka, in Hungary, the precipitation method was formerly in use; pot furnaces and graphite crucibles were employed. The charges consisted of 20 to 22 lbs. of antimony sulphide, with iron, potash, and pan scale (from salt-works). There were only two operations in the process.

At Linz and Schleiz in Germany, and at Alais in France, reverberatory furnaces are still in use. There is a great loss due to volatilisation in these furnaces; and hence condensing flues are connected with the furnaces for the collecting of the metallic fume. The bed must also be tight enough to prevent any loss due to leakage.

According to M. Herrenschildt, it is better to cover the bed of the reverberatory furnace with a thin layer of regulus in order to prevent the corrosion of the scoria.

3. **Direct Processes, i.e. Extraction of Metallic Antimony direct from the Ore.**—(a) *Bath Furnaces.*—T. C. Sanderson has patented\* a process for the smelting of antimony sulphide in a bath of ferrous

\* United States patent No. 714,040, Nov. 18, 1902.

sulphide on the hearth of a reverberatory furnace. After the hot ore has been charged and thoroughly rabbled, iron is added, the temperature of the furnace raised, and, when the decomposition is complete, the antimony tapped; the tap-hole is closed as soon as the iron sulphide appears. Slag is drawn through the working doors; and the increase of iron sulphide obtained during the operation is removed until the bath is reduced to its original depth. This method is said to have given good results, and has been in successful operation for more than a year.

Cookson patented\* in 1902 a process very similar to that of Sanderson. In fact, Cookson's and Sanderson's patents are copies of a similar patent by Herrenschmidt (No. 296,200, Jan. 16, 1900, France), shown in fig. 54.

(b) *Water-jacket or Blast Furnaces.*—Hering has experimented with shaft furnaces for the treatment of liquation residues by the precipitation method. Although his experiments have not been continued, yet good results might be obtained if rich ores were treated.

According to Herrenschmidt, rich ore can be treated directly in a water-jacketed furnace. Temperature = 1000° to 1100° C. Air-blast = 10 c. of mercury. About 12 to 14 per cent. of antimony can be recovered from the condensing chambers. Coke used = about 300 kgs. per ton.

(c) *Converters.*—According to Germot,† sulphide ore can be smelted in a converter into which air is blown. The air burns part of the sulphur of the ore, with the production of sulphurous acid and the metal itself. The operation is made continuous by the addition of more ore. The sulphurous acid produced escapes through a pipe at the upper part of the converter, together with the antimony sulphide fumes. If a current of air is made to act on these fumes, oxysulphide or antimony oxide will be produced, according to the amount of air admitted.

The products of the extraction of crude antimony‡ are unrefined antimony and slags. The former contains many foreign elements, as shown in the analyses given in the table on p. 120.

This impure antimony has to be refined. The slags obtained from

\* French patent No. 324,864, Sept. 30, 1902.

† A. Germot, *Revue des Produits Chimiques*, Dec. 15, 1907. Similar to Herrenschmidt's French patent No. 333,340, June 24, 1903.

‡ The term "crude antimony," meaning the unrefined metal, must be distinguished from the term "antimony crude," which means the liquated antimony sulphide.

the extraction by the roasting and reduction method consist principally of silicates, while those obtained by the precipitation method are

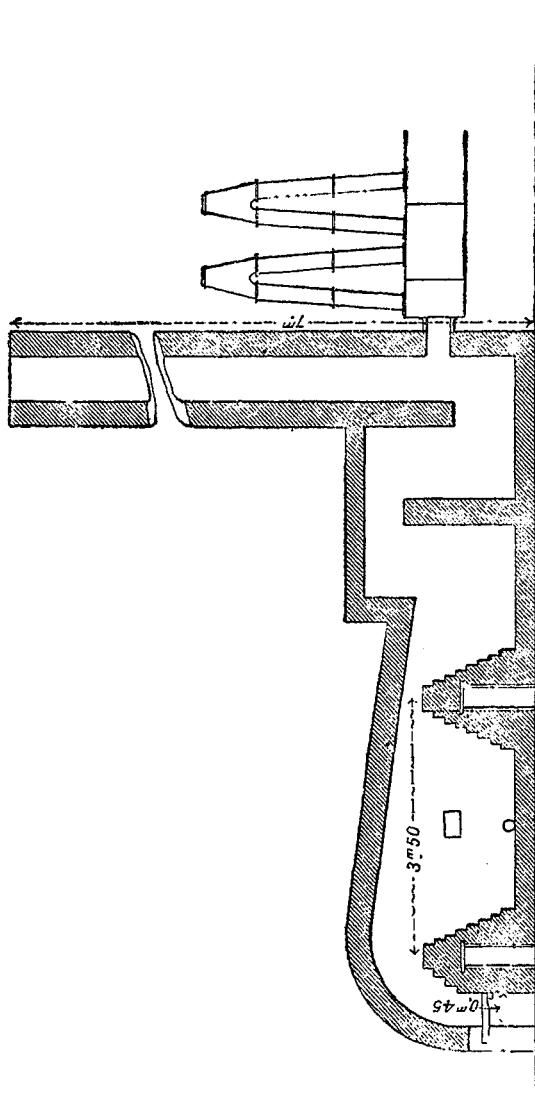


FIG. 64.

silicates and sulphides. They are thrown away if they are not sufficiently rich to be used in the first smelting of the ores.

The by-products produced in all these processes are liquation residues, matte, slags, refinery slags, and flue dust. They are added to the charges in smelting the ore, if they are sufficiently rich; the liquation dross, however, is subjected to a preliminary roasting, and the flue dust is intimately mixed with lime, before smelting. Liquation residues are also sometimes treated separately in shaft furnaces.

Method of extraction Furnace used Analyst	1. 2.		3. 4.		5. From Fahl-ore- spiess desilverised by amalgamation in the Stephan Works.
	Precipitation	Reverberatory Helmhacker.	By reduction of oxidised ores. Shaft furnace.		
Sb . . . . .	94.5	84.0	97.2	95.0	90.77
S . . . . .	2.0	5.0	0.2	0.75	2.0
Fe . . . . .	3.0	10.0	2.5	4.0	...
Co . . . . .	...	...	...	...	} 1.50
Ni . . . . .	...	...	...	...	
Cu . . . . .	...	...	...	...	5.73
As . . . . .	0.25	1.0	0.1	0.25	...
Au . . . . .	traces	...	...	...	...

4. Other Processes.—(α) At the Stephan Works, in Upper Hungary, antimony is extracted from the spiess, which has been desilverised by amalgamation. The spiess is obtained from the smelting of fahl-ores. The antimony is extracted by using pyritic ores in a shaft furnace. The copper is thereby converted into sulphide by the sulphur of the pyrites, and the impure antimony obtained is refined.

(β) Pelatan \* smelts the following mixture in a reverberatory furnace :—

Oxide of antimony . . . . .	53
Sulphide of antimony . . . . .	40
Coal . . . . .	7
	100

It is only necessary to liquate the rich sulphide ore and to oxidise the poor sulphide ore in order to obtain the sulphide and the oxide required for the production of the metal. Refining can be effected with an alkaline flux.

(γ) Basse patented † in 1907 the following process. The advantages of this process are :—

\* French patent No. 210,331, Dec. 19, 1890.

† French patent No. 375,872, March 19, 1907.



- (a) The suppression of any loss due to charging and to the activity of reaction.
- (b) The protection of the bed and the wall of the furnace.
- (c) The elimination of a great proportion of dirt and residues.
- (d) An increased yield of metal.

The substances are mixed in the proper proportions, moulded into briquettes of a convenient size, dried, and charged into a reverberatory furnace for the production of the metal.

The ingredients forming the briquettes are mixed in the following proportions by weight:—

(a) Oxide of antimony, powdered . . . . .	100
Charcoal, powdered . . . . .	15
Dried carbonate of soda, powdered . . . . .	2
Lime, powdered . . . . .	2
Water . . . . .	15
(b) Sulphide of antimony, powdered . . . . .	100
Iron filings or shavings . . . . .	10
Charcoal, powdered . . . . .	20
Dried carbonate of soda, powdered . . . . .	2
Lime, powdered . . . . .	2
Water . . . . .	15
(c) Sulphide of antimony, powdered, or oxide of anti- mony, powdered . . . . .	35
Antimonate of oxide of antimony . . . . .	60
Iron filings or shavings . . . . .	8
Charcoal . . . . .	20
Carbonate of soda . . . . .	3
Lime, powdered . . . . .	2
Water . . . . .	15

(d) The process \* for the extraction of gold from antimony ore, as patented by M. Herrenschildt, is as follows:—

This process is based upon the principle that, when antimony sulphide and the metal itself are melted together, the gold contained in the sulphide passes into the metal. The direct use of the metal can be dispensed with by, for instance, melting antimony sulphide and antimony oxide together with coal. The metallic antimony formed in this reaction extracts the gold from the sulphide.

A mixture is made of the antimony ore or of antimony crude with the metal or its oxide, in such proportion as will yield one-tenth of the metal in the ore as charged into a reverberatory furnace, a rotatory furnace, or a crucible. The auriferous antimony thus

\* French patent No. 350,013, June 23, 1904.

obtained can be treated with bisulphide of sodium or bisulphide of calcium; or it can be melted in a crucible with sufficient sulphur to convert nine-tenths of the metal into sulphide, while the remaining one-tenth contains all the gold. This alloy of antimony and gold can be treated with nitric acid so as to extract all the gold.

## II. EXTRACTION BY WET METHODS.

There have been many wet processes proposed for treating poor ores or liquation residues, but none have been practicable on a large scale.

Haremain has devised a process of extracting antimony from antimonial lead ores by roasting the crushed ore with alkaline carbonate and carbon. The result is a double sulphide of alkali and antimony, which, on being lixiviated, yields the precious metal and lead. The antimony is precipitated as a sulphide by the addition of an acid, preferably sulphuric acid, with the formation of an alkaline sulphate which can be recovered for future use.

N. W. Edwards proposes to treat gold- and silver-bearing antimony ores by lixiviation with a 7 per cent. solution of calcium sulphide, preferably cold, in large vats provided with stirring apparatus. The resulting reaction is that the antimony is dissolved as sulphide, while the gold is left behind with the residues. The gold thus obtained can be recovered by any of the ordinary methods. The solution obtained above is then drawn off and is treated with carbonic acid obtained by burning lime. The calcium is precipitated, as carbonate, by the carbonic acid, and is filtered off. Upon the further treatment of the solution by carbonic acid, the antimony sulphide is finally precipitated. The hydrogen sulphide evolved during the reaction may be used to regenerate calcium sulphide solution by bubbling it through milk of lime.

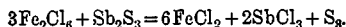
According to Hargreaves, finely powdered ore can be treated with hot hydrochloric acid. Lime is used to neutralise the solution, which is then to be treated with zinc or iron for precipitation of the antimony. The precipitated metal is to be washed successively with antimony chloride solution, hydrochloric acid, and water, and then fused with potash in crucibles.

Smith's method is similar to the one just described.

Hering also proposes to treat liquation residues by hydrochloric

acid. The chloride thus formed in solution is treated with water, which precipitates it as basic chloride; the chloride solution may be precipitated by hydrogen sulphide.

Rud. Koepp & Co. patented a process to use ferric chloride as a solvent,



This reaction goes on better in the presence of hydrochloric acid or haloid salts.

MacArthur's process is as follows:—The ore is ground small enough to pass through 20-mesh, and is treated with a solution of sodium hydroxide of not more than 2 per cent. strength, at a temperature of 100° C. The filtered solution is precipitated by carbon dioxide obtained from a lime-kiln. The antimony precipitate obtained is in the form of a red amorphous sulphide, which is collected in a filter-press, while the filtrate, containing sodium carbonate, is causticised by lime from the kiln, ready for further use. The process is therefore continuous.

Silver-bearing antimonial fahl-ores free from lime can be heated with Glauber salt and coal in order to convert the antimony into the double sulphide of sodium and antimony. Sulphur dioxide may then be used to decompose the leached salt, with the formation of antimony sulphide and sodium thiosulphate, the former of which can be treated for antimony in the ordinary manner. Any silver or copper in the ore would be left behind in the residues from the leaching process.

Of all the wet processes that have been proposed to treat antimony ore, especially ore containing gold, that of M. Herrenschildt seems superior to all others for practical application on a large scale. The following is a description of this process\* :—

(a) *Concentration*.—The mineral, ground either in crushing or in ball mills, is allowed to pass through sieves, the dimension of whose mesh can only be determined by successive trials. With an endless belt concentrator, the following products are obtained :—

The *concentrates*, to be de-antimonised.

The *mixed materials*, to be passed back to the concentrator.

The *tailings*, to be rejected.

The *concentrates* consist principally of iron pyrite, mispickel, and stibnite, as well as all the gold contained in the ore.

\* *Rapport de M.M. Pelatan et Lévat, Ingénieurs civils des Mines, sur le traitement des minerais auro-antimonieux par le procédé de M. Herrenschildt.* Paris, 1904 (pamphlet).

The following analyses refer to material from the mine La Lucette ; the quantities are those yielded per ton :—

	Waste ground by		Concentrates from Waste.		Mixed Materials.	Tailings.
	Crushing Mill.	Ball Mill.	Sample I.	Sample II.		
Antimony, kilos .	10·9	9·5	114·1	97·5	14·6	5·1
Gold, grammes .	6	5	34	214	1	traces

(b) *The Treatment of the Concentrates.*—They are lixiviated in agitators with a solution of sodium sulphide. The sulphide of antimony is dissolved as double sulphide of antimony and sodium, and the gold is left in the residues.

The liquor thus obtained is heated with the sulphurous acid coming direct from the roasting of pyritic ores or of the sulphide of antimony, obtained in the same process from a previous treatment. The antimony sulphide thus precipitated has a red colour. The gold residue can be treated in a reverberatory furnace in the presence of litharge. The gold can be extracted by cupellation or by oxidation with nitrate of soda.

The process is profitable with an ore containing :—

Antimony, 4 per cent., or 40 kilos per ton.  
Gold, 12 grms. per ton.

The profit is 21 frs. per ton, after subtracting the expenses. One ton of ore may cost only 6 frs. This result has been obtained at Genest (Mayenne); France.

Lyte proposes to roast antimony-bearing lead, silver, and copper ores in the presence of chlorides, to condense the antimony vapour in a solution of salt, and to precipitate the metal by iron or zinc. This process requires complicated condensing apparatus.

The Utah Antimony Company, of Garfield Co., Utah, has been able to obtain a concentrate containing 65 per cent. antimony from ore containing only 11 per cent. of that metal. The mill is capable of producing 10 tons of concentrate per day.

### III. EXTRACTION BY ELECTROLYTIC METHODS.\*

It has been proposed to treat poor sulphide antimony ores, and the residue from the liquation of richer ores, with solutions of alkali-

\* *Electric Smelting and Refining* of Dr W. Borchers, translated by W. G. McMillan, pp. 476-487 ; London, C. Griffin & Co., 1904.

metal and alkaline-earth metal sulphides. The resulting reaction is the production of a solution of soluble thio-antimonates,  $\text{Na}_3\text{SbS}_4$  or  $\text{Ca}_3(\text{SbS}_4)_2$ , and thio-antimonites,  $\text{Na}_3\text{SbS}_3$  or  $\text{Ca}_3(\text{SbS}_3)_2$ . These solutions can be electrolysed with the greatest ease.

The results of the experiments made by Borchers in 1886 prove that antimony was deposited in equal quantity both from the thio-antimoniate and thio-antimonite. If a sodium thio-antimonate solution be used, it is only necessary to add either sodium sulphide or sodium hydroxide, in such quantity that there is at least one atom of sodium for every atom of sulphur, in order to prevent the separation of sulphur at the anode. In other words, the action takes place best when three molecules of sodium sulphide ( $\text{Na}_2\text{S}$ ) are present for each molecule of antimony sulphide ( $\text{Sb}_2\text{S}_3$ ).

The relative distribution of the elements before and after the experiment is shown in the following table:—

	Antimony.	Sodium.	Sulphur.	Oxygen.
	Kgrms.	Kgrms.	Kgrms.	Kgrm.
Before electrolysis— In form of salts, etc. . . .	2·440	1·840	2·560	0·020
After electrolysis— In metallic form . . . .	2·437	...	...	...
In solution—				
2·410 kgrm. $\text{NaSH}$ . . . .	...	0·990	1·377	...
1·202 ,, $\text{Na}_2\text{S}_2$ . . . .	...	0·503	0·699	...
1·491 ,, $\text{Na}_2\text{S}_2\text{O}_8 + 5\text{H}_2\text{O}$	...	0·275	0·384	0·288
	<u>2·437</u>	<u>1·768</u>	<u>2·460</u>	<u>0·288</u>

The loss of antimony (3 grms.) is so small that the precipitation may be considered as practically quantitative. The loss of sodium and sulphur is due to the fact that the solution clinging to the antimony after the powder had been removed was not added to the rest of the liquid.

The experiments, as carried out by Borchers, also show a peculiar fact, that with the same expenditure of current the same quantity of antimony is deposited, whether it exists in the solution as the trivalent or as the pentavalent antimony.

*Practical Working of the Electrolytic Process.*—The sodium sulphide solution in the conical iron vessels (figs. 55–58, a) is treated and agitated by means of steam introduced through the steam-pipe b. As soon as the solution is boiling, the finely divided ore is sprinkled into

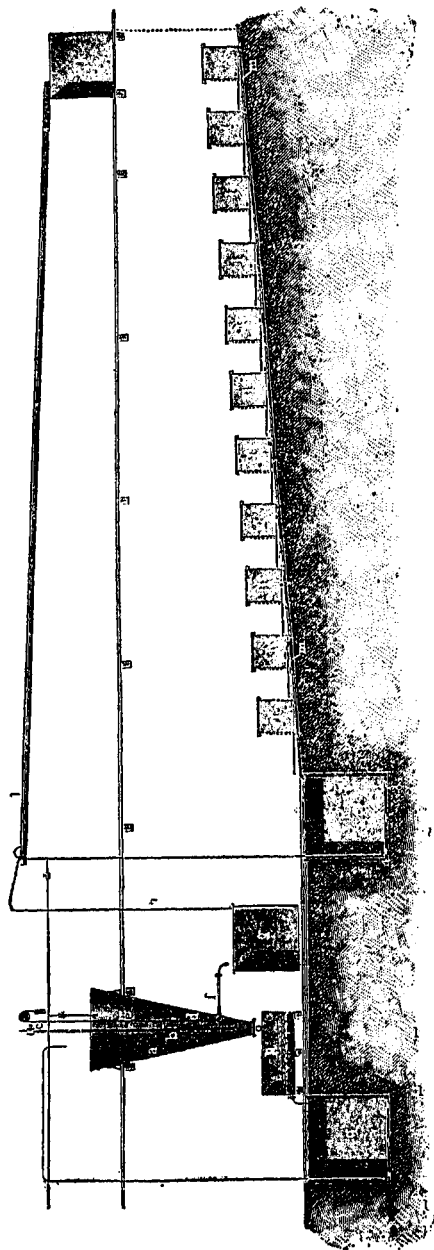


FIG. 55.

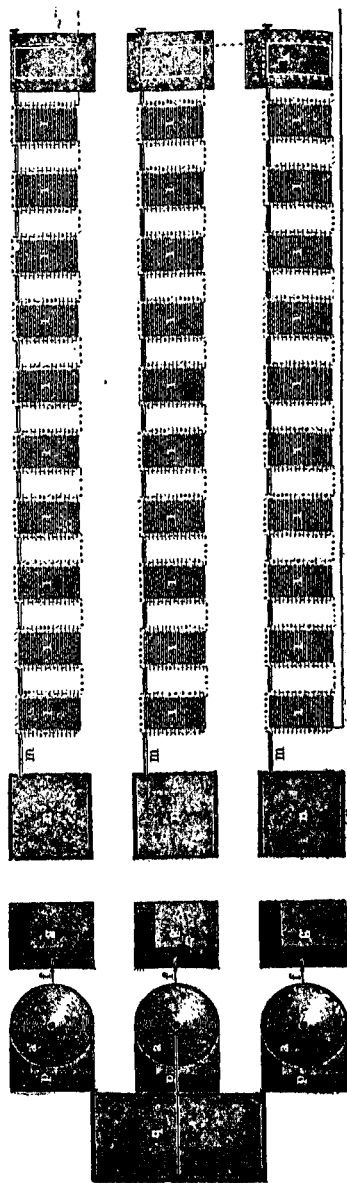


FIG. 56.

it. The presence of sodium hydrosulphide or of polysulphides is not objectionable so long as the proper proportion of sulphur to sodium is kept (by the addition of soda); that is, every atom of oxidisable sulphur must be accompanied by an atom of sodium capable of neutralisation.

Antimony glance is best suited for the treatment. For each molecule of antimony trisulphide there should be present in the solution three molecules of sodium sulphide; and after the extraction is complete the concentration should not exceed 12° Baumé (or 9° to 10°, if hot). To the electrolyte should be added 3 per cent. of common salt, which not only assists the clearing of the solution by the separation of dissolved sulphide of iron, but also reduces the electrical resistance of the solution.

After the ore has been added the whole mass is stirred thoroughly

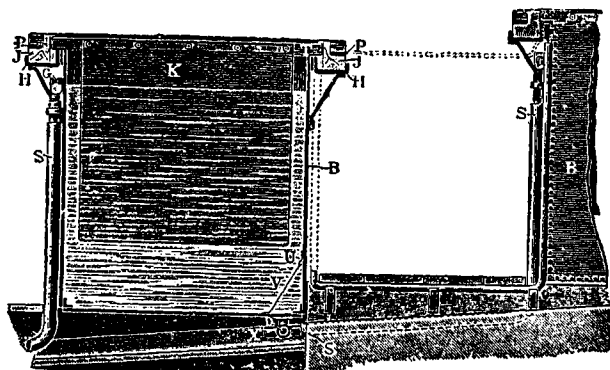


FIG. 57.

by a current of injected steam for an hour or longer. Air is admitted from time to time through *c* on the steam-pipe *b*.

After two or three hours, when the mass has been sufficiently heated and stirred, and the insoluble portion of the charge has settled, the clear solution is drawn off, *f*, into the leaching vessel, *g*, from which it is pumped through the pipe *b* and the channel *i* to the reservoir *k*. The bell-shaped siphon arrangement, *d*, is used to ensure that only the clear liquor is drawn off. From the reservoir, the liquor is allowed to flow through successive electrolyte tanks, *l*; finally, after being exhausted of its antimony, it flows through the channel *m* into the tank *n*, from which it may be raised for further circulation, or may be pumped to another part of the works for the recovery of the thiosulphate, sulphur, or sodium chloride.

The residues from the first extraction are treated with fresh

sodium sulphide solution and then boiled repeatedly with water; they are then allowed to pass through *o* into the filter *p*, where they are washed again with hot water. The wash-waters collected in the holder *q* are used again for washing other residues. Such a plant can extract 6 to 8 cwts. of antimony from its ores containing less than 10 per cent. of the metal in twelve hours.

Figs. 57 and 58 show the arrangement of the electrolytic baths on a large scale. *A* are the anodes, *K* the cathodes, which are hung in iron baths. The cathodes are of sheet-iron and bolted on to the rails *T*, and rest directly upon the rim of the baths, so that the baths also serve as cathodes. The anodes are plates of lead suspended

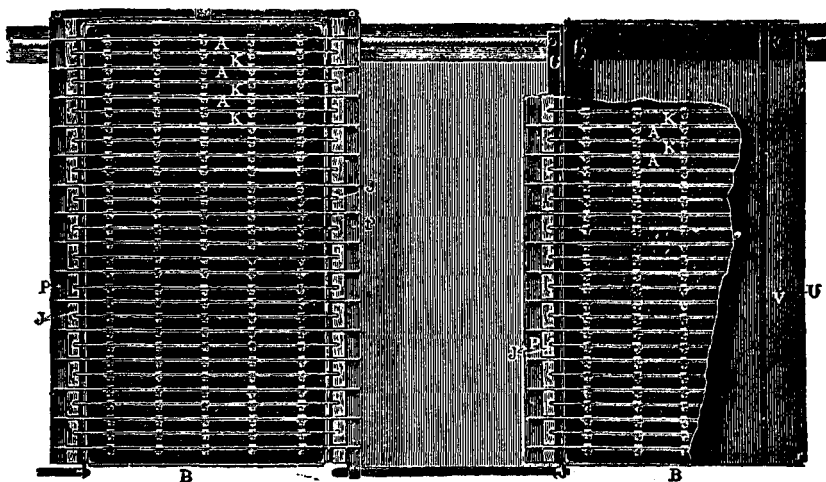


FIG. 58.

from iron rails, resting upon the positive leads, which are isolated by resting on the wooden bars *J*. The electrolyte is fed through the three-way cock *D* under the bath, since it becomes less dense as the antimony is removed. The outlet is through *G* by means of the rubber pipes *S* into the next bath. In order to effect an even distribution of the incoming electrolyte, a plate, *V*, is riveted upon and along the bottom of the bath; over this plate is another one, *U*, which is so attached that there is a little space between the two, the two thus forming a channel.

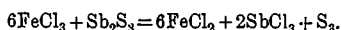
With concentrated solutions electrolysis may be commenced with a current of 100 to 150 amperes per square metre (0.064 to 0.1 ampere per square inch), which may gradually be reduced to 40 or 45



amperes (0.026 to 0.03 ampere per square inch). The necessary E.M.F. is about 2 volts per bath.

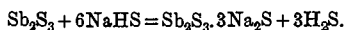
The metal thus obtained is in the pulverulent form or in lustrous scales, according to the density of the current used.

Koepp's method is to treat antimony sulphide with ferric chloride, thus :—

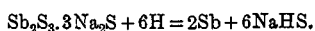


The solution is electrolysed at a temperature of 50° C. between lead plates. Antimony is deposited upon the cathode and ferric chloride upon the anode. The current used is 3.7 amperes per square foot. The use of chlorides as electrolytes precludes the possibility of the process becoming practical.

Siemens and Halske use as solvent either the sulphides, hydro-sulphides, or polysulphides of the alkalis. When the finely ground ore is thus lixiviated, a double salt is formed, *e.g.* with NaHS :—



The liquor is then led into the cathode division of a bath. The bath is divided up by diaphragms into series of anodes and cathodes ; the former are made of carbon or platinum, and are closed and made gas-tight ; the latter are made of copper or antimony plates. The reaction at the cathode end is as follows :—



In this way, not only is metallic antimony obtained, but also the NaHS solution is regenerated and used to dissolve more of the sulphide.

Another process by Siemens is to electrolyse a solution of the double salt formed by treating antimony sulphide with sulph-hydrate of calcium, barium, strontium, or magnesium. Without the use of diaphragms, the hydrogen liberated at the cathode end combines with the sulphur of antimony sulphide, and the antimony is deposited, while at the same moment the sulph-hydrates of other metals are formed, to be in turn converted into disulphides by the oxygen developed in the reaction.

These disulphides are treated with carbon dioxide, obtained by heating a mixture of the carbonates and sulphur, the result being the formation of the carbonates of calcium, barium, strontium, and magnesium, sulphur and hydrogen sulphide. These, with the exception of the hydrogen sulphide evolved, are heated in the absence of air, when carbon dioxide and the caustic alkaline earths are formed. The carbon dioxide is used to decompose disulphide solutions, and the basic oxides are treated with the hydrogen

evolved in the above reaction, in order to produce fresh quantities of the sulph-hydrate solution.

Izart describes a process for the extraction of antimony by dissolving antimony ores with sodium sulphide. The solution is electrolysed in a vat divided, by a diaphragm, into a cathode compartment, into which the solution is put, and an anode compartment, which is filled with a 17 per cent. caustic soda solution. Sufficient ammonium chloride is added to the soda solution as will raise its specific gravity to that of the antimony solution. At Cassagnes, France, the process yielded a lustrous scaly deposit of metallic antimony: the current density was 0.8 ampere per square decimetre; the E.M.F., 1.6 volts; the yield, 76 per cent.; the output per kilowatt, 0.55 kg. antimony, which was finally raised to 0.621 kg.

At Lixa, near Oporto, Portugal, the following process, for the extraction of both antimony and gold from impure antimony, had been tried, and was finally given up on account of high working cost:—Plates of the impure antimony were used as anodes, while the electrolyte was a solution of antimony trichloride, made by dissolving the trichloride in a concentrated solution of salt, potassium chloride, or ammonium chloride strongly acidified with hydrochloric acid. When current was passed, the antimony dissolved out from the anode was deposited on the cathode; while the gold, in the form of fine powder, fell to the bottom of the cell.

In Sanderson's process, a solution of butter of antimony, in a very concentrated solution of sodium, potassium, or ammonium, acidified with hydrochloric acid, is used as an electrolyte, in which are suspended antimony anode plates containing gold. When a current is passed, the antimony is deposited on the cathode and the gold particles fall to the bottom of the vat. This process is too costly; moreover, a chloride solution can never afford a good deposit.

Betts, at a meeting of the American Electro-chemical Society, September 18, 1905, stated that an acid ferric chloride solution attacks stibnite with ease, producing a solution of ferrous and antimonious chlorides and a residue of sulphur; from this solution metallic antimony and ferrous chloride can be recovered electrolytically.

#### IV. REFINING OF ANTIMONY.

Unrefined antimony, as already stated, usually contains sulphur, iron, arsenic and copper, and frequently lead. These impurities, with the exception of lead, can be eliminated partly by oxidising and slagging agents, partly by sulphurising agents, and partly by chlorinating agents. Soda or potash or antimony glass (antimony oxy-

sulphide) removes sulphur by fusion, and converts arsenic into arseniate of soda or potash. The conversion of copper and iron into their sulphides by sulphide of antimony can be facilitated by the addition of soda or potash, or of Glauber salt and charcoal. These sulphides form a slag with the sulphide of sodium produced from the reduction of the Glauber salt, and with the soda or potash present. These sulphides are easily removed by antimony glass.

The use of common salt, carnallite, or magnesium chloride to volatilise some of the foreign metals present as chlorides, and to slag others, may also occasion great loss of metal due to volatilisation.

As lead can easily be separated from its oxide or sulphide by metallic antimony, the above-mentioned methods are ineffective for its elimination. It can, however, only partially be eliminated by chloridising, which, as previously hinted, causes great loss due to volatilisation. Mitscherlich suggested that the elimination of lead should be effected before the smelting of antimony sulphide by the addition of 4 per cent. of iron, which removes all the lead and a comparatively small amount of antimony.

In commerce, the purity of antimony regulus is judged by the appearance of the fern-like "star" on its surface.

If the metal is impure, or if the pure metal has been exposed during solidification, or if the slag covering sets before the metal does, or if a trace of undecomposed slag or potash comes into contact with the surface, the characteristic fern-like structure is not exhibited.

1. **Refining in Pot Furnaces.**—This kind of furnace is, or has been, in use at Septèmes in France, in England, and at Oakland in California. The fuel consumption is great, and therefore it is advisable to use it for small quantities only.

At Septèmes the furnace held thirty crucibles, the shape of the furnace being that of a barrel cut lengthwise through the middle. Its dimensions were:—

Length . . . . .	7 feet.
Breadth across each end . . . . .	4 "
Breadth in the middle . . . . .	5 "
The bed was 6 inches lower than the bridge.	
The height of the roof above the bridge . . . . .	8 inches.
" " " the middle of the bed . . . . .	1 foot 6 inches.
" " " the end where the flue left the furnace . . . . .	10 inches.
Length of fireplace . . . . .	5 feet.
Breadth " " . . . . .	1 foot 8 inches.
Depth " " from roof to bars . . . . .	1 " 4 "
Width of working door in the longer front side . . . . .	1 " 8 "

The crucibles were made of fire-clay, and could stand five or six charges each, each charge being 48·5 lbs. of impure antimony. To each charge were added 13 to 17 lbs. of flux, which was a mixture of sulphate and carbonate of soda, with a little salt and pure oxidised antimony ores. The fusion lasted six hours, with a consumption of 450 to 550 lbs. of coal. A low red heat is necessary.

In England the process of refining and restarring the star-bowls is as follows:—The lumps of metal, when cold, are removed from the mould and are thoroughly cleaned from the adhering skin of slag by chipping with sharp hammers, this part of the work being sometimes done by women. Unless this cleaning process is carefully done, it is well-nigh impossible to obtain good stars on the finished metal. The chippings are returned to the second smelting. Having been cleaned, the star-bowls are broken small. The charge made is about 84 lbs., together with enough flux to surround the ingots completely; the quantity is generally 8 lbs. for ingots of the ordinary shape. The melting takes place in the crucibles standing close to the fireplaces, where the fusion is most rapid. The metal is charged first and is closely watched; as soon as it begins to melt, the flux is added; and as soon as the fusion appears to be complete the furnace-man stirs the mixture once round only with an iron rod, and the charge is then poured out. The flux is used over and over again, being regenerated by the addition of carbonate of potash. The ingots must be completely surrounded by the flux; there must be a thin layer of it between the mould and the metal, and also the whole surface of the ingot must be covered by the flux to a depth of a quarter of an inch. Any traces of the flux still adhering to the ingot are removed by washing in warm water, with the assistance of a little sharp sand.

For a charge of 60 to 70 lbs. of bowl-metal, with 1 to 2 lbs. American potash and 10 lbs. of slag, obtained from a previous charge of French metal, the time required is three-quarters of an hour.

The slag obtained shows whether the operation is complete or not. It should be smooth and of a deep black colour.

The process of refining as practised in Tuscany is as follows:—The broken-up impure metal is mixed with one-eighth by weight of carbonate of soda, and one-sixth by weight of sulphide of antimony. This mixture is placed in a Hesse crucible. The metallic button thus obtained is again fused with carbonate of soda and a little nitrate of potash.

2. Refining in Reverberatory Furnaces.—Reverberatory furnaces are, or were, used at Milleschau, at Bányá, at Siena, and at Oakland. The bed of the furnace should be tight, and should be made of materials capable of resisting the action of the fused alkalis used. The best material is partly weathered granite, newly cut stone being unfavourable. A mixture of burnt and raw clay can be used, if such stone is not available. In this case the mixture should be rammed hard into an iron pan.

Figs. 59, 60, 61 show the construction of a furnace of this kind as built by Hering at Milleschau and as recommended by Helmhacker.

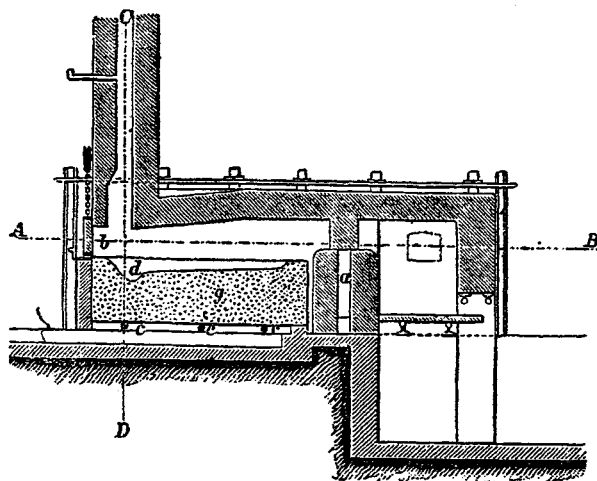


FIG. 59.—Section E F.

The following is a description of figs. 59, 60, 61 :—

- g*, Bed of granite block.
- c*, Three iron rollers carrying the granite.
- f*, Three railway bars for the rollers.
- d*, A depression or sump in the bed, in which the antimony collects and from which it can be ladled.
- b*, Working door; to facilitate working, the later patterns of furnace are provided with two doors, one on each side of the flue end of the furnace; one being used for drawing the slag, the other for ladling out the metal and charging.
- a*, A vertical channel inside the fire-bridge, for preheating the air, and thereby aiding the combustion of the fire gases. The air-current admitted into these vertical channels is regulated by a

horizontal flue running through the bridge lengthwise, the flue being provided with a slide, and the chimney with a damper. The charge for a furnace of such dimensions is 1200 to 1500 lbs., exclusive of the fluxes.

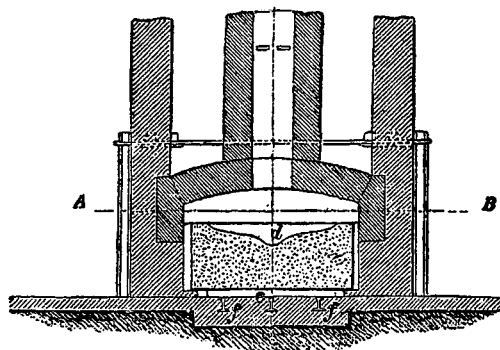


FIG. 60.—Section CD.

At Bánya the bed is built of fire-clay 11 inches thick, well rammed into an iron box 13 feet long by 8 feet 2 inches wide. A charge consists of 10 cwts. only of the unrefined metal.

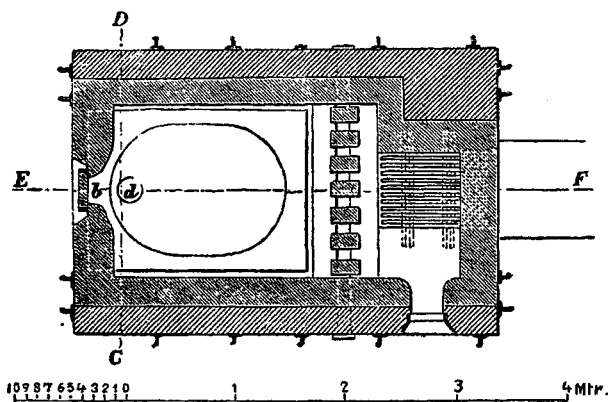


FIG. 61.—Section A B. 1 metre = 3.28 feet.

At Milleschau, where the above-described furnace is in use, the very impure antimony is refined first by soda and then by antimony glass, while the purer sorts are refined by antimony glass alone. The tetroxide of antimony used in making antimony glass is

obtained in the form of crusts, formed in the hottest part of the chimney.

According to Helmhacker, the refining process is as follows:—

Twelve hundred to 1500 lbs. of impure antimony are charged into the furnace, previously heated to a red heat. As soon as the metal is melted, generally in less than half an hour, 3 to 7 per cent. of soda, with which is mixed a little coke-dust or fine charcoal, is added, according to the purity of the metal. After this the heat is raised to bright redness in order to fuse the soda. During the charging and the fusion, vapour of antimonious and arsenious oxides is given off.

The slag gradually becomes thicker and thicker, and consequently, after about three hours, the bubbles, which at first were numerous, rise very slowly through the slag. The slag is then very carefully skimmed off through the working door.

Up to this point the iron and sulphur persist as impurities in the metal. They are removed by adding ingredients capable of forming antimony glass, such as oxysulphide of antimony. For each 100 lbs. of antimony in the charge, 3 lbs. of liquated sulphide of antimony and  $1\frac{1}{2}$  lbs. of antimony tetroxide are thrown in, and, as soon as these are fused,  $4\frac{1}{2}$  lbs. more of potash or white flux are added.

Care must be taken that the bath of metal is completely covered with the fluxes.

The metal can be ladled out at the end of a quarter of an hour, but this must be done cautiously, in order to secure the starred appearance of the ingots. When cold, the slag covering the ingots can be broken off by means of a hammer.

Three charges of 1300 to 1500 lbs. each can be refined in one of these furnaces in twenty-four hours, with a consumption of 1300 lbs. of coal.

The slag obtained in the final process of refining is called *star slag*, which consists principally of antimony glass, and contains from 20 to 60 per cent. of antimony; it is generally used over again for refining. When it becomes too impure for this purpose, it is charged along with the ore for the first smelting. The other slags obtained in the course of refining are also added to the charges of ore for smelting. The impurities found in the *star slag* are sulphides of iron and nickel, iron oxides and silica.

The loss due to volatilisation amounts to 20-30 per cent. The flue dust consists principally of the trioxide and tetroxide. The cost of refining is said to be  $2\frac{1}{2}$  to 3 marks per 100 kilos. (*i.e.* 1s. 3d. to 1s. 7d. per cwt.).





(a) *Refined Antimony*.—The composition of the metals taken from different sources can be seen from the following table:—

	I.	II.	III.	IV.	V.	VI.
Source	{ Lipto Szt. Miklos, Hungary. }	California.		{ Samples for tenders at the Royal Docks at Wilhelmshaven. }		
Analyst	Hirzel.	Booth, Garret, Blair.		Himly.		
Sb	98·27	98·34	99·081	98·98	98·81	98·87
Cu	0·54	0·021	0·052	0·01	0·02	0·02
Fe	0·63	0·144	0·039	0·35	0·34	0·16
Pb	...	0·410	0·538	0·34	0·34	0·73
As	...	1·008	0·036	0·09	0·36	0·09
Bi	0·36	...	...	...	...	...
S	...	0·064	0·254	0·23	0·12	0·11
Co	...	...	...	...	...	...
Ni	...	0·013	trace.	...	...	...

(β) *Refinery slag* generally contains from 20 to 60 per cent. of antimony, and is a mixture of soda, sodium sulphantimoniate, antimony trioxide and tetroxide, ferrous oxide, iron sulphide, arsenic oxide, and smaller proportions of silica and alumina; it is added to charges of ore.

(γ) *Star slag* consists essentially of antimony glass, and is used repeatedly until it becomes too poor and impure; it is then added to charges of ore.

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## CHAPTER VI.

### THE ANTIMONY PREPARATIONS AND THEIR USES.

THE principal uses of antimony, arranged in the order of importance, are as follows :—

1. Alloys.
2. Pigments and paints.
3. Medicine.
4. Colouring matter in glass-making and in the preparation of artificial gems.
5. Colouring matter in pottery-making.
6. Colouring matter for the manufacture of cloth and paper.
7. Mordants.
8. Corrosive for dyeing.
9. Vulcanising rubber.
10. Coating articles.
11. For the manufacture of aniline yellow and aniline red.
12. For the fabrication of dice-boxes, for the cartridges of the new firearms, and other objects, for artillery uses.
13. Miscellaneous uses.

We shall now take up the treatment of each in the order given.

#### 1. Alloys.

The principal alloys of antimony are :—

- (a) Britannia metal.
- (b) Bearing or anti-friction metal.
- (c) Type-metal.
- (d) Hard lead.
- (e) Others of less importance.

(a) **Britannia Metal.**—This alloy is generally used to make spoons, cans, articles of luxury, etc. It is practically an alloy of tin and

antimony, in variable proportions, with smaller quantities of copper, zinc, lead, bismuth, or other metals.

The following table, according to Long, shows the variation of the properties of the alloys of tin and antimony, as different proportions of the two are taken :—

Composition of Alloys.			Specific Gravity.			
Sb.	Sn.	Atomic Formulae.	Found.	Calculated.	Difference.	
					Expansion.	Contraction.
100·0	...	Sb	6·713	...	...	...
92·6	7·4	Sb <sub>12</sub> Sn	6·739	6·752	0·013	...
89·2	10·8	Sb <sub>8</sub> Sn	6·747	6·770	0·023	...
88·1	11·9	Sb <sub>4</sub> Sn	6·781	6·817	0·036	...
67·7	32·3	Sb <sub>2</sub> Sn	6·844	6·889	0·045	...
51·4	48·6	SbSn	6·929	6·984	0·055	...
34·5	65·5	SbSn <sub>2</sub>	7·023	7·082	0·059	...
26·0	74·0	SbSn <sub>3</sub>	7·100	7·133	0·033	...
17·4	82·6	SbSn <sub>5</sub>	7·140	7·186	0·046	...
9·5	90·5	SbSn <sub>10</sub>	7·208	7·234	0·026	...
5·0	95·0	SbSn <sub>20</sub>	7·276	7·262	...	0·014
2·1	97·9	SbSn <sub>50</sub>	7·279	7·281	0·002	...
1·0	99·0	SbSn <sub>100</sub>	7·284	7·287	0·003	...
...	100·0	Sn	7·294	...	...	...

The addition of antimony to tin gives an alloy that possesses a silver-white appearance, and whose melting point is higher, and hardness greater, than the corresponding quantities of tin alone. The brittleness increases and the malleability decreases as the proportion of antimony increases. An alloy consisting of 80 per cent. tin and 20 per cent. antimony is sufficiently malleable to be hammered and rolled in the cold. It is by keeping close to this proportion that the best alloys of tin and antimony, for making pots and engravers' plates, are obtained. According to Chaudet, 10 parts of tin to 1 part of antimony form a perfectly ductile alloy.

The alloy is white in colour, with a bluish tint, and takes a high polish. The amount of copper used must always be limited, as it tends to give a yellowish tint to the appearance and diminishes its fusibility. Good alloys show a fine-grained, jagged fracture; and if it exhibits a crystalline structure, they either contain too much antimony, or the union among the constituents is not intimate enough, thus necessitating their remelting. Iron and zinc are objectionable,

as they increase the hardness and brittleness. Lead is advantageous in cast work by making the alloy more fusible, but it impairs the colour and lustre. Arsenic induces brittleness, even in small quantities.

The essential point in the preparation of Britannia metal is to make the tin harder, tougher, more sonorous, and more easily polished. The alloy gives castings as fine and sharp as those made with the most fluid alloys of tin and lead, copper and zinc, etc. It acquires a finer polish than alloys of tin and lead, as the latter are too soft to sustain the action of emery and other polishing materials. Bismuth increases the fusibility.

The best way to prepare the alloy is to melt the copper first, then to add the antimony with a portion of the tin, and finally the remaining tin.

Dr Karmarsh states that Britannia metal, when subjected to rolling, has its specific gravity diminished. He explains this by saying that the particles, under the pressure of the rolls, have a tendency to become separated.

The following is a list of the principal alloys of tin and antimony in commercial use:—

	Tin.	Anti- mony.	Copper.	Zinc.	Bis- muth.	Lead.	Other Metals.
English metal (Britannia metal)	94	5	1	...	...	...	...
„	90	6	2	...	2	...	...
„	90	7	3	...	...	...	...
„	89·3	7	1·8	...	...	1·8	...
„	85·47	9·66	1·81	3·06	...	...	...
„	85	5	3·5	1·5	5	...	...
„	80	10	9	...	...	1	...
„ (Hobson)	109 lbs.	9 lbs.	3 lbs	...	...	...	3 oz. man- ganese
„	75	8·5	...	...	8	8·5	...
„ (sheet)	90·6	7·8	1·5	...	...	...	...
„ (cast)	90·6	9·2	0·2	...	...	...	...
Queen's metal	50½-75½	16½-8½	...	...	16½-8	16½-8	...
„	88·5	7·1	3·5	0·9	...	...	...
„ or pewter	88·5	7	3·5	...	1	...	...
English Tutania	25	25	...	...	25	...	brass 25
German „	7	92	1	...	...	...	...
Engestrund „	7	62	31	...	...	...	...
Ashberry metal	80	14	2	1	...	...	nickel 3
„	79	15	3	2	...	...	1
„	77·08	19·40	...	2·80	...	...	...
Minofer	68·5	18·2	3·3	10	...	...	...

	Tin.	Anti- mony.	Copper.	Zinc.	Bis- muth.	Lead.	Other Metals.
German metal .	72	24	4	...	...	...	...
„ .	84	9	2	5	...	...	...
„ .	20	64	10	6	...	...	...
Lega per vasellame di stagno	90	9	1	...	...	...	...
Metallo argentino di Parigi	84.44	14.5	...	...	...	0.06	...
Britannia metal .	85.7	10.4	1.0	2.9	...	...	..
„ .	81.9	16.2	...	1.9	...	...	...
Plate pewter. .	89.3	7.1	1.8	...	1.8	...	...
Métal argentin .	85.5	14.5	...	...	...	...	...
Poterie d'étain des ouvriers de Paris	90	9	1	...	...	...	...
Métal du prince Robert for covers	84.75	15.25	...	...	...	...	...
English pewter for drinking-cups	88.42	7.16	3.54	0.88	...	...	...
Queen's metal for English tea-pots	73.36	8.88	...	...	8.88	8.88	...
Complex English metal	87	6	2	nickel 2	0.5	tungs- ton 1.5	brass 1
Britannia ware made in Sheffield	3½ parts	28 parts	8 parts	...	...	...	brass 8 parts
For plugs of stop- cocks	80	20	...	...	...	...	...
For seats of stop- cocks	86	14	...	...	...	...	...
Algiers metal .	90	10	...	...	...	...	...
„ .	75	25	...	...	...	...	...

(b) **Bearing or Anti-friction Metal.**—This is sometimes known as white metal. This metal is generally an alloy of tin, antimony, and copper; but rarely it is composed of lead, antimony, and tin, or of zinc, antimony, and tin; or still more rarely of lead, zinc, and tin, or of zinc, tin, and copper, etc.

There are two kinds of bearings: one for heavy loads and a large number of revolutions, and the other for light loads and a small number of revolutions. The former require the use of red brass; the latter, that of white metal.

White metal enables the axle to run with extreme smoothness. Its hardness depends upon the amount of copper content.

The following is a list of the principal varieties of white metal, as used in industries:—

	Tin.	Ant.	Copper.	Zinc.	Iron.	Lead.
English, for heavy loads . . .	17.47	...	5.62	76.14	...	...
"    medium " . . .	76.7	15.5	7.8	...	...	...
"    "    "    " . . .	72.0	26.0	2.0	...	...	...
For mills . . .	15	...	3	40	...	42
"    heavy axles . . .	72.7	18.2	9.1	...	...	...
"    "    "    " . . .	38	6	1	47	...	4
"    rapidly revolving axles . . .	17	77	6	...	...	...
Bearings of great hardness . . .	5	...	2.5	...	70	...
"    "    "    " . . .	12	82	4	2	...	...
Bearings (cheap)* . . .	2	2	8	88	...	...
"    "    "    " . . .	1.5	1.5	7	90	...	...
Bavaria, durable cold running . . .	90	8	2	...	...	...
Austrian Govt. railroad . . .	90	7	3	...	...	...
Distributing slide valves . . .	83.2	11.2	5.6	...	...	...
{ Westphalia Bahn . . .	82	11	7	...	...	...
{ Magdeburg-Halber- ständter . . .	74	15	11	...	...	...
{ Saarbrücken . . .	85	10	5	...	...	...
{ Bergisch-Märkische . . .	80	12	8	...	...	...
{ Diverse Bahnen (recom- mended) . . .	85	10	5	...	...	...
{ Magdeburg-Leipziger . . .	91	6	3	...	...	...
{ Rheinische . . .	82	12	6	...	...	...
{ Ostbahn . . .	...	16	...	...	...	84
{ Berlin-Hamburger . . .	20	20	...	...	...	60
{ Oppeln-Tarnowitz . . .	42	16	...	...	...	42
Analysis made by Dudley in laboratory of Pennsylvania R.R. Co. { Car-box metal . . .	...	14.88	...	trace	0.61	84.33
{ Anti-friction metal . . .	...	11.93	...	...	...	88.32
{ American " " . . .	...	19.60	...	0.93	0.65	78.44
{ Magnolia metal . . .	...	16.45	bismuth trace	trace	trace	83.55
"    "    "    " . . .	5	15	...	...	...	80
Babbitt's anti-friction metal † . . .	83.3	8.3	8.3	...	...	...
Original Babbitt metal . . .	89	7.3	3.7	...	...	...

(c) **Type-metal.**—It is essentially an alloy of lead, antimony, and tin, with, occasionally, the addition of copper. One way of manufacturing the alloy is as follows:—Heat strongly 2 kilos. of tin in a

\* Siemens and Halske, equal parts of zinc and cadmium and 10 per cent. Sb.

† It can be made thus:—Melt separately 4 parts of copper, 12 parts of Banca tin, and 8 parts of antimony regulus, and, after fusion, add 12 parts of tin. The antimony is added to the first portion of the tin after its fusion, and the copper is introduced after the vessel is taken off the fire and before its content is poured out. The charge is kept from oxidation by a layer of powdered charcoal. A small percentage of aluminium added to the mixture gives a good result.

The German Babbitt metal is somewhat harder than that used in the United States, and for some uses is probably too hard. Many railroad companies in the United States buy a hard Babbitt metal and reduce it with pure tin to suit various requirements, e.g. :—

German railway specimen . . .	83.3 tin.	11.1 Sb.	5.6 Cu.
U.S. " " . . .	88.9 "	7.4 "	3.7 "

crucible, and, after its fusion, add 1 kilo. of copper, in shreds of plate, 5 kilos. of lead, and finally, after strong heating, 2 kilos. of antimony. Add to this mixture 1 kilo. of common type-metal (made from 25 kilos. of lead and 5 kilos. of antimony).

The following is a list of the common type-metals:—

	Lead.	Antimony.	Tin.	Copper.
Type-metal . . . . .	55	30	15	...
" . . . . .	60	25	15	...
" . . . . .	70	18	10	2
" . . . . .	82	14.8	3.2	...
" . . . . .	55	22.7	22.1	...
" . . . . .	61.8	18.8	20.2	...
" . . . . .	69.2	19.5	9.1	1.7
" . . . . .	80	20	...	...
" . . . . .	50	27.77	..	bismuth 22.23
" . . . . .	65.1	5.82	...	bis. 29.58
" . . . . .	66.66	33.34	...	...
Stereotype plate . . . . .	85.71	14.29	...	...
" . . . . .	70	15	...	bismuth 15
Linotype metal . . . . .	84.5	13.5	2	...
Type-metal . . . . .	72	18	25	...

(d) Hard Lead.—It is a particularly useful alloy, suitable for many technical purposes in which the lead, when used alone, possesses too low a melting-point; and further, it is used to make cocks and valves that come into contact with acids in chemical works. It is obtained from antimony ore containing much lead, and also as a by-product from smelting works. Its usual composition is 22 per cent. Sb and 78 per cent. Pb.

Antimony-lead alloys, according to Matthiessen:—

Composition.			Specific Gravity.			
Antimony.	Lead.	Atomic Formula.	Found.	Calculated.	Difference.	
					Exp.	Cont.
100	...	Sb	6.713	...	...	...
54.1	45.9	Sb.Pb	8.201	8.268	0.067	...
37.1	62.9	SbPb	8.989	9.045	0.056	...
22.7	77.3	SbPb <sub>2</sub>	9.811	9.822	0.011	...
16.4	83.6	SbPb <sub>3</sub>	10.144	10.211	0.067	...
10.5	89.5	SbPb <sub>5</sub>	10.586	10.599	0.013	...
5.5	94.5	SbPb <sub>10</sub>	10.930	10.952	0.022	...
2.3	97.7	SbPb <sub>25</sub>	11.194	11.196	0.002	...
...	00	Pb	11.376	...	...	...

(e) **Other Alloys of Less Importance.**—An alloy for making the nails to be used in ships consists of : tin 50 per cent., lead 33 per cent., and antimony 17 per cent. ; or 3 parts tin, 2 parts lead, and 1 part antimony. It is specially resistant against the continued action of water and atmosphere.

Metallic mirrors, buttons, etc., have been made from the following alloys :—

Antimony, silver, copper, zinc.
„ tin, zinc, steel.
„ copper, iron, lead.
„ copper, tin, zinc.
„ copper, tin, lead.

*Alloys of Antimony and Hydrogen.*—Antimony hydride is rather a chemical compound than an alloy, and is generally in the form of a gas. As a solid alloy it can be obtained by sending a current through a dilute sulphuric acid bath, the metal antimony being then negative. The hydrogen thus disengaged unites with the antimony to form brown flakes. If bichloride of mercury is introduced into the bath, an alloy consisting of hydrogen, antimony, and mercury is obtained, which becomes very unstable as soon as the galvanic current is stopped. The phenomenon of dissociation is accompanied by a development of heat and electricity, thus producing a reversing secondary current. Although the study of this curious and delicate reaction is still not far advanced, yet the results already obtained promise well for its future use in the manufacture of secondary poles and accumulators.

*Antimony Amalgam.*—Mercury dissolves antimony in different proportions, and forms white alloys, the fluidity of which decreases proportionately as the percentage of antimony increases. When in a solid state they are so fragile that they break up under the slightest shock. They are of theoretical interest only.

*Alloys of Antimony and the Alkalies.*—Potash and soda are reduced with great facility by carbon in the presence of antimony, forming alloys which may contain the alkaline metals up to 25 per cent. This alloy is ordinarily prepared by heating to red heat for two or three hours a mixture of 6 parts of tartar emetic and 1 part of nitre, or equal parts of antimony and roasted cream of tartar. The metallic button thus obtained is very compact, greenish gray in colour, brittle, and lamellar in structure. It possesses some of the properties of potassium ; when exposed to humid air it inflames rapidly ; in water, it sets the hydrogen free, leaving behind a residue of antimony, while the potash remains in solution. In contact with mercury, the anti-

mony is isolated, while the potassium forms an amalgam with the mercury. An explosive alloy can be made by calcining for three hours a mixture of 100 parts of tartar emetic, 3 parts of lamp-black; or 100 parts of metallic antimony, 75 parts of roasted cream of tartar, and 12 parts of lamp-black. The crucible used for this purpose must be coated with a thin layer of carbon to prevent adhesion. This alloy may be used in the manufacture of matches that are damp-proof.

*Cooke's Alloys.*—Two crystallised compounds of antimony and zinc are known, with  $Sb_2Zn_3$  and  $Sb_2Zn_2$  as formulæ. The former is prepared by melting together 57 parts of antimony and 43 parts of zinc. After carefully stirring the mixture, it is allowed to cool in the crucible until a crust is formed on the surface, which is then pierced and the liquid portion poured off. The interior of the crucible is then seen to be covered with magnificent prismatic crystals, terminating in points.

The latter,  $Sb_2Zn_2$ , is prepared in the same manner with 68·5 parts of antimony and 31·5 parts of zinc (*Fremy*). These two alloys possess the property of decomposing water at  $100^\circ C.$ ; thus, 200 grms. of  $Sb_2Zn_3$  can set free 130 c.c. of hydrogen gas in ten minutes. This decomposition can be accelerated by adding a few drops of chloride of platinum: 200 grms. of  $Sb_2Zn_2$  can then set free 244 c.c. of hydrogen gas in ten minutes. Cooke has recommended the use of these two alloys for the production of pure hydrogen in the laboratory.

*Réaumur's Alloys.*—When a mixture of 70 parts of antimony and 30 parts of iron is heated to a white heat in a crucible, the resulting alloy is very hard, white in colour, and slightly magnetic, the hardness being increased in proportion as the quantity of iron is increased. It is always formed when iron is used to excess in reducing antimony sulphide.

*Alloys of Antimony and Gold.*—Antimony has such great affinity for gold that a very minute quantity of antimony vapour will modify its ductility. The alloys are straw-yellow, the fracture being grainy and dull, like that of porcelain. They are used in jewelry.

*Alloys of Antimony and Copper.*—Equal parts of the two metals form an alloy having a beautiful violet colour.\* In combination with tin, the alloy is used in industries.

*Alloys of Antimony and Silver.*—They are white and brittle.

*Alloys of Antimony and Aluminium.*—These alloys, discovered recently, have been studied by M. Pécheux. Von Aubel (1895) obtained the alloy  $SbAl$ , which melts at  $1080^\circ$ ; L. Guillet (1902) obtained the alloys  $SbAl$ ,  $SbAl_3$ ,  $SbAl_4$ , and  $SbAl_{10}$ , which turn to a

\* It is known as "regulus of Venus."



black powder. Since then Pécheux has been able to obtain the alloys:  $SbAl_{20}$ , density = 2.73;  $SbAl_{35}$ , density = 2.7;  $SbAl_{38}$ , density = 2.662; and  $SbAl_{40}$ , density = 2.598. The melting-point of these four alloys is between 760° and 730°, while those of antimony and aluminium are 460° and 650° respectively. They expand on solidifying, are sonorous, offer resistance to filing, but are somewhat brittle, and can be slightly bent. They are of a bluish-gray colour, and do not alter in air or water at ordinary temperatures. The alloy  $SbAl_{30}$ , however, decomposes water at 100° C. The lightness, malleability, and durability of these alloys may render them useful in the construction of ships for the navy, submarine vessels, automobile conveyances, and air-ships.

An alloy of antimony and arsenic is very fusible, very hard and brittle, and is not of practical use.

An alloy of antimony and nickel is brittle, and has a lead colour.

Alloys of antimony and bismuth have the following composition, according to Holzmann:—

Composition			Specific Gravity.			
Sb.	Bis.	Atomic Formula.	Found.	Calculated.	Difference.	
					Exp.	Cont.
100°	...	Sb	6.713	...	...	...
54.0	46.0	$Sb_2Bi$	7.864	7.856	...	0.008
37.1	62.9	$SbBi$	8.392	8.385	...	0.007
22.7	77.3	$SbBi_2$	8.886	8.888	0.002	...
12.8	87.2	$SbBi_4$	9.277	9.272	...	0.005
8.9	91.1	$SbBi_5$	9.435	9.433	...	0.002
...	100	Bi	9.823	...	...	...

It may be assumed that the volume remains constant, the differences between the specific gravities found and calculated being negligible.

**Remarks on the Preparation of Useful Alloys.**—In working with antimony alloys it is important to cast them at a temperature as low as possible, and to pour into cold moulds, so as to aid rapid solidification and obtain a fairly uniform mass instead of an eutectic alloy. Brass moulds must be used for casting, and must be coated on the interior with a mixture of lamp-black and oil of turpentine, or lamp-black alone, to prevent any adhesion of the alloy to the mould. Red chalk mixed to a uniform mass with water can also be used.

The mixture for an alloy must be thoroughly stirred. If the alloy

on fracture shows a non-homogeneous structure, it requires to be rapidly remelted under a layer of charcoal, so as to prevent oxidation.

Fig. 62 shows a smelting furnace for the production of alloys of antimony with other metals.

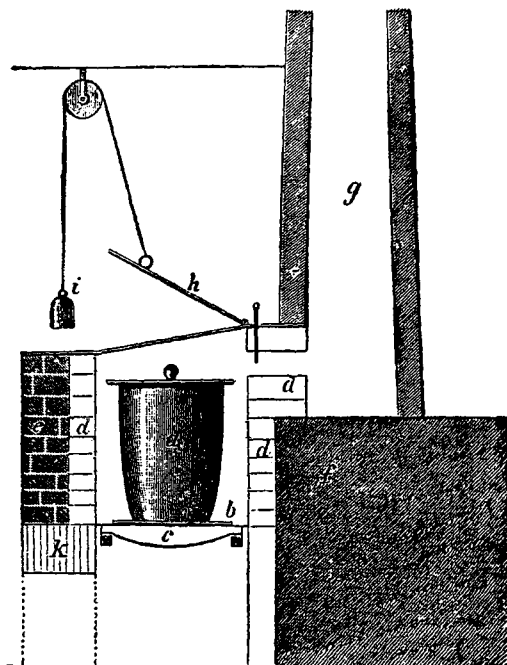


FIG. 62.—Scale =  $\frac{1}{4}$ .

- |                       |                            |
|-----------------------|----------------------------|
| a, Graphite crucible. | f, Ground.                 |
| b, Cast-iron plate.   | g, Chimney.                |
| c, Grate.             | h, Iron cover for furnace. |
| d, Fire-brick.        | i, Balancing weight.       |
| e, Common brick.      | k, Arch.                   |

## 2. Pigments and Paints.

(a) **Antimony White.**\*—The process for forming it, as given by MM. *Bolierre, Ruolz, and Rousseau*, is as follows †:—In a brick oven or a cast-iron furnace, a draught of air and a jet of steam regulated for

\* Taken from the translation by Fesqueat.

† Vide "Volatilisation Process" under *Metallurgy*.

each kind of sulphide is thrown upon the heated surface of antimony sulphide. Sulphur escapes as sulphurous acid, which may be saved, and the antimony is converted into white oxide, which is collected in receivers placed at the end of the heating apparatus. This product may be ground immediately with oil. It does not require drying, pulverising, sifting, etc. The covering power is twice that of white lead.

The process of MM. *Vallé* and *Barreswill* is as follows:—Algaroth powder, an oxychloride of antimony, is obtained by treating  $Sb_2S_3$  with HCl.  $H_2S$  is made to burn, and the sulphurous acid produced is employed in lead chambers for the manufacture of sulphuric acid. The clear and settled chloride of antimony is decomposed by water. The hydrochloric acid resulting from this decomposition (with a little antimony) is used for condensing HCl gas, or for separating the gelatin from bones; also for manufacturing new antimony white, by treating with HCl either the residue of antimony ore calcined at a low temperature, or the product of the action of  $H_2SO_4$  upon the  $Sb_2S_3$ . The sulphurous acid resulting from the treatment is used for the manufacture of sulphuric acid.

MM. *Hallett* and *Stenhouse's* process:—A natural oxide of antimony, or an ore in which the sulphide and the oxide are associated together, is used. The mineral is pulverised and is separated from the gangue by washing or by some mechanical device. The heavy portion thus obtained is calcined in a reverberatory furnace, and from it the sulphur is driven off as sulphuric acid. The residue consists mostly of antimonious acid, which, after being further powdered, is mixed with oil or varnish. The product may occasionally contain a little lead, copper, or iron, which has the effect of diminishing its whiteness. Hence it is mostly used for inferior painting.

Antimony-white paint can withstand the action of water, is as opaque as white lead, is scarcely acted upon by sulphurous fumes or sulphuretted hydrogen, is durable for outside-work painting, and is not poisonous.\* Furthermore, it possesses more body than zinc white, covers better, and is cheaper.

\* In 1850, J. Brachet, Professor of General Pathology at the *École de Médecine*, Paris, in discussing the lead-paint question, stated: "Is it possible, in the painting of buildings, to replace white lead by some other metallic substances less poisonous? Is it possible to employ white oxide of antimony, as proposed by Ruolz? . . . In order to dispense with the use of lead paint, it is necessary to have a great quantity of this mineral. If one could open up some of these mines, he would then do a great service, not only to industries and arts in general, but above all to humanity. It is to be hoped that the government will encourage this branch of industry. . . . The great problem of preventing lead disease will thus

The following gives a comparison of the prices of the three kinds of paint in actual use,\* the rates being taken from the *Revue des produits chimiques*:—

White lead,	100 kilos. † at	61 fr.	.	.	.	.	61 fr.
Oil,	30	„	140	„	.	.	42 „
	130 kilos. cost .	.	.	.	.	.	103 „
	100	„	.	.	.	.	79·20 „
Zinc white,	100 kilos. at	82·50 fr.	.	.	.	.	82·50 fr.
Oil,	60	„	140	„	.	.	84·0 „
	160 kilos. cost .	.	.	.	.	.	166·50 „
	100	„	.	.	.	.	104·05 „
Antimony white,	100 kilos. at	85 fr.	.	.	.	.	85 fr.
Oil,	50	„	140	„	.	.	70 „
	150 kilos. cost .	.	.	.	.	.	155·5 „
	100	„	.	.	.	.	103·66 „

Experience shows that the following ratio must be taken for painting a given surface with the three kinds of paint, separately—

$$\begin{array}{ccc} \text{Kil.} & \text{Kil.} & \text{Kil.} \\ \text{Zn : Sb : Pb} & = & 100 : 120 : 130. \end{array}$$

But, in order to obtain the same hue for the three cases, experience shows that it is necessary to apply:—

1 coat of lead at	102·96 fr.	.	.	.	.	102·96 fr.
2 coats of antimony at	124·39 fr.	.	.	.	.	248·78 „
3 „ zinc at	104·05 fr.	.	.	.	.	312·15 „

From these it can be seen that antimony white is a good substitute for white lead, from the point of view of hygiene and technology.

M. G. Hyvert recommends the following process ‡:—Carbonate of soda is melted with a mixture of antimony and saltpetre or sodium dioxide, and a solution of sulphate of alumina is used to treat the waters of lye-washing. Good results can also be obtained by treating antimony oxide, together with pulverised bauxite, with silicate of soda, the product being treated with lye-washing and

be solved.” Also the *Chambre de Commerce de Montluçon* adopted, Oct. 13, 1901, the proposition to replace the use of lead paint by that of antimony white, and to encourage the general public to use it from the hygienic point of view. With regard to this question, consult *La Crise du Plomb*, par G. Hyvert, 1901.

\* Taken from *La Crise du Plomb*, p. 28.

† 1 fr. = 9½ pence; 1 kilo. = 2¼ lbs.

‡ French patent, June 18, 1901.

dried at 100°. Again, a mixture of bauxite and antimonious acid may first be treated with steam, and then calcined slowly under a current of carbonic acid gas. Finally, the antimonates of manganese and of zinc give a good white colour.

(b) **Antimony Black.**—It is obtained by treating antimony solutions with zinc or iron. The deposit thus obtained is in the form of powder, and is used to bronze metals or plaster.

(c) **Antimony Vermilion.**—Lampadius, in 1853, proposed using the red sulphide of antimony as a pigment, which, as he observed, covers well when employed with water, but possesses less body when ground with oil.

M. E. *Mathieu-Plessy* writes thus\* :—"The product to which I give the name vermilion of antimony is the result of a new modification of the sulphide of antimony which I obtain from the decomposition of hyposulphite of soda in the presence of chloride of antimony.

"Among the phenomena of double decomposition, so characteristic of the nature of mineral substances, none is more striking than the production of the orange-yellow sulphide of antimony by means of sulphuretted hydrogen or of an alkaline sulphide. If the latter reagent, from long exposure to the air, be partly transformed into hyposulphite, it may give with a proto-salt of antimony variously coloured precipitates, the colour depending on the degree of oxidation. These variations, which may have been already observed, will be easily explained by the reaction studied by myself, which gave the key for obtaining a red sulphide of antimony entirely distinct from the well-known ones hereafter mentioned.

"I refer to the orange-yellow sulphide, produced by the reaction of sulphuretted hydrogen upon the proto-chloride of antimony, the black native sulphide, and the brown-red sulphide, a modification of the preceding one, which was observed for the first time by Fuchs, and has recently been studied by Mr Rose.

"It is not sufficient, however, to put the proto-chloride of antimony and the hyposulphite of soda in contact with each other to obtain the sulphide of antimony with all the brightness which it is able to acquire. In order always to arrive at the desired result, I have been obliged to make numerous trials and to vary the proportions of the reagents and the temperature. At last I have succeeded in finding out a process which is satisfactory in regard to the quality of the product and the facility of its preparation.

"Believing that the vermilion of antimony might find its applica-

\* *Bull. de la Société industrielle de Mulhouse*, vol. xxvi. pp. 297 et seq.

tion in the arts, I have examined its preparation from beginning to end, and I have therefore aimed at producing hyposulphite of soda and the chloride of antimony on a manufacturing scale. In regard to the hyposulphite of soda, and in order to avoid crystallisations, which require a special apparatus, I followed a process which gave me this salt in a state of sufficient purity, at a time when its preparation was but little understood. The process was based upon the employment of the sulphide of soda.

"In my researches I have demonstrated that this salt should be employed in the natural state, in order to avoid the reaction of the sulphurous acid upon the hyposulphite resulting in the Langlois salt, which, being also decomposed, becomes sulphate of soda. In the preparation of the sulphite I have followed the process of M. Camille Koechlin, which consists in burning sulphur in a convenient apparatus. It consists of a sieve holding large crystals of soda, suspended in a cask open at the top. The bottom is connected by means of a pipe with a small clay furnace, upon which the sulphide is thrown in small quantities at a time.

"The combustion of the sulphur is regulated by means of a trap-door; the draught is good, and after two or three days the crystals of soda are transformed. Should there be portions unacted upon, the easily crumbling sulphite is rubbed off, and the core of carbonate is replaced in the cask. A solution of 25° Bé. strength is made from the sulphite, and is afterwards heated and saturated with crystals of soda. When the addition of this salt ceases to produce an effervescence (litmus paper does not give sufficient indications), or rather, when a diluted sample of the liquor produces a slight disengagement of carbonic acid by the addition of hydrochloric acid, then sublimed sulphur is put in, and the mixture is heated for three hours upon a water-bath. During that time the evaporated water is replaced and the mass is frequently stirred. The cold liquor is diluted with water until the strength is 25° Bé.

"The protochloride of antimony is easily prepared by boiling in hydrochloric acid the powdered native sulphide of antimony. When the disengagement of hydrosulphuric acid begins to be slow, the whole is boiled for a few minutes. After cooling, the clear liquid is decanted.

"In order to obviate the inconvenience of the production of sulphuretted hydrogen, the gas is collected in a solution of soda, or it is burned at the end of a glass tube connected with the vessel where the reaction takes place. If a burning alcohol lamp be placed at the end of the tube, the combustion of the gas will not be arrested, even

should the gas be accompanied by a large proportion of steam. The chloride of antimony thus obtained is diluted with water to 25° Bé.

“The two solutions of antimony and of hyposulphite being prepared, we proceed as follows:—We pour into a stoneware vessel 4 litres of chloride of antimony, 6 litres of water, and 10 litres of hyposulphite of soda. The precipitate caused by the water is rapidly dissolved in the cold by the hyposulphite. The vessel is then placed in a hot-water bath, where the temperature of the mixture is gradually raised. At about 30° C. the precipitate of sulphite begins to form; it is orange-yellow at first, and becomes darker afterwards. At 55° C. the vessel is removed from the water-bath and the precipitate is allowed to settle, which it does rapidly. The mother-liquors are decanted, and the deposit is washed, first with water holding  $\frac{1}{15}$  of HCl, and afterwards with ordinary water. Lastly, the precipitate is collected upon a filter and dried. The wet vermilion of antimony is of an exceedingly bright red colour; after drying, it loses part of its brightness. This pigment may be prepared in the cold, but the product is finer and more constant if we operate in the manner just described.

“Being certain to reproduce my new sulphide whenever it is desired, I have undertaken its analysis. But as the determination of the antimony is very difficult, and as there is no known method sufficiently accurate for the purpose, I have determined the sulphur and calculated the antimony by difference. It has also been necessary to determine the proportion of water. Moreover, I have compared the orange-yellow sulphide with my own, and the result is:—

0·668 of orange-yellow sulphide loses 0·038 at 200° C.  
0·808 of red sulphide loses 0·009 at 200° C.

“This proves that the vermilion of antimony is an anhydrous substance, and that the above shown is due to imperfect drying.

“There now remains to prove by analysis that the vermilion of antimony differs from the orange-yellow sulphide by only one equivalent of water. This explains the new properties of the red sulphide. I have found by analysis:—

Water . . . . .	1·1
Sulphur . . . . .	26·7
Antimony (by difference) . . . . .	72·2
	<hr/>
	100·0

which composition proves that the equivalents of sulphur and antimony are in the ratio 3 : 1.”

M. E. Kopp\* says:—"The sulphide of antimony, according to its physical state and its mode of preparation, may present very varied colorations. It is crystalline and black-gray in the native state. When kept in the molten state for a long time and suddenly cooled, it becomes hyacinth-red. Precipitated by sulphuretted hydrogen from an antimonious solution, it is of an orange colour more or less red. In the kermes state it is red-brown. Lastly, when obtained from the reaction of a soluble hyposulphite upon the chloride of antimony, its red colour is more or less bright, and more or less orange or crimson, in accordance with the temperature employed and the concentration of the liquors.

"This latter reaction was indicated by several chemists, who gave recipes for the regular manufacture of the fine red sulphide of antimony, which was called vermilion of antimony.

"All of these methods are based upon the employment of hyposulphite of soda and chloride of antimony in quite concentrated solutions, and they present various inconveniences.

"In the process which I have followed, the vermilion of antimony is obtained by the reaction of the chloride of this metal upon a dilute solution of hyposulphite of lime; and the mother-liquors are used several times, and are thrown away only after they contain too great a proportion of chloride of calcium.

"I am going to describe successively the various operations in the manufacture of the red sulphide of antimony.

"1. *Preparation of the Chloride of Antimony.*—The decomposition of the sulphide by HCl is very easy in experimental laboratories, but the operation presents great difficulties when we have to work upon large quantities of materials.

"After a series of experiments (employment of leaden vessels, heating stoneware vessels in sand and pitch baths, etc.), I found that it was much better to roast the sulphide of antimony at a moderate temperature in contact with air and steam. The greater part of the sulphide is converted into oxide of antimony, and the sulphurous acid produced in the manufacture of the hyposulphite of lime. The oxide of antimony is then easily dissolved in commercial hydrochloric acid.

"If, during the oxidation of the sulphide of antimony, there is produced a certain proportion of antimonious acid, but slightly soluble in HCl, it may be saved by collecting the residues from the treatment with hydrochloric acid, and washing them with chloride of calcium or hyposulphite of lime, which dissolves the adherent

\* *Bulletin de la Société industrielle de Mulhouse*, vol. xx. pp. 379 et seq.



chloride of antimony. They are then dried and melted with a certain proportion of antimony sulphide and quicklime, in order to transform the whole into antimony green. The addition of a small quantity of quicklime is intended for decomposing the small proportion of chloride of antimony which may still remain in the residues.

"2. *Preparation of the Hyposulphite of Lime.*—This salt is cheaply prepared by the action of sulphurous acid upon the sulphide or polysulphide of calcium, or the oxysulphide. The sulphurous acid is produced by burning brimstone or roasting pyrites or sulphide of antimony.

"The polysulphide of calcium is prepared by boiling finely ground sulphur with newly slaked lime and sufficient water. It is advantageous to add to this solution of polysulphide a certain proportion of powdered oxysulphide of calcium, which is the residue of the lixiviation of crude soda. In the absence of oxysulphide, quicklime may be added.

"Sulphurous acid, in its reaction upon the sulphide and oxysulphide of calcium, sets sulphur free and forms a sulphite of lime, which, in the presence of sulphur and undecomposed sulphide, is soon transformed into hyposulphite of lime. The reaction is aided by the elevation of temperature which takes place in the apparatus.

"The liquor is examined now and then to see whether it is alkaline, neutral, or acid. As soon as it has become slightly acid, it is run from the apparatus into a large settling-tank, where it generally becomes neutralised by a certain quantity of undecomposed oxysulphide of calcium held in it. If, after stirring for some time, the liquor preserves its acid reaction, sulphide of calcium is added until complete neutralisation is effected, which is ordinarily made apparent by a black precipitate of sulphide of iron.

"After settling for some time, the clear liquid is decanted, and forms a solution of nearly pure hyposulphite of lime. The same vessel is subsequently used for neutralising the liquors obtained during the process of manufacture.

"3. *Preparation of Vermilion of Antimony.*—The red sulphide of antimony is prepared with the above solutions of chloride of antimony and of hyposulphite of lime.

"The apparatus consists simply of several wooden tanks, holding from 20 to 30 hectolitres each, and raised about 1 metre above the floor. These tanks are so arranged that they may be heated by steam, passed through a copper or lead pipe, opening about 2 decimetres from the bottom, or, what is preferable, through a coil of

pipes, the condensed steam of which may be carried outside, without being mixed with the liquors. In this manner we avoid the useless dilution of the liquors producing the vermilion of antimony.

"When the pressure of the boilers has reached two or three atmospheres, the tanks are filled with the solution of hyposulphite of lime up to seven-eighths of their height. We then pour the solution of chloride and antimony into the first tank, 2 or 3 litres at a time. There is formed a white precipitate which is rapidly dissolved at the beginning; but when solution becomes slow, even when the liquor is stirred, the addition of chloride of antimony is discontinued, because there should always be a certain excess of hyposulphite of lime.

"The liquor of the tank should be perfectly clear and limpid; if there is any white precipitate, it should be dissolved by adding small quantities of hyposulphite.

"Steam is then let in, and the temperature of the liquors is gradually raised to 50° or 60° or even 70° C. while stirring goes on. The reaction soon becomes manifest; the liquid is successively coloured a straw-yellow, then a pure lemon-yellow, orange-yellow, orange, reddish-orange, and lastly a very deep and bright orange-red. The steam is then stopped, and the acquired heat of the liquid, aided by a slow stirring, is sufficient to complete the reaction, and impart to the colour its maximum of intensity. Should the heating be continued, the red-orange colour would pass successively to a pure red, then to a more or less crimson red, which in its turn would grow darker and darker, and become brown, blackish brown, and, lastly, nearly black.

"We see that by graduating the temperature it is possible to obtain all the intermediate hues between orange and brown-black. The tank is covered, and the coloured precipitate is allowed to deposit.

"The clear and limpid liquor, which smells strongly of sulphurous acid, is decanted through holes bored in the tank at different heights, and is conducted by means of leaden pipes or wooden troughs into a large quantity of sulphide and oxysulphide of calcium. The sulphurous liquor regenerates a certain proportion of hyposulphite of lime.

"As the solution of chloride of antimony always contains a large proportion of chloride of iron, it becomes easy to watch the working of this latter operation. All the iron remains in solution in the mother-liquors of the sulphide of antimony; but as soon as these are brought in contact with sulphide of calcium the insoluble sulphide of iron is formed. As long as the black precipitate remains, the mother-liquors, charged with sulphurous acid, have not been added

in excess; but when they are in excess the black precipitate disappears, owing to its being changed into the soluble hyposulphite of iron. The contents of the reservoir are then well stirred, and, if necessary, sulphide of calcium is added, until the black precipitate of sulphide of iron reappears and remains permanent. At the same time a certain proportion of hyposulphite of iron should remain in solution. This condition is easily fulfilled when we operate upon a sufficiently large amount of materials. After the precipitate has settled the liquor is decanted, and is a neutral solution of hyposulphite of lime, with a certain proportion of hyposulphite of iron and of chloride of calcium.

“We should carefully avoid, in this regeneration of the hyposulphite of lime, leaving in an excess of sulphide of calcium, which will impair the coloration of the vermilion by causing the formation of the ordinary orange-yellow sulphide of antimony. Therefore, if the solution of hyposulphite of lime be yellow and alkaline, a liquor charged with sulphurous acid should be added, until complete neutralisation of the alkaline reaction.

“This solution of hyposulphite of lime, like the first, is employed in the preparation of a new quantity of vermilion of antimony. The mother-liquors, charged with sulphurous acid, are again neutralised in the large reservoir by a new proportion of sulphide and oxy-sulphide of calcium, and so on, until the liquors become so much loaded with chloride of calcium that it becomes necessary to throw them away, or to reserve them for some other purpose. But this takes place only after twenty or thirty operations.

“It is even possible to save the sulphurous acid in these exhausted mother-liquors, by saturating them with a milk of lime. This produces a precipitate of oxide of iron and of sulphite of lime, and leaves chloride of calcium only in the mother-liquors. The precipitate, mixed with sulphide of calcium, is transformed by sulphurous acid into the hyposulphites of lime and iron. And if the proportion of iron be too great, it may be precipitated by a slight excess of milk of lime.

“The precipitate of vermilion of antimony left on the bottom of the first tank is received into a conical cloth filter, and the drained liquors are added to those of the reservoir. The tank is then rinsed with tepid water, which is made to pass through the filter.

“The washing of the vermilion should be done very carefully, and it is often necessary to empty the contents of the filter into a large volume of pure water and to wash the filtrate several times by decantation. The red sulphide is afterwards filtered again and dried

at the ordinary temperature or in a stove-room the temperature of which is not over 50° to 60° C.

“While the precipitate is settling in the first tank, a similar operation takes place in the second, and then in the third. During that time the first tank has been emptied, and its mother-liquors have been regenerated. These are then brought back into the first tank, and another precipitation of vermilion of antimony takes place, and so on.

“4. *Properties of the Vermilion of Antimony.*—The vermilion of antimony is in the state of a very fine powder, without taste or smell, and is insoluble in water, alcohol, or essential oils. It is but little acted upon by the weak acids, even when concentrated, or by the powerful inorganic acids which have been diluted with water. It stands the latter acids better than the ordinary sulphide of antimony. Concentrated and hot hydrochloric acid dissolves it, with formation of sulphuretted hydrogen and chloride of antimony. Nitric acid oxidises it, with the production of sulphuric and antimonie acids. The vermilion of antimony is not sensibly acted upon by ammonia or the alkaline carbonates; on the other hand, the powerful caustic alkalies, such as potash, soda, baryta, strontia, and lime, decompose it and form combinations which are colourless, or nearly so. The colour is therefore destroyed; consequently this pigment should not be mixed with alkaline substances. A high temperature blackens it, and should the heat be such as to melt it, it becomes ordinary sulphide of antimony.

“The vermilion of antimony is an opaque pigment, without much lustre or brightness, when mixed with water, thickened by gummy or gelatinous substances. On the other hand, when ground in oil or varnishes, it acquires great intensity and brightness of color, and has good body or covering power, being superior in that respect to red lead, orange mineral, the red subchromate of lead, and cinnabar or mercury vermilion. A well-prepared vermilion of antimony, ground in oil, gives possibly the purest red color; that is to say, it is not tinged orange, or pink, or crimson; but it often has a brownish hue. It is perfectly unalterable by air or light, and may be mixed with white lead, which is not blackened by it, even after several years. It does not assist or hinder the drying of oil. Therefore the vermilion of antimony is a pigment especially fitted for oil-painting, and its low price and covering power render it advantageous for carriage and house painting.”

(d) *Antimony Yellow.*—(a) *Naples Yellow.*—This pigment, which is obtainable by combining lead oxide and antimonie acid together,

has been found native in the lavas of Vesuvius. There exist many processes for manufacturing it. According to Brunner, a German chemist, it can be produced thus:—A mixture of 2 parts of tartar emetic and 4 parts of marine salt is calcined gently in a Hesse crucible just to the point of fusion. After cooling, the mass is crushed and then washed with water.

(β) Messrs *Hallet* and *J. Stenhouse* in 1861 took out a patent in England for manufacturing antimony yellow. This is produced by using the oxides and the sulphides of antimony, with variable proportions of antimony, oxide of iron, silica, water, and sometimes arsenic, giving rise to various hues from a light yellow to a yellowish red. The gangue is removed as far as possible by picking and washing the ore, after which it is ground and sifted. The ground mass is introduced into large crucibles, muffles, or reverberatory furnaces, where it is carefully calcined at a dull red heat with access of air. The mass is constantly stirred in order to prevent too high an elevation of its temperature. During the operation, the powder emits steam, sulphur, sulphurous acid, fumes of antimony and arsenic, and becomes less fusible. The calcination lasts for from two to three hours, and is completed when vapours and fumes are no longer disengaged and when all the antimony has been transformed into anhydrous antimonious acid. The impure antimonious acid is reduced to an impalpable powder by grinding and levigation. After drying, it forms with oil, varnish, etc., a pigment which may be combined with oxides or salts, such as zinc oxide, white lead, chromate of lead. The yellow pigment is obtained when the following constituents are mixed together: 8 parts of native oxide of antimony, or of the oxide mixed with the sulphide, or the impure antimonious oxide obtained by the above-mentioned process; 3 parts of red lead or litharge; and 1 part of oxide of zinc. This mixture is powdered and calcined in crucibles, muffles, or furnaces, until combination is effected and the final yellow colour has appeared. The mass is then finally powdered and ground in oil or in varnish. By varying the proportions, one can obtain various tones and hues of Naples yellow:—

	I.	II.	III.	IV.	V.	VI.
Antimonious acid . . . . .	4	1	3	1	1	2
Oxide of lead . . . . .	2	2	3	1	1	1
Oxide of zinc . . . . .	1	1	1	1	...	...

In trade this pigment goes under various names, such as Naples yellow, jaune, solid yellow, antimony yellow.

(γ) *The Process of Meromé.*—A mixture of 3 parts of finely

powdered bismuth, 24 parts of powdered stibnite, and 64 parts of saltpetre is melted and is poured, while molten, into water. The mass thus obtained is brittle and is finely powdered, washed and dried, and is melted with 128 parts of litharge and 8 parts of sal ammoniac. This yellow pigment has almost fallen into disuse, because of its instability and the high price of bismuth.

(d) The *yellow pigment* can also thus be obtained:—Melt together 16 parts of litharge, 1 part of sal ammoniac,  $\frac{1}{2}$  part of antimonate of bismuth (obtained by heating a mixture of 30 parts of bismuth, 240 parts of antimony sulphide, and 640 parts of nitre), and, after complete fusion, pour into water.

(e) *Antimony Yellow of a Permanent Character (Fr. jaunes fixes)*.—This can be obtained by employing antimonic acid, produced by treating the perchloride of antimony with water and the residue with hydrochloric acid. It can also be prepared by slowly calcining antimonate of protoxide of iron, obtained by double decomposition, in the air. The result thus obtained is very resistant to the action of sulphurous vapour. When chloride of antimony is treated with a current of sulphuric acid vapour, the resulting pigment is still more resistant to the action of sulphurous vapour. Sulphuric acid, which, as a rule, is very injurious to Naples yellow and blackens it, is in this case a good agent for vivifying the colour. Various hues of yellow pigment can be obtained by adding to it an oxysulphide formed by the action of sulphantimonate of sodium in a solution of sulphate of zinc. The precipitate is a very deep orange-yellow, very insoluble, and is dried at 50°. A mixture of this with the persulphide in various proportions will produce hues of colour from lemon-yellow to orange yellow.

(e) *Antimony Blue*.—This pigment is, as yet, without an equal in the manufacture of artificial flowers. It is thus produced:—A dilute solution of potassium ferrocyanide is added to a clear solution of metallic antimony in aqua regia. According to Krauss, this is merely a Prussian blue obtained from the ferrocyanide used, which is decomposed by the strong acid, with evolution of hydrocyanic acid, the antimony thus possessing no colouring principle.

(f) *Antimony Violet*.—This is obtained by mixing antimony vermilion and either antimony blue or other kinds of blue together.

(g) *Antimony Green*.—This is obtained by the mixing of antimony yellow and antimony blue in different proportions.

(h) *Antimony Orange*.—R. Wagner recommended the use of sulpho-antimonite of barium mixed with artificial sulphate of baryta (*blanc fixe*) as furnishing good pigments for painting.

This pigment can be produced thus:—

Finely powdered sulphate of baryta . . . .	2 parts.
Native sulphide of antimony . . . . .	1 part.
Powdered charcoal . . . . .	1 „

This mixture is calcined in a crucible of clay or graphite for several hours up to red heat. The crucible should remain closed until it becomes cold, because the carbonaceous matter contained in it might become inflamed, with explosion, if it remained open. The calcined mass is then boiled in water, and the insoluble residue—the sulphide of barium and calcium—is used in the mixing of the material for another operation. The filtered liquid has a pale-yellow colour. Dilute sulphuric acid is then added to it until the orange colour is entirely precipitated. The colour thus produced is mixed with *blanc fixe*. If a purer orange hue is desired, the solution of sulpho-antimonite of barium is boiled with  $\frac{1}{2}$  part of sublimed sulphur. The sulpho-antimonite of barium is then transformed into sulpho-antimonate, which has a composition analogous to that of Schlippe's salt.

A yellowish orange colour is obtained when a dilute solution of sulpho-antimonate of sodium is treated with a mixture consisting of 1 kilo. of quicklime, dissolved in 25 litres of cold water, 1 kilo. of sulphate of iron protoxide, 1 kilo. of sulphate of zinc, and alum in amount varying according as the colour is required to be of a more yellowish or less red hue.

(i) **Orange-red Sulphide of Antimony.**—The patent of MM. *Leclair* and *Barruel* is to the following effect:—1 part of natural  $Sb_2S_3$  is pulverised and dissolved, with the aid of heat, in 7 parts of hydrochloric acid at 20° Bé. The hydrogen sulphide given off from the first operation is condensed in a solution of milk of lime. When all the sulphide is dissolved, the acid solution of antimony chloride is poured into stoneware vessels which have holes at different heights. The liquor is diluted with water until it becomes turbid and a white precipitate appears. Then this is put into demijohns and is submitted to a stream of hydrogen sulphide. The liquor is occasionally stirred with a wooden stick, and the vessels covered to prevent the escape of the hydrogen sulphide, which is, however, led to a solution of milk of lime by means of tubes, and is absorbed therein. The sulphide thus obtained is washed and dried in a stove-room heated to from 40° to 50° C., but not higher; otherwise it loses much water and turns black.

(j) **Miscellaneous Pigments.**—(a) A yellowish-red pigment can be obtained by melting a mixture of 8 parts of the oxide with 2 parts of the sulphide together. This is known as crocus.

(β) When 8 parts of the oxide are melted with 4 parts of the sulphide, the resulting product has a dark-brown colour, and is known as foie d'antimoine.

(γ) **Antimonite of lead.**—This is prepared by treating 50 parts of metallic antimony with 20 parts of concentrated sulphuric acid, thereby obtaining sulphate of antimony. This salt is heated until the evolution of acid fumes has ceased, and is then calcined in a crucible with 21 parts of dry carbonate of soda, with the production of antimonious acid. The fused material is boiled in water, and the solution is decomposed by neutral acetate of lead. The precipitate obtained is antimonite of lead, which can be collected on a filter-cloth and then dried upon bricks in a stove-room heated to 60° C.

(δ) **Antimonate of lead** is thus prepared :—A mixture of 1 part of antimony sulphide and 5 parts of nitrate of potash is deflagrated in a red-hot crucible, or upon the bed of a reverberatory furnace. The calcined product is dissolved in boiling water, and the solution thus obtained is decomposed by neutral acetate of lead. The precipitate is then washed and dried. The antimonate of lead thus obtained is white and heavy, and possesses a certain body.

(ε) **Kermes.**—Its colour is brownish yellow. It can be prepared thus :—

*Dry Method.*—In a crucible is melted a mixture of 5 parts of antimony sulphide and 3 parts of dry carbonate of soda. The mass, after complete cooling, is treated with 80 parts of boiling water.

*Wet Method.*—Boil, for three-quarters of an hour, 1 part of pulverised antimony sulphide with 22 parts of dry carbonate of soda, in 250 parts of water.

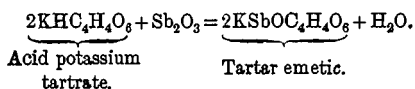
### 3. Medicine.

Antimony, by itself, cannot produce any effect upon the human system, but only as a salt capable of being decomposed by the fluids of the body, especially in the tartarised form, which, being the most soluble, has properly superseded other forms. According to Orfila, Flandin, Danger, and Milon, the solutions of antimony salts rapidly permeate the animal system and are readily eliminated with the urine. Under certain circumstances the salts of antimony contained in the solutions are deposited in the tissues, especially in the liver, the spleen, and the kidneys.

Several doctors, such as Navies, Van der Bosch, Hahnemann, Strack, Philip, have recommended the use of the salts of antimony in the treatment of colic induced by lead paint.

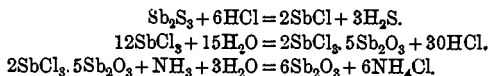


**Official Preparation of Tartar Emetic** (antimonii et potassii tartras):—Oxide of antimony in very fine powder, 2 oz. ; bitartrate of potassium, fine powder,  $2\frac{1}{2}$  oz. ; distilled water, 18 fl. oz. To the water, previously heated to boiling-point in a glass vessel, add the powders, previously mixed, and boil for an hour ; filter liquid while hot, and set it aside for crystallisation.



In small doses, it seems to increase the activity of the function of secretion, particularly of the mucous membranes ; in large doses it causes vomiting. It is also used in some eruptive or exanthematous fevers, in catarrhal affections, and as an ointment to be applied externally.

**Official Preparation of Antimony Trioxide** (antimonii oxidum) :—Sulphide of antimony in very fine powder, 4 oz. troy ; hydrochloric acid, 18 oz. troy ; nitric acid, 1 oz. troy ; liquor ammoniæ,  $1\frac{1}{2}$  fl. oz. ; distilled water. The sulphide is put into a flask containing hydrochloric acid, and is then digested by means of a sand-bath until effervescence ceases. Then add nitric acid gradually. When the nitrous acid vapours have ceased to be given off, the solution is allowed to cool. Add half a pint of water and filter. Pour the filtered liquid gradually into 12 pints of water, constantly stir it, and allow the precipitate to subside. Decant the liquid and wash the precipitate twice, on each occasion with 8 pints of water. Then transfer it to a muslin filter to drain, and wash it until the acid reaction ceases. Introduce it into a vessel and subject it to the action of liquor ammoniæ for two hours. Then transfer it to a muslin filter and wash it until the filtrate gives no precipitate when silver nitrate is added. Dry it finally in a gentle heat.



This oxide is used in the preparation of tartar emetic.

**Antimonii Sulphidum**,  $\text{Sb}_2\text{S}_3$ , is used almost exclusively in veterinary practice as an alterative.

**Other Antimony Compounds for Medical Purposes.**—When crude antimony is powdered and is mixed with thrice its weight of nitrate of potash, and projected gradually into a red-hot crucible, it detonates, producing a white oxide combined with sulphate of potash. This is the “solvent of Rotrou or unwashed calx of antimony” of the old

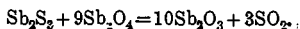
chemists. If the sulphate of potash be separated by repeated affusion of water, we have the calcined antimony of the London Pharmacopœia, which is "ceruse of antimony, or diaphoretic antimony."

By varying the proportions of nitrate of potash and sulphide of antimony, one is able to obtain different strengths of the resulting compounds, known as "mild antimonial emetic of Boerhaave," "crocus antimonii, crocus metallorum, or hepar antimonii," "crocus antimonii mitrior," and "crocus antimonii medicinalis."

Antimony trichloride, in liquid form, goes under the names "liquor stibii muriatici," "butyrum antimonii liquidum," "cauterium antimoniale." Besides these may be mentioned kermes (pulvis Carthusianorum,  $Sb_2S_3$  + variable  $Sb_2O_3$ ), antimony pentasulphide (golden sulphide of antimony,  $Sb_2S_5$ ), Algaroth powder ( $SbO_2Cl$ ), Schlippe's salt ( $Na_3SbS_4 \cdot 9H_2O$ ), antimoniate of quinine, etc.

#### 4. Colouring Matter in Glass-making and in the Preparation of Artificial Gems.

When antimony tetroxide is fused with antimony sulphide in suitable proportions, the resulting product is the trioxide, which always contains more or less of the sulphide.



The colour of the impure trioxide varies according to the quantity of sulphide it contains. This is known as "antimony glass," and is used as a colouring matter in glass-making and in the preparation of artificial gems.

#### 5. Colouring Matter in Pottery-Making.

The use of antimony in pottery coloration was known to the ancients. This is evident from the fact that the Chinese have used the oxide for a long time in the preparation of the yellow background and of carnation. Nowadays various shades of the same colour can be obtained by the addition of either zinc oxide or of tin oxide, which has the effect of brightening the colour; or of iron oxide, to deepen the general tone of the colour; or of the oxides of chromium and cobalt, to give a greenish tint to it.

**Yellow Pigment that can be Vitrified.**—This is produced by combining the oxide of lead with that of antimony or with the antimonate of potash, obtained by heating a mixture of 2 parts of metallic antimony and 5 parts of nitre in a crucible to red heat. The residue is washed with cold water. This, with the addition of various proportions of oxides of zinc and iron and sometimes tin, is mixed

with the flux of Sèvres No. 2, which is composed of 6 parts of minium, 2 parts of sand, and 1 part of melted borax.

*Yellow No. 2* (for hard porcelain):—

Minium . . . . .	400 parts.
Crystallised boric acid . . . . .	90 „
Sand . . . . .	120 „
Diaphoretic antimony . . . . .	120 „
Red oxide of iron . . . . .	30 „

*Yellow No. 3* (for hard porcelain):—

Minium . . . . .	420 parts.
Crystallised boric acid . . . . .	90 „
Sand . . . . .	120 „
Diaphoretic antimony . . . . .	12 „
Flower of zinc . . . . .	30 „

*Yellow No. 4*:—

No. 2 flux . . . . .	880 parts.	840 parts.
Flower of zinc . . . . .	35 „	40 „
Yellow hydrate of oxide of iron . . . . .	70 „	80 „
Diaphoretic antimony . . . . .	15 „	40 „

*Yellow No. 6* (for stoneware or glazed earthenware):—

	Pale.	Yellow.	Golden Yellow.
Antimonate of potassium . . . . .	60	60	60
Minium . . . . .	90	60	90
Carbonate of soda . . . . .	10	15	...
Hydroxide of iron . . . . .	...	12	56

*Clear Yellow No. 9*.—This is suitable for hard porcelain ; but it is equally applicable for enamel and light porcelain :—

Orange mineral . . . . .	120 parts.
Sand d'Étampes . . . . .	40 „
Melted borax . . . . .	40 „
Acid antimonate of potash . . . . .	40 „
Hydrated carbonate of zinc . . . . .	30 „

*Middle Yellow No. 10*:—

Orange mineral . . . . .	120 parts.
Sand d'Étampes . . . . .	40 „
Melted borax . . . . .	40 „
Acid antimonate of potash . . . . .	40 „
Hydrated carbonate of zinc . . . . .	20 „
Hydroxide of iron . . . . .	20 „

*Deep Yellow* No. 11.—This is made like No. 10, but 20 parts of coleothar or of red oxide are substituted for the carbonate of zinc and the yellow oxide of iron.

*Other yellows are :—*

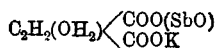
No.		Flux No. 2.	Antimonate of Potash.	Carbonate of Zinc.	Red Oxide of Iron.
41	B. Clear yellow for brown or green	75	17	8	...
42	P.F. Jonquil yellow . . . .	79	14	7	...
43	Deep yellow for brown or green .	75	17	4	4
46	Deep yellow . . . . .	75	17	...	8
47	Pale yellow for carnation . . .	84	4	4	8

## 6. Colouring Matter for the Manufacture of Cloth and Paper.

The oxysulphide of antimony ( $\text{SbS}_2\text{O}$ ) has been used for this purpose.

## 7. Mordants.

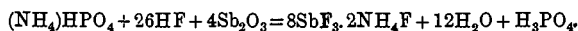
The salts of antimony used as mordants are of two kinds—either basic or acid ; the former is used for thickening, the latter for decolorising. The ordinary mordants are tartar emetic, double oxalate of potassium and antimony, and fluoride of antimony. They are always used after the application of tannin, when they form antimony tannates. Oxymuriate of antimony is another form of mordant. It is sold as a concentrated solution, made by dissolving metallic antimony in a mixture of hydrochloric acid and nitric acid, diluted very cautiously to  $80^\circ$  Tw. (specific gravity 1.4). The tartar emetic, as used, has the formula :—



Of late, double fluoride of antimony and potassium, or of antimony and sodium, have been used as substitutes for tartar emetic ; also double oxalate of antimony and potassium,  $\text{SbK}_3(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ , double fluoride,  $\text{SbF}_3 \cdot \text{NaF}$ , and the salt  $\text{SbF}_3(\text{NH}_4)_2\text{SO}_4$  are used. The essential thing for an antimony salt for use as a mordant is that it shall be soluble in water, not be liable to precipitate antimony oxide, and yet be readily decomposable.

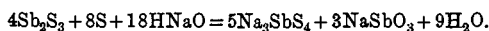
### 8. Mordant for Dyeing.

Fluoride of antimony,  $\text{SbF}_3$ , is used as a mordant for dyeing. According to Rad (1890), the following reaction occurs:—

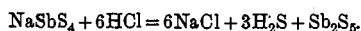


### 9. Vulcanising Rubber.

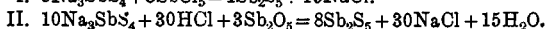
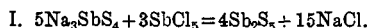
The so-called *Goldschwefel* (antimony pentasulphide,  $\text{Sb}_2\text{S}_5$ ) is used for this purpose. It is thus made:—Powdered antimony sulphide is heated with sulphur and sodium hydroxide:



From this solution the so-called Schlippe's salt,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$  crystallises out.  $\text{HCl}$  is then added to it:



According to Bertsch and Harmsen, the following reactions may occur:—



### 10. Coating Articles.

Metallic antimony can be used to paint objects with, giving them a polished-steel appearance. It is called "iron black" (*Eisenschwarz*) in trade, and can be obtained by precipitating a solution of antimony salt with zinc. It can also be used for bronzing gypsum.

The *beurre d'antimoine* ( $\text{SbCl}_3$ ) can be used for bronzing copper and iron, and preserving them from being oxidised by the deposition of a thin layer produced by the action of the copper or the iron upon the chloride.

M. George Hyvert recommended the use of antimony fluoride to get rid of vegetable parasites that are so injurious to iron structures and rails.\*

### 11. For the Manufacture of Aniline Yellow and Aniline Red.

Antimonic acid,  $\text{HSbO}_3 + 2\text{H}_2\text{O}$ , has replaced arsenic acid in the manufacture of aniline yellow and aniline red.

\* At present the railway companies in England and in the United States use a solution of arsenic compounds for this purpose.

## 12. For the Fabrication of Dice-boxes, etc.

An alloy of lead and antimony is used.

## 13. Miscellaneous Uses.

(a) If fluoride of antimony is heated with the sulphide, the sulphochloride is formed. It is used in medicine, or as a corrosive and macerating agent for wool.

(b) It has been proposed to use *beurre d'antimoine* in the manufacture of matches without phosphorus.

(c) Oxide of antimony is used in the manufacture of artistic *abat-jour* (lamp-shades) and *réflecteur en verre jaune opaque* (yellow opaque glass reflector).

(d) Antimony salts, particularly combined with fibrocol,\* are very good antiseptics for incorporation with lime-wash and with the paste † used in the *papiers couchés* of painters.

(e) Thermo-electric couples.

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\* Proposed by Hyvert in his book *Le Fibrocol*.

† Ordinary paste is a colloidal substance, giving rise to anticelluloid fermentation due to *Bacillus amylobacter* and *Bacillus butyricus*.

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## CHAPTER VII.

### THE ANALYSIS OF ANTIMONY COMPOUNDS.

THIS chapter is divided into the following parts :—

- A. Qualitative determination.
- B. Quantitative determination.
  - 1. Dry method—fire assaying.
  - 2. Wet methods.
    - (a) Gravimetric.
    - (b) Volumetric.
    - (c) Electrolytic.
- C. Special methods.

#### A. Qualitative.

The following is taken from Crookes\* :—

“(a) Minerals which contain antimony, when heated alone before the blowpipe on charcoal, or with the addition of 3 or 4 parts of fusion mixture ( $K_2CO_3 + Na_2CO_3$ ), yield dense white fumes of antimonious oxide, which in great measure escape into the atmosphere, but which also in part become deposited on the charcoal support, forming a well-marked white sublimate, or incrustation of the oxide.

“These results, though certainly in most cases very useful indications, do not furnish, to the satisfaction of the mineralogist, sound, conclusive evidence of the presence of antimony in the mineral tested, seeing that several other bodies occurring in the mineral world give, when heated before the blowpipe, exactly the same or nearly similar reactions. As a consequence of the hitherto inconclusive blowpipe evidence, mineralogists have usually considered it essential when engaged in correct work to supplement those indications by means of the accurate but tedious method of the ordinary wet way qualitative chemical analysis.

\* *Select Methods in Chemical Analysis*, by Sir W. Crookes, pp. 372 *et seq.* 4th edition, 1905. Longmans, Green & Co.

“With a view to remove the necessity of consuming so much valuable time over the certain identification of antimony, Alexander Johnstone proposes the following exceedingly simple test, which he discovered and successfully applied while working among the various metallic ores of antimony.

“To the white coat which will invariably form on the charcoal if the mineral containing antimony be properly treated and heated before the blowpipe, add, by means of a narrow glass tube, a single drop of ammonium sulphide. If the white sublimate is composed of antimonious oxide, then the portion touched by the drop (or the part touched by the edge of the drop) will immediately become converted into the well-known and highly characteristic reddish or orange antimony sulphide.

“As no other white coat producible on charcoal by heating a mineral in the blowpipe flame becomes reddish or distinctly orange in colour when treated as above with ammonium sulphide, the value of this easily applied test must at once be apparent.

“(β) In the examination of mineral bodies for antimony the test substance is often roasted in an open tube for the production of a white sublimate. Dr E. Chapman, Professor of Mineralogy at Toronto, recommends for the detection of antimony in this substance the following process—a method more especially available when the operator has only a portable blowpipe-case at his command:—The portion of the tube to which the chief part of the sublimate is attached is to be cut off by a triangular file, and dropped into a test-tube containing some tartaric acid dissolved in water. This being warmed or gently boiled, a part at least of the sublimate will be dissolved. Some potassium bisulphate—either alone, or mixed with some sodium carbonate and a little borax, the latter to prevent absorption—is then to be fused on charcoal in a reducing flame; and the alkaline sulphide thus produced is to be removed by the point of the knife-blade and placed in a small porcelain capsule. The hepatic mass is most easily separated from the charcoal by removing it before it has time to solidify. Some of the tartaric acid solution is then to be dropped upon it, when the well-known orange-coloured precipitate of antimony sulphide will at once result.

“In performing this test, it is as well to employ a somewhat large fragment of the test substance, so as to obtain a thick deposit in the tube. It is advisable also to hold the tube in not too inclined a position, in order to allow but a moderate current of air to pass through it; and care should be taken not to expose the sublimate to the action of the flame, otherwise it might be converted almost wholly

into a compound of antimonious and antimonie acids, the greater part of which would remain undissolved in the tartaric acid. A sublimate of arsenious acid, treated in this manner, would, of course, yield a yellow precipitate, easily distinguishable by its colour, however, from the deep-orange antimonial sulphide. The crystalline character, etc., of this sublimate would also effectually prevent any chance of misconception.

“(γ) Dr A. Weller proceeds as follows for the estimation of antimony:—Antimonie acid and antimonie oxide, and in like manner antimony penta- and tri-chloride, can be most easily distinguished from each other by their different behaviour with potassium iodide. The property of the former, when in hydrochloric solution, of separating two atoms of iodine from potassium iodide for each atom of antimony can be used for the qualitative estimation of antimony. In order to verify this method, weighed quantities of finely pulverised pure metallic antimony are oxidised in a flask at a gentle heat with potassium chlorate and hydrochloric acid, and the excess of chlorine is expelled by strong heating. The solution of antimony pentachloride thus obtained is introduced into the flask of Bunsen's chlorine distillation apparatus by means of hydrochloric acid, considerably diluted and mixed with a sufficiency of perfectly pure potassium iodide, avoiding too great an excess. The liberated iodine is distilled into dilute solution of potassium iodide, observing all the precautions laid down by Bunsen, and especially cooling the retort well in flowing water. When cold the distillate is titrated in the usual manner by means of very dilute sulphurous acid and an iodine solution of known strength. The distillation requires from five to ten minutes. Particularly important is the fact that stannic acid and stannic chloride in acid solutions do not decompose potassium iodide. This behaviour renders it possible to estimate antimony in presence of tin, as in alloys, easily and accurately. The tin is calculated as difference.”

The detection of the impurities accompanying the sulphide can be made thus:—The mineral is pulverised and is heated with concentrated hydrochloric acid, until all of it enters into solution. The lead will separate out in the form of lead chloride, upon the cooling of the liquid. Water added to the clear supernatant liquid will cause the precipitation of antimony oxychloride ( $\text{SbOCl}$ ), a white powder, while iron and copper remain in solution. Copper may be detected by the blue coloration when a few drops of ammonia are added to the filtrate, while the presence of iron may be proven by the addition of a solution of potassium ferrocyanide.

## B. Quantitative.

1. **Dry Method.**—*Fire Assaying.*—Dr J. Clark says (*Journ. Soc. Chem. Ind.*, 1896) that fire-assay for antimony ore is inaccurate, and refers to Carnot's investigation upon the same subject (*Annales des Mines*, vol. i.), wherein it was shown that results were rarely within 8 or 9 per cent. of the truth.

In assaying antimony ores it is necessary to determine one of the following things :—

( $\alpha$ ) The pure sulphide of antimony (antimony crude) which the ore may contain.

( $\beta$ ) The metallic antimony (antimony regulus) which the ore may yield.

( $\alpha$ ) *The Determination of the Sulphide of Antimony.*—The ore is first broken into small pieces, which are then charged into a crucible with perforated bottom. This is fitted into a second crucible for about half its depth. The lid of the first crucible and the joint between the two crucibles should be luted with fire-clay and sand. Only the upper crucible is heated, while the lower one is allowed to protrude into the ash-pit of the furnace. Thus the sulphide is melted and collects in the lower crucible.

( $\beta$ ) *The Determination of Metallic Antimony.*—

1. The ore is in the oxide state :—

Ore . . . . .	10 grms.
Soda ( $\text{NaHCO}_3$ ) . . . . .	25 ,,
Argol . . . . .	5 ,,
Salt . . . . .	cover.

The heat must be carefully regulated, and the assay should be taken off the fire as quickly as possible.

2. The ore is a sulphide or an oxide :—

Ore . . . . .	10 grms.
Cyanide of potassium . . . . .	35-40 ,,
Salt . . . . .	cover.

The heat applied must be low, and the operation must be a quick one

The button obtained should be cleaned by washing only, and not by hammering, as it is brittle. The button could be tested for iron or other impurities present. The foreign metals can be separated by treating the broken button with concentrated nitric acid, which converts the antimony into an antimonic acid precipitate. Filter, wash, dry, and ignite. The weight multiplied by 0.790067 gives the metallic antimony. Often this step is unnecessary, as the

volatilised antimony can more than counterbalance the impurities that may be present.

2. Wet Methods.—(a) *Gravimetric.*—(a) *Determination as Trisulphide,  $Sb_2S_3$ .*— $H_2S$  is passed for twenty minutes into the cold solution of an antimonite or antimonate. The solution is then heated to

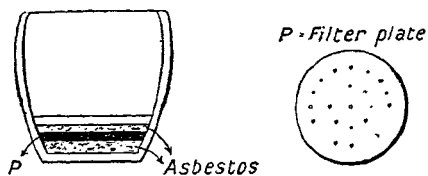


FIG. 63.

boiling, the current of  $H_2S$  being still maintained up to fifteen minutes after the commencement of boiling. The dense precipitate is then filtered through a Gooch crucible.\* It is then washed with 50 to 75 per cent. of very dilute and hot acetic acid into which  $H_2S$  has been passed, dried, and heated in a Paul's drying-oven to  $230^\circ$  for not

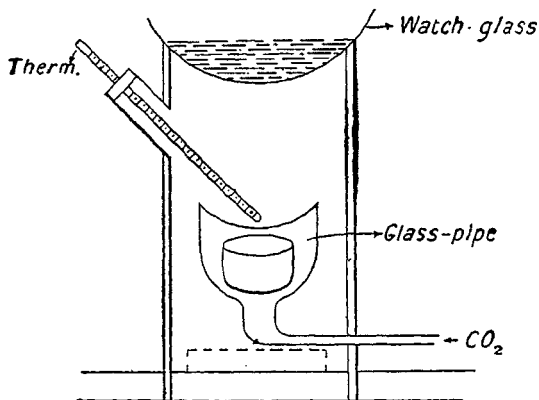


FIG. 64.

more than half an hour. The sulphur volatilised from the precipitate is collected in watch-glasses. As soon as all the sulphur has been driven off, the crucible is allowed to cool and is weighed.

( $\beta$ ) *Determination as Tetroxide,  $Sb_2O_4$ ,* according to Rössing.—The sulphide of antimony, precipitated from a hot solution, is washed (1) with hot water, (2) with alcohol, (3) with a mixture of alcohol

\* For a short description of this crucible, *vide* pp. 24–25, Hall's *Analytical Chemistry*, vol. ii.; N. Y., Wiley & Sons, 1905.

and carbon bisulphide, (4) with alcohol alone, and (5) with ether. Dry the precipitate by warming it slightly. Remove as much precipitate as possible from the filter on to a watch-glass, and use hot ammonium sulphide to dissolve the remaining portion upon the filter-paper, which is then evaporated to dryness in a weighed crucible. The main part of the precipitate is then added to the crucible. Pass fuming nitric acid into the crucible covered with a watch-glass. After the first violent action is over, the crucible is heated in a water-bath until the evolution of gas has entirely ceased. Remove the watch-glass and evaporate the contents of the crucible to dryness. In order to oxidise all the sulphur, this operation is repeated. The  $H_2SO_4$  formed is eventually driven off by careful heating over a free flame. The open crucible is placed in the opening of an inclined disc of asbestos board, and the temperature is gradually increased until the full heat of the Teclu burner is obtained.

( $\gamma$ ) *Estimation of Antimony in Native Sulphide of Antimony*, according to Crookes.—The mineral is powdered, and 20 grains of it are taken. They are treated with a slight excess of HCl, and the mixture is gently heated until the  $H_2S$  has completely evaporated. The solution is then filtered, and the filter is washed with dilute HCl. The solution is then slowly evaporated in the flask until it is concentrated enough and freed from the excess of HCl. The antimony is now in the form of trichloride. A newly prepared solution of gallic acid is carefully added to a slight excess. Hot water is next added, and the precipitate of antimony bigallate is washed, dried, and weighed. The filtrate can be tested for iron, lead, copper, silver, arsenic, and, sometimes, zinc, cobalt and other metals remaining in solution. As iron is difficult of complete separation in the presence of gallic acid, other well-known methods are used for its determination.

According to Mr L. Parry, the determination of antimony by the gravimetric method, especially if estimated as  $SbO_3$ , is quite unreliable.

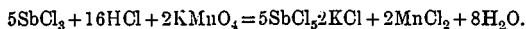
( $b$ ) *Volumetric.*—( $a$ ) *Mohr's Method.*\*—Conversion of antimonious acid in alkaline solution into antimonic acid by iodine.

Antimonious oxide, or any of its compounds, is dissolved in tartaric acid and water; sodium carbonate is used to neutralise any excess of the acid used; then a cold saturated solution of sodium bicarbonate is added in the proportion of 10 c.c. to about 0.1 gramme  $Sb_2O_3$ ; to the clear solution starch is added, and  $\frac{N}{10}$  iodine until the blue colour appears. This operation must be done quickly, as when the bicar-

\* This is a useful method when copper is absent.

bonate is added the metal is soon precipitated as antimonious hydrate, upon which the iodine has no effect.

( $\beta$ ) *Volumetric Method of Petriccioli and Reuter.*—The antimony ore is crushed, and 0.5 to 1 gramme of it is taken and treated first with 50 c.c. of hot water and then with 50 c.c. of pure strong hydrochloric acid. It is heated on a sand-bath up to 70° C. All the antimony is then dissolved in about from thirty to sixty minutes. It is next filtered and the residue washed, first with water containing HCl and then with pure water. The filtrate, after the addition of some tartaric acid, is diluted to 750 c.c. and heated to 79° C.  $H_2S$  is passed through to obtain the precipitate. This is filtered, washed with  $H_2S$  water, and rinsed back into the original precipitation vessel with the aid of hot water. Add 50 c.c. of strong HCl and warm the solution (but avoid boiling) until no more  $H_2S$  is evolved. Dilute the liquid until a milkiness is just observed; this turbidity is removed by adding HCl drop by drop. Then titrate with potassium permanganate. The reaction occurring is represented as follows:—



The end-point of the reaction is sharp. If 5.27 grammes of pure potassium permanganate be dissolved per litre of solution, 1 c.c. will be equivalent to 1 per cent. of antimony with 1 gramme of the original sample.

( $\gamma$ ) H. Causse,\* in *Comptes Rendus*, 1897, describes a new method for the volumetric estimation of antimony, which is based upon the fact that antimonious acid, free or combined, reduces iodic acid, with the formation of antimonic acid and the liberation of a proportionate amount of iodine, the reaction being thus:—



The solutions required are: iodic acid, 50 grms. in 250 c.c.; decinormal sodium thiosulphate; 20 per cent. potassium iodide; and starch paste. Into the flask of a Fresenius or Mohr's iodometric apparatus, 0.5–0.6 gramme of antimonious oxide is weighed, 20–25 c.c. of iodic acid are added, and 10 c.c. of potassium iodide solution are placed in the condensing apparatus. The contents of the flask are boiled until colourless, and the collected iodine determined with thiosulphate. From antimony compounds the sulphide is precipitated by sulphuretted hydrogen, then dissolved in HCl, and the oxide obtained by the action of sodium carbonate. The halogen acids, sulphurous acid, and sulphuretted hydrogen must be dissolved in

\* Taken from *Mineral Industry*.



tartaric acid or potassium bitartrate, which are without action on iodic acid.

(8) Joseph Hanns,\* in *Chemiker Zeitung*, 1897, proposes to determine antimony volumetrically by precipitating it as sulphide, filtering and washing the precipitate with water; the precipitate is washed into a beaker and ferric sulphate added (either in powder or in solution) in the proportion of 6 parts to 1 part of antimony sulphide. The solution is then boiled for fifteen minutes. The reaction is:—



The contents of the beaker are then diluted considerably, and 15 c.c. of concentrated sulphuric acid are added for each gramme of ferric sulphate used. The solution is then cooled quickly to 25° C., and titrated to a faint rose colour with potassium permanganate. The permanganate solution is made up to a strength of 1 to 1.5 grammes per litre and is standardised against antimony trioxide. The amount of antimony sulphide in the precipitate treated with the ferric sulphate should not exceed 0.2 to 0.3 gramme.

(ε) Dr Clark,\* in *Journ. Soc. Chem. Ind.*, 1896, recommends for antimony ores and alloys a modification of Mohr's method † of titration with  $\frac{N}{10}$  solution of iodine:—

α<sub>1</sub>. If the ore is free from arsenic and iron, dissolve in HCl, drive off H<sub>2</sub>S by heat, add tartaric acid or Rochelle salt, make alkaline with NaHCO<sub>3</sub>, and titrate.

β<sub>1</sub>. If iron is present, dissolve in HCl, precipitate with H<sub>2</sub>S, redissolve in HCl, and proceed as before.

γ<sub>1</sub>. If arsenic is present, dissolve in HCl + Fe<sub>2</sub>Cl<sub>6</sub> and distil off the arsenic; precipitate Sb with H<sub>2</sub>S, and proceed as under β<sub>1</sub>. The arsenic distilled off may be condensed and estimated by titration with  $\frac{N}{10}$  solution of iodine.

δ<sub>1</sub>. When the ore or alloy contains tin, dissolve in HCl + Fe<sub>2</sub>Cl<sub>6</sub>, distil off As, precipitate Sb with metallic iron, redissolve, after washing in HCl plus a little KClO<sub>3</sub>, filter off the insoluble impurities derived from the iron, precipitate Sb with H<sub>2</sub>S, and proceed as under γ<sub>1</sub>.

According to Mr L. Parry, the most accurate and practical methods are, titration of Sb<sub>2</sub>O<sub>3</sub> with iodine in alkaline solution, and titration of iodine liberated by action of SbCl<sub>5</sub> on KI in HCl solution.

\* Taken from *Mineral Industry*.

† Vide paragraph (α) of the present chapter.

The other volumetric methods that may be mentioned are:—

- (1) Solution of precipitated Sb in  $H_2SO_4$  and titration with  $KMnO_4$ .
- (2) Titration of precipitated Sb with  $FeCl_3$  in a boiling HCl solution.
- (3) Titration of precipitated Sb with bichromate after solution in  $FeCl_3$ .

(c) *Electrolytic*.—(a) According to Smith, antimony, when precipitated from a solution of its chloride, or from that of antimony potassium oxalate, does not adhere well to the cathode. From a solution of potassium antimonyl tartrate it is deposited very slowly. A cold ammonium sulphide solution is good, but its use is not pleasant. Hence potassium or sodium sulphide is resorted to, but must not contain iron or alumina. The antimony solution, mixed with 80 c.c. of sodium sulphide (sp. gr. 1.13–1.15), is diluted with water to 125 c.c., and acted upon at  $60^\circ$ – $65^\circ$  by a current of N.D.<sub>100</sub> = 1 ampere and 1.1–1.7 volts. Two hours are required to fully precipitate the metal. Then treat the metal with water and pure alcohol. Dry it at  $90^\circ$ . The solution must be absolutely free from polysulphides. But as the antimony sulphide obtained in the ordinary course of analysis always contains sulphur, this must be eliminated. Add 50–70 c.c. of a 25 per cent. solution of sodium sulphite to the solution after the addition of sodium sulphide in excess; then heat the liquid until it is completely decolorised, and allow it to cool. It is best to pass a current of 0.25 ampere. Wash deposit with water, alcohol, and ether.

( $\beta$ ) The sulpho-salts of antimony, as proposed by Parrodf and Mascazzini, Luckow, Classen and V. Reiss, and Classen and Ludwig, are the best for obtaining an antimony deposit by electrolysis.

“The determination of antimony by the electrolysis of its sulpho-salts is one of the most convenient and useful of all electrolytic methods, and is one that is frequently used in actual practice. It is especially convenient, because the form of solution in which the antimony is obtained in the usual course of separation from the other metals can be directly electrolysed.

“A solution of 1 grm. tartar emetic in water is treated with a solution of sodium sulphide until the precipitate which first forms is redissolved. The mixture, after dilution to 150 c.c., is electrolysed at normal temperature with a current of 0.5 to 1.0 ampere and 1.3 to 1.8 volts. To see whether all the antimony has been deposited, a small test portion of the electrolyte is taken and is heated with a few drops of dilute sulphuric acid, and if antimony is present there will appear a reddish colour. One may raise the basin to see whether

any electrolysis is still proceeding on the newly attacked part of the electrode; but this is not satisfactory. Generally at the cathode the antimony deposit is bright, metallic, and silver-gray in colour, and the anode is covered with sulphur. The sulphide solution must not contain any polysulphides. They are, however, produced in the electrolyte during the course of the electrolysis; and, as soon as they are discovered, hydrogen peroxide must be added, and also a fresh amount of sodium monosulphide. If the current used is allowed to continue for too long a time, the edges of the deposit may be dissolved; and this redissolved antimony cannot be separated from the electrolyte. Hence it is preferable to carry out the electrolysis with hot solutions and strong currents in a short time. The deposit of antimony on the platinum electrode can be removed by means of hot nitric acid, or be converted into the white oxide of antimony, which is redissolved by adding tartaric acid and rinsing out with hot water.\*

### C. Special Methods.

1. *For Alloys of Tin, Lead, Antimony, and Copper containing little Arsenic*; such as type-metal, solder, anti-friction metals, etc.†

$\text{SbCl}_5$  in  $\text{HCl}$  solution oxidises  $\text{KI}$ . The liberated iodine may be titrated with stannous chloride—not with *hypo*.

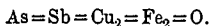
In this method the presence of tin (as  $\text{SnCl}_4$ ) and lead has no effect whatever on the titration; indeed, the titration is done with  $\text{SnCl}_2$ . Copper, arsenic, and iron, when present in solution in their highest state of oxidation, are reckoned as antimony, and should be estimated and allowed for, this being preferable to separating the  $\text{Sb}$  from them.  $\text{Fe}$  is rarely present, but in the case of alloys with *more than 1 per cent.*  $\text{As}$ , it is advisable to dissolve in aqua regia and to separate the  $\text{Sb}$  and  $\text{As}$  as sulphides, as it appears that in some cases, when an alloy rich in arsenic and tin is boiled with  $\text{HCl}$ , there is a considerable evolution of  $\text{H}_2\text{As}$ . This matter is under investigation. Arsenic, however, is rarely present in the above alloys in quantities greater than 1 per cent. 1–3 grms. of fine filings are weighed into a 16-oz. flask and boiled gently with 150 c.c.  $\text{HCl}$  until action ceases and most of the  $\text{Pb}$  and  $\text{Sn}$  is dissolved. To complete the solution, add cautiously a cold saturated solution of  $\text{KClO}_3$ , which also peroxidises the metals. After solution is complete, add a little  $\text{KClO}_3$ , and make sure that excess of chlorine is present. The solution is diluted with

\* Taken from Neumann's work.

† Taken from *The Assay of Tin and Antimony*, by L. Parry, *Mining Journal* Office, London, 1906.

rather less than an equal bulk of water, and boiled until free from chlorine. In practice, half an hour is a sufficient length of time; the most practical and most delicate test of the absence of free chlorine in the cold solutions is the sense of smell. The assays should not be boiled to a smaller bulk than 150 c.c., as the chloride of antimony is volatile. Allow the assay to cool; when quite cold, fill the flask with  $\text{CO}_2$  from a Kipp apparatus charged with marble and  $\text{HCl}$ , add 20 c.c. of a fresh 20 per cent. solution of  $\text{KI}$ , and titrate as rapidly as possible with stannous chloride. This is made by dissolving 10 grms. of tin, or 20 grms.  $\text{SnCl}_2$  2 aq., in 300 c.c.  $\text{HCl}$  and diluting to 1 litre. It should be kept under  $\text{CO}_2$ , and must be standardised, every time it is used, against a standard solution of bichromate made by dissolving exactly 16 grms. of fine  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1 litre of distilled water. 100 c.c. bichromate = 2 grms.  $\text{Sb}$ , and 100 c.c.  $\text{SnCl}_2$  = about 1 gm.  $\text{Sb}$ . The assays, if overdone, are brought back with the standard bichromate (rapidly), but should only require a few drops at most, otherwise the accuracy of the assay is impaired.

The assays have a great tendency to absorb oxygen after titration; hence the necessity for a  $\text{CO}_2$  atmosphere and rapid titration, especially in presence of  $\text{As}$  and  $\text{Cu}$ . Further, the reaction in the case of  $\text{As}$  is not instantaneous, and only proceeds to completion at the same rate as the iodine is liberated by  $\text{SnCl}_2$ —being to some extent reversible. Acid solutions of  $\text{AsCl}_3$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{FeCl}_2$ , and of  $\text{KI}$  readily absorb oxygen from the air, while  $\text{SbCl}_3$  is scarcely affected. The bichromate remains quite constant, and it may be standardised against pure iron as a check on the weighing up. In standardising the stannous chloride, pour a little  $\text{KI}$  solution and starch paste into an 8-oz. flask, fill the flask with  $\text{CO}_2$ , and run in rapidly 20 c.c.  $\text{SnCl}_2$  from the burette. Then titrate rapidly with  $\text{K}_2\text{Cr}_2\text{O}_7$ .



1 per cent.  $\text{As}$  = 1.6 per cent.  $\text{Sb}$ . 1 per cent.  $\text{Cu}$  = 0.945 per cent.  $\text{Sb}$ .

1 per cent.  $\text{Fe}$  = 1.03 per cent.  $\text{Sb}$ .

2. *Analysis of Antimony Ore* (the following is an abstract from Thos. Brown, Jr.'s, article on the determination of antimony in ores, in the *Journ. of Am. Chem. Soc.*, Sept. 1899).—Impurities such as silica, iron, and lime would not materially interfere with the schemes of analysis used. Lead, mercury, copper, tin, and arsenic, when found in quantities larger than traces, should be separated from the antimony when its determination is by the method of sulphides; also tin and arsenic when the oxide method is used. A preliminary qualitative test should always be made for the

purpose of modifying the sulphide method, and a quantitative one in order to estimate the true market value of the ore.

Lead is determined both qualitatively and quantitatively as the orange-yellow chromate ( $\text{PbCrO}_4$ ). For the qualitative test the finely ground ore is boiled with concentrated nitric acid for several minutes, and, if a sulphide, until the sulphide of antimony is entirely converted into the insoluble white oxide, then cooled and diluted. Ammonia is added in excess, then acetic acid in excess, and the whole heated for several minutes in order to bring the lead salt thoroughly into solution. The insoluble matter is now filtered off, and the filtrate treated with an excess of potassium bichromate, which precipitates the lead as chromate from this ammonium acetate and acetic acid solution. The lead can also advantageously be determined quantitatively in this form from the sulphide precipitate remaining on the filter after separating the Sb from the metals of the fifth group.

For arsenic a combination of the Canby and Mohr methods is used. One gramme of the finely powdered ore is mixed in a porcelain crucible with 8 to 10 parts of a mixture of equal parts of sodium carbonate and nitre, gradually brought to fusion over a burner or in a muffle, and kept so for five minutes or longer. The fused mass is allowed to cool, disintegrated in hot water, and the insoluble matter filtered off. The filtrate is now acidified with  $\text{HNO}_3$  and the carbonic and nitrous acid gases boiled off. An excess of an emulsion of zinc oxide is added; and should an unusually heavy precipitate of gelatinous silica and alumina be produced, a second filtration is necessary, also an extra addition of zinc oxide to the filtrate before the precipitation of the arsenic. This is precipitated as the reddish-brown silver arsenate ( $\text{Ag}_3\text{AsO}_3$ ) by the addition of silver nitrate in slight excess, accompanied by vigorous stirring.

The precipitate, mixed with zinc oxide, is filtered, washed with cold water until the washing shows no silver reaction, and dissolved off the filter with hot dilute nitric acid, catching the solution and washings in a beaker free from chlorine. When cold, this is titrated for silver with a solution of potassium or ammonium thiocyanate, using 1 c.c. of saturated solution of ferric sulphate as indicator, and titrating to the same pale amber-yellow colour as was obtained in standardising the solution against pure silver. For the standard silver solution 1 grm. of the pure metal is dissolved in  $\text{HNO}_3$ , boiled to expel red fumes, and diluted to 100 c.c. For the standard thiocyanate solution  $9\frac{3}{10}$  grms. of potassium thiocyanate or  $7\frac{6}{10}$  grms. of ammonium thiocyanate are dissolved and diluted to

1 litre; then 1 c.c. = 0.010 grm. silver, and 108 silver = 25 arsenic. This same treatment, somewhat modified, is used in testing the ore qualitatively for arsenic. After fusion, the addition of acid, boiling, and the addition of zinc oxide in excess, the whole is filtered, and the neutral filtrate tested for arsenic as before.

Ores are divided into three classes: (1) the soluble ores, such as stibnite; (2) the practically insoluble ores, such as cervantite; (3) the partially soluble ores, as oxysulphides (stibnite mixed with cervantite). Ores of the first class are thus treated:—1 grm. of the finely ground ore is treated in a No. 3 beaker with 25 c.c. of concentrated HCl, covered and boiled until apparently decomposed and the solution does not occupy more than 15 c.c. in bulk. About 2 grms. of tartaric acid are added, and as soon as these are dissolved from 4 to 6 drops of concentrated HNO<sub>3</sub> are also added, and the whole boiled for a short period. On cooling and diluting, H<sub>2</sub>S is passed through for about an hour, and the Sb precipitated as sulphide. After warming slightly, it is allowed to stand in the cool for an hour or more and then filtered. These precautions having been attended to, no more Sb will be precipitated either on standing or passing additional H<sub>2</sub>S. If lead or other metals of the fifth group have been found, it may be necessary to dissolve the precipitate in excess of ammonium sulphide. The antimony is again precipitated as before. The precipitate, in any case, is well washed, and dried in an air-bath at 110° C. to constant weight. As the precipitate contains a certain amount of free sulphur, it is necessary to determine the amount of black anhydrous antimonious sulphide it contains. This is done by weighing a certain amount of the precipitate into a platinum boat, which is placed in a combustion tube and the free sulphur driven off in a stream of CO<sub>2</sub>.

The insoluble ores,\* are best treated by fusion with a flux composed of equal parts of flower of sulphur and sodium carbonate. One gramme of ore is used to eight or more parts of the mixed flux. The mixture is put in a crucible of 40 c.c. capacity, covered with a portion of flux, placed in the muffle, and heated cautiously to fusion, which takes place in about ten minutes. Many precautions have to be observed, as it is very difficult to fuse the readily volatile antimony, even at a low heat, without loss. The mass, when fused, is dissolved in hot water, and the solution, which contains the antimony, filtered off

\* A. Chippendale (*Eng. and Min. Journal*, May 12, 1900) recommends the use of potassium-iodide, to be added occasionally to the boiling concentrated HCl solution containing the oxide ores. When dissolved, the antimony may be determined by the usual methods.

from the sulphide of iron and those of the fourth group. The antimony is precipitated as sulphide by adding a slight excess of HCl.

The partially soluble ores require double treatment as above.

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## CHAPTER VIII.

### THE PRODUCTION AND VALUATION OF ANTIMONY ORE.

THE following is a list of the most important antimony minerals, with their antimony content:—

These con- stitute the ore of antimony.	{	Senarmonite . . . . .	83·56 per cent. Sb.
		Valentinite . . . . .	83·56 ,,
		Cervantite . . . . .	79·20 ,,
		Kermesite . . . . .	75·30 ,,
		Stibnite . . . . .	71·80 ,,
		Volgerite . . . . .	58·91 ,,
		Guejarite . . . . .	58·50 ,,
		Berthierite . . . . .	57·00 ,,
		Livingstonite . . . . .	53·12 ,,
		Zinkensite . . . . .	42·60 ,,

The market of antimony ore is, in a general way, confined to a few smelters and their agents, and the price is chiefly a mere matter of private contract, generally according to the principle of sliding scales.

French dealers have made use of the following formula for the determination of the value of antimony ore:—

$$p = \frac{t}{100} \left( 1 - \frac{1}{a} \right) (c - f),$$

in which :

$p$  = the value of 1000 kilos. or 1 metric ton of mineral.

$\frac{t}{100}$  = the tenor of the ore determined by fire-assay.

$\frac{1}{a}$  = the loss in smelting.

$c$  = the value of regulus in francs per metric ton.

$f$  = cost of smelting and profit of the smelter per metric ton of regulus.

The loss in smelting may be calculated as 10 per cent. of the metallic tenor of the ore. The cost of smelting may roughly be estimated at 350 to 500 frs., or at £14 to £18, per ton of metal

produced. In calculating the loss, the following may be adhered to :—

	9 per cent.	for ore of 55	per cent.	Sb or more.
10	”	”	50	” to 55 per cent.
11	”	”	45	” ” 50 ”
15	”	”	40	” ” 45 ”
18	”	”	35	” ” 40 ”
20	”	”	less than 35	per cent. Sb.

With English buyers the price is generally paid per unit of antimony in ore. Thus, in 1904, 4s. to 5s. per unit was paid for 50 per cent. sulphide ore, when regulus was worth from £25 to £35; in 1905, 6s. to 8s., when regulus was sold at from £35 to £60; in 1906, 8s. to 15s., and in some cases above 15s., when the price of regulus rose from £60 to £120. Some dealers still offer ores to smelters on the old formula:  $0.9T(P - 330) = V$ , c.i.f., in which T = antimony content in percentage, P = market price of regulus, and V = value in francs c.i.f. Havre, Marseilles, Antwerp, or Hamburg.

American buyers commonly make a basis of \$1 per unit (22.4 lbs.), when the metal is worth 8 c. per lb., for ore containing about 50 per cent. Sb, with a variation of one-third of the difference in the market price for the metal per 2240 lbs. up or down. Thus, with the metal at 8 c. per lb. or \$179.20 per 2240 lbs., the value of an ore containing 52 per cent. Sb is \$52 per ton of 2240 lbs. If the price for the metal is 10 c. per lb. or \$224 per 2240 lbs., the addition of  $\frac{1}{3}(\$224 - \$179.20) = \$14.93$  is made, giving the ore a value of \$66.93.

The phrase “cost of smelting” means :—

- (a) Direct operating without general expense.
- (b) Including general expense.
- (c) Direct operating, including general expense, *plus* amortisation charges.\*

A Belgian dealer offers to buy ores on the formula: †

$$P = R \times 90 \left( \frac{T \cdot 8}{100} \right) - £6,$$

in which

P = price per ton of antimony ore.  
 R = price in £ of regulus in London.  
 T = analysis of ore in percentage.

M. F. T. Havard classifies antimony ore under the following heads :—

- (a) Auriferous, with 40 to 70 per cent. of antimony in the form of sulphide, several ounces of gold, together with, in some cases, payable

\* Taken from *The Eng. and Min. Journal*, N.Y., p. 124, Jan. 11, 1908.

† Private communication.

silver. The value per unit of antimony is according to market condition. Gold is generally paid for at 75s. per oz.; sometimes, however, no pay is given for the precious metals.

(b) The same class of auriferous ore, but with less than 40 per cent. of antimony; sometimes with payable silver. Pay is given for precious metals as under (a).

(c) Antimony ore, both sulphide and oxide, free from precious metals, with from 40 to 70 per cent. antimony.

(d) The same class of ore as (c), but with less than 40 per cent. antimony.

(e) Mixed copper, antimony, and zinc ores, nearly always carrying some lead and silver, in which antimony is paid for at prices varying from the price of lead to 5s. per unit.

(f) Lead concentrate and high-class lead ore, with 40 to 60 per cent. lead, 3 to 10 per cent. antimony, and generally carrying some silver. Antimony is usually sold at lead-price by the mines, and also sometimes by dealers, on the consideration that they receive the resulting hard lead at an advantage on the market price.

The extraordinary fluctuations of prices of regulus in the years 1906 and 1907 may be attributed to various causes.

The sudden rise of the metal from its normal rate of about £40 to £120 per ton in 1906 may be due to the following causes\* :—

(a) Increased demand in the machine industries.

(b) Partial replacement of tin, now scarce and expensive, by antimony in alloys, Babbitt and bearing metal.

(c) A change in the quality of the ore coming on the market from high grade to low grade, as workings in the mines reached greater depths.

(d) The general increase in prices of all metals as compared with the constant value of gold.

(e) The increase in the production of antimony oxide in place of its metal, for the manufacture of antimony pigments.

(f) Its replacing soft lead for acid-proof linings and other purposes.

(g) The sulphide being used in greater quantities than ever in the rubber industry for the purposes of vulcanisation.

(h) Its great demand during the Russo-Japanese war for artillery uses.†

(i) Speculation.

\* From F. T. Havard, "The Antimony Industry," *The New Zealand Mines Record*, April 16, 1907.

† The author was informed of this by a French dealer in antimony, but was unable to verify the statement.



## VALUE OF ANTIMONY REGULUS.

Year.	Per ton.		Year.	Per ton.	
	Low.	High.		Low.	High.
1875	£ 50	£ 59	1893	£ 37	£ 43
1876	55	69	1894	32	37
1877	48	50	1895	31½	33
1878	48	50	1896	29½	30½
1879	50	70			
1880	60	75			
1881	55	60			
1882	42	55			
1883	36	40	1897	7	7½
1884	40	45	1898	8	9·75
1885	35	39	1899	10	11
1886	29½	35	1900	10	10·50
1887	30	40	1901	10	10·25
1888	39	50	1902	9·2	10
1889	45	75	1903	6·56	8·25
1890	70	76	1904	6½	8½
1891	40	72	1905	8·375	14·5
1892	43	52			

(Cookson's, N. Y.)

Cents per lb.      Cents per lb.

## AVERAGE PRICES IN CENTS PER LB.

	1906.			1907.		
	Cookson's.	Hallet's.	Ordinaires.	Cookson's.	Hallet's.	Ordinaires.
January . . .	15·0	14·0	13·5	25·906	25·219	24·156
February . . .	16·0	15·0	14·25	25·062	24·062	23·437
March . . .	17·5	16·5	16·15	24·900	23·750	23·025
April . . .	21·31	20·81	20·25	24·125	21·344	20·875
May . . .	25·25	24·38	23·31	21·937	18·562	17·750
June . . .	26·0	25·0	24·0	15·750	13·812	12·650
July . . .	25·25	24·25	23·19	11·875	10·500	10·125
August . . .	25·0	24·0	22·75	10·906	9·687	9·375
September . . .	24·5	24·0	22·25	10·750	10·000	9·650
October . . .	25·2	24·81	23·63	11·750	10·406	10·047
November . . .	26·14	25·25	24·50	11·000	9·937	8·906
December . . .	26·25	25·24	24·70	9·662	9·050	8·088
Average . . .	22·78	21·94	21·73	16·969	15·527	14·840



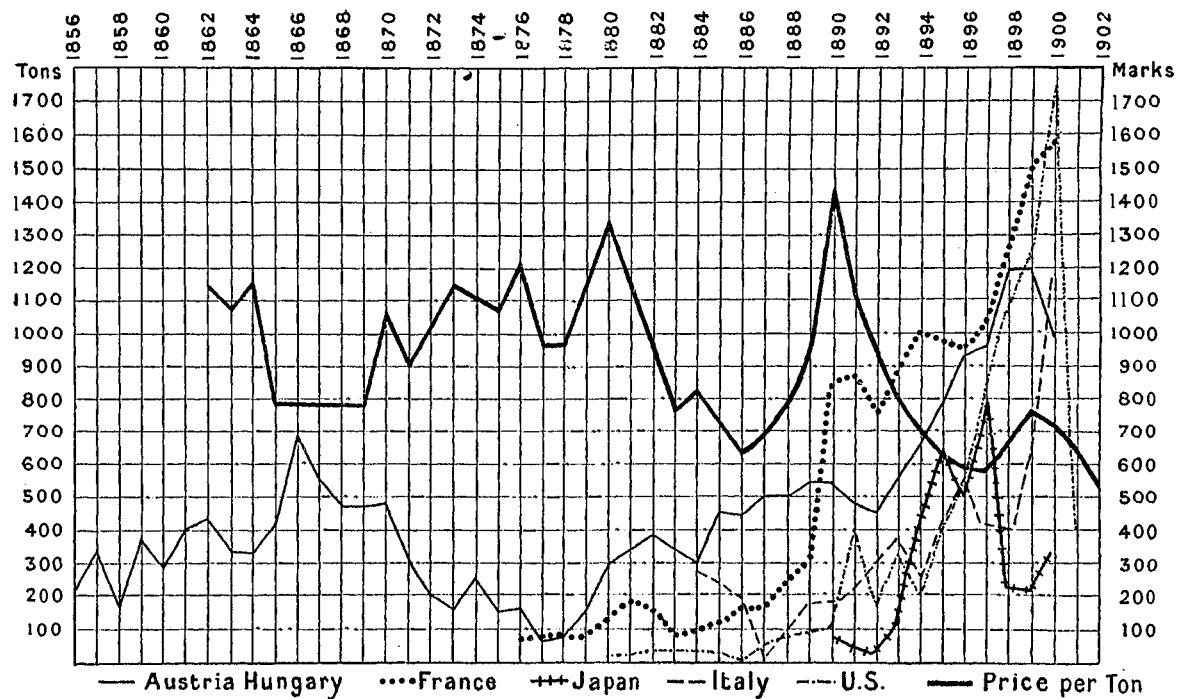


Fig. 65.

1 MARK = ABOUT \$0.238  
20.43 MARKS = £1

Now the sudden fall of the metal from its normal rate of about £40 to £35 may be due to the following causes\* ;—

(a) The market for needle antimony had, to a large extent, been artificially sustained by a considerable proportion of the Chinese output being held in strong hands on the Continent. With the appearance of larger quantities of ore from North Africa, Turkey, and Australia, the holders became afraid, and needle antimony was allowed to drop.

(b) The decline was accelerated by financial depression in the United States, and a consequent diminution of demand.

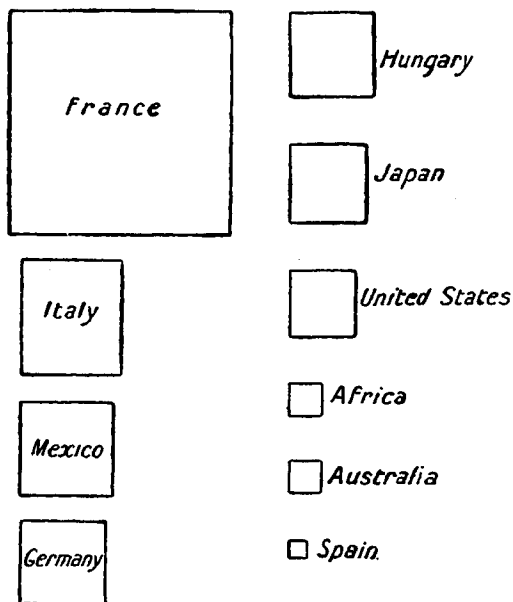


FIG. 66.

Within the last few years Japan has ceased to be a factor in the antimony market. The United States cannot produce antimony with profit at prices below 20 c. per lb. Australia and China are likely to become the principal producers of antimony ores. Perhaps, with better facilities of transportation, the South American mines could be worked with profit.

\* From p. 124, *The Eng. and Min. Journal*, Jan. 1908.

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## CHAPTER IX.

### THE PRINCIPAL MINES AND SMELTING WORKS OF ANTIMONY.

THE following is a list of the principal mines and smelting works of antimony that have been, or are still being, worked :—

#### I. MINES.

- (1) *Algeria*.—Taya, Sempsa, Djebel-Hamimat.
- (2) *Asia Minor*.—Smyrna.
- (3) *Australia*.—Macleay district, at Hargreaves Falls and Aberfoil, Armidale (New South Wales), Costerfield (Victoria), and Queensland.
- (4) *Austria-Hungary*.—Besztercebanya (Schemnitz), Michaelsberg, Moldau River and Kuttenberg (Bohemia), Bánya, Szálouak, Rosenau, Liptau, Neusohl, Magurka, Kremnitz, Rechnitz Mountains between Aranyidka and Rosenau.
- (5) *Borneo*.—Sarawak.
- (6) *Canada*.—West Gore (Hants Co.), M'Dougal (Nova Scotia), Prince-William (New Brunswick).
- (7) *Chile*.—Antofagasta.
- (8) *China*.—Province Hunan.
- (9) *France*.—La Lucette, Licoulne, Bessade, Loubelzac, Ouche, Conches, etc. Besides these, there are twenty-six principal mines in France, including Corsica.
- (10) *Germany*.—Arnsberg (Westphalia), Hoffnung (near Brück), Goldkronach (Fichtelgebirge), Caspari mine near Mentrop.
- (11) *Italy*.—Meria, Ersa, Luri (provinces Grosseto and Cagliari), Pereta (Tuscany), Cettine di Cotoruiano and Tocchi (province Sienna), Ponte a Rosaio (province Sienna), San-Basilio, Ballao, Su-Suergin mine near Villasalto (district Lanusei, Sardinia), Roccalumera, Letoianni, and Francavilla (Sicily).
- (12) *Japan*.—Itshinokawa (Shikoku), Nakase, Nara, Ehiune, Yamaguchi, Nii-gori, Ojoinumura.

- (13) *Mexico*.—Sonora.  
 (14) *Peru*.—Mollendo.  
 (15) *Portugal*.—Tapada, Lixa, Gondomar, Braganza, Corcega.  
 (16) *Servia*.—Styria, Kik, Stolitza, Zavorie.  
 (17) *Spain*.—Salamea de la Serena (near Badajoz), San Jose, Genara, Caurel, Perseverance, Huelva, Leon, Oviedo, Ribas.  
 (18) *Turkey*.—Allkhur, Aidin.  
 (19) *United States*.—Ballarat (South California), Coyote Creek (Iron Co., Utah), Beulah (near Austin, Nevada), Thompson's Fall (Montana), Sevier Co. (Arkansas)

## II. SMELTING WORKS.

(1) *Austria-Hungary*.—Szalouak, Budweis (Bohemia), Stephan Works, Milleschau (Bohemia), Magurka, Rosénau, Gross-Göllnitz; Schönberg, Proutkovitz (Bohemia) (owned by Milleschauer Berg- und Hüttenwerks Actiengesellschaft); Příklad (Bohemia) (owned by Emil Pohok).

(2) *Belgium*.—Antwerp (owned by Société Industrielle de Beerse).

(3) *Canada*.—West Gore (Nova Scotia) (owned by St Helens Metal Recovery Co.).

(4) *China*.—Hankow (owned by Carlowitz & Co.).

(5) *England*.—Newcastle-on-Tyne (owned by Cookson & Co.); Hallett & Fry, Johnson & Matthey, Pontifex & Wood, Mathison & Co. (in London).

(6) *France*.—The principal smelting works are situated at Conches (Cantal), Blesle and Brionde (Haute-Loire).

The principal smelters are: (a) Emmanuel Chatillon (Conches, Blesle, and Brionde); (b) Société Franco-Italienne (Brionde); (c) Paul et Cie. (Collet-de-Dèze); (d) Basse Vitalis (Blesle); (e) Herrenschildt (Genest).

Other smelting centres are: La Lincoule (Haute-Loire), Bouc and Septèmes (Rhône), Alais, Malbosc (Ardèche).

(7) *Germany*.—Linz (Schleiz), Dusseldorf, Wolfsberg (Harz).

(8) *Italy*.—Genoa (owned by Miniere e Fonderie d'Antimonio, Società Anonima), Siena (Tuscany), Florence, Ponte a Rosaio (Sienne), Su-Suergin.

(9) *Japan*.—Osaka, Sanchoba, Sunohara.

(10) *Servia*.—Kostajnik (Dina Rian).

(11) *United States*.—Chelsea (Sta'en Island, N.Y.), Chapman Smelting Co., San Francisco (owned by Mathison & Co., London).

III. PRINCIPAL AGENTS FOR ANTIMONY.

- (1) *England*.—Hardy, Seligmann & Co., Billiter Buildings, London,  
E C.
- (2) *Belgium*.—W. Flecken (Antwerp).
- (3) *France*.—H. Partin (Paris).
- (4) *Germany*.—A. Auerbach (Hamburg).
- (5) *The United States*.—The American Metal Co. (N.Y.).

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