$$Sb_2S_3 \ + \ 6HCl \ = \ 2SbCl_3 \ + \ 3H_2S$$

<div style="text-align:center">

Sulphide of antimony.    Hydrochloric acid.    Chloride of antimony.    Sulphuretted hydrogen.

</div>

This solution, cleared by subsidence, is what is commonly known as *Butter of antimony* (*Liquor Antimonii Chloridi*, B. P.). If pure sulphide has been used in its preparation, the liquid is nearly colorless; but much of that met with in veterinary pharmacy is simply a by-product in the generation of sulphuretted hydrogen from native ferruginous sulphide of antimony and hydrochloric acid, and is more or less brown from the presence of chloride of iron. It not unfrequently darkens in color on keeping; this is due to absorption of oxygen from the air and conversion of light-colored ferrous into dark-brown ferric chloride or oxychloride.
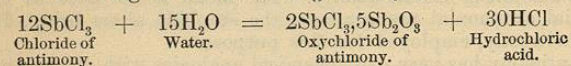
*True butter of antimony* ($Sb\overset{\cdots}{C}l_3$) is obtained on evaporating the above solution to a low bulk, and distilling the residue. The butter condenses (as a white crystalline semi-transparent mass in the neck of the retort); at the close of the operation it may be easily melted and run down in a bottle, which should be subsequently well stoppered.

*Pentachloride of antimony* ($SbCl_5$), or *antimonic chloride*, is a fuming liquid, obtained on passing chlorine over the lower chloride.

### Oxychloride of Antimony. Antimonious Oxychloride.

*Second Synthetical Reaction.*—Pour the solution of chloride of antimony produced in the last reaction into several ounces of water; a white precipitate of oxychloride of antimony ($2SbCl_3,5Sb_2O_3$) falls, some chloride of antimony remaining in the supernatant acid liquid.
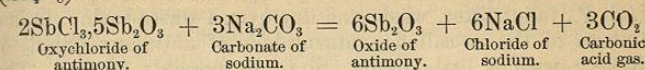
This is the old *pulvis Algarothi, pulvis angelicus,* or *mercurius vitæ.* On standing under water it gradually becomes crystalline.

$$12SbCl_3 \ + \ 15H_2O \ = \ 2SbCl_3,5Sb_2O_3 \ + \ 30HCl$$

<div style="text-align:center">

Chloride of antimony.    Water.    Oxychloride of antimony.    Hydrochloric acid.

</div>

### Oxide of Antimony. Antimonious Oxide.

Well wash the precipitate with water, by decantation (*vide* p. 109), and add solution of carbonate of sodium; the chloride remaining with the oxide is thus decomposed, and oxide of antimony ($Sb_2O_3$) alone remains. This is *Antimonii Oxidum,* U. S. P. It is of a light buff or grayish-white color, or quite white if absolutely free from iron, insoluble in water, soluble in hydrochloric acid, fusible at a low red heat. The moist oxide of antimony may be well washed and employed for the next reaction, or dried over a water-bath. At temperatures above 212° oxygen is absorbed, and other oxides of antimony formed. The presence of the latter is detected on boiling the powder in solution of acid tartrate of potassium, in which
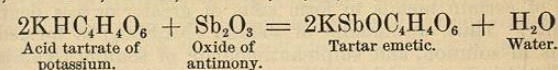
oxide of antimony ($Sb_2O_3$) is soluble, but *antimonic anhydride* ($Sb_2O_5$) and the double oxide or so-called *antimonious anhydride* ($Sb_4O_8$) are insoluble.

$$2SbCl_3,5Sb_2O_3 \ + \ 3Na_2CO_3 \ = \ 6Sb_2O_3 \ + \ 6NaCl \ + \ 3CO_2$$

<div style="text-align:center">

Oxychloride of antimony.    Carbonate of sodium.    Oxide of antimony.    Chloride of sodium.    Carbonic acid gas.

</div>

*The higher oxide of antimony* ($Sb_2O_5$), termed antimonic oxide or anhydride, corresponding with arsenic anhydride, is obtained on decomposing the pentachloride by water, or on boiling metallic antimony with nitric acid. The variety obtained from the chloride differs in saturating power from that obtained from the metal, and is termed metantimonic ($\mu\varepsilon\tau\alpha$, *meta*, beyond).

### Tartar Emetic.

*Third Synthetical Reaction.*—Mix the moist oxide of antimony obtained in the previous reaction with about an equal quantity of cream of tartar (6 of the latter to 5 of the dry oxide) and sufficient water to form a paste; set aside for a day to facilitate complete combination; boil the product with water, and filter; the resulting liquid contains the oxy-tartrate of antimony and potassium ($KSbOC_4H_4O_6$), potassio-tartrate of antimony, tartrated antimony, or tartar emetic (emetic, from ἐμέω, *emeō*, I vomit; tartar, from τάρταρος, *tartaros* See Index).

$$2KHC_4H_4O_6 \ + \ Sb_2O_3 \ = \ 2KSbOC_4H_4O_6 \ + \ H_2O$$

<div style="text-align:center">

Acid tartrate of potassium.    Oxide of antimony.    Tartar emetic.    Water.

</div>

On evaporation the salt is obtained in colorless transparent triangular-faced crystals of the above composition, with a molecule of water of crystallization, forming the *Antimonii et Potassii Tartras,* U. S. P., $2KSbOC_4H_4O_6,H_2O$.

The formula for tartar emetic is apparently inconsistent with the general formula for tartrates ($R'R'C_4H_4O_6$); this will be subsequently fully explained in connection with Tartaric Acid. The salt appears to be an oxytartrate ($KSbC_4H_4O_6O$).

Tartar emetic is soluble in water, and slightly so in proof-spirit. Dissolved in sherry wine, it forms the official *Vinum Antimonii,* U. S. P.

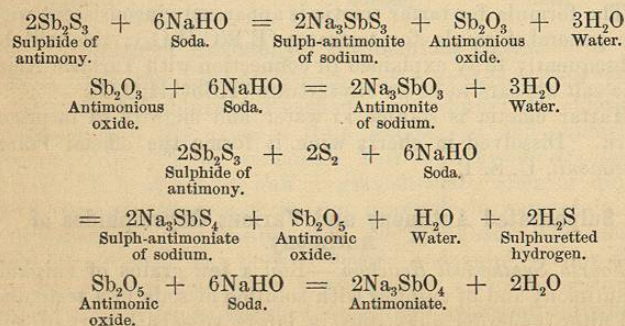### Sulphurated Antimony and Various Oxysulphides of Antimony.

*Fourth Synthetical Reaction.*—Boil a few grains of sulphide of antimony and of sulphur with solution of soda in a test-tube, and filter (or larger quantities in larger vessels, 1 part of sulphide to 12 of soda, and 30 of water for 2 hours, frequently stirring, and occasionally replacing water lost by evaporation).

Into the filtrate, before cool, stir diluted sulphuric acid until the liquid is slightly acid to test-paper ; a brownish-red precipitate of oxysulphide of antimony, *Antimonium Sulphuratum*, U. S. P., falls ; filter, wash, and dry over a water-bath. It is a mixture of the so-called pentasulphide of antimony ($Sb_2S_5$ or $Sb_3S_5S_2$) with a little oxide ($Sb_2O_3$ or possibly $Sb_3S_5$). The oxide results from the double decomposition of sulphide of antimony and soda.
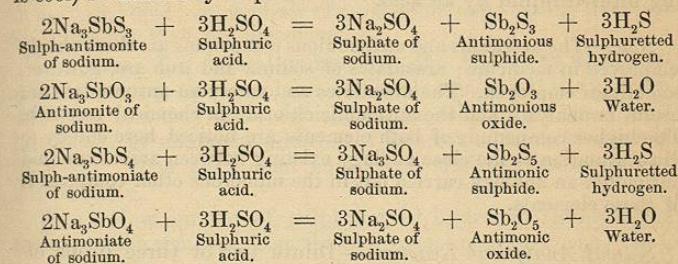
These are some of the many varieties of *mineral kermes*, so called from their similarity in color to the *insect kermes*. *Kermes* is the name, now obsolete, of the *Coccus Ilicis*, a sort of cochineal insect, full of reddish juice, and used for dyeing from the earliest times. The term *mineral kermes* was apparently applied originally to the amorphous or precipitated orange sulphide of antimony ($SbS_3$). It afterward included any oxysulphide and pentasulphide. A brownish-red variety may be prepared without the addition of any free sulphur. The color of the precipitate is affected by the temperature as well as state of dilution of the alkaline liquid when the acid is added. When the alkaline liquid is boiled, especially if long exposed to air, oxygen is absorbed by some of the antimony, whose sulphur, uniting with the trisulphate, forms a portion of the lighter yellow pentasulphide.

*Explanation of Processes.*—The sulphides and oxides of antimony, like those of arsenicum, react with the sulphides, hydrates, and oxides of certain metals to form salts of greater or less degree of solubility. Thus, antimonite of sodium ($Na_3SbO_2$) is formed and remains in solution, and sulph-antimonite of sodium ($Na_3SbS_3$) is formed and is deposited in brilliant yellow tetrahedral crystals when a hot alkaline solution of the trisulphide of antimony is set aside to cool. Sulphur, being present, is slightly soluble in antimoniate of sodium ($Na_3SbO_4$), and sulph-antimoniate of sodium ($Na_3SbS_4$) is produced.

$$2Sb_2S_3 + 6NaHO = 2Na_3SbS_3 + Sb_2O_3 + 3H_2O$$

Sulphide of antimony. Soda. Sulph-antimonite of sodium. Antimonious oxide. Water.

$$Sb_2O_3 + 6NaHO = 2Na_3SbO_3 + 3H_2O$$

Antimonious oxide. Soda. Antimonite of sodium. Water.

$$2Sb_2S_3 + 2S_2 + 6NaHO$$

Sulphide of antimony. Soda.

$$= 2Na_3SbS_4 + Sb_2O_5 + H_2O + 2H_2S$$

Sulph-antimoniate of sodium. Antimonic oxide. Water. Sulphuretted hydrogen.

$$Sb_2O_5 + 6NaHO = 2Na_3SbO_4 + 2H_2O$$

Antimonic oxide. Soda. Antimoniate.

In the hot solutions of these sulphur salts and oxygen salts sulphide and oxide of antimony are soluble, and are reprecipitated in

an indefinite state of combination, partially on cooling or wholly on the addition of acid. The acid also decomposes the oxysalts with precipitation of oxides, and the sulphur salts with precipitation of sulphides of antimony. The acid should be added to the liquids before much oxysulphide has deposited (that is, before the solution is cool) if uniformity of product is desired.

$$2Na_3SbS_3 + 3H_2SO_4 = 3Na_2SO_4 + Sb_2S_3 + 3H_2S$$

Sulph-antimonite of sodium. Sulphuric acid. Sulphate of sodium. Antimonious sulphide. Sulphuretted hydrogen.

$$2Na_3SbO_3 + 3H_2SO_4 = 3Na_2SO_4 + Sb_2O_3 + 3H_2O$$

Antimonite of sodium. Sulphuric acid. Sulphate of sodium. Antimonious oxide. Water.

$$2Na_3SbS_4 + 3H_2SO_4 = 3Na_2SO_4 + Sb_2S_5 + 3H_2S$$

Sulph-antimoniate of sodium. Sulphuric acid. Sulphate of sodium. Antimonic sulphide. Sulphuretted hydrogen.

$$2Na_3SbO_4 + 3H_2SO_4 = 3Na_2SO_4 + Sb_2O_5 + 3H_2O$$

Antimoniate of sodium. Sulphuric acid. Sulphate of sodium. Antimonic oxide. Water.

The oxide and sulphide indicated in these equations, together with excess of sulphide of antimony originally dissolved by the alkaline liquid, are all precipitated when the acid is added, and form the varieties of *kermes*. Kermes may be formed by union as well as by aqueous solution of the components. The student is strongly recommended carefully to study the foregoing paragraphs, for, although neither the official nor any other variety of *kermes* is itself of much importance in modern practical pharmacy, a thoughtful consideration of the chemistry will, by revealing chemical actions and analogies that are general, sow the seeds of chemical principles in the mind.

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The previous four synthetical reactions illustrate the official processes for the respective substances. The solution of chloride of antimony is only used in the preparation of oxide ; the oxide, besides its use in the preparation of tartar emetic, is mixed with twice its weight of phosphate of calcium (purified bone-earth) to form *Pulvis Antimonialis*, U. S. P., or "*James's Powder*."

*Sulphides* and *hydride* of antimony are incidentally mentioned in the following analytical paragraphs.

*(b) Reaction having Analytical Interest (Tests).*

*First Analytical Reaction.*—Through an acidified antimonial solution pass sulphuretted hydrogen ; an orange precipitate of amorphous sulphide of antimony falls. It has the same composition as the crystalline black sulphide ($Sb_2S_3$), into which, indeed, when dried, it is quickly converted by heat. Like sulphide of arsenicum, it is soluble in alkaline solutions. Collect a portion on a filter, and, when well drained, add *strong* hydrochloric acid ; it dissolves—unlike sulphide of arsenicum.

A higher sulphide of antimony ($Sb_2S_5$), corresponding to the higher sulphide of arsenicum, exists. It is formed on passing sulphuretted hydrogen through an acidified solution of the higher chloride ($SbCl_5$), or on boiling black sulphide of antimony and sulphur with an alkali, and decomposing the resulting filtered liquid by an acid.

*Note.*—The arsenious and antimonious compounds are those chiefly employed in medicine; arseniates of sodium and iron are, however, sometimes employed. The arseniates and rarely an antimoniate are useful in analysis, and the antimonic chloride in chemical research. The higher compounds of both elements are noticed here chiefly to draw attention to the close analogy existing between arsenicum and antimony, an analogy carried out in the numerous other compounds of these elements.

*Second Analytical Reaction.*—Dilute two or three drops of the solution of chloride of antimony with water; a precipitate of oxychloride occurs, the formation of which has been explained under the similar synthetical reaction. The occurrence of this precipitate distinguishes antimony from arsenicum, but is a reaction that cannot be fully relied upon in analysis, because requiring the presence of too much material and the observance of too many conditions. Add a sufficient quantity of hydrochloric acid to dissolve the precipitate, and boil a piece of copper in the solution, as directed in the corresponding test for arsenicum (*vide* page 170); antimony is deposited on the copper. Wash, dry, and heat the copper in a test-tube as before; the antimony, like the arsenicum, is volatilized off the copper and condenses on the side of the tube as white oxide, but the sublimate, from its low degree of volatility, condenses close to the copper; moreover, it is destitute of crystalline character—that is to say, it is *amorphous* (*a*, *a*, without; μορφη, *morphē*, shape).

Shake out the copper, and boil water in the tube for several minutes. Do the same with the arsenical sublimate similarly obtained. The deposit of arsenic slowly dissolves, and may be recognized in the solution by ammonio-nitrate of silver; the antimonial sublimate is insoluble.

*Third Analytical Reaction.*—Perform the experiments described under Marsh's test for arsenicum (pp. 170, 171), carefully observing all the details there mentioned, but using a few drops of solution of chloride of antimony or tartar emetic instead of the arsenical solution. Antimoniuretted hydrogen, or hydride of antimony ($SbH_3$), is formed and decomposed in the same way as arseniuretted hydrogen.

To one of the arsenicum spots on the porcelain lid (p. 171) add a drop of a solution of "chloride of lime" (bleaching-powder); it quickly dissolves. Do the same with an antimony spot; it is unaffected.

Heat more quickly causes the volatilization of an arsenicum than an antimony spot; sulphydrate of ammonium more readily dissolves the antimony than the arsenicum.

Boil water for several minutes in the beaker or wide test-tube containing the arsenious sublimate (page 171); it slowly dissolves, and may be recognized in the solution by the yellow precipitate given on the addition of solution of ammonio-nitrate of silver. The antimonial sublimate, similarly treated, does not dissolve.

Pass a slow current of sulphuretted hydrogen through the delivery-tube removed from the hydrogen-apparatus (page 171), and, when the air may be considered to have been expelled from the tube, gently heat that portion containing the deposit of arsenicum; the latter will be converted into a *yellow* sublimate of sulphide of arsenicum. Remove the tube from the sulphuretted-hydrogen apparatus, and repeat the experiment with a similar antimony deposit; it is converted into *orange* sulphide of antimony, which, moreover, owing to inferior volatility, condenses nearer to the flame than sulphide of arsenicum.

Pass dry hydrochloric acid gas through the two delivery-tubes. This is accomplished by adapting first one tube and then the other by a cork to the test-tube containing a few lumps of common salt, on which a little sulphuric acid is poured during the momentary removal of the cork. The sulphide of antimony dissolves and disappears; the sulphide of arsenicum is unaffected.

*Thorough conception of the chemistry of arsenicum and antimony will be obtained on constructing equations or diagrams descriptive of each of the foregoing reactions.*

*Antidote.*—The introduction of poisonous doses of antimonials into the stomach is fortunately quickly followed by vomiting. If vomiting has not occurred, or apparently to an insufficient extent, any form of tannic acid may be administered (infusion of tea, nutgalls, cinchona, oak-bark, or other astringent solutions or tinctures), an insoluble tannate of antimony being formed, and absorption of the poison consequently somewhat retarded. The stomach-pump must be applied as quickly as possible.

Recently precipitated moist ferric hydrate is also, according to T. and H. Smith, a perfect absorbent of antimony from its solutions, the chemical actions being probably, they say, similar to that which takes place between ferric hydrate and arsenious anhydride. It may be given in the form of a mixture of per-chloride of iron either with carbonate of sodium or with mag-nesia.

These statements may be verified by mixing together the various substances, filtering, and testing the filtrate for antimony in the usual manner.

DIRECTIONS FOR APPLYING THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE OF THE ELEMENTS ARSENICUM AND ANTIMONY.

Acidify the liquid with hydrochloric acid, and pass through it sulphuretted hydrogen—

A *yellow* precipitate indicates arsenicum.

An *orange* precipitate indicates antimony.

The result may be confirmed by the application of other tests.

DIRECTIONS FOR APPLYING THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF BOTH ARSENICUM AND ANTIMONY.

Acidify a small portion of the liquid with hydrochloric acid, and pass through it sulphuretted hydrogen.

*Note* I.—If the precipitate by sulphuretted hydrogen is unmis-takably orange, antimony may be put down as present, and arseni-cum only further sought by the application of Fleitmann's test to the solution of the sulphide in aqua regia* freed from sulphur by boiling, or, better, to the original solution.

*Note* II.—Sulphide of antimony is far less readily soluble than sulphide of arsenicum in solution of carbonate of ammonium. But this fact possesses limited analytical value; for the color of the sul-phides is already sufficient to distinguish the one from the other when they are unmixed; and when mixed, much sulphide of anti-mony will prevent a little sulphide of arsenicum from being dis-solved by the alkaline carbonate, while much sulphide of arsenicum will carry a little sulphide of antimony into the solution. When the proportions are, apparently, from the color of the precipitate, less wide, solution of carbonate of ammonium will be found useful in

* *Aqua Regia* is a mixture of fifteen parts hydrochloric and four parts nitric acid. It was so called from its property of dissolving gold, the "king" of metals.

roughly separating the one sulphide from the other. On filtering and neutralizing the alkaline solution by an acid, the yellow sulphide of arsenicum is reprecipitated. The orange sulphide of antimony will remain on the filter.

*Note* III.—Solution of bisulphite of potassium is said by Wöhler to be a good reagent for separating the sulphides of arsenicum and antimony, the former being soluble, the latter insoluble in the liquid.

*Note* IV.—Another reagent for separating the sulphides of arsen-icum and antimony is *strong* hydrochloric acid. As little water as possible must be present. On boiling, the sulphide of antimony dis-solves, while the sulphide of arsenicum remains insoluble. The liquid slightly diluted, filtered, more water added, and sulphuretted hydrogen again transmitted, gives orange sulphide of antimony. The process should previously be tried on the precipitated mixed sulphides. The presence of arsenicum may be confirmed by the application of Fleitmann's test to the original solution.

*Note* V.—If the precipitate by sulphuretted hydrogen is unmis-takably yellow, arsenicum may be put down as present, and any antimony detected by the previous or one of the following two pro-cesses. These two processes are rather long, and require much care in their performance, but are useful, because a small quantity of antimony in much arsenicum, or *vice versâ*, may be detected by their means.

*First Process.*—Generate hydrogen and pass it through a small wash-bottle containing solution of acetate of lead, to free the gas from any trace of sulphuretted hydrogen it may pos-sess, and then through a dilute solution of nitrate of silver con-tained in a test-tube. When the apparatus is in good working order, pour into the generating-bottle the solution to be ex-amined, adding it gradually to prevent violent action. After the gas has been passing for five or ten minutes, examine the contents of the nitrate-of-silver tube; arsenicum, if present, will be found in the solution in the state of arsenious acid,

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 3Ag_2;$$

while antimony, if present, will be found in the black precipi-tate that has fallen, according to the following equation:—

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$
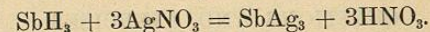
The arsenious radical may be detected in the clear, filtered, supernatant liquid, which still contains much nitrate of silver, by cautiously neutralizing with a very dilute solution of am-monia, or by adding a few drops of solution of ammonio-nitrate of silver, yellow arsenite of silver being produced. The anti-mony may be detected by washing the black precipitate, boil-ing it in an open dish with solution of tartaric acid, acidulating with hydrochloric acid, filtering, and passing sulphuretted hy-

drogen through the solution—the orange sulphide of antimony being precipitated (Hofmann).

*Second Process.*—Obtain the metallic deposit in the middle of the delivery-tube, as already described under Marsh's test. Act on the deposit by sulphuretted hydrogen gas, and then by hydrochloric acid gas, as detailed in the third analytical reaction of antimony (p. 182). If both arsenicum and antimony are present, the deposit, after the action of sulphuretted hydrogen, will be found to be of two colors, the yellow sulphide of arsenicum being usually further removed from the heated portion of the tube than the orange sulphide of antimony. Moreover, subsequent action of hydrochloric acid gas causes disappearance of the antimonial deposit, which is converted into chloride of antimony and carried off in the stream of gas.

The chief objection to this process is the liability of the operator mistaking sulphur, deposited from the sulphuretted hydrogen gas by heat, for sulphide of arsenicum. But the presence or absence of arsenicum is easily confirmed by applying Fleitmann's test to the original solution, while the process is most useful for the detection of a small quantity of a salt of antimony when mixed with much of an arsenical compound.

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The laboratory student may now proceed to the analysis of aqueous solution of salts of any of the metallic elements hitherto considered. The method followed may be that for the separation of the previous three groups, sulphuretted hydrogen being first passed through the solution to throw out arsenicum and antimony. The whole scheme of analysis is given on the next page. Three or four solutions should be examined before proceeding to the last group of metals.

Learners who have no opportunity of working at practical analysis will gain much knowledge by endeavoring not to remember, but to understand these methods of separating elements from each other in a solution containing several compounds.

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## QUESTIONS AND EXERCISES.

269. What is the composition and source of the *Black Antimony* of pharmacy?

270. In what alloys is metallic antimony a characteristic ingredient?

271. What is the quantivalence of antimony as far as indicated by the formulæ of the official preparations?

272. By a diagram show how "Butter of antimony" is prepared.

273. Write out equations or diagrams expressive of the reactions which occur in converting chloride of antimony into oxide.

274. What is the formula of Tartar Emetic?

275. Explain the official process for the preparation of Oxysulphide of Antimony (*Antimonium Sulphuratum*, U. S. P.) by aid of diagrams.

276. Give a comparative statement of the tests for arsenicum and antimony.

277. How is antimony detected in the presence of arsenicum?

278. How may arsenicum and iron be distinguished analytically?

279. Describe a method by which antimony, magnesium, and iron may be separated from each other.

280. Draw out an analytical chart for the examination of an aqueous liquid containing salts of arsenicum, zinc, calcium, and ammonium.

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## COPPER, MERCURY, LEAD, SILVER.

These metals, like arsenicum and antimony, are precipitated from acidified solutions by sulphuretted hydrogen, in the form of sulphides; but the sulphides, unlike those of arsenicum and antimony, are insoluble in alkalies. The atom of copper is usually bivalent, $Cu''$; mercury bivalent in the mercuric salts, $Hg''$, and univalent in the mercurous salts, $Hg'$; lead sometimes quadrivalent, $Pb''''$, but generally exerting only bivalent activity, $Pb''$; and silver univalent, $Ag'$.

## COPPER.

Symbol Cu.   Atomic weight 63.4.

*Source.*—The commonest ore of this metal is *copper pyrites*, a double sulphide of copper and iron, raised in Cornwall; Australia and Russia supply *malachite*, a mixed carbonate and hydrate; much ore is also imported from Spain and from South America. It is smelted in enormous quantities at Swansea, South Wales, a locality peculiarly fitted for the operation on account of its proximity to the coal-fields and its position as a sea-coast town—these advantages at all times ensuring cheap fuel and freightage to the different metallurgical establishments. An economical method of smelting copper pyrites and other sulphides has recently been introduced by Hollway. After the sulphide is once melted air is driven, not over, as usual, but through the mass; the combustion of the sulphur then becomes self-supporting and is greatly accelerated.

*Alchemy.*—The alchemists termed this metal *Venus*, perhaps on account of the beauty of its lustre, and gave it her symbol ♀, a compound hieroglyphic also indicating a mixture of gold ☉ and a certain hypothetical substance called acrimony ✠, the corrosive nature of which was symbolized by the points of a Maltese cross. To this day the blue show-bottle in the shop-window of the pharmacist is occasionally ornamented by such a symbol, indicative, possibly, of the fact that the blue liquid in the vessel is a preparation of copper.

*Coinage.*—The material of British copper coinage is now a bronze mixture composed, in 100 parts by weight, of 95 copper, 4 tin, and 1 zinc, the same as in the copper coinage of France. The penny