## Arsenicum.

*Third Synthetical Reaction.*—Place a grain or less of arsenic at the bottom of a narrow test-tube, cover it with about half an inch or an inch of small fragments of dry charcoal, and hold the tube, nearly horizontally, in a flame, the mouth being loosely covered by the thumb. At first let the bottom of the tube project slightly beyond the flame, so that the charcoal may become nearly red hot; then heat the bottom of the tube. The arsenic will sublime, become deoxidized by the charcoal, carbonic oxide being formed, and the element *arsenium*, sometimes termed arsenicum, and also formerly called *arsenic*, be deposited in the cooler part of the tube as a dark mirror-like incrustation.

There is a characteristic odor, resembling garlic, emitted during this operation, probably due to a partially oxidized trace of arsenicum, which escapes from the tube; for arsenic does not give this odor; moreover, arsenicum being a freely oxidizable element, its vaporous particles could scarcely exist in the air in an entirely unoxidized state.

*Metallic arsenicum* may be obtained in large quantities by the above process if the operation be conducted in vessels of commensurate size. But performed with great care, in narrow tubes, using not charcoal alone, but *black flux* (a mixture of charcoal and carbonate of potassium obtained by heating acid tartrate of potassium in a test-tube or other closed vessel till no more fumes are evolved), the reaction has considerable analytical interest, the garlic odor and the formation of the mirror-like ring being highly characteristic of arsenicum. Compounds of mercury and antimony, however, give sublimates which may be mistaken for arsenicum.

## Arsenic Acid and other Arseniates.

*Fourth Synthetical Reaction.*—Boil a grain or two of arsenic with a few drops of nitric acid until red fumes cease to be evolved; evaporate the solution in a small dish to dryness, to remove excess of nitric acid; dissolve the residue in water; the product is Arsenic acid ($H_3AsO_4$).

Arsenic acid, when strongly heated, loses the elements of water, and arsenic anhydride remains ($As_2O_5$).

Arsenic anhydride readily absorbs water and becomes arsenic acid ($H_3AsO_4$). Arsenic acid is reduced to arsenious by the action of sulphurous acid $H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$.
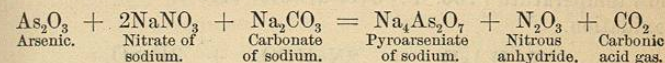
Salts analogous to arsenic acid, the arseniate of hydrogen, are termed *arseniates*, and have the general formula $R'_3AsO_4$. The ammonium arseniate ($NH_4)HAsO_4$ may be made by neutralizing arsenic acid with ammonia. Its solution in water forms a useful reagent. ——Arsenic acid is used as an oxidizing agent in the manufacture of the well-known dye, magenta.

Arsenite and arseniate of sodium are used in the cleansing operations of the calico-printer.

## Pyroarseniate and Arseniate of Sodium.

*Fifth Synthetical Reaction.*—Fuse two or three grains of common white arsenic ($As_2O_3$) with nitrate of sodium ($NaNO_3$) and dried carbonate of sodium ($Na_2CO_3$) in a porcelain crucible, and dissolve the mass in water; solution of arseniate of sodium ($Na_2HAsO_4$) results.

$$As_2O_3 + 2NaNO_3 + Na_2CO_3 = Na_4As_2O_7 + N_2O_3 + CO_2$$

Arsenic.    Nitrate of sodium.    Carbonate of sodium.    Pyroarseniate of sodium.    Nitrous anhydride.    Carbonic acid gas.

The official proportions (B. P.) are 10 of arsenic to $8\frac{1}{2}$ of nitrate of sodium and $5\frac{1}{2}$ of dried carbonate, each powdered, the whole well mixed, fused in a crucible at a red heat till effervescence ceases, and the liquid poured out on a slab. The product is pyroarseniate of sodium ($Na_4As_2O_7$). Dissolved in water, crystallized and dried, the salt has the formula $Na_2HAsO_4,7H_2O$ (*Sodii Arsenias*, U. S. P.).

$$Na_4As_2O_7 + 15H_2O = 2(Na_2HAsO_4,7H_2O).$$
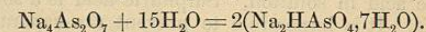
Heated to 300° F. the crystals lose all water. A solution of 1 part of the anhydrous salt ($Na_2HAsO_4$) in 99 of water forms the *Liquor Sodii Arseniatis*, U. S. P. The anhydrous salt is used in this preparation because the crystallized is of somewhat uncertain composition. The fresh crystals are represented by the formula $Na_2HAsO_4,12H_2O$ (= 53.7 per cent. of water); these soon effloresce and yield a stable salt having the formula $Na_2HAsO_4,7H_2O$ (= 40.4 per cent. of water). To avoid the possible employment of a mixture of these bodies, the invariable anhydrous salt is officially used, constancy in the strength of a powerful preparation being thereby secured.
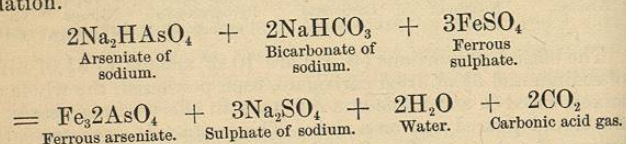
The student will find useful practice in verifying the above numbers representing the centesimal proportion of water in the two arseniates of sodium. This will readily be accomplished if what has already been stated respecting a symbol representing a number as well as a name, and the remarks concerning a molecular weight, be remembered.

The shape of each of the two varieties of arseniate of sodium ($Na_2HAsO_4,12H_2O$, and $Na_2HAsO_4,7H_2O$) is identical with that of the corresponding phosphate of sodium ($Na_2HPO_4,12H_2O$, and $Na_2HPO_4,7H_2O$); the structure of the molecule of the 12-arseniate is the same as that of the 12-phosphate, and the 7-arseniate as that of the 7-phosphate; the two former are isomorphous, the two latter are isomorphous. This is only one instance of the strong analogy of arsenicum and its compounds with phosphorus and its corresponding compounds. The preparation and characters of the next substance, arseniate of iron, will remind the learner of phosphate of iron.

## Arseniate of Iron. Ferrous Arseniate.

*Sixth Synthetical Reaction.*—To a hot solution of arseniate of sodium add a little solution of bicarbonate of sodium, and

then solution of ferrous sulphate ; a precipitate of ferrous arseniate occurs ($Fe_32AsO_4$) (*Ferri Arsenias*, B. P.). On the large scale $15\frac{3}{4}$ parts of dried arseniate dissolved in 100 of hot water, and $20\frac{3}{4}$ of sulphate in 120 of hot water, with $4\frac{1}{2}$ of bicarbonate of sodium, may be employed. The precipitate should be collected on a calico filter, washed, squeezed, and dried at a low temperature (100° F.) over a water-bath to avoid excessive oxidation.

$$2Na_2HAsO_4 \quad + \quad 2NaHCO_3 \quad + \quad 3FeSO_4$$

Arseniate of　　　Bicarbonate of　　　Ferrous
sodium.　　　　　sodium.　　　　　　sulphate.

$$= Fe_32AsO_4 \quad + \quad 3Na_2SO_4 \quad + \quad 2H_2O \quad + \quad 2CO_2$$

Ferrous arseniate.　　Sulphate of sodium.　　Water.　　Carbonic acid gas.

*The use of the bicarbonate of sodium* is to ensure the absence of free sulphuric acid in solution. Sulphuric acid is a solvent of ferrous arseniate. It is impossible to prevent the separation of sulphuric acid, if only ferrous sulphate and arseniate of sodium be employed. At the instant of precipitation ferrous arseniate is white, but rapidly becomes of a green or greenish-blue color, owing to absorption of oxygen and formation of a ferroso-ferric arseniate. When dry it is a tasteless, amorphous, much oxidized powder, soluble in acids.

The *Hydride* and *Sulphides of Arsenicum*, and the *Arsenites* and *Arseniates of Copper* and of *Silver*, are mentioned in the following analytical paragraphs :—

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

*First Analytical Reaction.*—Repeat the third synthetical reaction, operating on not more arsenic than has about the bulk of a small pin's head, and using not charcoal alone, but the *black flux* already mentioned (p. 166), or a well-made and perfectly dry mixture of charcoal and carbonate of potassium obtained by heating the bicarbonate of potassium. The tube employed should be a narrow test-tube, or, better, a tube (easily made from glass tubing) having the following (Berzelius's) form :—

Fig. 33.
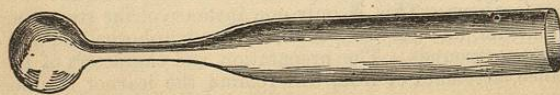


The arsenic and black flux are placed in the bulb of the tube, which is then heated in a flame ; the arsenicum condenses on the constricted portion of the tube. If now the bulb be carefully fused off in a flame, the arsenicum may be chased up and

down the narrower part of the tube until the air in the tube has reoxidized it to arsenious anhydride.

If the operation has been performed in a less delicate manner in an ordinary test-tube, cut or break off portions of the tube containing the sublimate of arsenicum, put them into a test-tube and heat the bottom of the latter, holding it nearly horizontally, and partially covering the mouth with the finger or thumb ; the arsenicum ($As_4$) will absorb oxygen from the air in the tube, and the resulting arsenious anhydride ($As_2O_3$) be deposited on the cool part of the tube in brilliant transparent, generally imperfect, octahedral crystals.
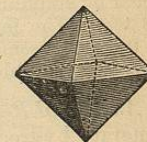
*Microscopic Test.*—Prove that the crystals are identical in form with those of common white arsenic, by heating a grain

Fig. 34.　　　　　　　　　　Fig. 34a.
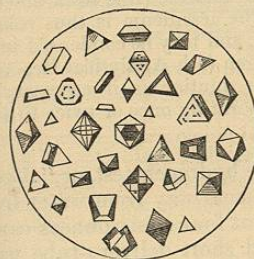


A sublimate of White Arsenic. (Magnified.)　　　A perfect Octahedron.

or less of the latter in another test-tube, examining the two sublimates by a good lens or compound microscope.

The appearance of a sublimate of arsenic is peculiar and quite characteristic. The primary form of each crystal is an octahedron (ὀκτὼ, *okto*, eight ; ἕδρα, *hedra*, side) (fig. 34*a*), or, rarely, a tetrahedron, and in a sublimate a few perfect octahedra are generally present. Usually, however, the crystals are modifications of octahedra, such as are shown in fig. 34—which is drawn from actual sublimates.

*Second Analytical Reaction.*—Place a thin piece of copper, about a quarter inch wide and half inch long, in a solution of arsenic, acidified by hydrochloric acid, and boil (nitric acid must not be present, or the copper itself will be dissolved) ; arsenicum is deposited on the plate in a metallic condition, an equivalent portion of copper going into solution. Pour off the supernatant liquid from the copper, wash the latter once or twice with water, dry the piece of metal by holding in the clean fingers and passing through a flame, and finally place it

8

at the bottom of a clean dry narrow test-tube or a Berzelius tube; sublime as described in the last reaction, again noticing the form of the resulting crystals.

This is commonly known as Reinsch's test of arsenicum, it having been introduced by Reinsch in 1843. The tube may be reserved for subsequent comparison with an antimonial sublimate (p. 186).

*Note.*—Copper itself frequently contains arsenicum, a fact that may not, perhaps, much trouble an operator so long as he is performing experiments in practical chemistry merely for educational purposes; but when he engages in the analysis of bodies of unknown composition, he must assure himself that neither his apparatus nor materials already contain the element for which he is in search.

*The detection of arsenicum in metallic copper* is best accomplished by distilling a mixture of a few grains of the sample with five or six times its weight of ferric hydrate or chloride (free from arsenicum) and excess of hydrochloric acid. The arsenicum is thus volatilized in the form of chloride of arsenicum, and may be condensed in water and detected by sulphuretted hydrogen (6th Analytical Reaction) or Reinsch's test. The ferric chloride solution is, if necessary, freed from any trace of arsenicum by evaporating once or twice to dryness with excess of hydrochloric acid.

*Third Analytical Reaction:* The hydrogen test, or "*Marsh's*" *test.*—Generate hydrogen in the usual way from water by zinc and sulphuric acid, a bottle of about four or six ounces capacity being used, and a funnel-tube and short delivery-tube passing through the cork in the usual manner (see following figure). Dry the escaping hydrogen (except in rough experiments, when it is unnecessary) by adapting to the delivery-tube, by a pierced cork, a short piece of wider tubing filled with fragments of chloride of calcium, *a*. To the opposite end of the drying tube fit a piece of narrow tubing ten or twelve inches long, made of hard German glass, and having its aperture narrowed by drawing out in the flame of the blowpipe. When the hydrogen has been escaping for a sufficient number of minutes, and at such a rate as to warrant the operator in concluding that all the air originally existing in the bottle has been expelled, set light to the jet, and then pour eight or ten drops of the aqueous solution of arsenic, or three or four drops of the acid or alkaline solution of arsenic, previously prepared, into the funnel-tube, washing the liquid into the generating-bottle with a little water. The arsenic is at once reduced to the state of arsenicum, and the latter combines with some of the hydrogen to form hydride of arsenicum or arseniuretted hydrogen gas ($AsH_3$). Immediately hold a piece of earthenware or porcelain (the lid of a porcelain crucible, *b*.

if at hand) in the hydrogen jet at the extremity of the delivery-tube; a brown spot of arsenicum is deposited on the

Fig. 35.
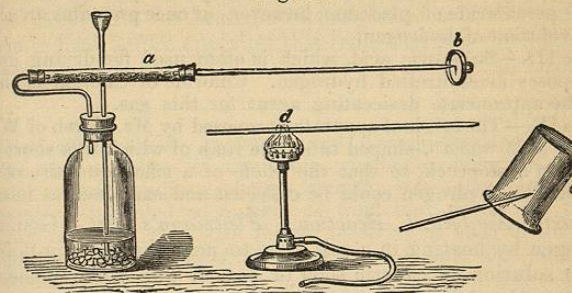


The Hydrogen Test for Arsenicum.

porcelain. Collect several of these spots, and retain them for future comparison with antimonial spots (p. 183).

The separation of arsenicum in the flame is due to the decomposition of the arseniuretted hydrogen by the heat of combustion. The cool porcelain at once condenses the arsenicum, and thus prevents its oxidation to white arsenic, which would otherwise take place at the outer edge of the flame.

Hold a small beaker, *c*, or wide test-tube over the flame for a few minutes; a white film of arsenic ($As_2O_3$) will be slowly deposited, and may be further examined in contrast with a similar antimonial film (p. 183).

During these experiments the effect produced by the arsenical vapors on the color of the hydrogen-flame will have been noticed; they give it a dull livid tint. This is characteristic.

Apply the flame of a gas-lamp to the middle of the hard delivery-tube, *d*; the arseniuretted hydrogen, as before, is decomposed by the heat, but the liberated arsenicum ($As_2$) immediately condenses in the cool part of the tube beyond the flame, forming a dark metallic mirror. The tube may be removed and kept for comparison with the antimonial deposit.

*Note* I.—Zinc, like copper, frequently itself contains arsenicum. When a specimen free from arsenicum is met with, it should be reserved for analytical experiments, or a quantity of guaranteed purity should be purchased of the chemical-apparatus maker. Sulphuric acid is more easily obtained free from arsenic.

*Note* II.—In delicate and important applications of Marsh's test, magnesium may be substituted for zinc with safety, as arsenicum

has not yet been, and is not likely to be, found in magnesium. Magnesium in rods is convenient for this purpose, and may be obtained from most dealers in chemicals. Both magnesium and zinc, if perfectly pure, react with acids extremely slowly; the addition of a little perchloride of platinum, however, at once promotes an abundant evolution of hydrogen.

*Note* III.—Sulphuric acid, which is often used for drying gases, decomposes arseniuretted hydrogen. Chloride of calcium is therefore the appropriate desiccating agent for this gas.

*Note* IV.—The original apparatus proposed by Mr. Marsh of Woolwich in 1836 was a U-shaped tube, one limb of which was short and closed by a stopcock, so that the whole of a small quantity of the arseniuretted hydrogen could be collected and examined at leisure.

*Fourth Analytical Reaction: Fleitmann's test.*—Generate hydrogen by heating in a test-tube to near the boiling-point a strong solution of caustic soda or potash and some pieces of zinc (or aluminium).

$$(Zn + 2NaHO = H_2 + Na_2ZnO_2—\text{zincate of sodium.})$$
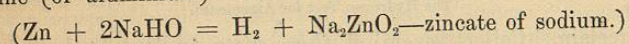
Add a drop of arsenical solution, and spread over the mouth of the tube a cap of filter-paper moistened with one drop of solution of nitrate of silver. Again heat the tube, taking care that the liquid itself shall not spirt up on to the cap. A plug of cotton-wool may even be placed in the mouth of the test-tube to prevent this spurting. The arsenic is reduced to arsenicum, the latter uniting with the hydrogen as in Marsh's test; and the arseniuretted hydrogen, passing up through the cap, reacts on the nitrate of silver, causing the production of a purplish-black spot.

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

*Note* I.—This reaction is particularly valuable, enabling the analyst to quickly distinguish arsenicum in the presence of its sister element antimony, which, although it combines with the hydrogen evolved from dilute acid and zinc, does not combine with the hydrogen evolved from solution of alkali and zinc, and therefore does not give the effect just described.

*Note* II.—Aluminium answers as well as zinc for Fleitmann's test (Gatehouse), or magnesium may be used; or, instead of zinc and alkali, weak sodium amalgam may be employed (Davy).

*Fifth Analytical Reaction—Bettendorff's Test.*—To a solution of chloride of tin in strong hydrochloric acid add a very small quantity of any arsenical solution. Arsenicum then separates, especially on the application of heat, giving the mixture a yellowish and then brownish hue or grayish-brown turbidity, or even a sediment of gray-brown flocks, according to the amount present. Much water prevents the reaction; its presence, there-

fore, must be avoided as for as possible; indeed a liquid saturated by hydrochloric acid gas gives best results. Arsenic in sulphuric or hydrochloric acid or in tartar emetic, etc., may be detected by this method. Nitrates, such as subnitrate of bismuth, must first be heated with sulphuric acid to remove the nitric radical before applying this reduction test for arsenicum. The stannous is converted to stannic salt during the reaction.

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*Distinction between Arsenious and Arsenic Combinations.*—The above tests are those of arsenicum, whether existing in the arsenious or arsenic condition, though from the latter the element is not generally eliminated so quickly as from the former. Of the following reactions, that with nitrate of silver at once distinguishes arsenious acid and other arsenites from arsenic acid and other arseniates.

*Mem.*—The exact nature of all these analytical reactions will be more fully evident if traced out by diagrams or equations.

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*Sixth Analytical Reaction.*—Through an acidified solution of arsenic pass sulphuretted hydrogen; a yellow precipitate of sulphide of arsenicum or arsenious sulphide ($As_2S_3$) quickly falls. Add an alkaline hydrate or sulphydrate to a portion of the precipitate; it readily dissolves. The precipitate consequently would not be obtained on passing sulphuretted hydrogen through an alkaline solution of arsenic. To another portion of the precipitate, well drained, add *strong* hydrochloric acid; it is insoluble, unlike sulphide of antimony. Neither sulphide is soluble in the *weak* acid.

*Note* I.—Cadmium also affords a yellow sulphide in an acid solution by action of sulphuretted hydrogen, but this sulphide is insoluble in alkaline liquids. Under certain circumstances, tin, too, yields a yellow sulphide; but tin is otherwise easily distinguished (*vide* Tin).

*Note* II.—A trace of sulphide of arsenicum is sometimes met with in sulphur (distilled from arsenical pyrites). It may be detected by digesting the sulphur in solution of ammonia, filtering, and evaporating to dryness; a yellow residue of sulphide of arsenicum is obtained if that substance be present.
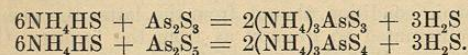
*Seventh Analytical Reaction.*—Through an acidified solution of arsenic acid, or any other arseniate, pass a rapid current of sulphuretted hydrogen; arsenic sulphide ($As_2S_5$) slowly falls. Brauner and Tornieck state that by a slow current the arsenic compound is gradually reduced to the arsenious and a yellow precipitate of arsenious sulphide and sulphur ($As_2S_3 + S_2$)

slowly falls. The precipitate is soluble in alkaline hydrates and sulphydrates. This reaction is more rapid if the solution be warmed.

*Chemical Analogy of Sulphur and Oxygen.*—The potassium arsenite and sulph-arsenite, arseniate and sulph-arseniate, have the composition represented by the following formulæ :—

$$K_3AsO_3 \qquad\qquad K_3AsO_4$$
$$K_3AsS_3 \qquad\qquad K_3AsS_4 ;$$

and the corresponding ammonium and sodium salts have a similar composition :—

$$6NH_4HS + As_2S_3 = 2(NH_4)_3AsS_3 + 3H_2S$$
$$6NH_4HS + As_2S_5 = 2(NH_4)_3AsS_4 + 3H_2S.$$

*Eighth Analytical Reaction.*—To an aqueous solution of arsenic add two or three drops of solution of sulphate of copper, and then cautiously add diluted solution of ammonia, drop by drop, until a green precipitate is obtained. The production of this precipitate is characteristic of arsenicum. To a portion of the mixture add an acid ; the precipitate dissolves. To another portion add alkali : the precipitate dissolves. These two experiments show the advantage of testing a suspected arsenical solution by litmus-paper before applying this reaction ; if acid, cautiously adding alkali, if alkaline, adding acid, till neutrality is obtained. (Or a special copper reagent may be used ; see a note to the Eleventh Analytical Reaction, below).

The precipitate is arsenite of copper ($Cu''HAsO_3$) or *Scheele's Green.* More or less pure, or mixed with acetate or, occasionally, carbonate of copper, it is used as a pigment under many names, such as Brunswick Green and Schweinfurth Green, by painters and others.

*Ninth Analytical Reaction.*—Apply the test just described to a solution of arsenic acid or other arseniate ; a somewhat similar precipitate of arseniate of copper is obtained.

*Tenth Analytical Reaction.*—Repeat the eighth reaction, substituting nitrate of silver for sulphate of copper ; in this case *yellow* arsenite of silver ($Ag_3AsO_3$) falls, also soluble in acids and alkalies.

*Eleventh Analytical Reaction.*—Apply the test to a solution of arsenic acid or other arseniate ; a *chocolate*-colored precipitate of arseniate of silver ($Ag_3AsO_4$) falls.

This reaction may be utilized for the detection of arsenic when occurring in ores and other substances as ordered by the U. S. Pharmacopœia in the case of *Antimonii Sulphidum Purificatum ;*

"If 2 gm. of the salt be mixed and cautiously ignited, in a porcelain crucible, with 8 gm. of pure nitrate of sodium, and the fused

mass boiled with 25 gm. of water, there will remain a residue which should be white, or nearly so, and not yellowish nor brownish (abs. of other metallic sulphides). On boiling the filtrate with an excess of nitric acid, until no more nitrous vapors are evolved, then dissolving in it 0.1 gm. of nitrate of silver, filtering again, if necessary, and cautiously pouring a few drops of water of ammonia on top, not more than a white cloud, but no red nor reddish precipitate, should appear at the line of contact of the two liquids (abs. of more than traces of arsenic)."

*Copper and Silver Reagents for Arsenicum.*—The last four reactions may be performed with increased delicacy and certainty of result if the copper and silver reagents be previously prepared in the following manner : To solution of pure sulphate of copper (about 1 part in 20 of water) add ammonia until the blue precipitate at first formed is nearly but not quite redissolved ; filter and preserve the liquid as an arsenicum reagent, labelling it *solution of ammonio-sulphate of copper* (B. P.). Treat solution of nitrate of silver (about 1 part in 40) in the same way, and label it *solution of ammonio-nitrate of silver* (B. P.). The composition of these two salts will be referred to subsequently.

*Arsenious and Arsenic Compounds.*—While many reagents may be used for the detection of arsenicum, only nitrate of silver, as already stated, will readily indicate in which state of oxidation the arsenicum exists ; for the two sulphides and the two copper precipitates, though differing in composition, resemble each other in appearance, whereas the two silver precipitates differ in color as well as in composition.
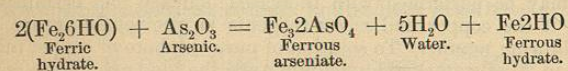
Soluble arseniates also give insoluble arseniates with solutions of salts of barium, calcium, zinc, and some other metals.

In group-testing, arsenicum, if existing as arsenic acid or other arseniate, is not readily affected by such tests as sulphuretted hydrogen or even hydrogen itself. Hence, if its presence in that state is suspected, the liquid under analysis should be warmed with a little sulphurous acid or oxalic acid, and then tested with sulphuretted hydrogen.

*Antidote.*—In cases of poisoning by arsenic or arsenical preparations, the most effective antidote is recently precipitated moist ferric hydrate (*Ferri Oxidum Hydratum,* U. S. P.). It is perhaps best administered in the form of a mixture or solution of ferric sulphate (*Liquor Ferri Tersulphatis,* U. S. P.) or perchloride of iron (*Liquor* or *Tinctura*) with carbonate of sodium—two or three ounces of the former to about one ounce of the crystals of the latter. Instead of the carbonate of sodium, about a quarter of an ounce of calcined magnesia may be used. (See *Ferri Oxidum Hydratum cum Magnesia,* U. S. P., page 149.) These quantities will render at least 10 grains of arsenic insoluble. Emetics should also be given, and the stomach-pump applied as quickly as possible.

The above statements regarding the antidote for arsenic may be verified by mixing the various substances together, filtering, and proving the absence of arsenicum in the filtrate by applying some of the foregoing tests.

*Mode of Action of the Antidote.*—The action of the carbonate of sodium or the magnesia is to precipitate ferric hydrate ($Fe_26HO$)—chloride of sodium ($NaCl$) or magnesium ($MgCl_2$) being formed, which are harmless, if not beneficial, under the circumstances. The reaction between the ferric hydrate and the arsenic results in the formation of insoluble ferrous arseniate.

$$2(Fe_26HO) + As_2O_3 = Fe_32AsO_4 + 5H_2O + Fe2HO$$
$$\text{Ferric hydrate.} \quad \text{Arsenic.} \quad \text{Ferrous arseniate.} \quad \text{Water.} \quad \text{Ferrous hydrate.}$$

The so-called Solution of Dialyzed Iron (see Index) is also, as might be expected from its composition, an antidote to arsenic. It should be administered with a little bicarbonate of either sodium or potassium, or with magnesia, or with any other salt which serves to neutralize any acid that may be present.

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## QUESTIONS AND EXERCISES.

249. What is the formula of a molecule of arsenicum?

250. In what form does arsenicum occur in nature?

251. Describe the characters of white arsenic.

252. Name the official preparations of arsenicum.

253. What proportion of arsenic ($As_2O_3$) is contained in *Liquor Potassii Arsenitis*, U. S. P., and in *Liquor Acidi Arseniosi*, U. S. P.?

254. By what method may arsenic be reduced to arsenicum?

255. Give the formulæ of arsenious and arsenic acids and anhydrides.

256. Explain, by diagrams, the reactions which occur in converting arsenic into Arseniate of Sodium by the process of the British Pharmacopœia.

257. Why is anhydrous instead of crystallized arseniate of sodium employed in the preparation of *Liquor Sodii Arseniatis*, U. S. P.?

258. In the preparation of Arseniate of Iron from ferrous sulphate and arseniate of sodium, why is acetate of sodium included?

259. Describe the manipulations necessary to obtain arsenic in its characteristic crystalline form.

260. How is Reinsch's test for arsenicum applied, and under what circumstances may its indications be fallacious?

261. Give the details of Marsh's test for arsenicum, and the precautions to be observed in its performance. Explain the reactions by diagrams.

262. What peculiar value has Fleitmann's test for arsenicum?

263. Describe the conditions under which sulphuretted hydrogen becomes a trustworthy test for arsenicum?

264. How may a trace of sulphide of arsenicum be detected in sulphur?

265. How are the salts of copper and silver applied as reagents for the detection of arsenicum?

266. How are arsenites distinguished from arseniates?

267. Mention the best antidote in cases of poisoning by arsenic, explain the process by which it may be most quickly prepared, and describe its action.

268. Do you know of any other antidote to arsenic? If so, describe the mode of administration.

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## ANTIMONY.

### Symbol Sb (Stibium).    Atomic weight 120.

*Sources and Uses.*—Antimony occurs in nature chiefly as sulphide, $Sb_2S_3$. The *crude* or *black antimony* of pharmacy is this native sulphide freed from impurities by fusion; it has a striated, crystalline, lustrous fracture; subsequently powdered, and if it contains any soluble salt of arsenicum, the latter removed by digestion in solution of ammonia, it forms the grayish-black, crystalline *Antimonii Sulphidum*, U. S. P. When this powder is washed with solution of ammonia to remove any traces of sulphide of arsenicum and dried, it forms the *Antimonii Sulphidum Purificatum*, U. S. P. The metal is obtained from the sulphide by roasting, the resulting oxide being reduced with charcoal and carbonate of sodium. Metallic antimony is an important constituent of *Type-metal*, *Britannia metal* (tea and coffee pots, spoons, etc.), and the best varieties of *Pewter*. The old *pocula emetica*, or everlasting emetic cups, were made of antimony; wine kept in them for a day or two was said to have acquired a variable amount of emetic quality. The metal is not used in making official antimonial preparations, the sulphide alone being, directly or indirectly, employed for this purpose.

Antimony has very close chemical analogies with arsenicum. Its atom, in the common salts, exerts trivalent activity (*e. g.*, $SbCl_3$), but sometimes it is quinquivalent (*e. g.*, $SbCl_5$).

Antimony, like arsenicum, unites with iodine to form a tri-iodide ($SbI_3$). A bromide ($SbBr_3$) is also known.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

#### (*a*) *Reactions having Synthetical Interest.*

### Chloride of Antimony.    Antimonious Chloride.

*First Synthetical Reaction.*—Boil half an ounce or less of sulphide of antimony with four or five times its weight of hydrochloric acid in a dish in a fume-chamber or in the open air; sulphuretted hydrogen is evolved, and solution of chloride of antimony, $SbCl_3$, is obtained.

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

Sulphide of antimony.   Hydrochloric acid.   Chloride of antimony.   Sulphuretted hydrogen.
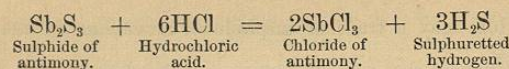
This solution, cleared by subsidence, is what is commonly known as *Butter of antimony* (*Liquor Antimonii Chloridi*, B. P.). If pure sulphide has been used in its preparation, the liquid is nearly color-less; but much of that met with in veterinary pharmacy is simply a by-product in the generation of 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 unfre-quently 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.
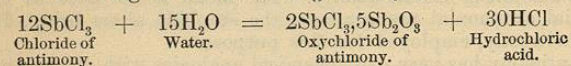
*True butter of antimony* ($Sb\bar{C}l_3$) is obtained on evaporating the above solution to a low bulk, and distilling the residue. The butter condenses (as a white crystalline semi-transparent mass in the neck of the retort); at the close of the operation it may be easily melted and run down in a bottle, which should be subsequently well stop-pered.

*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.
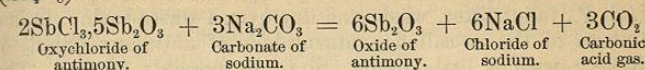
This is the old *pulvis Algarothi*, *pulvis angelicus*, or *mercurius vitæ*. On standing under water it gradually becomes crystalline.

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

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

### 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
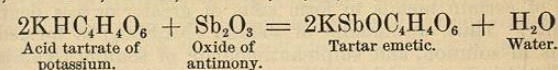
oxide of antimony ($Sb_2O_3$) is soluble, but *antimonic anhydride* ($Sb_2O_5$) and the double oxide or so-called *antimonious anhydride* ($Sb_4O_8$) are insoluble.

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

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

*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 anti-mony with nitric acid. The variety obtained from the chloride differs in saturating power from that obtained from the metal, and is termed metantimonic (μετα, *meta*, beyond).

### Tartar Emetic.

*Third Synthetical Reaction.*—Mix the moist oxide of anti-mony 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 anti-mony and potassium ($KSbOC_4H_4O_6$), potassio-tartrate of anti-mony, tartrated antimony, or tartar emetic (emetic, from ἐμέω, *emeō*, I vomit; tartar, from τάρταρος, *tartaros* See Index).

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

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

On evaporation the salt is obtained in colorless transparent triangular-faced crystals of the above composition, with a mole-cule of water of crystallization, forming the *Antimonii et Po-tassii 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 sul-phide to 12 of soda, and 30 of water for 2 hours, frequently stirring, and occasionally replacing water lost by evaporation).