Very pure, antimony-free arsenic is produced from magnesium ammonium arsenate. A solution of arsenic acid is mixed with chemically pure MgCl$_2$ and ammonia is slowly added. The initial precipitate is discarded and the middle fractions are collected. Then the material is repeatedly dissolved and precipitated in a similar fashion, the number of such treatments depending upon the purity of the starting materials. In each case, the first and last fractions are discarded. After final washing, the material is dried. The magnesium ammonium arsenate thus obtained is mixed with sugar charcoal; pure As is sublimed from the mixture by heating, preferably in vacuum.

De Pasillé recommends that ammonium arsenate be reduced in an ammonia stream at 1000°C. According to Geach, very pure As can also be obtained by reduction of chemically pure As$_2$O$_3$ with Zr metal and subsequent sublimation. Impurities other than Sb can be removed by sublimation in vacuum (Geach).

PROPERTIES:
M.p. 817° (under pressure), b.p. 633°; d. 5.78. Rhombohedral crystals with a gray metallic luster. Brittle. Hardness (Mohs) 3.5.

REFERENCES:

YELLOW ARSENIC

Yellow As is formed when the vapor is cooled suddenly. In the Erdmann and Unruh method, the As vapor is added directly to CS₂, which serves as the solvent, because the yellow form converts to the gray with exceptional ease, particularly in the light. Figure 200 illustrates the apparatus employed. The aluminum tube α (wall thickness 3 mm., inside diameter 20 mm., length 1 m.) is wrapped with a 2-mm. thickness of asbestos paper (b), which is cemented in place with water glass. A closely fitting, 40-cm. iron tube ε is pushed over the tube. The end of the Al tube projecting 50 cm. is closed with a one-hole cork and connected to a CO₂ source via a wash bottle containing H₂SO₄. The other end of the Al tube is reinforced with asbestos and water glass to provide a good seal with the conical aperture of tube f, even though that end of the tube is very hot during operation because of the necessity of preventing condensation and consequent plugging with As. Receiver γ is a 12-cm. I.D. sphere with U tube f attached. Dry CO₂ at about −20°C is introduced through a tube adjacent to the thermometer. The receiver stands in ice-water bath and holds about 300 ml. of CS₂. A second and a third receiver, identical but containing only about 100-120 ml. of CS₂ each, are connected in line with the first. All three vessels are placed in the ice-water bath, which is covered to exclude light. The level of ice water must extend above the conical connection of tube f. The Al tube is charged with pure As.

Fig. 200. Preparation of yellow arsenic. a) Aluminum tube; b) asbestos insulation; d) asbestos paper heat insulation; f) inlet tube; g) receiver.
and brought to low red heat by a gas flame or an electric furnace. The thin oxide layer on the As is immediately removed by heating the material in a stream of CO₂. Then an additional CO₂ stream is admitted through the aluminum tube. Thus, the As vapor which distills over is cooled with the —20°C CO₂ and is immediately absorbed in the cold CS₂. The solution is filtered and concentrated on a water bath, to about half the original volume. It is then evaporated to saturation in a large diameter test tube. Finally, it is cooled to —70°C in a Dry Ice-acetone bath, whereupon the As precipitates. The supernatant liquid is decanted and the As is dried in vacuum. All the operations, particularly those with the concentrated solutions, must be performed as far as possible in the absence of light. About 12 g. of yellow arsenic is obtained from the solution in the first receiver and another 4 g. from the second. There is none in the third.

**PROPERTIES:**

Yellow powder, converting to gray As in less than one minute when exposed to sunlight. Soluble in CS₂. Cubic crystals. d. (20°C) 1.97.

Solubility in 100 ml. of CS₂

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Yellow As, g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>+46</td>
<td>11</td>
</tr>
<tr>
<td>+18 to 20</td>
<td>7.5—8</td>
</tr>
<tr>
<td>+12</td>
<td>5.5—6</td>
</tr>
<tr>
<td>0</td>
<td>3.8—4</td>
</tr>
<tr>
<td>—15</td>
<td>2—2.5</td>
</tr>
<tr>
<td>—60 to —80</td>
<td>0.8—1.0</td>
</tr>
</tbody>
</table>

**REFERENCES:**

A. Stock and W. Siebert. Ber. dtsch. chem. Ges. 37, 4572 (1904); 38, 966 (1905).

**Arsine**

\[
\text{AsH}_3
\]

1. \[ \text{Na}_3\text{As} + 3 \text{NH}_4\text{Br} = 3 \text{NaBr} + 3 \text{NH}_3 + \text{AsH}_3 \]

The reaction is run in liquid NH₃, using the reactor illustrated in Fig. 201. First the required amount of Na is placed in \( \alpha \) and dry NH₃ is condensed over it. The required amount of powered As is then added. By turning and tapping the bulb, dry NH₄Br, which has
been weighed into the flask at the right, is added to a. The evolving

gas is scrubbed with water, dried with P₂O₅, and condensed in a

trap cooled with liquid nitrogen. It can be purified by vacuum
distillation in the apparatus used for

SbH₃ (p. 599, Fig. 203, or Part I, p. 67).

II. \( \text{As}_2\text{Zn}_3 + 3 \text{H}_2\text{SO}_4 = 3 \text{ZnSO}_4 + 2 \text{AsH}_3 \)

\[
\begin{array}{cccc}
345.9 & 294.2 & 484.3 & 44.8 (155.8)
\end{array}
\]

To obtain the required zinc alloy, an

intermediate alloy is first prepared by

fusing the quantity of Zn computed from

\[
2\text{As} + 3\text{Zn} = \text{As}_2\text{Zn}_3
\]

149.8 196.1 345.9

in a closed crucible, to which a portion of

the As is added. After cooling, the alloy

is pulverized, the rest of the As is added,

and the fusion in the closed crucible is

repeated. After cooling and grinding, the

alloy is placed in a reaction flask equipped

with a dropping funnel and a ground joint.

The air is displaced with a stream of H₂,

and boiled 30% H₂SO₄ is then added drop-by-drop. The gas thus

generated contains only 0.5% impurities. It is scrubbed with KOH

solution, dried with solid KOH and P₂O₅, and purified by condensa-

tion and vacuum distillation at low temperature.

III. Arsine can also be prepared in the familiar manner involving

addition of a solution of As₂O₃ in HCl to zinc granules and dilute

H₂SO₄. However, the gas thus generated contains no more than 25%

AsH₃.

IV. In the Nast method, an Mg–Al–As alloy is decomposed with very
dilute sulfuric acid. Fractionation of the resulting gases in a Stock

vacuum apparatus also permits isolation (even though in a very

small quantity) of As₂H₄ (diarsine), an analog of N₂H₄ and P₂H₄.

V. According to Stone and Burg, treatment of AsCl₃ with LiAlH₄ in

absolute ether gives AsH₃ in a 70% yield.

PROPERTIES:

M.p. \(-113^\circ\text{C}\), b.p. \(-58.5^\circ\text{C}\). Colorless gas and liquid. Exceptionally poisonous. Sensitive to \(\text{O}_2\). Unstable on porous surfaces.

REFERENCES:

**Sodium Dihydrogen Arsenide**

\[ \text{Na} + \text{AsH}_3 = \text{NaAsH}_2 + \frac{1}{2}\text{H}_2 \]

Gaseous arsine is introduced into a solution of sodium in liquid NH$_3$ at $-78^\circ$C. The arsine apparatus described in Fig. 201 is employed. Approximately 1 g. of sodium is placed in the side bulb and about 50 ml. of NH$_3$ is condensed in \( \alpha \). Then the Na is added to the NH$_3$ by rotation of the bulb, and dissolved while the flask is cooled with Dry Ice. A stream of AsH$_3$ is then introduced, while the flask is still in the cold bath. The solution, initially dark blue, becomes lighter and finally turns yellow. When the color changes, the NH$_3$ is evacuated. The residue is NH$_3$-free NaAsH$_2$ which appears on the reactor walls as pale-yellow crystals.

Potassium dihydrogen arsenide can be produced in a similar fashion.

**Other preparative methods:**

\[ \text{(C}_6\text{H}_5\text{)}_3\text{CNa} + \text{AsH}_3 = \text{(C}_6\text{H}_5\text{)}_3\text{CH} + \text{NaAsH}_2 \]

**Properties:**

Decomposes rapidly in air, generating heat and leaving a brown residue of unknown composition. Stable in vacuum, in the absence of air. Hydrolyzes in H$_2$O, forming AsH$_3$.

See also the preparation and properties of the analog NaPH$_2$.

**References:**


Arsenic Trichloride

AsCl$_3$

I.  

$$2\text{As} + 3\text{Cl}_2 = 2\text{AsCl}_3$$

149.8  212.7  362.5

Pulverized As is placed in a retort with a filler tube or in a boat inserted into a Pyrex tube. Dry Cl$_2$ is passed over the material. The As usually ignites and burns in the Cl$_2$ stream. If necessary, the reaction may be initiated by slight heating. A long cooling tube attached to the reaction tube (or to the neck of the retort) delivers the product to a distillation flask serving as receiver. At the end, a small quantity of As powder is added to the distillation flask to bind the dissolved Cl, and the contents are distilled. The material fractionated over As powder is completely pure.

II.  

$$4\text{As}_2\text{O}_3 + 3\text{S}_2\text{Cl}_2 + 9\text{Cl}_2 = 8\text{AsCl}_3 + 6\text{SO}_2$$

791.3  405.1  638.2  1450.2  384.4

A mixture of 140 g. of As$_2$O$_3$ and 100 g. of S$_2$Cl$_2$ is prepared in a flask, and dry Cl$_2$ is introduced. When most of the material has reacted, another 60 g. of As$_2$O$_3$ is added, and additional Cl$_2$ is introduced. Finally, the product is distilled directly from the flask, in the presence of some metallic arsenic.

III.  

$$\text{As}_2\text{O}_3 + 6\text{HCl} = 2\text{AsCl}_3 + 3\text{H}_2\text{O}$$

197.8  218.8  362.5  54.0

The As$_2$O$_3$ is distilled from concentrated hydrochloric acid in a stream of HCl.

PROPERTIES:

Formula weight 181.28. Colorless, oily liquid. Fumes in air. Extremely toxic (skin poison). Solidifies at $-16.2^\circ$C to colorless crystals with a pearly sheen. B.p. 130.2$^\circ$C; d. 2.2. Soluble in H$_2$O and HCl. Dissolves alkali iodides, sulfur, phosphorus, and oils.

REFERENCES:

**Arsenic Tribromide**

**AsBr₃**

I. \[2 \text{As} + 3 \text{Br}_2 = 2 \text{AsBr}_3\]

\[
\begin{array}{ccc}
149.8 & 479.5 & 629.3
\end{array}
\]

A boat is placed in a Pyrex tube and filled with As powder. A stream of dry \(\text{N}_2\), saturated with \(\text{Br}_2\) vapor by passage through a \(\text{Br}_2\)-filled wash bottle, is passed over the As. The tube is inclined toward the receiver and connected with the latter by means of an asbestos-paper-sealed adapter. The tube is heated until the onset of reaction. The product is distilled from the receiver over As powder.

II. \[2 \text{As}_2\text{O}_3 + 3 \text{S} + 6 \text{Br}_2 = 4 \text{AsBr}_3 + 3 \text{SO}_2\]

\[
\begin{array}{ccc}
395.6 & 96.2 & 959.0 & 1258.6 & 192.2
\end{array}
\]

A mixture of 26.5 g. of \(\text{As}_2\text{O}_3\), 6 g. of sulfur, and 64 g. of \(\text{Br}_2\) is heated in a 300-ml. flask in a metal bath. After about seven hours, the rising vapors are no longer colored brown with bromine. A preheated suction filter is employed for filtering. The product is very pure. Further purification involves distillation over As as in method I.

**PROPERTIES:**

Formula weight 314.66. Colorless, deliquescent, rhombic prisms. M.p. 31.2°C, b.p. 221°C; d₄ 3.66. Fumes in humid air and is hydrolyzed by water.

**REFERENCES:**


**Arsenic Triiodide**

**AsI₃**

I. \[\text{As} + \frac{3}{2} \text{I}_2 = \text{AsI}_3\]

\[
\begin{array}{ccc}
74.9 & 380.7 & 455.6
\end{array}
\]

A \(\text{CS}_2\) or ether solution of \(\text{I}_2\) is refluxed with excess As powder until the iodine color disappears. This is followed by rapid filtration. The product is then allowed to crystallize. Concentration of the solution yields additional crystals. The product is recrystallized from \(\text{CS}_2\) or ether.
Other preparative methods:

II. \[ \text{As}_2\text{O}_3 + 6\text{HCl} + 6\text{KI} = 2\text{AsI}_3 + 6\text{KCl} + 3\text{H}_2\text{O} \]

\[
\begin{array}{ccccccc}
197.8 & 218.8 & 996.1 & 911.3 & 447.3 & 54.0 \\
\end{array}
\]

A solution of 10 g. of KI in 10 ml. of H\(_2\text{O}\) is added to a hot solution of 2 g. of As\(_2\text{O}_3\) in 30 ml. of hydrochloric acid (d. 1.19), whereupon a yellow crystalline powder precipitates. This is suction-filtered and washed with concentrated hydrochloric acid (d. 1.12) until no KCl residue is seen when the wash liquid is evaporated on a watch glass. The product can be further purified by recrystallization as described above.

III. In the Oddo method, the product is obtained from As\(_2\text{O}_3\), iodine, and sulfur, in a procedure identical to that described for AsBr\(_3\). However, 102 g. of iodine is used in the present case. After heating for 14 hours, the product can be purified by recrystallization as described above.

PROPERTIES:

Lustrous, trigonal red leaves or platelets. Rhombohedral. M.p. 141.8°C, b.p. 403°C; d.\(_{25}\) 4.688. Soluble in H\(_2\text{O}\), ether, CS\(_2\), xylene, and various other organic solvents. Sparingly soluble in strong HCl. In air, gradually decomposes into AS\(_2\text{O}_3\) and iodine.

REFERENCES:


Arsenic Diiodide

AsI\(_2\)

\[
\text{As} + \text{I}_2 = \text{AsI}_2
\]

74.9  253.8  328.7

A mixture of 20 g. of I\(_2\) and 20 g. of powdered As is placed in a tube, and all air is displaced by repeated evacuation and filling
with CO$_2$. The tube is sealed in a stream of CO$_2$. The tube is then heated in an inclined position for seven hours at 240°C, and permitted to cool in the same position to enable the product to gather and solidify at one end. To recrystallize the product, the section containing the product is broken off. It is immediately placed in flask $a$ of the apparatus illustrated in Fig. 202, prefilled with air-free, $P_2O_5$-dried CO$_2$ from $b$. The flask capacity is 300–400 ml. and it contains about 150 ml. of dry xylene. Stopper $c$ is then pushed firmly into place while $d$ is left loose. The xylene is then boiled (continued passage of CO$_2$) until the AsI$_2$ dissolves. After that, $d$ is tightened in place, $c$ is removed, and adapter $e$, containing a hard folded filter paper, is put in its place. Flask $h$ is then placed over $e$ while a constant flow of CO$_2$ is maintained. After $h$ has been filled with CO$_2$ (in about 5 minutes) the solution is transferred into $h$ via filter $r$ by slowly tilting the apparatus. The solution must remain boiling hot. The CO$_2$ inlet is then transferred to $g$ and the stopper connecting $h$ to $e$ may be removed. The product is permitted to cool in the CO$_2$ stream; the AsI$_2$ precipitates as long red prisms.

![Fig. 202. Purification of arsenic diiodide.](image)

To separate the AsI$_2$, a fairly coarse fritted glass filter $i$, attached to suction flask $k$, is placed over the neck of flask $h$. Carbon dioxide is introduced through a tube in the stopper of $k$. When the whole system has been filled with CO$_2$ via $g$, the apparatus is turned upside down and the AsI$_2$ drops onto the fritted filter. It is then suction dried in a stream of CO$_2$. Removal from the filter must also be done in a stream of CO$_2$ and in the absence of moisture. The aspirator is turned off, the system is filled with CO$_2$, and flask $h$ is removed quickly and replaced by an adapter $l$ which fits the fritted filter. The adapter is sealed to the filter with large-diameter rubber hose (e.g., bicycle inner tube). Then CO$_2$ passage from
below is resumed. Several previously prepared storage tubes may now be attached at the other end of the adapter. These are filled with CO₂, the AsI₂ is poured in, and the tubes are sealed with a torch.

**PROPERTIES:**

Red prisms. M.p. 128-130°C. Exceptionally unstable in air. Disproportionates in water to As and AsI₂.

**REFERENCES:**


**Diarsenic Trioxide**

\[
\text{As}_2\text{O}_3 (\text{As}_4\text{O}_6)
\]

\[
2 \text{AsCl}_3 + 3 \text{H}_2\text{O} = \text{As}_2\text{O}_3 + 6 \text{HCl}
\]

To obtain a pure product, 150 g. of As₂O₃ is treated with concentrated HCl in the apparatus shown in Fig. 231, and AsCl₃ is slowly distilled in a stream of HCl. To remove SbCl₃ from the oily layer in the first condensation trap, the material is shaken repeatedly with 2/3 its volume of concentrated hydrochloric acid until the aqueous layer is free of Sb (tested by the method of Foulk and Horton, i.e., distilling off the bulk of dissolved AsCl₃ and precipitating the strongly acid solution with H₂S. The precipitate is filtered off, the solution diluted, and the H₂S bubbling is resumed; Sb precipitates as an orange-red solid. If SbCl₃ is present only in traces, the precipitate appears only after one or two days of standing in an atmosphere of H₂S). The pure AsCl₃ is hydrolyzed in vigorously stirred boiling water and As₂O₃ crystallizes out on cooling.

**PROPERTIES:**

White powder. There are two crystalline modifications, monoclinic claudetite (m.p. 313°C) and cubic arsenolite (m.p. 275°C). A cold solution of As₂O₃ in hydrochloric acid always separates arsenolite. Claudetite can be obtained by heating moist arsenolite for several days at 100 to 200°C. In addition, there is a vitreous
form of $\text{As}_2\text{O}_3$. In the vapor and in nitrobenzene the formula is $\text{As}_4\text{O}_6$. The structure is analogous to that of $\text{P}_4\text{O}_6$. B.p. 465°C; sublimes at 195°C in a stream of $\text{N}_2$.

REFERENCES:

**Orthoarsenic Acid**

$$\text{H}_3\text{AsO}_4$$

$\text{As}_2\text{O}_3 + 2\text{HNO}_3 + 3\text{H}_2\text{O} = \text{N}_2\text{O}_3 + 2\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

197.8 126.0 54.0 76.0 301.8

Arsenic trioxide (100 g.) is placed in a ground joint flask and 100 ml. of concentrated $\text{HNO}_3$ (d. 1.38) is slowly added from a dropping funnel. The mixture is then heated. The nitric oxides are passed through concentrated $\text{H}_2\text{SO}_4$ to obtain nitrosyl hydrogen sulfate. When the evolution of nitrogen oxides ceases, the supernatant liquid is decanted from the undissolved material and evaporated to dryness. The residue is taken up in some $\text{H}_2\text{O}$ and filtered through a glass frit, and the solution is evaporated until a thermometer in the liquid reads 130°C. The solution, which has a honeylike consistency when cold, is left to crystallize in a refrigerator (in a desiccator over $\text{H}_2\text{SO}_4$). Beautiful transparent crystals of $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ precipitate. If the crystallization is done at $-30^\circ\text{C}$, the hydrate $\text{H}_7\text{AsO}_6$ may be formed, but only if the solution is held for a few days at this temperature. If the solution is evaporated until a b.p. of 175°C is reached, $\text{As}_2\text{O}_5 \cdot 5/3\text{H}_2\text{O}$ precipitates.

**PROPERTIES:**

All the hydrates lose their water on heating above 250–300°C and convert to $\text{As}_2\text{O}_5$.

$\text{H}_3\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$: transparent, large, hygroscopic crystals.

$\text{As}_2\text{O}_5 \cdot 5/3\text{H}_2\text{O}$: dull, granular crystalline mass.

REFERENCES:
A. Simon and E. Thaler. Z. anorg. allg. Chem. 161, 143 (1927); 246, 19 (1941).
Sodium Dihydrogen Orthoarsenate

\[
\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}
\]

\[
\text{H}_2\text{AsO}_4 + \text{NaOH} = \text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}
\]

A 5N solution of \(\text{H}_3\text{AsO}_4\) is neutralized with caustic soda to the methyl orange end point and then evaporated until crystallization begins. The crude salt which precipitates on cooling is dissolved in water to make a saturated solution at 100°C (75.3 g./100 g. \(\text{H}_2\text{O}\)), and is then cooled to 0°C with stirring. The fine, crystalline precipitate is suction-filtered, washed with some ice water, and dried over \(\text{P}_2\text{O}_5\).

**PROPERTIES:**

White crystalline powder. d 2.53. Loses water of crystallization when warmed and passes through the stages \(\text{NaH}_2\text{AsO}_4 \rightarrow \text{Na}_2\text{H}_2\text{As}_2\text{O}_7 \rightarrow \text{Na}_3\text{H}_2\text{As}_3\text{O}_{10}\), finally converting to \(\text{NaAsO}_3\) above 230°C.

REFERENCE


**Ammonium Orthoarsenate**

\[
(\text{NH}_4)_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}
\]

\[
\text{H}_2\text{AsO}_4 + 3\text{NH}_3 + 3\text{H}_2\text{O} = (\text{NH}_4)_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}
\]

A saturated aqueous orthoarsenic acid solution is saturated with gaseous \(\text{NH}_3\). Beautiful crystals of ammonium orthoarsenate precipitate immediately.

**PROPERTIES:**

Rhombic crystalline lamellae. Loses \(\text{NH}_3\) and \(\text{H}_2\text{O}\) in air and converts to the monohydrogen salt. On heating, the aqueous solution loses so much \(\text{NH}_3\) that the solution corresponds at the end to the dihydrogen salt.

REFERENCES:


**Tetraarsenic Tetrasulfide**

\[
\text{As}_4\text{S}_4
\]

\[
\text{As} + \text{S} = \frac{1}{4}\text{AsS}
\]

Equimolar quantities of As and S are placed in a thick-walled, sealed tube and fused together at 500–600°C in a N\(_2\) atmosphere. The product is sublimed in vacuum.

**PROPERTIES:**

Deep red, lustrous monoclinic crystals. Vapor density measurements at 550°C indicate As\(_4\)S\(_4\). M.p. 320°C, b.p. 565°C; d 3.5. Occurs in nature as realgar.

**REFERENCE:**


**Diarsenic Pentasulfide**

\[
\text{As}_2\text{S}_5
\]

\[
2\text{H}_3\text{AsO}_4 + 5\text{H}_2\text{S} = \text{As}_2\text{S}_5 + 8\text{H}_2\text{O}
\]

Pure As\(_2\)S\(_5\) can be obtained by precipitation of orthoarsenic acid solutions only if the aqueous acid is treated with twice its volume of concentrated (d 1.19) hydrochloric acid, and a fast stream of H\(_2\)S is bubbled through the ice-cooled solution for about an hour. The flask must be cooled even during the HCl addition and no temperature rise should be allowed. The precipitate is washed with water and alcohol and dried at 100°C.

**PROPERTIES:**

Somewhat brighter yellow than the trisulfide. Decomposes into As\(_2\)O\(_3\), S, and As\(_2\)S\(_3\) when boiled with H\(_2\)O.

**REFERENCES:**

**Ammonium Thioarsenate**

\[(\text{NH}_4)_2\text{AsS}_4\]

\[
\text{As}_2\text{S}_3 + 3(\text{NH}_4)_2\text{S} = 2(\text{NH}_4)_2\text{AsS}_4
\]

310.2 204.5 514.6

A solution of \(\text{As}_2\text{S}_3\) in excess \((\text{NH}_4)_2\text{S}\) is prepared with moderate heating and thoroughly extracted with hot alcohol. Cooling results in precipitation of colorless crystals of the salt. After suction filtering, the product is washed with alcohol.

**PROPERTIES:**

Formula weight 257.29. Prisms. In air, the surface yellows. Melts on heating and decomposes to \(\text{As}_2\text{S}_3\), S, and ammonium sulfide.

**REFERENCE:**


**Sodium Thioarsenate**

\[\text{Na}_3\text{AsS}_4\cdot8\text{H}_2\text{O}\]

\[
3\text{Na}_2\text{S} + \text{As}_2\text{S}_3 + 2\text{S} = 2\text{Na}_3\text{AsS}_4
\]

234.1 246.0 64.1 544.3

A solution of 20 g. of \(\text{As}_2\text{O}_3\) in hot NaOH is strongly acidified with HCl. Then \(\text{As}_2\text{S}_3\) is precipitated by bubbling \(\text{H}_2\text{S}\) through the hot solution. Filtering and thorough washing with dilute HCl follows. One half of a solution of 24 g. of NaOH in 100 ml. of water is saturated with \(\text{H}_2\text{S}\) and mixed with the other half. The thus obtained \(\text{Na}_2\text{S}\) solution is used to dissolve \(6.4\) g. of sulfur and the \(\text{As}_2\text{S}_3\). The mixture is evaporated on a steam bath until a crystalline surface layer forms. It is then left to crystallize in the cold.

**PROPERTIES:**

Formula weight 416.275. Monoclinic prisms, colorless to pale yellow. Readily soluble in \(\text{H}_2\text{O}\) and stable in air. Acidification of the solution results in precipitation of copious quantities of \(\text{As}_2\text{S}_6\).

**REFERENCES:**

McCay. Z. analyt. Chem. 34, 725 (1895).
Sodium Monothioorthoarsenate

Na$_3$AsO$_3$S·12H$_2$O

6 NaOH + As$_2$O$_3$ + 2 S = 2 Na$_3$AsO$_3$S + 3 H$_2$O

240.0 197.8 64.1 447.9 54.0

Arsenic trioxide (20 g.) is dissolved in a solution of 24 g. of NaOH in 100 ml. of H$_2$O and the mixture is boiled with 6.5 g. of S for half an hour. It is filtered hot and evaporated on a steam bath until crystallization. It is then permitted to cool and the crystals are suction filtered.

PROPERTIES:


REFERENCES:


Sodium Dithioorthoarsenate

Na$_3$AsO$_3$S$_2$·11H$_2$O

6 NaOH + As$_2$S$_3$ + 2 S = 2 Na$_3$AsO$_3$S$_2$ + H$_2$S + 2 H$_2$O

240.0 246.0 64.1 480.0 34.1 36.0

A mixture of 24.6 g. of moist, freshly precipitated As$_2$S$_3$ and 6.4 g. of finely ground sulfur is prepared and a solution of 24 g. of NaOH in 200 ml. of water added. This new mixture is allowed to stand for 12 hours, with frequent agitation, until the bulk of the sulfur has dissolved. It is then filtered, and the filtrate is evaporated until crystallization, at which point it is allowed to cool. The crystallized substance consists of very pure Na$_3$AsO$_3$S$_2$·11H$_2$O. Additional product is obtained from the mother liquor; it is, however, contaminated with thio- and monothioarsenates.

PROPERTIES:


REFERENCE:

Antimony

Chemically pure Sb can be produced by reduction of $\text{Sb}_2\text{O}_5$ with hydrogen or, more simply, with KCN. Equal parts of the dried oxide and chemically pure KCN are mixed and the mixture is fused in a porcelain crucible. After cooling, the block of metal is freed of surface impurities by boiling with water and remelted. The starting $\text{Sb}_2\text{O}_5$ is best purified by conversion to $\text{HSbCl}_3$ through repeated recrystallization from pure, concentrated hydrochloric acid (Groschuff method). Lautié recommends vacuum distillation of the metal at 800°C for final purification.

PROPERTIES:


REFERENCES:

E. Groschuff. Z. anorg. allg. Chem. 103, 164 (1918).

Stibine (Antimony Hydride)

$\text{SbH}_3$

I. $\text{Mg}_3\text{Sb}_2 + 6 \text{HCl} = 2 \text{SbH}_3 + 3 \text{MgCl}_2$

A mixture of 20 g. of finely pulverized Sb and 40 g. of Mg powder is placed in a sheet-iron trough (70 cm. long) which is inserted into a 25-mm.-diameter iron tube. The mixture is then heated in a stream of $\text{H}_2$. When the tube glows, the flame is extinguished and the tube is allowed to cool in the stream of $\text{H}_2$. The alloy should be sintered but not fused. The tube contents are sieved and the coarse fraction is repulverized. The gray-black powder should pass through a screen with 0.5-mm. openings. In decomposition the powder is added to the acid and not vice versa. Where small quantities are involved, this can be done in the manner described for $\text{AsH}_3$ (p. 593). The acid is placed in flask $a$ of Fig. 203 and Mg–Sb alloy in the side bulb. The powder is added to the flask by turning and tapping the bulb. However, it is better to employ an automatic charging
apparatus, illustrated in Fig. 203. The vessel \( b \) containing the Sb-Mg powder is fitted on top of flask \( g \). A hard rubber rod \( d \) (a thick knitting needle if available) is positioned axially in vessel \( b \) and rotating in the mercury seal \( c \). The lower end of the rod is conical, with a few spiral grooves at the bottom. Slow rotation of the rod permits a uniform powder flow into \( g \). The latter contains preboiled, dilute hydrochloric acid (\( d = 1.06 \)) and is cooled with an ice-salt bath. The air is displaced with \( H_2 \) prior to addition of the alloy powder. The interior of empty tube \( e \) is coated with \( P_2O_5 \) powder, while a glass bead-\( P_2O_5 \) mixture is placed in drying tubes \( f \). The evolving gas passes through \( e \) and \( f \) for drying and is frozen in trap \( k \), cooled with liquid nitrogen. The product gas contains about 15% SbH\(_3\). At the end of the run (SbH\(_3\) evolution is readily controlled by adjustment of the rate of rotation of the feed rod; it continues for a few hours) all the SbH\(_3\) is displaced from \( g \) into \( k \) with a stream of \( H_2 \). Capillary \( i \) is melted and the sealed apparatus is evacuated. The trap contents are melted; a small forerun is distilled into \( l \), while the main fraction is collected in \( m \). Constrictions \( n \) and \( p \) are then melted and the material distilled into ampoules \( r \), observing the vacuum on gauge \( q \). The distillation temperature is 65-75°C.

Other preparative methods: The electrolytic preparation method of Reismann, Berkenblit, Haase and Gaines uses a Pt anode and a Pt/Ir cathode in an electrolyte consisting of 1.7 liters of 4N \( H_2SO_4 \), 80 g. of tartaric acid, and 8 g. of Sb.
PROPERTIES:

Formula weight 124.78. Cubic crystals. The gas decomposes readily, evolving heat (the decomposition may become explosive). Since a flame may not be brought near the SbH₃, the storage flask may be torch-sealed only if the contents are frozen at liquid N₂ temperature or a long capillary is interposed between the seal point and the flask. M.p. -91°C, b.p. -17°C, d (-17°C) 2.2. Slowly decomposes into the elements just above the b.p. Extremely toxic. Five volumes of H₂O dissolve one volume of SbH₃. Cubic crystals.

REFERENCES:

H. Reckleben and A. Gütting. Z. analyt. Chem. 49, 73 (1910);
F. Paneth. Z. Elektrochem. 26, 453 (1920);
H. J. S. Weeks. Recueil Trav. Chim. Pays-Bas 43, 649 (1924); 44, 201, 795 (1925);
A. Stock and W. Doht. Ber. dtsch. chem. Ges. 35, 2274 (1902);
G. V. Teal. US Patent 2 391 280 (1945);

Antimony (III) Chloride

SbCl₃

I. \[2\text{Sb} + 3\text{Cl}_2 = 2\text{SbCl}_3\]

A few pieces of pure Sb are placed in glass tube \(r\) (Fig. 204), and a stream of dry Cl₂ is introduced through side arm \(a\) of the flask. Tube \(r\) rests on an asbestos-lined iron trough inclined slightly toward the flask. Once the reaction has started, it is necessary to add fresh pieces of Sb only from time to time. This is done by removing stopper \(c\), which is only loosely inserted. Plugging does not occur since the chloride is kept fluid in the narrow 8-mm. section of tube \(r\) by absorbing Cl₂. When enough crude chloride is collected in the flask, the Cl₂ stream is interrupted and a few pieces of Sb are placed in the flask. Heat is then applied and finally some more Sb powder is added to eliminate the last of the SbCl₅. Finally, the SbCl₃ is purified by distillation.

II. A solution of 25 g. of finely pulverized stibnite in 150 ml. of concentrated hydrochloric acid is prepared with heating and filtered
Fig. 204. Preparation of antimony (III) chloride. \( r \) Glass tube, straight section about 60 cm. long, inside diameter 1.5 cm., 0.8 cm. in constricted section. Walls 1.5-2 mm. thick.

after cooling. The operation must be conducted under a hood. The filtrate is fractionated in the presence of 2 g. of Sb, the flask being closed with an asbestos stopper. The condenser is air cooled. The forerun (boiling up to 120°C) is discarded. The fraction boiling above 200°C is retained. This portion is fractionated once more in the presence of 1 g. of Sb powder, and only the fraction boiling at 223°C is collected.

Fig. 205. Purification of antimony (III) chloride by sublimation. \( t \) Drying tube.

A particularly pure preparation can be obtained by resublimation of the SbCl₃. In this procedure, a two-liter distillation flask \( k \) is placed on a steam bath (see Fig. 205) while the upper part of the sphere is cooled with running water. Some SbCl₃ is placed in the flask. When enough fine, long crystals have deposited on the cold upper part and no unsublimed SbCl₃ is left on the bottom, the flask is left to cool without being disturbed. Then the readily detached crystals are transferred (with tapping) into flask \( v \). The entire apparatus must, of course, be carefully dried.
PROPERTIES:

Formula weight 228.1. Colorless; when sublimed, long, fine, rhombic crystals. M.p. 72.9°C, b.p. 223.0°C; d° 3.14. Hygroscopic. Fumes in air. Highly corrosive. Soluble in small amounts of H₂O. In large quantities of H₂O, hydrolyzes to SbOCl. Soluble in cold alcohol, CS₂, and in ether; soluble in alkali chloride solutions, forming salts of hexachloroantimony(III) acid. Used for bronzing iron articles. The high cryoscopic constant (18.4) and its ability to dissolve many substances render SbCl₃ suitable for molecular weight determinations.

REFERENCES:

P. Hensgen. Recueil Trav. Chim. Pays-Bas 9, 301 (1890);
J. Kendall, E. D. Crittenden and H. K. Miller. J. Amer. chem. Soc. 45, 967 (1923);
G. Langguth. Chim. Ind. 25, 22 (1931);
O. Werner. Z. anorg. allg. Chem. 181, 154 (1929);

**Antimony (V) Chloride**

\[
\text{SbCl}_3
\]

\[
\text{SbCl}_3 + \text{Cl}_2 = \text{SbCl}_5
\]

A sample of SbCl₃ is melted in a ground joint Claisen flask. A gas inlet tube passes through one stopper. Chlorine is introduced, at first with heating and then without. When the liquid is saturated, the inlet tube is replaced by a capillary and the flask, which has a vacuum receiver, is evacuated. To remove the excess Cl₂, a stream of air dried with \(\text{P}_2\text{O}_5\) is drawn through the apparatus by suction, followed by distillation of the flask contents at 14 mm. At this pressure, the SbCl₅ distills over at 68°C. The yield is 85%.

PROPERTIES:

Colorless liquid; fumes strongly in air. M.p. 4.0°C, b.p. (14 mm.) 68°C; (760 mm.) about 140°C (dec.); d° 2.346. On addition of a small quantity of H₂O, forms the hydrates SbCl₅·H₂O and SbCl₅·4H₂O. With addition of larger amounts of water, hydrolyzes to Sb₂O₅. Vapor pressure 6 mm. (51°C), 9 mm. (58°C).
ARSENIC, ANTIMONY, BISMUTH

REFERENCES:

O. Ruff. Ber. dtsch. chem. Ges. 42, 4026 (1909);
W. Biltz and K. Jeep. Z. anorg. allg. Chem. 162, 34 (1927);

**Antimony (III) Oxide Chloride**

\[
\text{SbCl}_3 + \text{H}_2\text{O} = \text{SbOCl} + 2 \text{HCl}
\]

A mixture of 70 ml. of \( \text{H}_2\text{O} \) and 100 g. of \( \text{SbCl}_3 \) is prepared, thoroughly stirred, and allowed to stand for several days. The crystals that precipitate are suction-filtered, pressed, washed with ether, and dried. Larger crystals are prepared, according to Edstrand, by heating \( \text{SbCl}_3 \) with absolute alcohol in a sealed tube at 150°C.

**Properties:**

- Colorless monoclinic crystals or crystalline powder. Soluble in hydrochloric and tartaric acids and in \( \text{CS}_2 \). Addition of water results in hydrolysis to \( \text{Sb}_2\text{O}_3 \). Heating to about 250°C results in formation of \( \text{Sb}_2\text{O}_5\text{Cl}_2 \). Above 320°C the product is \( \text{Sb}_2\text{O}_3 \).

**References:**

A. Sabanjew. Z. f. Chem. 14, 206 (1871);
J. M. van Bemmelen, P. A. Meerburg and U. Huber Noodt. Z. anorg. allg. Chem. 33, 290 (1903);

**Hexachloroantimonic (V) Acid**

\[
\text{Sb}_2\text{O}_3 + 8 \text{HCl} + 2 \text{Cl}_2 + 6 \text{H}_2\text{O} = 2 \text{HCl}_4 \cdot 4.5 \text{H}_2\text{O}
\]

A sample of \( \text{Sb}_2\text{O}_3 \) is dissolved in twice its weight of concentrated hydrochloric acid, and saturated with \( \text{Cl}_2 \). When the solution becomes greenish yellow, it is concentrated somewhat on a water
bath, gaseous HCl is added, and the mixture is allowed to crystal-
lize overnight at 0°C in a desiccator over H$_2$SO$_4$ (seedling should
be used if possible). The crystals that precipitate are suction-
filtered on a glass suction filter and repeatedly washed with ice-
cold concentrated hydrochloric acid. By concentration, additional
crystal fractions can be obtained from the mother liquor and the
wash liquids, after another treatment with HCl gas. The crystalline
fractions thus obtained can then be repeatedly recrystallized from
concentrated hydrochloric acid (seed crystals should be set aside).
The compound K$_2$SbCl$_6$·H$_2$O precipitates as greenish octahedral
crystals if KCl, instead of HCl, is added to the concentrated solu-
tion.

**PROPERTIES:**

44°C. Effloresces over concentrated H$_2$SO$_4$. Readily soluble in
ethanol, acetone, glacial acetic acid, and small amounts of H$_2$O.
Hydrolyzes in excess H$_2$O. Alcohol and acetone solutions give a
neutral reaction.

**REFERENCES:**

(1905);
E. Groschuff. Z. anorg. allg. Chem. 103, 147 (1918);
F. Seel. Z. anorg. Chem. 252, 24 (1943).

**Nitrosyl Chloroantimonate (V)**

\[
\text{NO(SbCl}_6\text{)}
\]

\[
\text{NOCl} + \text{SbCl}_5 = \text{NO}_2\text{SbCl}_6
\]

A solution of two moles of NOCl in a small quantity of dried
CCl$_4$ is cooled in an ice-salt bath. Moisture must be absent. A
solution of one mole of SbCl$_5$ in a small quantity of CCl$_4$ is added
dropwise. The yellow precipitate is suction-filtered, washed with
some cold CCl$_4$, and vacuum dried over P$_2$O$_5$.

The corresponding nitryl chloroantimonate (V) can be prepared,
according to Seel, by co-condensation of SbCl$_5$, Cl$_2$, and NO$_2$Cl.
It is a colorless salt.

**PROPERTIES:**

Yellow crystals, can be sublimated in a CO$_2$ stream at 150°C.
Melts in a closed tube at 170°C. Decomposes in moist air.
REFERENCES:

H. Rheinboldt and R. Wasserfuhr. Ber. dtsch. chem. Ges. 60, 732 (1927);
F. Seel. Z. anorg. Chem. 252, 24 (1943);

**Antimony (III) Bromide**

\[
\text{SbBr}_3
\]

\[
\text{Sb} + 3 \text{Br} = \text{SbBr}_3
\]

121.8 239.7 361.5

Antimony and bromine react with the appearance of a flame. The material can be prepared in exactly the same manner as described for As: a N\(_2\) stream, saturated with Br\(_2\), is passed over Sb powder and the products are trapped in a receiver. Another method is to add very small portions of Sb powder through a vertical reflux condenser set on a Pyrex flask containing a solution of Br\(_2\) in CS\(_2\). Then the Br\(_2\) excess and the CS\(_2\) are distilled off. The flask contents are distilled in a sausage distillation flask. Purification may be accomplished by recrystallization from CS\(_2\) or, better still, via the Jander and Weis procedure, by redistillation over Sb powder and KBr in a stream of dry CO\(_2\). The apparatus illustrated in Fig. 205a is employed. Flask \(a\) contains SbBr\(_3\), placed over Sb powder and KBr. A very large first cut is distilled into receiver \(v\), while dry CO\(_2\) is passed through the apparatus from \(b\). Then \(v\) is removed, CO\(_2\) is introduced in at the right, and the major fraction is distilled from \(b\) onto the chemically pure Sb. The material is again distilled from \(b\), and again a large first cut is discarded. Finally, the main fraction is distilled into receivers attached with ground glass joints.

**PROPERTIES:**


REFERENCES:

J. Niklés. J. Pharm. (3) 41, 145 (1862);
A. C. Vournasos. Z. anorg. allg. Chem. 192, 372 (1930);
W. Biltz and A. Sapper. Z. anorg. allg. Chem. 203, 282 (1932);

Fig. 205a. Purification of antimony (III) bromide.

Antimony (III) Iodide

\[ \text{SbI}_3 \]

\[ \text{Sb} + \frac{3}{2} \text{I}_2 = \text{SbI}_3 \]

A solution of 14 g. of I₂ in 300 ml. of toluene is refluxed with 7 g. of finely pulverized Sb until the iodine color disappears. The yellow-green solution is filtered from the unconverted Sb (best practice is to use an immersion suction filter and propel the fluid with compressed CO₂) and allowed to crystallize, whereupon SbI₃ precipitates as red leaflets. These are freed of toluene in a vacuum desiccator at 40°C and then resublimed in a flow of CO₂ or in vacuum. The SbI₃ distills between 180 and 200°C. The yield is 80%.

PROPERTIES:

Red, crystalline flakes; trigonal. In addition to the red trigonal form \[ d (22°C) 4.92 \], there are two greenish modifications, one rhombic and one monoclinic. \[ d (17°C) 4.77 \]. When fused, a pomegranate-red liquid. The vapor is orange red. M.p. 170°C, b.p. 401°C. Hydrolyzes in H₂O to a yellow oxyiodide.

REFERENCES:

Ammonium Hexabromoantimonate (IV)

\[(\text{NH}_4)_2\text{SbBr}_6\]

\[\text{SbBr}_3 + \frac{1}{2} \text{Br}_2 + 2 \text{NH}_4\text{Br} = (\text{NH}_4)_2\text{SbBr}_6\]

A 4.9-g. sample of \(\text{NH}_4\text{Br}\) is dissolved in 50 ml. of concentrated (48\%) hydrobromic acid with gentle warming and the solution is then cooled. A portion of the \(\text{NH}_4\text{Br}\) precipitates as a very fine powder but redissolves on addition of 50 ml. of concentrated \(\text{H}_2\text{SO}_4\) (use cooling). A solution of 9 g. of \(\text{SbBr}_3\) and 0.65 ml. of \(\text{Br}_2\) in 10 ml. of concentrated hydrobromic acid is then added to the mixture. The \((\text{NH}_4)_2\text{SbBr}_6\) precipitates virtually quantitatively. It is suction filtered, washed three times with 4 ml. of concentrated hydrobromic acid, and dried in a vacuum desiccator over KOH. The drying process, usually complete after two days, involves loss of Br, and the substance takes on a dirty olive-green color. After drying, the composition of the substance corresponds approximately to the formula \((\text{NH}_4)_2\text{SbBr}_5\). If the drying is longer, the color becomes lighter and more bromine is lost. To rebromite the substance, it is placed in a desiccator over concentrated \(\text{H}_2\text{SO}_4\) and kept there for a day under bromine vapor. The excess \(\text{Br}_2\) is then evacuated. The preparation is then pure and corresponds to the formula \((\text{NH}_4)_2\text{SbBr}_6\).

**PROPERTIES:**

Crystallizes in deep-black octahedra, stable in dry air. Moisture produces hydrolytic decomposition. Soluble in 2N hydrochloric acid; can be recrystallized (with loss of Br) from concentrated hydrobromic acid. Crystal structure: similar to \(\text{K}_2\text{PtCl}_6\).

**REFERENCES:**

F. Ephraim and S. Weinberg. Ber. dtsch. chem. Ges. 42, 4450 (1909);
K. A. Jensen. Z. anorg. allg. Chem. 232, 193 (1937); 252, 317 (1944);

Antimony (III) Oxide

\[\text{Sb}_2\text{O}_3\]

\[2\text{SbCl}_3 + 3 \text{H}_2\text{O} = \text{Sb}_2\text{O}_3 + 6 \text{HCl}\]

A solution of \(\text{SbCl}_5\) in some highly concentrated hydrochloric acid is diluted with water. The resulting precipitate is repeatedly
washed and decanted with water and is then boiled repeatedly with dilute ammonia until the solution is free of halogen ions. It is then decanted repeatedly with water, washed on a filter, and dried. Other antimony compounds may be used in similar fashion to prepare \( \text{Sb}_2\text{O}_3 \) by hydrolysis.

**PROPERTIES:**

White, crystalline powder; cubic (senarmontite) or rhombic (valentinite); transformation point \( 570^\circ\text{C} \pm 10^\circ\text{C} \). Hydrolysis yields the metastable valentinite. When treated with alkali, converts gradually to senarmontite. \( d_4^{25} 5.19 \) (cubic), \( 5.79 \) (rhombic); b.p. \( 1425^\circ\text{C} \); m.p. \( 655^\circ\text{C} \). Sublimes in vacuum at \( 400^\circ\text{C} \). Slightly soluble in \( \text{H}_2\text{O} \). Heating gives a reversible yellow color.

**REFERENCES:**

E. J. Roberts and F. Fenwick. J. Amer. Chem. Soc. 50, 2133 (1928);
M. C. Bloom and M. J. Buerger. Z. Kristallogr. 96, 367 (1937);
M. J. Buerger and S. B. Hendricks. Z. Kristallogr. 98, 29 (1938);

**Antimony (V) Oxide**

\( \text{Sb}_2\text{O}_3 \)

\[ \text{II. } 2\text{SbCl}_5 + 5\text{H}_2\text{O} = \text{Sb}_2\text{O}_3 + 10\text{HCl} \]

The \( \text{Sb}_2\text{O}_3 \) required for the preparation of chemically pure \( \text{Sb} \) is made by hydrolysis of hexachloroantimonic acid. The latter is dissolved in some double-distilled water, and the cold solution is diluted with more water. Then C. P. ammonia is added and the solution is heated on a water bath until the \( \text{Sb}_2\text{O}_3 \) precipitate settles. Decantation follows, then repeated washing with chemically pure water and another decantation. Finally, the precipitate is suction filtered through a paper filter. The substance is dried in a dish by heating on a water bath.

\[ \text{II. } 2\text{SbCl}_5 + 5\text{H}_2\text{O} = \text{Sb}_2\text{O}_3 + 10\text{HCl} \]

A mixture of \( \text{SbCl}_5 \) in 20 to 25 times its weight of cold water is prepared. After a few hours, the precipitate is filtered and washed with cold water. It is dried at \( 275^\circ\text{C} \) to constant weight.
III. Another method of preparation is the precipitation of a potassium antimoniate solution with nitric acid, followed by thorough washing and drying as above.

**PROPERTIES:**

Fine, pale yellow powder. Cubic. Slightly soluble in H₂O. d 3.78. Loses oxygen on heating above 300°C and gradually converts to Sb₂O₅. New studies have shown that the compound does not correspond fully to Sb₂O₅, but that it is always somewhat hydrated. When heated for a long time, its composition corresponds to the formula Sb₂O₅ • SbOOH. It seems questionable whether pure Sb₂O₅ exists at all.

**REFERENCES:**

K. Dihlström and A. Westgren. Z. anorg. allg. Chem. 235, 153 (1937); 239, 57 (1938);

**Hydrated Antimony (V) Oxide**

\[
\text{Sb}_2\text{O}_5 \cdot (\text{H}_2\text{O})_x
\]

\[
2\text{SbCl}_3 + x\text{H}_2\text{O} = \text{Sb}_2\text{O}_5 \cdot (\text{H}_2\text{O})_{x-5} + 10\text{HCl}
\]

598.1 \( x \cdot 18 \)
532.5 \( + 18 \cdot (x-5) \) \( 364.7 \)

I. Antimony (V) chloride (100 ml.) is added dropwise and with vigorous stirring and constant cooling to 0°C to 7.5 liters of ice-cold saturated chlorine water. The liquid becomes cloudy. The copious precipitate is repeatedly washed and decanted with nine-liter portions of water and then purified for 23 days in a rapid dialyzer. The material is filtered through a leaf filter and spread on a clay plate, where it is left to dry in the air. After a number of months, the preparation analyzes as Sb₂O₅ • 4.58 H₂O.

II. If precipitation is performed at 100°C with only two liters of the precipitation liquid, followed by purification and drying as described in I, the resulting crystals are larger and have the composition Sb₂O₅ • 4.40 H₂O.

**PROPERTIES:**

Insoluble or very slightly soluble in moderately concentrated alkalis and acids. Opaque, white, highly adsorptive mass. Isothermal dehydration at room temperature produces one definitely identified hydrate, 3 Sb₂O₅ • 5H₂O, which can be prepared by heating for many days in a sealed tube at 300°C.
REFERENCES:
G. Jander, Koll. Z. 23, 130 (1918);
G. Jander and A. Simon. Z. anorg. allg. Chem. 127, 71 (1923);

Diantimony Tetroxide

\[ 2 \text{Sb}_2\text{O}_5 = 2 \text{Sb}_2\text{O}_4 + \text{O}_2 \]

647.0 615.0

Antimony (V) oxide is ignited to red heat for about two weeks in a Pt crucible at 800-900°C. Other method: boiling \( \text{Sb}_2\text{O}_3 \) with nitric acid, evaporating until fuming, and igniting as above.

PROPERTIES:
Minute, lustrous crystals, yellow when heated. Infusible. Decomposes to \( \text{Sb}_2\text{O}_3 \) and \( \text{O}_2 \) at very high temperatures. Virtually insoluble in water, dilute acids and alkalis. Soluble in hot concentrated HCl and concentrated \( \text{H}_2\text{SO}_4 \). d. 6.6-7.5. Cubic or rhombic crystals.

REFERENCES:
K. Dihlström and A. Westgren. Z. anorg. allg. Chem. 235, 153 (1937); 239, 57 (1938).

Antimony(III) Sulfate

\[ \text{Sb}_2\text{(SO}_4)_3 \]

291.5 294.2 531.7 54.0

Long, silky needles of \( \text{Sb}_2\text{(SO}_4)_3 \) precipitate on cooling. These are suction filtered on a glass filter crucible and dried on a clay dish. The substance can be obtained free of \( \text{H}_2\text{SO}_4 \) by washing with xylene. Washing is continued until the wash liquor obtained by shaking the xylene with water no longer gives an acid reaction. The crystals are converted to an amorphous mass on washing, but the salt is then very pure.
10. ARSENIC, ANTIMONY, BISMUTH

PROPERTIES:

Colorless crystals, deliquesce in air. Cold water decomposes the substance to a basic sulfate. Complete hydrolysis results on boiling with water. d 3.62.

REFERENCE:

S. Metzl. Z. anorg. allg. Chem. 48, 143 (1906).

**Antimony (III) Oxide Sulfate**

\[ (\text{SbO})_2\text{SO}_4 \]

\[
\text{Sb}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{O} = (\text{SbO})_2\text{SO}_4 + 2 \text{H}_2\text{SO}_4
\]

531.7 36.0 371.6 196.2

Antimony sulfate is treated with 10 times its weight of cold water, the mixture is thoroughly stirred and allowed to stand overnight in the cold. It is then suction-filtered and dried at 100°C.

PROPERTIES:

White powder, insoluble in water, soluble in dilute tartaric acid.

REFERENCE:

S. Metzl. Z. anorg. allg. Chem. 48, 143 (1906).

**Sodium Thioantimonate (V)**

\[ \text{Na}_3\text{SbS}_4 \cdot 9 \text{H}_2\text{O} \]

\[
\text{Sb}_2\text{S}_3 + 8 \text{NaOH} + 6 \text{S} = 2 \text{Na}_3\text{SbS}_4 + \text{Na}_2\text{SO}_4 + 4 \text{H}_2\text{O}
\]

339.7 320.0 192.4 638.0 142.0 72.1

1. A solution of 15 g. of SbCl₃ in 600 ml. of dilute hydrochloric acid is prepared. If a precipitate is produced as a consequence of hydrolysis, concentrated hydrochloric acid is added until the solution becomes clear. Then H₂S is bubbled through the solution, and the precipitate of Sb₂S₃ is filtered off. It is mixed with 60 ml. of 20% NaOH; 6 g. of S (powder form) is added and the mixture is boiled with constant stirring until the orange-red color turns yellow. The water lost on boiling should be replaced from time to time. The solution is filtered through a fluted filter and
evaporated until crystallization begins. If the solution becomes turbid, a few drops of 20% NaOH are added until it clears. After complete cooling, the crystalline precipitate is suction-filtered, washed with some alcohol, and dried in a desiccator over quicklime to which a few drops of ammonium sulfide solution have been added. The mother liquor can be further concentrated. The preparation can be purified by recrystallization from weakly alkaline solution (a few milliliters of sodium hydroxide are added to the water).

SYNONYM:
Schlippe's salt.

PROPERTIES:

Formula weight $\text{(Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O)} = 481.14$. Bright yellow, large, tetrahedral crystals. Effloresces readily in air.

REFERENCES:
C. F. von Schlippe. Schweiggers Journ. f. Chem. and Physik 33, 320 (1821);
H. and W. Biltz. Ubungsbeispiele aus der unorganischen Experimentalchemie [Practical Problems in Experimental Inorganic Chemistry], Leipzig, 1920, p. 133;

**Bismuth**

$\text{Bi}$

The chemically pure bismuth oxide starting material is prepared from highest purity commercial bismuth nitrate. This is dissolved at $18^\circ\text{C}$ in one half its weight of 8% nitric acid. An equal weight of concentrated nitric acid is added, and the solution is cooled to $0-10^\circ\text{C}$ while well stirred. The resulting crystalline slurry is suction-filtered on a coarse fritted glass filter and washed with some ice-cold, concentrated nitric acid. Further quantities of nitrate may be obtained by concentrating the mother liquor. The purification is repeated as many times as necessary; the nitrate product is decomposed to the basic nitrate by heating in a porcelain dish at $110^\circ\text{C}$ and this is then converted to the oxide by igniting. The oxide is mixed with half its weight of pure KCN and reduced in a porcelain crucible. Reduction in a flow of $\text{H}_2$ is less convenient.
Impurities in the Bi metal thus purified cannot be detected by chemical or spectroscopic means.

Bismuth metal can be purified to a considerable extent by slow crystallization in a large diameter Vycor test tube under paraffin oil. It is permitted to cool, while stirring with a perforated glass ladle, and the precipitated crystals are scooped out of the melt (it must be borne in mind that bismuth expands on solidification and may burst the test tube. A dish is therefore placed underneath). The crystals are melted. This treatment removes all impurities except for Sb, which forms mixed crystals with the bismuth.

PROPERTIES:


REFERENCES:

O. Honigschmid and L. Birckenbach. Z. Elektrochem. 26, 403 (1920);
J. Löwe. Z. analyt. Chem. 22, 498 (1883);
R. Schneider. J. prakt. Chem. 50, 461 (1894);
F. Mylius. Z. anorg. allg. Chem. 96, 237 (1916);

Bismuth (III) Chloride

BiCl₃

\[
2 \text{Bi} + 3 \text{Cl}_2 = 2 \text{BiCl}_3
\]

418.0 212.7 630.7

A boat containing Bi is placed in a Vycor tube and heated in an electric furnace. A two-way stopcock permits introduction of either pure N₂ or Cl₂. The air is displaced with N₂ and the apparatus is dried by heating and passage of N₂. Then the chlorine stream is introduced and the temperature is raised until the reaction begins. The BiCl₃ sublimes into the part of the tube that is cooled by a water jacket or with wet filter paper. After about an hour the formation of BiCl₃ ceases. The Cl₂ is displaced with N₂, and the chloride is quickly removed from the tube (Honigschmid describes a special emptying device).

Other preparative methods: solution of Bi₂O₃ in hydrochloric acid, drying on a water bath, and distilling the residue in a stream of CO₂.
PROPERTIES:


REFERENCES:


Bismuth Dichloride

\[ \text{BiCl}_2 \]

\[ \text{Bi} + \text{Hg}_2\text{Cl}_2 = \text{BiCl}_2 + 2\text{Hg} \]

209.0 472.1 279.9 401.2

An equimolar mixture of Hg₂Cl₂ and powdered Bi is heated for two hours in a sealed tube at 250°C. After heating, the BiCl₂ is separated from the Hg and reheated in the tube.

PROPERTIES:

Microscopically small, black crystals, insoluble in organic solvents. M.p. 163°C; d 4.86. At 300°C, it decomposes to Bi + BiCl₃. When heated in air, produces Bi₂O₃, BiOCl and Cl₂. With H₂O decomposes to BiOCl, Bi and HCl. Yields BiCl₃ with I₂.

REFERENCES:


Bismuth Oxide Chloride

\[ \text{BiOCl} \]

\[ \text{BiCl}_2 + \text{H}_2\text{O} = \text{BiOCl} + 2\text{HCl} \]

315.4 18.0 260.5 72.9

A solution of 3 g. of Bi₂O₃ in 300 ml. of hydrochloric acid (d 1.05) is heated to boiling, at which point 2.5 liters of boiling water is added. Boiling is continued until the initial precipitate
has redissolved. The solution is then allowed to cool until crystallization sets in. The BiOCl precipitate is filtered by suction.

**Properties:**
Colorless, crystalline powder, very slightly soluble in H₂O. d 7.72. Tetragonal.

**References:**

**Bismuth (III) Bromide**

BiBr₃

\[
2 \text{Bi} + 3 \text{Br}_2 = 2 \text{BiBr}_3
\]

The same type of reaction vessel is employed as in the preparation of BiCl₃. A stream of N₂ dried with concentrated H₂SO₄ is passed through a wash bottle filled with Br₂. This flask is slightly heated by a surrounding warm water bath. The N₂-Br₂ mixture then passes through a P₂O₅ drying tube. The apparatus used for preparation of this gaseous mixture is illustrated in Fig. 206.

Fig. 206. Generation of a stream of dry bromine vapor for preparation of bismuth (III) bromide.

*Other method:* Bismuth powder is placed in a retort, Br₂ is poured over it, and the mixture is allowed to stand for a few days and then distilled. It is also possible to heat Br₂ with Bi in a round-bottom flask equipped with a reflux condenser. In both cases purification is by vacuum distillation.

**Properties:**
Formula weight 448.75. Orange-yellow, crystalline mass. M.p. 218 °C, b.p. 441 °C; d. 5.7. Produces BiOBr with H₂O.
REFERENCES:

O. Hönigschmid and L. Birckenbach. Z. Elektrochem. 26, 403 (1920);

**Bismuth Oxide Bromide**

\[ \text{BiOBr} \]

\[ \text{BiBr}_3 + \text{H}_2\text{O} = \text{BiOBr} + 2\text{HBr} \]

A solution of 3 g. of Bi₂O₃ in 50 ml. of hydrobromic acid (d 1.38) is heated to boiling. It is then diluted with 1.5–1.6 liters of boiling water and boiling is continued until the initial precipitate redissolves. The BiOBr crystallizes on cooling in ice. It is washed with dilute hydrobromic acid and then with pure water.

**PROPERTIES:**

Colorless square crystals or colorless crystalline powder. Very stable, melts at red heat. Soluble in concentrated hydrobromic acid.

**Bismuth (III) Iodide**

\[ \text{BiI}_3 \]

I.

\[ \text{Bi} + \frac{3}{2}\text{I}_2 = \text{BiI}_3 \]

Iodine (20 g.) is ground with 45 g. of finely powdered Bi in a mortar and then rapidly placed in a retort. The mixture is heated until reaction begins. At the end of the reaction, a stream of CO₂ is passed through the warm retort to remove unreacted iodine. The iodide is then sublimed in a stream of CO₂. Smaller quantities can also be prepared by placing the mixture in a boat inserted into a Vycor tube, heating, and then subliming the BiI₃ in a CO₂ stream.

II.

\[ \text{BiCl}_3 + 3\text{HI} = \text{BiI}_3 + 3\text{HCl} \]

A solution of BiCl₃ in hydrochloric acid is precipitated with concentrated hydriodic acid. The precipitate is filtered in a fritted glass suction funnel and washed free of Cl ions with concentrated
hydriodic acid. The crystals are dried in vacuum over $\text{P}_2\text{O}_5$. They are then heated in vacuum nearly to the melting point and finally sublimed by stronger heating.

**Properties:**

Dark crystals with metallic luster. Very similar in appearance to iodine. M.p. slightly above $400^\circ \text{C}$. Slightly soluble in alcohol, benzene, and toluene.

**References:**

L. Birckenbach. *Ber. dtsch. chem. Ges.* 40, 1404 (1907);

### Bismuth Oxide Iodide

\[
\text{BiI}_3 + 2\text{KOH} = \text{BiOI} + 2\text{KI} + \text{H}_2\text{O}
\]

A precipitate of BiOI is formed when BiI$_3$ is shaken with some dilute KOH. It is suction-filtered, washed and dried.

**Other preparative methods:** A solution of 20 g. of Bi(NO$_3$)$_3$ in 30 g. of glacial acetic acid is stirred into a cold solution of 7 g. of KI and 10 g. of sodium acetate in 400 ml. of H$_2$O. When the precipitate becomes brick red, it is filtered off, washed and dried.

A solution of 0.25 g. of Bi$_2$O$_3$ in 40 ml. of hydriodic acid (d. 1.2) is diluted with six liters of water. The whole is heated on a water bath; crystalline BiOI immediately precipitates.

A solution of 30.5 g. of BiONO$_3$ in 30 ml. of concentrated nitric acid is mixed with 60 ml. of H$_2$O and 60 ml. of glycerol. The solution is stirred with 125 ml. of 25% sodium hydroxide and 175 ml. of H$_2$O. The clear solution is diluted with H$_2$O to one liter. Then a solution of 33 g. of KI in 50 ml. of H$_2$O plus 60 ml. of acetic acid is added. After two hours it is suction filtered and washed. The yield is 32 g. of 91% pure material.

**Properties:**

Brick-red crystalline powder or copper-colored crystals. Only slightly attacked by hot water. Fuses at red heat with partial decomposition.

**References:**

Bismuth Oxide Nitrite

\[
\text{BiONO}_2
\]

\[
\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O} + \text{NaNO}_2 = \text{BiONO}_2 + 2\text{HNO}_3 + \text{NaNO}_3 + 4\text{H}_2\text{O}
\]

A mixture of 48.4 g. of crystalline bismuth (III) nitrate and 18.2 g. of mannitol is ground in a mortar. The mass is kneaded thoroughly until it is viscous and sticky. It is then allowed to stand until it can be readily stirred with the pestle. Then 100 to 300 ml. of water is added. (The mixture must not be allowed to stand for a long time without water, since it will decompose with generation of NO\(_2\).) The mixture is stirred until dissolved; it is filtered and a solution of NaNO\(_3\) added. A thick slurry of BiONO\(_2\) \cdot 1/2H\(_2\)O crystals precipitates. The slurry is suction-filtered and washed until it no longer shows an acid reaction. It is then dried on clay.

**PROPERTIES:**

Formula weight (BiONO\(_2\) \cdot 1/2H\(_2\)O) 280.0. Yellow-white crystals. Loses NO\(_2\) above 60°. Loses its water of crystallization in vacuum over H\(_2\)SO\(_4\).

**REFERENCE:**


Bismuth (III) Phosphate

\[
\text{BiPO}_4
\]

\[
\text{Bi(NO}_3)_3 + \text{H}_3\text{PO}_4 = \text{BiPO}_4 + 3\text{HNO}_3
\]

I. A bismuth (III) nitrate solution (prepared as described above under BiONO\(_2\)) is precipitated by H\(_3\)PO\(_4\) or a phosphate solution. The precipitate is removed by suction filtration and washed. II. A mixture of 15 g. of Bi(NO\(_3\))\(_3\) \cdot 5H\(_2\)O and 7 g. of Na\(_2\)HPO\(_4\) \cdot 12H\(_2\)O is placed in a large flask with some water and concentrated
nitric acid and heated on a water bath. Water is added dropwise until microscopic crystals precipitate.

PROPERTIES:

When prepared as described in method I, it contains three moles of water of crystallization. Preparations produced as described in method II contain no water of crystallization. Does not melt on heating. Only slightly soluble in water and dilute acids. Not hydrolyzed by boiling water. d. 6.323. The anhydrous form is monoclinic.

REFERENCE:

**Bismuth (III) Borate**

\[ \text{BiBO}_3 \cdot 2 \text{H}_2\text{O} \]

\[
4 \text{Bi(NO}_3)_3 + \text{Na}_2\text{B}_4\text{O}_7 = 4 \text{BiBO}_3 + 10 \text{HNO}_3 + 2 \text{NaNO}_3
\]

\[
(5 \text{H}_2\text{O}) \quad (10 \text{H}_2\text{O}) \quad (2 \text{H}_2\text{O})
\]

1940.4 381.4 1215.4 630.2 170.0

A solution of bismuth (III) nitrate and mannitol, prepared as described above under BiONO\(_2\), is precipitated with borax solution. The finely granular crystal powder is removed by suction, washed and dried.

PROPERTIES:

Formula weight (BiBO\(_3\)·2H\(_2\)O) 303.85. White powder. Attacked by water and alkalis.

REFERENCE:

**Sodium Bismuthate**

\[ \text{NaBiO}_3 \]

A) ANHYDROUS

\[
\text{Bi}_2\text{O}_3 + 3 \text{Na}_2\text{O}_2 = 2 \text{NaBiO}_3 + \frac{1}{2} \text{O}_2 + 2 \text{Na}_2\text{O}
\]

466.0 234.0 560.0 124.0

Dry Bi\(_2\)O\(_3\) is mixed with half its weight of Na\(_2\)O\(_2\) and heated in a vessel protected from access of moisture and CO\(_2\). The initial
heating (to 350°C) is rapid. It is then continued to about 600°C until gas generation ceases. The cooled sample should evolve no gas when carefully immersed in water. It is preferable to work with sintered magnesia crucibles.

**PROPERTIES:**

Yellow powder. Rapidly oxidizes acidified manganese (II) sulfate solution to permanganate.

**B) HYDROUS**

\[
\text{Bi}_2\text{O}_3 + 6 \text{NaOH} + 2 \text{Br}_2 = 2 \text{NaBiO}_3 + 4 \text{NaBr} + 3 \text{H}_2\text{O}
\]

A suspension of 170 g. of Bi$_2$O$_3$ in 1.5 liters of 40% sodium hydroxide is vigorously stirred and oxidized at the boiling point by gradually added Br$_2$ (300 g.). The brown precipitate formed is filtered off, washed with 40% sodium hydroxide, and suspended in three liters of H$_2$O. The suspension is now agitated for a while, until the color changes from brown through light brown to yellow. The precipitate is then allowed to settle; it is filtered, added to 1.5 liters of 53% NaOH, and refluxed for one half hour. The resultant brown precipitate is readily filtered off after settling. It is washed with 50% sodium hydroxide, placed, while still damp, in three liters of H$_2$O, and briefly agitated. When the yellow precipitate settles, it is filtered, thoroughly washed with water, and finally dried on clay. The yield is 170 g.

**PROPERTIES:**

Formula weight 280.0. Fine yellow needles. Variable water content may go as high as 5 H$_2$O. The usual formula is NaBiO$_3$·3.5 H$_2$O. Reacts with acids with partial decomposition and formation of higher bismuth oxides; oxidizes Mn(II) in H$_2$SO$_4$ to MnO$_4$ in the cold.

**REFERENCES:**


**Potassium Bismuthate**

\[
\text{KBiO}_3
\]

\[
\text{Bi}_2\text{O}_3 + 6 \text{KOH} + 2 \text{Br}_2 = 2 \text{KBiO}_3 + 4 \text{KBr} + 3 \text{H}_2\text{O}
\]

A suspension of 165 g. of Bi$_2$O$_3$ in 1.5 liters of 50% potassium hydroxide is oxidized at the boiling point (as described above for
NaBiO₃) with small portions of Br₂ (total 500 g.). A dark violet precipitate results. Now, an additional 500 ml. of hot 40\% potassium hydroxide is added and the material is filtered after settling. The precipitate is washed with 40\% potassium hydroxide, suspended in 3–5 liters of H₂O, and agitated for a while. The liquid is decanted after some hours; the solid is washed with cold H₂O and filtered. The bright red precipitate is dried over H₂SO₄ in a desiccator. The yield is 205 g. of KBiO₃· 1/3 H₂O. Formula weight (anhydrous) 296.1.

REFERENCE:

Dibismuth Tetroxide
Bi₂O₄

\[
2 \text{KBiO}_3 + 2 \text{HClO}_4 = 2 \text{KClO}_4 + \text{Bi}_2\text{O}_4 + \text{O}_2
\]

Potassium bismuthate (see above) (50 g.) is boiled for about 10 hours in a large excess of 10\% perchloric acid, until a slight residue of only 1–2 g. of an orange-red precipitate is left. The precipitate is filtered off, washed and dried. This is hydrated Bi₂O₄.

REFERENCE: